SCIENCE FINDER
Keywords: Electrothermal Vaporizer and ICPMS

APP* = Application (224)
FUN* = Fundamental (77)
REV* = Review (42)
DISS* = DISSERTATION (3)
TOTAL=346

APP* 1) Xia, L., B. Hu, et al. "Single-drop microextraction combined with low-temperature electrothermal vaporization ICPMS for the determination of trace Be, Co, Pd, and Cd in biological samples." Analytical chemistry FIELD Publication Date:2004 May 15 76(10): 2910-5.

A new method of single-drop microextraction combined with low-temperature electrothermal vaporization (LTETV)-ICPMS was proposed for the determination of trace Be, Co, Pd, and Cd with benzoylacetone (BZA) as both extractant and chemical modifier. Several factors that influence the microextraction efficiency, such as sample flow rate, microdrop volume, and extraction time, were investigated and the optimized microextraction conditions were established. Be, Co, Pd, and Cd in the postextraction organic phase were directly determined by LTETV-ICPMS with the use of BZA as chemical modifier. The chemical modification of BZA in LTETV-ICPMS was studied, and the factors affecting the formation of chelates and vaporization/transportation of chelates were investigated. Under the optimized conditions, the detection limits of the method were 0.12, 0.99, 1.5, and 0.27 pg/mL for Be, Co, Pd, and Cd, and the relative standard deviations for 0.1 ng/mL Be, Co, Pd, and Cd were 16, 14, 14, and 11%, respectively. After 10 min of extraction, the enrichment factors were 160 (Be), 125 (Co), 40 (Pd), and 180 (Cd). The proposed method was applied to the determination of trace Be, Co, Pd, and Cd in biological reference materials, and the determined values were in good agreement with the certified values.

APP* 2) Chaudhary-Webb, M., C. Paschal Daniel, et al. "Determining lead sources in Mexico using the lead isotope ratio." Salud p'ublica de M'exico FIELD Publication Date:2003 45 Suppl 2: S183-8. FIELD Reference Number: FIELD Journal Code:0404371 FIELD Call Number:.

OBJECTIVE: Lead poisoning can, in some cases, be traced to a specific route or source of exposure on the basis of the individual's blood lead isotope ratio. To assess the major source of lead exposure among women residing in Mexico City, we compared blood, ceramic, and gasoline lead isotope ratios. MATERIAL AND METHODS: The study population, randomly selected from participants of a large trial, (1/1996-12/1996) comprised of 16 women whose lead levels exceeded 10 micrograms/dl and who reported using lead-glazed ceramics. Lead isotope ratios were performed on a Perkin Elmer 5000 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) interfaced with a Perkin Elmer HGA-600MS Electrothermal Vaporization System (ETV). RESULTS: The isotope ratios (206Pb/204Pb, 207Pb/204Pb, and 208Pb/204Pb) of both the blood specimens and their corresponding ceramic specimens were highly correlated, with r = 0.9979, r2 = 0.9958, r = 0.9957, r2 = 0.9915 and r = 0.9945, r2 = 0.9890 values for the three isotope ratios, respectively, suggesting that the lead exposure most likely resulted from the use of these ceramic. Measurements of lead isotope ratios from leaded gasoline in use at the time of blood sampling, differed from those in blood and ceramics. CONCLUSIONS: Determining lead isotope ratios can be an efficient tool to identify a major source of lead exposure and to support the implementation of public health prevention and control measures. This paper is available too at: http://www.insp.mx/salud/index.html. Female; Human

REV* 3) Heumann Klaus, G. "Isotope-dilution ICP-MS for trace element determination and speciation: from a reference method to a routine method?" Analytical and bioanalytical chemistry FIELD Publication Date:2004 Jan 378(2): 318-29.

This critical review discusses the conditions under which inductively coupled plasma-isotope dilution mass spectrometry (ICP-IDMS) is suitable as a routine method for trace element and element-speciation analysis. It can, in general, be concluded that ICP-IDMS has high potential for routine analysis of trace elements if the accuracy of results is of predominant analytical importance. Hyphenated techniques with ICP-IDMS suffer both from lack of commercially available isotope-labeled spike compounds for species-specific isotope dilution and from the more complicated system set-up required for species-unspecific ICP-IDMS analysis. Coupling of gas or liquid chromatography with species-specific ICP-IDMS, however, enables validation of analytical methods involving species transformations which cannot easily be performed by other methods. The potential and limitations of ICP-IDMS are demonstrated by recently published results and by some unpublished investigations by our group. It has been shown that possible loss of silicon as volatile SiF4 during decomposition of a sample by use of hydrofluoric acid has no effect on trace silicon determination if the isotope-dilution step occurs during digestion in a closed system. For powder samples, laser ablation ICP-IDMS can be applied with an accuracy comparable with that only available from matrix-matched standardization, whereas the accuracy of electrothermal vaporization ICP-IDMS was strongly dependent on the element determined. The significance of easy synthesis of isotope-labeled spike compounds for species-specific ICP-IDMS is demonstrated for monomethylmercury and Cr(VI). Isotope-exchange reactions between different element species can prevent the successful application of ICP-IDMS, as is shown for iodinated hydrocarbons. It is also shown for monomethylmercury that species transformations during sample-pretreatment steps can be followed by species-specific ICP-IDMS without loss of accuracy. A relatively simple and time-efficient procedure for determination of monomethylmercury in environmental and biological samples is discussed. The method, which entails a rapid microwave-assisted isotope dilution step and in-situ extraction of the derivatized species, has good potential for routine application in the future.

FUN* 4) Hayashi, H., T. Honda, et al. "Simultaneous determination of trace elements in minute samples by electrothermal-vaporization/low-pressure helium-ICP-MS." Analytical sciences : international journal of the Japan Society for Analytical Chemistry FIELD Publication Date:2003 May 19(5): 791-3. FIELD Reference Number: FIELD Journal Code:8511078 FIELD Call Number:.

Electrothermal vaporization with two filaments was studied for low-pressure helium-ICP-MS. A 10-microl volume of sample was dried and vaporized, and then introduced to the ICP. With this technique, four elements were simultaneously determined with the acceptable precisions (RSD ca. 10%). The detection limit based on 3 sigma of background signals approached the fractional ppb range. The proposed method was successfully applied to the analysis of the certified reference material for human hair.

APP* 5) Vanhaecke, F., M. Resano, et al. "Determination of platinum and rhodium in environmental matrixes by solid sampling-electrothermal vaporization-inductively coupled plasma mass spectrometry." Analytical chemistry FIELD Publication Date:2002 Dec 1 74(23): 6040-8.

Electrothermal vaporization from a graphite furnace was used in combination with inductively coupled plasma mass spectrometry (ICPMS) for the determination of Pt and Rh in environmental matrixes. Solid samples of tunnel dust, grass, and atmospheric aerosol collected on a cellulose filter could be analyzed directly, such that sample dissolution-which is not self-evident for the determination of platinum group metals-could be avoided. By heating the graphite furnace according to a multistep temperature program, spectral interferences were avoided, since a "dry" plasma was obtained, while "parent" ions such as Cu, Zn, and Pb, giving origin to interfering molecular ions, were vaporized during the thermal pretreatment step. For tunnel dust, the most demanding sample matrix, a mixture of HCl and HF was used as a modifier to stimulate the vaporization of matrix components during the thermal pretreatment step and, hence, to alleviate matrix-induced analyte signal suppression during the actual vaporization step. Calibration was accomplished by means of single standard addition with an aqueous standard solution. The results obtained agreed within the experimental uncertainty with the corresponding reference values (certified values or results obtained using pneumatic nebulization ICPMS), while relative standard deviations of < or = 15% were typical for both Pt and Rh. In all samples, a Pt/Rh ratio of approximately 6-8 was established. For a typical sample mass of 2 mg, limits of detection were 0.35 ng/g for Pt and 0.05 ng/g for Rh. Support, Non-U.S. Gov't

APP* 6) Chassaigne, H., C. C. Chery, et al. "Development of new analytical methods for selenium speciation in selenium-enriched yeast material." Journal of chromatography. A FIELD Publication Date:2002 Nov 8 976(1-2): 409-22.

A sequential extraction allowing the discrimination of water-soluble and non-soluble selenium fractions has been developed to evaluate the availability of selenium (Se) in an Se-enriched yeast candidate reference material. The fractionation of selenium-containing compounds in the extracts was achieved on preparative grade 200 Superdex 75 and columns. It showed that water-soluble selenium is present in several fractions with a large mass distribution. Low-molecular- (< or = 10,000) and high-molecular-mass selenocompounds (range 10,000-100,000) were considered separately for further experiments. The analytical approach for low-molecular-mass selenocompounds was based onanion-exchange HPLC with on-line inductively coupled plasma (ICP) MS for quantitative analysis. Selenocystine, selenomethionine, selenite and selenate were quantified in the fractions isolated in preparative chromatography. The study revealed the existence of various unidentified Se species in yeast material. The Se-containing proteins in the yeast material have been further separated and selenium quantified by the combination of gel electrophoresis and electrothermal vaporization-ICP-MS. This new approach allows the separation of the proteins with high resolution by sodium dodecylsulfate-polyacrylamide gel electrophoresis and the sensitive determination of selenium in the protein bands.

APP* 7) Tanaka, M. and M. Takahashi "Depth profiling of ultra trace metal impurities in polytetrafluoroethylene wares by surface scraping and acid-vapor extraction followed by ICP-MS analysis." Analytical sciences : international journal of the Japan Society for Analytical Chemistry FIELD Publication Date:2002 Oct 18(10): 1099-103.

This paper describes the development of the depth profiling method of ultra trace metal impurities in polytetrafluoroethylene (PTFE) wares based on contamination-free sampling followed by acid-vapor extraction and its application to evaluate the washing method for PTFE wares. A contamination-free sampling process was achieved by scraping the surface of PTFE wares with the cleft face of a silicon wafer followed by exposing the PTFE scraped to highly pure acid-vapor. The concentration of metal impurities in extractants was determined by ICP-MS equipped with an electrothermal vaporizer (ETV-ICP-MS). The blank values of Al, Cr, Fe, Ni and Cu by the depth profiling method were 0.006, 0.004, 0.005, 0.002 and 0.003 ng, respectively. By analyzing the depth profile of beakers, the distributions of ultra trace (ng g(-1) level) metal impurities were clarified. An examination of the washing methods by the depth profiling method also clarified that exposing to acid-vapor was more effective than the acid-dipping method for the elimination of metal impurities.

REV* 8) Vanhaecke, F., M. Resano, et al. "Electrothermal vaporisation ICP-mass spectrometry (ETV-ICP-MS) for the determination and speciation of trace elements in solid samples - A review of real-life applications from the author's lab." Analytical and bioanalytical chemistry FIELD Publication Date:2002 Sep 374(2): 188-95.

The use of electrothermal vaporisation (ETV) from a graphite furnace as a means of sample introduction in inductively coupled plasma mass spectrometry (ICP-MS) permits the direct analysis of solid samples. A multi-step furnace temperature programme is used to separate the vaporisation of the target element(s) and of the matrix components from one another. Sometimes, a chemical modifier is used to enable a higher thermal pre-treatment temperature, by avoiding premature analyte losses (stabilisation) or promoting the selective volatilisation of matrix components. In almost all instances, accurate results can be obtained via external calibration or single standard addition using an aqueous standard solution. Absolute limits of detection are typically 1 pg, which corresponds to 1 ng/g for a typical sample mass of 1 mg. Real-life applications carried out in the author's lab are used to illustrate the utility of this approach. These applications aim at trace element determination in industrial and environmental materials. The industrial materials analysed include different types of plastics - Carilon, polyethylene, poly(ethyleneterephtalate) and polyamide - and photo- and thermographic materials. As samples from environmental origin, plant material, animal tissue and sediments were investigated. Some applications aimed at a multi-element determination, while in other, the content of a single, but often challenging, element (e.g., Si or S) had to be measured. ETV-ICP-MS was also used in elemental speciation studies. Separation of Se-containing proteins was accomplished using polyacrylamide gel electrophoresis (PAGE). Subsequent quantification of the Se content in the protein spots was carried out using ETV-ICP-MS. As the volatilisation of methylmercury and inorganic mercury could be separated from one another with respect to time, no chromatographic or electrophoretic separation procedure was required, but ETV-ICP-MS as such sufficed for Hg speciation in fish tissue.

APP* 9) Gelaude, I., R. Dams, et al. "Direct determination of methylmercury and inorganic mercury in biological materials by solid sampling-electrothermal vaporization-inductively coupled plasma-isotope dilution-mass spectrometry." Analytical chemistry FIELD Publication Date:2002 Aug 1 74(15): 3833-42.

This paper reports on the use of solid sampling-electrothermal vaporization-inductively coupled plasma mass spectrometry (SS-EIV-ICPMS) for the direct and simultaneous determination of methylmercury and inorganic mercury in biological materials. The main advantage of this fast and sensitive method is that no sample preparation is required. In this way, the sample throughput can be considerably increased, problems of contamination and analyte losses are kept to a minimum and, even more important, the original chemical form of the different analyte species in the solid samples is preserved. To achieve this goal, a solid sample is inserted into a graphite furnace of the boat-in-tube type and is subsequently submitted to an appropriate temperature program, leading to the separate vaporization of methylmercury and inorganic mercury, which are transported into the ICP by means of an argon carrier gas. The separation was accomplished within 75 s. For the quantification of the two peaks, species-unspecific isotope dilution was used. For this purpose, a stable flow of argon loaded with gaseous Hg isotopically enriched in 200Hg was generated using a permeation tube that was constructed in-house. Its emission rate was determined by collecting the mercury released during a given time interval on a gold-coated silica absorber, after which the amount collected was released by heating of the absorber and determined by cold vapor atomic absorption spectrometry (CVAAS) and cold vapor atomic fluorescence spectrometry (CVAFS). A reference material from the Canadian National Research Council (NRC) (TORT-2) was used to assess the accuracy of the method. For the application of the method to samples with diverse mercury contents, the spike/sample ratio can be optimized by varying the emission rate of the permeation tube simply by adapting its temperature. To prove the feasibility of this approach, two reference materials (BCR 463 and DORM-2) with a methylmercury content more than 10 times higher than that of TORT-2 were also analyzed. The detection limits obtained for 1 mg of sample (2 ng g(-1) and 6 ng g(-1) for methylmercury and inorganic mercury, respectively) were found to be sufficiently low for this kind of application and are competitive when compared to other techniques. Support, Non-U.S. Gov't

FUN* 10) Venable John, D., D. Langer, et al. "Optimizing the multielement analysis capabilities of an ICP quadrupole mass spectrometer using electrothermal vaporization sample introduction." Analytical chemistry FIELD Publication Date:2002 Aug 1 74(15): 3744-53.

A mathematical solution and an experimental procedure are described for calculating the maximum number of transient signals, such as those obtained using ETV sample introduction into an ICPMS, that can be monitored by a scanning spectrometer, such as a quadrupole mass analyzer. The total number of masses that can be monitored per ETV firing is shown to be dependent on the values chosen for data collection (i.e., scan time and dwell time) and the necessary limits of detection required by the method. The theory shows the effect that statistical noise, peak shapes, and inconsistent peak appearance times have on the overall variance calculated for the sample concentration based on total counts or "peak area". Also included in the variance calculation is the contribution made by the autosampler as an example of one type of error that is not associated with the data collection parameters. The theory is validated by two experiments where 21 and 68 transient signals are monitored per ETV firing; and as predicted, a 10 ppb sample is accurately quantified with precision better than 9% in both cases.

APP* 11) Bettinelli, M., S. Spezia, et al. "Determination of rare earth elements in urine by electrothermal vaporization inductively coupled plasma mass spectrometry." Rapid communications in mass spectrometry : RCM FIELD Publication Date:2002 16(6): 579-84.

A method was developed for the determination of rare earth elements (REEs) in urine with electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICPMS). The undiluted sample was directly injected into the graphite tube and trifluoromethane (Freon-23) was used as chemical modifier in order to reduce the vaporization temperature and the memory effect of most of the lanthanides. The detection limits were in the range 1-10 ng/L with relative standard deviation of 3-5% at concentration levels of 1microg/L, and less than 10-15% at 100 ng/L. Two different procedures, external calibration and a standard additions method, were evaluated to measure the concentration levels of lanthanides in the urine samples and the second procedure was considered to be the best choice for calibration in this work. The level of REEs in urine of 50 healthy volunteers was in the range 5-20 ng/L, above the detection limit of ETV-ICPMS. Copyright 2002 John Wiley & Sons, Ltd. Female; Human; Male

APP* 12) Keith-Roach Miranda, J., S. Sturup, et al. "Comparison of two ICP-MS set-ups for measuring 99Tc in large volume water samples." Analyst FIELD Publication Date:2002 Jan 127(1): 70-5.

Large volume fjord and seawater samples have been radiochemically prepared for ICP-MS analysis in order to test the robustness of the procedure and to carry out a comparison of two ICP-MS set-ups. A sector field instrument (MicroMass PT2) coupled with an ultrasonic nebuliser and a quadrupole ICP-MS (Perkin-Elmer Elan 6000) coupled with an electrothermal vaporisation (ETV) unit were used. The results showed that the radiochemical procedure was robust, removing Ru and Mo to acceptable levels, and that the two set-ups gave results that were in agreement. The correlation coefficient between the sets of 11 results was 1.0 +/- 0.05. The importance of establishing the matrix effect when using an ETV is discussed. Comparative Study; Support, Non-U.S. Gov't

APP* 13) Hayashi, H., T. Tanaka, et al. "Electrothermal vaporization on a tungsten filament for the determination of arsenic in chloride solutions by low-pressure helium ICP-MS." Analytical sciences : international journal of the Japan Society for Analytical Chemistry FIELD Publication Date:2001 Jan 17(1): 171-3.

A combined method of electrothermal vaporization and low-pressure helium ICP-MS was developed for the determination of traces of arsenic in chloride solutions, because serious spectral interference occurred in conventional argon ICP-MS. On a tungsten filament was placed 5 microl of a sample and heated electrothermally to remove the solvent. The resulting residue on the filament was covered with a vaporization chamber, and after reducing the pressure to ca. 5 Torr, it was rapidly heated by discharging a high-capacity condenser (0.22 F). The vapor of arsenic was transferred to a helium plasma with a stream of carrier gas for the determination. The background was not observed at m/z of 75, which allowed the determination of arsenic at ng/ml levels in chloride solutions. Sodium chloride significantly enhanced the intensity of the arsenic signal, whereas other chlorides, including KCl, MgCl2, CaCl2 and NH4Cl, suppressed the analytical signals. This enhancement due to sodium ions seems to be a peculiar phenomenon to the helium ICP. The proposed method can be applied to direct determinations of as low as 0.9 ng/ml of arsenic in seawater.

FUN* 14) Friese, K. C., U. Watjen, et al. "Analyte transport efficiencies in electrothermal vaporization for inductively coupled plasma mass spectrometry." Fresenius' journal of analytical chemistry FIELD Publication Date:2001 Aug 370(7): 843-9.

A modified graphite furnace for solid-sampling atomic absorption spectrometry as an electrothermal vaporizer (ETV) was coupled to a Perkin-Elmer/Sciex ELAN 6000 ICP mass spectrometer. The integrals obtained from electrothermal vaporization of aliquots containing As, Cd, Cu, Co, Fe, Mn, Pb, Se, and Zn were compared with those obtained from pneumatic nebulization of the same aqueous standard solution. The pneumatic nebulizer was calibrated by weighing the mass of aqueous aerosol trapped on a filter. With "wet plasma" conditions maintained also for measurements with the ETV and reference signals for analyte signals obtained with the calibrated pneumatic nebulization, the transport efficiency of the ETV system, e.g. the ratio of the analyte amount introduced into the plasma to that amount dosed into the vaporizer, was determined. The transport efficiency of two different tube and interface designs has been evaluated. Investigations with and without the use of trifluoromethane as reactive gas, with different furnace heating rates, and with varying gas flows were performed. In general, the tube equipped with a nozzle led to generally higher transport efficiency than the standard tube. Without trifluoromethane transport efficiencies ranged from 10% to 35% with the standard tube and from 15% to 50% with the nozzle-type tube. With addition of 2 mL min(-1) trifluoromethane to the argon flow of 400 mL min(-1) through the tube, transport efficiencies from 20% to 70% and from 70% to 100% were achieved with the standard and nozzle-type tubes, respectively.

APP* 15) Song, M., T. U. Probst, et al. "Rapid and sensitive determination of radiocesium (Cs-135, Cs-137) in the presence of excess barium by electrothermal vaporization-inductively coupled plasma-mass spectrometry (ETV-ICP-MS) with potassium thiocyanate as modifier." Fresenius' journal of analytical chemistry FIELD Publication Date:2001 Jul 370(6): 744-51.

An electrothermal vaporization-inductively coupled plasma-mass spectrometric (ETV-ICP-MS) method based on selective volatilization of cesium with KSCN as modifier has been developed for determination of radiocesium, i.e. 135Cs and 137Cs, in the presence of isobaric barium. A 10,000 times excess of barium, which was volatilized at a temperature of 1,100 degrees C, resulted only in a 1% signal increase in the signal of mass 135 amu. The recommended concentration of KSCN is 0.3 mM, and pretreatment and volatilization temperatures are 400 degrees C and 1,100 degrees C, respectively. A ramp time of 1 s is recommeded for the volatilization step. The achieved limit of detection for 135Cs is 0.2 pg/mL (10 microBq/mL) and 4 fg (0.2 microBq) absolute for a sample volume of 20 microL. This means a limit of detection for 137Cs of 0.2 pg/mL (0.6 Bq/mL) and of 4 fg (0.01 Bq) absolute. Signal variations of 135Cs and 137Cs, respectively, in spiked samples with various matrices were investigated.

APP* 16) Friese, K. C., K. H. Grobecker, et al. "Development of an electrothermal vaporization ICP-MS method and assessment of its applicability to studies of the homogeneity of reference materials." Fresenius' journal of analytical chemistry FIELD Publication Date:2001 Jul 370(5): 499-507.

A method has been developed for measurement of the homogeneity of analyte distribution in powdered materials by use of electrothermal vaporization with inductively coupled plasma mass spectrometric (ETV-ICP-MS) detection. The method enabled the simultaneous determination of As, Cd, Cu, Fe, Mn, Pb, and Zn in milligram amounts of samples of biological origin. The optimized conditions comprised a high plasma power of 1,500 W, reduced aerosol transport flow, and heating ramps below 300 degrees C s(-1). A temperature ramp to 550 degrees C ensured effective pyrolysis of approximately 70% of the organic compounds without losses of analyte. An additional hold stage at 700 degrees C led to separation of most of the analyte signals from the evaporation of carbonaceous matrix compounds. The effect of time resolution of signal acquisition on the precision of the ETV measurements was investigated. An increase in the number of masses monitored up to 20 is possible with not more than 1% additional relative standard deviation of results caused by limited temporal resolution of the transient signals. Recording of signals from the nebulization of aqueous standards in each sample run enabled correction for drift of the sensitivity of the ETV-ICP-MS instrument. The applicability of the developed method to homogeneity studies was assessed by use of four certified reference materials. According to the best repeatability observed in these sample runs, the maximum contribution of the method to the standard deviation is approximately 5% to 6% for all the elements investigated.

APP* 17) Okamoto, Y. "Generation of a methylbismuth species and its electrothermal vaporization for the determination of bismuth by inductively coupled plasma mass spectrometry." Fresenius' journal of analytical chemistry FIELD Publication Date:2000 Feb 366(3): 309-11.

Inorganic bismuth(III) was converted to a methylbismuth species, possibly trimethylbismuth, by a thermochemical reaction with methyllithium. It instantly vaporized and was then introduced into the ICP ion source to detect the 209Bi signal. Utilizing an exchangeable small sample cuvette placed on the tungsten boat furnace for the reaction was very favorable from the viewpoints of easy handling, no memory effect, and maintenance of furnace conditions. In this manner, the analyte was vaporized at quite a low temperature (150 degrees C). The detection limit (3sigma) was 0.13 pg of bismuth and the precision in relative standard deviation for 5.0 pg of bismuth was determined to be 3.8% (n = 7).

APP* 18) Uggerud, H. and W. Lund "Determination of arsenic by inductively coupled plasma mass spectrometry--comparison of sample introduction techniques." Fresenius' journal of analytical chemistry FIELD Publication Date:2000 Sep-Oct 368(2-3): 162-5.

A comparison is made of four sample introduction techniques for the determination of As by inductively coupled plasma mass spectrometry. The techniques studied were 1) flow injection with pneumatic nebulization (FIA-PN), 2) direct electrothermal vaporization (ETV), 3) continuous hydride generation (HG) and 4) hydride generation with in situ trapping followed by electrothermal vaporization (HG-ETV). It was found that FIA-PN and ETV gave similar detection limits in concentration units (about 20 pg mL(-1)), although ETV had a much lower absolute detection limit (0.2 pg). Sample introduction by hydride generation gave an inferior detection limit (100-200 pg mL(-1)), also in combination with in situ trapping and ETV, owing to the blank signal from traces of As in NaBH4 which is difficult to eliminate. The results indicate that the more elaborate sample introduction techniques based on ETV and HG may not offer significant advantages compared to normal solution nebulization for the determination of As in simple sample matrices such as natural fresh waters, where matrix removal is not required.

APP* 19) Okamoto, Y. "Direct determination of lead in biological samples by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) after furnace-fusion in the sample cuvette-tungsten boat furnace." Fresenius' journal of analytical chemistry FIELD Publication Date:2000 Jun 367(3): 300-5.

The newly conceived electrothermal vaporization (ETV) system using a tungsten boat furnace (TBF) sample cuvette was designed for the direct analysis of solid samples with detection by inductively coupled plasma mass spectrometry (ICP-MS). Into this small sample cuvette, a solid mixture of the biological samples and diammonium hydrogenphosphate powder as a fusion flux was placed and situated on a TBF. Tetramethylammonium hydroxide solution was added to the mixture. After the on-furnace digestion had been completed, the analyte in the cuvette was vaporized and introduced into the ICP mass spectrometer. The solid samples were analyzed by using a calibration curve prepared from the aqueous standard solutions. The detection limit was estimated to be 5.1 pg of lead, which corresponds to 10.2 ng g(-1) of lead in solid samples when a prepared sample amount of 1.0 mg was applied. The relative standard deviation for 8 replicate measurements obtained with 100 pg of lead was calculated to be 6.5%. The analytical results for various biological samples are described.

APP* 20) Miller, R. T., P. Martasek, et al. "Zinc content of Escherichia coli-expressed constitutive isoforms of nitric-oxide synthase. Enzymatic activity and effect of pterin." Journal of biological chemistry FIELD Publication Date:1999 May 21 274(21): 14537-40. FIELD Reference Number:

Recently, we obtained x-ray crystallographic data showing the presence of a ZnS4 center in the structure of Escherichia coli-expressed bovine endothelial nitric-oxide synthase (eNOS) and rat neuronal nitric-oxide synthase (nNOS). The zinc atom is coordinated by two CXXXXC motifs, one motif being contributed by each NOS monomer (cysteine 326 through cysteine 331 in rat nNOS). Mutation of the nNOS cysteine 331 to alanine (C331A) results in the loss of NO. synthetic activity and also results in an inability to bind zinc efficiently. Although prolonged incubation of the C331A mutant of nNOS with high concentrations of L-arginine results in a catalytically active enzyme, zinc binding is not restored. In this study, we investigate the zinc stoichiometry in wild-type nNOS and eNOS, as well as in the C331A-mutated nNOS, using a chelation assay and electrothermal vaporization-inductively coupled plasma-mass spectrometry. The data reveal an approximate 2:1 stoichiometry of heme to zinc in (6R)-5,6,7,8-tetrahydro-L-biopterin-replete, wild-type nNOS and eNOS and show that the reactivated C331A mutant of nNOS has a limited ability to bind zinc. The present study substantiates that the zinc in NOS is structural rather than catalytic and is important for maintaining optimally functional, enzymatically active, constitutive NOSs. Support, Non-U.S. Gov't; Support, U.S. Gov't, P.H.S.

FUN* 21) Mahoney, P. P., S. J. Ray, et al. "Preliminary investigation of electrothermal vaporization sample introduction for inductively coupled plasma time-of-flight mass spectrometry." Analytical chemistry FIELD Publication Date:1999 Apr 1 71(7): 1378-83.

The coupling of an electrothermal vaporization (ETV) apparatus to an inductively coupled plasma time-of-flight mass spectrometer (ICP-TOFMS) is described. The ability of the ICP-TOFMS to produce complete elemental mass spectra at high repetition rates is experimentally demonstrated. A signal-averaging data acquisition board is employed to rapidly record complete elemental spectra throughout the vaporization stage of the ETV temperature cycle; a solution containing 34 elements is analyzed. The reduction of both molecular and atomic isobaric interferences through the temperature program of the furnace is demonstrated. Isobaric overlaps among the isotopes of cadmium, tin, and indium are resolved by exploiting differences in the vaporization characteristics of the elements. Figures of merit for the system are defined with several different data acquisition schemes capable of operating at the high repetition rate of the TOF instrument. With the use of both ion counting and a boxcar averager, the dynamic range is shown to be linear over a range of at least 6 orders of magnitude. A pair of boxcar averagers are used to measure the isotope ratio for silver with a precision of 1.9% RSD, despite a cycle-to-cycle precision of 19% RSD. Detection limits of 10-80 fg are calculated for seven elements, based upon a 10-microL injection.

APP* 22) Lee, K. H., S. H. Liu, et al. "Determination of cadmium and lead in urine by electrothermal vaporization isotope dilution inductively coupled plasma mass spectrometry." Analyst FIELD Publication Date:1998 Jul 123(7): 1557-60.

Electrothermal vaporization isotope dilution inductively coupled plasma mass spectrometry (ETV-ID-ICP-MS) was applied to the determination of Cd and Pb in urine samples. The isotope ratios for each element in each analytical run were calculated from the peak areas of each isotope. A relatively low vaporization temperature was used, which separated the analyte from the major matrix components and improved the ion signals of Cd and Pb significantly. Various chemical modifiers were tested to obtain the best signal of Cd and Pb. After preliminary studies, 1% HNO3 was added to the samples as the chemical modifier. The ETV-ID-ICP-MS method was applied to the determination of Cd and Pb in freeze-dried urine reference material NIST SRM 2670 and several fresh urine samples. The results for NIST SRM 2670 agreed satisfactorily with the certified values. The results for other samples obtained by isotope dilution and the method of standard additions agreed satisfactorily. The detection limits were 0.02 and 0.005 ng ml-1 for Cd and Pb, respectively. The precision between sample replicates was better than 11% for all determinations. Human; Support, Non-U.S. Gov't

APP* 23) Michalke, B. and P. Schramel "Selenium speciation in human milk with special respect to quality control." Biological trace element research FIELD Publication Date:1997 Winter 59(1-3): 45-56.

Selenium- (SE) organo compounds of pooled human milk (7th-14th d after delivery) were separated by centrifugation and subsequent size-exclusion chromatography (SEC) as described in ref. (1). The SEC fractions were used for Se determinations by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) in parallel to identification procedures of the organic ligands by two different capillary zone electrophoresis (CZE) methods. Further, the combination of isotachophoresis- (ITP) CZE with ETV-ICP-MS was used for final identifications. Mass balances were carried out at each analytical step for quality assurance. Reinjection experiments were performed to check the stability of Se-organo compounds during the analytical procedure. These quality-control experiments showed that no species transformations took place during the analytical procedure, and the Se species were native in human milk. The identification and quantification of organic ligands were clear and resulted in values of 2 (+/- 0.2) mg/L GSH/GSeH, 2 (+/- 0.22) mg/L cystamine/Se-cystamine, 4 (+/- 0.4) mg/L cystine/ Se-cystine, and 1 (+/- 0.18) mg/L methionine/Se-methionine. Unfortunately, a differentiation between sulfur (S) and Se analogs was not possible with the applied CE methods. The Se values per organic ligand were determined as 2.5 (+/- 0.23) mg/L associated with GSH (as GSeH), 3.1 (+/- 0.31) mg/L associated with cystamine (as Se-cystamine), 5.2 (+/- 0.4) mg/L associated with cystine (as Se-cystine), and 1 (+/- 0.1) mg/L associated with methionine (as Se-methionine). Female; Human

APP* 24) Grunke, K., H. J. Stark, et al. "Determination of traces of heavy metals (Mn, Cu, Zn, Cd and Pb) in microsamples of teeth material by ETV-ICP-MS." Analytical and bioanalytical chemistry FIELD Publication Date:1996 Mar 354(5-6): 633-5.

Heavy metal levels in tooth compartments would appear to be a suitable indicator of long-term exposure. A method has been developed to assess the heavy metal levels (Mn, Cu, Zn, Cd and Pb) in tooth compartments like dentin and enamel. For the simultaneous determination of these elements in small dentin sample amounts (in some cases less than 1 mg) inductively coupled plasma mass spectrometry with electrothermal vaporization was the method of choice. Sample preparation, method development and first results of the application of the method for the analysis of tooth compartments have been described. Variation in the elemental concentrations depending on the kind of tooth and the sampling position have been observed. The method is useful for epidemiological studies of the heavy metal exposure of children.

APP* 25) Wei, W. C. and M. H. Yang "Determination of phosphorus and arsenic in trichlorosilane by electrothermal vaporization-inductively coupled plasma mass spectrometry with prior concentration by cuprous chloride." Analytical and bioanalytical chemistry FIELD Publication Date:1995 Sep 353(2): 167-70. FIELD Reference Number: FIELD Journal Code:101134327 FIELD Call Number:.

A method for the determination of trace impurities of phosphorus and arsenic in trichlorosilane with prior separation followed by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) has been developed. The preconcentration of the analytes from the sample matrix was made by adding cuprous chloride to a 10 mL trichlorosilane sample for the formation of non-volatile compounds with the elements of interest. Upon evaporation of trichlorosilane, the analytes retained in the residue were then determined in the presence of copper as modifier by ETV-ICP-MS. The dual role of cuprous chloride both in the preconcentration and instrumental determination was investigated and discussed. By meticulous control of experimental conditions, limits of detection for these two elements as low as sub-ng/g can be achieved. The method was applied to the determination of phosphorus and arsenic in a commercially available trichlorosilane sample.

APP* 26) Michalke, B. and P. Schramel "Hyphenation of capillary electrophoresis to inductively coupled plasma mass spectrometry as an element-specific detection method for metal speciation." Journal of chromatography. A FIELD Publication Date:1996 Oct 25 750(1-2): 51-62.

A stepwise development for the use of capillary electrophoresis and inductively coupled plasma mass spectrometry (ICP-MS) for speciation investigations is presented. The high resolution power of CE is used for the separation of metal species, whereas ICP-MS is taken for element-specific detection with low detection limits. This contribution starts with an off-line combination of both instruments. Separation and identification of species in model solutions and real samples are shown by scanning UV detection at the CE unit with subsequent metal quantification in peak related fractions, applying electrothermal vaporization ICP-MS. Finally, first separations are demonstrated, using the on-line hyphenation with a laboratory-made nebulizer. Here, standard solutions are separated and monitored by UV and ICP-MS. Stability of electrical current during nebulization was checked and a possibly interfering suction flow was estimated. After optimization sufficient electropherograms were obtained. Advantages and problems are discussed for both modes. Human

APP* 27) McKay, K. "New techniques in the pharmacokinetic analysis of cancer drugs. II. The ultratrace determination of platinum in biological samples by inductively coupled plasma-mass spectrometry." Cancer surveys FIELD Publication Date:1993 17: 407-14.

The use of ICP-MS and its various sample introduction techniques has great potential in extending the time scale of study for the pharmacokinetics of platinum containing anti-tumour drugs. Electrothermal vaporization ICP-MS can be used to measure very small samples with very low concentrations. Speciation studies of platinum in tissues can be carried out with HPLC-ICP-MS over longer time periods. Finally, LA-ICP-MS is potentially useful for studying the spatial distribution of platinum in tissues and tumours.

APP* 28) Whittaker, P. G., T. Lind, et al. "Inductively coupled plasma mass spectrometric determination of the absorption of iron in normal women." Analyst FIELD Publication Date:1989 Jun 114(6): 675-8.

The determination of iron isotope ratios in blood, without prior sample preparation, using inductively coupled plasma mass spectrometry (ICP-MS) with sample introduction by electrothermal vaporisation (ETV) is described. Following oral administration of 5 mg of enriched 54FeSO4 and intravenous administration of 200 micrograms of 57FeSO4 to non-pregnant women, the 54Fe: 56Fe and 57Fe: 56Fe isotope ratios in serum were measured reliably within 20 min per sample in quintuplicate. Changes in the fractional absorption of iron during human pregnancy could therefore be assessed.

APP* 29) Newman, R. A., S. Osborn, et al. "Determination of tellurium in biological fluids by means of electrothermal vaporization-inductively coupled plasma-mass spectrometry (ETV-ICP-MS)." Clinica chimica acta; international journal of clinical chemistry FIELD Publication Date:1989 Feb 15 179(2): 191-6.

REV* 30) Park, C. J. and G. E. M. Hall (1986). "Electrothermal vaporization as a means of sample introduction into an inductively coupled plasma mass spectrometer: a preliminary report of a new analytical technique." Paper - Geological Survey of Canada 86-1B: 767-73.

Development work in the application of electrothermal vaporization as a means of sample introduction into an inductively coupled plasma mass spectrometer is described. Preliminary results obtained in the anal. of various matrixes for Mo, W, Tl, and Fe are illustrated by measurement of isotope ratios, and the potential and usefulness of isotope diln. measurement is demonstrated. The anticipated value of such a technique is expected to be seen in the direct anal. of seawater at and below the part-per-billion level and in the detn. of elements in geol. materials whose natural abundance is below 1 mg g-1. Relative std. deviations in the range of 1-2% at the picogram level are obtained.

APP* 31) Robinson, R., M. Bell, et al. (1987). A comparison of trace level concentrations for silver, arsenic, barium, cadmium, and lead in drinking waters obtained by inductively coupled plasma-mass spectrometry and electrothermal-vaporization atomic absorption spectroscopy, Los Alamos Natl. Lab.,Los Alamos,NM,USA. FIELD URL:: 45 pp.

Data obtained by inductively coupled plasma-mass spectrometry (ICP-MS) and electrothermal-vaporization at. absorption spectroscopy (ETVAA), for concn. of Ag, As, Ba, Cd, and Pb in drinking water specimens, spiked analyte recoveries, and control samples are compared. The goal was to obtain EPA approval for the ICP-MS as an alternate anal. technique. Similar concns. for those metals in the natural waters were obtained by both methods. Several of the spike recoveries and control sample recoveries, however, varied significantly. Those recoveries indicated a greater level of confidence for the As and Ba anal. data obtained using the ICP-MS method. In addn., ICP-MS has rigid multielement anal. technique capabilities with limits of quantification and data confidence comparable to those of ETVAA. Those multielement capabilities and the relative ease of obtaining data make ICP-MS the preferred anal. technique.

APP* 32) Date, A. R. and Y. Y. Cheung (1987). "Studies in the determination of lead isotope ratios by inductively coupled plasma mass spectrometry." Analyst (Cambridge, United Kingdom) 112(11): 1531-40.

The application of inductively coupled plasma-mass spectrometry to the detn. of lead isotope ratios in geol. materials is described. Data presented for a series of lead mineral concs. are compared with ref. values obtained by conventional solid source thermal ionization mass spectrometry. The simultaneous detn. of lead isotope ratios and trace elements is carried out in a rapid anal. mode. The application of an electrothermal vaporization technique for small soln. aliquots is described. Lead isotope ratio data for the

United States Geol. Survey std. ref. silicate rock BCR-1, obtained without sepn. of lead from the matrix, are compared with previously published values obtained after sepn.

APP* 33) Park, C. J. and G. E. M. Hall (1987). "Analysis of geological materials by inductively coupled plasma mass spectrometry with sample introduction by electrothermal vaporization. Part 1. Determination of molybdenum and tungsten." Journal of Analytical Atomic Spectrometry 2(5): 473-80.

The detn. of molybdenum and tungsten at low levels in geol. materials by isotope diln. inductively coupled plasma mass spectrometry with sample introduction by electrothermal vaporization is reported. This technique eliminates the need for the laborious, time-consuming sepn. steps assocd. with sample introduction by conventional nebulization which not only impede productivity but also introduce analyte contamination. Anal. by isotope diln. is shown to be necessary in order to achieve precision values of less than 5% relative std. deviation in the measurement step. Memory effects are evident in the detn. of W due to carbide formation during ashing, in spite of the presence of Freon gas during vaporization. Detn. limits of 0.03 mg g-1 for Mo and 0.06 mg g-1 for W are obtained. Results for std. ref. materials analyzed by this procedure compared well with literature values.

APP* 34) Park, C. J., J. C. Van Loon, et al. (1987). "Design and optimization of an electrothermal vaporizer for use in plasma source mass spectrometry." Canadian Journal of Spectroscopy 32(2): 29-36.

An electrothermal vaporizer (ETV) was developed for sample introduction into a plasma for inductively coupled plasma-source mass spectrometry. The device was designed with due consideration of flow dynamics and gas temp. distributions within the system. In this regard, to prevent sample loss on glass and tubing surfaces, a 5-mL vol. exists between the top filament surface and the inside surface of the glass envelope to allow condensation of the aerosol into microparticulates therein. The ETV is oriented vertically and the carrier gas is injected tangentially to spiral the sample upwards and to minimize sample loss on glass and tubing surfaces. Transport efficiency depends on the element but is > 80% (compared to < 20% for most previously reported devices) for all the elements studied (Cd, Pb, Cu, Fe, Ni).

APP* 35) Park, C. J., J. C. Van Loon, et al. (1987). "Sample analysis using plasma source mass spectrometry with electrochemical sample introduction." Analytical Chemistry 59(17): 2191-6.

A detailed procedure is outlined for the anal. of practical samples by plasma mass spectrometry with an electrothermal vaporizer for sample introduction. Results were obtained for the detns. of As, Cu, Mn, Pb, Rb, V, Zn, and Ag in National Bureau of Stds. (NBS) orchard leaves (SRM 1571) and oyster tissue (SRM 1566) and of Pb in a human blood sample used in an interlab. comparison study. Simultaneous multimass anal. is demonstrated for Pb isotopes in NBS 981. Generally, the results agreed with certified values. Abs. detection limits at the picogram level were obtained that are 10- to 1000-fold better than those reported for inductively coupled plasma at. emission spectrometry and 10-fold better than those obtained by nebulization with inductively coupled plasma mass spectrometry. Relative std. deviations ranged from 2% to 13%.

APP* 36) Hall, G. E. M., J. C. Pelchat, et al. (1988). "Relative merits of two methods of sample introduction in inductively coupled plasma mass spectrometry: electrothermal vaporization and direct sample insertion." Journal of Analytical Atomic Spectrometry 3(6): 791-7.

Two alternative sample-introduction techniques to conventional nebulization in anal. by inductively coupled plasma mass spectrometry, namely, electrothermal vaporization and wire loop direct sample insertion, are compared. Both enjoy certain advantages over pneumatic nebulization; these include a low sample vol. requirement, higher sensitivity and reduced oxide and hydroxide formation. Although introduction by direct sample insertion is not subject to loss of analyte during transport to the plasma, it is less applicable to the anal. of solns. with significant concns. of salt (higher than 1%) than electrothermal vaporization is. Performances are compared in the anal. of the river water ref. material SLRS-1, directly for Mn, As and Pd and for Au after extn. of the chloride complex AuCl4-into iso-Bu Me ketone. Impurities of Fe, Mo and Ni in the wire loop precluded their detn. by direct sample insertion.

APP* 37) Park, C. J. and G. E. M. Hall (1988). "Analysis of geological materials by inductively coupled plasma mass spectrometry with sample introduction by electrothermal vaporization. Part 2. Determination of thallium." Journal of Analytical Atomic Spectrometry 3(2): 355-61.

The application of inductively coupled plasma mass spectrometry with sample introduction by electrothermal vaporization to the detn. of Tl in geol. materials was studied. Two commonly used decompn. procedures, both employing HF and oxidizing acids but one also incorporating fusion of the residue with LiBO2, were tested. Good accuracy and precision were achieved in the direct anal. of the acid leachates, as demonstrated by the results for international ref. materials. A detection limit of 9 ng g-1 of Tl was obtained, with an av. precision of 4% relative std. deviation in the range 5-1400 ng g-1. However, a spectral interference caused by a high concn. of Pb necessitated sepn. of Tl by the extn. into iso-Bu Me ketone prior to anal. for those samples whose Pb contents were >500 mg g-1.

APP* 38) Gregoire, D. C. (1988). "Determination of platinum, palladium, ruthenium, and iridium in geological materials by inductively coupled plasma mass spectrometry with sample introduction by electrothermal vaporization." Journal of Analytical Atomic Spectrometry 3(2): 309-14.

The application of electrothermal vaporization as a means of sample introduction for the detn. of some of the platinum group metals by inductively coupled plasma mass spectrometry (ICP-MS) has been studied. Rock powders were decompd. using the nickel sulfide fire assay technique. Samples of 10 g were preconcd. to a final soln. vol. of 0.5 mL. Sample solns. were analyzed for the platinum group elements using the method of stable isotope diln. Optimum plasma operating conditions were different for the detn. of the platinum group metals when dry aerosols were introduced into the plasma or when soln. nebulization was used. Pyrolytic graphite coated cryst. filaments were used for the vaporization of acidic sample solns. The addn. of 500 ppm of Ni as nitrate resulted in up to a ten-fold enhancement in the analyte ion count rate. A smaller effect was obsd. for Cu for which the nitrate was more effective than the chloride for producing signal enhancements. The addn. of 500 ppm of Ni as nitrate was used as a matrix modifier for the detn. of the platinum group elements in geol. materials. Quant. anal. data for a series of ultramafic rock samples detd. by neutron activation anal., soln. nebulization ICP-MS and electrothermal vaporization ICP-MS compared well with one another.

FUN* 39) Darke, S. A., C. J. Pickford, et al. (1989). "Study of electrothermal vaporization sample introduction for plasma spectrometry." Analytical Proceedings 26(11): 379-81.

The relative merits of an ETV (electrothermal vaporization) system were investigated for the introduction of samples into the ICP (inductively coupled plasma) as solns. and slurries. The results show that the sample vapor produced can be analyzed by both ICP-OES (optical emission spectrometry) and ICP-MS (mass spectrometry). The use of various matrix modifiers was assessed for improving the transport of lead to the plasma. An improved signal/background was obtained by using 1000 mg mL-1 phosphate soln. as a modifier, but lead transport to the plasma at high temps. was not improved. Improved limits of detection for lead were obtained with the ETV system with both ICP-OES and ICP-MS compared with pneumatic nebulization. Values detd. for lead in fly ash slurries by ETV-ICP-OES and ETV-ICP-MS were in good agreement with those obtained by soln. nebulization ICP-MS. The introduction of NBS fly ash soln. on to the graphite rod caused rapid deterioration of the rod and resulted in high values for lead compared with the certificate value. Methods are being considered to prevent deterioration of the graphite in the presence of acids.

APP* 40) Forster, A. R., R. A. Howard, et al. (1989). Method and apparatus for analysis of material involving electrothermal vaporization and inductively coupled plasma mass spectrometry. U.S. Us, (Shell Oil Co., USA). 11 pp.

Methods and app. are provided for qual. and quant. detn. of constituents of a sample of material. The method preps. the sample for anal. by mixing the sample with a preselected quantity of a preselected material that serves to transport and project the sample. The mixt. may be pyrolyzed and/or injected into a plasma. A spectrometric detection is made of the sample in the plasma. The app. is a modified electrothermal-vaporization furnace, whose sample outlet is connected to the sample inlet of an inductively coupled plasma-mass spectrometer (ICP-MS). An addnl. gas (e.g., O) injection line is provided between the sample outlet of the furnace and the sample inlet of the ICP-MS. Application to biol. samples is indicated.

APP* 41) Dunn, C. E., G. E. M. Hall, et al. (1989). "Platinum-group metals in common plants of northern forests: Developments in analytical methods, and the application of biogeochemistry to exploration strategies." Journal of Geochemical Exploration 32(1-3): 211-22.

All Pt-group metals (PGM) in ashed plant tissues, from an area of Pt ore mineralization in Saskatchewan, were detd. by neutron activation anal. of a NiS fire assay bead. Concns. of ? 1350 ppb Pd, 880 ppb Pt, 49 ppb Rh, 37 ppb Ru, 24 ppb Ir, and 15 ppb Os occur in ashed twigs of black spruce (Picea mariana), indicating that the ratios of PGM uptake are about the same as those occurring in the bedrock. Plants growing on drift-covered diabase, known to have .apprx.100 ppb PGM, contain ?77 ppb Pt in ash, demonstrating the potential value of biogeochem. methods in helping to delineate PGM-contg. zones. Twigs of black spruce, jack pine, and labrador tea appear to be the optimum sample media in this environment. A rapid multi-element neutron activation anal. by direct irradn. of tissue permits detn. of 0.05 ppb Ir in dry material, or 2 ppb Ir in ashed samples. Any detectable Ir probably indicates enrichment of PGM in the substrate. Comparison of several wet-chem. anal. methods indicates that the optimum (cost-effective) technique for detecting 1-2 ppb Pt, Pd, or Rh in 2-g samples of ash is by Te copptn. (following fusion and dissoln.), and anal. by inductively coupled plasma-mass spectroscopy with sample introduction by electrothermal vaporization. However, care must be taken to ensure complete dissoln. of all PGM in the ash.

APP* 42) Matsunaga, H., N. Hirate, et al. (1989). "Determination of trace amounts of uranium and thorium in silicon and silicon dioxide by electrothermal vaporization/ICPMS." Bunseki Kagaku 38(2): T21-T25.

A sensitive and accurate detn. method for ultratrace amts. of U and Th in semiconductor materials such as Si and SiO2 has been investigated by using electrothermal vaporization method (ETV) and inductively coupled plasma mass spectrometry (ICPMS). The electrothermal vaporizer is constructed with an advanced graphite furnace vaporizer and a tantalum tube (0.5 mm thick), which is inserted into a graphite tube. The semiconductor materials are dissolved by a mixt. of HF, HNO3, and H2SO4 then evapd. to fumes. After each residue is dild. to a const. vol. with pure water, U and Th contents are measured by ETV-ICPMS. With this method, the detn. of sub-ppt U and Th in Si crystal, SiO2 powder and quartz glass became possible. The recovery percentages were 93-104%.

APP* 43) Whittaker, P. G., T. Lind, et al. (1989). "Inductively coupled plasma mass spectrometric determination of the absorption of iron in normal women pregnancy." Analyst (Cambridge, United Kingdom) 114(6): 675-8.

The detn. of Fe isotope ratios in blood, without prior sample prepn., using inductively coupled plasma mass spectrometry (ICP-MS) with sample introduction by electrothermal vaporization (ETV) is described. Following oral administration of 5 mg of enriched 54FeSO4 and i.v. administration of 200 mg of 57FeSO4 to nonpregnant women, the 54Fe:56Fe and 57Fe:56Fe isotope ratios in serum were measured reliably within 20 min per sample in quintuplicate. Changes in the fractional absorption of Fe during human pregnancy could therefore be assessed.

APP* 44) Newman, R. A., S. Osborn, et al. (1989). "Determination of tellurium in biological fluids by means of electrothermal vaporization-inductively coupled plasma-mass spectrometry (ETV-ICP-MS)." Clinica Chimica Acta 179(2): 191-6.

The antitumor Te compd. As-101 (ammonium trichloro[dioxoethylene-O,O']tellurate) was added to human plasma or urine and the levels of Te were detd. by ETV-ICP-MS. The lower limits of detection in urine were 2.7 and 7.6 ng/mL and, in plasma, they were 5.7 and 10.3 ng/mL for isotopes 130 and 126, resp.

APP* 45) Hall, R. J. B., M. R. James, et al. (1990). "The feasibility of the use of electrothermal vaporization inductively coupled plasma mass spectrometry for the determination of femtogram levels of plutonium and uranium." Special Publication - Royal Society of Chemistry 85(Plasma Source Mass Spectrom.): 145-54.

An inductively coupled plasma-mass spectrometric method was developed for the detn. of femtogram Pu and U. The elec. vaporization technique was employed for sample introduction which distinctly improved the anal. sensitivity. The method was applied to the ultratrace detn. of plutonium in urine. A limit of detection of 107 atoms was obtained for Pu-242 and Pu-244. The linear range was 5-500 fg Pu. The relative std. deviation was 8% for an injected concn. of 50 fg Pu.

FUN* 46) Dittrich, K., I. Mohamad, et al. (1990). "Introduction of microsamples into plasmas." Special Publication - Royal Society of Chemistry 85(Plasma Source Mass Spectrom.): 18-24.

By the combination of electrothermal vaporization (ETV) with inductively coupled plasma-at. emission spectrometry (ICP-AES) and ICP-mass spectrometry (MS) techniques, sample introduction efficiency, and as a result the abs. detection limits, have been dramatically improved for microsamples, in comparison to normal nebulization techniques. The one step procedure, furnace at. nonthermal excitation spectrometry (FANES), gives much better detection limit for easily and more moderately vaporizable elements than the ETV ICP-AES techniques. The reason for this is the direct vaporization of the sample into the plasma. In addn., when compared to ETV-at. absorption spectrometry (AAS), FANES also offers a strong enhancement due to the degree of ionization in this source. Therefore, it can be recommended to test this technique also in combination with MS detection. An addnl. advantage of this set up should lie in the vaporization, excitation and ionization under vacuum conditions.

APP* 47) Toole, J., A. S. Hursthouse, et al. (1990). "The determination of actinides in environmental samples by ICP-MS." Special Publication - Royal Society of Chemistry 85(Plasma Source Mass Spectrom.): 155-62.

The results presented here illustrate that accurate assays of Pu, U, and Np are achievable in a wide range of environmental matrixes using inductively coupled plasma-mass spectrometry (ICP-MS). Research and development at Scott. Univ. Res. React. Cent., United Kingdom is working towards their simultaneous detn. (including Th) in environmental materials. Improvements in actinide detection limits of about two orders of magnitude by the use of electrothermal vaporization (ETV-ICP-MS) are anticipated, and studies with this add-on facility, in collaboration with VG Elemental, have now commenced. Compared to the alpha spectrometric method, the ICP-MS is simple, fast, and requiring no complicated prior sepn. procedures.

APP* 48) Marshall, J. and J. Franks (1990). "Multielement analysis and reduction of spectral interferences using electrothermal vaporization inductively coupled plasma-mass spectrometry." Atomic Spectroscopy 11(5): 177-86.

A description is given of the exptl. arrangement for the electrothermal vaporization of discrete liq. samples directly into an inductively coupled plasma-mass spectrometer (ICP-MS). The simultaneous detection of 21 elements at part per billion levels is possible using this technique. Specific improvements in detection for phosphorus compared to normal ICP-MS operation are achieved by removal of spectral interference at mass 31 due to the presence of water derived polyat. NOH. Spectral interferences in the detection of vanadium in a hydrochloric acid matrix and titanium in a sulfuric acid matrix are reduced or eliminated.

FUN* 49) Shen, W. L., J. A. Caruso, et al. (1990). "Electrothermal vaporization interface for sample introduction in inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 5(6): 451-5.

An electrothermal vaporization (ETV) device was developed for inductively coupled plasma mass spectrometry by modifying a com. graphite furnace unit. A detailed description of the modifications are presented. The new ETV interface is designed to increase sample transport efficiency by converting analyte vapor into microparticles in the furnace. The characterization and optimization of the device are also discussed. Ten consecutive firings of a 30-pg sample of Pb resulted in a relative std. deviation (RSD) of 4%

peak height and 1.6% RSD of peak-area measurements. The abs. detection limit, detd. by comparing the response obtained for a 3-mL sample of 10 ng mL-1 of Pb soln. in 1% HNO3 with that obtained for blanks contg. 1% HNO3 only, was 10 and 14 fg, for a dwell time of 10 ms, for peak area and peak height, resp. The linear dynamic range for Pb extends over 3 orders of magnitude, from 300 fg to 300 pg.

APP* 50) Shibata, N., N. Fudagawa, et al. (1990). "Vaporization characteristics of rare earth elements in tungsten furnace/ICP-MS." Bunseki Kagaku 39(6): 353-8.

Signal profiles of rare earth elements (REEs) obsd. as the signal-time curves were investigated by inductively coupled plasma mass spectrometry (ICP-MS) using W boat electrothermal vaporization (ETV) device as a sample introduction system. Twenty-microliters of REE std. solns. applied on the W-boat were heated to produce the profiles. Both the Ar-H carrier gas flow rates supplied into the glass chamber and the heating temp. of the W-boat. Signal appearance times and the peak times of REEs were later than those of common metals such as Pb or Co. This suggests that REEs are not easily vaporized on the W-boat. REEs which have higher m.ps. showed profiles with later peak times and more significant memory effects. Thes results indicate that the signal profiles of REEs are dependent on the m.ps. of the elements.

FUN* 51) Tsukahara, R. and M. Kubota (1990). "Some characteristics of inductively coupled plasma-mass spectrometry with sample introduction by tungsten furnace electrothermal vaporization." Spectrochimica Acta, Part B: Atomic Spectroscopy 45B(7): 779-87.

The performance of an inductively coupled plasma-mass spectrometer with an electrothermal vaporizer (ETV) has been investigated as a function of several parameters assocd. with ETV operation. A tungsten ribbon furnace was used as the ETV device. To prevent oxidn. of the furnace material, argon with a small amt. of added hydrogen was supplied as the carrier gas. By lowering the vaporization temp., the greatest signals were obtained at higher flow rates of the carrier gas. The amt. of tungsten evapd. from the furnace material was low enough to avoid matrix effects. Water was removed by drying at 100 Deg for 65 s reduce the formation of ArO, and consequently the detection limit of Fe was improved to 0.3 pg. The detection limits for Co and Pb were 0.02 and 0.008 pg, resp.

APP* 52) Gregoire, D. C. (1990). "Sample introduction techniques for the determination of osmium isotope ratios by inductively coupled plasma mass spectrometry." Analytical Chemistry 62(2): 141-6.

Reported are the relative merits of three sample introduction techniques for the detn. of osmium isotope ratios by inductively coupled plasma mass spectrometry (ICP-MS). These are electrothermal vaporization (ETV), osmium tetroxide vapor generation (VG), and conventional soln. nebulization (SN). When Te was used as a matrix modifier, ETV was 3 orders of magnitude more sensitive (in terms of signal intensity) for osmium detns. than were either SN or osmium tetroxide VG. The sensitivity of SN was increased by a factor of 30 by nebulizing Os as the dissolved tetroxide rather than in its reduced form. Osmium isotope ratios were detd. with a precision of 0.2% relative std. deviation by using soln. nebulization, 0.3% by using vapor generation, and 0.5% by using electrothermal vaporization.

REV* 53) Henry, R. (1991). "Why should I use ICP-MS for multielement environmental analysis?" Proceedings of the Annual ISA Analysis Division Symposium 25(Edmonton Spring Symp., 1991, Pt. 2): 101-15.

A review, with 3 refs., on the use inductively coupled plasma-mass spectrometry (ICP-MS) for multielement environmental anal. covers plasma mol. ions, interface design, instrumentation overview, detection limits, interferences, electrothermal vaporization ICP-MS, and very high resoln. ICP-MS.

APP* 54) Etoh, T., M. Yamada, et al. (1991). "Electrothermal vaporization inductively coupled plasma mass spectrometric (ETV-ICP-MS) determination of impurities in photoresist for very large scale integrated circuit (VLSI)." Analytical Sciences 7(Suppl., Proc. Int. Congr. Anal. Sci., 1991, Pt. 2): 1263-4.

A method was developed for the detn. of Na, Fe, Mn, Ni and Cu in photoresist for VLSI by ETV-ICP-MS. Photoresist samples were dild. 10 times with an ethoxy Et acetate (EEA). The std. addn. method was used for the detn. of impurities. Ashing temp., vaporization temp. and carrier gas flow rate were optimized for impurities and some mol. ions in the photoresist. The anal. results obtained were in good agreement with those obtained by graphite furnace at. absorption spectrometry (GFAAS). The detection limits of Na and Fe in photoresist were 0.06 ppb 0.2 ppb, resp.

REV* 55) Fisher, C. G. (1991). "Where to next? The future role of ICP-MS." Atomic Spectroscopy 12(Spec. Issue): 239-46.

A review with no refs. The developments of Perkin-Elmer instruments for at. absorption spectrometry, progress in inductively coupled plasma (ICP)-at. emission spectrometry and ICP-mass spectrometry for anal. are discussed. The discussion includes mixed gas plasmas, desolvation techniques, projected advances in software for ICP-MS, principal component anal., quality control, slurry sampling electrothermal vaporization, glow discharge and spark ablation, isotopic capabilities of ICP-MS, and the use of ICP-MS for anal. of semiconductor materials, environmental and biol. anal.

APP* 56) Scott, R. D., M. S. Baxter, et al. (1991). "Detection of actinides in environmental samples by inductively coupled plasma mass spectrometry." Analytical Proceedings 28(11): 382-4.

This work has concd. on three main areas: (a) an investigation of the chem. processing which is necessary for the detection of actinides in environmental samples; (b) the detn. of 237Np and a comparison of the results with those obtained by a-spectrometry and neutron-activation anal.; and (c) establishment of detection limits both in conventional liq. nebulization and in electrothermal vaporization.

REV* 57) Borsier, M. (1991). "Hyphenation techniques: recent progress in combination methods using inductively coupled plasma (ICP) sources." Spectra 2000 159((Suppl.)): 5-8.

Coupling various techniques with ICP plasmas enlarges their domain of use. This paper reviews some aspects of these new developments with 12 refs. Spark and laser ablation enable direct introduction of solid into the plasmas and spot anal. Flow injection anal. and electrothermal vaporization are used for microsamples anal. Use of ICP detection for chromatog. is enlarging the possibilities in metal speciation.

APP* 58) Imakita, T., H. Horii, et al. (1991). "Determination of trace amount of bismuth in iron and steel by inductively coupled plasma mass spectrometry with sample introduction by electrothermal vaporization." Tetsu to Hagane 77(11): 1944-50.

The performance of an inductively coupled plasma-mass spectrometer with an electrothermal vaporizer was studied as a function of several parameters assocd. with vaporizer operation. Signal profiles of Bi in some acid solns. were detd. using a pyro-coated graphite tube as the vaporizer device. Signal appearance time of Bi in HNO3 was later than that in HCl, and the signal intensity of Bi in HNO3 was lower than that in HCl. Ni in HNO3 increased the signal intensity of Bi in HCl and in aqua regia. The detection limit at the sub-picogram level, which was 50 times better than that obtained by the nebulization method. The method was also used to detn. Bi content in Fe, and the detection limit was increased 20 times, but the Ni effect was not found.

APP* 59) Ida, I., K. Isobe, et al. (1991). "Application of electrothermal vaporization for inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry." Tetsu to Hagane 77(11): 1936-43.

The use of electrothermal vaporization (ETV) as a means of sample introduction provides a lot of advantages over conventional pneumatic nebulization for inductively coupled plasma at. emission spectrometry (ICP-AES) and mass spectrometry (ICP-MS). Compared with the nebulization method, the ETV system needs smaller sample vol. and higher sample transport efficiency can be attained. Application of the ETV system for ICP-AES made it possible to improve the detection limits of Al, Cr, Cu with sufficient precisions. Vaporization behavior of Cu in the presence of a large excess of Fe considerably depended on the heating program and the amt. of Fe. Copper in pure iron ref. materials were successfully detd. by controlling the heating program and matrix matching of calibration stds. For ICP-MS, spectral interferences arising from water and/or acids in sample soln. were removed with the ETV system. Rapid scan monitoring capability of ICP-MS made it possible to do multielemental anal. Sufficient sensitivity equiv. to the nebulization method was attained for the simultaneous measurement of twenty five elements, but precisions were poor because the signals obtained with the ETV were transient and optimum heating programs were different for each element.

APP* 60) Voellkopf, U., A. Guensel, et al. (1991). "Applications of ICP-MS with sample introduction by electrothermal vaporization and flow injection techniques." Appl. Plasma Source Mass Spectrom., [Sel. Pap. Int. Conf.], 2nd: 162-77.

Flow injection hydride generation sample introduction was used for the inductively coupled plasma-mass spectrometry (ICP-MS) detn. of As, Se, Sb, Hg, and Bi. Optimization and interference studies were performed. The method was applied to ref. samples and seawater. Sensitivity and precision expts. were performed for Mn, Ni, Co, Cu, Rh, In, Pb, and Bi applying optimized single element electrothermal vaporization and spectrometer conditions. The method was applied to a certified ref. sample.

REV* 61) Hulmston, P. and R. C. Hutton (1991). "Analytical capabilities of electrothermal vaporization-inductively coupled plasma-mass spectrometry." Spectroscopy (Duluth, MN, United States) 6(1): 35-8.

A general outline is given of the potential capabilities of electrothermal vaporization (ETV)-inductively coupled plasma-mass spectrometry (ETV-ICP-MS). ETV as a means of sample introduction into an ICP-MS instrument is a relatively new approach to the elemental and isotopic detn. of trace elements that offers rapid, quant., and sensitive anal. of small samples. Operational aspects of the technique are outlined, examples are provided that demonstrate the anal. performance currently attainable, and applications are discussed.

FUN* 62) Shibata, N., N. Fudagawa, et al. (1991). "Electrothermal vaporization using a tungsten furnace for the determination of rare-earth elements by inductively coupled plasma mass spectrometry." Analytical Chemistry 63(6): 636-40.

In electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) using a tungsten furnace, the effect of vaporizing parameters on signals and the performance of the ETV technique in the measurement of rare-earth elements (REEs) were investigated. A mixt. of Ar and H was used as the carrier gas to transport sample materials to the ICP. In a transient signal obsd., the signal appearance time and the peak time of oxide ions (MO+) were earlier than those of singly charged element ions (M+). The MO+/M+ ratio reached the min. at an Ar gas flow rate of 1.0 L min-1. Also, it increased as the heating temp. of the furnace rose, though the rate of increasing decreased with increasing H gas flow rate. The ratios for 11 REEs tested were in a range 10-3 to 10-5, 2 or 3 orders of magnitude smaller than those obtained by the conventional nebulization technique (NEB-ICP-MS). The precision for La was 1-2% at abs. amts. above 1 pg. The detection limits for 14 REEs were 0.0001-0.0006 ng mL-1, 1 order of magnitude better than those obtained by NEB-ICP-MS.

FUN* 63) Imakita, T., H. Horii, et al. (1992). "Determination of trace amounts of bismuth in iron and steel by inductively coupled plasma-mass spectrometry with sample introduction by electrothermal vaporization." Proceedings of the Chemists' Conference 44TH: 44-50.

The performance of an inductively coupled plasma-mass spectrometer with an electrothermal vaporizer (ETV-ICP-MS) has been investigated as a function of several parameters assocd. with ETV operation. Signal profiles of bismuth in some acid solns. were measured using a pyro-coated graphite tube as the ETV device. The signal appearance time of bismuth in nitric acid occurred later than that in hydrochloric acid, and the signal intensity of bismuth in nitric acid was less than that in hydrochloric acid. The use of nickel as a modifier for bismuth in nitric acid increased the intensity to that of bismuth in both hydrochloric acid and in aqua regia. The detection limit at the sub-picogram level was improved by a factor of fifty over that obtained by nebulization with ICP-MS. The method was applied to the detn. of bismuth in iron. A detection limit of 0.01 ppm was obtained, which was a 20-fold increase on that obtained by nebulization with ICP-MS. However, the signal intensity of bismuth in iron soln. was depressed to half that obtained in the absence of iron, and nickel used as a modifier did not improve the sensitivity. Bismuth content was detd. in certified ref. materials of iron dissolved in aqua regia, and the results agreed with the ref. values.

APP* 64) Pinkston, T. L. (1992). "Multi-element determination of trace contaminants in photoresist materials by inductively coupled plasma mass spectrometry." Future Pract. Contam. Control, Proc. Int. Symp. Contam. Control, 11th: 535-40.

Advanced photoresist chems. used in the manuf. of semiconductors are now being produced with extremely low levels of trace metallic impurities. The use of inductively coupled plasma mass spectrometry allows for the rapid anal. of these chems. with sensitivity similar to furnace at. absorption and with minimal sample prepn. Sample introduction methods currently being used include ultrasonic nebulization (USN) and electrothermal vaporization (ETV).

APP* 65) Van Loon, J. C., C. J. Park, et al. (1992). "New sample introduction techniques for ICP-MS." Guangpuxue Yu Guangpu Fenxi 12(3): 59-64.

The most exciting development in trace element anal. is the introduction of plasma-source mass spectrometry. ETV (electrothermal vaporizer) used to vaporize liq. and solid samples into plasma was studied in this paper. The results show that using ETV device results in the detection limit improvement of one of two orders of magnitude compared to conventional nebulization method. The proposed device is suitable for acid digested samples, vol. limited sample, viscous liqs. and solids samples. The ETV also eliminates the interferences from vaporization, acid anions and spectral interference. Fly ash, sediment and liver are analyzed using the proposed app.

FUN* 66) Al-Maawali, S. and C. L. Chakrabarti (1992). "Use of magnesium/palladium chemical modifiers for the determination of voltaile elements by electrothermal vaporization ICP-MS: effect on mass transport efficiency." Spectrochimica Acta, Part B: Atomic Spectroscopy 47B(9): 1123-32.

Vaporization of nanogram quantities of Ag, Sn, Pb with mixed chem. modifier Pd(NO3)2 + Mg(NO3)2 (Pd:Mg mole ratio of 0.228:1) resulted in a five-fold enhancement in peak area sensitivity for these elements in electrothermal vaporization-inductively coupled plasma-mass spectrometry. A smaller enhancement effect was obsd. when the palladium in the above chem. modifier was used in the chloride form. Anal. precision was improved significantly when the above mixed chem. modifier was used. The linearity and the slope of anal. calibration curves were dependent on the presence of concomitant elements. For a single element (without matrix), peak area counts increased much faster than linearly with increased sample mass. However, in the presence of ng quantities of concomitant, the calibration curves increased in slope and became linear. Because the addn. of modifier did not enhance atom formation in graphite-furnace at. absorption spectroscopy, these phenomena were largely attributable to a change in the mass transport efficiency of the sample from the ETV to the argon plasma caused by the presence of matrix elements vaporized with the analyte. The effect of concomitant elements on the linearity of ETV-ICP-MS anal. calibration curves and on the role of matrix components and compn. on the mass transfer efficiency is discussed.

APP* 67) Ruth, K., P. Schmidt, et al. (1992). "ICP-MS applications in silicon semiconductor manufacturing." Spectroscopy (Duluth, MN, United States) 7(9): 36-9.

Advances in the electronic industry toward large-scale integration of semiconductor devices have placed strict demands on the ability to measure and monitor ultratrace levels of impurities. These chem. contaminants, even at part-per-billion levels, can cause elec. component failures and ultimately result in lower yields. Silicon semiconductor manufg. particularly requires cleanliness throughout the entire process. This article describes the use of inductively coupled plasma-mass spectroscopy (ICP-MS) to assess and monitor impurity levels in silicon and cleaning chem. baths during different stages of processing. Here, the ICP-MS instrument is operated in two sample introduction modes - nebulization and electrothermal vaporization - to handle \"problem\" elements and low sample vols. Instrument optimization techniques and capabilities for this application are also discussed.

FUN* 68) Daniels, R. S., D. C. Wigfield, et al. (1992). "Mathematical modeling of atom loss in delivery tubing." Canadian Journal of Chemistry 70(7): 1978-84.

A math. model is presented to establish a relationship between the quantity of trace analyte vapor lost to the surface of delivery tubing and the tubing diam., while in transit between stages of an instrument. Cold-vapor at. absorption spectrometry for mercury, hydride generation techniques, and interfaces like the interface between electrothermal vaporization and inductively coupled plasma mass spectrometry all risk significant analyte loss before measurement. The results of this modeling substantiate the results of limited exptl. work published elsewhere suggesting the use of the smallest possible tubing diam. for the delivery of at. vapor through a tube. This diam. is calculable using Poiseuille's formula. Using this model, kinetic theory, and exptl. data, the sticking probability for mercury on latex tubing is calcd. to be approx. 1.6 * 10-6.

APP* 69) Ulrich, A., W. Dannecker, et al. (1992). "Use of electrothermal vaporization inductively coupled plasma mass spectrometry for single-element and multi-element determinations." Analytical Proceedings 29(7): 284-6.

If ETV-ICP-MS is to be used as a multi-element technique, compromise conditions for ETV temp.-time programs are required. Optimum detection limits, however, are only achieved with single-element ETV parameters and single-ion monitoring ICP-MS conditions. Particularly, elements which are difficult to det. with conventional soln. ICP-MS, such as 56Fe, 32S (oxide interferences) and 75As in chloride matrixes (mol. ion interferences) can be detected with high sensitivity. In this paper the influence of ramp time on the vaporization step, temp.-time program for ETV multielement detn., recovery, precision and reproducibility under multielement conditions, and single-element detns. for interfered elements are discussed.

APP* 70) Ulrich, A., C. Huchulski, et al. (1992). "Use of electrothermal vaporization inductively coupled plasma mass spectrometry for element determinations in complex matrixes, such as sandstone samples." Analytical Proceedings 29(7): 282-4.

The use of electrothermal vaporization-inductively coupled plasma-mass spectrometry (ETV-ICP-MS) for trace element detn. in sandstone samples is presented. The results were compared to those obtained by electrothermal at. absorption spectrometry.

FUN* 71) Gregoire, D. C. (1992). "Electrothermal vaporization for inductively coupled plasma mass spectrometry: new applications in mass spectrometry and graphite furnace atomic absorption spectrometry." Analytical Proceedings 29(7): 276-7.

A comparison is provided for graphite furnace at. absorption spectrometry (GFAAS) and electrothermal vaporization-inductively coupled plasma-mass spectrometry (ETV-ICP-MS) to show how data obtained from both techniques under similar exptl. conditions can be combined to provide new information not evident using either technique in the area of trace metal detn. The application of chem. modifiers in ETV-ICP-MS was discussed.

REV* 72) Hall, G. E. M. (1992). "Inductively coupled plasma mass spectrometry in geoanalysis." Journal of Geochemical Exploration 44(1-3): 201-49.

A review with many refs. Inductively coupled plasma mass spectrometry (ICP-MS) has had a profound effect in the discipline of geoanal. since its com. availability in 1983. In particular, the ability to det. precious metals, rare earth elements (REEs) and refractory elements such as Hf, Ta and W at their natural levels in geol. materials has dramatically improved through the application of this highly sensitive, multielement technique. Its capability to measure individual isotopes was directed mainly towards the Re-Os chronometer pair in ore genesis studies, and to a lesser extent to the quantitation of Pb isotope ratios. The impact of ICP-MS to date in exploration geochem. is reviewed in this paper, together with a description of the instrumentation, the principles of the technique and the procedures suitable for its optimal use. As with every anal. technique, ICP-MS suffers from interferences; although the degree of spectral interference is lower than in ICP at. emission spectrometry (ICP-AES), the opposite is true in the case of matrix-induced effects. Its intolerance towards solns. contg. high concns. of dissolved solids (>0.2%) has fostered research into modes of sample introduction other than conventional nebulization. Applications of alternate means of introduction based upon electrothermal vaporization, laser ablation, slurry nebulization and flow injection are discussed here. Waters are an ideal medium for anal. by ICP-MS, though there are as yet only a few studies examg. the potential use of this sample type in geochem. As happened in the 1980s with the complementary technique of ICP-AES, the 1990s will see the establishment of ICP-MS as a rugged, efficient anal. tool in prodn.-oriented labs. together with continuing research into design improvements and new applications.

APP* 73) Shibata, N., N. Fudagawa, et al. (1992). "Determination of trace metals in potassium hydrogen phthalate by inductively coupled plasma mass spectrometry." Analytica Chimica Acta 265(1): 93-101.

Metal impurities contained in high-purity potassium hydrogen phthalate reagents were detd. by inductively coupled plasma mass spectrometry (ICP-MS) with sample introduction by electrothermal vaporization (ETV). The impurities were sepd. from the matrix constituents by ion-exchange sepn. using a Chelex-100 resin before measurement in order to minimize the effect of spectroscopic interferences peculiar to ICP-MS. Ion exchange-ETV-ICP-MS yielded low detection limits in the range 1-10 ng g-1 for eight elements, which were one or two orders of magnitude better than those obtained by conventional nebulization (NEB) ICP-MS. The anal. results for five kinds of potassium hydrogen phthalate reagents agreed satisfactorily with those obtained by direct NEB-ICP-MS and/or ETV-ICP-MS.

FUN* 74) Ediger, R. D. and S. A. Beres (1992). "The role of chemical modifiers in analyte transport loss interferences with electrothermal vaporization ICP-mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 47B(7): 907-22.

A modification of a com. at. absorption graphite furnace was used as a sampling cell for electrothermal vaporization inductively coupled plasma-mass spectrometry (ETV-ICP-MS). The characteristics of four chem. modifiers used with this ETV-ICP-MS system were evaluated for a suite of 20 analyte elements. Sensitivity enhancements due to presence of the modifiers were obsd. for all elements. A given quantity of modifier resulted in greater relative enhancements for small analyte amts. than for large analyte amts. Enhancements were similar for elements of differing volatilities and chem. behavior. This characteristic led to the conclusion that the modifiers acted primarily as phys. carriers of vaporized analyte that would otherwise condense on cool surfaces within the ETV cell and on the transport line between the cell and the ICP. The function of modifiers as phys. carriers of analyte elements may become as important for ETV-ICP-MS as their traditional graphite furnace at. absorption role as chem. active reagents. For ETV-ICP-MS devices that exhibit analyte transport loss, modifiers are likely to be a necessary ingredient to successful quant. results for analyses in which the stds. have differing compns. than the samples.

REV* 75) Gregoire, D. C., M. Lamoureux, et al. (1992). "Electrothermal vaporization for inductively coupled plasma mass spectrometry and atomic absorption spectrometry: symbiotic analytical techniques." Journal of Analytical Atomic Spectrometry 7(4): 579-85.

New techniques have been developed for investigating fundamental phenomena occurring during electrothermal vaporization (ETV) as applied to at. absorption spectrometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS). The different nature of electrothermal AAS (ETAAS) and ETV-ICP-MS data make possible the melding of information from both techniques in order to differentiate solid-phase and gas-phase chem. reactions leading to vaporization and atomization and elucidate the mechanism of matrix interferences and the chem. involved in chem. modification. The significance of chem. modification for ETV-ICP-MS is demonstrated and the use of ETV-ICP-MS in assisting ETTAS for rapid method development is shown. The importance of mass transport effects in ETV-ICP-MS is demonstrated, which indicates that knowledge of the phys. and chem. form of the analyte and matrix components is important to the practical application of ETV-ICP-MS to chem. anal. Nonspectroscopic or matrix interferences in ETV-ICP-MS are more severe than in soln. nebulization ICP-MS.

REV* 76) Baumann, H. (1992). "Solid sampling with inductively coupled plasma-mass spectrometry - a survey." Fresenius' Journal of Analytical Chemistry 342(12): 907-16.

This survey presents the approaches to solid sample introduction with inductively coupled plasma-mass spectrometry (ICP-MS), including electrothermal vaporization, direct sample insertion, laser ablation, arc nebulization, and slurry nebulization. The main characteristics of these sample introduction techniques with regard to their combination with ICP-MS are discussed and examples of applications are given. The anal. aspects of these relatively new techniques are critically evaluated.

APP* 77) Voellkopf, U., M. Paul, et al. (1992). "Analysis of solid samples by ICP-mass spectrometry." Fresenius' Journal of Analytical Chemistry 342(12): 917-23.

ICP-mass spectrometry is typically used as a technique for very rapid multielement anal. at trace and ultra-trace levels of solns. by continuous sample aspiration and nebulization. However, ICP-MS is well suited to be used as a detector for other sample introduction devices. For the anal. of solid samples laser sampling and electrothermal vaporization accessories may be used as sample introduction devices for ICP-MS. Laser sampling permits the anal. of many different types of solid materials. For solid sampling ETV-ICP-MS anal. it is of advantage to reduce the sample to a fine powder prior to anal. For automated anal. powders may be introduced as slurries into the graphite furnace by means of a slurry sampling device. Since appropriate certified solid ref. materials are not always available for calibration, or since they are not certified for all analyte elements of interest, the analyses discussed in this contribution were performed semiquant. The instrument response function was established using ref. materials which were similar in their compn. to the samples. The results of semiquant. bulk analyses of glass (NIST 612) and geol. material (USGS GXR-3) by laser sampling ICP-MS are in good agreement with the certified values. The concns. of the analytes detd. in the glass sample were in the range of 10 mg/g to 80 mg/g. The lowest analyte concn. in the geol. sample was 0.4 mg/g (Eu) and the highest was approx. 186 mg/g (Fe). The precision achieved was in the order of 5% to 15%. Laser sampling ICP-MS is not only suitable to bulk anal. but also to analyses where spatial information is required. As an example for such an application the detn. of Pb in a wine bottle cork stopper is discussed. The slurry sampling technique was used for the semiquant. anal. of NIST coal ref. samples by electrothermal vaporization ICP-MS. The accuracy achieved with this approach was within a factor of +-2 of the ref. values.

FUN* 78) Shibata, N., N. Fudagawa, et al. (1992). "Effects of hydrogen mixed with argon carrier gas in electrothermal vaporization-inductively coupled plasma-mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 47B(4): 505-16.

In inductively coupled plasma-mass spectrometry with sample introduction by tungsten furnace electrothermal vaporization, the effects of adding hydrogen to the argon carrier gas on the signals of background ions (Ar+, ArH+, N+, O+, OH+) and analyte ions (In+, Tl+, Pb+, Ag+, Bi+, Te+) were investigated. These ion signals increased as the flow rate of hydrogen was increased, and the signal enhancement rates were dependent on the ionization potentials of the test species. An optical fiber system was used to obtain information on the electron no. d. (ne) and excitation temp. (Tex) at the interface region between the sampling and skimmer cones. The values of ne in the interface plasma were of the order of 1013 cm-3 and those of Tex were about 5400 K, though these values may reflect the characteristics of the barrel shock. Hydrogen addn. caused a rise in Tex and an increase in ne at the interface region. This results in an enhanced ionization of the analytes. An increase in the ion species like Ar+ and ArH+ at the interface region may also promote the ionization through collisions or charge transfer.

FUN* 79) Byrne, J. P., C. L. Chakrabarti, et al. (1992). "Mechanisms of chloride interferences in atomic absorption spectrometry using a graphite furnace atomizer investigated by electrothermal vaporization inductively coupled plasma mass spectrometry. Part 1. Effect of magnesium chloride matrix and ascorbic acid chemical modifier on manganese." Journal of Analytical Atomic Spectrometry 7(2): 371-82.

The interference by magnesium chloride with the atomization of manganese in electrothermal at. absorption spectrometry (ETAAS) has been investigated using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). The ETV-ICP-MS allows the direct observation of the loss of manganese during the charring step, and thereby allows differentiation between the manganese loss during charring and the loss due to formation of mol. species during atomization. The mechanism of interference by magnesium chloride is dependent on the charring temp. At temps. above 700 DegC, the manganese is lost during charring; this loss occurs as the magnesium chloride matrix undergoes hydrolytic decompn., and the manganese is carried away from the graphite furnace with the hydrogen chloride gas generated by the hydrolysis reaction. At charring temps. lower than 700 DegC the suppression of manganese at. absorption signal is due to vapor-phase interference caused by formation of manganese chloride during atomization. The addn. of ascorbic acid, as a chem. modifier, removes interferences in both the higher and the lower charring temp. regions. The results obtained by ETV-ICP-MS show that, for charring temps. above 700 DegC, ascorbic acid prevents the loss of manganese during charring. This effect is explained by retardation of hydrolysis of the magnesium chloride matrix by the chem. modifier, ascorbic acid.

APP* 80) Kawanabe, I., G. Murase, et al. (1993). "Direct evaluation-inner ICP-MS for ultrapure chemicals." Semiconductor Pure Water and Chemicals Conference 12th: 27-44.

Authors think that \"Direct Evaluation\", i.e., direct injection of chems. into plasma without preconcn. process, is essential for the inductively coupled plasma mass spectrometry (ICP-MS) to evaluate the semiconductor-garde chems. This makes it possible to avoid contamination from the pretreatment and to increase the measuring throughput. Using the Nebulizer ICP-MS with anticorrosive injection system and the electrothermal vaporization (ETV) ICP-MS, we studied the direct injection measuring method, using various chems. such as HF, HNO3 and H2O2. Characteristic spectra features of plasma-borne mol. ions under coexistence of these chems. in plasma were examd. first. Formation of fluorine-relating mol. ions, nitrogen or oxygen-relating mol. ions and argon-relating mol. ions was identified. In addn., we checked the detection limit of each impurity element in HF. As a result, we confirmed that the relatively good detection limit as low as 0.5 ppb was obtained in the case of elements such as Cr, Ni and Zn which tend to be interfered by the mol. ion peaks. It was also revealed that the detection limit was lower than 0.1 ppb in the case of elements such as Li, Be, Mg, Mn and Ga which were less likely to be interfered by the mol. ion peaks. Fe which is affected by 40Ar16O+, cannot be accurately quantified by the nebulizer ICP-MS. We therefore employed the ETV-ICP-MS to directly evaluate Fe. We found that the detection limit was at the level of approx. 0.2 ppb.

REV* 81) Stefanova, V., V. Kmetov, et al. (1993). "Pulse techniques for sample introduction in the inductively-coupled-plasma mass spectrometry." Analytical Laboratory 2(3): 159-75.

A review is presented with 117 refs. with discussion on general characteristics of the ICP-MS method, continuous nebulization, arc and spark nebulization, laser ablation, electrothermal vaporization (open and tube type cells), thermo-spray, and flow injection. Crit. evaluation and comparison with other methods are presented.

APP* 82) Argentine, M. D. (1993). Analysis of trace impurities in organometallic semiconductor grade reagent materials using electrothermal vaporization - inductively coupled plasma spectrometry. Univ. Massachusetts,Amherst,MA,USA. FIELD URL:: 225 pp.

REV* 83) McKay, K. (1993). "New techniques in the pharmacokinetic analysis of cancer drugs II. The ultratrace determination of platinum in biological samples by inductively coupled plasma-mass spectrometry." Cancer Surveys 17(Pharmacokinetics and Cancer Chemotherapy): 407-14.

A review with 17 refs. The use of ICP-MS and its various sample introduction techniques has great potential in extending the time scale of study for the pharmacokinetics of platinum contg. antitumor drugs.

Electrothermal vaporization ICP-MS can be used to measure very small samples with very low concns. Speciation studies of platinum in tissues can be carried out with HPLC-ICP-MS over longer time periods. Finally, LA-ICP-MS is potentially useful for studying the spatial distribution of platinum in tissues and tumors.

APP* 84) Hall, G. E. M. and J. C. Pelchat (1993). "Determination of palladium and platinum in fresh waters by inductively coupled plasma mass spectrometry and activated charcoal preconcentration." Journal of Analytical Atomic Spectrometry 8(8): 1059-65.

A method was developed to analyze fresh waters for Pd and Pt by inductively coupled plasma mass spectrometry following preconcn. of the analytes by adsorption onto activated charcoal. Two modes of sample introduction were used: nebulization (NEB) and electrothermal vaporization (ETV). Using a 1 L sample vol. and a preconcn. factor of 200, detection limits are in the range 0.3-0.8 ng L-1 for both elements, with little difference between NEB or ETV introduction. Precision is typically 10% relative std. deviation at the 5 ng L-1 level and 4-5% at 10-fold higher concns. of Pd and Pt. Addn. of 10 mL of concd. HCl per L of sample is necessary to maintain these elements in soln. at their natural levels in waters, well below 50 ng L-1, and even then stability beyond about 20 days is questionable. Application of the method to waters collected from various mineralized sites in Canada indicated that dispersion patterns can be identified, but max. concns. of sol. Pd and Pt are low and for the most part less than 5 ng L-1. As the preconcn. procedure is also suitable for Au and Rh, this method can be extended to include their measurement.

APP* 85) Sturgeon, R. E., S. N. Willie, et al. (1993). "Determination of ultratrace levels of heavy metals in Arctic snow by electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 8(8): 1053-8.

Application of electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) to the direct detn. of trace heavy metals in surface samples of Arctic snow is described. Limits of detection by ETV-ICP-MS are in the fg range, viz., 29, 57, 86, 120, 140, 360, 420, 470, 870 and 3200 for Tl, Cs, Pb, Mn, Co, V, Cu, Ni, Cd and Cr, resp. Direct quantification against simple aq. stds. is feasible using NaCl soln. as a carrier. The latter was obtained in a high-purity form through diln. of the sea-water ref. material National Research Council of Canada (NRCC) NASS-3. Assessment of accuracy was accomplished by anal. of the river water ref. material SLRS-2 (NRCC) and by comparative anal. of the samples by electrothermal atomization at. absorption spectrometry.

APP* 86) Obata, T., Y. Kobayashi, et al. (1993). "Determination of ultratrace amounts of uranium and thorium in yttrium by the ion-exchange separation/ICP-MS." Bunseki Kagaku 42(11): 763-6.

A method has been developed for the 0.01 ng/g level detn. of uranium and thorium in yttrium by electrothermal vaporization(ETV)/ICP-MS. An ion-exchange technique was applied for the sepn. of uranium and thorium from yttrium and other elements in the sample. Although U and Th were adsorbed on an anion-exchange resin, yttrium was not adsorbed in a 7M nitric acid soln. Uranium and thorium were eluted with a 1M hydrofluoric acid-0.1M hydrochloric acid mixt. The eluted soln. was evapd. to dryness and dissolved again with 1M hydrochloric acid. Uranium and thorium in the soln. were further sepd. from traces of concomitant elements by a cation-exchange resin. Uranium was eluted with 2M hydrochloric acid. After yttrium, lanthanum, cerium, praseodymium and neodymium were eluted with 4M nitric acid and 4M hydrochloric acid, and thorium was eluted with a 1M hydrofluoric acid-0.1M hydrochloric acid mixt. The eluted solns. of uranium and thorium were combined and evapd. to dryness. The residue was dissolved with 1M hydrochloric acid. Uranium and thorium were detd. by ETV/ICP-MS using tungsten and molybdenum boats, resp., because the tungsten boat contained high level of thorium and the molybdenum boat contained uranium. The detn. limits of uranium and thorium were 0.003 and 0.005 ng/g, resp.

FUN* 87) Sparks, C. M. and J. Holcombe (1993). "Particle size distribution of sample transported from an electrothermal vaporizer to an inductively coupled plasma mass spectrometer." Spectrochimica Acta, Part B: Atomic Spectroscopy 48B(13): 1607-15.

The particles exiting the graphite furnace electrothermal vaporizer (ETV) cell of a com. ETV inductively coupled plasma mass spectrometer (ICP-MS) were size characterized. There were a large no. of particles leaving a furnace heated with no sample. Assuming all the particles were graphitic, .apprx.0.1 mg of material exited the ETV. A common analyte carrier, NaCl, was also characterized and exhibited a bimodal size distribution with a consistent absence of particles in the 0.2-0.3 mm region, which may be explained by the presence of 2 mechanisms responsible for NaCl particle formation. The mass spectral signals of Na+ and C+ indicated the NaCl and C particles were temporally sepd. Several parameters were varied (i.e. heating rates, gas flows, transport tube geometries) and their impact on the size distribution was noted. ETV heating rates for 440 and 2000 K s-1 and Ar flows of 1.0 and 1.8 1 min-1 produced a statistically insignificant change in the no. of particles or their size distribution, except for the 0.3-0.5 mm regime with the varying heating rates. Varying transport tube lengths from 0.2-2.0 m showed subtle effects that were notable for large particles and long tubes.

APP* 88) Nakamura, Y., Y. Kobayashi, et al. (1993). "Determination of ultratrace amounts of uranium and thorium in aluminum and aluminum alloys by electrothermal vaporization/ICP-MS." Bunseki Kagaku 42(9): 525-30.

A method has been developed for detg. 0.01 ng g-1 level of uranium and thorium in aluminum and aluminum alloys by electrothermal vaporization (ETV)/ICP-MS. To eliminate interferences an ion-exchange technique was applied to sep. uranium and thorium from aluminum and other elements. It is known that uranium is adsorbed on an anion-exchange resin and thorium is adsorbed on cation-exchange resin. However, aluminum and copper were eluted with 6 M hydrochloric acid. The sample was dissolved with hydrochloric acid contg. copper which was added for anal. of pure aluminum, and then oxidized with hydrogen peroxide. Concn. of hydrochloric acid in the soln. was adjusted to 6 M, and the soln. was passed through the mixed ion-exchange resin column. After the uranium and thorium were eluted with 1M hydrofluoric acid-0.1 M hydrochloric acid, the soln. was evapd. to dryness. It was then dissolved with 1 M hydrochloric acid. Uranium and thorium were detd. by ETV/ICP-MS using tungsten and molybdenum boats, resp., since the tungsten boat contained high-level thorium and the molybdenum boat contained uranium. The detn. limit of uranium and thorium were 0.003 and 0.005 ng g-1, resp.

FUN* 89) Gregoire, D. C. and R. E. Sturgeon (1993). "Background spectral features in electrothermal vaporization inductively coupled plasma mass spectrometry: molecular ions resulting from the use of chemical modifiers." Spectrochimica Acta, Part B: Atomic Spectroscopy 48B(11): 1347-64.

The formation of background polyat. ions in electrothermal vaporization inductively coupled plasma mass spectrometry is reported. Vaporization temps. ranging from 800 to 2500 DegC were studied. Carbon-contg. polyat. ions interfere with the detn. of Mg, Si, Ti, Ca and Cr. Polyat. ions resulting from the vaporization of ascorbic acid, sodium chloride, magnesium nitrate, nickel nitrate and palladium nitrate chem. modifiers were studied. Microgram quantities of chem. modifier resulted in oxide and argide polyat. ion intensities equiv. to picogram background equiv. masses for interfered analyte isotopes. In most cases alternative analyte isotopes free of interference were available. The formation of carbide or nitride modifier mol. ions was not obsd. The argon dimer could be used as a diagnostic tool to indicate plasma loading effects and matrix suppression effects resulting from the use of chem. modifiers.

FUN* 90) Shibata, N., N. Fudagawa, et al. (1993). "Oxide formation in electrothermal vaporization inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 48B(9): 1127-37.

In electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) using a tungsten furnace, the effects of plasma parameters and removal of solvent on interfering monoxide ion signals were investigated in order to det. rare earth element (REE) impurities in high-purity REE oxide samples without spectral interferences. The monoxide ion to element ion ratio (MO+/M+) was dependent on the plasma parameters, showing a decreasing tendency with increasing rf power. To reduce spectral interferences, the plasma parameters were chosen so as to attain a larger analyte signal and smaller MO+/M+

for a matrix element. The effect of oxide interferences on analyte signal could be further reduced by proper selection of integration time of the ion count. Also, a theor. calcn. of MO/M, assuming the Boltzmann equil. of MO in the ICP, was performed to elucidate the mechanism related to oxide formation. In nebulization ICP-MS, exptl. MO+/M+ values for REEs were in good agreement with theor. MO/M ones, which indicates that oxide ion species in ICP-MS may be derived from undissociated MO and/or MO+ in the ICP. In ETV-ICP-MS, however, exptl. MO+/M+ values were two orders of magnitude larger than theor. ones, probably owing to the air entering the ICP. Under the optimized conditions that the oxide formation was minimized, the use of the ETV technique enabled us to det. Tb and Lu impurities at a concn. level of 0.01 mg g-1 in high-purity Gd2O3.

APP* 91) Bailey, E. H., A. J. Kemp, et al. (1993). "Determination of uranium and thorium in basalts and uranium in aqueous solution by inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 8(4): 551-6.

Methods are described for the simultaneous detn. of uranium and thorium in basaltic rocks at concns. from mg kg-1 (ppm) to mg kg-1 (ppb) levels and for uranium in soln. at femtogram levels. The technique for basalts does not require preconcn. and samples are taken into soln. using a conventional rapid acid digestion method. The results obtained agree, in general, within 10% of published values for eight basalt ref. materials. In addn., optimum conditions with respect to acidic media and storage vessel were ascertained as 5% HNO3 and high-d. polyethylene, resp. The method is applicable to a wide range of silicate rocks and other geol. materials. For the detn. of uranium at sub-ng mL-1 concns., such as occur in natural waters, sample introduction by electrothermal vaporization was investigated using several matrixes. Complexation of uranium with EDTA prior to anal. proved successful at levels down to 0.5 fg mL-1. Routine detn. of such low concns. is thus feasible.

FUN* 92) Byrne, J. P., M. M. Lamoureux, et al. (1993). "Mechanisms of chloride interferences in atomic absorption spectrometry using a graphite furnace atomizer investigated by electrothermal vaporization inductively coupled plasma mass spectrometry. Part 2. Effect of sodium chloride matrix and ascorbic acid chemical modifier on manganese." Journal of Analytical Atomic Spectrometry 8(4): 599-609.

The interference by sodium chloride with the atomization of manganese in electrothermal at. absorption spectrometry (ETAAS) has been investigated using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). The ETV-ICP-MS technique allows direct observation of the signals of manganese along with matrix components during both the pyrolysis and the atomization step of ETAAS, and thereby allows differentiation between the manganese loss from the furnace during pyrolysis and the loss due to formation of mol. species during atomization. The mechanism of interference by sodium chloride is independent of the pyrolysis temp. The loss of manganese does not occur during pyrolysis, but is due to vapor-phase interference caused by the formation of manganese chloride during atomization. The addn. of ascorbic acid, as a chem. modifier, removes the interference by sodium chloride at all pyrolysis temps. investigated (450-1100 DegC). In ETV-ICP-MS, when the sample of manganese contains only the sodium chloride matrix, the chloride appearance time coincides with that of the manganese suggesting a gas-phase interference mechanism. The addn. of ascorbic acid promotes an early release of chloride during the atomization cycle. The chloride appearance temp. is approx. 250 DegC lower than that of the manganese (~1200 DegC). In ETAAS this difference in the two temps. reduces the amt. of residual chloride left in the graphite furnace at the manganese appearance time, thereby eliminating the interference of sodium chloride with manganese.

APP* 93) Nicholson, S., T. W. Sanders, et al. (1993). "The determination of low levels of technetium-99 in environmental samples by inductively coupled plasma-mass spectrometry." Science of the Total Environment 130-131: 275-84.

99Tc is produced in nuclear fission with a yield approx. comparable to that of 90Sr and 137Cs, and it has been released into the environment during the last 40 yr primarily as a result of nuclear fuel reprocessing. It is a beta emitter with a long half life, and its concn. in environmental materials is usually detd. radiometrically. An alternative to radiometric methods which uses inductively coupled plasma-mass spectrometry and which is not subject therefore to interferences caused by ionizing emissions from other radionuclides present in the sample is described. A chem. sepn. is carried out to conc. Tc and to remove mass and matrix interferences. The application of the method to det. Tc concns. in environmental materials from the Irish Sea is discussed. Limits of detection are comparable with those obtained with radiometric methods, but may potentially be significantly improved by developments in the instrumentation such as using electrothermal vaporization. A further advantage of this technique is the rapid data acquisition (following chem. sepn.) of 1 min per sample compared with several hours for radiometric detns.

APP* 94) Richner, P. and S. Wunderli (1993). "Differentiation between organic and inorganic chlorine by electrothermal vaporization inductively coupled plasma mass spectrometry: application to the determination of polychlorinated biphenyls in waste oils." Journal of Analytical Atomic Spectrometry 8(1): 45-9.

Inductively coupled plasma mass spectrometry (ICP-MS) can be used as a screening test for chlorinated org. compds. such as polychlorinated biphenyls (PCBs) in oils. An upper limit for the PCB concn. can be deduced from the Cl concn. Due to the contamination of oils with inorg. Cl, a differentiation between org. Cl (PCB-Cl) and inorg. Cl is necessary. Electrothermal vaporization ICP-MS achieves this using a temp. program having one step at 400 Deg, to vaporize the PCBs, and a second at 2650 Deg, to vaporize inorg. Cl compds. Detection limits are 0.5-10 mg PCB/g of oil depending on the nature of the oil and the degree of chlorination of the PCB.

APP* 95) Ren, J. M. (1994). Direct solid sample analysis by electrothermal vaporization inductively coupled plasma atomic emission spectrometry and mass spectrometry. McGill Univ.,Montreal,QC,Can. FIELD URL:: 164 pp.

FUN* 96) Nonose, N. and M. Kubota (1994). "Effect of secondary discharge on spectroscopic and non-spectroscopic interferences in inductively coupled plasma mass spectrometry." Symposium on Plasma Science for Materials 7TH: 7-14.

In inductively coupled plasma mass spectrometry (ICP-MS), the effect of secondary discharge occurring at the tip of sampling cone on spectroscopic and non-spectroscopic interferences was studied with and without shielding of ICP. In the spectroscopic interference, the formation of polyat. ion species due to (ArX+), closely related to chem. reactions occurring at the interface region, was suppressed under the condition that the secondary discharge was eliminated. In the non-spectroscopic interference, addn. of halogen matrix enhanced analyte signals only when the desolvation or electrothermal vaporization devices were used as sample introduction systems. The lower the ionization potential of halogen the larger the signal enhancement ratio of analytes. Addnl. the secondary discharge increased analyte signals, resulting from promotion of ionization of halogen in the interface region.

APP* 97) Argentine, M. D. and R. M. Barnes (1994). "Electrothermal vaporization-inductively coupled plasma mass spectrometry for the analysis of semiconductor-grade organometallic materials and process chemicals." Journal of Analytical Atomic Spectrometry 9(12): 1371-8.

Electrothermal vaporization inductively coupled plasma mass spectrometry was applied to the detection and detn. of volatile and nonvolatile impurities in semiconductor-grade trimethylaluminum and the process chems. phosphorus tribromide and P oxychloride. Adaptation of a graphite furnace combined with initial sub-ambient temps. permits the direct anal. of otherwise hard-to-handle samples. Nonvolatile impurities (Al, Ca, Cd, Cr, Cu, Fe, Ga, In, Mg, Mn, Ni, Pb, Si, Sn, Zn) are detected and detd. readily because of complete analyte and matrix sepn. Volatile impurities (Ga, Si, Sn, Zn) are also detected, but detn. is limited owing to nonspectral mass spectrometric effects resulting from concurrent matrix evapn. Semiquant. anal. was applied successfully for rapid, multielemental impurity screening of electrothermally vaporized samples.

REV* 98) Darke, S. A. and J. F. Tyson (1994). "Review of solid sample introduction for plasma spectrometry and a comparison of results for laser ablation, electrothermal vaporization, and slurry nebulization." Microchemical Journal 50(3): 310-36.

The relative merits of three solid sample introduction techniques for inductively coupled plasma at. emission spectroscopy and inductively coupled plasma mass spectrometry were evaluated. The techniques studied were laser ablation (LA), slurry nebulization, and slurry introduction via electrothermal vaporization. The application of each technique to the quantification of Ba and Pb in geochem. samples was described and the results obtained for each technique were compared. To help in assessing the potential of the systems described here a simple classification of the agreement obtained between found and known values was proposed allowing a comparison of these results with other results published in the literature to be made. Problems encountered during the evaluation of the techniques were described and, for LA, the assocd. problems led to the development of a modified sampling system which was used in a study of some fundamental aspects of LA as a method of solid sample introduction. Possible routes for improvement in sampling and transport are suggested, including use of reactive gases, ablation under stopped flow conditions and removal of large particles by gravitational settling. A review with 165 refs.

FUN* 99) Gray, D. J., S. Wang, et al. (1994). "Stability and sensitivity enhancement using ETV-ICPMS." Applied Spectroscopy 48(11): 1316-20.

The interfering of an electrothermal vaporization (ETV) unit to an inductively coupled plasma mass spectrometer (ICPMS) produces a powerful system for ultra-low-level compositional anal. of micro-vol. samples, as well as decreasing some of the mol. interferences inherent in a conventional-nebulization ICPMS. Some problems still remain with this technique in respect to signal variation, sample heating profiles, and instrument tuning parameters. Advances are presented concerning the instrumental conditions necessary for lowering signal variation. These include optimization of dry-plasma tuning of the spectrometer lens stack, furnace cooling/heating, and tube mounting. Novel ways of enhancing sensitivity by multiple deposition, preconcn., and chem. modification have been studied with particular emphasis on uranium and radium detn.

FUN* 100) Gilmutdinov, A. K., A. E. Staroverov, et al. (1994). "Kinetics of release of carbon and carbon monoxide from a graphite furnace investigated by electrothermal vaporization inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 49B(10): 1007-26.

Detection of C-contg. mols. released during the high temp. heating of a dry, unloaded HGA-type graphite furnace (GF) was undertaken by interfacing the GF to an ICP-MS. Desorption of O2 (as CO) chemisorbed onto the GF surface can be discriminated from that produced as a result of continuous oxidn. of the surface by gaseous O2 impurity. Because plasma-induced dissocn. of CO is negligible, signals arising from C do not have to be deconvoluted from those of CO. To a 1st approxn., the formation of C and CO can be treated as independent processes. A theor. anal. of the transient exptl. signals is presented.

APP* 101) Hoffmann, E., C. Luedke, et al. (1994). "Electrothermal vaporization for simultaneous multi-element determination." Journal of Analytical Atomic Spectrometry 9(11): 1237-41.

New techniques were developed for anal. of microsamples. A modification of a graphite furnace for furnace atomization nonthermal excitation spectrometry (FANES) was used in electrothermal vaporization inductively coupled plasma mass spectrometry. The figures of merit, such as the max. mass which can be introduced into the plasma (25 mg), the detection limits of a no. of elements (Ag: 0.02 pg; Co: 0.3 pg; Mn: 0.2 pg) in concd. nitric acid, the dynamic range of calibration curves and the influence of sodium on anal. signals are studied and compared to the ones obtained for FANES.

FUN* 102) Becker, S. and A. V. Hirner (1994). "Coupling of inductively coupled plasma mass spectrometry (ICP-MS) with electrothermal vaporization (ETV)." Fresenius' Journal of Analytical Chemistry 350(4-5): 260-3.

An inductively coupled plasma mass spectrometer (ICP-MS) was coupled online with an electrothermal vaporization (ETV). The influence of aerosol gas flow as well as the variation of the coupling distance on the signal intensity was studied and compared with the results of hydraulic high-pressure nebulizer (HHPN) measurements. Also, temp. programs known from graphite furnace at. absorption spectroscopy (GFAAS) were applied to ETV-ICP-MS. All optimization of temp. programs, calibration series based on mono-element and multi-element solns. were carried out. The dynamic range and the detection limits of the method were detd. Using internal standardization it was tried to improve linearity and reproducibility. Internal standardization does not have a great impact on linearity, but may be a useful tool to improve reproducibility. However, the latter is still low.

APP* 103) Richner, P., D. Evans, et al. (1994). "Applications of laser ablation and electrothermal vaporization as sample introduction techniques for ICP-MS." Fresenius' Journal of Analytical Chemistry 350(4-5): 235-41.

The field of applications of ICP-MS can be further increased using special sample introduction techniques such as laser ablation (LA) and electrothermal vaporization (ETV). In both cases a tandem source for mass spectrometry is formed by the sample introduction device and the ICP. The 1st source is specifically designed for the volatilization of a sample and it can be used to introduce selectively only certain parts of a sample into the ICP-MS, based either on local distribution (LA) or volatility (ETV). Applications of LA-ICP-MS are the detn. of distribution patterns of minor constituents in solid samples such as ceramics, alloys or hard biol. structures. Homogeneity testing in the 1st two types of samples or detn. of distribution patterns of trace elements in the latter can be carried out rapidly with high spatial resoln. on a multielemental basis. The possibility of online sepn. between fractions of different volatility in a sample with ETV-ICP-MS is demonstrated for volcanic eruption products and other samples.

FUN* 104)Gregoire, D. C., D. M. Goltz, et al. (1994). "Vaporization of acids and their effect on analyte signal in electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 9(9): 919-26.

The vaporization properties of HCl and HNO3 under various furnace heating conditions were studied. Drying-step temps. of 140 Deg (50 s) and pyrolysis-step temps. of 400 Deg (10 s) were effective in volatilizing most of the chloride from 10 mL of 1% vol./vol. HCl, however, a small amt. (40 ng) of acid was retained on the graphite even after pyrolysis at 400 Deg. Under the same exptl. conditions, HNO3 was completely volatilized from the graphite tube. The effect of a range of concns. of HCl, HNO3, H2SO4 and H3PO4 on analyte signals was studied for Co, Cu, Ag, Cs, Pb, Bi and U. Analyte signals were enhanced by as much as a factor of two in the presence of 1% vol./vol. HNO3 and H2SO4. H3PO4 suppressed analyte signals for Ag and Bi and the use of HCl resulted in relatively small changes in analyte sensitivity. The use of a pyrolysis step in the heating programmed reduced the effects assocd. with acid matrixes, but at the expense of signal intensity. A mixed modifier-carrier reduced the matrix effects assocd. with H2SO4 and H3PO4 and essentially eliminated them for NHO3 and HCl.

FUN* 105) Byrne, J. P., D. M. Hughes, et al. (1994). "Mechanism of volatilization of tungsten in the graphite furnace investigated by electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 9(9): 913-17.

The mechanism of volatilization of W from a graphite substrate was studied using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). Vaporization temps. in the range 800-2700 Deg were studied. In this temp. region two distinct vaporization processes occur, resulting in two sep. ETV-ICP-MS peaks for W. The earlier peak appears at temps. >=850 Deg and is attributed to the volatilization of W oxide. At temps. >2500 Deg a 2nd peak appears when W carbide is vaporized from the graphite surface. NaCl and NaF chem. modifiers are ineffective in preventing the formation of W carbide. The signal-to-background ratio (S/N) for W varies with vaporization temp., with the optimum S/N and min. limit of detection (0.51 pg) being obtained at vaporization temps. around 110 Deg.

APP* 106) Wildner, H. and G. Wunsch (1994). "Ultratrace analysis in high purity phosphorus by thermal trace-matrix-separation via ETV-ICP-MS." Journal fuer Praktische Chemie/Chemiker-Zeitung 336(5): 408-14.

Elemental (red) P can be effectively volatilized and sepd. from ultra trace contaminants by electrothermal vaporization (ETV) in a graphite furnace. The tube must be covered with WC and some H added to the transport Ar. Detection limits of 0.01 to 10 ng/g in the P sample are obtained for most analytes by ICP-MS in single ion monitoring mode. Exceptions are some carbide forming elements (B, Si, V), some contaminants from graphite (B, Si) and some easily volatile traces (As, Sb, Te, I). ETV in multi element scan mode or alternatively wet chem. trace matrix sepn. (SMT) with an cation exchanger plus nebulizer aspiration allow detection limits about one order higher. The proposed technique requires a min. of chem. manipulation and therefore reduces risk of contamination.

APP* 107) Gregoire, D. C. and J. Lee (1994). "Determination of cadmium and zinc isotope ratios in sheep's blood and organ tissue by electrothermal vaporization inductively coupled plasma mass spectrometry. Invited lecture." Journal of Analytical Atomic Spectrometry 9(3): 393-7.

Samples were digested with nitric acid using a microwave oven. Cadmium and Zn were sepd. from matrix components using adsorption chromatog. prior to isotope ratio measurement by electrothermal vaporization inductively coupled plasma mass spectrometry. A concn. factor of 35 was achieved. Limits of detection for the detn. of Cd and Zn in blood were 0.34 and 0.40 pg g-1, resp. Cadmium isotope ratios (111Cd:106Cd; 111Cd:110Cd) were detd. with a precision of 2-3% for both peak height and area count measurements. Zinc isotopes ratios (68Zn:67Zn; 68Zn:66Zn) were detd. with a precision of 2% for peak height measurements and 1% for peak are count measurements.

APP* 108) Gregoire, D. C., N. J. Miller-Ihli, et al. (1994). "Direct analysis of solids by ultrasonic slurry electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 9(5): 605-10.

The direct anal. of solids using ultrasonic slurry electrothermal vaporization inductively coupled plasma mass spectrometry is reported. National Inst. of Stds. and Technol. (NIST) Std. Ref. Material (SRM) 1632a Trace Elements in Coal (Bituminous), Total Diet SRM 1548 and National Research Council of Canada LUTS-1 Lobster Hepatopancreas RM were analyzed for a no. of elements including Ni, Cu, Cr, Pb, Mn and Co. As a consequence of matrix effects, most analytes were detd. using the method of std. addns., although Ni, Cu, Pb and Mn in NIST coal and Pb in LUTS-1 were successfully detd. by external calibration using aq. stds. With the exception of Cr in the coal sample, excellent agreement was obtained between the concn. detd. and the certified range. Monitoring of the Ar dimer during the high temp. vaporization cycle is an effective means of assessing matrix effects and selecting calibration strategies for individual analytes. Calcd. limits of detection range from 0.07 ng g-1 for Co to 3.2 ng g-1 for Cr in 2 mg samples.

FUN* 109) Lamoureux, M. M., D. C. Gregoire, et al. (1994). "Modification of a Commercial Electrothermal Vaporizer for Sample Introduction into an Inductively Coupled Plasma Mass Spectrometer. 1. Characterization." Analytical Chemistry 66(19): 3208-16.

Modifications to a com. graphite furnace were made for its use as a sample introduction device with an inductively coupled plasma mass spectrometer (ICP-MS) and to allow simultaneous measurement of the at. absorption and mass spectrometric signals. The effect of the internal Ar carrier gas flow, the total Ar carrier gas flow, and the vaporization temp. on the integrated ion intensity for Ag was studied. An abs. limit of detection of 0.23 pg was obtained for Ag when vaporization took place from a graphite platform in the presence of sodium chloride chem. modifier. The utility of simultaneously measuring electrothermal atomization at. absorption (ETAA) and ETV-ICP mass spectrometric signals was demonstrated by studying the interference of MgCl2 on the detn. of Mn by ETAAS. This study provided direct evidence for preatomization loss of Mn when vaporized in the presence of MgCl2.

FUN* 110) Lamoureux, M. M., D. C. Gregoire, et al. (1994). "Modification of a Commercial Electrothermal Vaporizer for Sample Introduction into an Inductively Coupled Plasma Mass Spectrometer. 2. Performance Evaluation." Analytical Chemistry 66(19): 3217-22.

The performance of a modified com. graphite furnace (ETV) used as a sample introduction device for inductively coupled plasma mass spectrometry (ICP-MS) was evaluated. This novel ETV system is based on the extn. of sample vapor through the dosing hole rather than 1 end of the graphite tube. Abs. limits of detection for Co, Cu, Mn, Nd, V, Y, Yb, and Zn were 0.075, 0.169, 0.072, 0.651, 0.236, 0.511, 0.042, and 0.617 pg, resp. These limits of detection are comparable to those obtained using a com. available electrothermal vaporization system. The sensitivity of 49 elements (the above-listed, minus V, plus Ag, As, Au, Ba, Be, Bi, Cd, Ce, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, La, Lu, Mo, Ni, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Sm, Sn, Sr, Tb, Te, Tl, Tm, and W) was detd. under various exptl. conditions, and in general, these improved when NASS-3 (seawater ref. material) was used as a chem. modifier. Increasing the vaporization temp. had a significant effect only on refractory, carbide-forming elements and rare earth elements. Vaporization from the graphite tube rather than from a platform surface gave better sensitivity for most elements.

FUN* 111) Beres, S., R. Thomas, et al. (1994). "the benefits of electrothermal vaporization for minimizing interferences in ICP-MS." Spectroscopy (Duluth, MN, United States) 9(1): 20-6.

The use of electrothermal vaporization (ETV) to reduce interferences arising from pneumatic nebulization with inductively coupled plasma-mass spectrometry (ICP-MS) is studied. By thermally and chem. sepg. matrix components from the analytes of interest, ETV can effectively reduce the deleterious effects caused by the introduction of the bulk matrix into the ICP-MS system. The capabilities of ETV-ICP-MS and the importance of the ETV sampling device design are illustrated with several practical applications.

FUN* 112) Byrne, J. P., D. C. Gregoire, et al. (1994). "Vaporization and atomization of boron in the graphite furnace investigated by electrothermal vaporization inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 49B(5): 433-43.

The vaporization and atomization of B in the graphite furnace were studied using both electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) and graphite furnace at. absorption spectrometry (GFAAS). The majority of the B is vaporized in mol. form and removed from the furnace at temps. well below the appearance temp. of at. B. The effect of Ni nitrate chem. modifier on the vaporization of B was also studied. The modifier is largely ineffective in preventing loss of B from the graphite furnace prior to atomization. The extent of this preatomization loss, both in the presence and absence of the modifier, is reported. For the detn. of boron by ETV-ICP-MS, the optimum sensitivity is obtained at a vaporization temp. of .apprx.1800 Deg, i.e. well below the max. possible vaporization temp. This sensitivity is enhanced by the addn. of the Ni modifier.

APP* 113) Ruth, K., P. Schmidt, et al. (1994). "Silicon wafer surface analysis by electrothermal vaporization inductively-coupled plasma mass spectrometry (ETV-ICP-MS)." Proceedings - Electrochemical Society 94-7(PROCEEDINGS OF THE THIRD INTERNATIONAL SYMPOSIUM ON CLEANING TECHNOLOGY IN SEMICONDUCTOR DEVICE MANUFACTURING, 1993): 565-72.

This work describes the use of ETV-ICP-MS as a complementary alternative anal. technique to assess metallic impurity levels on Si wafer surfaces. Instrument capabilities and limitations toward this application are discussed.

APP* 114) Manninen, P. K. G. (1994). "Determination of extractable organic chlorine by electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 9(3): 209-11.

Extractable org. Cl (EOCI) is a sum parameter used to describe the org. Cl concn. in solid or liq. samples that can produce injurious effects on health. A new method is presented for the detn. of EOCI.

Inductively coupled plasma mass spectrometry (ICP-MS) is not esp. suitable for the detn. of Cl owing to the high ionization energy of Cl. However, when electrothermal vaporization (ETV) is compared with ICP-MS, the sensitivity is high enough to facilitate sum parameter anal. from limited sample vols. Et acetate was used as an extn. solvent. Cl was detd. by collecting data during heating by monitoring m/z 35 using the single-ion monitoring mode. The detection limit for EOCI by ETV-ICP-MS is .apprx.10 ng.

APP* 115) Seubert, A. and R. Meinke (1994). "Online coupled ion chromatography-ICP-(AES,MS) and electrothermal vaporization-ICP-MS in use for ultra trace analysis of high purity rhenium." Fresenius' Journal of Analytical Chemistry 348(8-9): 510-19.

This work presents the benefits of coupling techniques such as Electrothermal Vaporization (ETV)-ICP-MS and Ion Chromatog. (IC)-ICP-(AES, MS) for ultra trace anal. in a high purity Re powder sample. Direct anal. using ICP-AES suffers from poor detection limits and allows trace anal. only >1 mg/g for most analytes. ICP-MS anal. of trace elements is more sensitive, but signal depression caused by the heavy Re-ions limits trace anal. to concns. of 50-100 ng/g analyte in the solid sample. Coupling Ion Chromatog. with ICP-spectrometers, combined with time resolved measurement (IC-ICP-TRM) of the elution signals, was used to enhance the sensitivity of both ICP-AES and ICP-MS. Resulting detection limits are in the very low ng/g to pg/g range. Coupling of ETV and ICP-MS offers the possibility of eliminating the volatile Re2O7 matrix by thermal pretreatment and allows ICP-MS measurements without matrix interferences caused by Re. Results from these methods are compared with Glow Discharge Mass Spectrometry (GDMS) anal., a semi-quant. solid state technique. The results are also compared with the manufacturers' specifications to show the power of modern routine anal. using ICP-AES or FAAS.

APP* 116) Durrant, S. F., A. Krushevska, et al. (1994). "Matrix separation by chelation to prepare biological materials for isotopic zinc analysis by inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 9(3): 199-204.

Following an evaluation of three chelating resins [Chelex-100, poly(dithiocarbamate) (PDTC) and carboxymethylated poly(ethylenimine)-poly(methylenepolyphenylene) isocyanate (CPPI)], a procedure was established with the last of these for the sepn. of Zn from biol. matrix elements prior to 70Zn:68Zn isotopic anal. by inductively coupled plasma mass spectrometry (ICP-MS). The method was verified by establishing Zn recoveries and by detg. its effectiveness in removing Cl and Na from buffered test solns. Calcium, Na, and Zn concn. data were detd. by inductively coupled plasma at. emission spectrometry. Chlorine was measured by electrothermal vaporization ICP-MS. The efficacy of the technique was demonstrated by the detn. of zinc isotope ratios in bovine milk and human urine. Results compared favorably with those obtained using a previously established extn. procedure.

APP* 117) Wang, J., J. M. Carey, et al. (1994). "Direct analysis of solid samples by electrothermal vaporization inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 49B(2): 193-203.

The direct anal. of solid samples by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) was demonstrated. This method provides a rapid alternative to traditional means of solid sample anal., as the sample pre-treatment procedures are eliminated or minimized. Three instrument calibration methods for the solid sample detns. such as liq. std., std. addn. and differing wts. of a std. ref. material were studied. Use of std. ref. materials for standardization, when available, provided for the best performance for the ETV-ICP-MS system. A simple and easy to use method of introducing the solid sample, with a well-defined mass, into the graphite furnace was developed.

APP* 118) Takenaka, M., M. Tomita, et al. (1994). "Depth profiling of ultratrace chromium, iron, nickel, and copper in silicon wafers by electrothermal vaporization/ICP-MS." Bunseki Kagaku 43(2): 173-6.

A method of etching micro thin layers for silicon wafers by a wet chem. technique has been developed. Ultratrace concn. of Cr, Fe, Ni, and Cu in the etching soln. were detd. by electrochem. vaporization ICP-MS (ETV/ICP-MS). Silicon wafers 0.01 to 10 mm thick could be dissolved by controlling the acidities of HF and HNO3 in the etching soln. The thickness was calcd. from the Si concn. of the etching soln. by ordinary spectrophotometry using the Molybdenum Blue method. Silicon wafers were etched by 10 mL of acid solns. contg. appropriate concns. of HF and HNO3. After the etching process, an aliquot of the soln. was used for Si measurement. The rest was dried, dissolved in water and then subjected to elemental anal. by ETV/ICP-MS. The micro depth profiling of Cr, Fe, Ni, and Cu of a ref. sample was done using the proposed method and showed good agreement with that obtained by SIMS. When a few practical silicon wafer samples were also analyzed by this method, it was found that different types of silicon wafer had clearly different depth profiles of elements. The detection limites were 0.005 ng/g for Cu and Ni, and 0.01 ng/g for Cr and Fe.

REV* 119) Balaram, V. (1995). "Developments and trends in inductively coupled plasma mass spectrometry and its influence on the recent advances in trace element analysis." Current Science 69(8): 640-9.

A review, with 77 refs. A brief introduction to the various instrumental methods such as at. absorption spectrometry, x-ray fluorescence spectrometry, neutron activation anal., inductively coupled plasma at. emission spectrometry, thermal ionization mass spectrometry, etc. are presented highlighting their relative merits and demerits. The history and developments of inductively coupled plasma mass spectrometry (ICP-MS) and its advantages and limitations over other multi-element instrumental techniques are reviewed. Extended capabilities by hyphenating ICP-MS to various other known sample introduction techniques such as flow-injection, electrothermal vaporization, chromatog. methods and laser ablation are discussed in brief. The recent development of high resoln. multi-collector double-focusing magnetic mass spectrometer with inductively coupled plasma at atm. pressure as source is also discussed. Some of the areas where more developments can be expected in future are suggested.

FUN* 120) Vanhaecke, F., G. Galbacs, et al. (1995). "Use of the Ar2+ signal as a diagnostic tool in solid sampling electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 10(12): 1047-52.

The utility of the Ar2+ signal (at mass-to-charge ratio m/z = 80) as a diagnostic tool in solid sampling electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) is reported. Simultaneous monitoring of the Ar dimer signal with the signal(s) of the analyte element(s) indicated that nonspectral interferences, caused by matrix components co-volatilizing with the analyte element(s), can strongly affect the analyte signal profiles in solid sampling ETV-ICP-MS of samples of biol. or environmental origin. This observation led to a more profound understanding of why, for a given matrix, the signal profiles strongly differ from one element to another, and why, for a given element, the signal profile is strongly dependent on the matrix. These matrix effects also cause a curvature in the sample mass response curves (analyte signal intensity as a function of sample mass). At least in some instances, the use of the Ar2+ signal as an internal std. allows (i) this nonlinearity to be cor. for and (ii) accurate anal. results to be obtained. Finally, simultaneous registration of the Ar dimer and the analyte signal(s) is useful during optimization of ashing and vaporization temps.

APP* 121) Ren, J. M., R. Rattray, et al. (1995). "Assessment of direct solid sample analysis by graphite pellet electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 10(11): 1027-9.

Graphite pellet vaporization was evaluated as a method for solid sample introduction for ICP-MS. A detection limit of 0.1 ppb of Cd was obtained indicating that the technique might be very useful for screening. The accuracy was poor using the technique of external stds. and four ref. materials, suggesting that the technique of std. addns. might be required if the technique was to be used for anything other than semi-quant. measurements.

APP* 122) Wei, W.-C., C.-J. Chen, et al. (1995). "Determination of boron using mannitol-assisted electrothermal vaporization for sample introduction in inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 10(11): 955-61.

The possibility of improving the detection sensitivity for boron using mannitol as a chem. modifier in electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) is presented. Expts. were performed by adding mannitol to a boron analyte soln. to form a boron-mannitol complex and then injecting the resulting product into the ETC-ICP-MS system for detn. The effect of mannitol on the signal pulse of boron was studied by monitoring the analyte through a heating cycle from 150 to 2600 Deg. The appearance of several marked signal pulses at 425-1500 Deg was obsd. and assumed to result from the vaporization of boron-mannitol complexes. The signal intensity of boron in the presence of mannitol is considerably enhanced in comparison with that in its absence. The optimization of the ETV and ICP parameters and the amt. of mannitol added and the comparison of mannitol with different modifier systems were subsequently studied. By following the established method the sensitivity for boron in the presence of mannitol can be improved by a factor of 84 compared with that without the modifier, and the limits of detection (3 s) achieved in the presence of mannitol can be >=0.2 ng mL-1 with a 20 mL injection. The large boron sensitivity enhancement in the presence of mannitol in ETV-ICP-MS is attributed to the formation of a boron-mannitol complex that is subsequently vaporized from the graphite surface and transported with the assistance of mannitol to the plasma. A novel application with mannitol, which acts both as a preconcg. agent for boron in the chem. sepn. process and as a modifier in the ETV-ICP-MS for the detn. of boron in trichlorosilane, is also presented.

FUN* 123) Fonseca, R. W. and N. J. Miller-Ihli (1995). "Analyte transport studies of aqueous solutions and slurry samples using electrothermal vaporization ICP-MS." Applied Spectroscopy 49(10): 1403-10.

Analyte transport of both aq. solns. and slurry samples was studied using ultrasonic slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry (USS-ETV-ICP-MS). The elements studied included V, Mn, Ni, Cu, and Pb, and the materials analyzed included NIST SRM 1548 Total Diet, SRM 1632a Coal, SRM 1566a Oyster Tissue, and NRCC LUTS-1 Lobster Hepatopancreas. The effect of microgram amts. of Pd as well as the effect of oxygen ashing on analyte transport were studied. Slurry samples have a better analyte transport in comparison to aq. solns. when no phys. carriers were added. Under these exptl. conditions, the detd. slurry concns. were apparently high when quantified using external calibration. Microgram amts. of Pd were used to study whether it was possible to reduce the difference in analyte transport between slurry samples and aq. stds. The use of microgram amts. of Pd resulted in signal intensity suppression. Such a signal redn. could be related to the presence of space charge effects or losses of analyte due to condensation of the phys. carrier together with the analyte on different parts of the ETV cells or the transfer line. However, quantitation for slurry samples was improved using Pd as a phys. carrier. Pd by itself was not completely effective for samples with high carbon content; therefore the effect of oxygen ashing combined with Pd was studied. An enhancement of signal intensities was obsd. when oxygen ashing was used, as well as a shift in the carbon signal to earlier times. In this case, signal enhancement was assocd. with an improvement in analyte transport caused by an increased no. of carbon particles leaving the furnace at the same time as the analytes studied. With oxygen ashing, slurry samples behaved more similarly to aq. solns., facilitating quantitation with aq. stds.

APP* 124) Gregoire, D. C. and H. Naka (1995). "Mechanism of vaporization of sulfur in electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 10(10): 823-8.

The mechanism is reported of the vaporization of sulfur using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). Studied were the vaporization characteristics of sulfuric acid, thiourea, potassium sulfate, ferric sulfate and magnesium sulfate. All compds. with the exception of potassium sulfate released sulfur as SO3 gas resulting from thermal decompn. of the sample. Potassium sulfate vaporized without decompn. The use of KCl, KNO3 and KOH as chem. modifiers was studied, with KOH being the most beneficial for the ETV-ICP-MS detn. of sulfur. The abs.

limit of detection for sulfur was 13 pg which corresponds to a relative limit of detection of 0.26 ng mL-1 using a 50 mL sample.

REV* 125) Liu, X. (1995). "Current status and prospect for the determination of rare earth elements by inductively coupled plasma mass spectrometry." Fenxi Huaxue 23(10): 1218-24.

A review with 77 refs. is given on the development of inductively coupled plasma mass spectrometric detn. of rare earth elements, including current status, spectral and non-spectral interferences, overcome of interference, laser ablation-ICP-MS, electrothermal vaporization-ICP-MS, ultrasonic nebulizer-ICP-MS and their development trends.

APP* 126) Wei, W.-C. and M.-H. Yang (1995). "Determination of phosphorus and arsenic in trichlorosilane by electrothermal vaporization-inductively coupled plasma mass spectrometry with prior concentration by cuprous chloride." Fresenius' Journal of Analytical Chemistry 353(2): 167-70.

A method for the detn. of trace impurities of phosphorus and arsenic in trichlorosilane with prior sepn. followed by electrothermal vaporization-inductively coupled plasma mass spectrometry (ETV-ICP-MS) was developed. The preconcn. of the analytes from the sample matrix was made by adding cuprous chloride to a 10 mL trichlorosilane sample for the formation of nonvolatile compds. with the elements of interest. Upon evapn. of trichlorosilane, the analytes retained in the residue were then detd. in the presence of copper as modifier by ETV-ICP-MS. The dual role of cuprous chloride both in the preconcn. and instrumental detn. was studied and discussed. By meticulous control of exptl. conditions, detection limits for these two elements as low as sub-ng/g can be achieved. The method was applied to the detn. of phosphorus and arsenic in a com. available trichlorosilane sample with satisfactory results.

FUN* 127) Goltz, D. M., D. C. Gregoire, et al. (1995). "Vaporization and atomization of uranium in a graphite tube electrothermal vaporizer: a mechanistic study using electrothermal vaporization inductively coupled plasma mass spectrometry and graphite furnace atomic absorption spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 50B(8): 803-14.

The mechanism of vaporization and atomization of U in a graphite tube electrothermal vaporizer was studied using graphite furnace at. absorption spectrometry (GFAAS) and electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). Graphite furnace AAS studies indicate U atoms are formed at temps. >2400 DegC. Using ETV-ICP-MS, an appearance temp. of 1100 DegC was obtained indicating that some U vaporizes as U oxide. Although U carbides form at temps. >200 DegC, ETV-ICP-MS studies show that they do not vaporize until 2600 DegC. At 2200-2600 DegC, U atoms in GFAAS are likely formed by thermal dissocn. of U oxide, whereas at higher temps., U atoms are formed via thermal dissocn. of U carbide. The origin of U signal suppression in ETV-ICP-MS by NaCl was also studied. At temps. >2000 DegC, signal suppression may be caused by the accelerated rate of formation of carbide species while at temp. <2000 DegC, the presence of NaCl may cause intercalation of the U in the graphite layers resulting in partial retention of U during the vaporization step. The use of 0.3% freon-23 (CHF3) mixed with the argon carrier gas was effective in preventing the intercalation of U in graphite and U carbide formation at 2700 DegC.

APP* 128) Conrad Gregoire, D., K. M. Ansdell, et al. (1995). "Trace analysis of single zircons for rare-earth elements, U and Th by electrothermal vaporization-inductively coupled plasma- mass spectrometry (ETV-ICP-MS)." Chemical Geology 124(1-2): 91-9.

A method is described for the trace anal. of single zircons for Y, La, Ce, Nd, Sm, Yb, Th and U by electrothermal vaporization-inductively coupled plasma-mass spectrometry (ETV-ICP-MS). Zircons are cleaned by an abrasion process and dissolved in HNO3 and HF in a pressure vessel. Following conversion to chlorides and evapn. to dryness, the dissolved zircon residue is re-dissolved in 500 mL of high-purity 2.5M HNO3. Analyte concns. were measured with a precision of approx. +-6%. Agreement between found and ref. values for BCS-388 zircon ref. material was excellent. Limits of detection for the anal. of a 10-mg zircon were 150 ng g-1 for Y, 90 ng g-1 for La, 115 ng g-1 for Ce, 65 ng g-1 for Nd, 180 ng g-1 for Sm, 22 ng g-1 for Yb, 190 ng g-1 for Th and 80 ng g-1 for U. Abs. limits of detection for a 10-mL soln. aliquot ranged from 4 to 36 fg (10-15 g). Zircon solns. were analyzed using external calibration by aq. stds. with the addn. of a mixed component carrier (NASS-3 open ocean seawater). No matrix or spectroscopic interferences were obsd. from major-element matrix components. The anal. of a typical set of single zircons gave concn. levels well above the limit of detection for all elements except La.

REV* 129) Matusiewicz, H. (1995). "Electrothermal vaporization sample introduction into plasma sources for analytical emission spectrometry." Advances in Atomic Spectroscopy 2: 63-138.

A review, with many refs., is given on historical, fundamental, and practical aspects of electrothermal vaporization (ETV) as a sample introduction technique for plasma sources in anal. emission spectrometry. Methods for ETV sample introduction into inductively coupled plasmas (for at. emission and mass spectrometry-AES and MS, resp.) microwave-induced plasmas (for MIP-AES and MIP-MS), d.c. plasmas (DCP), and capacitively coupled microwave plasmas (CCMP) are reviewed and evaluated critically and the performance of plasma sources for real sample detns. is evaluated. The advantages and disadvantages, limitations, figures of merit and ease of operation, as compared to conventional pneumatic nebulization and other sample introduction techniques, are described.

FUN* 130) Imai, S., Y. Nishiyama, et al. (1995). "Investigations of pyrolyzed ascorbic acid in an electrothermal graphite furnace by inductively coupled argon plasma mass spectrometry and Raman spectroscopy." Journal of Analytical Atomic Spectrometry 10(6): 439-42.

The characteristics of pyrolyzed ascorbic acid were studied by electrothermal vaporization inductively coupled Ar plasma mass spectrometry (ETV-ICP-MS) and Raman spectrometry. The signals from the ETV-ICP-MS instrumentation for m/z values of 13, 24, 44, and 52, corresponding to polyat. species of 13C, 12C, 12C, 12C16O2, and 12C40Ar, resp., indicated 3 signals in the atomization cycle corresponding to: (i) gaseous compds., such as hydrocarbons, CO and CO2 at <580 K; (ii) active C species at 600-1100 K; and (ii) thermally stable C species at 1200-2400 K. After the ETV-ICP-Ms measurements, more thermally stable C residues (i.e., soot) were confirmed in the graphite furnace by eyesight. Raman spectra of pyrolyzed ascorbic acid on the pyrolytic graphite (PG) coated graphite furnace inner wall showed that the thermally stable C residues were released via decompn. into active C species with increasing pyrolysis temp., and part of the residue remained at 2150 K. Raman spectra of the C residues on a nonpyrolytic graphite coated graphite furnace wall after repetitive (100 times) pyrolysis of 5% (m/v) ascorbic acid soln. at >2500 K showed the formation of a PG phase.

APP* 131) Nickel, H. and Z. Zadgorska (1995). "A new electrothermal vaporization device for direct sampling of ceramic powders for inductively coupled plasma optical emission spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 50B(4-7): 527-35.

In spite of many important advantages of electrothermal vaporization of solid samples combined with inductively coupled plasma spectrometry (ETV-ICP-OES) the method was not exploited to its full potential as a routine anal. mainly due to unsatisfactory reproducibility. The design of the system which transports the analytes into the plasma is recognized as one of the main factors influencing effective transport. Development of a reliable means of combining an ETV device with an ICP would be very useful when direct anal. of trace elements in ceramic powders is needed. This paper describes the construction of an ETV-ICP system for direct anal. of ceramic powders through in situ thermochem. processing. The system is based on in-line elec. resistive heating of a graphite crucible with powd. silicon carbide mixed with a CoF2 + BaO modifier in a proportion 1:1:1. The transport path was shortened to 9 mm from the orifice of the crucible to the bottom of a modified injector tube. No material was deposited on the injector tube based on washing the tube and analyzing the soln. by ICP-OES. Initial assessment by peak area integration of emission signals of 5 mg silicon carbide powder shows that the level of detection lies approx. in pg level for Ti, V, Al and Fe. The system has no memory effect. The ETV unit could be used both by ETV-ICP-OES and ETV-ICP-MS.

APP* 132) Moens, L., P. Verrept, et al. (1995). "Solid sampling electrothermal vaporization for sample introduction in inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 50B(4-7): 463-75.

Solid sampling using electrothermal vaporization is an attractive sample introduction method for at. absorption spectrometry (AAS), inductively coupled plasma at. emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). For AAS, the method is well established. The techniques needed to apply SS-ETV in ICP-based methods are described, with the emphasis on the coupling of different types of ETV-devices to the inductively coupled plasma torch and on the requirements for the spectrometer and the data acquisition and handling system. Though standardization is not straightforward, std. addn. and external calibration with solid stds. yield accurate results. The latter is demonstrated by the anal. of std. ref. materials. Figures of merit for SS-ETV-ICP-AES and SS-ETV-ICP-MS are presented. The literature concerning ICP-AES and ICP-MS (methods and applications) is briefly reviewed and new results of SS-ETV-ICP-MS anal. of SRMs are presented.

FUN* 133) Hughes, D. M., C. L. Chakrabarti, et al. (1995). "Seawater as a multi-component physical carrier for ETV-ICP-MS." Spectrochimica Acta, Part B: Atomic Spectroscopy 50B(4-7): 425-40.

The beneficence of NASS-3 sea water in enhancing analyte response in ETV-ICP-MS was studied from a mechanistic viewpoint. Seawater serves as a multi-component phys. carrier which acts primarily to increase the transport efficiency of analytes having wide ranging volatiles. A study of the major components of seawater revealed that HCl, released upon the hydrolysis of $MgCl2$, is most beneficial to very volatile elements (Cd, Rb, Cs and Tl), volatilization of NaCl affects elements of intermediate volatility (Pb, Ag, In, Ga and Bi), and MgO vaporization increases the transport efficiency of involatile elements (Co). Analyte signal enhancements were reduced or signal suppression occurred when NaCl or NASS-3 was added in amts. >0.07 mg. The carrier that caused the least signal suppression when used at high concn. was HCl. Decreasing the ETV heating rate enhances the effect of the phys. carrier if the matrix element and analyte co-vaporize.

REV* 134) Olson, L. K., N. P. Vela, et al. (1995). "Hydride generation, electrothermal vaporization and liquid chromatography as sample introduction techniques for inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 50B(4-7): 355-68.

A review, with 63 refs., is given. Although the most common method of sample introduction for inductively coupled plasma-mass spectrometry (ICP-MS) used in pneumatic nebulization, it suffers from limitations particularly with respect to the transport efficiency. In an effort to improve the analyte transport to the plasma, many alternative techniques were studied, including electrothermal vaporization (ETV) and hydride generation, among others. Flow injection and liq. chromatog., although they employ pneumatic nebulization, also were studied as sample introduction techniques due to the ability to analyze small vol. samples and obtain speciation information. Here, some advances in sample introduction for ICP-MS is discussed including hydride generation and ETV techniques. Recent studies in HPLC-ICP-MS will also be described. Advantages and disadvantages of each method will be reviewed together with the application to some representative samples.

FUN* 135) Vanhaecke, F., S. Boonen, et al. (1995). "Solid sampling electrothermal vaporization inductively coupled plasma mass spectrometry for the determination of arsenic in standard reference materials of plant origin." Journal of Analytical Atomic Spectrometry 10(2): 81-7.

The direct detn. of As in solid samples of plant origin using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) is reported. The 1st phase of the work consisted of an optimization of the carrier gas flow rate and the heating cycle of the modified graphite furnace (ashing and vaporization temps.). A systemic study of the signal profiles (signal intensity as a function of time) showed that As coming from the solid samples and As coming from liq. stds. added to the solid material, only showed an analogous behavior on condition that these liq. spikes were previously dried before the solid sample was introduced into the sample boat. The potential of the technique was assessed by establishing figures of merit and analyzing some std. ref. materials for As. An abs. limit of detection of .apprx.1 pg was established for As, corresponding to a relative limit of detection of .apprx.1 ng g-1 for a typical sample mass of 1 mg. Results obtained for the As content in the samples analyzed were not deteriorated by the presence of Cl, as even on addn. of amts. of Cl exceeding the Cl content of the samples no 40Ar35Cl+ interference on the 75As+ signal could be established. For the detn. of As in these ref. materials of plant origin, several methods of calibration were studied, including external calibration using both liq. and solid stds. and single std. addn. The use of an internal std. (Sb) was studied and its requirement was assessed as being from advisable to imperative, depending on the calibration method used. Although several methods offered possibilities for accurate detn. (mean deviation between ETV-ICP-MS results and certified values <10%), single std. addn. was assessed to be the most practicable and straightforward method.

APP* 136) Santosa, S. J. and S. Tanaka (1995). "Inductively coupled plasma mass spectrometry for sequential determination of trace metals in rain and river waters using electrothermal vaporization." Analytical Letters 28(3): 509-34.

The sequential detn. of Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, and Pb in rainwater and river water samples was studied using an inductively coupled plasma mass spectrometry (ICP-MS) with a graphite rod electrothermal vaporizer in the presence of the mixed modifier of Pd nitrate and Mg nitrate. The sensitivity enhancements due to the modifier were obsd. for all analytes. Detection limits as high as 0.52, 0.13, 0.89, 0.35, 1.76, 0.5, 0.9, 0.5, 0.04, 1.03, 0.28, 0.07, 0.1, and 3.78 pg, resp., for Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, and Pb were obtained. The repeatability of sample solns. were very good, i.e. 1-7% (as a coeff. of variation) and the recoveries of elements were good enough, i.e. 81-106%, using a std. addn. method. There was no difference between the results obtained by nebulizer ICP-MS and those obtained by this method, except for Zn and As.

APP* 137) Tsoupras, G. (1996). "ICP-MS application to semiconductor processing chemical materials analysis." Analusis 24(9-10): M23-M28.

The anal. results of metallic impurities found in semiconductor grade chems. are reported. The HP-4500 ICP-MS instrument was used to analyze, in concd. acids, all metallic traces required by the semiconductor manufacturers. Electrothermal vaporization (ETV) and microconcentric nebulization (MCN) enabled the anal. of small vols. and difficult matrix samples. The Shield Torch system, under cool plasma conditions, virtually eliminates the interferences due to the plasma gas (Ar) polyat. ions that affect the anal. of the important microcontaminants such as K, Ca, and Fe. The method of std. addns. was used to quantitate the analytes. Detection limits for all metallic impurities were substantially lower than required by the industry.

FUN* 138) Sparks, C. M. (1996). Sample transport in electrothermal vaporization-inductively coupled plasma-mass spectrometry. Univ. of Texas,Austin,TX,USA. FIELD URL:: 181 pp.

APP* 139) Walther, A., G. Werner, et al. (1996). "Use of electrothermal-vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) for determination of suspended-matter components." CANAS '95, Colloquium Analytische Atomspektroskopie, Konstanz, Germany, Apr. 2-7, 1995: 561-566.

ETV-ICP-MS was employed for the anal. of suspended matter collected from aquatic systems. By the addn. of Pd as modifier, high recoveries were obtained for As, Bi, Cd, Li, Sb, Se, Sn, and Zn. The detn. limits were, in ng/mL: As, 0.04; Bi, 0.0003; Cd, 0.01; Li 0.05;, Sb, 0.02; Se 1.24;. Sn 0.05; and Zn 0.35.

FUN * 140) Hoffmann, E., C. Luedke, et al. (1996). "Studies of internal standardization in electrothermal-vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) with a transversely heated graphite tube." CANAS '95, Colloquium Analytische Atomspektroskopie, Konstanz, Germany, Apr. 2-7, 1995: 157-162.

For the first time, a transversely heated electrothermal vaporizer was used in combination with ICP-MS. A direct and brief connection to the injector tube of the ICP torch provided the condition that only low transport losses of the sample vapor occurred. With this arrangement, one can attain not only an increase in the ion intensity, but one can also decrease the well-known bending of the calibration curves in the lower concn. range, caused by long-term heating of the graphite tubes, with longer lines to the plasma. Moreover, the memory effect is lower. Measurements with Pb and Cd resulted in an improvement in the reproducibility of the anal. signal by internal standardization. In the ETV-ICP-MS, the analyte element itself can also be an internal std,. esp. if it possesses >1 stable isotope. The solvents for these analyses were water and HCl solns.

APP* 141) Wanner, B., P. Richner, et al. (1996). "Use of modifiers in electrothermal-vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS)." CANAS '95, Colloquium Analytische Atomspektroskopie, Konstanz, Germany, Apr. 2-7, 1995: 143-148.

The use of modifiers, such as NH4F, NH4Cl, CCl2F2, and CHF3, for the detn. of difficultly volatile elements, such as lanthanum and uranium and for the detn. of boron by electrothermal-vaporization inductively coupled plasma mass spectrometry is described. The abs. detection limit was 2-6 pg for boron, and 10 fg for lanthanum and uranium.

APP* 142) Schramel, P. and I. Wendler (1996). "Inductively coupled plasma mass spectrometry (ICP-MS) with electrothermal vaporization (ETV)." CANAS '95, Colloquium Analytische Atomspektroskopie, Konstanz, Germany, Apr. 2-7, 1995: 137-142.

The capabilities of inductively coupled plasma mass spectrometry coupled with electrothermal vaporization for detn. of trace elements in medicinal, biol., and environmental samples is discussed and illustrated by detn. of selenium, molybdenum, and platinum, and detn. of cadmium and lead in seawater.

FUN* 143) Ortner, H. M., U. Rohr, et al. (1996). "Studies of graphite tube corrosion by gravimetry and electrothermal-vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS)." CANAS '95, Colloquium Analytische Atomspektroskopie, Konstanz, Germany, Apr. 2-7, 1995: 89-96.

Graphite tubes that wear coated with pyrolytic carbon showed less mass loss with the no. of thermal cycles in the conditioning process as measured by gravimetry. In the ETV-ICP-MS tests, the corrosion rate for coated and uncoated tubes was greater in atomization-annealing test conditions than for drying-ashing test conditions.

FUN* 144) Fonseca, R. W. and N. J. Miller-Ihli (1996). "Influence of sample matrix components on the selection of calibration strategies in electrothermal vaporization inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 51B(13): 1591-1599.

Quantification of both digested and slurry samples were studied using ultrasonic slurry electrothermal vaporization inductively coupled plasma mass spectrometry (USS-ETV-ICP-MS). The results of external calibration using aq. stds., method of addns., and In as an internal std. were compared. The elements studied include: Mn, Ni and Cu and the materials analyzed include: NIST SRM 1548 total diet and SRM 1549 milk powder. Pd was used as a phys. carrier and O ashing was used to remove the org. part of the slurry matrix. Different degrees of matrix suppression effects were obsd. when different skimmer cones were employed. Aging of the skimmer cone and consequent loss of its original circular symmetry and decrease in orifice size resulted in differences in sampling of the ion beam and changes in the degree of matrix effects were obsd. as the skimmer cone was rotated. The presence of matrix suppression effects is evidenced by strong suppressions in the Ar2, C and analyte signals. When matrix suppression effects were present, the method of external calibration provided low recoveries (av. accuracy 73 +- 12%), therefore it was necessary to use the method of addns. to compensate for these problems, providing an av. of 108 +- 13%. When matrix effects were absent, the external calibration method resulted in an av. accuracy of 101 +- 16%.

APP* 145) Galbacs, G., F. Vanhaecke, et al. (1996). "Determination of cadmium in certified reference materials using solid sampling electrothermal vaporization inductively coupled plasma mass spectrometry supplemented with thermogravimetric studies." Microchemical Journal 54(3): 272-286.

The present study describes the application of solid sampling electrothermal vaporization inductively coupled plasma mass spectrometry (SS-ETV-ICP-MS) for the direct detn. of Cd in five certified ref. materials of plant, soil, and sediment origin. The work incorporates the optimization of the most important instrumental parameters (furnace heating program, carrier gas flow rate, plasma forward power) and notes significant differences in signal response behavior of samples of different origin. The applicability of TG coupled to mass spectrometry for the optimization of SS-ETV-ICP-MS was also evaluated. TG information and data were thoroughly exploited in every phase of the study. Figures of merit, such as abs. limits of detection (0.2-0.5 pg Cd in 1 mg sample), sensitivities (0.45-2.0 105/ng Cd), and precision (5-10% relative std. deviation), were also assessed. Three methods of standardization, including solid calibration using certified ref. materials, generalized simplified std. addn., and multiple std. addn., were tested, out of which the method of multiple std. addn. is the most practical and reliable.

FUN* 146) Doherty, W., P. M. Outridge, et al. (1996). "Technique for the introduction of dry atomic vapors for improved optimization and diagnostic studies of laser ablation inductively coupled plasma spectrometry." Journal of Analytical Atomic Spectrometry 11(11): 1123-1126.

An ETV technique is described for introducing internal stds. (IS) into the sample carrier gas emanating from LA cells. Unlike 'wet-dry' dual flow systems, this method introduces the stds. as a dry vapor prior to the spectrometer torch, thereby avoiding the polyat. ion interferences assocd. with wet plasmas and the need for specially designed dual flow torches and nebulizers. The IS elements behave similarly to ablated analyte elements and polyat. Ar ions of similar mass under changing instrument conditions (lens settings and forward power). The technique offers improved dry plasma spectrometer optimization over previous methods, and the opportunity for sepg. and studying confounded LA and plasma phenomena such as the sources of signal noise and nonspectroscopic interferences. The system is easy to operate, and currently produces IS signal stability of ?1% relative std. deviation over 15 min and ?5% over 1 h. With further refinements in stability, internal standardization of spectrometer operation will also be possible.

FUN* 147) Nonose, N., N. Matsuda, et al. (1996). "Signal enhancement effect of halogen matrix in electrothermal vaporization-inductively coupled plasma-mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 51B(12): 1551-1565.

In W furnace electrothermal vaporization(ETV)-inductively coupled plasma mass spectrometry(ICP-MS), the presence of halogen matrixes caused a signal enhancement for volatile elements such as Zn, Cd and Pb, whose halides melting and b.ps. were relatively low. To clarify the mechanism of signal enhancement in ETV-ICP-MS, the effects of chem. interaction between analytes and halogen matrixes on the surface of ETV furnace, the transport efficiency of vaporized analytes from the furnace into the ICP and the phys. properties of the ICP itself and of the micro plasma (interface plasma) in the interface region between the sampling and the skimmer cones were studied by at. absorption and at. emission spectrometry. Among the effects mentioned above, neither the chem. interaction on the surface of the ETV furnace nor the transport efficiency of vaporized analytes could be related to the analyte signal enhancements. The degree of enhancement depends on the ionization potential of the coexisting halogen and was not caused by a variation in the phys. properties of the ICP but rather by a variation of those of the interface plasma. Probably the halogen matrixes affects the phys. properties of the interface plasma, contributing to the promotion of the ionization of analytes.

APP* 148) Alvarado, J. S. and M. D. Erickson (1996). "Determination of long-lived radioisotopes using electrothermal vaporization-inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 11(10): 923-928.

A general method for the detn. of long-lived radioisotopes by integrating electrothermal vaporization and inductively coupled plasma-mass spectrometry (ETV-ICP-MS) to vaporize environmental samples with complex inorg. matrixes is described. The method required no sample pre-treatment and minimized sample size. The rationale was to use chem. modifiers such as CHF3 to form metal fluorides with much lower boiling-points than other metal compds. (such as oxides and carbides). Given sufficiently high temps. and long reaction times, samples in other chem. forms are converted into elemental halides and vaporized. The characterization and application of ETV-ICP-MS for the detn. of radioisotopes is described. The detection limits for 99Tc, 238U, 236U, 232Th, 230Th and 226Ra were similar to those obtained with ultrasonic nebulization (USN-ICP-MS). Abs. detection limits ranged from 0.5 fg for 226Ra to 5 fg for 238U. Anal. calibration plots wee linear at 2-3 orders of magnitude. Matrix effects caused by Group IA and IIA elements were minimized by changing the nature of the sample and by using temporal-thermal programming without affecting anal. performance. Comparison studies between ETV-ICP-MS and classical radiometric techniques were performed for various environmental samples.

APP* 149) Riter, K. L., O. I. Matveev, et al. (1996). "The determination of lead in whole blood by laser enhanced ionization using a combination of electrothermal vaporizer and flame." Analytica Chimica Acta 333(1-2): 187-192.

A system for electrothermal vaporization - laser enhanced ionization spectrometry (ETV-LEIS), developed in this lab., was used for the detn. of lead concns. in whole blood. Blood stds. from the Centers for Disease Control (CDC) and the National Institute of Stds. and Technol. (NIST) were dild. 21:1 with ultrapure water and analyzed. Good agreement was found between the CDC and NIST stds. A linear anal. curve was obtained with a detection limit (3s) of 8.9*10-3mgdl-1 (890 fg abs.) for lead in whole blood. This compares favorably with other current methods for blood-lead detns. including isotope diln. inductively coupled mass spectrometry (ID-ICP-MS) and graphite furnace at. absorption spectrometry (GFAAS).

APP * 150) Laly, S., K. Nakagawa, et al. (1996). "Optimization of electrothermal vaporization, inductively coupled plasma mass spectrometry conditions for the determination of iron, copper, nickel and zinc in semiconductor grade acids." Spectrochimica Acta, Part B: Atomic Spectroscopy 51B(11): 1393-1401.

An electrothermal vaporization (ETV) unit, for introducing samples with high acid concn. and low vol., into inductively coupled plasma (ICP) has been described. Some features of ETV-ICP-MS for single-element detn. have been investigated. A no. of studies have been carried out to investigate the optimum operating conditions such as vaporization temp., vaporization interval and carrier gas flow rate. The study highlights the detn. of Fe, Ni, Cu and Zn. For all elements except Zn, a vaporization temp. > 2700 Deg was selected. In accordance with the vaporization nature, elements were placed in two groups for multi-element detns. The first group consisted of Fe, Cu and Ni and the second group of Zn. On the basis of the detns., we derived the detection limits of these elements in 6 in. wafer for our future studies. The results obtained are compared with those of other existing methods.

APP* 151) Yan, X., T. Tanaka, et al. (1996). "Electrothermal vaporization for the determination of halogens by reduced pressure inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 51B(11): 1345-1353.

Trace level quantities of some halogen elements are detd. by coupling tungsten filament electrothermal vaporization (ETV) with reduced pressure argon inductively coupled plasma mass spectrometry (ICP-MS). Microliter aq. samples of chlorides, bromides and iodides were loaded on the tungsten wire, where they were dried at const. current and then vaporized by using a high-capacity condenser discharge. On decreasing the pressure of the plasma, analyte intensity increased sharply. The reduced pressure ICP is seen to give a much narrower, more intense signal profile. The detection limits for bromine and chlorine improved about 1 times compared with an atm. pressure ICP ionization source. An electron collision ionization mechanism may contribute most to halogen ionization for reduced pressure ICP. The linear dynamic range was over three orders of magnitude. The precision was generally between 3-8%. Matrix effect was investigated with Na as a matrix element. Abs. detection limits for the elements studied are in the picogram to subnanogram range.

APP* 152) Liaw, M.-J. and S.-J. Jiang (1996). "Determination of copper, cadmium and lead in sediment samples by slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 11(8): 555-560.

Ultrasonic slurry sampling-ETV-ID-ICP-MS was applied to the detn. of Cu, Cd and Pb in several sediment samples. The influence of instrument operating conditions, slurry prepn., and nonspectroscopic and spectroscopic interferences on the ion signals and accuracy and precision of isotope ratio detn. was studied. The isotope ratios of each element were calcd. from the peak areas of each injection peak. The precision of isotope ratio detn. was better than 5%. The method was applied to the detn. of Cu, Cd and Pb in a harbor sediment ref. material (PACS-1) and in a sediment sample collected from the Taiwan Straits. The accuracy was better than 6% and the precision was better than 12%. The concns. of Cu, Cd and Pb detd. in the sediment samples by the ID method were compared with the results of external calibration and std. addns. methods.

APP* 153) Chapple, G. and J. P. Byrne (1996). "Direct determination of trace metals in sea-water using electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 11(8): 549-553.

A method is described for the direct anal. of five transition elements (Co, Cu, Mn, Ni, V) in sea-water using ETV-ICP-MS. Interferences from the sea-water matrix were eliminated by a combination of in situ sepn. of analyte and matrix components in the ETV, and use of HNO3 as a chem. modifier. The HNO3 facilitates the removal of chloride from the sea-water matrix during the sample drying stage, while optimization of the ETV heating program allows for effective sepn. of residual matrix and analyte species, thus reducing ionization suppression and space charge effects in the ICP-MS. Calibration stds., prepd. by spiking a sea-water matrix stripped of trace metals by ion exchange, gave excellent linearity and allowed for direct detn. of selected analytes without the use of std. addns. Detection limits ranged from 0.003 mg L-1 for V to 0.14 mg L-1 for Cu. The precision and accuracy of the method were checked by anal. of two certified ref. sea-waters.

APP* 154) Samuel, L., K. Nakagawa, et al. (1996). "Optimization of ETV-ICP-MS conditions for the determination of multi-elements in semiconductor grade acids." Fresenius' Journal of Analytical Chemistry 356(1): 31-36.

The performance of an electrothermal vaporization (ETV) unit as a sample introduction device for an inductively coupled plasma mass spectrometer (quadrupole-ICP-MS) was evaluated. The technique has several advantages over the conventional nebulization method. Some features of ETV-ICP-MS for single element detn. were studied. Attempts were made to optimize the exptl. parameters such as vaporization temp., vaporization interval and carrier gas flow rate. The study highlights the detn. of Cr, Mn, Al and Na. A compromise condition for multielement detn. was suggested and tested from single-element optimum conditions obtained. 25 mL soln. was used for the anal. Results obtained for the anal. of conc. HCl samples are also reported.

APP* 155) Berryman, N. G. and T. U. Probst (1996). "Parameter optimization of electrothermal vaporization inductively coupled plasma mass spectrometry for oligoelement determination in standard reference materials." Fresenius' Journal of Analytical Chemistry 355(7-8): 783-788.

The operational parameters of the graphite furnace for electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS), i.e. the internal carrier gas flow rate, the total carrier gas flow rate, the sample pretreatment temp. and the volatilization temp., are optimized for oligoelement detns. (75As, 9Be, 112Cd, 50Cr, 65Cu, 103Rh, 123Sb). The volatilization temps. of As and Cr are compared to those obtained by graphite furnace at. absorption spectrometry (GFAAS). Several modifiers Mg(NO3)2, Pd(NO3)2, Mg(NO3)/Pd(NO3)2, Ni(NO3)2 alone and in combination with NaCl was varied to find the optimal modifier conditions. ETV-ICP-MS signal enhancements by a factor of 10 to 130 resp. to those of conventional nebulization were obtained. The optimized parameters are evaluated by analyzing the water std. ref. NIST 1643c and the aqua regia soln. of the lake sediment ref. material BCR 280.

FUN* 156) Goltz, D. M., D. C. Gregoire, et al. (1996). "Characterization and evaluation of Mo, Ta, Re and W metal vaporization surfaces for electrothermal vaporization ICP mass spectrometry." Canadian Journal of Applied Spectroscopy 41(3): 70-76.

The utility of using metal foil inserts within a graphite tube to provide an alternative vaporization surface for ETV-ICP-MS was studied. Four different metal surfaces: Mo, Ta, Re and W were studied and their performance compared to that of graphite. Expts. to det. plasma loading caused by vaporization of metal showed that at temp. >2000 Deg, significant quantities of metal were volatilized. Signals for volatile elements were not affected by the vaporized metal, however, signals for relatively involatile elements were suppressed because these elements are co-vaporized at high temps. with metal originating from the vaporization surface. Calibration curves were obtained and anal. figures of merit calcd. for Yb, Ho, Ag, Th and U. In general, higher signals were achieved with a metal vaporization surface however this increase in sensitivity was counterbalanced by higher blank signals (compared to graphite) and poor signal reproducibility resulting in poorer limits of detection when using metal vaporization surfaces.

APP* 157) Wanner, B., P. Richner, et al. (1996). "The role of modifiers in electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) for the determination of B, La and U." Spectrochimica Acta, Part B: Atomic Spectroscopy 51B(8): 817-827.

The role of modifiers in electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) for the detn. of refractory elements such as La or U and carbide forming elements such as B was studied. Solns. of NH4F, NH4Cl, NH4Br, NaCl, NaF, NH4HSO4, (NH4)2HPO4, the gaseous halogenated hydrocarbons CHF3 and CCl2F2 and HCl were used as modifiers. The mechanism of the modifier effect and the influence of modifiers on sensitivity enhancement were studied. The sensitivity enhancements are great enough to achieve abs. detection limits of 2-6 pg for boron and 10 fg for La and U. The signal reproducibility is 0.5-3.0% for a concn. of 1 mg/L La and U, and 20 mg/L boron. Therefore, by adding modifiers, the use of ETV-ICP-MS can be extended to trace element detn. of refractory and carbide forming elements in ml amts. of sample.

APP* 158) Luedke, C., E. Hoffmann, et al. (1996). "Particle analysis of car exhaust by ETV-ICP-MS." Fresenius' Journal of Analytical Chemistry 355(3-4): 261-263.

Particulates of platinum group elements (Pt, Rh, Pd, Ir) emitted in automotive catalyst exhaust were measured down to the pg/m3 level. Samples were taken from a std. type three-way catalyst equipped gasoline engine, running on a computer controlled dynamometer. Particulates in catalyzed car exhaust were sampled fractionated according to size by using the cascade impactor with sep. targets mounted underneath each nozzle. The targets, small flat disks made of pure graphite, were subsequently analyzed by electrothermal vaporizer-inductively coupled plasma-mass spectrometer (ETV-ICP-MS) without any preparatory steps.

APP* 159) Li, H., B. Gong, et al. (1996). "Tributyl Phosphate as a Sensitivity-Enhancing Solvent for Organotin in Carbon Furnace Atomic Absorption Spectrometry." Analytical Chemistry 68(13): 2277-2280.

Tri-Bu phosphate (TBP) is a sensitivity-enhancing solvent for organotin compds. in graphite furnace at. absorption spectrometry; Bu2Sn(O2CCH3)2, Bu2Sn(O2CC11H23)2, Bu3SnCl, and Bu4Sn all give 1 order of magnitude higher sensitivities in TBP than in toluene or EtOAc. The sensitivities are enhanced further 1-2 orders of magnitude in TBP, when PdCl2(MeCN)2 is added as a matrix modifier in the org. solvent. Among the four organotin compds., Bu2Sn(O2CCH3)2 and Bu2Sn(O2CC11H23)2 give better sensitivities than Bu3SnCl and Bu4Sn in the absence of Pd in any org. solvent, which suggests that the O atom in the Sn compd. might form Sn oxides that are resistant to volatilization loss during ashing. Scanning electron microscopic, electrothermal vaporization ICPMS, and powder x-ray diffraction studies show that the final products before atomization include P-contg. compds. Sn2P2O7, SnP2O7, and Pd9P2, besides Sn-Pd alloys, PdSn, Pd3Sn, Pd2Sn, Pd3Sn2, and PdSn3. These P-contg. compds. would more efficiently stabilize Sn and suppress Sn vaporization loss during ashing, to give higher sensitivity.

APP * 160) Naka, H. and D. C. Gregoire (1996). "Determination of trace amounts of sulfur in steel by electrothermal vaporization-inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 11(5): 359-363.

A method is described for the detn. of trace amts. of S in steel by ETV-ICP-MS. The effect of Fe, Cu, Al, Si, V, Co, Ni, Cr, Mo, Ti, Mn and W on S signals and the use of KOH as a chem. modifier were studied. Most concomitant elements affected the intensity and shape of the S ETV-ICP-MS signal. The addn. of KOH as a chem. modifier only partially eliminated these interference effects. The use of isotope diln. calibration and the removal of Fe by solvent extn. with 4-methylpentan-2-one were used to compensate for interference effects. A precision of +-0.2 mg g-1 at an S concn. of 2 mg g-1 was achieved. The limit of detection for S in steel was 0.05 mg g-1.

APP* 161) Escobar, M. P. (1996). Determination of wear metals in lubricating oil by electrothermal vaporization inductively coupled plasma mass spectrometry. Univ. of Florida,Gainesville,FL,USA. FIELD URL:: 177 pp.

APP* 162) Gruenke, K., H. J. Staerk, et al. (1996). "Determination of traces of heavy metals (Mn, Cu, Zn, Cd and Pb) in microsamples of teeth material by ETC-ICP-MS." Fresenius' Journal of Analytical Chemistry 354(5-6): 633-5.

Heavy metal levels in tooth compartments would appear to be a suitable indicator of long-term exposure. A method has been developed to assess the heavy metal levels (Mn, Cu, Zn, Cd, and Pb) in tooth compartments like dentin and enamel. For the simultaneous detn. of these elements in small dentin sample amts. (in some cases <1 mg), inductively coupled plasma mass spectrometry with electrothermal vaporization was the method of choice. Sample prepn., method development, and first results of the application of the method for the anal. of tooth compartments have been described. Variation in the elemental concns. depending on the kind of tooth and the sampling position have been obsd. The method is useful for epidemiol. studies of the heavy metal exposure of children.

APP* 163) Anon (1996). "HP introduces the first benchtop electrothermal vaporization system designed expressly for ICP-MS." Chromatographia 42(3/4): 238-42.

APP* 164) Boonen, S., F. Vanhaecke, et al. (1996). "Direct determination of Se and As in solid certified reference materials using electrothermal vaporization inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 51B(2): 271-8.

Firstly, electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) was successfully applied for the direct detn. of Se in solid certified ref. materials (CRMs) of both biol. and environmental origin. Secondly, to exploit one of the most important advantages of ICP-MS (the multi-element capability), Se and As were detd. simultaneously in two CRMs (Sea lettuce and Estuarine sediment), the potential of ETV-ICP-MS for accurate mono-element detn. of As in solid CRMs having been proven in a previous study. For both the mono-element and the multi-element detns., several parameters (ashing and vaporization temp., carrier gas flow rate) were studied systematically to obtain optimized conditions. Both the linearity of the mass response curves and the signal profiles (signal intensity as a function of time) were examd. Abs. detection limits, based on the 3s criterion, are .apprx.1 pg. Using single std. addn. for calibration and Sb as an internal std., accurate results were obtained for both the mono-element detns. of Se (mean relative difference with the certified value of 6.5%) and the multi-element detns. of Se and As (mean relative difference with the certified values of, resp., 6.6% for Se and 7.2% for As).

APP* 165) Komoda, M., K. Chiba, et al. (1996). "Determination of trace impurities on silicon-wafer surface by isotope dilution analysis using electrothermal vaporization/inductively coupled plasma mass spectrometry." Analytical Sciences 12(1): 21-5.

The feasibility of coupling the isotope diln. (ID) anal. and the electrothermal vaporization/inductively coupled plasma mass spectrometry (ETV-ICP-MS) was studied to det. trace impurities on Si-wafer surface precisely. The precision of the isotope ratio measurement was studied for single element and sequential two-element detn. by ETV-ICP-MS. In the case of the single element detn., 0.1 ng ml-1 of Cu in a 20 mL sample could be measured with relative std. deviation <6%, and 1 ng ml-1 of Cu and Zn could be measured with relative std. deviation <5% in the sequential two-element detn. Coupling of ID and ETV-ICP-MS was applied to det. trace impurities of Cu, Zn and Pb, which were collected by etching a Si-wafer surface with a vapor mixt. of HNO3 and HF. The amt. of etching soln. obtained from one Si-wafer was .apprx.200 mL. Those impurities were detd. at 3 * 108-8.7 * 109 atoms cm-2 with an relative std. deviation of 2% by ID-ETV-ICP-MS. The amt. of Cu on the Si-wafer surface was also detd. by calibration method with ETV-ICP-MS and by graphite furnace at. absorption spectrometry. The results obtained by these three different methods agreed well with each other.

APP* 166) Escobar, M. P., B. W. Smith, et al. (1996). "Determination of metallo-organic species in lubricating oil by electrothermal vaporization inductively coupled plasma mass spectrometry." Analytica Chimica Acta 320(1): 11-17.

We have developed a method for the detn. of Al, Mg, Fe, and Y metallo-org. compds. in lubricating oil by electrothermal vaporization inductively coupled plasma mass spectrometry. A pneumatically-operated graphite plug holder was added to the ETV so that the dosing hole could be plugged during the ETV heating cycle.

FUN* 167) Sparks, C. M., J. A. Holcombe, et al. (1996). "Sample retention in the transport tubing between an electrothermal vaporizer and an inductively coupled plasma mass spectrometer." Applied Spectroscopy 50(1): 86-90.

The transport tube between a com. electrothermal vaporizer (ETV) and the torch for an inductively coupled plasma mass spectrometer (ICP-MS) was analyzed for sample that had been vaporized. A common analyte carrier, NaCl, and Ag were the primary samples analyzed. It was found that approx. 10% of the sample was retained in the transport tubing. This percentage could be varied by changing the total mass of sample vaporized, probably because of the smaller particles being formed. A temp. distribution of the argon gas in the transport tube was also obtained for max. power heating of the ETV, for a one-second vaporization step, and for various flow rates.

APP* 168) Hastings, D. W., S. R. Emerson, et al. (1996). "Determination of Picogram Quantities of Vanadium in Calcite and Seawater by Isotope Dilution Inductively Coupled Plasma Mass Spectrometry with Electrothermal Vaporization." Analytical Chemistry 68(2): 371-7.

The authors developed a method to measure picogram quantities of V in calcite and seawater by isotope diln. (ID) inductively coupled plasma mass spectrometry using electrothermal vaporization (ETV) to introduce the sample into the plasma. A 50V isotope spike enriched to 44 atom % was equilibrated with samples, followed by chem. purifn. by cation exchange chromatog. Samples were introduced into the ETV unit with a Pd modifier and heated to 1000 Deg. This quant. eliminates the ClO+ isobaric interference with V at m/z 51 for solns. up to 0.5 N HCl. The procedural blank was 0.27 pg of V. Corrections for 50Ti and 50Cr, which interfere with the 50V signal, were made by measurement of 49Ti and 53Cr. These isobaric interferences and variable ArC levels were the limiting sources of error in the ID measurement and diminished the detection limit to 6 pg of V. The detection limit for nonisotope diln. applications was 0.3 pg of V. Measurement precision on the same sample of dissolved calcite over one run was +-3% (1s). Accuracy was confirmed by detn. of V stds. in CaCO3 and by comparative measurement with ID thermal ionization mass spectrometry and graphite furnace at. absorption spectroscopy.

FUN* 169) Fonseca, R. W., N. J. Miller-Ihli, et al. (1997). "Effect of oxygen ashing on analyte transport efficiency using ETV-ICP-MS." Applied Spectroscopy 51(12): 1800-1806.

Oxygen ashing was used in electrothermal at. absorption spectroscopy to eliminate org. matrix sample components and is particularly useful when doing direct solids anal. of biologicals using ultrasonic slurry sampling. Oxygen ashing also proved to be useful for the anal. of slurry samples using ultrasonic slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry (USS-ETV-ICP-MS). The effect of oxygen ashing on analyte transport in USS-ETV-ICP-MS was evaluated. Oxygen ashing in the presence of Pd modifier (Pd/O2) enhances analyte transport efficiency, possibly as a result of an increase in the no. of carbon particles present in the graphite furnace during the vaporization step. These carbon particles act as a phys. carrier, providing a surface on which the analytes can condense to be transported more efficiently. The carbon particles act as a phys. carrier, providing a surface on which the analytes can condense to be transported more efficiently. The carbon produced at earlier times, with Pd/O2, may be the result of either dissocn. or fracture of the graphite during the rapid heating of the furnace. Pd, which was initially added to act as a phys. carrier, also seems to be acting as a catalyst for carbon oxidn. The shift in the carbon signal toward earlier times when using oxygen ashing was carbon signal toward earlier times when using oxygen ashing was obsd. only when Pd was present. Scanning electron micrographs of a home-made graphite platform revealed that portions of the graphite substrate were missing when Pd/O2 was used and that clearly visible pits were found in the graphite. Oxygen ashing combined with 1 mg Pd improves quant. results by removing the org. part of the matrix present in slurry samples while enhancing analyte transport efficiency by providing carbon particles that serve as a phys. carrier.

APP* 170) Byrne, J. P., R. S. C. McIntyre, et al. (1997). "Determination of chromium by electrothermal vaporization inductively coupled plasma mass spectrometry." Canadian Journal of Analytical Sciences and Spectroscopy 42(4): 95-101.

When electrothermal vaporizers constructed from graphite are used for the detn. of chromium by ETV-ICP-MS, isobaric interferences are caused by carbon argides. Methods for minimizing these interferences were studied and are reported. These include (a) use of 53Cr as the isotope of choice for anal., (b) redn. of the temp. at which the analyte is vaporized from the ETV and (c) addn. of a chem. modifier (8-hydroxyquinoline) to assist volatilization of chromium at lower temps. This strategy results in a significant improvement in the signal to background ratio for Cr and improves its limit of detection by a factor of twenty. Three soln. phase halide modifiers were also studied. Although these were used to assist the lower temp. volatilization of refractory elements with ETV-ICP-AES, they proved to be of no benefit for the ETV-ICP-MS anal. of Cr. Addn. of modifiers such as NH4F and NaOCl caused increased background signals from carbon argides because of addnl. carbon removed from the surface of the ETV in the presence of these modifiers.

FUN* 171) Byrne, J. P., D. C. Gregoire, et al. (1997). "Vaporization and atomization of the platinum group elements in the graphite furnace investigated by electrothermal vaporization-inductively coupled plasma-mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 52B(11): 1575-1586.

The mechanisms by which the Pt group elements (PGEs) are vaporized in the graphite furnace were studied using electrothermal vaporization-inductively coupled plasma-mass spectrometry (ETV-ICP-MS). Probably five of these elements (Ru, Rh, Pd, Ir and Pt) are reduced to their metallic state in the graphite furnace and then vaporized by direct sublimation of the metal. For Os, the vaporization mechanism is different. In the presence of HNO3, two distinct vaporization processes are obsd. Volatile oxides of Os are released at low temps., but some of this oxide is reduced to relatively involatile Os metal which is then vaporized when the temp. is increased >2000 Deg. The addn. of TeCl2 chem. modifier has minimal effect on the vaporization mechanism and sensitivity for detn. for five of the PGEs. For Os, however, the anal. sensitivity and limit of detection was improved when Te modifier was used in conjunction with a lower vaporization temp. of 1400 Deg. Optimum conditions for the detn. of the PGEs by ETV-ICP-MS are reported, along with their abs. limits of detection; these range from 0.015 pg for Ir to 0.25 pg for Os.

FUN* 172) Grunke, K., H. J. Stark, et al. (1997). "Removal of water and hydrogen from graphite tubes investigated by electrothermal vaporization inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 52B(9,10): 1545-1550.

Inductively coupled plasma-mass spectroscopy (ICP-MS) detection can be applied to study fundamental processes in the graphite furnace. The retention and high-temp. release of water/hydrogen and carbon under various furnace heating conditions are described. Different feasible monitor masses were studied and the signal for 36ArH+ (m/z = 37) is indicative of the amt. of water present. The release of carbon was monitored by measuring the integrated signal at m/z = 13. In the authors' study no water was found in the vaporization step using blank correction of a dry tube. However, the authors obsd. an 36ArH+ signal when the dry graphite tube was heated, even after up to 50 such heating cycles. This behavior was studied by monitoring the intensity of the 36ArH+ signal in long-term expts. with pyrolytic graphite-coated and uncoated tubes. The effect of release of water/hydrogen and carbon was significantly higher for the uncoated tubes. The source of the evolved hydrogen causing the 36ArH+ signal probably is the graphite material of the tube. The influence of the effect on selected analyte ETV-ICP-MS signals (Al, V, Cu, Pb) is described.

APP* 173) Grunke, K., H. J. Stark, et al. (1997). "An investigation of different modifiers in electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS)." Fresenius' Journal of Analytical Chemistry 359(4-5): 465-468.

The suitability of 11 modifiers (Pd-, Mg-, K-, Ca-, and NH4-salts) for electrothermal vaporization coupled to inductively coupled plasma mass spectrometry (ETV-ICP-MS) for the detn. of Mn, Cu, Zn, Cd, and Pb was studied. Solns. contg. varying quantities (10-2000 ng abs.) of these salts were added to 4 different amts. of analyte to study their suitability as modifier and their mass dependent influence. The best sensitivity enhancement for all elements tested was achieved with IrCl3 and PdCl2. From a comparison of the effect of PdCl2 vs. Pd(NO3)2 it was concluded that the mechanism of matrix modification also depends on the chem. form of the modifier. Particularly, for the volatile elements Cd and Zn differences in the behavior of the different chem. compds. of 1 metal (e.g. Pd) is evident, which shows that the enhancement effect is a result of the stabilization of the analytes in the graphite tube prior to vaporization and the improvement of the transport efficiency after vaporization.

APP* 174) Moor, C., P. Boll, et al. (1997). "Determination of impurities in micro-amounts of silver alloys by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) after in-situ-digestion in the graphite furnace." Fresenius' Journal of Analytical Chemistry 359(4-5): 404-406.

Forgeries of antique silver objects can be identified by their fingerprints of impurities. The dissoln. of the samples causes severe problems since Au and Ag have to be dissolved simultaneously. To overcome that difficulty and to minimize the amt. of sample, an ETV-ICP-MS method is presented based on solid sampling and an in situ digestion with HNO3 in a graphite tube. Detns. of Au, Bi, Cd, Pb, Sb, Sn, and Zn were performed in a range of 10-10.000 ppm and with an accuracy of 10-50%. Less than 1 mg sample material was required.

APP* 175) Uggerud, H. T. and W. Lund (1997). "Use of palladium and iridium as modifier in the determination of arsenic and antimony by electrothermal vaporization inductively coupled plasma mass spectrometry, following in situ trapping of the hydrides." Journal of Analytical Atomic Spectrometry 12(10): 1169-1174.

A study was made of Pd and Ir as modifiers in the detn. of As and Sb by electrothermal vaporization inductively coupled plasma mass spectrometry, following hydride generation and in situ trapping of the hydrides in the graphite furnace (HG-ETV-ICP-MS). The trapping temp. was 300 Deg and the vaporization temp. 2300 Deg. The signal intensities of As and Sb increase with decreasing vol. and concn. of the Pd modifier soln.; therefore, a low vol. (10-20 mL) land concn. (10-20 mg L-1) of modifier seems advisable. The obsd. effects were probably due to changes in the transport of analyte to the plasma, because the same effects were not obsd. when the trapped hydrides were detd. by electrothermal at. absorption spectrometry. Also Ir can be used as a modifier in HG-ETV-ICP-MS; Ir and Pd are about equally efficient for this purpose. The advantages of using Ir as modifier are discussed.

APP* 176) Bitterli, B. A., H. Cousin, et al. (1997). "Determination of metals in airborne particles by electrothermal vaporization inductively coupled plasma mass spectrometry after accumulation by electrostatic precipitation." Journal of Analytical Atomic Spectrometry 12(9): 957-961.

A method to det. metals in airborne particles by electrothermal vaporization ICP-MS after sampling by electrostatic pptn. into a graphite tube is described. A mobile sampler was used to collect samples. Calibration was performed with dried aerosol produced by the nebulization of a std. soln. For Cr, Fe, Mn, Cu, Zn, Sr, Cd, Sb, Ba and Pb, the abs. detection limits were in the picogram range. The high sensitivity allowed the monitoring of several metals in ambient air with a time resoln. of hours. The precision was 10-15%. The addn. of 5 mg g-1 of Na (as NaNO3) to the std. solns. improved the signal intensities and reduced the curvature of the calibration curves. The influence of CHF3 was studied but subsequently abandoned owing to a general increase not only of the signals but also of the background.

APP* 177) Berryman, N. and T. Probst (1997). "Rapid determination of 90Sr by electrothermal vaporization-inductively coupled plasma mass spectrometry (ETV-ICP-MS)." Radiochimica Acta 76(4): 191-195.

A 2-step temp. program was developed to det. 90Sr in highly active samples in the presence of Zr. In a first step, Sr is volatilized at 2400 Deg using Ar as a carrier gas, while Zr is completely retained in the graphite tube. It is removed in a second step by adding 0.1% CHF3 to the Ar carrier gas and increasing the temp. to 2650 Deg. Even a 100fold excess of Zr has no detrimental effects on the detn. of 90Sr. The detection limit is 2 pg/mL (10 Bq/mL) without using a modifier.

APP* 178) Takenaka, M., Y. Yamada, et al. (1997). "Determination of ultratrace metallic impurities in silicon wafers by acid vapor decomposition/electrothermal vaporization ICP-MS." Bunseki Kagaku 46(9): 743-747.

An acid vapor decompn. was developed for detn. of ultratrace-level impurities (Cr, Fe, Ni, and Cu) in Si wafers. The wafer surface was exposed with HF/HNO3 to form (NH4)2SiF6, which was dissolved in 5 mL H2O, decompd. with 0.1 mL aqua regia, dried, and dissolved in H2O/H2SO4 to give a sample soln. for electrothermal vaporization ICP-MS. The result showed fine agreement with that obtained by a wet-etching method. The blank level were 10 pg/g for Cr and Fe, 5 pg/g for Ni and Cu.

APP* 179) Willie, S. N., D. C. Gregoire, et al. (1997). "Determination of inorganic and total mercury in biological tissues by electrothermal vaporization inductively coupled plasma mass spectrometry." Analyst (Cambridge, United Kingdom) 122(8): 751-754.

A rapid method for the detn. of total and inorg. mercury in biol. tissues is presented using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV ICP-MS). Samples were solubilized using tetramethylammonium hydroxide. For the detn. of total mercury, sample aliquots (10 mL) are dried and vaporized into the plasma. For the detn. of inorg. mercury, iodoacetic acid, sodium thiosulfate, and acetic acid are added to the sample, cleaving the methylmercury from the tissue. Volatile methylmercury iodide is formed and removed from the ETV as the sample dries, leaving only inorg. mercury to be quantified. A limit of detection of 0.05 mg g-1 in solid samples was obtained. National Research Council of Canada ref. materials DORM-2 (dogfish muscle), DOLT-2 (dogfish liver), and TORT-2 (lobster hepatopancreas) were used to assess the accuracy of the method.

APP* 180) Fairman, B. and T. Catterick (1997). "Simultaneous determination of arsenic, antimony and selenium in aqueous matrixes by electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 12(8): 863-866.

A method for the simultaneous detn. of AS, Se and Sb in aq. matrixes by ETV-ICP-MS was developed. Complex interactions between the analytes and various chem. modifiers are described. A mixed modifier of Pd(NO3)2-Ni(NO3)2 was finally selected for quant. multi-element anal. Criteria of merit of the proposed method include a 0-100 ng g-1 linear range for As and Sb and 0.5-100 ng g-1 for Se. Internal standardization using Te was used to help produce repeatability of 3.9% for As, 6.9% for Se and 2.1% for Sb at the 1 ng g-1 level. Detection limits of 0.03, 0.08 and 0.01 ng g-1 for As, Se and Sb, resp., are routinely achievable. The accuracy of the proposed method was demonstrated with the anal. of several ref. waters. A severe neg. interference on Se by high HCl concns. could be overcome using a Pd(NO3)2-Mg(NO3)2-ascorbic acid chem. modifier.

APP* 181) Csato, I., G. Zaray, et al. (1997). "Direct analysis of silicon carbide powder by total reflection x-ray fluorescence spectrometry." Applied Spectroscopy 51(7): 1067-1072.

Three silicon carbide powders having different grain size distributions were analyzed by total reflection X-ray fluorescence (TXRF) spectrometry with the application of slurry sampling. For the elements investigated (Fe, Ti, V, Cu, Ni, and Ca) the line-to-background ratios show a max. value at a surface concn. of 12.5 mg/min2. For the realization of this surface concn., a 25-mL aq. slurry with a concn. of 1% (m/V) and pH of 10 was dropped onto the hydrophobic quartz carrier plate. For quantification of the intensity data, gallium was added as an internal std. to the slurries. Under these exptl. conditions, the anal. data of the fine-grained powders (80-90% of the powder particles were less than 1.5 mm) are in good agreement with concns. detd. in various labs. by inductively coupled plasma at. emission spectrometry (ICP-AES), ICP mass spectroscopy (MS), electrothermal vaporization- (ETV)-ICP-AES, slurry sampling graphite furnace at. absorption spectroscopy (GF-AAS), and neutron activation methods. Powders with a mean grain size greater than 1.5 mm deviate much more from the ref. data. Calcd. limits of detection (LODs) range from 2 to 25 mg/g. The precision expressed as relative std. deviation (RSD) varies between 4 and 14% for Fe, Ti, and V, whose concns. in the fine-grained silicon carbide samples exceed by a min. of tenfold their limits of detection; however the precision is very poor for Cu (66.6%) and Ni (62.3%), which have concns. near the limits of the detection.

APP* 182) Liaw, M.-J., S.-J. Jiang, et al. (1997). "Determination of mercury in fish samples by slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 52B(6): 779-785.

Ultrasonic slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry (USS-ETV-ICP-MS) has been applied to the detn. of mercury in several fish samples. The effects of instrument operating conditions and slurry prepn. on the ion signals are reported. Palladium was used as modifier to delay the vaporization of mercury. As the vaporization behavior of mercury in fish slurry and aq. soln. is quite different, the std. addn. method was used for the detn. of mercury in ref. materials. The detection limit of mercury estd. from the std. addn. curve was in the range 0.002-0.004 mg g-1 for different samples. This method was applied to the detn. of mercury in dogfish muscle ref. material (DORM-1 and DORM-2) and dogfish liver ref. material (DOLT-1). Accuracy was better than 4% and precision was better than 7% with the USS-ETV-ICP-MS method.

APP* 183) Santosa, S. J., S. Tanaka, et al. (1997). "Sequential determination of trace metals in sea water by inductively coupled plasma mass spectrometry after electrothermal vaporization of their dithiocarmabamate complexes in methyl isobutyl ketone." Environmental Monitoring and Assessment 44(1-3): 515-528.

A sensitive method for sequential detn. of V, Mn, Fe, Co, Ni, Cu, Zn, Mo and Sb in sea water using an inductively coupled plasma mass spectrometry (ICP-MS) after electrothermal vaporization of their dithiocarbamate complexes in Me iso-Bu ketone (MIBK) has been investigated. All analyte elements were simultaneously concd. 20 fold in a single ext. and introduced into the plasma using a graphite rod electrothermal vaporizer (ETV). A sensitivity enhancement due to a chem. modification using a mixed modifier of palladium nitrate and magnesium nitrate was obsd. for all analyte elements. The limits of detection of the method ranged from 2 ng L-1 for Co to 329 ng L-1 for V. For the replicate detns. of analyte elements in a sea water sample, the repeatability was within 10% (as a coeff. variation), except for V (12.8%). The recovery test performed on a sea water sample resulted in values ranging from 87% for Sb to 119% for V. With the exception of Mo, the application of this method for the detn. of the analyte elements in sea water samples collected from the surface to the depth of 5000 m at the sampling station of 34 Deg12.08'N, 141 Deg57.50'E (Oct. 12, 1994) in the northwest Pacific Ocean resulted in vertical distributions and concn. ranges which were in a good agreement with those reported in literatures.

APP* 184) Hughes, D. M., D. C. Gregoire, et al. (1997). "The vaporization of phosphorus compounds and the use of chemical modifiers for the determination of phosphorus by electrothermal vaporization inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 52B(4): 517-529.

The spectral interference on 31P+ from the 14N16O1H+ polyat. ion was essentially eliminated using electrothermal vaporization sample introduction for ICP mass spectrometry (ETV-ICP-MS). Vaporization of P from an electrographite surface stabilized P to higher vaporization temps. when compared to pyrolytic graphite but resulted in high background signals due to memory effects. The thermal vaporization characteristics of (NH4)2HPO4, H3PO4, Na2HPO4, K2HPO4 and Ca(H2PO4)2.H2O were studied. Most P compds. undergo thermal decompn. as the graphite tube is heated and are vaporized as metaphosphates. Iron is a common matrix element in geol. materials and many finished products such as steels. The presence of 1 mg of Fe can cause suppression of the P signal. This interference is most pronounced at high graphite tube heating rates. Nickel, La and Zr were used as chem. modifiers to stabilize P to higher vaporization temps. through compd. formation allowing for the removal of matrix components prior to the volatilization of P. Lanthanum and P when vaporized together gave a thermally stable P species, most likely LaP. As a modifier, however La is not suitable due to the high background signal (memory effect) produced when vaporized esp. on an electrographite surface. Although Ni is effective in thermally stabilizing P, large quantities of the metal are co-vaporized with P resulting in analyte signal suppression. Zirconium is the best modifier for removing the interference produced from the presence of an iron matrix and could be added in large amts. without itself causing P signal suppression. An abs. detection limit of 4 pg was obtained for P vaporized in the presence of 2 mg of zirconium.

FUN* 185) McIntyre, R. S. C., D. C. Gregoire, et al. (1997). "Vaporization of radium and other alkaline earth elements in electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 12(5): 547-551.

The mechanism of vaporization and optimum exptl. conditions was reported in the detn. of Ra and other alk. earth elements (Be, Mg, Ca, Sr, and Ba) by electrothermal vaporization-inductively coupled plasma mass spectrometry (ETV-ICP-MS). Calcd. and published data along with new exptl. results suggested that these elements are vaporized from the surface of the graphite tube as oxides. These oxides are then transported to the argon plasma where dissocn. and ionization take place. Appearance temps. and max. pyrolysis temps. obtained exptl. generally agreed with values obtained using graphite furnace at. absorption spectrometry (GFAAS). For Ra, the optimum pyrolysis and vaporization temps. were 1400 and 2500 Deg, resp. Dild. (1:500) seawater, used as a phys. carrier, was effective in improving sensitivity when used in small quantities, but caused significant suppression of the Ra signal when the analyte was co-vaporized with quantities (>40 mg) of salt. An abs. limit of detection of 1.7 fg was obtained, corresponding to 34 fg/mL in a 50 ml sample.

REV* 186) Gregoire, D. C. (1997). "Electrothermal vaporization sample introduction for inductively coupled plasma mass spectrometry: current status and future prospects. Barringer Award Lecture." Canadian Journal of Analytical Sciences and Spectroscopy 42(1): 1-9.

Electrothermal vaporization as a mode of sample introduction for inductively coupled plasma mass spectrometry offers the analyst a means of analyzing microliter sample vols. or microgram to milligram quantities of solids. The technique reduces oxide formation in the Ar plasma by a factor of 20 and reduces the formation of polyat. ions originating from matrix material by a factor of 50. Analyte is vaporized as the element or in combined form as an oxide or halide species. For this reason, sensitivities for refractory elements are orders of magnitude greater than can be achieved using other micro-anal. techniques such as GFAAS. Although there are many attractive anal. features that can be attributed to ETV-ICP-MS, its ability to handle complex liqs., slurries and solids as well as to take advantage of new developments is mass spectrometer technol. are perhaps its greatest strengths.

APP* 187) Santosa, S. J., S. Tanaka, et al. (1997). "Inductively coupled plasma mass spectrometry for the sequential determination of trace metals in seawater after electrothermal vaporization of their dithiocarbamate complexes in methyl isobutyl ketone." Fresenius' Journal of Analytical Chemistry 357(8): 1122-1127.

A sensitive method was developed for the sequential detn. of V, Mn, Fe, Co, Ni, Cu, Zn, Mo, and Sb in seawater using inductively coupled plasma mass spectrometry (ICP-MS) after electrothermal vaporization of their dithiocarbamate complexes in Me iso-Bu ketone (MIBK). After complexion with Na diethyldithiocarbamate (NaDDTC), all trace analyte elements were simultaneously sepd. from seawater matrix and concd. 20-fold in a single ext. of MIBK, followed by introduction of 10 mL of the ext. into Ar plasma using a pyrolytic graphite rod electrothermal vaporizer (ETV). Sensitivity enhancement due to chem. modification using a mixed modifier of Pd(NO3)2-Mg(NO3)2 was obsd. for all the elements. The limits of detection ranged from 2 ng/L for Co to 329 ng/L for V. For replicate detns. of the elements in seawater, the repeatability was within 10% (as a coeff. variation), except for V (12.8%). The recovery test performed on a seawater sample resulted in a range value from 87% for Sb to 119% for V. The method was successfully applied to seawater samples collected from the surface to the depth of 5000 m at a sampling station in the northwest Pacific Ocean.

APP* 189) Hauptkorn, S., V. Krivan, et al. (1997). "Determination of trace impurities in high-purity quartz by electrothermal vaporization inductively coupled plasma mass spectrometry using the slurry sampling technique." Journal of Analytical Atomic Spectrometry 12(4): 421-428.

A method was developed for the detn. of 14 relevant trace impurities in high-purity quartz based on ETV-ICP-MS using slurry sampling. The ETV device consisted of a double layer tungsten coil. Exptl. conditions were optimized with respect to the temp. program, the carrier gas flow, the internal diam. of the aerosol tubing, ICP-MS measurement parameters and internal standardization. Excluding U, calibration had to be carried out by the std. addns. method because of nonspectral matrix interferences. For U, simple quantification via calibration curves, recorded with aq. stds., was possible. The obsd. interferences also aggravated the background evaluation, which seriously limited the detn. of Al and Fe. The method was applied to the detn. of Al, Ba, Co, Cr, Cu, Fe, Li, Mg, Mn, Na, Pb, Sr, U and Zn in two quartz samples of different grades of purity. The accuracy of the results was checked by their comparison with those obtained by independent methods including instrumental neutron activation anal. The achievable detection limits are between 2 ng/g (Li, U) and 70 mg/g (Al).

REV* 190) Wennrich, R., K. Grunke, et al. (1997). "Environmental analyses with electrothermal-vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS)." Nachrichten aus Chemie, Technik und Laboratorium 45(3): 291-295.

The principles and application of the ETV-ICP-MS with a comparison with other ICP-MS techniques were reviewed (18 refs.). Examples for the application in environmental trace analyses different tooth materials, and ref. substances of sediments and suspended matter were given.

FUN* 191) Nakamura, Y., K. Takahashi, et al. (1997). "Evaluation of electrothermal vaporization, emission intensity-time-wavelength measurement and time resolution combined with an axially viewed horizontal inductively coupled plasma using an echelle spectrometer with wavelength modulation." Journal of Analytical Atomic Spectrometry 12(3): 349-354.

ETV using a tungsten boat furnace was studied in combination with an axially viewed (end-on) horizontal ICP for improvement in sensitivity. A high-dispersion echelle spectrometer in which wavelength modulation and 2nd-deriv. signal detection are incorporated was used. Time-resolved spectra were obtained by using an emission intensity-time-wavelength profiling method. To obtain a high S/B, the heating program of the ETV system, the flow rate of the transport gas and the delay time are important in addn. to the plasma conditions. Once the optimum conditions were established, reproducible peak appearance times can be obtained. The net emission intensity, repeatability and limit of detection (LOD) obtained by ETV end-on ICP-AES were compared with those obtained by end-on pneumatic nebulization ICP-AES. The improved LODs were close to those obtained by pneumatic nebulization ICP-MS. Discrimination between the Fe impurity in the tungsten boat and spiked Fe was possible using time resoln. Trace amts. of Mn and Al in a large amt. of Mo and Fe, resp., were time-resolved at neighboring wavelengths. The chem. species of the vaporized materials were identified by x-ray microanal. The main disadvantage of the method is that nitric and sulfuric acids cannot be used.

APP* 192) Gregoire, D. C. and M. d. L. Ballinas (1997). "Direct determination of arsenic in fresh and saline waters by electrothermal vaporization inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 52B(1): 75-82.

A method is described for the direct detn. of arsenic in fresh and saline waters by electrothermal vaporization inductively coupled plasma mass spectrometry. Arsenic could be detd. directly in waters contg. up to 10,000 mg mL-1 NaCl without interference from the formation of 75ArCl+. For non-saline waters, arsenic was detd. directly with the addn. to both aq. calibration stds. and samples of 0.1 mg each of Pd and Mg to act as phys. carriers. For the anal. of 1000 Deg, while the sep. addn. of 8 mg of ammonium nitrate was used to remove chloride from the sample. This eliminated series spectral interference on 75As+ from 75ArCl+. Although the ArCl+ spectral interference was completely eliminated, residual Na co-volatilized with As caused signal suppression, requiring the use of the method of std. addns. for calibration. An abs. limit of detection limit for As of 0.069 pg was obtained corresponding to 6.9 pg mL-1 in a 10 mL sample.

APP* 193) Hinds, M. W., D. C. Gregoire, et al. (1997). "Direct determination of volatile elements in nickel alloys by electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 12(2): 131-135.

A method is described for the direct detn. of Bi, Pb and Te in solid Ni alloys by ETV-ICP-MS. Samples are introduced into the graphite tube as small filings or chips weighing up to 3 mg. Using dild. sea water as a phys. carrier, both Bi and Pb could be detd. in solid Ni using external calibration with aq. samples although results for Pb were biased low. Better results in terms of accuracy and precision were obtained when solid root-mean-square (Ni) were used for calibration. LODs of 14 and 44 ng g-1 were obtained for Bi and Pb, resp., using a reduced sensitivity mode (OmniRange). Based on signals obtained for soln. stds. measured at the highest sensitivity, LODs of 0.002 and 0.004 ng g-1 are possible for Bi and Pb, resp. The detn. of Te by this technique was not successful using either soln. or solids calibration. Te did not show a linear instrument response with concn., which was probably due to an interaction between the Te and one or more matrix components in the solid phase that alters the release mechanism(s) for Te from those obsd. for Pb and Bi.

FUN* 194) Vanhaecke, F., S. Boonen, et al. (1997). "Isotope dilution as a calibration method for solid sampling electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 12(2): 125-130.

The present paper reports on the use of isotope diln. as a method of calibration for solid sampling ETV-ICP-MS. The possibilities and limitations of this calibration strategy were evaluated by detg. the Cd or Se content in solid CRMs of different origin. Since isotope ratios are only slightly affected or not affected at all by (i) matrix effects, (ii) signal drift and instrument instability and (iii) variations in the vaporization and/or transport efficiency, isotope diln. allows accurate analyses to be carried out (mean deviation between solid sampling ETV-ICP-MS results and certified values <10%). The precision attainable is detd. by the sample homogeneity and is hence comparable to that obtained using other calibration techniques, such as (i) external calibration with either a solid std. or an aq. std. soln. or (ii) std. addns. An important advantage of isotope diln. over the aforementioned calibration techniques for solid sampling ETV-ICP-MS, however, is that the use of an elemental internal std. is no longer required. For some materials, accurate anal. results could not be obtained as at least one of the isotopes involved is subject to spectral interference. The use of several parameters allowing spectral interferences to be detected is discussed. Finally, solid sampling ETV-ICP-MS was used for the detn. of the Cd content in tobacco as a 'real-life' sample and the results obtained using isotope diln. and single std. addn. for calibration were compared with one another and with the result obtained (after taking the ample into soln.) using pneumatic nebulization ICP-MS.

APP* 195) Chang, C.-C. and S.-J. Jiang (1997). "Determination of copper, cadmium and lead in biological samples by electrothermal vaporization isotope dilution inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 12(1): 75-80.

Electrothermal vaporization isotope diln. inductively coupled plasma mass spectrometry (ETV-ID-ICP-MS) was applied to the detn. of Cu, Cd and Pb in several biol. samples. The isotope ratios for each element in each anal. run were calcd. from the peak areas of each isotope. Various chem. modifiers tested to obtain the optimum signal of Cd and Pd were selected. The pyrolytic graphite platforms of the graphite tubes were then pretreated with Pd by three different methods, thermal pretreatment, electroplating and sputtering, and after careful evaluation of the anal. performance of these methods, thermal pretreatment of the platform with Pd before each anal. was selected. The ETV-ID-ICP-MS method was applied to the detn. of Cu, Cd and Pb in dogfish liver ref. material DOLT-1, dogfish muscle ref. material DORM-1 and freeze-dried urine std. ref. material NIST SRM 2670. The results agreed satisfactorily with the certified values.

APP* 196) Yu, L., S. R. Koirtyohann, et al. (1997). "Simultaneous determination of aluminum, titanium and vanadium in serum by electrothermal vaporization-inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 12(1): 69-74.

The systemic distribution of corrosion and wear products from total joint replacement devices in the human body needs to be better understood. This requires the measurement of metal ions, esp. Al, Ti and V, at ppb and sub-ppb levels in serum and other org. matrixes. Both ETAAS and NAA are reported for detg. some of the elements, but neither is completely suitable for detg. all three elements in serum at the levels encountered in control subjects and in patients with well-functioning devices. A method is described for the simultaneous detn. of Al, Ti and V in serum using ETV-ICP-MS. Spectral interferences from the serum matrix were circumvented or alleviated by the careful selection of anal. masses, chem. modifiers and the temp. program of the electrothermal vaporizer. The serum matrix influences the transport of analytes (carrier effect) from the furnace to the plasma. The carrier effect was cor. by using major component matrix matching with internal standardization, and good recovery was obtained. Detection limits of 0.7, 0.4 and 0.1 ppb in serum were obtained for Al, Ti and V, resp. NIST SRM 1598 Bovine Serum and a pooled human serum were analyzed. The Al concn. found was 3.8 +- 0.8 ppb while the V concn. was below the detection limit of 0.1 ppb, compared with the certified value for Al of 3.7 +- 0.9 ppb and the information value for V of 0.06 ppb (no value is given for Ti in SRM 1598). The Ti value obtained for the pooled human serum sample was within the concn. range previously reported for normal human serum.

APP* 197) Benyounes, M. E., J. P. Byrne, et al. (1998). "Investigation of the mechanism of vaporization of the platinum group elements in ETV-ICP-MS." EnviroAnalysis, Proceedings of the Biennial International Conference on Chemical Measurement and Monitoring of the Environment, 2nd, Ottawa, ON, Canada, May 11-14, 1998: 521-528.

The mechanism of vaporization of platinum group elements (PGEs) in a graphite furnace was studied using electrothermal vaporization-inductively coupled plasma-mass spectrometry (ETV-ICP-MS). The results suggest that five of these elements (Ru, Rh, Pd, Ir and Pt) are reduced to the metallic state and vaporized by direct sublimation of the metal in the graphite furnace. For Os, two distinct vaporization processes were obsd.: volatile oxides of Os were released at low temps., but some of this oxide was reduced to relatively nonvolatile Os metal, which was then vaporized >2000 Deg. The addn. of the TeCl2 chem.

modifier improves the anal. sensitivity and limit of detection for Os, which was then vaporized at 1400 Deg. No effect on the other PGEs was obsd.

APP* 198) Grunke, K. (1998). Studies of electrothermal vaporization as a sample feed technique for inductively coupled plasma mass spectrometer (ETV-ICP-MS) with special consideration of transport phenomena, Universitat Dortmund,Germany. FIELD URL:: i-viii, 1-185.

Fundamental examns. were carried out on electrothermal vaporization and transport processes in ETV-ICP-MS for environmental pollution monitoring by simultaneous detn. of Mn, Cu, Zn, Cd, and Pb in samples of human tooth compartments. The parameters were optimized with respect to the anal. task. Influences of the length, diam., and material of the transport duct and of the amt. of analyte on transport losses were studied. Effects of the release of H, H_2O, and C from graphite tubes were examd. Expts. with different modifiers and various analyte quantities showed that the effect of a modifier depends on the element to be detd. Particles generated by ETV were collected on a support and characterized by electron-optical methods. Finally, ETV-ICP-MS was applied to the detn. of heavy metal traces in compartments of human teeth, including the Pb isotope ratio. Different distributions for the various metals were found in the teeth caused by different enrichment mechanisms.

FUN* 199) Bjorn, E., W. Frech, et al. (1998). "Investigation and quantification of spectroscopic interferences from polyatomic species in inductively coupled plasma mass spectrometry using electrothermal vaporization or pneumatic nebulization for sample introduction." Spectrochimica Acta, Part B: Atomic Spectroscopy 53B(13): 1765-1776.

A new method for quantification of spectral interferences based on analyte isotope ratio measurements in the presence of various concns. of a specific matrix is presented. Within the method, a tolerance level is used, defined as the matrix concn. at which the ratio between analyte isotopes with and without interferences is altered by 10% compared to a pure water ref. std., normalized with respect to the analyte concn. in the solns. This can be used to est. the lowest analyte concn. which can be detd. with a defined accuracy in the presence of a known concn. of a specific matrix. Regarding spectroscopic interference effects, comparative results for sample introduction into the ICP-MS by electrothermal vaporization (ETV) and nebulization are presented for common matrix - (Ca, Na, K, Cl, P, O) and analyte (Cr, Ni, Cu, As, Se) elements. With the exception of the spectral overlap of 31P2+ on 62Ni+, spectroscopic interferences were reduced by 1-2.5 orders of magnitude when using ETV for sample introduction. Reasons for the increase in the spectral interference of 31P2+ on 62Ni+ are discussed. For sample introduction by neutralization, it was found that spectral interferences from CaO+ on 58Ni+ and 60Ni+ were reduced in the presence of phosphate.

FUN* 200) Alary, J.-F. and E. D. Salin (1998). "Quantitation of water and plasma diagnosis for electrothermal vaporization-inductively coupled plasma-mass spectrometry: the use of argon and argide polyatomics as probing species." Spectrochimica Acta, Part B: Atomic Spectroscopy 53B(12): 1705-1721.

The water content of the carrier flow originating from an electrothermal vaporization unit (ETV) attached to an inductively coupled plasma mass spectrometer was monitored by following the argon hydride ion (ArH+) at m/z = 37. The goal was to measure the water expelled by the ETV at sample vaporization and evaluate the influence of this parameter on the ion-generation efficiency. Linear responses from the argon hydride were obtained when the water loading in the plasma injector flow was increased from 0 to 3.3 mg/min. Other argides and water-derived species (Ar+, Ar2+ and O2+) were also monitored simultaneously and the effects from operating parameters were calcd. for each species. The magnitude of these effects can eventually be used as diagnosis tools. It was also found that signals for zinc, copper, lead, antimony and arsenic were greatly influenced by slight variations in water loading at low water levels. These signal fluctuations are greatly attenuated and transient shapes restored by convoluting each element transient with the ArH+ or Ar2+ curves that were recorded simultaneously. Envisioned applications that would benefit from a water-enhanced signal include spray electrothermal vaporization, direct sample insertion and laser ablation for inductively coupled plasma-mass spectrometry. The argon dimer Ar2+ seems more appropriate for making the correction since it provides a direct insight on the plasma temp. and provides a robust signal.

APP* 201) Pozebon, D., V. L. Dressler, et al. (1998). "Determination of Mo, U and B in waters by electrothermal vaporization inductively coupled plasma mass spectrometry." Talanta 47(4): 849-859.

A method for the detn. of Mo, U and B in waters by inductively coupled plasma mass spectrometry, using an electrothermal vaporizer for sample introduction, is described. For Mo and U, NH4F was chosen as modifier and for B, synthetic sea water plus mannitol were used. The modifier effect was verified and the optimized pyrolysis and vaporization temps. were obtained from pyrolysis and vaporization curves, together with the transient signals of the analytes. The masses of the modifiers added to the tube were also optimized. The detection limits were 0.018 or 0.30 ng mL-1 for Mo, 0.03 ng mL-1 for U and 0.68 ng mL-1 for B. The analytes were detd. in certified waters and the obtained results agree with the certified or recommended values or, in the case of B in sea waters, with the values obtained by other methods. Uranium could not be measured in the sea water samples due to strong memory effect.

APP* 202) Rosland, E. and W. Lund (1998). "Direct determination of trace metals in sea-water by inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 13(11): 1239-1244.

The direct detn. of trace metals in seawater by inductively coupled plasma mass spectrometry (ICP-MS) is described, based on sample introduction by flow injection anal. (FIA) and electrothermal vaporization (ETV). FIA-ICP-MS was used for the detn. of Mn, Mo and U; 500 mL of 1+9 dild. seawater were injected in a carrier stream of 0.028 mol/L HNO3. The detection limits were 0.7 mg/L Mn, 1.4 mg/L Mo and 0.10 mg/L U. ETV-ICP-MS was used for the detn. of Cd and Pb. The analytes were vaporized as chlorides at 800 Deg, without interference from the matrix elements. The detection limits were 4.1 ng/L for Cd and 0.8 ng/L for Pb. The FIA-ICP-MS and ETV-ICP-MS results were validated by analyzing a ref. seawater sample (NASS4).

APP* 203) Lee, K.-H., S.-J. Jiang, et al. (1998). "Determination of mercury in urine by electrothermal vaporization isotope dilution inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 13(11): 1227-1231.

Electrothermal vaporization isotope diln. inductively coupled plasma mass spectrometry (ETV-ID-ICP-MS) was applied to the detn. of mercury in urine samples. The isotope ratio of mercury in each anal. run was calcd. from the peak area of each isotope. Various modifiers were tested in order to obtain the greatest sensitivity for mercury. After preliminary studies, a mixed modifier of palladium, Mg(NO3)2 and 2% HCl was used. The ETV-ID-ICP-MS method was applied to the detn. of mercury in NIST SRM 2670 Toxic Metals in Freeze-Dried Urine and several fresh urine samples collected from graduate students. The results obtained for NIST SRM 2670 agreed satisfactorily with the certified values. The results for other samples analyzed by isotope diln. and by the method of std. addns. agreed satisfactorily. The detection limit of mercury, calcd. from the std. addns. calibration plot, was about 0.02 ng ml-1 with the ETV-ICP-MS method. The precision between sample replicates was better than 8% for all detns.

REV* 204) Becker, J. S. and H.-J. Dietze (1998). "Inorganic trace analysis by mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 53B(11): 1475-1506.

A review with 269 refs. Mass spectrometric methods for the trace anal. of inorg. materials with their ability to provide a very sensitive multielemental anal. were established for the detn. of trace and ultratrace elements in high-purity materials (metals, semiconductors and insulators), in different tech. samples (e.g. alloys, pure chems., ceramics, thin films, ion-implanted semiconductors), in environmental samples (waters, soils, biol. and medical materials) and geol. samples. Whereas such techniques as spark source mass spectrometry (SSMS), laser ionization mass spectrometry (LIMS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), glow discharge mass spectrometry (GDMS), secondary ion mass spectrometry (SIMS) and inductively coupled plasma mass spectrometry (ICP-MS) have multielemental capability, other methods such as thermal ionization mass spectrometry (TIMS), accelerator mass spectrometry (AMS) and resonance ionization mass spectrometry (RIMS) were used for sensitive mono- or oligoelemental ultratrace anal. (and precise detn. of isotopic ratios) in solid samples. The limits of detection for chem. elements using these mass spectrometric techniques are in the low ng g-1 concn. range. The quantification of the anal. results of mass spectrometric methods is sometimes difficult due to a lack of matrix-fitted multielement std. ref. materials (SRMs) for many solid samples. Therefore, owing to the simple quantification procedure of the aq. soln., inductively coupled plasma mass spectrometry (ICP-MS) is being increasingly used for the characterization of solid samples after sample dissoln. ICP-MS is often combined with special sample introduction equipment (e.g. flow injection, hydride generation, HPLC or electrothermal vaporization) or an off-line matrix sepn. and enrichment of trace impurities (esp. for characterization of high-purity materials and environmental samples) was used to improve the detection limits of trace elements. Also, the detn. of chem. elements in the trace and ultratrace concn. range is often difficult and can be disturbed through mass interferences of analyte ions by mol. ions at the same nominal mass. By applying double-focusing sector field mass spectrometry at the required mass resoln. - by the mass spectrometric sepn. of mol. ions from the analyte ions - it is often possible to overcome these interference problems. Com. instrumental equipment, the capability (detection limits, accuracy, precision) and the anal. application fields of mass spectrometric methods for the detn. of trace and ultratrace elements and for surface anal. are discussed.

REV* 204) Sneddon, J. and M. G. Heagler (1998). "Determination of mercury by atomic spectroscopy: application to fish." Advances in Atomic Spectroscopy 4: 213-229.

The use of various at. spectroscopic techniques including cold-vapor at. absorption spectrometry, cold-vapor at. fluorescence spectrometry, electrothermal atomization at. absorption spectrometry, inductively coupled plasma-mass spectroscopy, and inductively coupled plasma-at. emission spectrometry for the detn. of mercury is described. A short overview of the history, current uses, and toxicity is described. The application of these various at. spectroscopic techniques to the detn. of mercury in fish is thoroughly detailed.

APP* 206) Hughes, D. M., D. C. Gregoire, et al. (1998). "Determination of trace amounts of phosphorus in high purity iron by electrothermal vaporization inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 53B(6-8): 1079-1085.

Trace amts. of P were detd. in high purity Fe using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). The Fe matrix was largely removed using solvent extn. with 4-methyl-2-pentanone. Zr was used as a chem. modifier to avoid interference arising from the residual Fe present after solvent extn. The use of Zr modifier did not result in P signal suppression as was obsd. when Ni and La were used as chem. modifiers. External calibration with aq. stds. yielded results in good agreement with ref. values. The detection limit achieved using this method was 0.008 ppm P in Fe.

FUN* 207) Majidi, V. and N. J. Miller-Ihli (1998). "Influence of graphite substrate on analytical signals in electrothermal vaporization-inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 53B(6-8): 965-980.

This paper describes electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) expts. for vaporization of Na, Mg, P, K, Ca, V, Mn, Ni, Cu, Ga, Mo, Pd, Ag, Cd, In, W, Au and Pb in single element and mixed element solns.; using both pyrocoated and oxygenated pyrocoated graphite substrates. During these expts. several species originating from the graphite surface (13C+, CO+ and C2+) were monitored. When samples were vaporized from a pyrocoated graphite surface, precisions of .apprx.20% for Ar2+, 200% for 13C+ and 60% for CO+ were obsd. in their integrated ion intensities. For vaporization from an oxygenated pyrocoated graphite surface, the variation in integrated ion intensities was significantly reduced; <5% for Ar2+, <20% for 13C+ and 40% for CO+. The results obtained from these expts. indicate that ETV-ICP-MS can be used effectively for trace and ultratrace quant. anal. For best anal. results with ETV-ICP-MS, it is prudent that a new oxygenated graphite surface be used along with matrix modifiers and the method addns. technique. Surface origin of the C2+ ion was also studied. The surface species responsible for the C2+ ion are not the major analyte carrier species from the ETV to the ICP-MS. This was substantiated by the observation that the C2+ signal appears as a well behaved peak, regardless of the surface condition or the analyte used. There is evidence to suggest that the C2+ comes from an aldehyde-type mol. surface species. The C2+ signal is only obsd. when metals were present in acidic sample solns. or when the graphite surface was oxygen treated. Metal catalyzed surface oxidn. is one possible explanation for the prodn. mechanism of the species leading to the C2+ ion. The origin of 13C+ and CO+ ions is also explained.

APP* 208) Chen, S.-f. and S.-j. Jiang (1998). "Determination of cadmium, mercury and lead in soil samples by slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 13(10): 1113-1117.

Ultrasonic slurry sampling-electrothermal vaporization-isotope diln.-inductively coupled plasma mass spectrometry (USS-ETV-ID-ICP-MS) was applied to the detn. of Cd, Hg and Pb in several soil samples. Palladium was used as the modifier. Since the sensitivities of the elements studied in soil slurry and aq. soln. were different, the isotope diln. method was used for the detn. of Cd, Hg and Pb in selected soil samples. The influences of instrument operating conditions, slurry prepn. and interferences on the ion signals and the accuracy and precision of isotope ratio detns. were reported. The isotope ratios of each element were calcd. from the peak areas of each injection peak. The precision of the isotope ratio detns. was better than 4%. This method was applied to the detn. of Cd, Hg and Pb in NIST SRM 2711 Montana soil ref. material and several soil samples collected from the Kaohsiung area. The results for the ref. sample NIST SRM 2711 Montana Soil agreed satisfactorily with the certified values. Results for other samples analyzed by the isotope diln. method and the method of std. addns. agreed satisfactorily. The precision was better than 5% and the accuracy was better than 2% with the USS-ETV-ID-ICP-MS method. Detection limits estd. from std. addn. curves were in the ranges 4-24, 2-19 and 5-76 ng g-1 for Cd, Hg and Pb, resp., in different samples.

APP* 209) Pozebon, D., V. L. Dressler, et al. (1998). "Determination of trace elements in biological materials by ETV-ICP-MS after dissolution or slurry formation with tetramethylammonium hydroxide." Journal of Analytical Atomic Spectrometry 13(10): 1101-1105.

A method to prep. biol. samples to be analyzed by electrothermal vaporization inductively coupled plasma mass spectrometry is proposed. A soln. or slurry was formed by mixing a sample aliquot, 20-100 mg, with a small vol., 10-200 mL, of a 25% m/v tetramethylammonium hydroxide soln. For animal tissues, complete dissoln. was obtained, whereas for the plant and whole egg materials, slurries were obtained. The slurries were stirred manually, every three readings, in the instrument. The pyrolysis and atomization temps. were optimized, using Pd as a carrier-modifier for As, Se, Te, Ag, Cr, Cu, V, Ni, Mn, Co and Cd. An Ir-coated tube was used for Pb, Sb, Sn and Bi. External calibration was used preferentially, but in some instances, the analyte addns. method was employed. Good results were obtained for four certified ref. materials. However, Cr and Cd could not be detd. in the bovine muscle sample owing to spectral interferences and matrix effects, resp.

APP* 210) Byrne, J. P. and G. Chapple (1998). "Direct determination of trace metals in seawater by electrothermal vaporization ICP-MS with Pd-HNO3 modifier." Atomic Spectroscopy 19(4): 116-120.

A method for the direct multi-element detn. of As, Pb, Sb, Sn, and Tl in seawater by electrothermal vaporization-inductively coupled plasma mass spectrometry (ETV-ICP-MS) was developed. In situ sepn. of the salt matrix and the analytes was achieved by thermal pretreatment in the graphite furnace, prior to analyte vaporization. Palladium modifier was used to stabilize the analytes during thermal pretreatment; 5% (vol./vol.) HNO3 was added to remove chloride from the matrix, thus reducing isobaric interference of 40Ar35Cl on 75As. Calibration was achieved using matrix-matched stds. prepd. in a blank seawater matrix from which trace elements were removed by ion-exchange on silica-immobilized 8-hydroxyquinoline.

Detection limits in the range 0.015-0.042 mg/L were obtained. Analyte spike recoveries were measured between 99 and 113%.

APP* 211) Buseth, E., G. Wibetoe, et al. (1998). "Determination of endogenous concentrations of the lanthanides in body fluids and tissues using electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 13(9): 1039-1049.

A method was developed for the detn. of endogenous concns. of the lanthanides in body fluids and tissues with electrothermal vaporization inductively coupled plasma mass spectrometry. The method was applied to the anal. of rat liver and human blood plasma as well as to some ref. materials,viz., Oyster Tissue, Bovine Liver, Seronorm Trace Element Serum and Human Hair. Microwave digestion in high-pressure containers was used to digest the various biol. materials. Analyses of undigested biol. tissues by slurry sampling and body fluids by direct injection were also performed. For undigested samples, hydrogen peroxide injected directly onto the sample inside the graphite furnace was found to be effective in preventing the build-up of ash in the furnace. Trifluoromethane (Freon-23) was used as an effective chem. modifier that lowered the vaporization temp. and the memory effect significantly for most of the lanthanides. The abs. detection limits were, with few exceptions, in the range 1-20 fg for all the lanthanides in the various biol. materials. The relative detection limits varied with the level of diln. and the method used. For Seronorm Trace Element Serum, the relative detection limits were in the range 0.05-1.2 ng l-1. The anal. results for slurry and digested samples of the same material were similar with respect to accuracy and precision. The intermediate precision, i.e., the overall relative std. deviation obtained for the CRMs analyzed on three different (not consecutive) days, was less than 25% for the lanthanides with concns. higher than 1 ng g-1 dry material. In the few cases where a certified or indicative value existed for the concns. of the lanthanides in the ref. materials, good agreement between these concns. and the concns. obtained in the present work was found. Blood plasma samples from 30 healthy volunteers and liver samples from ten unexposed rats were analyzed. All the lanthanides were above the detection limit in the various samples analyzed.

APP* 212) Li, Y.-C., S.-J. Jiang, et al. (1998). "Determination of Ge, As, Se, Cd and Pb in plant materials by slurry sampling-electrothermal vaporization-inductively coupled plasma-mass spectrometry." Analytica Chimica Acta 372(3): 365-372.

Ultrasonic slurry sampling-electrothermal vaporization-inductively coupled plasma-mass spectrometry (USS-ETV-ICP-MS) has been applied to the detn. of Ge, As, Se, Cd and Pb in plant samples. The influences of instrument operating conditions and slurry prepn. on the signals were reported. Since the sensitivities of the elements in various plant slurries were quite different, std. addn. was used. Detection limits of Ge, As, Se, Cd and Pb estd. in different samples from the std. addn. curve were in the range 2.1-14, 3.8-6.5, 14-18, 1.8-12, and 7.8-18 ng g-1, resp. This method has been applied to the detn. of Ge, As, Se, Cd and Pb in tomato leaves ref. material (NIST SRM 1573a) and a ganoderma sample obtained from the local market. The anal. results of the tomato leaves ref. sample did agree with the certified values. Precision was better than 24% for all detns. with the USS-ETV-ICP-MS method.

APP* 213) Ulieru, D. G. (1998). "Trace contaminants from photoresist materials by modern spectrometry determination." Proceedings of SPIE-The International Society for Optical Engineering 3332(Metrology, Inspection, and Process Control for Microlithography XII): 721-726.

The modern semiconductor manufg. used advanced photoresists chems. with extremely low levels of trace metallic contaminants. The use of Inductively Coupled Plasma Spectrometry (ICP-MS) allows for the rapid anal. of these chems. with sensitivity similar to furnace at. absorption and with minimal sample prepn. Sample introduction methods currently being used include ultrasonic nebulization (USN) and electrothermal vaporization (ETV).

FUN* 214) Pozebon, D., V. L. Dressler, et al. (1998). "Study of interferences from Na and Cl using ETV-ICP-MS." Atomic Spectroscopy 19(3): 80-88.

The effects of Cl, Na and NaCl on the signal of the isotopes 46Ti, 47Ti, 49Ti, 53Cr, 54Fe, 55Mn, 62Ni, 63Cu, 67Zn, 70Ge, 75As, and 77Se were studied by comparing pneumatic nebulization vs. electrothermal vaporization (ETV) as sample introduction systems for anal. by inductively coupled plasma mass spectrometry (ICP-MS). Signal suppression by Na and polyat. ion interferences produced by Na and Cl were quantified using pneumatic nebulization. Using ETV, the Na and Cl polyatomics, which interfere at the m/z ratio of most of the isotopes, were not formed to a significant extent for concns. up to 3000 mg/mL Na and Cl of the potential interferents. However, above this concn., significant signal suppression was found for 67Zn and 70Ge, even at a high pyrolysis temp. High blank values were found for 53Cr and 54Fe due to the formation of ions involving H, C, and N. Two certified seawater samples were analyzed directly using HNO3 as a chem. modifier and matrix matching external calibration. The values obtained for Ni, Cu, V, and Mn agreed well with the certified concns. For As and Se, Pd nitrate was used as the modifier. The calibration was performed by the method of std. addns. Se could not be measured in the seawater samples since the concns. were below the limit of quantitation (LOQ).

APP* 215) Lee, K.-H. and S.-H. Liu (1998). "Determination of cadmium and lead in urine by electrothermal vaporization isotope dilution inductively coupled plasma mass spectrometry." Analyst (Cambridge, United Kingdom) 123(7): 1557-1560.

Electrothermal vaporization isotope diln. inductively coupled plasma mass spectrometry (ETV-ID-ICP-MS) was applied to the detn. of Cd and Pb in urine samples. The isotope ratios for each element in each anal. run were calcd. from the peak areas of each isotope. A relatively low vaporization temp. was used, which sepd. the analyte from the major matrix components and improved the ion signals of Cd and Pb significantly. Various chem. modifiers were tested to obtain the best signal of Cd and Pb. After preliminary studies, 1% HNO3 was added to the samples as the chem. modifier. The ETV-ID-ICP-MS method was applied to the detn. of Cd and Pb in freeze-dried urine ref. material NIST SRM 2670 and several fresh urine samples. The results for NIST SRM 2670 agreed satisfactorily with the certified values. The results for other samples obtained by isotope diln. and the method of std. addns. agreed satisfactorily. The detection limits were 0.02 and 0.005 ng ml-1 for Cd and Pb, resp. The precision between sample replicates was better than 11% for all detns.

APP* 216) Chen, S.-f. and S.-j. Jiang (1998). "Determination of arsenic, selenium and mercury in fish samples by slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 13(7): 673-677.

Ultrasonic slurry sampling-electrothermal vaporization inductively coupled plasma mass spectrometry (USS-ETV-ICP-MS) was applied to the detn. of Ge, As, Se and Hg in several fish samples. The influences of instrument operating conditions and slurry prepn. on the ion signals were investigated. Palladium and thioacetamide were used as modifiers to reduce the loss of Hg during drying. Since the sensitivities of Ge, As, Se and Hg in various fish slurries and aq. soln. were different, the std. addns. method was used for the detn. of Ge, As, Se and Hg in these fish samples. This method was applied to the detn. of Ge, As, Se and Hg in dogfish muscle ref. material (DORM-2), dogfish liver ref. material (DOLT-1) and a com. swordfish sample. The results agreed with the certified values. The precision between sample replicates was better than 11% with the USS-ETV-ICP-MS method. Detection limits calcd. from std. addn. curves were about 7, 19, 31 and 34 ng/g for Ge, As, Se and Hg, resp., in different samples.

APP* 217) Mierzwa, J. and M.-h. Yang (1998). "Electrothermal vaporization-inductively coupled plasma mass spectrometry for determination of metal impurities in slurries of aluminum oxide." Journal of Analytical Atomic Spectrometry 13(7): 667-671.

A new anal. procedure for the direct detn. of metal impurities in Al oxide by ultrasonic slurry sampling-electrothermal vaporization-inductively coupled plasma mass spectrometry (ETV-ICP-MS) is reported. The elements studied include Cr, Cu, Ga, Fe, Mg, Mn, Na, V and Zn. Two samples of fine alumina powder (including the certified ref. material NIST SRM 699) were used in this study without any addnl. pre-treatment. Anal. results of the external calibration using aq. stds., the external calibration using matched matrix stds. and the std. addns. method are presented and compared. The most appropriate (av. accuracy of 97 +- 5.5% for sample NIST SRM 699) was the std. addns. procedure of calibration. An acceptable agreement was found between the results of the slurry sampling procedure and the certified or ref. values, the repeatability of measurements was always better than 13.6%. Some other anal. figures-of-merit,e.g., limits of detection, are also presented. The abs. limits of detection (for the anal. of 15 mL samples) ranged from 0.8 to 8.3 pg. The speed and multi-element anal. potential of this technique seem to be very advantageous.

APP* 218) Caroli, S., O. Senofonte, et al. (1998). "Certified reference materials for research in Antarctica: the case of marine sediment." Microchemical Journal 59(1): 136-143.

A multielemental certified ref. material based on Antarctic marine sediment was prepd. in the framework of the Italian Programma Nazionale per la Ricerca in Antartide (PNRA, National Program for Research in Antarctica) and was coordinated by the Istituto Superiore di Sanita (ISS, National Institute of Health). The sediment was collected during the 9th Italian Expedition (1993-1994) in Antarctica in Terra Nova Bay (Ross Sea) at a depth of 80 m, stored at -20 Deg in polyethylene containers, and shipped to the ISS. The sediment was subjected to preliminary treatment at the Institute for Ref. Materials and Measurements (IRMM, Joint Research Center of the European Commission, Geel Establishment, Geel, Belgium). This treatment consisted of sieving, drying, jet milling, sampling, moisture detn., particle size detn., and microscopic examn. The final product turned out to contain mostly particles smaller than 90 mm (97% of total mass); particles larger than 150 mm were practically absent. The fraction between 90 and 150 mm comprised mainly org. material homogeneously distributed over the sediment. Five hundred two brown glass bottles (polyethylene insert and plastic screw cap; capacity 120 mL) could be thus filled with this material, each bottle contg. about 75 g of the sediment. The certification project was accomplished with the active participation of eight internationally reputed labs. from various countries (Belgium, Denmark, Hungary, Italy, Spain, and United States). The instrumental techniques resorted to in the certification exercise included cold vapor at. absorption spectrometry, electrothermal atomization at. absorption spectrometry, flame at. absorption spectrometry, inductively coupled plasma at. emission spectrometry, inductively coupled plasma mass spectrometry, isotope diln. inductively coupled plasma mass spectrometry, isotope diln. mass spectrometry, neutron activation anal., solid sampling Zeeman electrothermal atomization at. absorption spectrometry, and Zeeman electrothermal atomization at. absorption spectrometry. The certified values established for some trace elements are as follows: Al, 67.1 +- 3.3 mg/g; As, 4.41 +- 1.06 mg/g; Cd, 0.538 +- 0.027 mg/g; Cr, 42.1 +- 3.4 mg/g; Co, 6.87 +- 0.31 mg/g; Fe, 24.4 +- 0.7 mg/g; Mn, 446 +- 19 mg/g; Ni, 9.56 +- 1.05 mg/g; Pb, 21.0 +- 2.9 mg/g; Zn, 53.3 +- 2.7 mg/g. In turn, addnl. elements were quantified by some participants. Homogeneity of the powd. sediment for the various analytes is such that intakes as low as 100 mg still show no deviation from the nominal values larger than the attached uncertainty. Intakes of 200 mg are, however, recommended to minimize any possible variations in concn. The product has an av. moisture content of 0.30 +- 0.03% on delivery.

APP* 219) McIntyre, R. S. C., D. C. Gregoire, et al. (1998). "The direct determination of radium in geological materials by slurry sampling electrothermal vaporization-inductively coupled plasma-mass spectrometry." Spectroscopy (Eugene, Oregon) 13(4): 18, 20-24.

A method for the detn. of Ra in geol. materials using slurry sampling electrothermal vaporization-inductively coupled plasma-mass spectrometry (ETV-ICP-MS) is proposed. The method was verified using four geol. ref. materials (BL-5, DH-1a, EJB 5-81 and SRM 4353). Ra signal suppression caused by the presence of org. and silicate components of the sample matrix were reduced using a high pyrolysis temp. and by the addn. of HF. The limit of detection was 186 fg/mL (ppq) for 226Ra for a 20 mL sample aliquot of slurry contg. 21 mg/mL of solid sample.

APP* 220) Pozebon, D., V. L. Dressler, et al. (1998). "Determination of copper, cadmium, lead, bismuth and selenium(IV) in sea-water by electrothermal vaporization inductively coupled plasma mass spectrometry after online separation." Journal of Analytical Atomic Spectrometry 13(5): 363-369.

A procedure for the detn. of Cu, Cd, Pb, Bi and SeIV in seawater by electrothermal vaporization inductively coupled plasma mass spectrometry, after online sepn. using a flow injection system, is proposed. Matrix sepn. and analyte preconcn. was accomplished by retention of the analytes complexed with the ammonium salt of O,O-diethyldithiophosphoric acid on C18 immobilized on silica in a minicolumn coupled directly to the autosampler arm of the vaporizer. The methanol used as eluent was vaporized after being automatically injected into the graphite tube, prior to the vaporization of the analytes. The conditions for the online complexation and sepn. as well as the vaporizer temp. program were optimized. The recoveries from seawater were 90-110%. The accuracy of the method was tested by the anal. of 2 certified seawaters, CASS-3 and NASS-4, from the National Research Council of Canada. The concn. of Bi in these seawaters was below the method detection limit. The relative std. deviation was <10% (n=6). The throughput was 22 samples/h and the vol. of sample consumed was only 2.3 mL. Tl and AsIII were also sepd. but their complexation in seawater was not efficient.

APP* 221) Li, Y.-C. and S.-J. Jiang (1998). "Determination of Cu, Zn, Cd and Pb in fish samples by slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry." Analytica Chimica Acta 359(1-2): 205-212.

Ultrasonic slurry sampling electrothermal vaporization isotope diln. inductively coupled plasma mass spectrometry (USS-ETV-ID-ICP-MS) has been applied to the detn. of Cu, Zn, Cd and Pb in several fish ref. samples. NH4NO3 was added to the sample soln. to work as a modifier. Since the sensitivity of the elements studied in fish slurry and aq. soln. was quite different, isotope diln. was used for the detn. of Cu, Zn, Cd and Pb in ref. samples. The influences of instrument operating conditions, slurry prepn., non-spectroscopic and spectroscopic interferences on the ion signals and accuracy and precision of isotope ratio detn. were reported. The isotope ratios of each element were calcd. from the peak areas of each injection peak. Precision of isotope ratio detn. was better than 6%. This method has been applied to the detn. of Cu, Zn, Cd and Pb in dogfish muscle ref. material (DORM-2), dogfish liver ref. material (DOLT-1) and oyster tissue (NIST SRM 1566a). Accuracy was better than 19% and precision was better than 14% with ultrasonic slurry sampling and electrothermal vaporization isotope diln. inductively coupled plasma mass spectrometry. Detection limits estd. from std. addn. curves were in the range of 5-50, 200-500, 8-20 and 20-50 ng g-1 for Cu, Zn, Cd and Pb, resp., in different samples.

APP* 222) Wildner, H. and G. Wuensch (1998). "Electrothermal vaporization-ICP-MS for the determination of metals in micro amounts of high-purity nonmetals (P, As, Sb, S, Se, Te, I)." Fresenius' Journal of Analytical Chemistry 360(5): 520-526.

A thermal trace-matrix sepn. procedure was developed for the detn. of ultratraces of metals in solid nonmetals (P, As, Sb, S, Se, Te, and I). These matrixes are dissolved in high-purity H2O2 to form the corresponding acids. By applying a suitable temp. profile, coating the graphite tube with WC and using H2 as a gaseous modifier >90% of the matrix can be removed. Analyte recoveries are 90-105% with a RSD of 5-10%. Since the sepn. principle is not specific, nonmetallic analytes show poor recoveries of 10-40% (20-100% RSD). Elements forming persistent carbides, such as refractory metals, require either HF or Freon as an addnl. modifier. Sepn. of the matrix leads to higher sensitivities, fewer spectral and non-spectral interferences, and to better precision. The graphite tube is only little contaminated and its lifetime is drastically increased. The improvements result in limits of detection in the lower pg/g-range in the solid nonmetals. Furthermore, this method can be employed for amts. of sample around 1 mg at abs. detection limits <1 pg. Best performance of the coupling of ETV to ICP-MS is only obtained in the single-ion monitoring mode which means only semi-sequential multi-element capabilities.

APP* 223) Michalke, B. and P. Schramel (1998). "Selenium speciation in human milk with special respect to quality control." Biological Trace Element Research 59(1-3): 45-56.

Se organo compds. of pooled human milk (7th-14th d after delivery) were sepd. by centrifugation and subsequent size-exclusion chromatog. (SEC). The SEC fractions were used for Se detns. by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) in parallel to identification procedures of the org. ligands by two different capillary zone electrophoresis (CZE) methods. Further, the combination of isotachophoresis- (ITP) CZE with ETV-ICP-MS was used for final identifications. Mass balances were carried out at each anal. step for quality assurance. Reinjection expts. were performed to check the stability of Se-organo compds. during the anal. procedure. These quality-control expts. showed that no species transformations took place during the anal. procedure, and the Se species were native in human milk. The identification and quantification of org. ligands were clear and resulted in values of 2 (+-0.2) mg/L GSH/GSeH, 2 (+-0.22) mg/L cystamine/Se-cystamine, 4 (+-0.4) mg/L cystine/Se-cystine, and 1 (+-0.18) mg/L methionine/Se-methionine. Unfortunately, a differentiation between S and Se analogs was not possible with the applied CE methods. The Se values per org. ligand were detd. as 2.5 (+-0.23) mg/L assocd. with GSH (as GSeH), 3.1 (+-0.31) mg/L assocd. with cystamine (as Se-cystamine), 5.2 (+-0.4) mg/L assocd. with cystine (as Se-cystine), and 1 (+-0.1) mg/L assocd. with methionine (as Se-methionine).

APP* 224) Nonose, N. and M. Kubota (1998). "Determination of metal impurities in sulfamic acid by isotope dilution electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 13(2): 151-156.

Metal impurities present at sub-ng/g to ng/g levels in high-purity sulfamic acid reagents were detd. by isotope diln. inductively coupled plasma mass spectrometry (ID-ICP-MS) with sample introduction by electrothermal vaporization (ETV). Matrix constituents causing suppression and enhancement of analyte signals were removed from the sample introduction system at the pyrolysis stage before ETV-ICP-MS measurement. As the ETV device, both tungsten and graphite furnaces were employed. In graphite furnace ETV-ICP-MS, it was necessary to use a chem. modifier in order to enhance the signal sensitivity and to obtain a linear calibration graph. In tungsten furnace ETV-ICP-MS, a linear relationship between the analyte mass and the signal was achieved without the use of a modifier, but the stability of the isotope ratio measurement was slightly poorer than that in graphite furnace ETV-ICP-MS. The relative std. deviations obtained by ETV-ICP-MS using both furnaces were 6-30%. The anal. results for two types of sulfamic acid reagent obtained by tungsten furnace ETV-ICP-MS agreed with those obtained by graphite furnace ETV-ICP-MS.

FUN* 225) Langer, D. and J. A. Holcombe (1999). "Simple transient extension chamber to permit full mass scans with electrothermal vaporization inductively coupled plasma mass spectrometry." Applied Spectroscopy 53(10): 1244-1250.

The design for an in-line transient extension (TEx) chamber was developed to provide a simple means of lengthening an electrothermal vaporizer (ETV) signal for the purpose of obtaining a full mass scan from a single ETV firing with inductively coupled plasma mass spectrometry (ICP-MS) detection. The TEx chamber is simply a flask (e.g., 100-500 mL) with a mated joint allowing the ETV-generated aerosol to enter the chamber in a pulse and exit the chamber exponentially dild. Characterization of the TEx chamber was completed with the use of the following metals: Ba, Be, Ce, Co, In, Mg, Pb, Th, and Tl. A decrease in peak area of 20 +- 4% was witnessed when the TEx chamber was put in-line between the ETV and the ICP-MS for all metals tested. Comparison of the peak areas obtained with and without the addn. of 10 mL of 100 ppm NaCl to the sample without the TEx chamber in-line resulted in increases from 8 to 40%, depending on the metal. Repetition of the expt. with the TEx chamber in line showed no appreciable difference in results. This outcome indicates that diln. in the TEx chamber does not influence the behavior (i.e., enhancement effect) of the carrier. Interrupting the carrier gas flow for up to 2 min after the TEx chamber was \"loaded\" with the aerosol caused decreases in peak area from 25 to 35%, depending on the length of time the sample was held in the chamber. This result is most likely due to settling/loss of the aerosol particles in the chamber. Addn. of 10 mL of 100 ppm NaCl to the sample showed a decrease in peak area of 30-43% when the sample was held for up to 2 min in the chamber, slightly higher than when no NaCl was present. A comparison of full mass scans taken with a concentric nebulizer and the ETV with an in-line TEx chamber using identical data collection rates and times showed that the TEx chamber can be used successfully as a method for both qual. and quant. identification of trace elements in an unknown soln. Detection limits for the nine metals tested with the TEx chamber in line are given.

APP* 226) Ben Younes, M. E., D. C. Gregoire, et al. (1999). "Vaporization and removal of silica for the direct analysis of geological materials by slurry sampling electrothermal vaporization-inductively coupled plasma-mass spectrometry." Journal of Analytical Atomic Spectrometry 14(11): 1703-1708.

Reported is a method for the removal of silica for the direct anal. of solid geol. samples high in silica content using slurry sampling electrothermal vaporization-inductively coupled plasma-mass spectrometry (ETV-ICP-MS). The ETV-ICP-MS vaporization curve for SiO2, sampled as a slurry, is reported for temps. ranging from 810-2600 Deg. This curve showed that silica was completely vaporized at a temp. of 2200 Deg. The effect of using HF as a chem. modifier to remove silica as the tetrafluoride was studied. HF could completely remove any Si attributed to silica if sufficient modifier were added and an adequate reaction time allowed. At reaction hold times that were less than optimal, two Si signals were obsd. The 1st signal, which appears at an earlier time and at a temp. <480 Deg, is attributed to the volatilization of silicon tetrafluoride. The 2nd signal, which appears at a later time and at a temp. of .apprx.2500 Deg, is attributed to the vaporization of residual unreacted SiO2 remaining in the graphite tube, or to the vaporization of a mixt. of SiO2 and SiC. 20 ML of 50% HF is effective in completely removing 0.125 mg of SiO2. No adverse effects including corrosive degrdn. of the graphite tube were obsd. over the lifetime of the tube, which exceeded 200 firings. Hydrofluoric acid chem. modifier was successful in removing virtually all the silica content in natural silicate std. ref. materials.

APP* 227) Ludke, C., E. Hoffmann, et al. (1999). "Determination of trace metals in size fractionated particles from arctic air by electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 14(11): 1685-1690.

Studies of element compn. in small atm. particles aid the clarification of processes such as long-range transport, deposition and transformation of particles and quantification of emission from natural and anthropogenic sources. For this purpose, a highly sensitive method was developed for the trace anal. of atm. particles. The particles were sampled and sepd. according to size, directly on sep. small graphite disks arranged behind the jet-nozzles of an eight-stage cascade impactor. To det. the elemental compn. of the particles, the electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) technique was applied. In an appropriately sealed electrothermal vaporizer, linked to an inductively coupled plasma mass spectrometer, the targets were heated and the sample vapor was swept by argon into the plasma. The system described was used for the anal. of long-range transported particles from Arctic air sampled at the German Arctic research station at Spitsbergen, Norway, in spring 1998. For the elements Mn, Fe, Co, Ni, Ag, Cd, Sn, Sb and Pb the trace element content per cubic meter of air was measured as a function of the aerodynamic particle diam. Air masses of different origin cause characteristic particle distributions at low changes in total dust burden. The relative detection limits for the elements measured in an air vol. of 0.275 m3 were detd. to be within 0.3-10 pg m-3; the overall anal. precision was around 20% for all trace metals.

APP* 228) Uggerud, H. T. and W. Lund (1999). "Modifier effects from palladium and iridium in the determination of arsenic and antimony using electrothermal vaporisation inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 54B(11): 1625-1636.

A study was made of the stabilizing and carrying effects of palladium and iridium as modifiers in the detn. of arsenic and antimony by electrothermal vaporization inductively coupled plasma mass spectrometry. The signal intensities of arsenic and antimony increase with decreasing vol. (50-10 mL) and concn. (5-40 mg/mL) of the palladium modifier soln. Similar effects were not obsd. for iridium. Palladium and iridium had about the same stabilizing effect on the analytes; significant loss of the analyte occurred at pyrolysis temps. >900 Deg. The two modifiers gave rise to about the same increase in signal intensity, but the transport mechanism is probably different. Iridium interacts with the graphite surface such as to make carbon the main carrier. But palladium probably acts as an active carrier.

APP* 229) Liao, H.-C. and S.-J. Jiang (1999). "EDTA as the modifier for the determination of Cd, Hg and Pb in fish by slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 14(10): 1583-1588.

Ultrasonic slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry (USS-ETV-ICP-MS) has been applied to the detn. of Cd, Hg and Pb in several fish samples. The influences of the instrument operating conditions and slurry prepn. on the ion signals were reported. In this study, a relatively low vaporization temp. was used which sepd. the analyte from the major matrix components and improved the ion signals significantly. EDTA was used as the modifier to enhance the ion signals. Since the sensitivities of Cd, Hg and Pb in various fish slurries and aq. soln. were quite different, the std. addn. method and isotope diln. method were used for the detn. of Cd, Hg and Pb in these fish samples. This method has been applied to the detn. of Cd, Hg and Pb in dogfish muscle ref. material (DORM-2) and a swordfish sample purchased from the market. The anal. results agreed with the certified values. The precision between sample replicates was better than 14% with the USS-ETV-ICP-MS method. Detection limits estd. from std. addn. curves were about 3-6, 3-9 and 6-7 ng g-1 for Cd, Hg and Pb, resp., in different samples.

APP* 230) Langer, D. and J. A. Holcombe (1999). "A method for the direct analysis of new and used lubricating oils using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICPMS)." Preprints - American Chemical Society, Division of Petroleum Chemistry 44(3): 274-278.

An anal. method was described for the direct anal. of trace metals in new and used lubricating oils using a graphite furnace by electrothermal vaporization (ETV) for sample introduction and an inductively coupled plasma mass spectrometry (ICPMS) for element quantification. This method allows for reproducible introduction of lubricating oils into a graphite furnace without a diln. or sample prepn. step and analyzed directly without diln. Quantification is carried out by aq. calibration stds. The \"frozen drop method\", in which a drop of a prepd. oil sample falls on a piece of dry ice, is solidified, and the solid sample is transfered manually and dropped into a modified graphite furnace, was investigated as an alternative to conventional acid digestion.

APP* 231) Liao, H.-C. and S.-J. Jiang (1999). "Determination of cadmium, mercury and lead in coal fly ash by slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 54B(8): 1233-1242.

Ultrasonic slurry sampling electrothermal vaporization isotope diln. inductively coupled plasma mass spectrometry (USS-ETV-ID-ICP-MS) was applied to the detn. of Cd, Hg and Pb in coal fly ash samples. Thioacetamide (TAC) was used as the modifier. Since the sensitivities of the elements studied in coal fly ash slurry and aq. soln. were quite different, isotope diln. method was used for the detn. of Cd, Hg and Pb in these coal fly ash samples. The isotope ratios of each element were calcd. from the peak areas of each injection peak. This method was applied to the detn. of Cd, Hg and Pb in NIST SRM 1633a coal fly ash ref. material and a coal fly ash sample collected from Kaohsiung area. Anal. results of ref. sample NIST SRM 1633a coal fly ash agreed satisfactorily with the certified values. The other sample detd. by isotope diln. and method of std. addns. was agreed satisfactorily. Precision was better than 6% for most of the detns. and accuracy was better than 4% with the USS-ETV-ID-ICP-MS method. Detection limits estd. from std. addn. curves were at 24-58, 6-28 and 108-110 ng g-1 for Cd, Hg and Pb, resp.

APP* 232) Liu, H. W., S. J. Jiang, et al. (1999). "Determination of cadmium, mercury and lead in seawater by electrothermal vaporization isotope dilution inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 54B(9): 1367-1375.

Electrothermal vaporization isotope diln. inductively coupled plasma mass spectrometry (ETV-ID-ICP-MS) was applied to the detn. of Cd, Hg and Pb in seawater. The isotope ratios of the elements studied in each anal. run were calcd. from the peak areas of each isotope. Various modifiers were tested for the best signal of these elements. After preliminary studies, 0.15% mass/vol. TAC (thioactamide) and 4% vol./vol.

HCl were added to the sample soln. to work as the modifier. The ETV-ID-ICP-MS method was applied to the detn. of Cd, Hg and Pb in NASS-4 and CASS-3 ref. seawater and natural seawater from Kaohsiung area. The results for ref. sample NASS-4 and CASS-3 agreed satisfactorily with the ref. values. Results for other samples detd. by isotope diln. and method of std. addns. agreed satisfactorily. Detection limits were approx. 0.002, 0.005 and 0.001 ng/mL for Cd, Hg and Pb in seawater, resp., with the ETV-ICP-MS method. Precision between sample replicates was better than 20% for most of the detns.

FUN* 233) Gercken, B., E. Felder, et al. (1999). "Identification of combinatorial chemistry compounds via elemental tagging and ETV/ICP-MS." Special Publication - Royal Society of Chemistry 241(Plasma Source Mass Spectrometry): 222-234.

This paper demonstrates how electrothermal vaporization (ETV)/ICP-MS can play an essential role in pharmaceutical drug discovery research.

REV* 234) Vanhaecke, F. and L. Moens (1999). "Recent trends in trace element determination and speciation using inductively coupled plasma mass spectrometry." Fresenius' Journal of Analytical Chemistry 364(5): 440-451.

A review with 120 refs. During the past decade, ICP-MS has evolved from a delicate research tool, intended for the well-trained scientist only, into a more robust and well-established anal. technique for trace and ultra-trace element detn., with a few thousand of instruments used worldwide. Despite this immense success, it should be realized that in its \"std. configuration\", i.e. equipped with a pneumatic nebulizer for sample introduction and with a quadrupole filter, ICP-MS also shows a no. of important limitations and disadvantages: (i) the occurrence of spectral interferences may hamper accurate trace element detn., (ii) solid samples have to be taken into soln. prior to anal. and (iii) no information on the \"chem. form\" in which an element appears can be obtained. Self-evidently, efforts are made to overcome the aforementioned limitations to the largest possible extent. The application of a double focusing sector field mass spectrometer in ICP-MS instrumentation offers a higher mass resoln., such that spectral overlap can be avoided to an important extent. Addnl., in a sector field instrument, photons are efficiently eliminated from the ion beam, resulting in very low background intensities, making it also very well-suited for extreme trace anal. Also the combination of the ICP as an ion source and a quadrupole filter operated in an \"alternate\" stability region, an ion trap or a FT ion cyclotron resonance mass spectrometer allows high(er) mass resoln. to be obtained. With modern quadrupole-based instruments, important types of spectral interferences can be avoided by working under \"cool plasma\" conditions or by applying a collision cell. The use of electrothermal vaporization (ETV) or esp. laser ablation (LA) for sample introduction permits direct anal. of solid samples with sufficient accuracy for many purposes. The application range of LA-ICP-MS has become very wide and the introduction of UV lasers has led to an improved spatial resoln. Solid sampling ETV-ICP-MS on the other hand can be used for some specific applications only, but accurate calibration is more straightforward than with LA-ICP-MS. Limited multi-element capabilities, resulting from the transient signals obsd. with ETV or single shot LA, can be avoided by the use of a time-of-flight (TOF) ICP-MS instrument. Finally, when combined with a powerful chromatog. sepn. technique, an ICP-mass spectrometer can be used as a highly sensitive, element-specific multi-element detector in elemental speciation studies. Esp. liq. (HPLC-ICP-MS) and, to a lesser extent, gas (GC-ICP-MS) chromatog. have already been widely used in combination with ICP-MS. In speciation work, sample prepn. is often obsd. to be troublesome and this aspect is presently receiving considerable attention. For GC-ICP-MS, new sample pretreatment approaches, such as headspace solid phase microextn. (headspace SPME) and the purge-and-trap technique were introduced. Also supercrit. fluid chromatog. (SFC) and capillary electrophoresis (CE) show potential to be of use in combination with ICP-MS, but so far the application ranges of SFC-ICP-MS and CE-ICP-MS are rather limited.

FUN* 235) Mora, J., L. Gras, et al. (1999). "Electrothermal vaporization of mineral acid solutions in inductively coupled plasma mass spectrometry: comparison with sample nebulization." Spectrochimica Acta, Part B: Atomic Spectroscopy 54B(6): 959-974.

The anal. behavior of an electrothermal vaporization (ETV) device for the introduction of mineral acid solns. in inductively coupled plasma mass spectrometry (ICP-MS) was evaluated. H2O, HNO3, HCl, HClO4 and H2SO4 in concns. within the 0.05-1.0 mol L-1 range were studied. For all the acids tested, increasing the acid concn. increases the ion signal and deteriorates the precision. The magnitude of the signal enhancement depends on the analyte and on the acid considered. Acid solns. give rise to ion signals that are 2-10 times higher than those with H2O. Among the acids tested, H2SO4 provides the highest signals. The addn. of Pd reduces matrix effects due to the acids and increases the signal in ETV ICP-MS. In comparison with conventional sample nebulization (CS), the ETV sample introduction system provides higher sensitivities (between 2 and 20 times higher) at the same acid concn. The magnitude of this improvement is similar to that obtained with a microwave desolvation system (MWDS). The ETV sample introduction system gives rise to the lowest background signals from matrix-induced species. Due to this fact, the limits of detection (LODs) obtained for the isotopes affected by any interference are lower for ETV sample introduction than those obtained with the CS and the MWDS. For the isotopes that do not suffer from matrix-induced spectral interferences, the ETV gives rise to LODs higher than those obtained with the CS. For these isotopes the lowest LODs were obtained with MWDS.

FUN* 236) Gregoire, D. C. and R. E. Sturgeon (1999). "Analyte transport efficiency with electrothermal vaporization inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 54B(5): 773-786.

Reported are results for the quant. detn. of abs. transport efficiency in electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) for the Perkin-Elmer HGA-600MS electrothermal vaporizer. The abs. transport efficiencies for Mo, In Tl and Bi were detd. using exptl. conditions typical of those applied to real anal. by ETV-ICP-MS. Expts. using an online filter trapping app. indicated that particles produced by the ETV device were smaller than 0.1 mm in diam. The nature and condition of the ETV graphite surface, the length of the transfer tube, and the effect that dild. seawater and palladium modifiers have on analyte transport efficiency were investigated. Transport efficiency was comparable for all elements studied and was enhanced with previously used, rather than new, graphite tubes and when seawater and palladium carriers were present. When analyte was vaporized without carrier from a new graphite tube, the transport efficiency to the plasma was approx. 10%. Approx. 70% of the total amt. of analyte vaporized was deposited within the ETV switching valve, 19% onto the transfer tubing and 1% onto the components comprising the torch assembly. These conditions represent the \"worst case scenario\", with analyte transport to the plasma increasing to approx. 20% or more with the addn. of carrier.

APP* 237) Lam, J. W. H., R. E. Sturgeon, et al. (1999). "Ultra-trace determination of Se in sediments by electrothermal vaporizer-inductively coupled plasma-mass spectroscopy: use of the ETV as a thermochemical reactor." Spectrochimica Acta, Part B: Atomic Spectroscopy 54B(3-4): 443-453.

The performance of electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) was evaluated for the ultra-trace detn. of total Se in sediment ref. materials. Citric acid, when combined with an appropriate thermal program, promoted the early release of Se in a mol. form from the graphite surface, effecting a sepn. of the analyte from the concomitant matrix, thereby demonstrating the use of the ETV as a thermochem. reactor. No special sample pretreatment is needed and an abs. detection limit of 10 pg was achieved. Concns. of Se in different sediment CRMs were detd. and results obtained by both isotope diln. (ID) and std. addn. (SA) methodologies were compared and evaluated. Mass bias effects prevented accurate application of ID techniques.

REV* 238) Sturgeon, R. E. and J. W. Lam (1999). "The ETV as a thermochemical reactor for ICP-MS sample introduction." Journal of Analytical Atomic Spectrometry 14(5): 785-791.

Electrothermal vaporization (ETV) for sample introduction into (inductively coupled) plasmas was explored for more than two decades, 1st for use with optical spectroscopy and subsequently with mass spectrometry. It is with the latter that its full potential was appreciated vis-a-vis soln. sample nebulization. Tandem coupling of an ETV to a plasma source elicits a no. of attractive features, not least of which is the explicit use of the device as a thermochem. reactor for in situ pretreatment of samples. This aspect of ETV use has not yet been sufficiently well explored, despite an accumulated body of literature in the related field of ETAAS, where judicious selection of thermal programs and chem. modifiers was extensively used to minimize anal. problems. Of particular interest for ETV sample introduction is the feasibility of using classical chem. modifiers or other reagents to alter the volatility of either the analyte or the concomitant matrix, thereby permitting a thermal or temporal sepn. of their release from the ETV surface. This approach may alleviate space charge interference effects, minimize polyat. ion interferences and effectively enhance resoln., permit direct speciation of trace element fractions in samples as well as serve as a 'crucible' for sample prepn. The literature in this field is reviewed, with 82 refs., and examples of such applications for ICP-AES and ICP-MS detection are presented.

REV* 239) Kikawada, Y. (1999). "Direct determination of trace elements in sea water by ICP-MS." Nippon Kaisui Gakkaishi 53(2): 115-116.

A review, with 4 refs., on the detn. of trace elements in seawater by inductively coupled plasma mass spectrometry with electrothermal vaporization, flow injection, and combination of electrothermal vaporization and flow injection.

REV* 240) Taylor, A., S. Branch, et al. (1999). "Atomic spectrometry update: Clinical and biological materials, foods and beverages." Journal of Analytical Atomic Spectrometry 14(4): 717-781.

A review with 593 refs. Anal. of clin. and biol. materials; general reviews and articles; sampling and sample prepn.; sample collection and pretreatment; solid and slurry sampling; sample digestion; preconcn.; developments in and applications of multielement techniques; at. emission spectrometry with the inductively coupled plasma and the microwave induced plasma; inductively coupled plasma mass spectrometry and other mass spectrometric techniques; overcoming interferences in quadrupole ICP-MS (Q-ICP-MS); multielement detn. by Q-ICP-MS; laser ablation ICP-MS; electrothermal vaporization ICP-MS; double focusing magnetic sector ICP-MS; detn. of stable isotopes by mass spectrometry; accelerator mass spectrometry; x-ray fluorescence spectrometry; other multielement techniques and studies; developments in single element techniques; ref. materials and quality assurance are discussed.

APP* 241) Truscott, J. B., L. Bromley, et al. (1999). "Determination of natural uranium and thorium in environmental samples by ETV-ICP-MS after matrix removal by online solid phase extraction." Journal of Analytical Atomic Spectrometry 14(4): 627-631.

An online solid phase extn. method was developed for the detn. of 238U and 232Th in biol. certified ref. material using inductively coupled plasma mass spectrometry (ICP-MS). Abs. detection limits were 2.7 pg and 3.1 pg for the detn. of 238U and 232Th, resp., both being blank limited. The result for the detn. of 238U in NASS-4 Open Ocean Sea H2O was 2.13 +- 0.28 ng ml-1 compared with a certified value of 2.68 +- 0.12 ng ml-1. The results for the detn. of 238U in SLRS-3 River H2O was 0.043 +- 0.002 ng ml-1 compared with an indicative value of 0.045 ng ml-1. Results for the detn. of 238U and 232Th in NIST 1575 Pine Needles were 14.6 +- 3.4 ng g-1 and 28.3 +- 4.5 ng g-1 resp. compared with certified values of 20 +- 4 ng g-1 and 37 +- 3 ng g-1, using a dry and wet ashing sample prepn. method. Results for the detn. of 238U and 232Th in NIST 1566a oyster tissue were 121 +- 21 ng g-1 and 29 +- 8 ng g-1 for 238U and 232Th compared to certified and indicative values of 132 +- 12 ng g-1 and 40 ng g-1, using the same method. When a Li metaborate fusion method was used, results for 238U and 232Th were 23.3 +- 2.0 ng g-1and 36.2 +- 5.6 ng g-1 resp. in NIST 1575 Pine Needles. The application of electrothermal vaporization ICP-MS (ETV-ICP-MS) to NASS-4 Open Ocean Sea H2O gave 2.81 +- 0.54 ng ml-1 and SLRS-3 River H2O 0.045 +- 0.004 ng ml-1 for 238U. When the fused NIST 1575 samples were analyzed using ETV-ICP-MS, results for 238U and 232Th were 19.5 +- 1.7 ng g-1 and 38.8 +- 2.2 ng g-1 resp. Abs. detection limits for ETV-ICP-MS were 30 fg and 9 fg for 238U and 232Th, resp., both being blank limited.

APP* 242) Hu, Y., F. Vanhaecke, et al. (1999). "Determination of ruthenium in photographic materials using solid sampling electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 14(4): 589-592.

Ru was detd. in photog. emulsions and films using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) after minimal sample pre-treatment (no sepn. or preconcn. required). The emulsion samples were either (i) converted into a colloidal soln. by dissoln. in warm water or dil. HNO3 (liq. sampling) or (ii) dried at 105 DegC (solid sampling) prior to anal. For the anal. of photog. films, only solid sampling, requiring no sample pre-treatment, was used. By optimization of the ETV heating program, online sepn. of Ru (analyte) and Ir (internal std.) from the Ag matrix was accomplished: ~90% of the Ag present was removed prior to the vaporization of Ru and Ir. Quantification of Ru was accomplished by single std. addn., whereby Ir was used as an internal std. The abs. limit of detection was found to be ~1 pg. The results obtained showed a good agreement with those obtained by pneumatic nebulization ICP-MS and/or electrothermal at. absorption spectrometry after sample dissoln.

APP* 243) Vanhaecke, F., M. Verstraete, et al. (1999). "Determination of the palladium content in a solid plastic material by electrothermal vaporization ICP-mass spectrometry (ETV-ICPMS)." Analytical Communications 36(3): 89-92.

Electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICPMS) was used to det. the Pd content in a solid aliph. polyketone. The presence of Pd in this material is attributed to the use of a Pd-contg. homogeneous catalyst for its prepn. By application of a multi-step heating program, the org. matrix could be selectively and completely removed prior to the vaporization of the analyte element.

APP* 244) Vanhaecke, F., I. Gelaude, et al. (1999). "Solid sampling electrothermal vaporization inductively coupled plasma mass spectrometry for the direct determination of Hg in sludge samples." Analytica Chimica Acta 383(3): 253-261.

Solid sampling electrothermal vaporization-inductively coupled plasma mass spectrometry (ETV-ICP-MS) was used for the direct detn. of Hg in sludge. Pretreatment was limited to drying, sieving and homogenization by shaking. One milligram amts. of the samples of interest were inserted into a graphite furnace coupled to a quadrupole-based ICP-MS for subsequent anal. The temp. program of the graphite furnace was selected such that Hg was vaporized and transported into the plasma at a relatively low temp. (.apprx.700 Deg). Under these conditions, co-volatilization of considerable amts. of the matrix, leading to signal suppression and hence, curvature of the mass response curve, could be avoided. Quantification was accomplished by external calibration, using a (solid) certified ref. material, with a matrix compn. comparable to that of the samples. The accuracy attainable was evaluated by (1) anal. of a sludge certified ref. material and (2) comparison of the ETV-ICP-MS result for a real-life sample with the aqua regia extractable Hg content, as detd. by pneumatic nebulization ICP-MS after sample processing according to the German std. DIN 38414-S7. Although in all cases, the precision was obsd. to be limited by the inhomogeneous distribution of the analyte element over the matrix, the ETV-ICP-MS result obtained for the sludge ref. material showed an excellent agreement with the certified value, while for the real-life sample, the av. ETV-ICP-MS result agreed within 10% with the aqua regia extractable content. The approach developed was used for the anal. of sludges sampled at different locations in Limburg, Belgium. For all but 1 sample, the Hg content was below the max. allowable content, as specified in Flanders.

APP* 245) Turner, J., S. J. Hill, et al. (1999). "The use of ETV-ICP-MS for the determination of selenium in serum." Journal of Analytical Atomic Spectrometry 14(2): 121-126.

The development of a novel procedure for the accurate detn. of selenium in serum using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) is described. The proposed method eliminates the need for a lengthy sample digestion procedure (a requirement with many methods for the anal. of biol. samples), utilizing a simple 1+19 diln. of the serum with 1% nitric acid. Many of the interferences normally assocd. with the detn. of selenium by ICP-MS are successfully eliminated with careful optimization of the ETV temp. program and modifier system. Anal. characteristics for 74Se, 77Se, 78Se and 82Se are reported, including detection limits (3s blank) of .apprx.0.1 ng/g for 77Se and 82Se. Short- and long-term reproducibility data between 4.7 and 4.9% and 3.2 and 3.8% (relative std. deviation) for 77Se and 82Se, resp., are shown. The accuracy of the method, which included Te as an internal std., was demonstrated with the anal. of three internal quality control samples and the certified ref. material NIST SRM 1598 (bovine serum). Results within 10% of the target value were achieved for three of the four isotopes studied, with slightly worse results for 78Se owing to the large interference from argon adduct ions on this isotope. Preliminary work involving the addn. of nitrogen to the argon aerosol carrier gas was successful in reducing the ArAr interference at m/z 78.

REV* 246) Nickel, H. and J. A. C. Broeckaert (1999). "Some topical applications of plasma atomic spectrochemical methods for the analysis of ceramic powders." Fresenius' Journal of Analytical Chemistry 363(2): 145-155.

A review with 68 refs. is given. The scope of a no. of plasma spectrochem. methods for the detn. of the main components and impurities in ceramic powders is described. These methods meet the requirements for the anal. characterization of new structural and functional ceramics for modern industrial applications and electronic devices. For ceramic powders, spectrochem. anal. with direct methods as well as anal. subsequent to sample dissoln. are discussed. Fusion is a powerful method for the dissoln. of ZrO2 ceramic powders, provided the fluxes are pure enough. For detns. in Al2O3, SiC, and ZrO2, it will be shown that ICP-MS is very useful. This is esp. true for trace anal. after matrix removal. The latter can easily be performed online in the case of the anal. of Al2O3 powders. For direct anal. of ceramic powders, the direct insertion of samples into the plasma, spark and are ablation, laser ablation, electrothermal vaporization and slurry nebulization are discussed. Particular attention is given to the direct anal. of ceramics in powder form (Al2O3, SiC, Si3N4, B4, WC) using ICP-AES with slurry nebulization as well as with direct sample insertion (DSI) and with electrothermal vaporization (ETV). For the two latter methods, the use of chem. modifiers for volatile compd. formation will be shown to be of great importance, and its features will be explained using thermochem. considerations.

DISS* 247) Langer, D. L. (2000). Electrothermal vaporization inductively coupled plasma mass spectrometry: fundamental studies and practical applications. Univ. of Texas,Austin,TX,USA. FIELD URL:: 149 pp.

APP* 248) Bettinelli, M., U. Baroni, et al. (2000). "Determination of trace elements in honey using ETV-ICP-MS." Atomic Spectroscopy 21(6): 195-204.

The presence of certain trace elements in bee honey is an indication of environmental pollution. Since sample prepn. before instrumental detn. can seriously influence the final result, an anal. procedure that uses a simple diln. of the sample before spectrometric measurements would be required to ensure low contamination levels of the samples and, consequently, adequate detection limits. Electrothermal Vaporization - Inductively Coupled Plasma Mass Spectrometry (ETV-ICP-MS) for the detn. of As, Be, Cd, Co, Cs, Cu, Li, Mn, Ni, Pd, Pb, Rb, Rh, Sb, Se, Sn, Te, Tl, and V in honey was evaluated. The results relative to Robinia and Eucalyptus honey were compared with those obtained by USN-ICP-MS after microwave-acid dissoln. of the sample and with those obtained by HR-ICP-MS. The detection limits were 0.1-0.5 ng/g for all elements with a precision at 10 ng/g, generally <5-10%.

APP* 249) Emons, H., A. Baade, et al. (2000). "Voltammetric determination of heavy metals in microvolumes of rain water." Electroanalysis 12(15): 1171-1176.

Anal. methods for the trace detn. of heavy metals in microvolumes of real water samples by stripping voltammetry at microelectrodes and microelectrode arrays were investigated. Voltammetric procedures at Au, Pt, and glassy carbon microelectrodes including appropriate measuring cells were developed and validated by the application of electrothermal vaporization-inductively coupled plasma-mass spectrometry (ETV-ICP-MS) as well as stripping voltammetry performed at conventionally sized Hg electrodes. The influence of a piezo actuator on the accumulation efficiency of the analyte at the electrode surface was tested. Detection limits in the low picogram range were achieved with anodic stripping voltammetry and Osteryoung-square-wave or differential pulse detection. The methods were applied to the detn. of Pb, Cd, Zn, and Cu in single raindrops and small vols. of rain water.

FUN* 250) Wei, W.-C., P.-H. Chi, et al. (2000). "Study on the effect of polyhydroxy compounds on the sensitivity enhancement of elements in electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 15(11): 1466-1473.

A new approach to matrix modification, in which polyhydroxy compds. (polyols) were used as complexing agents, was evaluated for the detn. of trace elements (B, As, Se, Sb, Cr and Mo) by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). The effects of eight kinds of polyhydroxy compds. on the sensitivity enhancement of elements were studied. The addn. of mannitol and sorbitol has the best effect for sensitivity enhancement of the tested elements (B, As, Se and Sb) by a factor of 2.5-84 compared to results without modifiers by electrothermal vaporization ICP-MS. The sensitivity enhancement is attributed to the fact that various polyhydroxy compds. form volatile complexes with the elements and assist in transporting them from the ETV system to the ICP-MS instrument. The instrumental parameters for ETV-ICP-MS, such as gas flow rate, ashing temp. and vaporization temp., were studied and optimized. With the established method, the limits of detection for the elements of interest in the presence of mannitol and sorbitol were .apprx.1-100 pg mL-1, which is .apprx.1-2 orders lower than levels achieved in the absence of them. The interferences from Ca, Mg, Na and K, which exist abundantly in natural water samples, on the anal. performance of the analytes were examd. The coexisting elements markedly changed the volatility of the analyte-polyol complexes, which resulted in a decrease in the detection sensitivity of the analytes. The established matrix modification system was applied to the detn. of elements (As, B, Se and Sb) in various water samples. The feasibility of the proposed method was tested by using NIST SRM 1643 C Water samples.

FUN* 251) Venable, J., T. Williamson, et al. (2000). "Characterization of pressure pulse and carrier gas flow changes resulting from pulsed heating in ETV-ICP-MS." Journal of Analytical Atomic Spectrometry 15(10): 1329-1334.

A simplistic model was formulated to show the effects of pulsed heating upon a flow of gas through an ETV. Using this model, a significant change in flow was predicted with a profile that increased sharply during the initial stages of heating, but then tapered off. Exptl., pressure and flow increases are coincident to the pulsed heating of an ETV, by using both a direct and an indirect method of detn. Direct measurement of both pressure and flow increases were acquired through the use of a probe that contained pressure, flow and temp. sensors. An indirect measurement of the pressure/flow pulse was obtained by monitoring the Ar2+, which is sensitive to the carrier gas flow rate. The pressure increase is minimal (<0.5 torr) while the flow increase was much more substantial (>100 mL min-1). The magnitudes of both pressure and flow increases are dependent upon the initial carrier gas flow rates. Due to the envisioned deleterious effects of the pressure/flow pulse, an attempt was made to sep. the arrival of the pulse at the plasma from the analyte signal by lengthening the transport tubing. In this manner, the analyte signal traveled at a velocity which was much less than that of the pressure pulse which propagates at the speed of sound in Ar. However, increased transport tubing lengths resulted in lower sensitivities and no significant gain in precision.

APP* 252) Shuai, Q., Y. Qin, et al. (2000). "Determination of rare earth impurities in high-purity lanthanum oxide using electrothermal vaporization/ICP-AES after HPLC separation." Analytical Sciences 16(9): 957-961.

A new method for detn. of trace rare earth impurities in high-purity La2O3 by HPLC combined with electrothermal vaporization inductively coupled plasma at. emission spectrometry (ETV-ICP-AES) is proposed. The chromatog. retention behaviors of matrix (La) and rare earth impurities were studied using 2-ethylhexyl hydrogen 2-ethylhexylphosphonate (P507) resin as the stationary phase and dil. nitric acid as the mobile phase. The use of EDTA as an eluent enables effective elution of rare earth impurities from a HPLC column. The influence of EDTA in ETV-ICP-AES was also discussed. The exptl. results showed that a favorable sepn. between matrix (La) and rare earth impurities could be obtained within 30 min. The method proposed was applied to the anal. of high-purity La2O3; the results obtained were in good agreement with those obtained by ICP-MS. Under the optimum conditions, the detection limits (DLs) for 14 rare earth elements (REEs) were in the range of 0.8 ng/mL (Yb) to 48 ng/mL (Ce). The recoveries of 14 REEs were at 90-110%.

FUN* 253) Hattendorf, B. and D. Gunther (2000). "Characteristics and capabilities of an ICP-MS with a dynamic reaction cell for dry aerosols and laser ablation." Journal of Analytical Atomic Spectrometry 15(9): 1125-1131.

The characteristics of a dynamic reaction cell (DRC), used to reduce interferences from mol. or elemental ions in an inductively coupled plasma quadrupole mass spectrometer (ICP-MS), were studied for dry sample introduction. The dependence of the signals from mol. ions formed in the ICP or in the interface region was monitored with the variation of the concn. of reaction or buffer gas used. The differences between wet aerosols, generated with a std. cyclonic spray chamber and concentric nebulizer, to dry aerosols, generated by a desolvating nebulizer or laser ablation, were detd. The comparison of prominent background signals to ion signals from selected analyte ions was used to det. parameters that lead to optimum signal/background ratios and anal. performance for laser ablation anal. NH3 and H were used as reactive gases in these expts. Addnl., He, Ne and Xe were used as a buffer gas to enhance thermalization in the DRC. The reaction rate with NH3 is distinctly higher than with H. However, side reactions with analyte ions, leading to addnl. interferences and analyte loss through the formation of clusters, were severe with NH3. H, having a smaller reactivity, reduces cluster formation and retains analyte sensitivity even at a high gas concn. It is therefore better suited for methods that allow only short measurement times, like laser ablation (LA) or electrothermal vaporization (ETV). The capabilities of the DRC for LA are demonstrated through the detn. of Ca in a quartz sample and Nb in a Cr matrix, which suffer from either Ar-ions or Ar-based interferences. Redn. of the background intensities and use of the most abundant isotope led to a redn. of the limit of detection for Ca in quartz by two orders of magnitude and an improvement of accuracy for the detn. of Nb in a Cr-matrix.

APP* 254) Maria Maia, S., J. Bento Borba da Silva, et al. (2000). "Determination of As, Mn, Pb and Se in coal by slurry electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 15(9): 1081-1086.

A method for the detn. of trace elements in coal by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS), introducing the sample as a slurry, is proposed. The slurry was prepd. by mixing the powd. coal (<45 mm) with aq. 5% vol./vol. nitric acid soln. in an ultrasonic bath. An ultrasonic probe was used to homogenize the slurry in the auto-sampler cup just before its introduction into the graphite tube. The best compromise conditions for the furnace temp. program, the amt. of palladium used as modifier, the carrier gas flow rate, etc., were detd. By introducing 10 mL of a 4.0 mg mL-1 coal slurry, using 3 mg of Pd as a modifier, and a pyrolysis temp. of 600 DegC, most of the obtained values for four coal ref. materials were well within the certified range, using external calibration with aq. solns. No carrier had to be added in addn. to the palladium modifier. Using a lower slurry concn. of 1.3 mg mL-1 and 2 mg of Pd as the modifier, the values obtained for lead were significantly lower than the certified ones. This problem could be solved in part by adding NaCl as a phys. carrier, in addn. to the palladium, showing that this carrier reduces the differences in the analyte transport from the sample and from the calibration solns. However, results for most elements, except for arsenic, tended to be a little low even under these conditions, hence, preference was given to the higher slurry concn.

APP* 255) Uggerud, H. and W. Lund (2000). "Determination of arsenic by inductively coupled plasma mass spectrometry - comparison of sample introduction techniques." Fresenius' Journal of Analytical Chemistry 368(2-3): 162-165.

A comparison is made of four sample introduction techniques for the detn. of As by inductively coupled plasma mass spectrometry. The techniques studied were (1) flow injection with pneumatic nebulization (FIA-PN), (2) direct electrothermal vaporization (ETV), (3) continuous hydride generation (HG) and (4) hydride generation with in situ trapping followed by electrothermal vaporization (HG-ETV). FIA-PN and ETV gave similar detection limits in concn. units (.apprx.20 pg mL-1), although ETV had a much lower abs. detection limit (0.2 pg). Sample introduction by hydride generation gave an inferior detection limit (100-200 pg mL-1), also in combination with in situ trapping and ETV, owing to the blank signal from traces of As in NaBH4 which is difficult to eliminate. The more elaborate sample introduction techniques based on ETV and HG may not offer significant advantages compared to normal soln. nebulization for the detn. of As in simple sample matrixes such as natural fresh waters, where matrix removal is not required.

APP* 256) Vanhaecke, F., M. Resano, et al. (2000). "Multielement Analysis of Polyethylene Using Solid Sampling Electrothermal Vaporization ICP Mass Spectrometry." Analytical Chemistry 72(18): 4310-4316.

Next to laser ablation (LA) also electrothermal vaporization (ETV) from a graphite furnace as a means of sample introduction opens possibilities for direct anal. of solid samples using inductively coupled plasma mass spectrometry (ICPMS). Solid sampling ETV-ICPMS is very well suited for the detn. of metal traces in polyethylene. A limited multielement capability is often cited as an important drawback of ETV-ICPMS. However, by studying the effect of monitoring an increasing no. of mass-to-charge ratios on the signal profile (integrated signal intensity and repeatability) of selected analyte elements, the multielement capability of (solid sampling) ETV-ICPMS was systematically evaluated, and the results obtained suggest that, with a quadrupole-based ICPMS instrument, at least 11 elements can be detd. \"simultaneously\" (from the same vaporization step), in essence without compromising the sensitivity or the precision of the results obtained. The \"simultaneous\" detn. of Al, Ba, Cd, Cu, Mn, Pb, and Ti in a polyethylene candidate ref. material has been accomplished, despite the large variation in analyte concn. (from 5 ng/g for Mn to 500 mg/g for Ti) and in furnace behavior (volatility) they exhibit. To avoid premature losses of Cd during thermal pretreatment of the samples, Pd was used as a chem. modifier. Two different calibration methods-external calibration using an aq. std. soln. and single std. addn.-were studied and the results obtained were compared with those obtained using neutron activation anal. (NAA) and/or with the corresponding (candidate) certified values (if available). Single std. addn. was shown to be preferable (av. deviation between ICPMS result and ref. value < 3%), although-except for Ba-acceptable results could also be obtained with external calibration.

FUN* 257) Bings, N. H., J. M. Costa-Fernandez, et al. (2000). "Time-of-flight mass spectrometry as a tool for speciation analysis." Spectrochimica Acta, Part B: Atomic Spectroscopy 55B(7): 767-778.

A review, with 41 refs., is given. Time-of-flight mass spectrometry (TOFMS) has recently been introduced as an alternative to scanning-based mass analyzers for use in elemental anal. Coupled with an inductively coupled plasma or alternative ion source, TOFMS can produce a complete at. mass spectrum in <50 ms. Because of this high spectral-generation rate, even very brief transient signals can be recorded with high fidelity. Also, each mass spectrum is derived from the same sub-microsecond pulse of ions, so high precision can be achieved by using either isotope-ratioing or internal standardization techniques. All these features make TOFMS attractive for the measurement of transient signals, such as those commonly encountered in speciation anal. The capabilities of TOFMS in speciation will be demonstrated through the coupling of gas chromatog. and capillary electrophoresis with an inductively coupled plasma-TOFMS. Addnl., the development of novel switched gas sampling glow discharge (GSGD) ionization sources will be described and their role in chem. speciation will be evaluated. The switched GSGD has the ability to collect both at. and mol. mass spectra in rapid succession, to provide addnl. information about chem. species. The coupling of various sample introduction systems (flow-cell, exponential dilutor, capillary gas chromatog. and electrothermal vaporization) to the GSGD is outlined.

FUN* 258) Venable, J. D. and J. A. Holcombe (2000). "Signal enhancements produced from externally generated 'carrier' particles in electrothermal vaporization-inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 55B(7): 753-766.

An externally generated carbon particle aerosol produced from the pyrolysis of hexane vapor was introduced into an electrothermal vaporization inductively coupled plasma mass spectrometer (ETV-ICPMS) system to probe possible carrier effects. Signal enhancements were seen upon the introduction of the externally generated aerosol for most metals studied. However, these enhancements are caused by changes in the plasma rather than increased transport from the ETV to the ICPMS. Because a pyrolyzed hydrocarbon was used to generate the aerosol, both hydrogen gas and carbon were introduced into the plasma. The source of the enhancements is believed to stem from an increased plasma temp. (from H2(g) addn.) which increases the kinetic energy of the ions and enhances the transmission through the ion lenses. The carbon may also contribute to improved ionization efficiencies for those analytes with ionization potentials between 8.5 and 11 eV. Thus, the addn. of the externally generated aerosol did produce signal enhancements, but the effect is believed to be unrelated to analyte transport and instead dependent upon changes in bulk properties of the plasma.

APP* 259) Liu, H.-W. and S.-J. Jiang (2000). "Determination of mercury and thallium in seawater by electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of the Chinese Chemical Society (Taipei) 47(3): 481-488.

Electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) has been applied to the detn. of Hg and Tl in seawater samples. Various modifiers were tested for the best signal of these elements. After preliminary studies, 0.3% EDTA, 0.1% m/v TAC and 1% vol./vol. HCl were added to the sample soln. to work as the modifier. Since the sensitivities of Hg and Tl in various seawater matrixes and aq. std. solns. were quite different, std. addn. method and isotope diln. method were used for the detn. of Hg and Tl in these seawater samples. This method was applied to the detn. of Hg and Tl in NASS-4 and CASS-3 ref. seawater samples and seawater samples collected from the Kaohsiung area. Results obtained by isotope diln. method and method of std. addns. agreed satisfactorily. Detection limits were in the range of 5-15 and 0.4-0.5 ng l-1 for Hg and Tl in seawater, resp., with the ETC-ICP-MS method. The precision between sample replicates was better than 18% for all the detns.

FUN* 260) Rybak, M. E. and E. D. Salin (2000). "Closed-system trapping method for the direct determination of transport efficiency in electrothermal vaporization sample introduction." Journal of Analytical Atomic Spectrometry 15(7): 883-887.

A novel closed-system for the direct detn. of analyte transport efficiency in electrothermal vaporization (ETV) sample introduction is described. A com. available gas-sampling bag filled with 100 mL of 10% HNO3 was connected to the exhaust of an ETV system and used to collect and seal the product of an electrothermal vaporization event. The bag was then manually agitated, and its liq. contents decanted and analyzed by soln. nebulization ICP-MS. Analyte transport efficiency values are in statistical agreement with those detd. by a ref. method on the same ETV system for a variety of volatile (As, Cd, Mn, Pb), nonvolatile (Cu, Ni) and refractory carbide forming (V) elements. This simple exptl. setup captures all of the analyte in a single soln., with the closed-system element of its design ensuring that this is done quant. Abs. detection limits for most elements were of the order of 0.1-10 ng abs. for the technique, making it well suited for analyte masses typically vaporized in ETV-ICP-OES. The relative merits of using this type of setup for the detn. of analyte transport efficiency in ETV sample introduction, along with exptl. considerations, are described.

APP* 261) Turner, J., S. J. Hill, et al. (2000). "Accurate analysis of selenium in water and serum using ETV-ICP-MS with isotope dilution." Journal of Analytical Atomic Spectrometry 15(6): 743-746.

A procedure for the detn. of Se in H2O and serum using electrothermal vaporization isotope diln. inductively coupled plasma mass spectrometry (ETV-ID-ICP-MS) is described. The 82Se:77Se isotope ratio was measured throughout, following spiking of the samples with a soln. contg. the enriched 77Se isotope. Elimination of interferences was achieved with an optimized ETV temp. program. Parameters such as peak measurement mode, dwell time, points per spectral peak and no. of replicates were evaluated to establish optimum conditions. The accuracy and precision of the method are demonstrated with the anal. of several certified ref. materials TMRAIN-95 (spiked rainwater), TMDA-54.2 (spiked soft H2O), LGC 6010 (hard drinking H2O) and NIST 1598 (bovine serum). Results for all ref. materials were within the certified limits. Isotope diln. anal. of TMRAIN-95, TMDA-54.2, LGC 6010 and NIST 1598 gave % relative std. deviation values (n = 3) of 0.80, 0.07, 0.48 and 0.06%, resp., compared with 5.50, 2.79, 1.15 and 0.92% obtained with the conventional ETV-ICP-MS procedure, thus illustrating improvements in precision with the ETV-ID-ICP-MS method. The uncertainties for the two methods were calcd. following ISO guidelines. The uncertainty for the IDMS procedure was 3.4 times smaller than that for the conventional ETV-ICP-MS method (2.26% and 7.73%, resp.).

APP* 262) Okamoto, Y. (2000). "Direct determination of lead in biological samples by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) after furnace-fusion in the sample cuvette-tungsten boat furnace." Fresenius' Journal of Analytical Chemistry 367(3): 300-305.

The newly conceived electrothermal vaporization (ETV) system using a tungsten boat furnace (TBF) sample cuvette was designed for the direct anal. of solid samples with detection by inductively coupled plasma mass spectrometry (ICP-MS). Into this small sample cuvette, a solid mixt. of the biol. samples and diammonium hydrogen phosphate powder as a fusion flux was placed and situated on a TBF. Tetramethylammonium hydroxide soln. was added to the mixt. After the on-furnace digestion had been completed, the analyte in the cuvette was vaporized and introduced into the ICP mass spectrometer. The solid samples were analyzed by using a calibration curve prepd. from the aq. std. solns. The detection limit was estd. to be 5.1 pg of lead, which corresponds to 10.2 ng g-1 of lead in solid samples when a prepd. sample amt. of 1.0 mg was applied. The relative std. deviation for 8 replicate measurements obtained with 100 pg of lead was calcd. to be 6.5%. The anal. results for various biol. samples are described.

APP* 263) Song, M. and T. U. Probst (2000). "Rapid determination of technetium-99 by electrothermal vaporization-inductively coupled plasma-mass spectrometry with sodium chlorate and nitric acid as modifiers." Analytica Chimica Acta 413(1-2): 207-215.

An electrothermal vaporization-inductively coupled plasma-mass spectrometric (ETV-ICP-MS) method based on the suppression of Ru by using HNO3 and Na chlorate as modifiers was developed for detn. of 99Tc in the presence of Ru. A 1000 fold excess of Ru in the presence of 100 pg/mL 99Tc resulted in an 4% signal increase in the signal of mass 99 amu. Both HNO3 and Na chlorate act in this case as chem. modifiers, rather than simply as mere phys. carriers. The recommended concns. of HNO3 and Na chlorate are 1 and 0.7%, resp. The limit of detection of 99Tc is 1.4 pg/mL (0.9 mBq/mL) and 28 fg (18 mBq) abs. The concn. of 99Tc in three spiked samples with various matrixes was detd.

APP* 264) Snell, J. P., E. Bjorn, et al. (2000). "Investigation of errors introduced by the species distribution of mercury in organic solutions on total mercury determination by electrothermal vaporization-inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 15(4): 397-402.

This paper presents a study into the potential and limitations of an ETV system for the detn. of total mercury, present as different species, in org. soln. The thermal and chem. stability of four mercury species in an electrothermal vaporizer, ETV, coupled to an inductively coupled plasma (ICP-MS) mass spectrometer was studied when samples of hydrocarbon products were introduced. Calibration by the method of isotope diln. was tested with an isotopically enriched std. of mercury diethyldithiocarbamate, 201HgDDTC, in toluene. Sulfur-contg. compds., different palladium solns. and gold metals were studied for use as matrix modifiers. A combination of Pd(NO3)2 in propanol with stabilizing additives applied as a permanent modifier (A. Asheim, poster presentation, 3rd European Furnace Symposium, Prague, 1998) and thionyl chloride injected with each sample gave the most effective stabilization of mercury species and reproducible signals with a relative std. deviation of 3% for 5 mg L-1 HgCl2. The recoveries, by isotope diln., of HgCl2 and CH3HgCl in natural gas condensates ranged between 100 and 115%, while for Hg0 and Me2Hg only 48-65% was recovered with optimized conditions. Losses of the latter two species occurred on drying of the sample in the furnace prior to heating to the pyrolysis temp. Systematic errors in total mercury detn. were, therefore, found to occur for samples contg. Hg0 or Me2Hg, even with isotope diln. calibration. The detection limit, based on 3s of 10 replicate measurements of the 202Hg+ signal for toluene spiked with 6 mg L-1 201HgDDTC, was 0.19 mg L-1.

APP* 265) Resano, M., M. Verstraete, et al. (2000). "Simultaneous determination of Co, Mn, P and Ti in PET samples by solid sampling electrothermal vaporization ICP-MS." Journal of Analytical Atomic Spectrometry 15(4): 389-395.

The coupling of a graphite furnace to an ICP mass spectrometer results in a method that combines the suitability of the graphite furnace for handling solid samples with the detection power of ICP mass spectrometry (ICP-MS). Surprisingly, the majority of previous work devoted to solid sampling electrothermal vaporization (ETV) ICP-MS has only dealt with the detn. of a single element, thereby wasting the pronounced multi-element capabilities of the detection method. In this work, solid sampling ETV-ICP-MS was used for the simultaneous detn. of Co, Mn, P and Ti in two PET (poly(ethylene terephthalate)) materials, showing the suitability of the approach used for this kind of anal. For this detn., the problems caused by the different furnace chem. of the elements had to be tackled. In order to enable the detn. of P, a combination of Pd and ascorbic acid was used as a chem. modifier. Different calibration methods-external calibration using either an aq. std. soln. or a solid std. and single std. addn.-were studied and the results obtained were compared with those obtained by (i) ICP at. emission spectrometry after sample dissoln. and (ii) X-ray fluorescence. External calibration using a solid external std. and single std. addn. were proved to be equally successful, but the latter is more practicable as only an aq. std. soln. is required.

APP* 266) Tanaka, T., K. Furuhashi, et al. (2000). "Electrothermal vaporization using a tungsten filament followed by ICP-MS for the determination of arsenic in microsamples." Bunseki Kagaku 49(2): 125-127.

A combined method of electrothermal vaporization and ICP-MS was studied for microtrace anal. A 5 mL vol. of a sample was placed on a W filament (0.2 mm in diam. * 45 mm) and desolvated electrothermally. Arsenic in the residue was then vaporized by increasing the temp. of the filament to 2450 Deg with the aid of a capacitor (0.22 F) and then carried in an Ar stream to an ICP torch. The filament was used repeatedly at least 100 times. The relative std. deviation (n = 10) for signal intensities of 15 pg As was .apprx.10%, with an abs. detection limit (3s) of 1 pg. The proposed method was applied to the detn. of As in a certified ref. human hair sample. The anal. results obtained for the sample (decompd. with 14 M HNO3 and H2O2) were 0.35 +- 0.03 mg g-1, which almost coincided with the certified values (0.31 +- 0.02 mg g-1).

APP* 267) Wu, H., N. Watanabe, et al. (2000). "Highly sensitive determination of trace rare-earth elements in ultra pure rare-earth compounds by combining ICP-MS with HPLC and electrothermal vaporization." Bunseki Kagaku 49(2): 91-97.

It is very difficult to accurately quantify trace rare-earth elements (REE) in ultra-pure rare-earth compds. by a single anal. method, such as ICP-AES, ICP-MS or electrothermal vaporization (ETV)/ICP-MS. The authors have developed a highly sensitive and efficient method by coupling the advantages of HPLC, ETV and ICP-MS. HPLC eliminated problems caused by matrix and severe overlapping of oxides and hydroxides peaks coming from the main component obsd. in ICP-MS. ETV greatly reduced the interference from additives contained in the eluent of HPLC, and provided an efficient introduction method for ICP-MS. The detection limits of other REE in pure Gd2O3 were 0.07-2 ng/g Gd. The method is applicable to analyses for 7-8 N pure metal and compds.

APP* 268) Coedo, A. G., T. Dorado, et al. (2000). "Slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry for steelmaking flue dust analysis." Spectrochimica Acta, Part B: Atomic Spectroscopy 55B(2): 185-196.

A com. at. absorption graphite furnace (AAGF), with a self-made adapter and valve system, was used as a slurry sampling cell for electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). The system was applied to the detn. of As, Sn, Sb, Se, Te, Bi, Cd, V, Ti and Mo in steelmaking flue dusts. Exptl. conditions with respect to ETV and ICP-MS operating parameters were optimized. Compared to aq. solns., slurry samples present better analyte transport. Microgram amts. of Rh were used to reduce the difference in analyte response in sensitivity for aq. solns. of the tested analytes. No such increasing effect was obsd. for slurry samples and aq. stds. An added quantity of Rh acting as modifier/carrier resulted in an increase for the same analytes in matrix-slurry solns., even the addn. of an extra Rh quantity resulted in a decrease in the signals. The effect of Triton X-100 (used as a dispersant agent) on analyte intensity and precision was also studied. External calibration from aq. stds. spiked with 100 mg ml-1 Rh was performed to quantified 0.010 g/100 mL slurry samples. Results are presented for a certified ref. elec. arc furnace flue dust (EAF): CRM-876-1 (Bureau of Anal. Samples Ltd., Cleveland, UK), a ref. sample of coke ashes X-3705 (from AG der Dillinger Huttenwerke, Germany), and a representative sample of EAF flue dust from a Spanish steelmaking company (CENIM-1). For the two ref. materials an acceptable agreement with certificate values was achieved, and the results for the CENIM sample matched with those obtained from conventional nebulization soln.

APP* 269) Okamoto, Y. (2000). "Generation of a methylbismuth species and its electrothermal vaporization for the determination of bismuth by inductively coupled plasma mass spectrometry." Fresenius' Journal of Analytical Chemistry 366(3): 309-311.

Inorg. Bi(III) was converted to a methylbismuth species, possibly trimethylbismuth, by a thermochem. reaction with methyllithium. It instantly vaporized and was then introduced into the ICP ion source to detect the 209Bi signal. Using an exchangeable small sample cuvette placed on the W boat furnace for the reaction was very favorable from the viewpoints of easy handling, no memory effect, and maintenance of furnace conditions. In this manner, the analyte was vaporized at quite a low temp. (150 Deg). The detection limit (3s) was 0.13 pg of Bi and the precision in relative std. deviation for 5.0 pg of Bi is 3.8% (n = 7).

FUN* 270) Ben Younes, M. E. M. (2001). Studies on the mechanisms of vaporization of analytes and matrices in electrothermal vaporization inductively coupled plasma mass spectrometry. Carleton Univ.,Ottawa,ON,Can. FIELD URL:: 180 pp.

DISS* 271) Venable, J. D. (2001). Fundamental studies of electrothermal vaporization as a sample introduction source for inductively coupled plasma mass spectrometry. Univ. of Texas,Austin,TX,USA. FIELD URL:: 156 pp.

REV* 272) Hieftje, G. M., J. H. Barnes, et al. (2001). "Evolution and revolution in instrumentation for plasma-source mass spectrometry." Pure and Applied Chemistry 73(10): 1579-1588.

Plasma-source mass spectrometry, usually as inductively coupled plasma mass spectrometry (ICP-MS), has matured into a widely accepted method for ultra-trace multielemental anal. However, the method exhibits shortcomings. For example, it does not provide adequate precision for isotope ratio measurements if many isotopes are to be detd. Also, isobaric overlaps (spectral interferences) can be very troublesome in some situations. Similarly, matrix interferences can adversely affect many detns. Yet, it is in the area of high-speed transient measurements that ICP-MS perhaps suffers its greatest weakness. When sampling devices such as flow injection, laser ablation, electrothermal vaporization, or chromatog. are employed, the user must choose between broad elemental or isotopic coverage and signal-to-noise ratio (SIN). In turn, compromised S/N means lower precision or poorer detection limits. Here, new instrumentation aimed at overcoming these limitations will be described. One system, based on a time-of-flight mass spectrometer, provides excellent detection limits, resolving power better than com. quadrupole mass filters, precision of at least 0.02% relative std. deviation in a ratioing mode, and extraordinarily high speed for use with transient sampling devices. The 2nd instrument is based on a sector-field mass spectrometer but, unlike other such units, is equipped with a focal-plane array detector. So equipped, the system can detect a broad mass range at once.

APP* 273) Mesquita da Silva, M. A., V. L. A. Frescura, et al. (2001). "Determination of noble metals in biological samples by electrothermal vaporization inductively coupled plasma mass spectrometry, following cloud point extraction." Spectrochimica Acta, Part B: Atomic Spectroscopy 56B(10): 1941-1949.

A simple sepn. procedure for noble metals based on cloud point extn. is proposed. The analyte ions in aq. acidic soln., obtained by the acid digestion of the samples, were complexed with O,O-diethyldithiophosphate and Triton X-114 was added as a nonionic surfactant. By increasing the temp. up to the cloud point, a phase sepn. occurs, resulting in an aq. phase and a surfactant-rich phase contg. most of the analytes that were complexed. The metals in the surfactant-rich phase were detd. by electrothermal vaporization inductively coupled plasma mass spectrometry. The extn. conditions as well as the instrumental parameters were optimized. Enrichment factors ranging from 7 (Rh) to 60 (Pt) and limits of detection from 0.6 (Pt) to 3.0 ng L-1 (Rh) were obtained in the digested samples. The extn. was not efficient for Ir. Among the ref. materials analyzed only one (SRM 2670, urine) presented recommended values for Au and Pt. Due to the nonavailability of adequate CRMs, accuracy was assessed by spiking known analyte amts. to the acid digests. Recoveries close to 100% were obsd. for all the studied elements but Ru. Poor agreement between found and recommended values was obsd. for nondigested urine sample, probably due to the carrier effect of coextd. residual matrix components. However, good agreement was reached after urine acid mineralization.

REV* 274) Balaram, V. (2001). "ICP-MS: a powerful tool for geochemical and mineral exploration studies." Indian Mineralogist 35(1): 34-55.

A review, with many refs. Inductively coupled plasma mass spectrometry (ICP-MS) was applied with increasing frequency in the geochem. and mineral exploration studies. During the last 17 yr since its com. introduction, this technique has dramatically simplified the anal. of different geol. materials such as, rocks, ores, minerals, soils, sediments and water for trace elements, rare earth elements (REE), platinum group elements (PGE), gold and refractory elements such as Hf, Nb, Ta, and W at their natural abundance levels. The high sensitivity, multi-element capability and the ability to det. isotopic ratios have led to the extensive use of ICP-MS in geochem. and mineral exploration studies. Currently, ICP-MS has the capability to routinely analyze 30-60 elements at and below ng/g levels with extremely high precision and accuracy (<5% RSD for most elements). ICP-MS was also proved to be a good choice for isotopic ratio anal. of B, Os, Re, Pb, and U. Though ICP-MS is primarily designed for the anal. of aq. samples, its range of applications can be widely extended using simple hyphenation to other sample introduction systems such as, laser ablation, electrothermal vaporization, flow-injection, and different chromatog. methods. Laser ablation as a method of sample introduction system for ICP-MS can produce spatial information on element and isotopic distributions in direct solid materials. The recent advances made in ICP-MS anal. technique are discussed in this paper besides describing an integrated approach for the quality assurance during the anal. measurements.

APP* 275) Caroli, S., O. Senofonte, et al. (2001). "Production of a new certified reference material for trace elements in Antarctic krill." Journal of Analytical Atomic Spectrometry 16(10): 1142-1146.

Under the coordination of the Istituto Superiore di Sanita (ISS), Rome, Italy, and of the Institute for Ref. Materials and Measurements of the Joint Research Center, European Commission (EC-JRC-IRMM), Geel, Belgium, a new certified ref. material (CRM) for trace elements based on Antarctic krill was produced. The instrumental techniques resorted to in the certification project included flame, hydride generation, cold vapor and electrothermal atomization at. absorption spectrometry (with and without Zeeman background correction), inductively coupled plasma at. emission spectrometry, quadrupole and magnetic sector high resoln. inductively coupled plasma mass spectrometry and neutron activation anal. The certified values established for selected trace elements are as follows (in mg g-1 +- the 95% confidence interval): As, 5.02+-0.40; Cd, 0.73+-0.06; Co, 0.110+-0.010; Cu, 65.2+-2.3; Fe, 56.6+-2.3; Mn, 4.12+-0.10; Ni, 1.28+-0.12; Pb, 1.11+-0.09; Se, 7.37+-1.13; and Zn, 66.0+-2.0. Each value was obtained by combining data of several labs. provided that four or more independent methods of anal. were used. For several other elements (Ag, Al, Br, Ca, Cl, Cr, Hg, I, K, Mg, Na, Rb, Sc, Sn, Sr and V) informative concns. were given whenever the above criteria could not be respected.

APP* 276) Hayashi, H., Y. Hara, et al. (2001). "Determination of trace iron by electrothermal vaporization/low-pressure helium ICP-MS." Bunseki Kagaku 50(9): 631-634.

Although ICP-MS offers a powerful multielement anal. method, the Ar gas severely interferes with the detn. of Fe because of the formation of large background spectra. A combined method of electrothermal vaporization (ETV) and low-pressure He-ICP-MS was therefore employed to overcome this problem. Mass spectral interferences, however, still occurred at m/z of 54 and 56, which were assigned to 40Ar'4N+ and 40Ar16O+, resp. The polyat. interferences were caused by leaks of the ambient air through the glass ETV chamber. The chamber was newly designed and constructed from Al with specially prepd. vacuum parts. A 5 mL vol. of the sample was placed. on a W filament and heated at 2.6 A for 100 s to remove the solvent. After evacuating the chamber to 5 torr, the filament was heated to 2500 Deg by the discharge of a high-capacity condenser (0.27 F) for evapg. the sample. The resulting plume was transported to the plasma torch with a stream of carrier gas for the detn. of the most abundant isotope, 56Fe+. The relative std. deviation for the signal intensity (50 pg of Fe, n = 9) was .apprx.13%. The detection limit based on 3s was 0.8 ng ml-1, which was 25-times lower compared with the conventional Ar ICP-MS.

FUN* 277) Venable, J. D., M. Detwiler, et al. (2001). "Multiplexed electrothermal vaporization sample introduction system for inductively coupled plasma spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 56B(9): 1697-1706.

A multiplexed electrothermal vaporization (ETV) system for sample introduction into an inductively coupled plasma was designed in an effort to increase sample turn-around time. W filaments (300 W), originally designed for overhead projectors, were chosen for use as ETVs to avoid the high power requirements assocd. with other ETV devices, e.g. graphite furnaces (2-3 kW). In short, the authors have multiplexed the thermal stages were multiplexed such that a vaporization event can take place every 20 s. This represents a significant increase in the throughput typically assocd. with ETV-ICPMS, which is normally .apprx.20-30 samples/h. Evaluated with respect to common figure of merit criteria, the performance of the multiplexed ETV system is similar to that seen with conventional graphite furnace ETV systems. However, several mass spectral interferences can be introduced by the presence of W into the plasma, which hinder the anal. of certain metals (Hg, Mo, etc.). Thus, other low power vaporizers (e.g. Re, Ta) should be considered for use in future systems.

APP* 278) Miller-Ihli, N. J. and S. A. Baker (2001). "Microhomogeneity assessments using ultrasonic slurry sampling coupled with electrothermal vaporization isotope dilution inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 56B(9): 1673-1686.

Ultrasonic slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry (USS-ETV-ICP-MS) is a very powerful technique for the direct anal. of solid materials prepd. as slurries. The use of isotope diln. USS-ETV-ICP-MS (USS-ETV-ID-ICP-MS) for micro-homogeneity characterization studies of powd. ref. materials based on elemental analyses, was studied. Slurry anal. conditions were optimized taking into consideration d., particle size, analyte extn., slurry mixing, analyte transport and sampling depth. Slurries were prepd. using 1-20 mg of material and adding 1.0 mL of 5% nitric acid diluent contg. 0.005% Triton X-100. Three ref. materials were analyzed (RM 8431a Mixed Diet, SRM 1548a Typical Diet and SRM 2709 San Joaquin Soil). Cu and Ni were detd. in each material and Fe was also detd. in RM 8431a Mixed Diet. ETV conditions were optimized and the benefit of using Pd as a carrier to enhance transport, combined with oxygen ashing was demonstrated. The accuracy of the method was verified by comparing anal. results with certified values. The precision of the method was demonstrated by comparing relative std. deviation's for slurry samples and aq. stds. and elemental homogeneity was quantified based on the slurry sampling variability. The representative sample mass analyzed was calcd. taking into consideration extn. of analyte into the liq. phase of the slurry. Representative sample masses of .apprx.4 mg of RM 8431a provided slurry sampling variabilities of 10% or less for Cu, Fe and Ni. Representative sample masses of .apprx.10 mg of SRM 1548a provided slurry sampling variabilities of .apprx.10% for Cu and Ni. Representative sample masses of .apprx.0.3 mg of SRM 2709 resulted in total anal. variabilities of <7%, highlighting the fact that the San Joaquin Soil is clearly the most homogeneous of the materials characterized.

FUN* 279) Resano, M., M. Verstraete, et al. (2001). "Evaluation of the multi-element capabilities of electrothermal vaporization quadrupole-based ICP mass spectrometry." Journal of Analytical Atomic Spectrometry 16(9): 1018-1027.

Electrothermal vaporization (ETV) ICP mass spectrometry is a method that combines the ability of the graphite furnace to handle complex samples with the detection power of ICP-MS. It is somewhat surprising, however, that most works reporting on the application of this method have only described the simultaneous (from the same tube firing) detn. of 1-3 elements. Different authors have attributed this fact to the limited capability of the quadrupole filter (the most commonly used mass spectrometer in ICP-MS instrumentation) to deal with the transient signals that electrothermal vaporization produces. Nevertheless, recent works suggest that the real multi-element capabilities of ETV quadrupole-based ICP-MS might have been largely underestimated. A systematic study of the no. of mass-to-charge ratios that can be simultaneously monitored in ETV quadrupole-based ICP-MS without degrading the precision, the sensitivity and the limits of detection was carried out. Three elements with different furnace behaviors (Cd, Co and Ti) were chosen for the study. The effect of the dwell time and the way of processing the anal. data were also evaluated. The results indicate that, when using ETV-ICP-MS with a quadrupole-based instrument, no detrimental effects on the precision, detection limits and sensitivity occur as long as a crit. value of three or four points to define the signal profile is achieved. This requirement corresponds to the possibility of monitoring >20 elements for a std. peak width of 1.5-2 s. Several options for further improvements are also discussed, including the possibility of sepg. (with respect to time) the vaporization of elements with different furnace behaviors.

APP* 280) Mestek, O., I. Tresl, et al. (2001). "Custom-made interface between electrothermal vaporizer and inductively coupled plasma-mass spectrometer: determination of nickel by isotope dilution in plant samples." Talanta 55(3): 595-603.

ICP-mass spectrometer Perkin Elmer Elan 6000 was adapted for ETV anal. by coupling with GBC GF 3000 graphite furnace atomizer. Both instruments were connected by a 25 cm long PTFE tubing of 6 mm i.d. and a custom-made interface. The app. was applied to nickel detn. using isotope diln. technique. The efficiency of analyte transfer through the interface was approx. 20%, however the incomplete transfer did not influence the blank values. Measured isotope ratio was very stable, whereas the magnitude of ion signal showed a little shift. CRM samples were analyzed after microwave decompn. and by slurry technique as well. Obtained results were compared with those of pneumatic sample nebulization after nickel sepn. on Chelex column. All tested techniques gave accurate results with comparable precision. However, the slurry technique allowed significant decreasing of the blank values and the limit of detection. The duration of anal. run can also be substantially shortened from several hours to a few minutes.

FUN* 281) Venable, J. and J. A. Holcombe (2001). "Peak broadening from an electrothermal vaporization sample introduction source into an inductively coupled plasma." Spectrochimica Acta, Part B: Atomic Spectroscopy 56B(8): 1431-1440.

Signal broadening using electrothermal vaporization with inductively coupled mass spectrometry (ETV-ICPMS) occurs at a rate much faster than would be predicted by simple longitudinal diffusion. A Monte Carlo simulation that focused on particle motion within the transport tubing was created to elucidate the causes of this dispersion within ETV-ICPMS. Several parameters, including the diffusion coeff., tube diam., transport tube length, and flow rate were varied to discern their role in signal broadening. Using typical instrumental parameters, the parabolic flow profile generated by laminar flow of the carrier gas is the primary cause of dispersion. Manipulating the aforementioned variables to lessen the effects of laminar flow decreased dispersion. Conversely, increasing the role of laminar flow promoted broadening. The broadening processes should be applicable to any transient introduction system where material must be transported to a detection system. Due to the difference in the rate of broadening expected for particles of different sizes, the simulation was used to calc. the av. size of particles generated in the ETV using different mass amts. of sample. No change in particle size (.apprx.1 nm) was seen for mass amts. ranging from 10-10,000 pg, which suggests that the particle no. is increased with increasing sample mass rather than the av. particle size. Using this method of detg. particle size, it might be possible to further evaluate the mechanisms of phys. 'carrier' action.

REV* 282) Infante, H. G., M. Heisterkamp, et al. (2001). "ICP-TOF-MS for rapid simultaneous multi-element analysis in fast transient signals." Spectra Analyse 30(220): 23-31.

A review, with refs., is given. The introduction of new Inductively Coupled Plasma Mass Spectrometry (ICP-MS) detectors with a time-of-flight mass analyzer MS (TOF) was recently proposed as an attractive alternative to the sequential systems for trace and ultra trace multi-element anal., esp. for the measurement of transient signals. The high spectral generation rate of the ICP-TOF-MS system (generating complete mass spectra at rates of 20,000 times every 2nd) along with the high precision achieved for ratioing techniques make ICP-TOFMS adequate to measure most transient signals (e.g. those commonly encountered in flow injection (FI), electrothermal vaporization (ETV), laser ablation and chromatog.) without a loss in fidelity or the introduction of spectral skew. Results obtained by axial ICP-TOFMS are presented for ultra-trace speciation anal. of organometallic compds. using ICP-TOFMS coupled to gas chromatog. (GC) or to HPLC as well as for the detn. of sub-parts-per-trillion of rare earth elements (REE) in natural waters after flow injection online sorption preconcn. in a knotted reactor (KR).

REV* 283) Resano, M., M. Verstraete, et al. (2001). "Direct determination of sulfur in Bisphenol A at ultratrace levels by means of solid sampling-electrothermal vaporization-ICP-MS." Journal of Analytical Atomic Spectrometry 16(8): 793-800.

It is known that the accurate detn. of ppm levels of sulfur in solid samples is very complicated. One of the approaches that have been evaluated in order to improve the detection limits for this element is the use of electrothermal vaporization (ETV) as an alternative means of sample introduction in ICP mass spectrometry. In this way, it is possible to achieve a significant decrease of the oxygen-based interferences. In this work, the possibilities of electrothermal vaporization ICP-MS for sulfur detn. are extended one step further, as the direct detn. of the analyte in two Bisphenol samples (about 0.3 and 2 mg g-1) is carried out. Bisphenol A is a precursor in the prodn. of polycarbonate and epoxy resins, in which sulfur is present as an impurity. 34S was the isotope selected for the detn. Palladium (0.5 mg) was found to be the best chem. modifier and is capable of both preventing analyte losses (up to a pyrolysis temp. of 400 DegC) and improving the sensitivity. Some evidence as to the way in which it may act is also presented. Nitric acid was added as well in order to favor an efficient matrix removal prior to the release of the analyte. The resulting solid sampling-electrothermal vaporization-ICP-MS method combines very interesting features for this particular element: a high sample throughput (20-25 min per sample), a low limit of detection (4 ng g-1) and a reduced risk of analyte losses and/or contamination. Moreover, it presents some advantages over the dedicated sulfur analyzers that are very popular in the industry: low sample consumption (a few milligrams), multi-element possibilities and the ability to use aq. std. solns. for calibration. On the other hand, the overall method cannot be considered as very economic, but, for many labs. that already own an ICP-MS instrument, the acquisition of an ETV device would be relatively inexpensive.

FUN* 284) Friese, K.-C., U. Watjen, et al. (2001). "Analyte transport efficiencies in electrothermal vaporization for inductively coupled plasma mass spectrometry." Fresenius' Journal of Analytical Chemistry 370(7): 843-849.

A modified graphite furnace for solid-sampling at. absorption spectrometry as an electrothermal vaporizer (ETV) was coupled to a Perkin-Elmer/Sciex ELAN 6000 ICP mass spectrometer. The integrals obtained from electrothermal vaporization of aliquots contg. As, Cd, Cu, Co, Fe, Mn, Pb, Se, and Zn were compared with those obtained from pneumatic nebulization of the same aq. std. soln. The pneumatic nebulizer was calibrated by weighing the mass of aq. aerosol trapped on a filter. With wet plasma conditions maintained also for measurements with the ETV and ref. signals for analyte signals obtained with the calibrated pneumatic nebulization, the transport efficiency of the ETV system, e.g. the ratio of the analyte amt. introduced into the plasma to that amt. dosed into the vaporizer, was detd. The transport efficiency of two different tube and interface designs was evaluated. Investigations with and without the use of trifluoromethane as reactive gas, with different furnace heating rates, and with varying gas flows were performed. In general, the tube equipped with a nozzle led to generally higher transport efficiency than the std. tube. Without trifluoromethane transport efficiencies ranged from 10% to 35% with the std. tube and from 15% to 50% with the nozzle-type tube. With addn. of 2 mL min-1 trifluoromethane to the argon flow of 400 mL min-1 through the tube, transport efficiencies from 20% to 70% and from 70% to 100% were achieved with the std. and nozzle-type tubes, resp.

APP* 285) Maia, S. M., M. G. R. Vale, et al. (2001). "Feasibility of isotope dilution calibration for the determination of thallium in sediment using slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 56B(7): 1263-1275.

Isotope diln. (ID) calibration was studied to establish accurate values for Tl in a variety of sediment ref. materials using slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) as the anal. tool. The pyrolysis curve, as well as the anal. of SRM 2704 Buffalo River Sediment, suggested that pyrolysis at 700 Deg could be used for this detn. The anal. results for a no. of river sediment ref. materials confirmed this finding; however, the results for marine sediments were far too high, indicating a serious problem with these samples. A careful study revealed the following interference mechanism as the most likely one. The chloride content of marine sediments is some 2 orders of magnitude higher than that of river sediments, and the chloride leaches out very easily into the aq. phase of the slurry. The Tl that is in soln. forms TlCl upon drying, which is easily volatilized and lost at pyrolysis temps. >400 Deg. As the enriched isotope spike was added in soln., and the original Tl is retained, at least in part, in the sediment particles, the spiked Tl is preferentially lost, leading to the excessively high anal. results. Accurate results for Tl in marine and river sediments could be obtained using pyrolysis temps. of 400 and ?700 Deg, resp. The detection limit calcd. from 3*SD (n=5) of the sediment with the lowest Tl content (HISS-1) was 0.003 mg/g. The precision at the 0.5-1.0-mg/g Tl level based on 5 consecutive readings was 1.3-4.0% RSD.

APP* 286) Song, M., T. U. Probst, et al. (2001). "Rapid and sensitive determination of radiocesium (Cs-135, Cs-137) in the presence of excess barium by electrothermal vaporization-inductively coupled plasma-mass spectrometry (ETV-ICP-MS) with potassium thiocyanate as modifier." Fresenius' Journal of Analytical Chemistry 370(6): 744-751.

An electrothermal vaporization-inductively coupled plasma-mass spectrometric (ETV-ICP-MS) method based on selective volatilization of cesium with KSCN as modifier was developed for detn. of radiocesium, i.e. 135Cs and 137Cs, in the presence of isobaric barium. A 10000 times excess of barium, which was volatilized at a temp. of 1100 Deg, resulted only in a 1% signal increase in the signal of mass 135 amu. The recommended concn. of KSCN is 0.3 mM, and pretreatment and volatilization temps. are 400 Deg and 1100 Deg, resp. A ramp time of 1 s is recommended for the volatilization step. The achieved limit of detection for 135Cs is 0.2 pg/mL (10 mBq/mL) and 4 fg (0.2 mBq) abs. for a sample vol. of 20 mL. This means a limit of detection for 137Cs of 0.2 pg/mL (0.6 Bq/mL) and of 4 fg (0.01 Bq) abs. Signal variations of 135Cs and 137Cs, resp., in spiked samples with various matrixes were studied.

APP* 287) Friese, K. C., K. H. Grobecker, et al. (2001). "Development of an electrothermal vaporization ICP-MS method and assessment of its applicability to studies of the homogeneity of reference materials." Fresenius' Journal of Analytical Chemistry 370(5): 499-507.

A method has been developed for measurement of the homogeneity of analyte distribution in powd. materials by use of electrothermal vaporization with inductively coupled plasma mass spectrometric (ETV-ICP-MS) detection. The method enabled the simultaneous detn. of As, Cd, Cu, Fe, Mn, Pb, and Zn in milligram amts. of samples of biol. origin. The optimized conditions comprised a high plasma power of 1500 W, reduced aerosol transport flow, and heating ramps below 300 Deg s-1. A temp. ramp to 550 Deg ensured effective pyrolysis of approx. 70% of the org. compds. without losses of analyte. An addnl. hold stage at 700 Deg led to sepn. of most of the analyte signals from the evapn. of carbonaceous matrix compds. The effect of time resoln. of signal acquisition on the precision of the ETV measurements was investigated. An increase in the no. of masses monitored up to 20 is possible with not more than 1% addnl. relative std. deviation of results caused by limited temporal resoln. of the transient signals. Recording of signals from the nebulization of aq. stds. in each sample run enabled correction for drift of the sensitivity of the ETV-ICP-MS instrument. The applicability of the developed method to homogeneity studies was assessed by use of four certified ref. materials. According to the best repeatability obsd. in these sample runs, the max. contribution of the method to the std. deviation is approx. 5% to 6% for all the elements investigated.

APP* 288) Pozebon, D., V. L. Dressler, et al. (2001). "Comparison of the performance of FI-ICP-MS and FI-ETV-ICP-MS systems for the determination of trace elements in sea water." Analytica Chimica Acta 438(1-2): 215-225.

The performance of two flow injection systems (FI) for on line sepn. and pre-concn. of Cu, Cd, Pb, Bi, Au, Ag, As(III) and Se(IV) in sea water and detn. by inductively coupled plasma mass spectrometry are compared. One system is coupled to the nebulizer of the spectrometer while the other one is coupled to an electrothermal vaporizer also coupled to the same spectrometer. The matrix sepn. and analyte pre-concn. are accomplished by retention of the analytes complexed with the ammonium salt of O,O-di-Et dithiophosphate on C18 immobilized on silica in a column coupled directly to the pneumatic nebulizer or to the auto-sampler arm of an electrothermal vaporizer. The eluate is on line dild. with water and introduced directly to the pneumatic nebulizer or vaporized after being automatically injected into the graphite tube, prior to the vaporization of the analytes. The conditions for the complexation-sepn. and elution were optimized. The accuracy was checked by the anal. of two certified sea waters, CASS-3 and NASS-4, from the National Research Council of Canada. Only As(III) could not be detd. in the sea water medium. The recoveries for the non-certified elements were in the range 90-110%. The relative std. deviation are <10% while the sampling frequencies are in the range 21-22 h-1, for both systems.

APP* 289) Tanaka, T., K. Furuhashi, et al. (2001). "Determination of ultratrace arsenic and selenium by electrothermal vaporization and ICP-MS." Bunseki Kagaku 50(6): 427-431.

A detachable sample-injector with a coiled tungsten filament (0.2 mm in diam. x 45 mm) was constructed for the effective introduction of tiny amts. of sample into ICP-MS. A 5 ml vol. of the sample was placed on a filament and an injector was inserted into a plasma torch. After desolvating the sample for 30 s with an elec. current of 2.6 A, and the filament was rapidly heated to ca. 2500 DegC by discharging a high-capacity condenser (0.54 F). The resulting vapor was transferred to the plasma with a stream of argon for the detn. of As and Se. The intensities of the anal. signals increased by almost 100 times as compared with the values in a previous study, where a looped tungsten filament was elec. heated outside the plasma torch. The abs. detection limits were 0.5 pg for As and 1.1 pg for Se with relative std. deviations of 10-14%. The filament was used at least 100 times without any distortion of the signal profiles. The proposed method was applied to the detn. of As and Se in certified ref. human hair. The anal. results were 0.29+-0.03 mg g-1 for As and 1.8 - 0.2 mg g-1 for Se, which are in good agreement with the certified values.

APP* 290) Huang, S.-J. and S.-J. Jiang (2001). "Determination of Zn, Cd, and Pb in vegetable oil by electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 16(6): 664-668.

The detn. of Zn, Cd and Pb in vegetable oil by electrothermal vaporization in combination with inductively coupled plasma mass spectrometry (ETV-ICP-MS) was investigated. An oil emulsion contg. 10% vol./vol. vegetable oil, 2% vol./vol. Triton X-100, 2% vol./vol. H2O2 and 0.4% vol./vol. HNO3 was prepd. This soln. was then injected into the ETV-ICP-MS system for the detn. of Zn, Cd, and Pb. A mixed modifier of Pd, HNO3, and H2O2 was used to improve the sensitivities and peak shapes of the elements studied. Since the sensitivities of the elements studied in vegetable oil emulsion and that of aq. soln. were quite different, the std. addn. method and isotope diln. method were used for the detn. of Zn, Cd, and Pb in selected vegetable oil samples. The influences of instrument operating conditions, modifier selection, emulsion prepn. and interferences on the ion signals were reported. This method was applied to the detn. of Zn, Cd, and Pb in sweet corn plumule and canola oil purchased from a local market. The anal. results of various vegetable oil samples detd. by the method of std. addns. and isotope diln. agreed satisfactorily. Precision between sample replicates was better than 10% with the ETV-ICP-MS method. Under the optimum operating conditions, the detection limit obtained from the std. addn. curve was 2.0, 0.1, and 0.2 ng mL-1 for Zn, Cd and Pb, resp., in prepd. emulsified solns., which corresponded to 20, 1, and 2 ng mL-1 for Zn, Cd, and Pb, resp., in the original oil samples.

APP* 291) Okamoto, Y. (2001). "Determination of fluorine in aqueous samples by electrothermal vaporisation inductively coupled plasma mass spectrometry (ETV-ICP-MS)." Journal of Analytical Atomic Spectrometry 16(6): 539-541.

By monitoring at. fluorine at mass 19, fluoride ions in aq. samples were detd. by using an inductively coupled plasma (ICP) quadrupole mass spectrometer. In order to prevent the decrease in the ionization efficiency of fluorine atom caused by introduction of water mist, electrothermal vaporization was used for sample introduction into the ICP. To prevent the loss of fluorine during the drying process, a small amt. of tetramethylammonium hydroxide soln. was placed as a chem. modifier into a tungsten boat furnace. After the evapn. of the solvent, the analyte instantly vaporized and was then introduced into the ICP ion source to detect the 19F+ ion signal. By applying an extreme distance from the ion source to the inlet orifice of the sampling cone, the mol. 18OH+ ion which would interfere in the detection of the 19F+ ion was completely degraded. By using this system, the detection limit (3s) of 0.29 mg of the aq. fluoride ion was achieved. The calibration curve was linear in the tested range of up to 100 mg of the fluoride ion. The relative std. deviation for ten replicate measurements was 3.6% for 5.0 mg of the fluoride ion.

APP* 292) Okamoto, Y., T. Fujiwara, et al. (2001). "Determination of bismuth in nonferrous alloys by inductively coupled plasma mass spectrometry combined with use of solid-phase methylation and electrothermal vaporization technique." Applied Spectroscopy 55(4): 514-516.

This note will discuss in detail, together with the application to the detn. of Bi in nonferrous metals, a more complex matrix. The most remarkable feature of the method is that Bi, the analyte, reacts with the methyllithium to form a volatile alkylmetal compd., while matrix metal ions such as Pb(II), Sn(II), Fe(III), etc., are retained in the vaporizer as the hydroxides due to the strong basicity of the reagent. Thus, interference-free detn. could be achieved. Also, this method offers several advantages over conventional nebulization, e.g., high sample conversion efficiency, small sample consumption, and matrix sepn.

APP* 293) Hayashi, H., T. Tanaka, et al. (2001). "Electrothermal vaporization on a tungsten filament for the determination of arsenic in chloride solutions by low-pressure helium ICP-MS." Analytical Sciences 17(1): 171-173.

A combined method of electrothermal vaporization and low-pressure He ICP-MS was developed for the detn. of traces of As in Cl- solns., because serious spectral interference occurred in conventional Ar ICP-MS. On a W filament was placed 5 ml of a sample and heated electrothermally to remove the solvent. The resulting residue on the filament was covered with a vaporization chamber, and after reducing the pressure to ca. 5 Torr, it was rapidly heated by discharging a high-capacity condenser (0.22 F). The vapor of As was transferred to a He plasma with a stream of carrier gas for the detn. The background was not obsd. at m/z of 75, which allowed the detn. of As at ng/mL levels in Cl- solns. NaCl significantly enhanced the intensity of the As signal, whereas other chlorides, including KCl, MgCl2, CaCl2, and NH4Cl, suppressed the anal. signals. This enhancement due to Na+ seems to be a peculiar phenomenon to the He ICP. The proposed method can be applied to direct detns. of as low as 0.9 ng/mL of As in seawater.

APP* 294) Yu, L. L., W. R. Kelly, et al. (2001). "Determination of sulfur in fossil fuels by isotope dilution electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 16(2): 140-145.

The detn. of S by soln. nebulization quadrupole inductively coupled plasma mass spectrometry (ICP-MS) is difficult because of interferences from oxygen dimer ions. The large 16O2+ ion current from the solvent water is a serious interference at 32S, the most abundant of the four isotopes, and precludes its measurement. The isotopic compn. of S varies in nature as a consequence of natural mass fractionation; therefore, high accuracy isotope diln. mass spectrometric (IDMS) detn. of sulfur requires that the ratio of 32S/34S be measured, for the two isotopes represent over 99% of natural sulfur. In this work, electrothermal vaporization was used to generate a water-free aerosol of the sample. Non-solvent sources of oxygen were investigated and the spectral background minimized. Further redn. of the oxygen dimer was achieved by using nitrogen as an oxygen-scavenger in the argon plasma. The isotope ratio of 32S/34S was used for the detn. of S by IDMS. The repeatability of the 32S/34S ratio in terms of the relative std. error (95% confidence level) of 6 replicate measurements of the spiked and the unspiked samples was about 0.3% and 0.7%, resp. The detection limit of the method was 4 ng g-1. Sulfur in two fossil fuel ref. materials was measured and the results were in good agreement (within 0.3%) with those obtained by the more precise thermal ionization mass spectrometry (TIMS) method.

APP* 295) Lu, H. H. and S. J. Jiang (2001). "Organic acids as the modifier to determine Zn, Cd, Tl and Pb in soil by slurry sampling electrothermal vaporization inductively-coupled plasma mass spectrometry." Analytica Chimica Acta 429(2): 247-255.

Ultrasonic slurry sampling electrothermal vaporization inductively-coupled plasma mass spectrometry (USS-ETV-ICP-MS) has been applied to the detn. of Zn, Cd, Tl and Pb in several soil samples. A mixt. of 1% m/v EDTA and 1.5% m/v of ascorbic acid was used as the modifier to enhance the ion signals. The influences of instrument operating conditions and slurry prepn. on the ion signals were reported. A relatively low vaporization temp. was used which sepd. the analyte from the major matrix components and improved the ion signals significantly. With ETV sample introduction device, spectroscopic and nonspectroscopic interferences were alleviated significantly. Since the sensitivities of Zn, Cd, Tl and Pb in various soil slurries and aq. soln. were different, std. addn. method and isotope diln. method were used for the detn. of Zn, Cd, Tl and Pb in these soil samples. This method has been applied to the detn. of Zn, Cd, Tl and Pb in NIST SRM 2711 Montana soil ref. material and several soil samples collected from Kaohsiung area. The anal. results were agreed with the certified values. The precision between sample replicates was better than 9% with USS-ETV-ICP-MS method. Detection limits estd. from std. addn. curves were about 260-620, 3-5, 0.3-1 and 9-20 ng g-1 for Zn, Cd, Tl and Pb, resp., in different samples.

APP* 296) Okamoto, Y., R. Kikkawa, et al. (2001). "External furnace-fusion digestion for the direct determination of lead in rock samples by inductively coupled plasma mass spectrometry (ICP-MS) using the tungsten boat furnace - sample cuvette technique." Journal of Analytical Atomic Spectrometry 16(1): 96-98.

A newly conceived electrothermal vaporization system using a W boat furnace (TBF)-sample cuvette technique was applied for the direct anal. of rock samples with detection by inductively coupled plasma mass spectrometry (ICP-MS). Into this sample cuvette made of W, the powd. rock sample and an aliquot of ammonium fluoride soln. were placed and the cuvette was heated on a hot-plate for digestion. After the decompn. had been completed, the cuvette was positioned on the TBF. The analyte in the cuvette was vaporized and introduced into the ICP mass spectrometer. Since the solid samples could be decompd. to ash completely in the cuvette and the majority of siliceous components were expelled prior to measurement, the sensitivity was the same as that of aq. stds. The most remarkable feature is that the small sample cuvette was used as a weighing dish, sample carrier, decompn. vessel and electrothermal vaporizer. Thus, the technique overcomes problems such as weighing small amts. of powd. samples, decompn. of solid materials, introduction of the samples into the TBF device and the easy removal of the residue. The method was successfully applied to the direct detn. of lead in several std. rock samples.

REV* 297) Patriarca, M., B. Rossi, et al. (2002). "Use of atomic spectrometry (ICP-MS) in the clinical laboratory." Advances in Atomic Spectroscopy 7: 1-51.

A review. Since its introduction as an anal. technique, at. spectrometry has found wide application in the clin. lab. More than 25 elements are important to human life, most of which present at trace or ultratrace levels. Several trace elements are routinely detd. in body fluids and tissues for the diagnosis and monitoring of genetic diseases, nutritional deficiencies and occupational or environmental exposure. The choice of the method to apply for the detn. of a specific trace element in a human sample requires a clear understanding of the clin. question and the relative performances and limitations of the available techniques. Inductively coupled plasma mass spectrometry (ICP-MS), the latest development of at. spectrometry, has the capabilities for the fast and simultaneous detn. of trace and ultratrace elements, with detection limits in most cases superior to graphite furnace at. absorption spectrometry. High resoln. ICP-MS can be used for the detn. of most elements in body fluids and tissues, requiring only minimal sample pretreatment. Some of the interferences limiting the application of quadrupole ICP-MS to biol. important elements have been overcome using alternative methods of sample introduction, such as electrothermal vaporization and hydride generation, online chromatog. sepn. of interfering species and modified plasma conditions (cool plasma). New instrumental developments (collision/reaction cell technol.) have been shown to reduce substantially the extent of major argide based interferences. Beside the detn. of the total content of trace and ultratrace elements in clin. samples, the identification of their chem. species is necessary in order to evaluate their bioavailability and relative toxicity. The online coupling of ICP-MS with sepn. techniques (HPLC, capillary electrophoresis) has been applied to the speciation of essential and toxic elements, such as As, Se and I, and to pharmacokinetic studies of metallodrugs. Stable isotopes are used as tracers in human studies to provide a direct assessment of the absorption, distribution and elimination of labeled compds. In comparison with other techniques for the identification of isotope compn., ICP-MS allows faster sample throughput with minimal sample prepn. and it is therefore more suitable for studies of mineral metab. In addn., the development of ICP-MS ref. methods based on isotope diln. can give an important contribution to the improvement of the quality and traceability of anal. data for trace elements in lab. medicine.

APP* 298) Dias, L. F., T. D. Saint'Pierre, et al. (2002). "Determination of arsenic, lead, selenium and tin in sediments by slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry using Ru as permanent modifier and NaCl as a carrier." Spectrochimica Acta, Part B: Atomic Spectroscopy 57B(12): 2003-2015.

A procedure for the detn. of As, Pb, Se and Sn in sediment slurries by electrothermal vaporization inductively coupled plasma mass spectrometry is proposed. The slurry, 1 mg ml-1, was prepd. by mixing the sample ground to a particle size ?50 mm with 5% vol./vol. nitric and 1% vol./vol. hydrofluoric acids in an ultrasonic bath. The slurry was homogenized with a const. flow of Ar in the autosampler cup, just before transferring an aliquot to the graphite furnace. The tube was treated with Ru as a permanent modifier, and an optimized mass of 1 mg of NaCl was added as a phys. carrier. The pyrolysis temp. was optimized through pyrolysis curves, and a compromised temp. of 800 Deg was used; the vaporization temp. was 2300 Deg. The effect of different acid concns. in the slurry on the analyte signal intensities was also evaluated. The accuracy of the method was assured by the anal. of certified ref. sediments MESS-2, PACS-2 and HISS-1 from the National Research Council Canada, SRM 2704 and SRM 1646a from the National Institute of Stds. and Technol. and RS-4 from a round robin test, using external calibration with aq. stds. prepd. in the same medium as the slurries. The obtained concns. were in agreement with the certified values according to the Student's t-test for a confidence level of 95%. The detection limits in the samples were: 0.17 mg g-1 for As; 0.3 mg g-1 for Pb; 0.05 mg g-1 for Se and 0.28 mg g-1 for Sn. The precision found for the different sediment samples, expressed as relative std. deviation was 1-8% for As, 2-9% for Pb, 6-12% for Se and 3-8% for Sn (n = 5).

APP* 299) Saint'Pierre, T. D., L. F. Dias, et al. (2002). "Determination of Cu, Mn, Ni and Sn in gasoline by electrothermal vaporization inductively coupled plasma mass spectrometry, and emulsion sample introduction." Spectrochimica Acta, Part B: Atomic Spectroscopy 57B(12): 1991-2001.

Trace metals in fuels, except in the case of additives, are usually undesirable and normally they occur in very low concns. in gasoline, requiring sensitive techniques for their detn. Coupling of electrothermal vaporization with inductively coupled plasma mass spectrometry minimizes the problems related to the introduction of org. solvents into the plasma. Also, sample prepn. as oil-in-H2O emulsions reduces problems related to gasoline anal. A method for detn. of Cu, Mn, Ni and Sn in gasoline is proposed. Samples were prepd. by forming a 10-fold dild. emulsion with a surfactant (Triton X-100), after treatment with concd. HNO3. The sample emulsion was pre-concd. in the graphite tube by repeated pipetting and drying. External calibration was used with aq. stds. in a purified gasoline emulsion. Six samples from different gas stations were analyzed, and the analyte concns. are in the mg L-1 range or below. The limits of detection were 0.22, 0.02, 0.38 and 0.03 mg L-1 for Cu, Mn, Ni and Sn, resp. The accuracy of the method was estd. using a recovery test.

APP* 300) Wende, M. C. and J. A. C. Broekaert (2002). "Direct solid sampling electrothermal vaporization of alumina for analysis by inductively coupled plasma optical emission spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 57B(12): 1897-1904.

A procedure based on electrothermal evapn. (ETV) and inductively coupled plasma at. emission spectrometry (ICP-OES) for the detn. of trace impurities in Al2O3 powders without any sample pretreatment is presented. With the aid of matrix modifier the transport and the evapn. efficiency for refractory compds. could be increased by forming halides with a lower b.p. As calibration is still a problem in direct solid sample anal., different calibration approaches including the use of certified ref. materials from NIST and std. addn. of aq. solns. of analytes were discussed. The accuracy obtained with calibration and with the std. addn. method was demonstrated for the elements Ca, Fe, Ga, Mg, Mn, Na, Ni and V for the case of Al2O3 NIST std. ref. material (SRM 699). The ETV-ICP-OES method was used for the anal. of Al2O3 powders with impurities in the low mg/g range and the results for the elements Ca, Fe, Ga, Mg, Mn, Na, Ni and V obtained with evapn. of discrete powder amts. with ETV-ICP-OES and slurry evapn. under the use of ultrasonic homogenization during the sampling and ETV-ICP-MS were shown to be in a good agreement.

FUN* 301) Bjoern, E., D. C. Baxter, et al. (2002). "Calibration errors due to variations in peak characteristics in the measurement of transient signals by inductively coupled plasma-scanning mass spectrometry." Journal of Analytical Atomic Spectrometry 17(12): 1582-1588.

The impact of variations in peak characteristics on the fidelity of transient signal measurement by inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS) was studied. Specifically, the question as to whether the multi-element capabilities or the accuracy in detd. analyte amts. were deteriorated compared to what is reported previously when not considering peak variations was addressed. The peak characteristics considered were the time of the signal max. (tpeak), the std. deviation of the assumed Gaussian input function generated by the sample introduction system (sG), and the time const. for signal decay (t). Studies of simulated exponentially-modified Gaussian peaks revealed that, for variations of peak characteristics within reasonable ranges, measurement noise and variations in tpeak, sG and t all contributed to calibration uncertainty. Electrothermal vaporization (ETV) and flow injection (FI) systems were used to exptl. generate transient signals of varying peak characteristics. Removing data points from the raw signals simulated the monitoring of up to 100 mass-to-charge ratios, allowing calibration data and analyte amts. to be detd. from the processed signals. To obtain calibration graph slopes with relative std. deviations <1% for the ETV-ICP-QMS system, it was found necessary to acquire 7-24 data points per peak for 50-5 ms dwell times. On this basis, the max. no. of mass-to-charge ratios that could be monitored in a typical ETV-ICP-QMS anal. was 4-10 using dwell times of 50-5 ms. With the FI-ICP-QMS system, variations in the peak characteristics between calibration stds. and samples meant that, to obtain <3% error in detd. analyte amts., at least 7 or 10 points per peak were required for external and internal standardization, resp. Variations in peak characteristics contributed more than measurement noise to the error in detd. analyte amts. In recent studies it is reported that 3-4 data points per peak are sufficient to accurately monitor a transient if peak variations are not considered, which, for typical ETV signals, would allow the monitoring of 20 mass-to-charge ratios during a single measurement cycle. Thus the multi-element capability of ICP-QMS when monitoring transient signals can be severely compromised by such variations.

REV* 302) Thomas, R. (2002). "Beginner's guide to ICP-MS part XIII-sampling accessories." Spectroscopy (Duluth, MN, United States) 17(11): 26-33.

A review of the different sampling tools that are crit. in enhancing the practical capabilities of inductively coupled plasma-mass spectrometry (ICP-MS) for real world samples. These sampling tools include laser ablation, flow injection, electrothermal vaporization, desolvation systems, and chromatog. devices. The discussion focuses on the basic principles of laser ablation and flow injection and the benefits they bring to ICP-MS.

APP* 303) Tanaka, T., Y. Ando, et al. (2002). "Preconcentration of traces of cobalt, nickel, copper and lead in water by thermoresponsive polymer-mediated extraction for tungsten filament electrothermal vaporization-inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 17(11): 1556-1559.

A simple and rapid preconcn. method was developed for the detn. of trace metals (Co, Ni, Cu, Pb) in H2O samples by electrothermal vaporization (ETV) inductively coupled plasma mass spectrometry (ICP-MS). The method is based on the thermoresponsive pptn. of a water-sol. polymer, poly(N-isopropylacrylamide) [PNIPAAm], from the aq. sample soln. and the simultaneous incorporation of hydrophobic metal chelates into the ppt. To a 100 mL sample soln. (pH 3) were added 20 mg of ammonium pyrrolidinedithiocarbamate (APDC), 60 mg of PNIPAAm, and 850 mg of NaNO3. When the soln. was warmed at 50 Deg, PNIPAAm pptd. to form a gum-like aggregate (polymer phase). Hydrophobic metal-APDC chelates were quant. incorporated into the polymer phase. The polymer phase was easily taken up and dissolved with DMF to prep. 1 mL of soln. A 5 mL aliquot of the resulting soln., contg. Pd as a modifier, was placed onto a doubly coiled W filament in an ETV system. Four metals (Co, Ni, Cu, and Pb) were simultaneously detd. with ETV-ICP-MS, whereas Cd gave very small signals probably due to the volatile property of the Cd-APDC chelate. Because of the highly efficient concn. (100-fold), the detn. of these heavy metal ions at pg ml-1 to ng ml-1 levels was successfully achieved. The precision and accuracy of the proposed method were evaluated by analyzing a certified H2O sample.

APP* 304) Tanaka, M. and M. Takahashi (2002). "Depth profiling of ultra trace metal impurities in polytetrafluoroethylene wares by surface scraping and acid-vapor extraction followed by ICP-MS analysis." Analytical Sciences 18(10): 1099-1103.

This paper describes the development of the depth profiling method of ultra trace metal impurities in polytetrafluoroethylene (PTFE) wares based on contamination-free sampling followed by acid-vapor extn. and its application to evaluate the washing method for PTFE wares. A contamination-free sampling process was achieved by scraping the surface of PTFE wares with the cleft face of a silicon wafer followed by exposing the PTFE scraped to highly pure acid-vapor. The concn. of metal impurities in extractants was detd. by ICP-MS equipped with an electrothermal vaporizer (ETV-ICP-MS). The blank values of Al, Cr, Fe, Ni and Cu by the depth profiling method were 0.006, 0.004, 0.005, 0.002 and 0.003 ng, resp. By analyzing the depth profile of beakers, the distributions of ultra trace (ng g-1 level) metal impurities were clarified. An examn. of the washing methods by the depth profiling method also clarified that exposing to acid-vapor was more effective than the acid-dipping method for the elimination of metal impurities.

APP* 305) Vanhaecke, F., M. Resano, et al. (2002). "Determination of Platinum and Rhodium in Environmental Matrixes by Solid Sampling-Electrothermal Vaporization-Inductively Coupled Plasma Mass Spectrometry." Analytical Chemistry 74(23): 6040-6048.

Electrothermal vaporization from a graphite furnace was used in combination with inductively coupled plasma mass spectrometry (ICPMS) for the detn. of Pt and Rh in environmental matrixes. Solid samples of tunnel dust, grass, and atm. aerosol collected on a cellulose filter could be analyzed directly, such that sample dissoln.-which is not self-evident for the detn. of platinum group metals-could be avoided. By heating the graphite furnace according to a multistep temp. program, spectral interferences were avoided, since a dry plasma was obtained, while parent ions such as Cu, Zn, and Pb, giving origin to interfering mol. ions, were vaporized during the thermal pretreatment step. For tunnel dust, the most demanding sample matrix, a mixt. of HCl and HF was used as a modifier to stimulate the vaporization of matrix components during the thermal pretreatment step and, hence, to alleviate matrix-induced analyte signal suppression during the actual vaporization step. Calibration was accomplished by single std. addn. with an aq. std. soln. The results obtained agreed within the exptl. uncertainty with the corresponding ref. values (certified values or results obtained using pneumatic nebulization ICPMS), while relative std. deviations of ?15% were typical for both Pt and Rh. In all samples, a Pt/Rh ratio of .apprx.6-8 was established. For a typical sample mass of 2 mg, limits of detection were 0.35 ng/g for Pt and 0.05 ng/g for Rh.

REV* 306) Vanhaecke, F., M. Resano, et al. (2002). "Electrothermal vaporization ICP-mass spectrometry (ETV-ICP-MS) for the determination and speciation of trace elements in solid samples - A review of real-life applications from the author's lab." Analytical and Bioanalytical Chemistry 374(2): 188-195.

A review. The use of electrothermal vaporization (ETV) from a graphite furnace as a means of sample introduction in inductively coupled plasma mass spectrometry (ICP-MS) permits the direct anal. of solid samples. A multi-step furnace temp. program was used to sep. the vaporization of the target element(s) and of the matrix components from one another. Sometimes, a chem. modifier was used to enable a higher thermal pre-treatment temp., by avoiding premature analyte losses (stabilization) or promoting the selective volatilization of matrix components. In almost all instances, accurate results can be obtained via external calibration or single std. addn. using an aq. std. soln. Abs. limits of detection are typically about 1 pg, which corresponds to 1 ng/g for a typical sample mass of 1 mg. Real-life applications carried out in the author's lab. were used to illustrate the utility of this approach. These applications aim at trace element detn. in industrial and environmental materials. The industrial materials analyzed include different types of plastics - Carilon, polyethylene, poly(ethyleneterephtalate) and polyamide - and photo- and thermog. materials. As samples from environmental origin, plant material, animal tissue and sediments were studied. Some applications aimed at a multi-element detn., while in other, the content of a single, but often challenging, element (e.g., Si or S) had to be measured. ETV-ICP-MS was also used in elemental speciation studies. Sepn. of Se-contg. proteins was accomplished using polyacrylamide gel electrophoresis (PAGE). Subsequent quantification of the Se content in the protein spots was carried out using ETV-ICP-MS. As the volatilization of methylmercury and inorg. Hg could be sepd. from one another with respect to time, no chromatog. or electrophoretic sepn. procedure was required, but ETV-ICP-MS as such sufficed for Hg speciation in fish tissue.

APP* 307) Kurogouch, H., H. Hayashi, et al. (2002). "Determination of traces of arsenic and selenium in human hair by electrothermal vaporization/ICP-MS." Bunseki Kagaku 51(9): 821-824.

ICP-MS combined with electrothermal vaporization (ETV) has excellent abs. detection limits, and hence allows the detn. of trace elements in very minute amts. of samples. ETV/ICP-MS was applied to the anal. of human hair for As and Se. A 0.50-mg wt. of a sample was decompd. with 10 mL of 14 mol L-1 HNO3 and 2 mL of 30% H2O2 in a PTFE high-pressure decompn. vessel. The resulting soln. was mixed with 25 mL of a 1 mmol L-1 KMnO4 soln. and evapd. to dryness. The residue was dissolved in 500 mL of 1 mol L-1 HNO3, and a 5-mL aliquot of the soln. was placed on a W filament. After drying the sample elec., the filament was rapidly heated to .apprx.2500 Deg by discharging a high-capacity condenser (0.54 F). The sample plume generated from the filament was transported to the plasma with a stream of Ar and the signal intensities of 75As+ and 82Se+ were measured by MS. The addn. of KMnO4 to the sample was essential for preventing serious losses (30-50%) of analytes during evapn. The accuracy of the proposed method was evaluated by analyzing a certified ref. material (As 0.31 +- 0.02 mg g-1, Se 2.0 +- 0.08 mg g-1). The results (n = 4) were in good agreement with the certified values: 0.30 +- 0.01 mg g-1 for As and 2.0 +- 0.2 mg g-1 for Se.

APP* 308) Ovari, M., G. Zaray, et al. (2002). "Solid sampling electrothermal vaporization inductively coupled plasma atomic emission spectrometric method for analysis of amphipods (Dikerogammarus villosus) samples." Microchemical Journal 73(1-2): 125-130.

A solid sampling electrothermal vaporization inductively coupled plasma at. emission spectrometric (ETV-ICP-AES) method was developed for detn. of Ag, Cd, Co, Cu, Mn, Pb and Zn in amphipods (Dikerogammarus vilosus) applied for river water monitoring. The org. part of the dried and homogenized samples was decompd. at 450 Deg in a quartz boat. Ashed sample (2 mg) was weighed into the graphite boat and the carbonates were decompd. by addn. of 40 mL 1 M nitric acid. The dried inorg. residue was introduced into the graphite furnace and vaporized at 1350 Deg applying Freon 22 gaseous halogenating agent. The calibration was carried out by dry residues of std. solns. The same amphipod sample was digested and analyzed by inductively coupled plasma mass spectrometry (ICP-MS). The anal. results show a difference between 2 and 25%.

APP* 309) Resano, M., M. Verstraete, et al. (2002). "Direct determination of trace amounts of silicon in polyamides by means of solid sampling electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 17(8): 897-903.

A method was developed for the fast and reliable detn. of silicon in polyamides (two samples with silicon contents of 10 and 50 mg g-1 were analyzed) by means of solid sampling electrothermal vaporization ICP-MS. For all silicon isotopes, the occurrence of spectral interferences was studied as a function of the vaporization temp. The benefits of the use of palladium as a chem. modifier were investigated. Finally, a vaporization temp. of 2400 DegC, monitoring of 29Si+ and the addn. of 1 mg of palladium were found to be the optimum conditions for the detn. The method finally proposed shows very interesting features for this particular element: the ability to use aq. std. solns. for calibration, a low sample consumption (a few milligrams only), a high sample throughput (20 min anal. time per sample), a low limit of detection (0.3 mg g-1) and a reduced risk of analyte losses and, particularly, of contamination. Addnl., the approach also exhibits multi-element capabilities.

APP* 310) Ho, C.-Y. and S.-J. Jiang (2002). "Determination of Cr, Zn, Cd and Pb in milk powder by slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 17(7): 688-692.

Ultrasonic slurry sampling electrothermal vaporization reaction cell inductively coupled plasma mass spectrometry (USS-ETV-RC-ICP-MS) was applied to the detn. of Cr, Zn, Cd and Pb in several milk powder samples. The influences of instrument operating conditions and slurry prepn. on the ion signals were reported. Ascorbic acid was used as the modifier to enhance the ion signals. The background ions at the chromium and zinc masses were reduced in intensity significantly by using 0.4 mL min-1 NH3 as reaction cell gas in the dynamic reaction cell (DRC) while a q value of 0.6 was used. Since the sensitivities of Cr, Zn, Cd and Pb in milk slurry and aq. soln. were quite different, the isotope diln. method was used for the detn. of Cr, Zn, Cd and Pb in these milk samples. This method was applied to the detn. of Cr, Zn, Cd and Pb in NIST SRM 1549 and NIST RM 8345 milk powder ref. material and a milk powder sample purchased from the market. The anal. results were agreed with the certified values. The method detection limits estd. from std. addn. curves were about 3, 37, 0.2 and 2 ng g-1 for Cr, Zn, Cd and Pb, resp., in the original milk powder.

APP* 311) Gelaude, I., R. Dams, et al. (2002). "Direct Determination of Methylmercury and Inorganic Mercury in Biological Materials by Solid Sampling-Electrothermal Vaporization-Inductively Coupled Plasma-Isotope Dilution-Mass Spectrometry." Analytical Chemistry 74(15): 3833-3842.

This paper reports on the use of solid sampling-electrothermal vaporization-inductively coupled plasma mass spectrometry (SS-ETV-ICPMS) for the direct and simultaneous detn. of methylmercury and inorg. mercury in biol. materials. The main advantage of this fast and sensitive method is that no sample prepn. is required. In this way, the sample throughput can be considerably increased, problems of contamination and analyte losses are kept to a min. and, even more important, the original chem. form of the different analyte species in the solid samples is preserved. To achieve this goal, a solid sample is inserted into a graphite furnace of the boat-in-tube type and is subsequently submitted to an appropriate temp. program, leading to the sep. vaporization of methylmercury and inorg. mercury, which are transported into the ICP by means of an argon carrier gas. The sepn. was accomplished within 75 s. For the quantification of the two peaks, species-unspecific isotope diln. was used. For this purpose, a stable flow of argon loaded with gaseous Hg isotopically enriched in 200Hg was generated using a permeation tube that was constructed inhouse. Its emission rate was detd. by collecting the mercury released during a given time interval on a gold-coated silica absorber, after which the amt. collected was released by heating of the absorber and detd. by cold vapor at. absorption spectrometry (CVAAS) and cold vapor at. fluorescence spectrometry (CVAFS). A ref. material from the Canadian National Research Council (NRC) (TORT-2) was used to assess the accuracy of the method. For the application of the method to samples with diverse mercury contents, the spike/sample ratio can be optimized by varying the emission rate of the permeation tube simply by adapting its temp. To prove the feasibility of this approach, two ref. materials (BCR 463 and DORM-2) with a methylmercury content more than 10 times higher than that of TORT-2 were also analyzed. The detection limits obtained for 1 mg of sample (2 ng g-1 and 6 ng g-1 for methylmercury and inorg. mercury, resp.) were found to be sufficiently low for this kind of application and are competitive when compared to other techniques.

APP* 312) Okamoto, Y., C. Konishi, et al. (2002). "Alkylating vaporization of tellurium using tungsten boat furnace-sample cuvette technique and its analytical application by inductively coupled plasma mass spectrometry (ICP-MS)." Journal of Analytical Atomic Spectrometry 17(6): 619-621.

Methyllithium was used as a chem. modifier for the electrothermal vaporization inductively coupled plasma mass spectrometric detn. of inorg. Te. Following the placing of an aliquot quantity of the aq. sample soln. into a small exchangeable cuvette and application of a drying process to expel all the H2O, the resulting residue contg. inorg. Te was reacted with the methyllithium. Elec. heating of the furnace stimulated the release of the volatile methyltellurium species, permitting the complete sepn. of the analyte from not only the matrix but also the methylating agent itself. As the result, the quant. generation and introduction of the analyte Te could be achieved. Although the volatile species was too insubstantial and too momentary to identify, it was presumed to be dimethyltellurium. The detection limit is 0.12 pg of Te, which corresponds to 1.2 pg mL-1 of the Te concn. when a sample injection vol. of 100 mL is applied. The relative std. deviation for 10 replicates of stds. each contg. 20 pg of Te(iv) is 2.0%.

APP* 313) Chery, C. C., H. Chassaigne, et al. (2002). "Detection and quantification of selenium in proteins by means of gel electrophoresis and electrothermal vaporization ICP-MS." Journal of Analytical Atomic Spectrometry 17(6): 576-580.

A method for the sepn. of selenium-contg. proteins and subsequent detection and quantification of selenium was developed. First, the proteins are fractionated by means of sodium dodecylsulfate PAGE (SDS-PAGE); subsequently, the bands of the gel, contg. the proteins, are analyzed by electrothermal vaporization (ETV)-ICP-MS to detect and quantify selenium. External standardization with the use of an internal ref. (Te) was applied. A detection limit of .apprx.40 pg Se per band and a recovery of .apprx.98% were obtained. A single measurement is accomplished in less than 4 min and thus a gel lane after a sepn. of .apprx.1.5 h, can be entirely analyzed with ETV-ICP-MS in 3.5 h. If limited to 10 bands, a gel lane is analyzed in 2 h (calibration included). The anal. is directly carried out on the stained gel, without blotting, which makes the anal. even more practical. This method was optimized using the selenoprotein glutathione peroxidase as model. Then, it was applied to the fractionation of proteins from a selenium-yeast candidate ref. material. The reconstructed Se electropherograms are presented and compared with the stained gels. The major advantages of this method are the high resoln. of the protein fractionation and the straightforward quantification of selenium.

REV* 314) Burguera, J. L. and M. Burguera (2002). "On-line flow injection-atomic spectroscopic configurations: road to practical environmental analysis." Quimica Analitica (Barcelona, Spain) 20(4): 255-273.

A review with refs. An overview is given on the development of flow injection at. spectrometry within the last four years, highlighting the main achievements and trends in the field covering the period 1985 to early 2001. Topics such as online flame at. absorption spectrometry, electrothermal at. absorption spectrometry, inductively coupled plasma optical emission spectrometry, inductively coupled plasma mass spectrometry, at. fluorescence spectrometry, atom trapping at. absorption spectrometry and chem. vapor generation processes were used to illustrate the versatility of coupling flow injection for environmental anal.

REV* 315) Jin, Q. (2002). "Some new advances in material analysis using plasma spectrometry." ISIJ International 42(Suppl.): S106-S113.

A review. Some new advances in material anal. using plasma spectrometry with an emphasis on the anal. of solids, esp. metals and alloys are reviewed. The plasma spectrometries reviewed include inductively coupled plasma (ICP)-, microwave plasma torch (MPT)-, glow discharge (GD)-, and laser-induced plasma (LIP)-at. emission spectrometry (AES)/mass spectrometry (MS). For direct anal. of solid materials the GD-AES/MS and LIPS will play a major role though electrothermal vaporization (ETV)-, laser ablation-ICP/MPT may also occupy some places.

APP* 316) Maurice, J. F., G. Wibetoe, et al. (2002). "Longitudinal distribution of thallium in human scalp hair determined by isotope dilution electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 17(5): 485-490.

A method for the direct detn. of the longitudinal distribution of thallium in human scalp hair using isotope diln. electrothermal vaporization inductively coupled plasma mass spectrometry (ID-ETV-ICP-MS) was developed. Cleaning of hair is considered to be a crit. step and of major importance with respect to the anal. procedure and results from analyses of unwashed and washed hair, using different washing procedures, were therefore compared. Small hair samples are difficult to handle and several methods to ease handling and introduction into the ETV were examd. Embedding hair strands in pressure-hardening glue before cutting them into 10 mm segments and injecting them with a solid sample injector proved to be the most successful. Several longitudinal concn. gradients were obtained of hair from a thallium-poisoned person. The thallium level in the root segment of the hair was about 0.4 mg g-1, which is several orders of magnitude larger than the concn. normally found in hair. The concn. level then dropped to about 0.01 mg g-1 close to the end of the 20 cm long hair strands analyzed. The concn. of thallium in hair from non-exposed persons was found to be below the limit of detection for the method, i.e. 0.7 pg abs. amt., corresponding to about 5 ng g-1 in dried hair using approx. 150 mg of sample for anal.

REV* 317) Hou, X. and B. T. Jones (2002). "Tungsten devices in analytical atomic spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 57B(4): 659-688.

A review. Tungsten devices were employed in anal. at. spectrometry for ~30 yr. Most of these atomizers can be elec. heated ?3000 Deg at very high heating rates, with a simple power supply. Usually, a tungsten device is employed in one of two modes: as an electrothermal atomizer with which the sample vapor is probed directly, or as an electrothermal vaporizer, which produces a sample aerosol that is then carried to a sep. atomizer for anal. Tungsten devices may take various phys. shapes: tubes, cups, boats, ribbons, wires, filaments, coils, and loops. Most of these orientations were applied to many anal. techniques, such as at. absorption spectrometry, at. emission spectrometry, at. fluorescence spectrometry, laser excited at. fluorescence spectrometry, metastable transfer emission spectroscopy, inductively coupled plasma optical emission spectrometry, inductively coupled plasma mass spectrometry, and microwave plasma at. spectrometry. The anal. figures of merit and the practical applications reported for these techniques are reviewed. Atomization mechanisms reported for tungsten atomizers are also briefly summarized. In addn., less common applications of tungsten devices are discussed, including analyte preconcn. by adsorption or electrodeposition and electrothermal sepn. of analytes prior to anal. Tungsten atomization devices continue to provide simple, versatile alternatives for anal. at. spectrometry.

APP* 318) Bettinelli, M., S. Spezia, et al. (2002). "Determination of rare earth elements in urine by electrothermal vaporization inductively coupled plasma mass spectrometry." Rapid Communications in Mass Spectrometry 16(6): 579-584.

A method was developed for the detn. of rare earth elements (REEs) in urine with electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICPMS). The undiluted sample was directly injected into the graphite tube and trifluoromethane (Freon-23) was used as chem. modifier in order to reduce the vaporization temp. and the memory effect of most of the lanthanides. The detection limits were in the range 1-10 ng/L with relative std. deviation of 3-5% at concn. levels of 1 mg/L, and less than 10-15% at 100 ng/L. Two different procedures, external calibration and a std. addns. method, were evaluated to measure the concn. levels of lanthanides in the urine samples and the second procedure was considered to be the best choice for calibration in this work. The level of REEs in urine of 50 healthy volunteers was in the range 5-20 ng/L, above the detection limit of ETV-ICPMS.

APP* 319) Resano, M., L. Balcaen, et al. (2002). "Multi-element analysis of a thermographic material by means of solid sampling-electrothermal vaporization-inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 57B(3): 495-511.

In spite of the advantages that the direct anal. of inorg. samples by solid sampling-electrothermal vaporization-inductively coupled plasma mass spectrometry (SS-ETV-ICP-MS) may offer, esp. in terms of sample throughput, most works until date have only dealt with less complicated org. matrixes. This paper reports on the direct detn. of 7 elements (Al, Mg, Mn, Ni, Sb, Ti, and Zr, with concns. ranging between 0.6 and 150 mg/g) in a thermog. material. This is a challenging application and can be used to assess the real possibilities of SS-ETV-ICP-MS for the anal. of inorg. samples. To cope with the complex compn. of the matrix (Ag, Si, and org. compds.), as well as with the different characteristics of the analytes, several approaches and chem. modifiers (HF, HCl, HNO3, and CH3Li) were studied. Finally, 2 different strategies were optimized. The simultaneous detn. of Al, Mg, Mn, Ni, Ti, and Zr is made possible by addn. of 20 mL of 23 M HF, which enables an efficient matrix removal at a pyrolysis temp. of 1200 Deg. On the other hand, due to the higher volatility of Sb, an alternative approach, consisting of the removal of the org. matrix at 800 Deg and the subsequent addn. of 20 mL of 0.12 M HCl, was used for the detn. of this element. In this way, Sb was efficiently vaporized at 1200 Deg as a chloride, prior to the vaporization of Ag and Si. Quant. results, obtained by aq. stds. for calibration, were very satisfactory in terms of accuracy. The RSD. ranged between 8 and 12%. The results are hence promising, illustrating that the possibilities of ETV to deal with complex matrixes are yet to be fully exploited.

APP* 320) Keith-Roach, M. J., S. Sturup, et al. (2002). "Comparison of two ICP-MS set-ups for measuring 99Tc in large volume water samples." Analyst (Cambridge, United Kingdom) 127(1): 70-75.

Large vol. fjord and seawater samples were radiochem. prepd. for ICP-MS anal. to test the robustness of the procedure and to carry out a comparison of 2 ICP-MS set-ups. A sector field instrument (MicroMass PT2) coupled with an ultrasonic nebulizer and a quadrupole ICP-MS (Perkin-Elmer Elan 6000) coupled with an electrothermal vaporization (ETV) unit were used. The radiochem. procedure was robust, removing Ru and Mo to acceptable levels, and the two set-ups gave results that were in agreement. The correlation coeff. between the sets of 11 results was 1.0 +-0.05. The importance of establishing the matrix effect when using an ETV is discussed.

APP* 321) Thomas, R. (2002). "A beginner's guide to ICP-MS. Part VIII - mass analyzers: Time-of-flight technology." Spectroscopy (Duluth, MN, United States) 17(1): 36-38, 40-41.

A review describes the time-of-flight (TOF) technol. used in inductively coupled plasma-mass spectrometry (ICP-MS) system. This technol. has the unique ability to sample all ions generated in the plasma at exactly the same time. The basic principles and the benefits of TOF analyzers for ICP-MS, as well as the different sampling approaches are described. The differences between orthogonal and on-axis TOF technol. are also discussed. The most exciting potential for TOF ICP-MS is in the multielement anal. of a rapid transient signal generated by sampling accessories such as laser ablation, electrothermal vaporization, and flow injection systems. To better understand how TOF technol. can help improve precision in ICP-MS, the major sources of instability are detd. The integration time of 3 s/mass is required to det. 10 elements in duplicate with good precision and detection limits.

APP* 322) Sun, Y. C. and C. H. Hsieh (2002). "Novel matrix modifier for direct determination of palladium in gold alloy by electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 17(2): 94-98.

The detn. of Pd in Au alloy by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) is difficult because of the presence of the Au matrix and the formation of Au-Pd intermetallic complexes. A new matrix modifier for removing the Au matrix was studied followed by direct detn. of Pd by ETV-ICP-MS using an aq. std. Different halides, such as KI, KIO3 and KCl, were evaluated for the removal of the Au matrix by formation of low b.p. auric halide complexes. The influence of the temp. program on the sepn. efficiency was also studied. A novel pre-reaction step was developed to improve the removal efficiency by enhancing the reaction between auric ions and halides. Under optimized conditions, .apprx.75% of 0.2 mg of Au matrix can be removed and a satisfactory anal. signal can be obtained. The precision of this method was .apprx.6% using KI as matrix modifier, and the accuracy was confirmed by the good agreement between the data obtained by the proposed method and those by a wet chem. technique. The detection limits obtained using the proposed method were >=0.1 mg g-1, making the method suitable for the detn. of Pd in Au alloy.

APP* 323) Vale, M. G. R., M. M. Silva, et al. (2002). "Control of spectral and non-spectral interferences in the determination of thallium in river and marine sediments using solid sampling electrothermal atomic absorption spectrometry." Journal of Analytical Atomic Spectrometry 17(1): 38-45.

The direct anal. of solid samples using electrothermal (graphite furnace) at. absorption spectrometry (ETAAS) has been investigated for the detn. of thallium in river and marine sediment ref. materials, because complete digestion of sediment samples requires the use of hydrofluoric acid and/or an alk. fusion, and the extn. with aqua regia might be incomplete and cause interferences in the detn. of thallium. The detn. of thallium in river sediments using direct solid sampling ETAAS was straight forward, and could be carried out with good accuracy even without the use of a chem. modifier or calibration against aq. stds. The anal. of marine sediments, in contrast, proved to be extremely difficult due to severe spectral and non-spectral interferences. The latter ones were caused by the relatively high chloride content of marine sediments, compared to river sediments, and could eventually be controlled by the addn. of ammonium nitrate as a chem. modifier together with ruthenium as a permanent modifier. The spectral interference could only be overcome with Zeeman-effect background correction, and was most likely caused by sulfate. After optimization of the procedure, thallium in marine sediment ref. materials could be detd. by calibration against a certified river sediment ref. material. According to the experience gained with river sediments, it might be assumed that aq. stds. could equally be used for calibration; this approach, however, was not further investigated. The results were in good agreement with non-certified 'information' values for thallium and with results obtained by ICP-MS using electrothermal vaporization and isotope diln. calibration. A characteristic mass of 13 pg was obtained, and the limit of detection of the proposed method, based on the zero-mass response (three times the std. deviation of 10 atomization cycles with empty platforms), was around 0.02 mg g-1 Tl.

APP* 324) Li, P.-C. and S.-J. Jiang (2003). "Electrothermal vaporization inductively coupled plasma-mass spectrometry for the determination of Cr, Cu, Cd, Hg and Pb in rice flour." Analytica Chimica Acta 495(1-2): 143-150.

Ultrasonic slurry sampling (USS)-electrothermal vaporization (ETV) dynamic reaction cell (DRC) inductively coupled plasma-mass spectrometry (ICP-MS) was applied to det. Cr, Cu, Cd, Hg and Pb in rice samples. The influences of instrument operating conditions and slurry prepn. on the ion signals were reported. Ascorbic acid was used as a modifier to enhance the ion signals. The background ions at the chromium masses were reduced in intensity significantly by using 0.4 mL min-1 NH3 as reaction cell gas in the dynamic reaction cell while a q value of 0.6 was used. Since the sensitivities of Cr, Cu, Cd, Hg and Pb in rice flour slurry and aq. soln. were quite different, std. addn. and isotope diln. methods were used for the detn. of Cr, Cu, Cd, Hg and Pb in these rice samples. This method was applied to the detn. of Cr, Cu, Cd, Hg and Pb in NIST SRM 1568a rice flour ref. material and two rice samples purchased from the market. The anal. results for the ref. material agreed with the certified values. The results for the rice samples for which no ref. values were available also are in good agreement between the isotope diln. and std. addn. methods. The method's detection limits estd. from the std. addn. plots were .apprx.0.44, 1.7, 0.4, 0.53 and 0.69 ng g-1 for Cr, Cu, Cd, Hg and Pb, resp., in the original rice flour.

FUN* 325) Ertas, G. and J. A. Holcombe (2003). "Determination of absolute transport efficiencies of Be, Cd, In, Pb and Bi for electrothermal vaporization sample introduction into an inductively coupled plasma using an in-line electrostatic precipitator." Spectrochimica Acta, Part B: Atomic Spectroscopy 58B(9): 1597-1612.

A novel lab.-constructed electrostatic precipitator for the detn. of analyte transport efficiencies from a tube furnace electrothermal vaporization (ETV) sample introduction system is described. This simple exptl. set up captures the analyte electrostatically using a neg. corona discharge. The abs. transport efficiencies using exptl. conditions typical of those applied to real anal. by ETV-ICP-MS were detd. for Be, Cd, In, Pb and Bi to be 26 +- 3, 39 +- 8, 35 +- 1, 50 +- 11 and 35 +- 1%, resp. Pd and NaCl were evaluated as carriers and only marginally increase analyte transport for the elements studied. Pd enhanced efficiencies 20-50% for all but Bi, which decreased by 17%. The NaCl produced transport enhancements of 10-50% for all five analytes. However, uncertainties in the measurements made several of the individual improvements statistically insignificant. The mean precipitator collection efficiency of the aerosol leaving the ETV for the five elements studied is >90% and was detd. using the ICP-MS signal with the in-line precipitator's voltage either on or off. While 30 ETV firings were used for a single efficiency detn., reasonable precision could be obtained with .apprx.10 firings while still employing reasonable analyte masses, i.e. .apprx.20 ng. The transport results are in good agreement with previous studies using similar ETV design and analyte masses.

FUN* 326) Bings, N. H. and Z. Stefanka (2003). "Development of a tungsten filament electrothermal vaporizer for inductively coupled plasma time-of-flight mass spectrometry and its possibilities for the analysis of human whole blood and serum." Journal of Analytical Atomic Spectrometry 18(9): 1088-1096.

A methodol. was developed using a W filament electrothermal vaporizer (WETV) as a sample introduction system, coupled to an inductively coupled plasma time-of-flight mass spectrometer (ICP-TOFMS), for rapid and simultaneous detn. of Cr, Cu, Li and Pb in human whole blood and serum samples. The design of the vaporizer is based on a W-filament from Osram, which is positioned in a low vol. (7.3 mL) quartz cell that is esp. suited for the evapn. of minute amts. of samples and is coupled to the plasma torch via an 8 cm (3 mm id) glass tube. The W coil was connected to the secondary side of a conventional a.c. power supply, the primary side of which was interfaced with a newly designed LabView-based controllable four-channel switch box. Each channel was attached to a sep. variable 0-220 V transformer, allowing indirect adjustment of the voltage on the secondary side of the power supply between 0 and 13.8 V. The voltage/current heating programs (drying, pyrolysis, vaporization and filament cleaning) for sample evapn. as well as the ICP-TOFMS operational parameters (carrier gas flow rate, modulation pulse width) for the simultaneous detn. of 17 isotopes were optimized using sequential and Modified Simplex algorithm-based optimization techniques. The compromise operation parameters of the WETV system for multielemental detns. are different for aq. std. solns., human whole blood and serum samples. An Ar carrier gas flow rate of 1.16 L min-1 provided optimum results for the detection of transient signals. By using 10 mL sample vols. of aq. multielemental std. solns. abs. detection limits (3s) at 0.007-0.1 pg for Ba, Cd, Co, Cr, Cu, Ga, In, Mn, Ni and Sr, 0.11-0.19 pg for Ag, As, Bi, Li, Pb and Pd and 11 pg for Fe, and a precision of 2-6% for 10 replicates of 5 ng mL-1 (20 ng mL-1 of Fe) multielemental sample solns. were achieved. The method accuracy was verified by the anal. of Ref. Materials SRM 909 (Human Serum) from NIST and 404108 (Human Whole Blood) from Nycomed Pharma regarding their Cr, Cu, Li and Pb concns. Except the addn. of a phosphate-based matrix modifier, followed by appropriate diln., no addnl. sample pretreatment was necessary. Internal standardization using multielemental solns. was used for calibration. Good agreement with the certified values was obsd. and the filament had a lifetime of >350 firings.

FUN* 327) Ertas, G. and J. A. Holcombe (2003). "Use of a simple transient extension chamber with ETV-ICPMS: quantitative analysis and matrix effects." Journal of Analytical Atomic Spectrometry 18(8): 878-883.

The transient extension (TEx) chamber was developed to provide a simple means of lengthening an electrothermal vaporizer (ETV) signal for the purpose of obtaining a full mass scan from a single ETV firing with inductively coupled plasma mass spectrometry (ICPMS) detection. The TEx chamber was used for quant. anal. of natural water (NIST SRM 1640). Quant. anal. was done for Co, Be, Pb, Sb and Cd. Detection limits for the five elements tested with the TEx chamber were in the 1-10 mg L-1 range when monitoring 256 masses during a single ETV firing. In general, there was no significant change in the analyte signal using palladium, sodium chloride or magnesium nitrate modifiers when comparing results with and without the TEx chamber.

APP* 328) Comte, J., P. Bienvenu, et al. (2003). "Determination of selenium-79 in solutions of fission products after pre-treatment by ion exchange chromatography and ETV-ICP-MS." Journal of Analytical Atomic Spectrometry 18(7): 702-707.

The work presented in this article concerns the development of a method for the detn. of selenium-79 in fission product (FP) solns. resulting from nuclear fuel reprocessing. 79Se (T1/2 = 106 yr) was measured using electrothermal vaporization coupled with inductively coupled plasma mass spectrometry (ETV-ICP/MS) after a single chem. sepn. step to ext. Se from the high activity soln. (1010 Bq L-1). The ion exchange method produced a soln. sufficiently decontaminated with respect to major b/g emitters and had a significant selenium recovery yield (85%). ETV parameters, for example furnace program, quantity of palladium nitrate used as chem. modifier, and gas flow rates, were optimized. The assocn. of ETV and chem. sepn. eliminated all the interferences normally assocd. with the detn. of 79Se. The concn. of 79Se measured in the fission products soln. was 0.43 mg L-1.

REV* 329) Thomas, R. (2003). "Beginner's guide to ICP-MS part XIV - sampling accessories, part II." Spectroscopy (Duluth, MN, United States) 18(2): 42,44,46,48,50,52,54.

Sampling accessories are considered crit. to enhance the practical capabilities of inductively coupled plasma-mass spectrometry (ICP-MS); since their development more than 10 yr ago, they have proved to be invaluable for difficult, real-world applications. In the first part of the tutorial on sampling accessories the author looked at laser ablation and flow injection techniques. In this second installment, the focus is on three other important sampling approaches: electrothermal vaporization, desolvation systems and chromatog. sepn. devices.

APP* 330) Maia, S. M., D. Pozebon, et al. (2003). "Determination of Cd, Hg, Pb and Tl in coal and coal fly ash slurries using electrothermal vaporization inductively coupled plasma mass spectrometry and isotopic dilution." Journal of Analytical Atomic Spectrometry 18(4): 330-337.

A method was studied for the detn. of Cd, Hg, Pb and Tl in coal and in coal fly ash, using slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry and isotope diln. The slurry, 25 mg ml-1, was prepd. by mixing the powd. sample (? 36-45 mm) with acid solns. (nitric acid for coal and nitric and hydrofluoric acids for coal fly ash) and submitting the mixt. to an ultrasonic agitation, letting it stand afterwards in a water bath at 60 Deg for 2 h. An ultrasonic probe was used to homogenize the slurry in the auto-sampler cup just before its introduction into the graphite tube. The best conditions were detd. regarding analyte sensitivity, furnace temp. program, amt. of modifier, acid concn., gas flow rate and particle size. For Hg, the pyrolysis stage was omitted and a low vaporization temp. was used (450-1000 Deg); the residual matrix was eliminated in the 1st step of the following cycle. The modifiers used were: Pd for Cd and Tl; Au, Ir or Pd for Hg; Ir or Pd for Pb. The accuracy of the method was checked by analyzing six certified coal ref. materials (SARM 20, SARM 19, BCR No. 40, BCR No. 180, BCR No. 181 and NIST 1630a) and one certified coal fly ash (NIST 1633b). With one exception (Hg in BCR No. 180), the found concns. were typically within 95% confidence interval of the certified values, or close enough to the recommended values, as long as the samples were ground to a small enough particle size. The limits of detection were typically around 0.08 mg g-1, 0.03 mg g-1, 1 mg g-1 and 0.02 mg g-1 for Cd, Hg, Pb and Tl, resp. The precision was also adequate with relative std. deviations of usually <5%.

APP* 331) Furtado da Silva, A., L. F. Dias, et al. (2003). "Determination of Hg and Tl in environmental reference materials using slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry with permanganate as modifier and calibration against aqueous standards." Journal of Analytical Atomic Spectrometry 18(4): 344-349.

A method for the detn. of Hg and Tl in environmental samples by slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry is proposed. The slurry is prepd. by mixing the sample, ground to a particle size of ?50 mm, with 5% vol./vol. nitric and 1% vol./vol. hydrofluoric acids in an ultrasonic bath, and leaving it to stand for 40 h before anal. The slurry was homogenized in the autosampler cup with a const. flow of argon, just before transferring an aliquot to the graphite furnace. Potassium permanganate in soln., in an untreated and a Ru-treated tube, as well as potassium and manganese in soln. were studied as modifiers and carriers. Best thermal stabilization and sensitivity were obtained with KMnO4 in an untreated tube, esp. for Tl. These conditions were adopted, together with the optimized pyrolysis temps. of 300 Deg for Hg and 500 Deg for Tl, and a vaporization temp. of 1000 Deg for both analytes. The accuracy of the method was assured by the anal. of eight certified ref. materials, using external calibration with aq. stds. prepd. in the same medium as the slurries. The limits of detection in the samples were 0.18 mg g-1 for Hg and 0.07 mg g-1 for Tl. The precision found for the different samples, expressed as relative std. deviation, was 0.8-11% for Hg and 1-9% for Tl (n = 3).

REV* 332) Martin-Esteban, A. and B. Slowikowski (2003). "Electrothermal vaporization - inductively coupled plasma-mass spectrometry (ETV-ICP-MS): A valuable tool for direct multielement determination in solid samples." Critical Reviews in Analytical Chemistry 33(1): 43-55.

A review. Solid Sampling-Electrothermal Vaporization-Inductively Coupled Plasma-Mass Spectrometry (SS-ETV-ICP-MS) is an attractive technique for the direct simultaneous detn. of trace metals in solid samples. During recent years, some important developments dealing with ETV-ICP coupling and with analyte transport efficiencies are reported, and so SS-ETV-ICP-MS has received a renewed interest by the at. spectroscopy community. Thus, the present review highlights the inherent capabilities of SS-ETV-ICP-MS for the simultaneous detn. of trace metals. Tech. aspects of ETV-ICP coupling as well as more recent applications are reported. This technique is a powerful tool for sorting out some of the current anal. challenges, and future advances are to be expected to widen the field of application.

APP* 333) Ben-Younes, M., D. C. Gregoire, et al. (2003). "Effectiveness of ammonia in reducing carbon-based polyatomic ion interferences in electrothermal vaporization collision cell inductively coupled plasma mass spectrometry." Spectrochimica Acta, Part B: Atomic Spectroscopy 58B(2): 361-372.

The effectiveness of NH3 gas used in a Dynamic Reaction Cell (DRC) in reducing or eliminating carbon-based polyat. ions in electrothermal vaporization (ETV) inductively coupled plasma mass spectrometry is reported. Ammonia gas was found effective in reducing interfering polyat. ions on both Cr and Mg isotope ions. The use of NH3 as a reaction gas for the redn. of polyat. ion interferences on Si was not fully successful. However, the LODs for 28Si+ and 29Si+ were greatly improved over conventional ICP-MS. Ammonia is unsuitable as a reaction gas for the detn. of 30Si+. Results of signal to background studies indicate that the exptl. conditions required to optimize the DRC were close for soln. nebulization and ETV for Cr only. For Mg and Si, different optimization conditions were required.

APP* 334) Ho, C.-Y. and S.-J. Jiang (2003). "Electrothermal vaporization inductively coupled plasma mass spectrometry for determination of vanadium and chromium in soils." Spectrochimica Acta, Part B: Atomic Spectroscopy 58B(1): 63-70.

Ultrasonic slurry sampling electrothermal vaporization dynamic reaction cell inductively coupled plasma mass spectrometry (USS-ETV-DRC-ICP-MS) was applied to det. of V and Cr in several soil samples. The influences of instrument operating conditions and slurry prepn. on the ion signals were studied.

Ascorbic acid was used as the modifier to enhance the ion signals. To save expt. time, an ultrasonic nebulizer was used for the selection of dynamic reaction cell (DRC) operating conditions. The background ions at the V and Cr masses were significantly reduced in intensity by using NH3 as reaction cell gas in the DRC. Std. addn. method was used for the detn. of V and Cr in these soil samples. This method was applied to the detn. of V and Cr in NIST SRM 2711 Montana soil and NIST SRM 2709 San Joaquin soil ref. materials and a soil sample collected from the Kaohsiung area. The anal. results of the ref. samples agreed with the certified values. The precision between sample replicates was better than 3% with the USS-ETV-DRC-ICP-MS method. The method detection limits estd. from std. addn. curves were .apprx.0.24 and 0.16 mg g-1 for V and Cr, resp., in the original soil sample.

FUN* 335) Parsons, P. J., Y. Zhou, et al. (2003). "Atomization and vaporization of lead from a blood matrix using rhodium-coated tungsten filaments with pseudo-simultaneous electrothermal atomic absorption and inductively coupled plasma mass spectrometric measurements." Journal of Analytical Atomic Spectrometry 18(1): 4-10.

In an effort to understand the pyrolysis and atomization behavior of Pb in a dil. blood matrix when detd. using a tungsten filament electrothermal at. absorption spectrometer (W-filament ETAAS), we directly coupled a W-filament ETAAS instrument (J. Anal. At. Spectrom., 2001, 16, 82) to an inductively coupled plasma mass spectrometer (ICP-MS). The W-filament instrument was operated both as an electrothermal atomizer (ETA) and as an electrothermal vaporizer (ETV). The exptl. arrangement was used to monitor simultaneously the analyte (208Pb), the permanent modifier (103Rh) coating the W surface, a surrogate for the org. components of the blood matrix (40Ar12C), and the metal atomizer (180W, 183W and 184W16O), while also measuring Pb by AAS pseudo-simultaneously. Electrothermal parameters used in the ETV/ETA expts. were precisely the same as those described previously (Spectrochim. Acta, Part B, 2002, 57, 727) for ETAAS work. This was necessary in order that the ICP-MS data could be used to observe the vaporization of analyte, matrix, modifier, and metallic atomizer throughout the electrothermal cycle. The purge gas used to transport vaporized material from the atomization cell to the ICP was Ar contg. 6% H2. Pseudo-simultaneous ETAAS and ETV-ICP-MS measurements of Pb in blood were achieved using this exptl. arrangement, with the MS signals appearing roughly 2 s after those by AAS, consistent with the delay caused by the 15 cm long Teflon transfer line connecting the two instruments. During pyrolysis, a strong signal obsd. at mass 52 is shown to be due to 40Ar12C; this signal increases as filament power for pyrolysis increases. When plotted, the data show the effective removal of much of the carbon-based matrix during pyrolysis, but without significant loss of analyte. In contrast, the pre-coated permanent modifier, Rh, is only lost during the final cleaning stage of the program in which max. power is necessary to remove the carbonaceous matrix. However, when Rh is added to the diluent, it is lost even during pyrolysis, and at a much lower temp. This explains why addn. of Rh directly to the diluent yields no modification benefits, and why periodic re-coating of the filament surface for the anal. is necessary.

FUN* 336) Balsanek, W. J., J. D. Venable, et al. (2003). "Generation of a square wave inductively coupled plasma scanning mass spectrometry signal using electrothermal vaporization sample introduction." Journal of Analytical Atomic Spectrometry 18(1): 59-64.

A device was designed to convert the typical skewed Gaussian shaped signal from an inductively coupled plasma mass spectrometer (ICP-MS) using electrothermal vaporization (ETV) into a square wave signal. The basis for such a transformation is centered on the assumption that the aerosol particles produced from ETV are aerodynamically small, and thus, have diffusive properties similar to gases, which makes them easy to mix and resistant to loss by settling. The ETV square wave signals were generated through the use of a stainless steel cylinder equipped with a motor driven piston assembly, which was used to trap the transient ETV signal and deliver a uniform d. aerosol to the ICP-MS. The length of the signal was controlled by the rate of travel of the piston during expulsion of the sample aerosol. A const. flow rate was achieved and maintained using a pressure sensor feedback to the motor driving the piston. The system was evaluated by quant. full mass scans on a variety of signal shapes including square wave signals, normal ETV signals, and broadened ETV signals generated using a single bead string reactor (SBSR). The square wave signals yielded precisions for quant. full mass scans of better than 10% relative std. deviation for most metals compared to .apprx.15% for SBSR broadened signals and 40% for normal signals. The improved precision was attributed to an increased duty cycle, but the increase did not become significant until >100 masses were monitored due to the relatively small amt. of temporal overhead time (fly-back time, amplifier settling time, etc.) relative to data collection periods. Because the ETV generated aerosol consists of aerodynamically small particles, there was only a minimal decrease (<2-11%) in the integrated signal area as a result of using the square wave generator.

APP* 337) Arslan, Z. and A. J. Paulson (2003). "Solid phase extraction for analysis of biogenic carbonates by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS): an investigation of rare earth element signatures in otolith microchemistry." Analytica Chimica Acta 476(1): 1-13.

Uptake of trace elements into fish otoliths is governed by several factors such as life histories and environment in addn. to stock and species differences. In an attempt to elucidate the elemental signatures of rare earth elements (REEs) in otoliths, a solid phase extn. (SPE) protocol was used in combination with electrothermal vaporization (ETV) as a sample introduction procedure for the detns. by inductively coupled plasma quadrupole mass spectrometry (ICP-MS). Effects of various parameters, such as carrier gas flow rate, atomization temp. and chem. modification, were examd. for optimization of the conditions by ETV-ICP-MS. Atomization was achieved at 2800 DegC. Lower temps. (i.e. 2600 DegC) resulted in severe memory problems due to incomplete atomization. Palladium was used as a chem. modifier. It was found that an increase in Pd concn. up to 0.5 mg in the injection vol. (70 ml) led up to four-fold enhancement in the integrated signals. This phenomenon is attributed to the carrier effect of Pd rather than the stabilization since no significant losses were obsd. for high temp. drying around 700 DegC even in the absence of Pd. Preconcn. was performed online at pH 5 by using a mini-column of Toyopearl AF-Chelate 650M chelating resin, which also eliminated the calcium matrix of otolith solns. After preconcn. of 6.4 mL of soln., the conc. was collected in 0.65 mL of 0.5% (vol./vol.) HNO3 in autosampler cups, and then analyzed by ETV-ICP-MS. The method was validated with the anal. of a fish otolith certified ref. material (CRM) of emperor snapper, and then applied to samples. Results obtained from otoliths of fish captured in the same habitat indicated that otolith rare earth element concns. are more dependent on environmental conditions of the habitat than on species differences.

FUN* 338) Hermann, G., A. Trenin, et al. (2004). "Platform-to-platform sample transfer, distribution, dilution, and dosing via electrothermal vaporization and electrostatic deposition." Spectrochimica Acta, Part B: Atomic Spectroscopy 59B(5): 737-748.

A novel system for solid sample pretreatment, handling and dosing for anal. at. spectrometry is described. A primary solid or liq. sample is vaporized in a graphite furnace and then condensed in a specially designed condensation zone. On the further transport path, the analyte aerosol can be dild. and distributed in pre-set ratios in the lab. made flow control system. Applying a corona discharge, aerosol particulates are then quant. re-collected by means of intra-furnace electrostatic pptn. on the platform of another graphite furnace or by external pptn. on one or a set of platforms. This makes possible to produce a set of secondary platforms with equal analyte compns. from one individual primary sample. Such multitudes allow sequential multi-element detns. with single-element instrumentation or comparative measurements with different techniques. Furthermore, the described procedure allows external thermal sample pretreatment with preceding pyrolysis and addnl. vaporization, condensation, and re-pptn. that significantly reduces or removes the sample matrix. Owing to different losses, transport efficiencies of electrothermal vaporization (ETV) instrumentation depend on analyte element, matrix, vaporization temp., ramp rate, and tube history. In order to reduce the losses and therewith such dependencies of the losses, new lab. constructed ETV unit with analyte condensation in an axially focusing upstream convection zone has been constructed. Anal. performance of the new setup is compared with the performance of a com. end-on flow-through ETV unit when analyzing both liq. dosed samples and certified solid ref. materials. The new system shows much higher transport efficiencies that are, in addn., more uniform for elements of different volatility. The effects of chem. sample modifiers and elements supporting analyte condensation are studied. Most of the anal. measurements were carried out with a continuum source coherent forward scattering multi-element spectrometer. Comparative measurements were also carried out independently in the co-authors' labs. with at. absorption and inductively coupled plasma mass spectrometry techniques.

FUN* 339) Martin-Esteban, A., B. Slowikowski, et al. (2004). "Correcting sensitivity drift during long-term multi-element signal measurements by solid sampling-ETV-ICP-MS." Talanta 63(3): 667-673.

Solid sampling-electrothermal vaporisation-inductively coupled plasma-mass spectrometry (SS-ETV-ICP-MS) is an attractive technique for the direct simultaneous detn. of trace elements in solid samples and esp. in long-term studies (i.e. assessment of the homogeneity of ref. materials). However, during these studies a downward drift in the instrument sensitivity has been obsd. due likely to deposits on the sampling and skimmer cones and on the ion lens of the mass spectrometer. Accordingly, in this paper, several means of correcting and/or suppressing sensitivity drift are proposed and evaluated for the monitoring of Cd, Cu, Hg, Mn, Pb, Sb, Se, Sn, Tl, U and V in different ref. materials of inorg. and org. (biol.) origin. From that studies, the combination of the use of the argon dimer as internal std. together with a modification in the ETV-ICP connection tube seems to be the best mean of getting stable sensitivity during at least 60 consecutive ETV runs.

APP* 340) Saint'Pierre, T. D., L. F. Dias, et al. (2004). "Determination of Cd, Cu, Fe, Pb and Tl in gasoline as emulsion by electrothermal vaporization inductively coupled plasma mass spectrometry with analyte addition and isotope dilution calibration techniques." Spectrochimica Acta, Part B: Atomic Spectroscopy 59B(4): 551-558.

The presence of some elements can be undesirable in gasoline, not only by the possibility of damage of the motor parts and poor performance of the fuel, but also because of the pollution caused by the release of toxic metals to the atm. by the combustion of the fuel. The gasoline sample prepn. as emulsion is an adequate method for the sample introduction for sensitive anal. methods. In this work, external calibration with aq. stds., analyte addn. and isotope diln. calibration techniques were employed for the detn. of Cd, Cu, Fe, Pb and Tl in gasoline by electrothermal vaporization inductively coupled plasma mass spectrometry. The concns. of Cu and Fe were addnl. detd. by electrothermal at. absorption spectrometry. The ETV program for the analytes in a gasoline sample emulsion was optimized and the detn. was carried out without modifier at 400 DegC pyrolysis and 1900 DegC vaporization temps. In these conditions, the external calibration against aq. stds. could not be applied for the anal. of gasoline as emulsion, since the results of recovery tests were not acceptable. The detn. by analyte addn. or isotope diln. employing these conditions could be carried out for Cd, Cu, Pb and Tl, but not for Fe. The use of 10 mg Pd in soln. as chem. modifier allowed the detn. of all studied analytes together, at 800 DegC pyrolysis and 2100 DegC vaporization temps. The limits of detection for the analytes in gasoline, by analyte addn. or by isotope diln., were better than 5 mg l-1. The measured concns. for all analytes by analyte addn. and by isotope diln. calibration techniques were mostly in agreement and the precision for both calibrations were also similar and adequate. Agreement was also found with concn. results for Fe and Cu obtained by ET AAS, without modifier.

REV* 341) Miro, M., J. M. Estela, et al. (2004). "Application of flowing stream techniques to water analysis Part III. Metal ions: alkaline and alkaline-earth metals, elemental and harmful transition metals, and multielemental analysis." Talanta 63(2): 201-223.

In the earlier parts of this series of reviews , the most relevant flowing stream techniques (namely, segmented flow anal., continuous flow anal., flow injection (FI) anal., sequential injection (SI) anal., multicommuted flow injection anal. and multisyringe flow injection anal.) applied to the detn. of several core inorg. parameters for water quality assessment, such as nutrients and anionic species including nitrogen, sulfur and halogen compds., were described. In the present paper, flow techniques are presented as powerful anal. tools for the environmental monitoring of metal ions (alk. and alk.-earth metals, and elemental and harmful transition metals) as well as to perform both multielemental and speciation anal. in water samples. The potentials of flow techniques for automated sample treatment involving online analyte sepn. and/or preconcn. are also discussed in the body of the text, and demonstrated for each individual ion with a variety of strategies successfully applied to trace anal. In this context, the coupling of flow methodologies with at. spectrometric techniques such as flame at. absorption spectrometry (FAAS), electrothermal at. absorption spectrometry (ETAAS), inductively coupled plasma mass spectrometry (ICPMS) or hydride-generation (HG)/cold-vapor (CV) approaches, launching the so-called hyphenated techniques, is specially worth mentioning.

APP* 342) Xia, L., B. Hu, et al. (2004). "Single-Drop Microextraction Combined with Low-Temperature Electrothermal Vaporization ICPMS for the Determination of Trace Be, Co, Pd, and Cd in Biological Samples." Analytical Chemistry 76(10): 2910-2915.

A new method of single-drop microextn. combined with low-temp. electrothermal vaporization (LTETV)-ICPMS was proposed for the detn. of trace Be, Co, Pd, and Cd with benzoylacetone (BZA) as both extractant and chem. modifier. Several factors that influence the microextn. efficiency, such as sample flow rate, microdrop vol., and extn. time, were investigated and the optimized microextn. conditions were established. Be, Co, Pd, and Cd in the postextn. org. phase were directly detd. by LTETV-ICPMS with the use of BZA as chem. modifier. The chem. modification of BZA in LTETV-ICPMS was studied, and the factors affecting the formation of chelates and vaporization/transportation of chelates were investigated. Under the optimized conditions, the detection limits of the method were 0.12, 0.99, 1.5, and 0.27 pg/mL for Be, Co, Pd, and Cd, and the relative std. deviations for 0.1 ng/mL Be, Co, Pd, and Cd were 16, 14, 14, and 11%, resp. After 10 min of extn., the enrichment factors were 160 (Be), 125 (Co), 40 (Pd), and 180 (Cd). The proposed method was applied to the detn. of trace Be, Co, Pd, and Cd in biol. ref. materials, and the detd. values were in good agreement with the certified values.

REV* 343) Mihaljevic, M., L. Strnad, et al. (2004). "Application of inductively coupled plasma mass spectrometry in geochemistry." Chemicke Listy 98(3): 123-130.

A review. This review covers principles and applications of ICP MS in geochem. and environmental sciences. The current popularity of ICP MS is attributed to very low detection limits for almost all elements across the Periodic Table, simple mass spectra and the ability to measure isotopic ratios. The most frequently analyzed groups of elements are described in relation to the occurrence of spectral and non-spectral interferences, methods of calibration and measurement, the instrumental arrangement and also the most frequent methods of decompn. of solid samples. Modifications of the way of introducing the sample, in particular the use of electrothermal vaporization and laser ablation, make the ICP MS a very effective instrumental method for trace anal. However, it is necessary to take into consideration the high costs of purchase and operation of the instrument.

APP* 344) Li, S., B. Hu, et al. (2004). "Direct determination of trace impurities in niobium pentaoxide solid powder with slurry sampling fluorination assisted electrothermal vaporization inductively coupled plasma mass spectrometry." Journal of Analytical Atomic Spectrometry 19(3): 387-391.

A method of fluorination assisted electrothermal vaporization inductively coupled plasma mass spectrometry (FETV-ICP-MS) was developed to directly det. the trace impurities in niobium pentaoxide solid powder in which a poly(tetrafluoroethylene) (PTFE) emulsion was used as fluorinating modifier to promote the vaporization of refractory elements from a graphite furnace and to avoid the formation of thermally stable carbides. The solid sample was introduced into the graphite furnace in the form of slurry without any chem. pretreatments. The electrothermal vaporizer device was connected to the ICP system by a lab.-built interface, and the flow rates of sample carrier gas and auxiliary carrier gas were optimized exptl. The potentially polyat. interferences resulting from the pyrolyzates of PTFE were evaluated. A new method by stepwise dilg. the sample matrix is proposed for investigating the matrix effect and the results showed that no obvious matrix effect was obsd. with a sample matrix (Nb2O5) concn. of less than 200 mg L-1. Under the optimal conditions, the abs. limits of detection for FETV-ICP-MS detn. of Ta, Ti, Cr, W, Ni, Cu and Mn were in the range of 0.026-1.1 pg. For one anal. run, only 0.002 mg of Nb2O5 sample was required. The proposed method has been applied to detg. the trace impurities in Nb2O5 powder, and both the results obtained from the external calibration method and the std. addn. method were in a good agreement with those obtained by conventional nebulization ICP-MS.

APP* 345) Vieira, M. A., T. D. Saint'Pierre, et al. (2004). "Determination of As, Hg, Se and Sn in sediment slurries by CVG-ETV-ICP-MS with trapping in an Ir treated graphite tube and calibration against aqueous standards." Journal of Analytical Atomic Spectrometry 19(2): 297-300.

A method for the simultaneous detn. of As, Hg, Se and Sn in sediment slurries using chem. vapor generation (CVG), in situ trapping electrothermal vaporization inductively coupled plasma mass spectrometry, is proposed. The vapors produced by the reaction of the sample slurry with the reducing agent are transported to the vaporizer and trapped at 150 Deg in a graphite tube, treated with Ir as a permanent modifier, before vaporization at 2000 Deg and transport to the plasma. The accuracy of the method was assured by the anal. of certified ref. sediment samples, using external calibration with aq. solns., prepd. in the same medium and subject to the same CVG and trapping procedure as the slurries. The obtained concns. were in agreement with the certified values, using the t-Student test for a confidence level of 95%. The detection limits, in ng g-1, were: 0.8 for Hg, 0.04 for As, 0.01 for Se and 0.30 for Sn.

REV* 346) Heumann, K. G. (2004). "Isotope-dilution ICP-MS for trace element determination and speciation: from a reference method to a routine method?" Analytical and Bioanalytical Chemistry 378(2): 318-329.

A review. This crit. review discusses the conditions under which inductively coupled plasma-isotope diln. mass spectrometry (ICP-IDMS) is suitable as a routine method for trace element and element-speciation anal. It can, in general, be concluded that ICP-IDMS has high potential for routine anal. of trace elements if the accuracy of results is of predominant anal. importance. Hyphenated techniques with ICP-IDMS suffer both from lack of com. available isotope-labeled spike compds. for species-specific isotope diln. and from the more complicated system set-up required for species-unspecific ICP-IDMS anal. Coupling of gas or liq. chromatog. with species-specific ICP-IDMS, however, enables validation of anal. methods involving species transformations which cannot easily be performed by other methods. The potential and limitations of ICP-IDMS are demonstrated by recently published results and by some unpublished studies by the group. Possible loss of silicon as volatile SiF4 during decompn. of a sample using hydrofluoric acid has no effect on trace silicon detn. if the isotope-diln. step occurs during digestion in a closed system. For powder samples, laser ablation ICP-IDMS can be applied with an accuracy comparable with that only available from matrix-matched standardization, whereas the accuracy of electrothermal vaporization ICP-IDMS was strongly dependent on the element detd. The significance of easy synthesis of isotope-labeled spike compds. for species-specific ICP-IDMS is demonstrated for monomethylmercury and Cr(VI). Isotope-exchange reactions between different element species can prevent the successful application of ICP-IDMS, as is shown for iodinated hydrocarbons. It is also shown for monomethylmercury that species transformations during sample-pretreatment steps can be followed by species-specific ICP-IDMS without loss of accuracy. A relatively simple and time-efficient procedure for detn. of monomethylmercury in environmental and biol. samples is discussed. The method, which entails a rapid microwave-assisted isotope diln. step and in-situ extn. of the derivatized species, has good potential for routine application in the future.