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In This Issue:

Determination of Uranium and Thorium at Trace and Ultratrace Levels in Urine by Laser Ablation ICP-MS

J.S. Becker, M. Burow, M.V. Zoriy, C. Pickhardt, P. Ostapczuk, and R. Hille 197

Multielemental Characterization of Nickel by Glow Discharge Quadrupole Mass Spectrometry

Raparthi Shekhar, J. Arunachalam, Niranjan Das, and A.M. Srirama Murthy........ 203

As, Bi, Se(IV), and Te(IV) Determination in Acid Extracts of Raw Materials and By-products From Coal-fired Power Plants by Hydride Generation-Atomic Fluorescence Spectrometry

Carmen Moscoso-Pérez, Jorge Moreda-Piñeiro, Purificación López-Mahía, Soledad Muniategui-Lorenzo, Esther Fernández-Fernández, and Darío Prada-Rodríguez 211

Determination of Arsenic and Selenium in Woodlice by GFAAS

Michael Raessler 217

Rapid Determination of Zinc in Foods by Flow Injection Analysis With Flame AAS Using Gradient Calibration Method

Jesús M. Anzano, Riana J. B. Heinemann, and José Mª Mir 221

ICP-OES Determination of Niobium, Tantalum, and Titanium at Trace to Percentage Levels in Varying Geological Matrices

R. Saran, C.R. Khorge, A. Premadas, and Vijay Kumar........ 226

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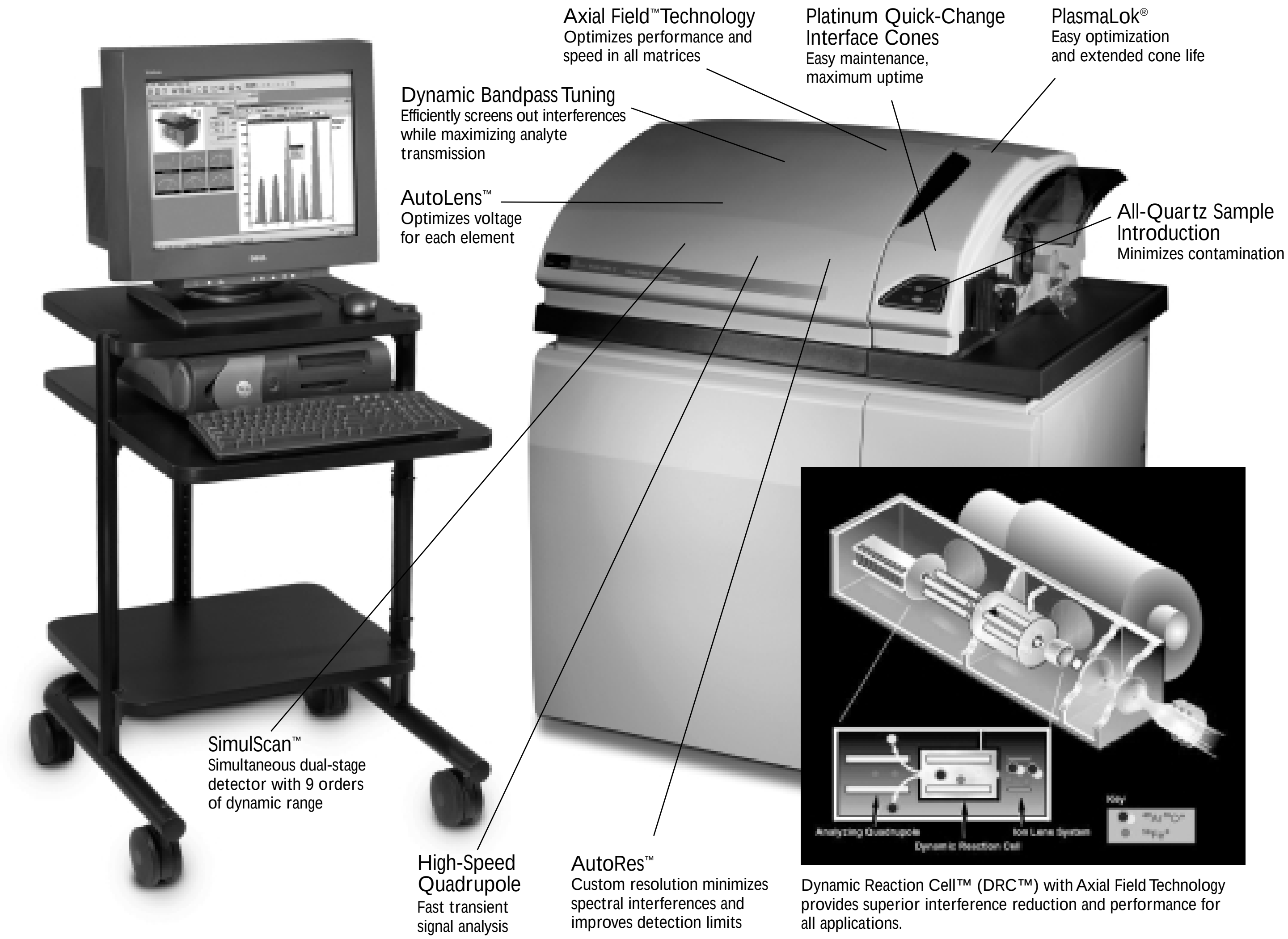

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Determination of Uranium and Thorium at Trace and Ultratrace Levels in Urine by Laser Ablation ICP-MS

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ABSTRACT

A new analytical procedure was developed for the determination of U and Th concentrations and the ^{235}U/^{238}U isotope ratio in urine at the trace and ultratrace levels by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). After drying, a homogeneous urine sample was analyzed directly by LA-ICP-MS. In order to study the figures of merit of the analytical methods developed, matrix-matched synthetic laboratory standards doped with ^{230}Th (IRMM 60), uranium with natural isotope composition (^{235}U/^{238}U = 0.00725), and uranium isotope standard reference material (NIST U-930) were prepared at low ng L^{-1} levels. The recovery for thorium and uranium concentration measured on a synthetic urine laboratory standard by LA-ICP-MS varied between 91 and 104%. The precision and accuracy of the analytical methods were determined for uranium in urine laboratory standards (at uranium concentrations of 0.1 ng mL^{-1}) to be 7% and <1%, respectively. The analytical technique developed was applied for ^{235}U/^{238}U isotopic ratio measurements in urine samples in order to detect possible incorporation of exposed persons to depleted or enriched uranium. This technique is of interest to forensic science particularly when only a small amount of dried urine sample is available for investigation.

INTRODUCTION

Determination of the concentration and isotope ratios of long-lived radionuclides, such as uranium and plutonium isotopes, thorium, ^{237}Np, ^{79}Se, ^{90}Sr, or ^{129}I, is required in environmental monitoring of nuclear contamination in nuclear safeguards and nuclear forensic studies (1–7). ^{238}U, ^{235}U, ^{234}U, and ^{232}Th are naturally occurring alpha-emitting long-lived radionuclides which are taken up daily at low levels with food and drinking water. Uranium with unnatural ^{235}U/^{238}U and ^{234}U/^{238}U ratios in comparison to the IUPAC table values (e.g., ^{235}U/^{238}U = 0.00725) and/or the evidence of ^{236}U at an abundance higher than observed in nature (^{235}U/^{238}U > 10^{-10}) demonstrates contamination of the urine sample of unnatural origin. Therefore, isotope ratio measurements are important because they can provide information on the origin of uranium (also thorium and plutonium). Due to different applications of uranium (e.g., in nuclear reactor technology, depleted uranium in ammunition) and thorium (as heat-resistant materials, e.g., in thorium alloys, welding rods, etc.), a careful monitoring of exposed persons is required in order to detect possible contamination with radionuclides.

Rapid analysis techniques are required especially for measurement of long-lived radionuclides in urine. Thermal ionization mass spectrometry (TIMS) has been used for many years as the standard technique for uranium isotope ratio measurements (8). The disadvantages of TIMS are time-consuming sample preparation steps and the need for a large volume of urine. In contrast, easy and fast monitoring is possible by the analysis of small volumes of body fluid (especially of urine) using inductively coupled plasma mass spectrometry (ICP-MS) (9–13). This is important for long-lived radionuclides at the trace and ultratrace levels in order to determine alpha-radiation emitters, such as uranium and thorium.

In addition to the determination of uranium and thorium in urine, which is a routine task in many laboratories, new analytical techniques have recently been proposed for the determination of Pu in urine at ultratrace levels using double-focusing sector field ICP-MS (ICP-SFMS) (14,15). Using a developed trace matrix separation technique, Pu isotope ratio measurements in urine were possible with detection limits at the attogram per mL level (10^{-18} g mL^{-1}) (14). Recently, we developed an analytical technique for the determination of ^{90}Sr in urine with a half-life $T_{1/2}$ of 29.1 years after separation and enrichment of the analyte with a detection limit at $0.4{*}10^{-15}$ g mL^{-1} (0.4 ppq) (16).

Laser ablation inductively coupled plasma source mass spectrometry (LA-ICP-MS) has become established as a very efficient and sensitive technique for the analysis of long-lived radionuclides in solid samples (1,17). Therefore, the application of LA-ICP-MS was studied for the direct determination of uranium and thorium concentrations and ^{235}U/^{238}U isotope ratios in a urine matrix in order to minimize the sample preparation steps and to reduce possible contamination during sample preparation. The often-discussed quantification problems in LA-ICP-MS can be solved by the application of matrix-matched synthetic standard materials. For this purpose, urine laboratory standards were prepared and analyzed by LA-ICP-MS in order to determine the precision and accuracy of the ana-

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lytical technique for the $^{235}U/^{238}U$ isotopic ratio, and to study the recovery of uranium and thorium at trace and ultratrace levels in a urine matrix. For quantification purposes, the isotope dilution technique is the method of choice and will be investigated for application in routine analysis by LA-ICP-MS.

The aim of the present work was to develop an analytical technique for direct uranium and thorium determination in urine at the trace and ultratrace levels by LA-ICP-MS, e.g., for forensic science, where only a very small amount of dried urine is available for investigation.

EXPERIMENTAL

ICP-MS Instrumentation

A quadrupole ICP-MS (ELAN® 6000 ICP-QMS, PerkinElmer SCIEX, Concord, Ontario, Canada) and a double-focusing sector field ICP-MS (ELEMENT, ThermoElectron Bremen, Germany), coupled with a laser ablation system from CETAC (LSX 200, Cetac Technologies, Omaha, NE, USA), were used for the determination of uranium concentrations and isotope ratios in urine samples. Measurements were made by LA-ICP-MS using a quadrupole-based system and a sector field instrument operating at low mass resolution. The experimental parameters were optimized with respect to maximum $^{238}U^+$ ion intensity. The optimized parameters of the laser ablation system used and the mass spectrometric measurements obtained on two different ICP mass spectrometers are summarized in Table I.

Samples and Isotope Standard Reference Materials

Urine samples were collected from adult volunteers in containers previously washed repeatedly with 2% (v/v) nitric acid in 18 MΩ cm water. Several human urine samples were investigated by LA-ICP-MS using the developed analytical techniques. A uranium certified isotope reference material NIST U-930 (NIST - National Institute of Standards and Technology, Gaithersburg, MD, USA) and a highly enriched ^{230}Th isotope standard (^{230}Th = 99.85%) IRMM-60 (IRMM - Institute for Reference Materials and Measurements, Geel, Belgium), or a $^{230}Th/^{232}Th$ isotope-mixed solution dissolved in 2% HNO_3 were doped in urine matrix and used for calibration of the proposed analytical procedures. Furthermore, freeze-dried urine (NIST 2670a) was available as a standard reference material in order to validate the uranium and thorium concentrations in this matrix.

Preparation of Synthetic Laboratory Standards

In addition to the standard reference material, freeze-dried urine (NIST 2670a), several suitable synthetic matrix-matched laboratory standards doped with natural uranium, thorium (^{232}Th=100 %), and an isotope standard solution [NIST U-930 or highly enriched ^{230}Th isotope standard (^{230}Th = 99.85%, IRMM-60)] at several concentrations (0.5, 1.25, and 2.5 µg L^{-1} for thorium and 0.25, 1.25, and 2.5 ng L^{-1} for uranium) were investigated. Urine laboratory standards were applied for quality control in order to evaluate the precision, accuracy, and limit of detection (LOD) of the new analytical method. After homogenizing the urine samples in an ultrasonic bath, a well-defined isotope standard solution (NIST U-930), ^{230}Th (IRMM-60), or a $^{230}Th/^{232}Th$ isotope-mixed solution dissolved in 2% HNO_3 was added. After drying under an IR lamp, a small amount of homogenized laboratory standard (less than 1 mg of dried urine) was analyzed by LA-ICP-MS.

Quantification Procedure

Two calibration strategies (external calibration and isotope dilution technique) were investigated by LA-ICP-MS using synthetic laboratory urine standards and the standard reference material freeze-dried urine (NIST 2670a). For all calibration curves measured by LA-ICP-SFMS via external calibration, the regression coefficient (R^2) was better than 0.99. In additional experiments, urine samples were doped

TABLE I
Experimental Parameters of LA-ICP-MS Measurements Using the ELAN 6000 (PerkinElmer Sciex, Canada) and ELEMENT (ThermoElectron, Bremen, Germany)

Laser Ablation		ICP-MS	ELEMENT	ELAN 6000
Wavelength (nm)	266	Mass resolution (m/Δm)	300	300
Pulse duration (ns)	5	Rf power (W)	1050	1200
Repetition frequency (Hz)	20	Carrier gas flow rate (L min^{-1})	0.92	0.77
Laser power density (W/cm²)	1.22 x 10^9	Dwell time (ms)	50	20
Energy/pulse (mJ)	4.3	Sweeps	5	10
Spot diameter (mm)	0.3	Replicates	10	10
Raster area (mm²)	5 x 0.5			

with uranium and thorium isotope-enriched solutions with the following isotope ratios: $^{235}U/^{238}U=17.34$ and $^{230}Th/^{232}Th=3.64$. The isotope dilution method was applied in LA-ICP-MS for different spike concentrations using the formula for isotope dilution analysis:

$$Q_s = Q_T \bullet (T–X)/(X–S) \bullet m_s/m_T$$

where

Q_s = element concentration in the sample

Q_T = element concentration in the highly enriched spike

X = isotopic ratio of the two selected isotopes in the mixture

T = isotopic ratio of the two selected isotopes in the spike

S = isotopic ratio of the two selected isotopes in the sample

m_s and m_T = atomic mass of the element in nature and of the isotopically enriched element, respectively.

RESULTS AND DISCUSSION

Recovery Studies for U and Th in Synthetic Laboratory Standards With Urine Matrix -- Accuracy and Precision of LA-ICP-MS

Determination of accuracy and precision of LA-ICP-MS using two ICP mass spectrometers together with recovery studies were performed on dried synthetic laboratory urine spiked with standard solutions having concentrations of 0.5, 1.25, and 2.5 ng L^{-1} for thorium and 0.25, 1.25, and 2.5 ng L^{-1} for uranium. The results of the recovery studies for thorium and uranium in synthetic laboratory standards are summarized in Table II. The recovery for the thorium measurements using the isotope dilution technique by LA-ID-ICP-MS varied between 97 and 104%, meaning that the accuracy of this analytical technique for Th determination at the ng L^{-1} level in a urine matrix was 4% and better. The recovery for uranium determination in dried urine at the low ng L^{-1} level by LA-ID-ICP-MS varied between 87 and 92%. The precision of the isotope dilution technique in LA-ICP-MS (between 1 and 5%) was slightly better for uranium than for thorium.

The accuracy and precision of LA-ICP-MS measurements for uranium and thorium at the ultratrace concentration levels was studied in freeze-dried urine standard reference material NIST 2670a. Figure 1 demonstrates the measured concentrations of U and Th for several repetitions of the analysis. Whereas the measured concentration of uranium in freeze-dried urine was determined as 0.103 ± 0.007 µg L^{-1} (certified concentration: 0.102 ± 0.002 µg L^{-1}), thorium at a significantly lower concentration was found to be 0.0053 ± 0.0007 µg L^{-1}, displaying excellent agreement with the certified value of 0.0053 ± 0.001 µg L^{-1}.

Comparison of Calibration Strategies in LA-ICP-MS

For evaluation of the quantification methods (external calibration using synthetic laboratory standards and isotope dilution analysis), urine samples doped with an enriched uranium isotope standard solution ($^{235}U/^{238}U = 17.34$) and ^{230}Th (0.3 µg L^{-1}), or with a thorium isotope-mixed solution ($^{230}Th/^{232}Th = 3.64$), were homogenized, dried, and investigated. The results of uranium and thorium determination in urine matrix by LA-ICP-MS using external calibration and isotope dilution calibration in LA-ICP-MS are summarized in Table III. The uranium concentration measured at 30 ng L^{-1} was found to be lower in LA-ICP-MS than in ICP-MS after microwave digestion due to possible contamination during sample preparation with the microwave. The thorium concentration in the urine matrix, which was one order of magnitude lower than uranium, was measured with 3.44 and 3.53 ng L^{-1}. This is in good agreement with the isotope dilution technique using ^{230}Th spike and the $^{230}Th/^{232}Th$ isotope-mixed solution for spiking the urine investigated. This result also agrees with the result determined by ICP-MS after microwave-induced digestion. The precision (RSD - relative standard deviation, n=3) of LA-ICP-SFMS measurements of thorium concentration at the low ng L^{-1} level was better than 10%. A significant improvement of precision in LA-ICP-MS for micro-local analysis was observed using the Nd-YAG laser from Bioptic (Berlin, Germany) (18).

TABLE II
Results of Recovery Studies for Determination of U and Th in Urine Matrix via Isotope Dilution Measured by LA-ICP-SFMS

Concn of doped thorium (ng L^{-1})	LA-ICP-MS[a] (ng L^{-1})	Recovery (%)	Concn of doped uranium (ng L^{-1})	LA-ICP-MS[b] (ng L^{-1})	Recovery (%)
0.5	0.52 ± 0.012	104	0.25	0.23 ± 0.003	91
1.25	1.25 ± 0.061	100	1.25	1.19 ± 0.05	87
2.50	2.49 ± 0.11	97	2.50	2.32 ± 0.09	92

[a] Isotope dilution using enriched ^{230}Th.
[b] Isotope dilution using enriched ^{235}U isotope standard solution.

Limit of Detection for U and Th Determination by LA-ICP-MS

Table IV summarizes the detection limits for uranium and thorium measured by LA-ICP-QMS (using ELAN 6000) and LA-ICP-SFMS (using ELEMENT). The detection limits for uranium and thorium determination in dried urine at the sub-ng L^{-1} levels are excellent considering the high salt content of the matrix. In general, the detection limits (using the 3 sigma criterion) in LA-ICP-MS in quadrupole ICP-MS are higher in comparison to the more sensitive sector field ICP-MS. The detection limit, e.g., of uranium in LA-ICP-SFMS with 0.1 ng L^{-1}, is the same as found in ICP-SFMS with pneumatic nebulization of digested and diluted urine sample (9). The detection limits in LA-ICP-MS are significantly lower than those of alpha spectrometry (2 to 3 orders of magnitude) (9) which is a more time-consuming technique in sample preparation and measurement. The advantage of LA-ICP-MS is its ability to analyze very small amounts of dried samples (analyzed volume: 1.25 mm^3) without the time-consuming analytical procedures when synthetic laboratory standards for calibration are prepared.

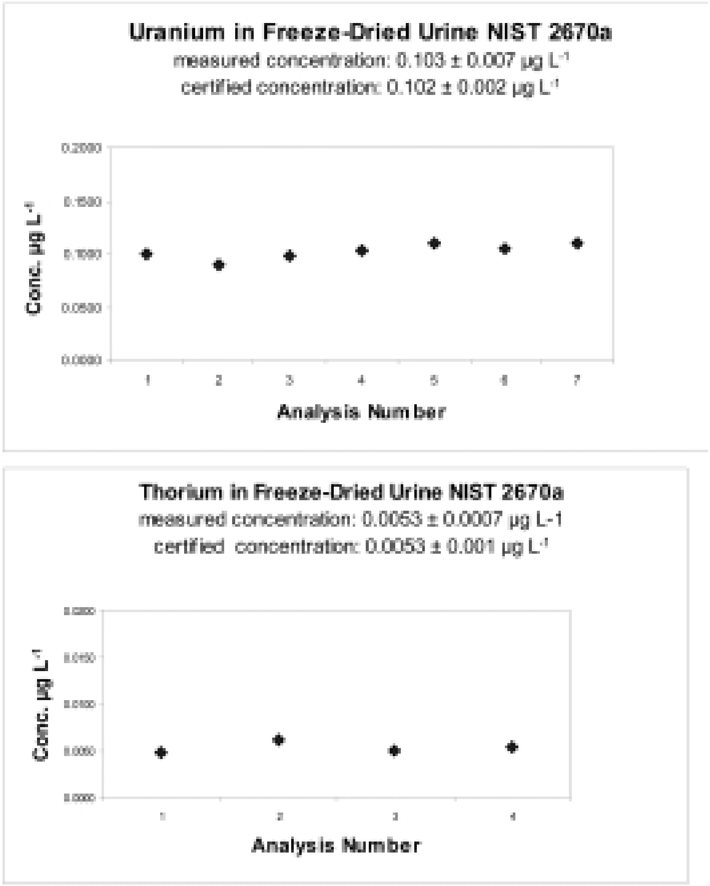

Fig.1. Precision and accuracy of LA-ICP-SFMS for (a) uranium and (b) thorium determination in freeze-dried urine NIST 2670a.

Results of U Concentration and Isotope Ratios in Real Urine Samples Measured by LA-ICP-MS

Due to the low detection limits in LA-ICP-MS, the double-focusing sector field mass spectrometer ELEMENT is the instrument of choice for the determination of uranium concentrations and isotope ratios in the sub-µg L^{-1} range. In Table V, uranium concentrations and $^{235}U/^{238}U$ isotope ratios of 10 real urine samples measured by LA-ICP-SFMS in routine mode are summarized. Thorium concentrations were also measured in real urine samples (see Table VI). The synthetic matrix-matched laboratory standards prepared for external calibration were used for a multitude of routine measurements. The uranium concentration in the examined urine samples varied between 0.066 and 0.167 µg L^{-1}. While in sample number 1, uranium with a natural isotope ratio ($^{235}U/^{238}U = 0.00725$) was detected, all other urine samples showed contamination with depleted uranium. The lowest $^{235}U/^{238}U$ isotope ratio was measured 0.0019. The developed analytical method is interesting for forensic applications where only a small amount of dried urine is available for investigation. First experiments on isotope ratio measurements using a cooled laser ablation chamber coupled to ICP-SFMS demonstrated a significant improvement in precision of isotope ratio measurements of uranium (18).

CONCLUSION

LA-ICP-MS is a powerful and sensitive analytical method for trace and ultratrace analysis and isotope ratio measurements of uranium and thorium in urine samples. The advantage of LA-ICP-MS is its ability to analyze a very small amount of dried sample and offering detection limits in the sub-ng L^{-1} range

TABLE III
Comparison of Different Calibration Techniques for the Determination of U and Th in Urine Matrix by LA-ICP-MS and ICP-MS After Microwave-induced Digestion

	External calibration using synthetic urine laboratory standard [a] (ng L^{-1})	Isotope dilution using an isotope-enriched ^{235}U standard solution[a] (ng L^{-1})	After microwave digestion using external calibration[b] (ng L^{-1})
U	33.8 ± 0.2	31.4 ± 0.2	34.4 ± 0.5

	Isotope dilution using ^{230}Th[a] (ng L^{-1})	Isotope dilution using ^{230}Th/^{232}Th isotope-mixed solution[a] (ng L^{-1})	After microwave digestion using external calibration[b] (ng L^{-1})
Th	3.53 ± 0.33	3.44 ± 0.30	3.32 ± 0.46

[a] Measured by LA-ICP-SFMS; [b] measured by ICP-SFMS.

TABLE IV
Detection Limits for U and Th in Urine Measured by LA-ICP-MS

Isotope	LA-ICP-QMS (ng L^{-1})	LA-ICP-SFMS (ng L^{-1})
^{238}U	6	0.1
^{232}Th	0.4	0.2

TABLE V
Results of Determination of U Concentration and Isotope Ratio Measurements by LA-ICP-SFMS on Several Urine Samples (n=3)

Sample	U (µg/L)	^{235}U/^{238}U
1	0.128 ± 0.030	0.0073 ± 0.002
2	0.066 ± 0.005	0.0026 ± 0.0002
3	0.130 ± 0.060	0.0036 ± 0.010
4	0.170 ± 0.040	0.0061 ± 0.001
5	0.073 ± 0.002	0.0029 ± 0.0001
6	0.127 ± 0.040	0.0061 ± 0.002
7	0.102 ± 0.020	0.0067 ± 0.001
8	0.163 ± 0.020	0.0024 ± 0.0003
9	0.167 ± 0.060	0.0037 ± 0.001
10	0.146 ± 0.040	0.0019 ± 0.004
Table value		0.00725

TABLE VI
Results of Determination of Th Concentration by LA-ICP-SFMS on Several Urine Samples (n=3)

Sample	Th (µg/L)
1	4.38 ± 0.26
2	7.22± 0.08
3	3.86 ± 0.17
4	8.34 ± 0.02
5	8.86 ± 0.49
6	19.9 ± 0.1
7	12.2 ± 0.1
8	14.1 ± 0.1

without requiring the time-consuming sample preparation steps, e.g., for use in forensic science applications.

For the further development of LA-ICP-MS into a routine analytical technique, a new experimental arrangement of solution-based calibration will be developed at our laboratory (19).

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Multielemental Characterization of Nickel by Glow Discharge Quadrupole Mass Spectrometry

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ABSTRACT

The assessment of nickel purity used in the preparation of Ni-based super-alloys has been carried out through multielemental analysis by Glow Discharge Quadrupole Mass Spectrometry. Relative Sensitivity Factor (RSF) values generated from certified iron matrix reference samples (NIST 1761 and 1762 low alloy steel) were found to be suitable for the computation of trace element concentrations.

Different wet chemical procedures were also carried out for the determination of different trace element constituents of the sample. The GD-QMS results were compared with those obtained through wet chemical methods. The GD-QMS results are in good agreement with those obtained from wet chemical procedures. A better assessment of nickel metal purity was achieved through GD-QMS. A variety of molecular ions formed through the reaction of nickel (matrix) with the discharge gas (argon) and other elements were observed.

INTRODUCTION

High purity nickel has been widely used as a major raw material in the manufacture of Ni-based super-alloys. These alloys are utilized for various applications such as advanced aero-engine, industrial, and marine applications (1). Advanced aero-engine super-alloys are designed almost to their performance limits by alloying with a number of at least 10 elements for optimum alloy characteristics. Contamination with unwanted elements from either raw materials, the melting crucible, or other refractory linings can affect the properties and performance of engine parts (2–4). Therefore, it is essential to develop analytical techniques for the accurate determination of impurity levels at every processing step starting from raw materials. As the nickel metal is the major component, many impurities in Ni-based super-alloy can come from the nickel metal used. Thus it is essential to determine the purity and levels of other trace constituents of nickel metal.

The impurity specifications of super-alloy (nickel, etc.) demand an overall multielemental the determination wherein some elements, even at levels of 0.5 mg kg^{-1}, are known to be detrimental to the performance of the super-alloy materials (4,5).

There are many analytical techniques developed for determination of trace constituents in metals. The solution-based multielemental techniques, such as inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS), require the separation of matrix/constituent elements to minimize interferences and signal suppressions. Chemical separation of the matrix from all other minor or trace constituents is not possible in a single step. Many separation procedures found in literature are suitable only for a group of elements at a time. Thus, trace element group separations using co-precipitation, solvent extraction, and ion exchange methods are often adopted.

Direct analysis of solid samples is an attractive choice. Glow discharge mass spectrometry (GD-MS) is a versatile multielemental technique suitable for such analyses since it is possible to carry out the simultaneous determination of elemental concentrations ranging from percentage levels to ultratrace levels with near uniform elemental sensitivity for the majority of elements. GD-MS is free from chemical blanks and requires only minimal sample preparation (6–8). However, quantitative analysis requires the generation of Relative Sensitivity Factors (RSF) which are obtained by using appropriate matrix-matched solid standard reference materials.

The high cost of the high resolution GD-MS systems has restricted their availability to but a few laboratories. The cost-effective quadrupole mass spectrometers (QMS) require extra effort for validating their usability in multielement trace determinations and assessing the purity of metals and alloys.

In this paper, the capabilities of GD-QMS for the multielement determination as well as the assay of the purity of a nickel (matrix) sample are reported. The discharge parameters, interferences due to discharge gas and matrix, use of RSF values generated on iron matrix standards for the multielement analysis of nickel and interfering analytes were investigated. Different wet chemical procedures were used for the determination of many trace constituents including

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the most crucial elements (4,5), i.e., Te, Bi, Tl, Se, and Pb in the nickel sample. A comparison of GD-QMS results with those obtained from various wet chemical methods is given.

EXPERIMENTAL

Instrumentation

A quadrupole GD-MS, Model GQ230 (VG Elemental, U.K.), was used for the analysis. This instrument was located in our Ultra Trace Analysis Laboratory, inside a class 200 clean room. The discharge was operated in current mode where the discharge voltage was adjusted by changing the flow rate of argon gas using a gas inlet valve. The discharge gas was argon of 99.9999% in purity, which is purified further by an in-line metal getter. The system interlock gate was operated using compressed argon gas (65 psi) of 99.9995% in purity. The dual detector system (Model No. 4870V, Galileo Electro-Optics Corp., Sturbridge, MA, USA) utilizes an electron multiplier for ion counting for trace elements (ion currents < 3 x 10^{-13} amp) and a Faraday cup for the measurement of major and minor elements (ion currents > 3 x 10^{-13} amp). The detector system provides a dynamic range of more than eight orders of magnitude (i.e., $1 \times 10^{-18} - 1 \times 10^{-9}$ amp). Instrument control and data acquisition were handled by Glo-Quad software. The peak jump mode was used for the data acquisition.

A 10-mm anode opening diameter flat sample holder was used. Two Teflon® spacers, each with a 1-mm thickness, and a 15-mm inner diameter (towards the sample) and 20-mm (towards anode) were used. The GD cell in the instrument was cryogenically cooled with liquid nitrogen in order to minimize residual gas contaminants.

Mass Calibration

A high-speed stainless steel (HSS) disc containing major elements, ranging from carbon to tungsten as constituents, was chosen for mass calibration. A small amount of solder (tin-lead alloy) material was also embedded into the HSS sample surface to add Sn (mid mass range ~ 120 amu) and Pb (higher mass ~ 208 amu) masses, as well as to get a better linear mass calibration at the entire mass range (lower masses to higher masses). The peak width (ΔM) was adjusted to 0.8 amu for all masses.

Collector Calibration

Collector calibration was done on a daily basis. The Faraday cup and Electron Multiplier detectors were cross-calibrated by measuring the signal intensity at mass 76 ($^{40}Ar^{36}Ar^{+}$). The detector calibration factor was adjusted to 2585±100 by adjusting the High Tension (HT) voltage (DC voltage, maximum of 3000 V, given to the detector as a bias voltage) to the electron multiplier just before starting the actual scanning. The collector calibration was done using a mass step of 0.01 amu and 120 points in peak scan.

Reagents and Containers

Sub-boiled HNO_3 and HCl, prepared using quartz sub-boiling units in our laboratory, were used throughout. Ultra-pure water (>18 MΩ resistivity) was obtained by passing through a combination of a reverse-osmosis (RO) system with mixed-bed ion exchanger and a Milli-Q™ water purification system (Millipore, Bangalore, India).

All stock standards of 1 mg/mL were prepared by dissolving 99.99% pure metals. Standards of required strength (of lower concentration) were prepared by sequential dilutions on a daily basis.

Sample Preparation for GD-QMS

The surface of the nickel sample in the form of a disc (20-mm diameter) was cleaned by isopropanol (using an ultrasonic cleaner) and dried under an infrared lamp. The sample was then inserted into the system and kept under vacuum for two minutes prior to analysis to remove the atmospheric contaminants. The discharge parameters were optimized to obtain maximum ion yield (500 K counts per second) for $^{58}Ni^{+}$. The optimized glow discharge parameters are listed in Table I. The sample surface was etched with GD plasma at 1.2 kV and 3.0 mA for nearly 60 minutes in order to eliminate the surface (embedded) contaminants. The analytical measurements were carried out at a mass step of 0.01 amu with 140 points in peak scan, but the peak integration was carried out at 0.8 amu relative to the center of the peak. The isotopes of the different elements were chosen by taking into account the abundance of the isotopes and the possibilities of interferences. Initially, a single scan for Faraday cup (major and minor elements) and 20 scans for electron multiplier (trace elements) were used for preliminary examination of the impurity levels in the sample. Upon such evaluation, 30–50 scans were chosen for the electron multiplier to improve the signal-to-noise ratio of the elements to be determined at ultratrace levels.

TABLE I
Discharge Parameters Used for the Analysis of Nickel Samples

Parameters	Values
Discharge voltage	1.2 kV
Discharge current	3.0 mA
Argon gas flow rate	39.8 sccm
Temperature during discharge	–180°C
Vacuum at qaudrupole region	5 x 10^{-7} mbar
Resolution	300 ($M/\Delta M$)

Wet Chemical Procedures

Sample Dissolution for Wet Chemical Procedures

Nickel samples in the form of a flat shape were cut into small pieces, etched with dilute HCl, and washed thoroughly with deionized water. Initially, dissolution was attempted in concentrated and dilute hydrochloric and nitric acid media separately. Only dilute nitric acid dissolved the nickel sample very quickly compared to the other media and, thus, was used for the dissolution of the nickel samples for all the wet chemical procedures.

Conversion of Acid Medium for the Nickel Sample

Some of the separation procedures required the sample to be present in the HCl medium. Hence, the sample present in the nitric acid medium was converted as follows: The nitric acid was evaporated to near dryness. Then, HCl of required molarity (depending on the separation procedure selected) was added, and evaporated to near dryness. The latter step was repeated in order to completely eliminate even traces of nitric acid. This conversion step took less time than for direct the dissolution of the nickel sample in the HCl medium.

Direct Determination of Trace Elements Using ICP-OES

Nickel sample solutions in the nitric acid medium were initially passed directly into ICP-OES at a concentration of 4 mg/mL nickel for the determination of trace constituents using the standard addition calibration method. All critical elements, as well as other trace elements, suffered from spectral line interferences and signal suppressions due to the matrix. With a dilution factor of 2, quantitative results were obtained for some elements (listed in Results and Discussion section) for which there were no spectral interferences due to the nickel matrix.

Matrix Separation Procedures

Ion Exchange Separation

An ion exchange procedure has been reported in the literature (9,10) for the separation of trace levels of nickel from many other elements. In one such procedure, nickel is adsorbed on a strong cation exchanger, and many trace elements are eluted with a solution containing 10% 6M HCl and 90% acetone. The same procedure has been tested for the separation of a nickel matrix from its trace constituents in order to preconcentrate and determine the trace elements.

Preparation of the Ion Exchange Column

A glass column (32 cm x 2 cm i.d.) with a leak-proof stopcock was used. About 21 g of a strong cation exchanger (Seralite SRC-120, 8% cross-linking) in H^+ form of mesh size of 50–100 was loaded after washing with water and soaking for 24 hours in 100 mL of a solution of 10% 6M HCl and 90% acetone. The approximate height of the resin bed was 8.5 cm, and the bed volume was around 26 cm^3. The resin bed was then washed again with a fresh solution mixture. Forty mL of a sample (approximately 150 mg) solution containing 10% 6M HCl and 90% acetone was passed through the column at a flow rate of 0.4 mL/min. Matrix nickel was adsorbed on the top layer of the resin bed as indicated by a thick green color of the layer. The unadsorbed trace elements were eluted with 40 mL of a fresh mixed solution containing 10% 6M HCl and 90% acetone. The acetone was evaporated (using hot plate) from the eluted solution and made up to 25-mL final volume. Process blanks, without the addition of sample material, and sample aliquots spiked with known amounts of trace elements to verify recoveries in each run, were treated similarly. The solutions were analyzed by ICP-OES using the standard addition calibration method. ICP-QMS analysis was carried out with rhodium as internal standard.

Solvent Extraction Using 4M HCl and TBP Solvent

Solvent extraction using Tri-Butyl Phosphate (TBP), as reported in the literature (11–14), indicates that trace elements (i.e., Te and Ga) can be separated selectively by extraction with TBP at various HCl concentrations (1M to 6M). Our experiment was carried out at 4M HCl and good recoveries were obtained for many elements. Hence, this method was adopted for the separation and determination of these trace elements from the nickel matrix.

A sample solution (~ 2 g) present in nitric acid medium was converted into 4M HCl medium and extracted with undiluted TBP solvent twice (1:1, 15 mL each). Nickel was retained in the aqueous phase, and trace elements were extracted into the organic phase. These trace elements were back-extracted twice into the aqueous phase with 4M HNO_3 solution (1:1). The aqueous solution was evaporated to near 1 mL and made up to 25-mL volume with Millipore™ water. Process blanks and sample solutions, spiked with known amounts of trace elements, were treated similarly. These solutions were analyzed by ICP-OES using the standard additions calibration method.

Solvent Extraction Using the Mixture 1M KI + 2M H_2SO_4 and MIBK

Many trace elements such as Cu, Ag, Sn, Pb and Bi were reported to be extracted selectively into Methyl Iso Butyl Ketone (MIBK) solvent from an iodide medium (1M KI + 2M H_2SO_4) (15,16). These trace elements are important elements since they have major effects on the properties of the final alloy. For example, bismuth is reported to be harmful when its concentration (4,5) exceeds 0.5 mg kg^{-1}.

A sample solution (~ 2 g) present in 1M KI + 2M H_2SO_4 was extracted with MIBK solvent twice (1:1, 15 mL each). Nickel was retained in the aqueous phase and the trace elements were extracted into the organic phase. These trace elements were then stripped back into 4M HNO_3 solution twice (1:1). Tin extracted into the organic solvent was also back-extracted into 4M HCl solution twice (1:1). Both solutions were mixed together and evaporated to near 1 mL and made up to 25 mL with Millipore water. Blank and sample solutions spiked with known amounts of trace elements were treated similarly. All solutions were analyzed by ICP-OES using the standard additions calibration method.

Solvent Extraction With MIBK-Benzene Mixture for Thallium Determination

Besides tellurium and bismuth, thallium is also a key impurity with a limit specified (4,5) to be within 0.5 mg kg^{-1} in the final alloy. Therefore, the determination of thallium is also essential and was carried out using the following procedure.

A simple solvent extraction procedure, developed earlier (17) for the determination of thallium in water samples at parts per billion levels, was investigated for the determination of thallium in nickel samples. A sample solution (~3 g) present in 10% HCl was extracted for two minutes with a mixed solution containing 40% MIBK and 60% benzene. The aqueous layer was discarded. The organic layer was shaken with 10 mL of 1% HCl for two minutes in order to strip elements that would interfere with the absorption of Tl from the organic phase. The aqueous layer was discarded. The organic layer was mixed with 0.01% crystal violet indicator (hexamethylenepararosaniline chloride, E. Merck, Darmstadt, Germany) and 10 mL of 10% HCl, and shaken for two minutes. After discarding the aqueous layer again, the organic layer was shaken with 10 mL of 1% HCl. The organic layer was separated and made up to 10 mL with freshly prepared organic solvent mixture. After filtering the organic solvent, the absorption at 582 nm was measured using spectrophotometry. Blanks and sample solutions spiked with known amounts of thallium were treated similarly.

Assay Analysis Using Dimethyl glyoxime (precipitation method)

An aliquot of the nickel sample (approximately 70 mg) was brought into chloride form and the nickel determined by gravimetry, following a standard procedure (18) using Dimethyl glyoxime (DMG) reagent.

RESULTS AND DISCUSSION

The GD-QMS technique is useful for the simultaneous determination of element concentrations ranging from the percentage levels to ultratrace levels in a single run. The quantitative results in GD-QMS require the development of matrix-specific RSF values, calculated from certified reference samples with the same or similar matrix composition of the sample to be analyzed. However, the availability of standard reference materials for high purity nickel, certified for all trace elements, is limited.

In the GD plasma, the atomization and ionization processes take place at two different regions. This phenomenon makes elemental ion yields more or less independent of matrix element. This advantage has been exploited in this analysis. Based on our earlier experience in the analysis of high purity antimony (19) and high purity cadmium (20), the suitability of RSF values generated from certified iron matrix reference materials for the multielement analysis of high purity nickel was investigated.

Thus, a set of RSF values were generated from iron matrix SRMs (NIST 1761 and 1762) and used for the determination of final concentrations of trace elements in nickel matrix samples. In order to check the accuracy of these results, the wet chemical procedures discussed in the Experimental section were carried out for the determination of many trace elements in nickel samples, including the most critical elements such as Bi, Te, Tl, Se, and Pb.

Performance of the Wet Chemical Procedures

Direct Analysis by ICP-OES

The direct analysis of a nickel sample solution (containing 2 mg/mL nickel) by ICP-OES was found suitable for the analytes B, Ti, Mn, Fe, and Cu. These analytes were found to be free from interferences and were quantified using the standard addition calibration method. The results are listed in Table II.

Ion Exchange Method

The separation procedure, using a strong cation exchanger with the solution containing 10% 6M HCl and 90% acetone as the eluent, provided very good separation of the matrix from the following elements (% recoveries given in parentheses): P (99%), Cu (101%), Ga (95%), Mo (67%), W (67%), Re (91%), Pb (97%). The matrix separation was found to be ~99.88%. Recovery of the selenium was found to be low (42%). The concentrations of these elements (P, Cu, Ga, Se, Mo, W, Re, Pb) were computed using the standard addition calibration method by ICP-OES and ICP-QMS. The results are listed in Table II.

This experiment has shown that the procedure adopted and used earlier for the separation of only trace level nickel from other trace elements, can also be used for the separation of matrix nickel from the above trace constituents. This method is also useful for the quantification of trace elements (P, Cu, Ga, Se, Mo, W, Re, and Pb) from the nickel matrix sample.

TBP Procedure

The separation method using TBP and 4M HCl gave a significant separation for the analytes V, Fe, Ga, and Te from the nickel matrix, which was retained in the aqueous phase only. These elements extracted into TBP solvent were back-extracted into the aqueous medium using 4M HNO_3. With this procedure, the matrix separation was found to be 99.83%. The % recoveries for these elements were V (75%), Fe (80%), Ga (76%) and Te (73%). The lesser recoveries were probably due to matrix suppression because of the high amount of nickel present in the solution. The final concentrations of these elements were calculated using the standard additions calibration method by ICP-OES and are listed in Table II.

KI+H_2SO_4 Procedure

The separation method using MIBK and 1M KI + 2M H_2SO_4, was found to be useful for the separation of Cu, Sn, Pb, and Bi present at trace and ultratrace levels in the nickel matrix sample. Using this procedure, matrix separation was found to be 98.15%. The % recoveries for these elements are: Cu (74%), Sn (87%), Pb (83%), Bi (73%). Final concentrations for the elements were computed using the standard additions calibration method. The results are listed in Table II.

Benzene and MIBK Mixture

The separation method using the MIBK and benzene mixture was found to be quite suitable for the determination of ultratrace levels of thallium in the nickel sample. The final concentration of thallium was computed using the standard additions calibration method and spectrophotometry. The results are listed in Table II.

Assay Analysis Using DMG

The assay of nickel, determined through the precipitation method using DMG, was 99.3±0.2%.

GD-QMS Results

Discharge Parameters

The influence of discharge current on the ion yield indicated (21) that the optimum discharge current is 3.0 mA (with a discharge voltage of 1.0 kV) for efficient sample cooling with reasonably low molecular ion interferences and maximum ion beam intensity. The 3.0 mA current results in the maximum ion beam intensity, the lowest level for the atmospheric gases (C^+, N^+, O^+) and the gas matrix combinations, and a drastically reduced contribution of molecular species (e.g., matrix dimers, argon dimers, argides, etc.). Thus, the discharge current was fixed at 3.0 mA using constant current mode. The discharge voltage of 1.2 kV resulted in a maximum ion intensity for $^{58}Ni^+$. Therefore, the discharge conditions of 1.2 kV and 3.0 mA were used for the analysis of the nickel sample.

Spectral Interferences in GD-QMS

Interferences Due to Nickel Matrix and Other Major Elements

Nickel has five natural isotopes: ^{58}Ni (abundance: 68.27%), ^{60}Ni (26.10%), ^{61}Ni (1.13%), ^{62}Ni (3.59%), and ^{64}Ni (0.91%). The higher abundance isotopes of nickel (58, 60, 62) produce molecular adducts in the GD plasma. Doubly charged ions of these isotopes ($^{58}Ni^{+2}$, $^{60}Ni^{+2}$, $^{62}Ni^{+2}$) interfere with silicon isotopes at masses 29 and 30 and with phosphorus at mass 31. The molecular ions due to the dimers of nickel, $^{58}Ni_2^+$, $^{58}Ni^{60}Ni^+$, $^{60}Ni_2^+$ (shown in Figure 1) were also noticed at masses of 116, 118, 120, respectively. The higher intensity at mass 120 as seen in Figure 1 is possibly due to additional isobaric interferences of the argon trimer, $^{40}Ar_3^+$. Many isotopes of tin are interfered with at these isobars.

TABLE II
Comparison of GD-QMS Values for Trace Elements in the Ni Sample With Wet Chemistry Values

Element (Isotope)	Wet Chemistry (mg kg^{-1})	GD-QMS Value (mg kg^{-1})
^{11}B	<8.30	7.97 ± 2.25
^{31}P	4.93	35.00 ± 5.79*
^{48}Ti	0.44	0.65 ± 0.17
^{51}V	0.24	0.19 ± 0.02
^{55}Mn	0.86	2.25 ± 0.05*
^{56}Fe	14.08	37.37 ± 1.81*
^{63}Cu	5.05	4.94 ± 0.23
^{71}Ga	0.47	1.53 ± 0.13*
^{82}Se	1.90	2.56 ± 0.12
^{95}Mo	0.31	0.45 ± 0.05
^{117}Sn	<2.31	2.17 ± 0.10
^{130}Te	<0.73	0.43 ± 0.04
^{186}W	0.46	0.22 ± 0.08
^{187}Re	0.06	0.07 ± 0.01
^{205}Tl	0.06	0.20 ± 0.03
^{208}Pb	1.83	1.79 ± 0.15
^{209}Bi	0.25	0.25 ± 0.02

*Spectral interference.

-- B, P, Ti, V, Mn, Fe, Cu, Ga, Sn, Te, Pb, Bi are determined by ICP-OES.

-- Se, Mo, W, Re are determined by ICP-QMS and Tl by spectrophotometry.

Molecular adducts (ions) with the monomers, dimers, and even trimers of discharge gas (argon) with the major isotopes of nickel (58 and 60) were also noticed in the spectrum. Isobars thus noticed were:
$^{58}Ni^{40}Ar^+$ (mass 98), $^{60}Ni^{40}Ar^+$ (mass 100), $^{58}Ni^{40}Ar_2^+$ (mass 138), $^{60}Ni^{40}Ar_2^+$ (mass 140), $^{58}Ni^{40}Ar_3^+$ (mass 178), and $^{60}Ni^{40}Ar_3^+$ (mass 180).

The intensities of these adducts are shown in Figure 1. Hence, some of the isotopes (^{98}Mo, ^{98}Ru, ^{100}Mo, ^{100}Ru, ^{138}Ba, ^{138}La, ^{140}Ce, ^{178}Hf, ^{180}Ta, and ^{180}W) suffer from these isobaric interferences in quadrupole-based GD-MS for the analysis of nickel metal. The level/extent of interference (apparent concentrations) due to these adducts on the isotopes ^{98}Mo, ^{100}Mo, ^{138}Ba, ^{178}Hf, and ^{180}Hf are estimated to be around 0.64%, 0.61%, 7 mg kg^{-1}, 658 mg kg^{-1}, and 157 mg kg^{-1}, respectively.

The GD-QMS analysis of the nickel sample showed that the sample contained C, N, O, and Cl. The ion beam ratio (IBR) concentrations of carbon, nitrogen, oxygen, and chlorine in the nickel sample were found to be 456 mg kg^{-1}, 185 mg kg^{-1}, 350 mg kg^{-1}, and 440 mg kg^{-1}, respectively. Some molecular interferences due to the above elements were also observed. The isotope of iron at mass 56 is interfered with by the molecular ion, ^{40}Ar^{16}O^{+}, and the single manganese isotope at mass 55 is interfered with by the molecular ion, ^{40}Ar^{14}N^{1}H^{+}. The molecular ion, ^{37}Cl^{16}O$_2^{+}$, interferes with gallium at m/z 69. The molecular ion formed with carbon and hydrogen, ^{58}Ni^{12}C^{1}H^{+}, interferes with the gallium isotope at mass 71. Another molecular ion, ^{58}Ni^{14}N$_2^{+}$ at mass 86, which interferes with strontium, was also observed. Besides these, the other molecular interferences, ^{58}Ni^{1}H^{+} and ^{40}Ar^{35}Cl^{+} on ^{59}Co and ^{75}As, were also observed.

Alternative isotopes with minimum or no isobaric interferences were used for the quantitation of these elements for which the isotopes of highest abundance suffered from spectral interferences. That is, isotope 117 for Sn, 95 for Mo, 137 for Ba, and 177 for Hf were used for the quantification in GD-QMS.

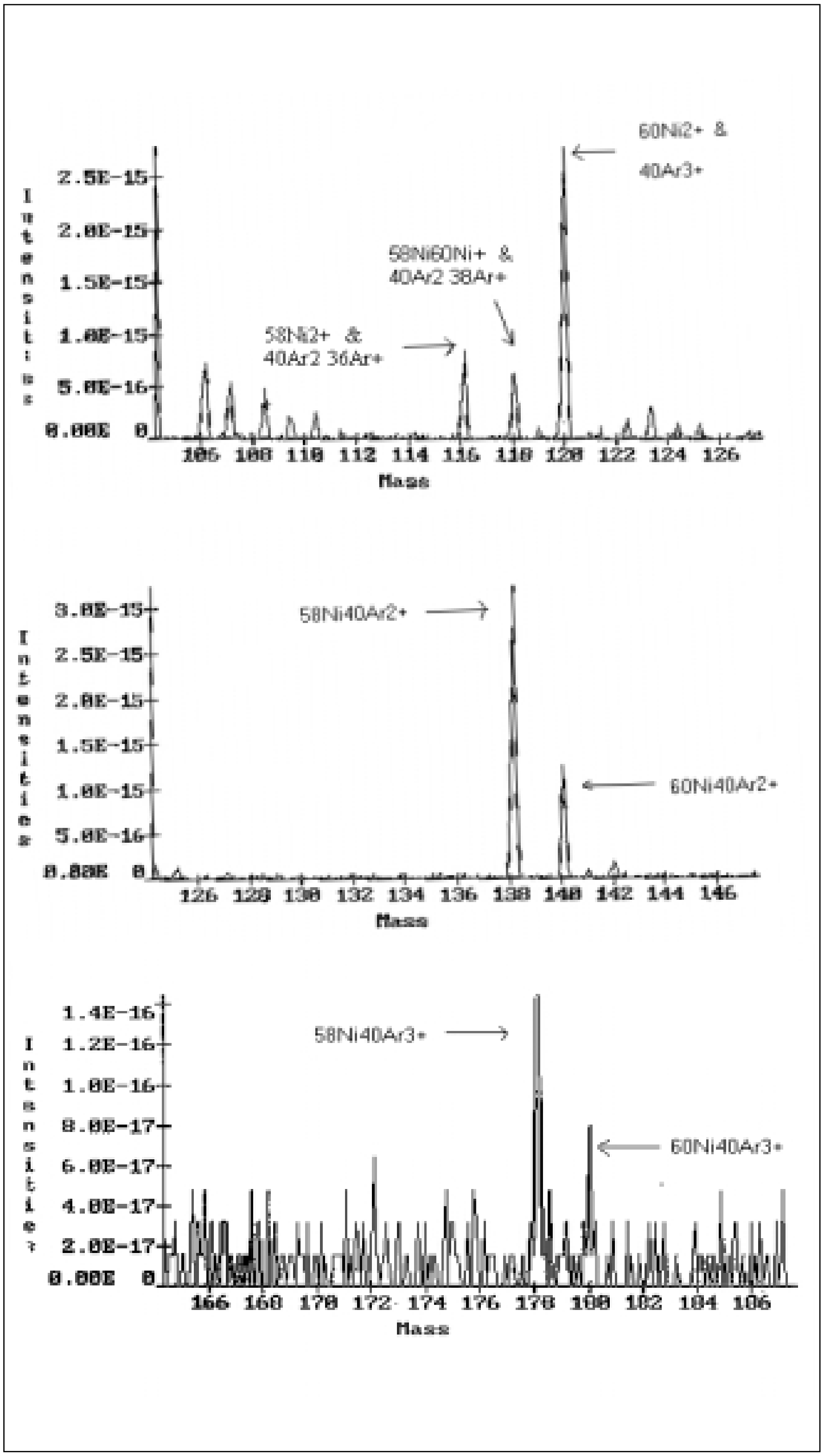

Fig. 1. GD Quadrupole Mass Spectrum for molecular adducts due to nickel matrix and discharge gas (argon) at a mass resolution of 300. Integration time is 40 ms.

Relative Sensitivity Factor and Quantitation in GD-QMS

The raw counts of each impurity element's isotope present in the nickel sample were normalized to 100% from their relative abundances. The ion beam ratio (IBR) values were generated by taking the ratio of abundancies corrected raw counts of each element to the total sum of corrected raw counts of all the elements, including the nickel isotope. The Relative Sensitivity Factor is the ratio of true concentration to the ion beam ratio (IBR).

The IBR data on Ni were corrected using RSF values generated from Low Alloy Steel NIST SRM 1761 and SRM 1762 (disk forms). The RSF value for nickel is 1.49 with respect to Fe. For the rest of the elements (not certified in above SRMs), the RSF values given by the instrument manufacturer with respect Fe matrix were used. The final computed concentrations are listed in Table II (along with wet chemistry values) and Table III (only GD-QMS values).

Comparison of GD-QMS Results

The GD-QMS results were compared with the results obtained by wet chemical methods. The results presented in Table II show extremely good agreement for B, Ti, V, Cu, Se, Mo, Sn, Te, W, Re, Tl, Pb, and Bi.

The higher GD values noted for some other elements (P, Mn, Fe, and Ga) are mainly due to isobaric interferences. The doubly charged ion of nickel, $^{62}Ni^{+2}$, interferes at mass 31 of phosphorus. The molecular ion of argon with nitrogen and hydrogen, $^{40}Ar^{14}N^{1}H^{+}$, interferes at mass 55 of manganese. Hence, phosphorous and manganese, both mono-isotopic elements, could not be determined accurately by GD-QMS.

In the case of iron, the higher GD value is due to the molecular ion, $^{40}Ar^{16}O^{+}$, formed with the argon and oxygen, which interfere iron at mass 56. The other isotopes of iron are even more severely interfered with by other molecular ions. Hence, only mass 56 was chosen for iron quantification and to identify the relative extent of interferences. The molecular interferences, $^{37}Cl^{16}O_2^{+}$ and $^{58}Ni^{12}C^{1}H^{+}$, affect the accurate measurement of gallium in nickel by GD-QMS. The extent of these interferences on P, Mn, Fe, and Ga are about 30 mg kg^{-1}, 1.4 mg kg^{-1}, 23 mg kg^{-1}, and 1 mg kg^{-1}, respectively, computed based on the corresponding wet chemistry values. The other impurity levels of the nickel obtained by GD-QMS, but not cross-validated by any other technique, are given in Table III. A list of elements that could be determined using GD-QMS and those that would require wet chemical methods are listed in Table IV.

The analyzed nickel metal sample was synthesised by an electro-refining process. The impurity levels in refined nickel synthesized from both processes (carbonyl-refining and electro-refining) reported by authors (22) are also listed in Table V. A comparison of the GD-QMS values with the reported values of nickel (electro-refining process) shows that the GD-QMS values are close to the reported values also.

Based on the GD-QMS analysis, the purity of the nickel sample was found to be 99.91%. This assessment was done based on the actual determination of many trace element concentrations. Their total concentration was subtracted from 100% rather than by the assay of matrix element alone as in the wet chemical procedure (99.3%). This indicates that a better assessment to the purity of nickel metal can be obtained by GD-QMS.

TABLE III
Other Trace Impurities Determined (only) by GD-QMS

Element	GD-QMS (mg kg^{-1})
^{34}S	11.44
^{45}Sc	2.13
^{52}Cr	23.62
^{59}Co	105*
^{66}Zn	2.70
^{75}As	25.42*
^{85}Rb	0.19
^{88}Sr	0.07
^{89}Y	0.01
^{90}Zr	1.24
^{103}Rh	0.05
^{109}Ag	0.85
^{114}Cd	2.18
^{121}Sb	0.73
^{133}Cs	0.72
^{137}Ba	0.57
^{177}Hf	0.09
^{181}Ta	0.23
^{195}Pt	0.35
^{197}Au	1.19
^{202}Hg	0.04

* Molecular interferences.

TABLE IV
Elements Determined by Different Techniques

Elements Cross-validated by Wet Chemical and GD-QMS Techniques	Elements Interfered in GD-QMS But Determined by Wet Chemical Techniques	Elements Determined Only by GD-QMS Technique
B, Ti, V, Cu, Se, Mo, Sn, Te, W, Re, Pb, Tl, Bi	P, Mn, Fe, Ga	S, Sc, Cr, Zn, As, Rb, Sr, Y, Zr, Rh,Ag, Cd, Sb, Cs, Ba, Hf, Ta, Pt, Au, Hg

TABLE V
Impurity Levels in Refined (Carbonyl-refining and Electro-refining) Nickel[a]

Element	Carbonyl-refining (mg kg^{-1})	Electro-refining (mg kg^{-1})
Sb	0.5	0.5
As	0.2	2
Bi	0.1	0.1
Cd	0.2	0.2
Co	3	2
Cu	5	1
Fe	100	3
Mn	NR[b]	0.5
Pb	0.2	1
P	0.5	1
Se	1	0.2
Ag	0.2	0.5
S	7	5
Ta	1	0.3
Te	0.5	0.5
Tl	0.1	0.5
Sn	0.5	0.2
Zn	0.5	1

[a] Published by Bromley et al. (22).
[b] NR=not recorded.

CONCLUSION

GD-QMS has been applied for the multi-element determination and purity assessment of a nickel sample. The RSF values generated from a certified iron matrix standard were found to be suitable for the analysis of a nickel matrix sample at trace and ultratrace levels, including the critical elements Bi, Te, Tl, Se, and Pb. A comparison of the GD results with the corresponding wet chemical values shows very good agreement between the two techniques.

The assay of purity by GD-QMS, based on the actual measurement of trace elements, provides a better basis for purity assessment. In addition, direct measurement by GD-QMS presents several advantages over conventional wet chemical methods in reducing the time-consuming chemical separation steps. GD-QMS, though requiring a compromise on the mass resolution and cost, was found to be quite useful in the analysis of a nickel sample of moderate purity (3N–4N), including the determination of certain 'soft' elements, that are reported to be critical for the properties of Ni-based super-alloys.

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As, Bi, Se(IV), and Te(IV) Determination in Acid Extracts of Raw Materials and By-products From Coal-fired Power Plants by Hydride Generation-Atomic Fluorescence Spectrometry

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ABSTRACT

Simple and sensitive procedures were developed for the determination of As, Bi, Se and Te in coal, fly ash, and slag samples involving microwave acid extraction and hydride generation atomic fluorescence spectrometry (HG-AFS). Hydrides were generated from hydrochloric acid medium using sodium tetrahydroborate. HG-AFS methods for As, Bi, Se and Te determinations were optimized by using experimental designs. The hydrochloric acid and sodium tetrahydroborate concentrations were in the 2.6–4.8 mol L^{-1} range and between 0.7–1% for all the metals studied. A microwave acid extraction procedure using aqua regia was used for solid samples treatment. The accuracy was studied using SRM 1632c (coal) and SRM 1633a (coal fly ash) reference materials. Detection limits in the 0.02–1.37 µg g^{-1} range were achieved. The methods were applied to several coal, fly ash, and slag samples from a coal-fired power plant.

INTRODUCTION

It is well known that coal-fired power plants produce large quantities of waste during coal combustion. The coal and ash particles generated in these procedures contain many potentially toxic compounds as organic compounds and trace elements (1). Some coals contain potentially toxic trace metals such as arsenic, mercury, and selenium, which are emitted to the atmosphere during the burning process and can become hazardous to human health. Thus, the determination of trace metals in coal and its by-products is very important.

Hydride generation atomic fluorescence spectrometry (HG-AFS) is a highly suitable technique for trace metal determination because of its high sensitivity, low sample volume, low reagent consumption, wide linear range, and the simple equipment required (2–11). The analytical methodologies most often used for trace metal determination in coal and coal combustion products are those that do not need a previous sample pre-treatment such as INAA (12), RNAA (13), XRF (14), and XAFS (15). These methods result in slight sample contamination but offer high-speed analysis. However, they require instrument calibration using reference materials, which is a very time-consuming process. Furthermore, these techniques require expensive instrumentation not available in many laboratories. In addition, the sensitivity achieved is not so high. Another group of methods, which includes atomic absorption spectrometry (AAS) (16-18), hydride generation atomic absorption spectrometry (HG-AAS) (19,20) and inductively coupled plasma mass spectrometry (ICP-MS) (21,22), requires a previous acid extraction procedure and results in very good detection limits. Measurements by HG-AFS or HG-AAS have greater tolerance to matrix interferences; however, these techniques require the sample to be in solution.

Microwave-assisted extraction methods using different acid mixtures for different kinds of samples have been proposed by several authors (5, 22–28). To achieve an adequate trace metal extraction from complex samples such as coal, fly ash, and slag samples, several authors employed aqua regia/HF mixtures. However, the use of HF mixtures results in poor accuracy when hydride generation techniques are used. This is due to the interference of fluorides in the reduction of As to arsine (29). The use of boric acid, which complexes the fluorides, is not able to remove fluoride interference (30).

The aim of this work was to develop methods for As, Bi, Se, and Te determination by hydride generation atomic fluorescence spectrometry in coal, fly ash, and slag samples collected from power plants in Spain. In general, samples have been extracted using an aqua regia mixture and microwave energy.

EXPERIMENTAL

Instrumentation

A Milestone MLS 1200 microwave oven (Sorisole, Italy), programmable for time and microwave power, was used for the metals extraction from the samples.

A PSA 10004 continuous-flow vapor system (PS Analytical, Sevenoaks, Kent, UK), equipped

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with a B-type gas-liquid separator and a PermaPure drier tube (PS Analytical,) was used for hydride generation. An Excalibur Millenium atomic fluorescence detector PSA 10.055 (PS Analytical), equipped with a boosted discharge hollow cathode lamp (BDHCL) (Superlamp; Photon, Victoria, Australia)was used as the AFS excitation source, a hydrogen diffusion flame as the atomization cell, and multi-reflectance filters (PS Analytical) to achieve isolation and reduction of flame emission. The instrumental conditions for the As, Bi, Se and Te determinations are listed in Table I.

Standard Solutions and Reagents

The following standard solutions were used:
As(III) chloride and Se(IV) chloride stock standard solution (1000 mg L^{-1}) (Panreac, Barcelona, Spain); As(V) (1000 mg L^{-1}) prepared from $Na_2HAsO_4 \bullet 7H_2O$, 98.5%, (Merck, Darmstadt, Germany); and bismuth and tellurium stock standard solution (1000 mg L^{-1}) (Panreac). Sodium tetrahydroborate (Aldrich) dissolved in 0.5% (w/v) of sodium hydroxide (Panreac) was used as the reducing solution; prepared daily and filtered before use. Hydrochloric acid solution was prepared from hydrochloric acid solution, 37% (Panreac). Hydrochloric acid and nitric acid, 36.5–38% and 69–70%, respectively (Baker, Phillipsburg, NJ, USA) were used for sample extraction.

All solutions were prepared from analytical reagent grade chemicals using ultrapure water, with a resistivity of 18 MΩ/cm, obtained from a Milli-Q™ water purification system (Millipore, Bedford, MA, USA).

Standard reference materials SRM 1632c (coal) and SRM 1633a (coal fly ash) from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) were used for the accuracy study.

TABLE I
Continuous Flow HG-AFS Operating Conditions for As, Bi, Se(IV), and Te(IV) Determination

Atomic Fluorescence Spectrometer Parameters				
	As	Bi	Se	Te
Wavelength (nm)	193.7	223.1	196.0	214.3
Primary current (mA)	27.5	12.0	20.0	15.0
Boost current (mA)	35.0	10.0	25.0	17.5
Gain	10	100	100	100
Delay time (s)	20	10	10	20
Measurement time (s)	74	50	50	20
Memory time (s)	40	40	40	40
Measurement mode	Height	Height	Height	Height
Continuous-flow Hydride Generation				
HCl (mol L^{-1})	4.8	4.8	2.6	3.0
$NaBH_4$ [%(w/v)]	1.0	0.7	0.7	0.8
Sample/HCl flow rate (mL min^{-1})	10	10	10	10
$NaBH_4$ flow rate (mL min^{-1})	7.5	5.0	7.5	5.0
Ar flow rate (mL min^{-1})	300	300	300	300

Microwave Acid Extraction Procedure

A 0.4000-g sample was weighed and placed into PTFE closed bombs. Then 6 mL and 2 mL of concentrated HCl and HNO_3 (aqua regia extraction) were added and the mixture subjected to microwave energy. The microwave energy program is listed in Table II. After microwave extraction, the acid liquid phase was filtrated (Whatman No. 40 paper filter). The solutions were made up to 25-mL volume with ultrapure water and kept in polyethylene bottles at 4°C until measurement.

Procedure for Measurements

The methods involve the continuous generation of As or Bi or Se or Te hydrides from acid extracts of solid samples. These samples were diluted with HCl (to a final HCl concentration of 4.8, 4.8, 2.6, and 3.0 mol L^{-1} for As, Bi, Se, and Te determination, respectively), then a reducing solution was added [1.0, 0.7, 0.7, and 0.8% (m/v) $NaBH_4$ for As, Bi, Se(IV), and Te(IV) determination, respectively]. The evolved hydrides were transferred to the atomic fluorescence detector using an argon flow rate of 300 mL min^{-1}. The operating conditions for HG-AFS are listed in Table I.

TABLE II
Microwave Acid Extraction Program

Step	Time (min)	Power (W)
1	5	300
2	3	650
3	3	450
4	3	0

Statistical Treatment of Data

For experimental design modeling, programs from Statgraphics Plus 4.0 routine (Statgraphics Graphics Corporation, USA) were used.

RESULTS AND DISCUSSION

Optimization of Operating Conditions Using Experimental Designs

Several parameters such as concentrations and flow rates of hydrochloric acid and sodium tetrahydroborate solution can affect the hydride generation efficiency. In addition, the influence of delay on the atomic fluorescence signal due to analysis time and memory time was also considered. Table III lists the upper and lower values of each factor studied. A 2^8*3/64 Plackett-Burman design (31), with 12 non-randomized runs and three degrees of freedom, was applied to select the significant variables, which were optimized by means of central composite designs or by using univariate approaches.

As Determination

The significant parameters obtained for As determination were sodium tetrahydroborate concentration, sodium tetrahydroborate flow rate, and analysis time, resulting in standardized effects (P=95%) higher than 3.2. These parameters were optimized using a 2^3+star central composite design. To help visualize the optimum from the central composite design, the contours of the response surface were plotted in Figure 1. In the contour plot, lines of constant response are drawn in the x_1, x_2 plane. Each contour corresponds to a particular height of the response surface. The results obtained (Figure 1) show an optimum value of 1% (m/v), 7.5 mL min^{-1}, and 74 s for sodium tetrahydroborate concentration, tetrahydroborate sodium flow rate, and analysis time, respectively.

Bi Determination

The sodium tetrahydroborate flow rate was the significant parameter, resulting in standardized effects higher than 3.2 (P=95%). These variables were optimized using a univariate approach. The optimum value was 5 mL min^{-1} .

TABLE III
Experimental Field Definition for the Plackett-Burman and Central Composite Designs

Key	Parameter	Low (–)	High (+)
A	HCl concentration (mol L^{-1})	3	4.8
B	$NaBH_4$ concentration [%(m/v)]	0.7	1
C	$NaBH_4$ flow rate (mL min^{-1})	5	10
D	Delay time (s)	10	20
E	Analysis time (s)	20	50
F	Memory time (s)	40	70
G	Dummy factor	-	+
H	Dummy factor	-	+

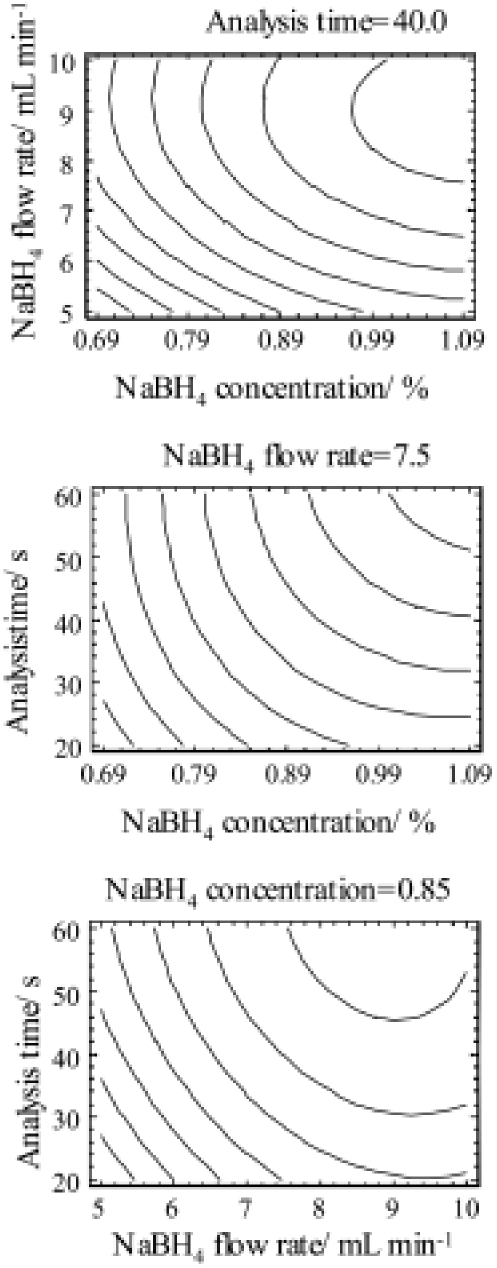

Fig. 1. Contours plot of the response surface for central composite design in As determination.

Se(IV) Determination

The significant parameters obtained for Se(IV) determination were hydrochloric acid concentration and sodium tetrahydroborate flow rate, resulting in standardized effects (P=95%) higher than 3.2. The optimum values obtained using a 2^2+star central composite design were 2.6 mol L^{-1} and 7.5 mL min^{-1} for hydrochloric acid concentration and sodium tetrahydroborate flow rate, respectively (Figure 2).

Te(IV) Determination

For the Te determination, the significant variables were sodium tetrahydroborate concentration and sodium tetrahydroborate flow rate (standardized effects higher than 4.3, P=95%). The optimum values of 0.8% (m/v) and 5 mL min^{-1} for sodium tetrahydroborate concentration and sodium tetrahydroborate flow rate, respectively, were optimized by using a 2^2+star central composite design (Figure 3).

For this study, the optimum values listed in Table I were used. The fixed values for the significant parameters (results from the Plackett-Burman designs) are also given in Table I.

Analytical Figures of Merit

Calibration and standard addition equations were obtained for the aqueous standard solutions of the digested coal, fly ash, and slag samples spiked with 0.5, 1.0, and 2.0 mg L^{-1} of Bi; or 0.5, 1.0, and 2.0 mg L^{-1} of Te; or 1.0, 2.0, and 4.0 µg L^{-1} of Se; or 25, 50, and 100 ng L^{-1} of As. The slopes of the calibration and standard addition graphs are similar (after application of the *t*-test resulting in a confidence level of 95%); which shows that matrix effects are not significant (Table IV).

Accuracy of the results was studied using the two standard reference materials SRM 1632 coal and SRM 1633 coal fly ash (Table V). These materials are not certified or indicative for Te determination. For Bi, the value obtained analyzing the reference material is indicative. An ANOVA test was performed to compare the certified and found concentration values. Results from the ANOVA test showed that there were no statistically significant differences between the means for all metals and both references materials analyzed. Thus, the results obtained are in agreement with the certified values.

TABLE IV
Calibration and Addition Slopes (L µg^{-1}) for As, Bi, Se, and Te Determination

Element	Gain	Calibration Slopes	Standard Addition Slopes Coal	Fly Ash	Slag	Coke
As	1	5.54	1.75	1.31	-	–
	10	50.0	-	-	52.08	49.70
Bi	1000	30.97	34.12	33.30	32.90	–
Se	10	46.90	46.80	49.70	46.80	53.80
Te	1000	37.40	19.0	46.55	27.97	–

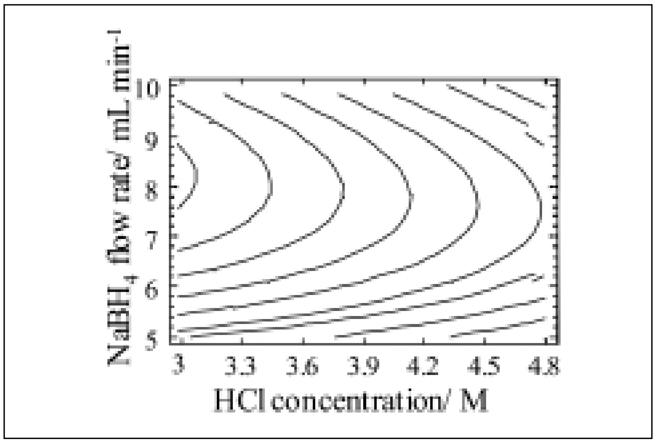

Fig. 2. Contours plot of the response surface for central composite design in Se determination.

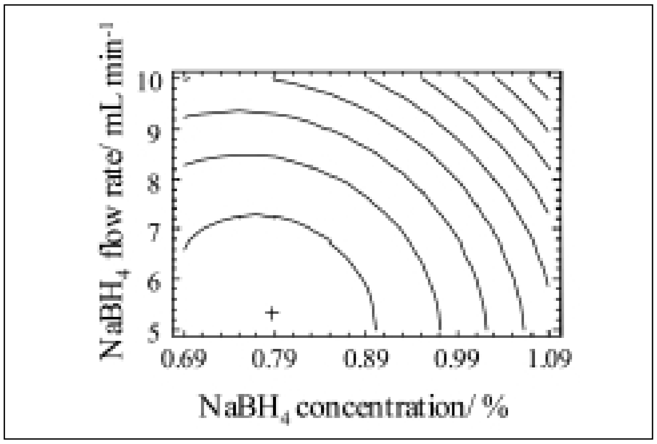

Fig. 3. Contours plot of the response surface for central composite design in Te determination.

TABLE V
Accuracy of Methods Obtained for As, Bi, and Se Determination Concentration[a] ±SD

		Certified Value	Obtained Value	R (%)
As	1632c (Coal)	6.18±0.27	5.96±0.11	96±1.8
	1633 (Coal Fly Ash)	145±15	132±0.57	91±0.4
Bi	1632c (Coal)	0.1*	0.09±0.01	90±10.0
Se	1632c (Coal)	1.326±0.071	1.23±0.01	93±0.7
	1633a (Coal Fly Ash)	10.3±0.6	10.40±0.06	101±0.6

[a] Concentration in μg g^{-1}.
*Indicative value.

TABLE VI
LOD and LOQ (μg g^{-1}) Obtained for As, Bi, Se, and Te Determination

	Coal		Fly Ash		Slag	
	LOD	LOQ	LOD	LOQ	LOD	LOQ
As	1.10	3.70	1.10	3.70	0.06	0.20
Bi	1.15	3.83	1.15	3.83	0.50	1.91
Se	0.02	0.08	0.04	0.16	0.02	0.08
Te	1.37	3.67	1.37	3.67	1.37	3.67

TABLE VII
As, Bi, Se and Te Concentrations and SD (μg g^{-1}) in Coal, Fly Ash, and Slag Samples (n=3)

Sample	As	Bi	Se	Te
Coal	113.5±1	1.9±0.1	0.85±0.05	2.5±0.2
Coal	41.4±1	3±0.1	4.5±0.3	3.2±0.9
Coal	41.4±1	2.1±0.1	5.1±0.1	<1.37
Coal	108.6±1	1.3±0.1	0.97±0.01	<1.37
Fly Ash	656.7±2	4.6±0.1	10.8±0.1	1.9±0.2
Fly Ash	778.1±1	<1.15	6.6±0.1	1.5±0.2
Fly Ash	190.8±2	5.1±0.1	6.5±0.1	2.7±0.1
Fly Ash	546±3	5.1±0.1	8.4±0.1	<1.37
Slag	6.4±0.2	1.8±0.2	1.7±0.1	<1.37
Slag	6.2±0.1	<0.50	1.2±0.1	2.2±0.1
Slag	3.6±0.2	<0.50	0.06±0.01	2.9±0.1
Slag	1.8±0.1	<0.50	0.12±0.05	1.4±0.3

The limit of detection (LOD) and limit of quantification (LOQ), defined as 3 sd/m and 10 sd/m, where sd is the standard deviation of 11 measurements of a blank and m is the slope of the calibration graphs, are listed in Table VI. The LOD and LOQ (expressed in μg g^{-1}) refer to amount of sample used for the microwave-acid extraction for each kind of sample and the dilution performed. The within-batch precisions obtained (relative standard deviation for 11 replicate measurements at different levels) are good, with RSDs (%) lower than 10% for all the elements studied.

Application

The acid-optimized procedures were applied to several coal, fly ash, and slag samples. Each sample was subjected twice to the microwave-assisted acid digestion. Aqueous calibrations were used for all metals and types of samples. Table VII lists the concentrations of each metal (n=3) together with the standard deviation (SD) values. As can be seen, the fly ash samples offer the highest As, Bi, and Se concentrations. This fact is in agreement with the partitioning behavior of these metals during coal combustion (32). These volatile and semi-volatile metals (class 2) are concentrated during coal combustion in fly ash. Thus, the levels of these trace elements are low in slag samples. On the other hand, As was the metal present in highest concentration in all samples studied.

CONCLUSION

The direct coupling of hydride generation to atomic fluorescence spectrometry results in a highly sensitive, accurate, and simple method for the determination of hydride-forming elements in samples from coal-fired power plants. For the metals studied, As concentrations were higher than Bi, Se, and Te concentrations; while Bi and Te concentrations were lowest. The accuracy studies show that the microwave-acid extraction procedure with aqua regia offers complete metals extraction from all samples.

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Determination of Arsenic and Selenium in Woodlice by GFAAS

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ABSTRACT

As and Se were determined in woodlice of the species *Porcellio scaber* (P. scab.) which were collected in pitfalls from a contaminated site near Jena, Thuringia, Germany. The animals were dried, ground, and digested using nitric acid combined with microwave-assisted high pressure digestion. Analysis of the samples was carried out by GFAAS with Zeeman background correction. The analytical method was developed based on two reference materials Dorm-2, Dogfish muscle (Squalus acanthias), and TORT-2, Lobster Hepatopancreas. The latter reference material was considered a close match to the matrix of the woodlice samples as both animal species are reported to store trace metals very efficiently in a particular section of their intestines: the hepatopancreas.

INTRODUCTION

Woodlice, *Porcellio scaber* (Latreille, 1804) are widespread in both rural and urban areas throughout Europe. They are relatively large, conspicuous, easily collected, and considered to be a good bioindicator of metal contamination of the terrestrial environment as well as of metal accumulation in the saprophagous food chains (1). Consequently, the trace metal content of woodlice is frequently used for risk assessment of a contaminated site. Although much information is available on the concentration of certain heavy metals such as Cd, Cu, Fe, and Zn in woodlice (2,3), little is known about the concentration of As and Se in these animals. This is surprising as both elements are known to be toxic, in particular if present in their mineral forms. This lack of data may be explained by the fact that trace determination of As and Se in complex matrices is still very demanding. Determinations by ICP-OES are often limited by the insufficient sensitivity of this technique at the ultratrace levels (detection limits for As and Se >20 µg/kg) (4) and the relatively high amounts of sample needed (several mL). On the other hand, analysis by quadrupole ICP-MS is severely hampered by the formation of cluster ions (5). For this reason, trace determination of As and Se is often carried out by atomic absorption spectrometry, either based on hydride-formation (6,7) or using a graphite furnace with Zeeman background correction (8,9). In the latter case, only µL amounts of sample are needed for one analysis which allows for several analyses from one sample, which is particularly beneficial when sample volume is limited.

Moreover, in animal samples characterized by elevated amounts of organic matter, the presence of organo-metallic compounds, e.g., arsenobetaine, has to be taken into consideration. Although being less toxic than their mineral congeners, these compounds are of particular importance due to their high stability which may cause problems in sample digestion. Consequently, both complete sample decomposition and quantitative recovery of As and Se were studied using the reference materials Dorm-2, Dogfish Muscle, and TORT-2, Lobster Hepatopancreas. Whereas a certified concentration of arsenobetaine is indicated in Dorm-2, the matrix of TORT-2 strongly resembles that of woodlice: both animal species store considerable amounts of trace metals in their hepatopancreas.

In this paper, a simple, rugged, but nonetheless sensitive method is presented for the determination of As and Se at the µg/kg (ppb) levels in woodlice samples based on microwave-assisted high-pressure digestion and analysis by graphite furnace atomic absorption spectrometry (GFAAS) with Zeeman background correction.

EXPERIMENTAL

Analyses by GFAAS

Analysis of the samples was carried out with a PerkinElmer® Model 3030 Zeeman atomic absorption spectrometer (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA), equipped with an AS-60 autosampler and an HGA®-600 graphite furnace. Pyrolytically coated graphite tubes with integrated platforms (PerkinElmer, Part No. B3001264) were used.

Argon (300 mL/min for As, 250 mL/min for Se) was used as the purge gas except during atomization (gas stop). As and Se absorbance was analyzed at the 193.7-nm and 196.0-nm lines, respectively (bandpass 0.7 nm for both elements). Integration time for all measurements was 5 s. PerkinElmer System 2 electrodeless discharge lamps (EDL) were used as the radiation sources.

A Pd-Mg modifier was used for both As and Se determinations: 300 µL of $Pd(NO_3)_2$ and 200 µL of $Mg(NO_3)_2 \cdot 6H_2O$ were diluted to 2 mL with HNO_3, 15%. Then 10 µL of this modifier was automatically

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added to 20 µL of each blank, standard, reference material, and sample. After appropriate dilution of the standard solutions, a four-point calibration at 5, 10, 15, and 20 µg/L for both As and Se was carried out. Evaluation of the data was based on peak area signals.

The furnace programs for both elements are summarized in Table I.

Reagents and Reference Materials

Arsenic and selenium standard solutions, 1 g/L (1000 ppm), HNO_3, 65%, Suprapur®, solutions of 10 g/L Mg as $Mg(NO_3)_2 \bullet 6H_2O$ and Pd as $Pd(NO_3)_2$, respectively, were obtained from Merck, Darmstadt, Germany. TORT-2, Lobster Hepatopancreas, and Dorm-2, Dogfish Muscle, were purchased from the National Research Council Canada, Ottawa. Ultrapure water (>18.2 MΩ/cm, MilliQ™, Millipore, Eschborn, Germany) was used throughout.

Sample Preparation

Woodlice of the species *P. scab.* were collected from the grounds of a former industrial site near Jena, Thuringia, Germany. Animals of about the same age and size were manually collected, separated, killed in a freezer, freeze-dried, and ground by a planetary ball mill (Retsch, Haan, Germany). About 30 animals treated in the manner described were then pooled to give an overall sample dry weight of almost 100 mg. These samples were then submitted to microwave-assisted high-pressure digestion (see below).

Sample Digestion

500 mg of reference material or 100 mg of sample was dissolved in 3 mL HNO_3, 65%, and submitted to a microwave-assisted high pressure digestion in a Multiwave® (Anton Paar, Austria). A six-position-rotor with 50-mL reaction vessels made of TFM (tetrafluor-modified polytetrafluoroethylene) was used. The maximum reaction temperature was 230°C with a maximum pressure of 30 bar. Overall digestion consisted of the following steps:
Step 1: increase of microwave power from 700 W to 1000 W during 10 min;
step 2: maintenance of microwave power at 1000 W for 10 min, and
step 3: cooling at zero microwave power for 15 min.
The whole digestion procedure took 35 min. To check for possible contamination of reagents and vessels, a blank was run with each series of reference materials and samples.

After digestion, the blank and reference materials were transferred to 50-mL glass vessels and filled to the mark with ultrapure water. In case of the woodlice samples, digestion solutions were transferred to 10-mL glass vessels as As and Se concentrations were expected to be considerably lower.

TABLE I
GFAAS Operating Conditions for As and Se Determination

Program	Furnace (°C)	Ramp Time (sec)	Hold (sec)	Gas (mL/min)	Analysis
As					
1	100	5	20	300	
2	130	10	50	300	
3	1100	20	30	300	
4	2200	0	4	0	X
5	2650	1	3	300	
Se					
1	100	1	30	250	
2	120	15	30	250	
3	600	20	40	250	
4	1000	15	45	250	
5	2100	0	5	0	X
6	2500	1	5	250	

RESULTS AND DISCUSSION

Detection Limits and Characteristic Mass

The detection limits were obtained by replicate analysis of 10 blanks, consisting of 3 mL HNO_3 65% Suprapur, brought to 50-mL volume with ultrapure water. The corresponding values were 1.4 µg/L (As) and 1.0 µg/L (Se). With respect to sample digestion and the final volume of the digestion solutions, the limits of determination for As and Se were 140 µg/L and 100 µg/L, respectively, for both reference materials and woodlice samples. The characteristic masses for As and Se were calculated to 21 pg and 29 pg, respectively, which were close to the tabulated values of 17 pg (As) and 30 pg (Se) (10).

Reference Materials

Concentrations of As and Se determined in the reference materials are summarized in Table II. Also provided are the certified concentrations together with the uncertainties which (according to the manufacturer) represent 95% confidence limits for an individual subsample. As mentioned in the experimental section, 500 mg of each reference material was digested. Studies in our laboratory with other elements revealed that the use of 500 mg of reference material leads to quantitative recovery of the certified concentrations with excellent RSD values (<1%) which can be traced to a high degree of sample homogeneity. Prior to analysis by GF-AAS, the digestion solutions were diluted as follows to fit in the calibration range: Dorm-2: 1:10 for As determination; no dilution for Se. TORT-2: 1:20 for As determination and 1:10 for Se determination.

As can be seen from the data in Table II, there is quantitative recovery for both As and Se in the two reference materials and the mean of six replicate analyses are listed. The results show that there was complete decomposition of the organic matter including the organo-metallic compounds, such as arsenobetaine, which makes up more than 90% of all As present in Dorm-2. This was confirmed by the absence of any precipitate or residue in the clear digestion solution. Based on these data and the principle of matrix-matching, it was concluded that the method is well-suited for the determination of As and Se in woodlice samples.

Woodlice Samples

The results of woodlice analysis are summarized in Table III. A total of 30 woodlice samples was analyzed. However, concentrations above the limit of determination could only be determined in six samples for As and in seven samples for Se. The concentrations ranged from 180–265 µg/kg for As and 170–340 µg/kg for Se with RSD values for both elements between 3–10%. Indicated is the mean of three analyses. These concentrations are remarkably lower than in the reference materials where both elements are present in the mg/kg (ppm) range. Moreover, these concentrations are also remarkably lower than those of other toxic elements, e.g., Cd, whose concentration is reported to be in the mg/kg range as well (2). Based on the data presented, it can be assumed that woodlice do not accumulate these elements very efficiently.

CONCLUSION

A multiwave-assisted high-pressure digestion combined with the analysis by GF-AAS was performed to determine the As and Se content of woodlice of the species *Porcellio scaber*. Despite the sensitivity of the method, As and Se concentrations in most animals were below the limits of determination for both elements. In future studies, enhancement of sensitivity is envisaged, i.e., preconcentration of the analytes prior to analysis.

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TABLE II
As and Se Concentrations in Dorm-2 and TORT-2; n=6

	Concentration (mg/kg)	Certified Concentration (mg/kg)
Dorm 2		
As	17.2 ± 1.0	18.0 ± 1.1
Se	1.28 ± 0.2	1.40 ± 0.09
TORT-2		
As	19.9 ± 0.4	21.6 ± 1.8
Se	5.68 ± 0.2	5.63 ± 0.67

TABLE III
As and Se Concentration in Woodlice Sample (n=3)
LOD = Limit of Determination
140 µg/kg for As
100 µg/kg for Se

Sample No.	As (µg/kg)	Se (µg/kg)
1–3	< LOD	< LOD
4	240 ± 10	< LOD
5	180 ± 15	< LOD
6	250 ± 19	< LOD
7–8	< LOD	< LOD
9	265 ± 20	< LOD
10–12	< LOD	< LOD
13	< LOD	190 ± 15
14	< LOD	170 ± 8
15–16	< LOD	< LOD
17	180 ± 12	< LOD
18	< LOD	< LOD
19	< LOD	225 ± 7
20	< LOD	< LOD
21	< LOD	285 ± 18
22	< LOD	< LOD
23	< LOD	295 ± 10
24–25	< LOD	< LOD
26	< LOD	230 ± 10
27	205 ± 8	< LOD
28	< LOD	< LOD
29	< LOD	340 ± 12
30	< LOD	< LOD

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Rapid Determination of Zinc in Foods by Flow Injection Analysis With Flame AAS Using Gradient Calibration Method

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ABSTRACT

A calibration method was developed using flow injection analysis (FI) with a Gradient Calibration Method (GCM). The method allows the rapid determination of zinc in foods (approximately 30 min) after treatment with concentrated sulphuric acid and 30% hydrogen peroxide, and analysis with flame atomic absorption spectrometry (FAAS). The method provides analytical results with a relative standard deviation of about 2% and requires less time than by conventional FI calibration.The electronic selection of different segments along the gradient and monitoring of the technique covers wide concentration ranges while maintaining the inherent high precision of flow injection analysis.

Concentrations, flow rates, and flow times of the reagents were optimized in order to obtain best accuracy and precision. Flow rates of 10 mL/min were selected for zinc. In addition, the system enables electronic dilution and calibration where a multipoint curve can be constructed using a single sample injection.

INTRODUCTION

According to their biological roles, food constituents are classified as essential or non-essential. Some essential metallic elements are present in foods at relatively high concentrations (e.g., calcium, magnesium, sodium), but others are present as trace elements (e.g., iron, copper, zinc) (1). Zinc is an essential mineral found in almost every cell. It stimulates the activity of approximately 100 enzymes, which are substances that promote biochemical reactions in the body. Zinc supports a healthy immune system, assists healing, helps maintain the sense of taste and smell, and is needed for DNA synthesis. Zinc also supports normal growth and development during pregnancy, childhood, and adolescence. Zinc is found in a wide variety of foods and for dietary control, knowing about the zinc content in foods is very important. Oysters contain more zinc per serving than any other foods, but red meats and poultry are the major source of zinc in the American diet. Other good food sources include beans, nuts, certain seafoods, whole grains, fortified breakfast cereals, and dairy products (2).

The determination of metals at trace levels requires either a larger sample amount or a pre-concentration step (3) in addition to very sensitive techniques. The use of large amounts of samples is sometimes problematic, or sensitive techniques are not available, while the use of a pre-concentration step increases analysis time, and can also be the source of random and bias errors.

Most methods of flow injection analysis (FI) are based on peak height (4) mainly because the inflection point on the FI response curve is easily localized. Experience has shown that in spite of non-equilibrium situations, FI yields easily reproducible and useful analytical readouts.

Some of the most exciting advances in flow injection analysis have involved gradient techniques. Due to the key role of dispersion controlled in space and time, these are based on the feasibility of identifying and selecting reproducibly suitable sections of the dispersed sample zone and exploiting the specific concentrations at these points for analytical purposes.

The gradient technique is not limited to reaction rate measurement or the stopped-flow approach. Electronic dilution and electronic calibration are two examples. Electronic calibration is based on the use of one standard solution from which the readout is extracted not only at the peak top, but also from suitable sections along the peak tail. The idea of using a single concentrated standard solution to generate a number of dilutions in a continuous flow for the purpose of instrument calibration is not new. The gradient dilution flask was introduced by Lovelock and later modified (5,6).

The simplest application of the gradient technique, called "electronic calibration," has been used in molecular spectroscopy with (7) and to correct for interferences in flame atomic absorption spectrometry (FAAS) (8,9)

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Calcium was determined in synthetic samples (containing silicon, phosphate, aluminum, vanadium, and titanium), and also in iron ore samples using calibration by the gradient ratio-standard addition method in flow injection FAAS (10).

In this paper, a sample treatment is described which allows destruction of the highly oleaginous organic matrix. In studies about acid attack, length of analysis time and required sample weight are of major interest in conjunction with FAAS, because this procedure would be useful in quality control food laboratories. In this work, we developed a straightforward, rapid sample attack method using sulphuric acid and hydrogen peroxide as an alternative to traditional dry ashing. The method allows the determination of zinc in food samples by FAAS in a highly convenient and expeditious manner.

EXPERIMENTAL

Instrumentation

PerkinElmer® Model 2100 atomic absorption spectrometer, equipped with a built-in microprocessor, screen and printer (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). The hollow cathode lamps employed were also obtained from PerkinElmer.

Manifold FI: Tubes of PTFE (0.5 mm i.d.) and peristaltic pump.

Six-way injection valve.

A schematic of the instrument setup used is shown in Figure 1. Measurements were processed using a Hewlett Packard PC computer equipped with Excel® software.

Reagents and Samples

Zinc standard of 1000 µg mL^{-1} and 1 g of metallic zinc to within 0.0001 g were dissolved in 10 mL of nitric acid. This solution was transferred quantitatively to a 1000-mL calibrated flask and diluted to volume with distilled water.

Commercially available food samples were used and the zinc content was determined by FAAS (11).

All solutions were prepared from analytical grade reagents. Additional diluted solutions of zinc were made by diluting appropriate volumes of the standards with distilled water immediately prior to use.

Sample Preparation

A sample (approximately 1.0 g) was weighed and placed into a 100-mL Kjeldhal flask and 2–3 mL of concentrated sulphuric acid was added. This solution was heated for 20 min, first gently and then more vigorously. Then, 4 mL of 30% hydrogen peroxide was added dropwise to de-colorize the solution. The mixture was vigorously boiled (to remove excess hydrogen peroxide) and allowed to cool. Finally, it was diluted to 25 mL with distilled water (12).

Procedure

All measurements were obtained under the conditions given in Table I. Water was used as the carrier fluid at the optimized flow rate of 10 mL min^{-1}.

For the Gradient Calibration Method, the elected standard solution of 2.5 µg mL^{-1} of zinc was injected into the system three times and the signals reported at 0.1-second intervals at the 213.9-nm wavelength. The food sample solution was also injected three times into the stream and the maximum absorbance values were recorded.

RESULTS AND DISCUSSION

Sample Attack

A 50% hydrogen peroxide solution affects a rapid attack of the sample. However, according to the Analytical Methods Committee (13), using a more readily available

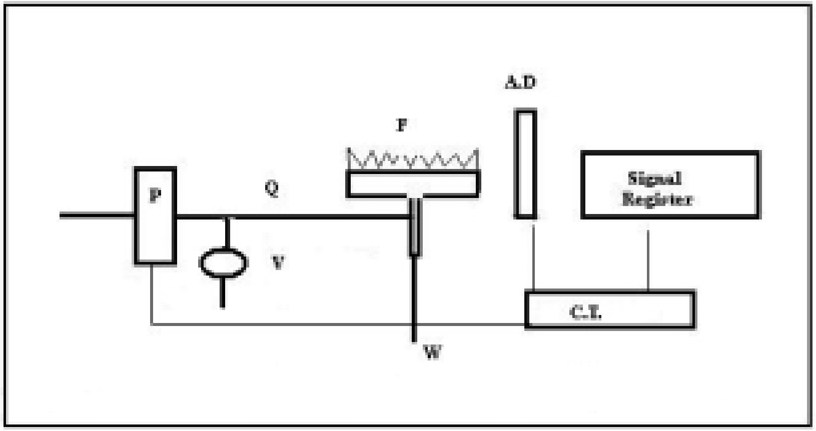

Fig. 1. Schematic of instrument setup: P=pump, Q=pumping rate, V=valve injection, C.T.=control timer and relay for pump control, F=flame, AD=absorbance detector.

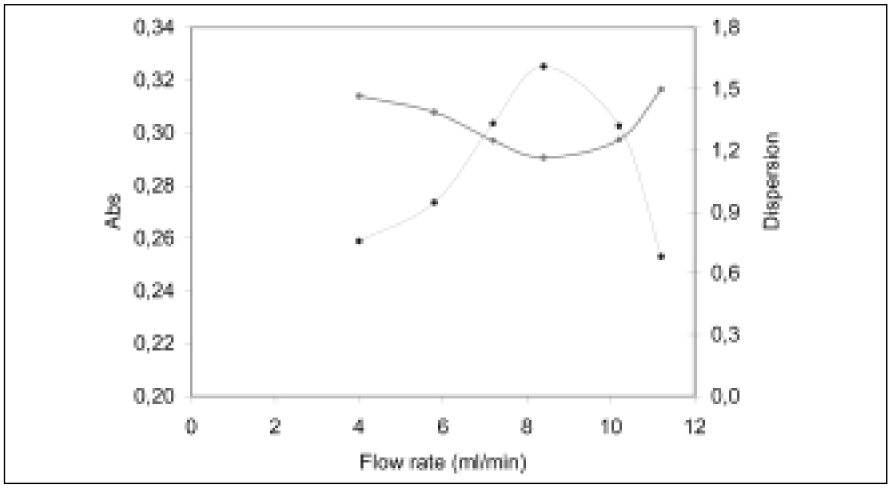

Fig. 2. Comparison between the values of absorbance and dispersion with variation in flow rate.

TABLE I
Instrument Parameters Used in the Determination of Zinc by AAS

Atomic Absorption Conditions	
Wavelength	213.9 nm
Intensity	20 mA
Slit width	0.7 nm
Working range	0-5 µg mL^{-1}
Burner distance below optic	10 mm
Flame	Air-acetylene
FIA Conditions	
Tubing i.d.	0.5 mm
Carrier flow rate	10 mL min^{-1}
Volume of the sample loop	86.39 mL
Time window	20 s
Time resolution	0.1 ms

30% reagent poses no special problem. In fact, by adding a slightly larger reagent volume prolongs the attack by a few minutes and removes the organic matter completely. The proposed procedure permits the effective dissolution of food samples in 30 minutes. The recoveries achieved in the determination of zinc were quite satisfactory (close to 100%).

The proposed method allows for the correct dissolution of food samples in approximately 30 minutes as follows:

- Treatment with sulphuric acid: 20 minutes
- Treatment with hydrogen peroxide: 5 minutes
- Removal of excess hydrogen peroxide: 5 minutes

In order to determine the possible influence of sample amount treated, different sample amounts were tested. It was observed that a relatively large amount of sample increased the time of the attack and produced incorrect results (the amount of zinc was less than estimated). In addition, it required a large amount of sulphuric acid for sample treatment which resulted in the precipitation of insoluble sulphates and did not produce expected results. It was found that best results were obtained when the sample amount was 1 g.

Flow Injection Methodology

The concentration, flow rate, and flow time of the reagents were optimized in order to obtain best accuracy and precision. Flow rates ranging from 3.5 to 10.0 mL/min were tested. A flow rate of 10 mL/min was selected for zinc because it showed best relation between signal/dispersion. High flow rates cause loss of sample and variability in the results; smaller values alter the signal as is shown in Figure 2. The minimum distance required between the tubes was 11 cm. Different internal tube diameters (0.3, 0.5, and 0.8 mm) were tested, but best results were obtained with the 0.5-mm tube. This size was selected for this work.

Gradient Calibration Method

A system based on the Gradient Calibration Method produces a purely exponential concentration gradient, so that $C=C_0 \exp (Qt/v)$, where C is the concentration at time t, C_0 is the original concentration at t=0, Q is the volumetric pumping rate, and V is the volume of the stirred tank. Therefore, this so-called logarithmic dilution method is based on knowledge of the pattern that the concentration gradient will follow, and allows an exact computation of C at any time t from Q, V, and C_0. But this approach is of limited value. First, it is impossible to construct a system where the very beginning of the dispersion curve will exactly fit the above expression. This means that the top of the peak will never be included in the logarithmic dilution profile, and is therefore lost as a source of information. Secondly, Q has to be found experimentally (and so does the V value, by extrapolation) so that some empirical factors must always be involved.

What is proposed here is an entirely empirical approach, based on identification of the pattern (which the concentration gradient follows) and its subsequent reconstruction into a calibration curve. Thus, whenever the instrument has to be recalibrated, say after a series of assays, a single injection will suffice to reconstruct a multipoint calibration curve. Thus, recalibration

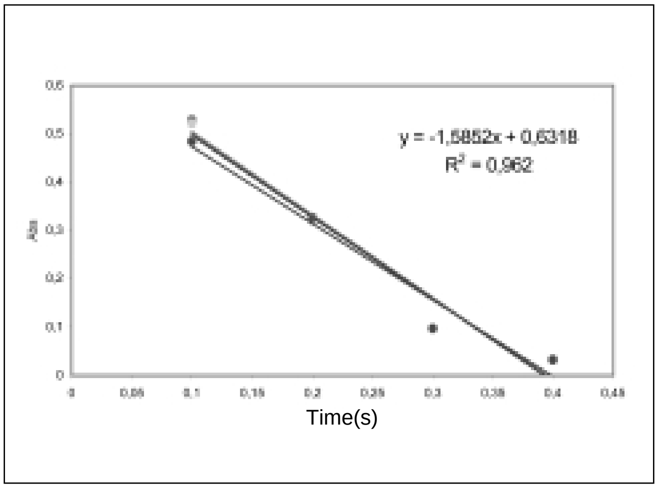

Fig. 3. Relation between time and absorbance with the 2.5-ppm zinc solution.

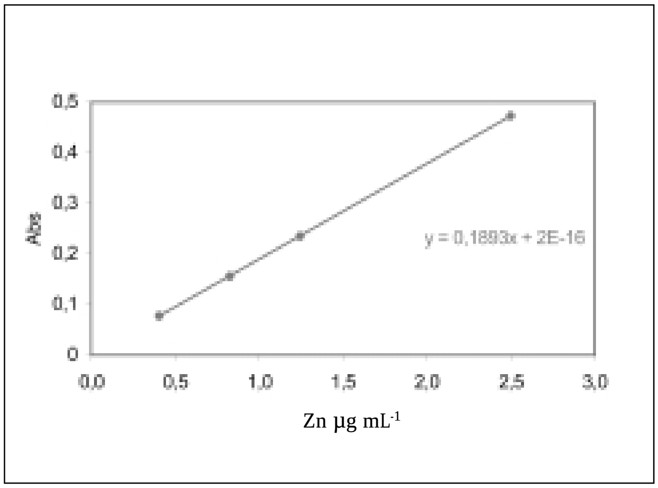

Fig. 4. Temporal calibration graph with 2.5-µg g^{-1} Zn solution.

will not rely on a single point (such as peak height of the most concentrated standard) which, as explained above, is most sensitive to variations of reagent concentration, but will be obtained from a number of points identified along the peak tail. Furthermore, variations in the pumping rate, which would have the most pronounced influence on the t_1 to ~n values, may easily be identified (and possibly corrected for) by checking the t_0–t_5 interval.

The maximum concentration of zinc was selected to produce the temporal calibration, where the values of absorbance at each 0.1-second interval were reported and used to build the concentration / time graph (Figure 3).

With the equation obtained graphically, the values of time were substituted and the values of absorbance recalculated. Then, knowing that the maximum absorbance corresponded to the concentration of 2.5 mg L^{-1}, the absorbance vs. concentration graph was obtained (Figure 4). With the calibration graph, the zinc concentration in the food samples could be calculated using only one standard.

Food Analysis

This analytical system was also used for the zinc determination in several food samples obtained from supermarkets in Zaragoza, Spain. The results are listed in Table II. It can be seen that the zinc content in these food samples varies from 13.07 to 53.89 µg g^{-1}. On the other hand, recovery values obtained by the standard addition method proved that the developed procedure is not affected by matrix interferences and can be used satisfactorily for the analysis of natural foods.

Table II lists the results obtained in the determination of zinc in foods using the flow injection and wet digestion procedures. As can be seen, the results are in agreement (according to the linear regression test and the paired *t*-test). The relative standard deviation (using temporal calibration) was close to 2% in the best cases. The results of our study are similar to those obtained in the determination of zinc in different foods by FI-FAAS and slurry nebulization (14).

CONCLUSION

The results obtained in the analysis of foods verify the accuracy and applicability of the methodology developed for zinc determination at the µg g^{-1} levels. The advantages of the present method include simplicity, short analysis time, low risk of contamination, and low analytical cost due to the reduction in reagent consumption. The on-line system using FAAS analysis allows the zinc determination in food samples at trace levels (detection limits of about 0.01 mg/L) with appropriate reliability.

Treatment of the food samples with sulphuric acid and 30% hydrogen peroxide allows atomic absorption determinations with the gradient technique. Under the working conditions used, the reagents employed do not significantly alter the flame atomic absorption of zinc, nor are there any interferences from other metals at their typical concentrations. As a result, zinc can be determined in aqueous solution by running a calibration curve from the gradient technique.

TABLE II
Results for the Determination of Zinc in Foods by Flow Injection FAAS Using Gradient Calibration Method (15,16)

		Samples			
		Chickpeas	Rice	Beans	Lentils
Discontinous[a]	Average, (µg g^{-1})	35.770	13.07	35.95	51.21
	Range (µg g^{-1})	35.54 – 38.27	11.99 – 13.55	32.44 – 39.28	50.09 – 51.93
	SD (µg g^{-1})	1.11	0.63	2.92	0.77
	RSD (%)	3.1	4.8	8.1	1.5
FI[b]	Average (µg g^{-1})	34.32	14.33	33.47	53.89
	Range (µg g^{-1})	31.09 – 35.81	13.90 – 14.65	30.90 – 36.16	47.03 – 55.89
	SD (µg g^{-1})	1.90	0.36	2.53	2.98
	RSD (%)	5.5	2.5	7.6	5.5
GCM[c]	Average (µg g^{-1})	38.33	16.90	37.42	53.27
	Range (µg g^{-1})	34.86 – 39.92	16.45 – 17.25	34.67 – 40.29	51.94 – 54.58
	SD (µg g^{-1})	2.04	0.38	2.72	1.02
	RSD (%)	5.3	2.2	7.3	1.9

[a] Discontinous: Traditional discontinuous calibration.
[b] FI: Conventional Flow Injection Analysis.
[c] GCM: Gradient Calibration Method

The flow injection methodology proposed for the determination of zinc in foods is fast, shows precision similar to the batch procedure, and provides similar accuracy. The proposed manifold designs can easily be adapted to any metal determination without important modifications.

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ICP-OES Determination of Niobium, Tantalum, and Titanium at Trace to Percentage Levels in Varying Geological Matrices

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ABSTRACT

A simple method is reported for the determination of niobium, tantalum, and titanium in geological samples by ICP-OES. Novelties of the method include preparation of a sample solution without the use of flux. The sample is decomposed by treating with hydrofluoric (HF) and sulfuric acid (H_2SO_4) mixture (10:3, v/v), heated to sulfuric acid fumes, cooled, and finally digested in 0.9M H_2SO_4 and 0.2–0.5M H_2O_2 to convert the elements into their peroxy complexes, adequately stable to prevent any hydrolysis or polymerization of the individual or combined analytes over a period of at least one week. The homogeneity of the solution is confirmed by the absence of any significant variation in analyte emission signals when determined by ICP-OES.

Niobium, tantalum, and titanium are determined, respectively, at the 316.340-nm, 240.063-nm, and 336.121-nm lines in an argon ICP after applying two suitable off-peak background correction points. The selection of the lines (with specified background correction) is based on their freedom from interelement and concomitant interferences at the levels studied, even though the lines are not the most sensitive for the respective elements. Iron at levels greater than 1 mg/mL elevates the background in the case of the tantalum and titanium lines, degrading the signal-to-noise ratio and the subsequent detection limits, and is removed by extraction with MIBK in HCl (4–6M). The presence of HCl does not cause hydrolysis nor suppression of the respective signals.

The efficacy of the method is validated by the determination of elements in the minerals columbite, tantalite, ilmenite, and ilmenorutile, other minerals and rocks (monazite, carbonatite), soil samples (in-house geological samples), and international geostandards IGS-33, IGS-34, SY-2, and SY-3. The values obtained are in good agreement with the gravimetric, spectrophotometric, and certified values, respectively. Niobium, tantalum, and titanium are determined down to the 10-ppm levels with RSDs of 1.3%, 1.7%, and 0.8%, respectively.

INTRODUCTION

Niobium and tantalum find wide application as construction materials in nuclear technology and engineering (1–3). The close ionic radii of Nb(V) (0.69 A°), Ta(V) (0.68 A°), and Ti(IV) (0.68 A°) result in their occurrence together in nature (4) and make their separation difficult. Besides, greater affinity for hydroxyl ions due to their relatively high ionic potential (>5.7 eV) makes them prone to hydrolysis in aqueous solutions (5). To avoid hydrolysis and also polymerization (especially of niobium and tantalum) and to prevent their subsequent loss, geological samples require decomposition with a suitable flux such as $KHSO_4$ (or potassium or ammonium bi-fluoride followed by fusion with $KHSO_4$) and digestion in the presence of α-hydroxycarboxylic acid (6). This makes the determination of niobium, tantalum, and titanium by inductively coupled plasma optical emission spectrometry (ICP-OES) difficult due to the presence of total dissolved salt concentrations (TDS) well above the tolerance levels.

A simple method is proposed for the preparation of sample solutions by acid digestion without the use of flux and α-hydroxycarboxylic acid, which increase the TDS beyond the tolerance levels. The sample is decomposed by treating it with a hydrofluoric and sulfuric acid mixture, heated to sulfuric acid fumes, cooled, and finally digested in 0.9M H_2SO_4 and 0.2–0.5 M H_2O_2.

A spectral interference study by Winge et al. (7), which pertains to the singly ionized emission lines of niobium, tantalum, and titanium in an argon ICP, reports interferences of iron or vanadium on most of the lines, but to a greater extent on the tantalum and titanium lines. Our study also revealed interelement interferences on some of these lines.

In the present work, Nb, Ta, and Ti are determined by ICP-OES utilizing the 316.340-nm, 240.063-nm, and 336.121-nm emission lines, respectively, in an argon ICP. The interelement interferences and also interferences due to vanadium and other concomitants are removed by applying two points off-peak background correction on either side of the analyte line. The interference of iron on niobium is removed by off-

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peak background correction. However, the presence of iron at levels greater than 1 mg/mL elevates the background for tantalum and titanium, degrades the signal-to-noise ratio and subsequently deteriorates their detection limits. The interference is overcome by qualitative extraction of iron by MIBK in the presence of 4–6 M HCl to bring the iron below the tolerance level for the determination of tantalum and titanium along with niobium. The procedure has been employed for the determination of niobium, tantalum, and titanium down to the 10-ppm levels in minerals rich in metals such as columbite, tantalite, ilmenite, and in carbonatite, monazite, rocks, and soil samples.

EXPERIMENTAL

Instrumentation

A GBC-Integra XM sequential ICP spectrometer (GBC Scientific Equipment Pty. Ltd., Melbourne, Australia) was used, equipped with a 0.75-m focal length Czerney Turner monochromator (1800 grooves/mm grating), a concentric glass nebulizer with cyclonic spray chamber, and an argon humidifier to prevent blockage in the nebulizer by high levels of dissolved solids. A fully automated instrument was used (see Table I).

Procedure

The samples (rich in analytes -- 0.100 g; rocks, soils, and other minerals - 0.500 g) were repeatedly (3–4 times) digested with a hydrofluoric acid-sulphuric acid mixture (10:3 v/v) in a platinum dish, heated to expulsion of sulphuric acid fuming, and cooled. The residue was digested in 0.9M H_2SO_4 and 0.2–0.5M H_2O_2 and made up to suitable volume (after filtration in case of calcium-rich samples such as carbonatite with CaO > 15%); a blank was prepared similarly.

Sample Solutions With Iron Greater Than 1 mg/mL

The sample solution was transferred to a separation funnel adding hydrochloric acid to give a final acidity between 4–6M HCl, then 25 mL of methyl isobutyl ketone (MIBK) was added, and the mixture shaken for 2 minutes. The phases were allowed to separate and the aqueous phase was collected in a beaker. The organic phase was washed with 10 mL of HCl (6M) and the separated aqueous layer was added to the earlier aqueous layer. The combined aqueous phase was evaporated to reduce the volume. The final solution was made up to 25-mL volume with 0.2–0.5 M H_2O_2.

RESULTS AND DISCUSSION

Preparation of Sample Solution

Although niobium, tantalum, and titanium are prone to easy hydrolysis and polymerization in aqueous solutions, the tendency is observed to a greater extent for niobium and tantalum. These phenomena create problems in obtaining clear solutions of the samples containing these elements, resulting in loss of analytes. The difficulty is usually overcome by decomposing the samples by direct fusion with $KHSO_4$, or after fusion with potassium or ammonium bi-fluoride (to remove fluoride), and dissolving the fused mass in hot boiling tartaric or citric acid (α-hydroxycarboxylic acid) or oxalic acid. The procedure introduces salts at concentrations much above the tolerance levels (10 mg/mL or 40 mg/mL with humidified argon) causing frequent blockage of the nebulizer. In the case of samples rich in niobium, tantalum, and/or titanium, dilution of the sample solution reduces the salt concentration, enabling their determination (8), although the advantage of the dynamic range of ICP remains poorly utilized. But other samples do not permit this type of reduction in TDS due to a low concentration of the analytes.

TABLE I
Instrumental Operating Conditions

GBC Integra XM Sequential Spectrometer	
RF Generator	40.68 M Hz
Incident Power	1.20 KW
Reflected Power	20 W
Plasma Argon	10 L/min
Auxiliary Argon	0.5 L/min
Nebulizer Argon	0.6 L/min
Argon Humidifier	Yes
Nebulizer Pressure	290 Kpa
Pump Speed	20%
Liquid Uptake Rate	2.6 mL/min
Flush Time	10 Sec
Viewing Height	11 mm
Integration Time :	
Scanning Mode	4.5 Sec
Analysis Mode	15 Sec
PMT Voltage	650 V

Decomposition of the samples with a mixture of $HF\text{-}H_2SO_4$ (10:3 v/v) in the proposed method and subsequent digestion with 0.9M H_2SO_4 in the presence of 0.2–0.5M H_2O_2 does not introduce salt, and the TDS is far below the tolerance levels. The complexation of niobium, tantalum, and titanium with H_2O_2 in the presence of H_2SO_4 prevents their hydrolysis and polymerization over a period of at least one week, as confirmed by the absence of a significant variation in the emission signal of the analytes. This results in a problem-free ICP-OES determination of niobium, tantalum, and titanium in the solution down to the 10-ppm levels with RSDs of 1.3%, 1.7%, and 0.8%, respectively.

Selection of Emission Lines for Determination of the Analytes

Most of the first four emission lines (7) of the three analytes suffer interferences from iron and vana-

TABLE II
Spectral Parameters for the Determination of Analytes

Element	Wave-length (nm)	Order	Window (nm)	No. of Steps	Time per Step (sec)	Off-peak BGC Correction Points	
						Left (nm)	Right (nm)
Nb	316.340	1	0.030	31	0.5	0.008	0.013
Ta	240.063	2	0.030	31	0.5	0.008	0.013
Ti	336.121	1	0.030	31	0.5	0.014	0.011

dium, and other elements. Using a 1-µg/mL solution of the analyte, we studied the spectral interference of concomitants (100 µg/mL and higher concentrations) within the wavelength range of ± 0.05 nm from the analyte line to examine their wing effect and the effect on background level. The final studies were made with a two-point off-peak background correction on the left and right side of the analyte over 0.03 nm (Table II).

The influence of concomitants on the selected lines for the analytes was examined by means of spectral scans of solutions of the concomitants (of known concentrations) as well as by measurement of the signals for these elements at the selected wavelengths using the specified background corrections. The concomitants include major and minor elements such as Ca (bulk being precipitated as $CaSO_4$ during sample preparation in H_2SO_4 medium), Mg, Al, Mn, Fe, etc., and traces like Cu, Ni, Co, Cr, Mo, W, Pb, Zr, the rare earth elements, U, V, or Th. The interference was considered to be negligible if their amounts (the maximum amount tested, 5 mg/mL) added to 1 µg/mL of an analyte produced an error of less than ± 1%. In other cases, the critical concentration ratio (CCR) was calculated (9). The results are listed in Table III.

It was observed that the most sensitive line for niobium at 309.418 nm suffers serious interference due to a direct overlap by V(II) at 309.42 nm besides other elements (such as Al, Cr, Cu, Fe, Mg, and V). The next most sensitive line for niobium at 316.340 nm in the present method suffers interferences from Ca, Cr, and Fe, but the specified background correction removes these interferences at the concentration levels studied.

Tantalum is determined at 240.063 nm since it is relatively free from titanium and other interferences, which is an advantage over the most sensitive Ta(II) line at 263.558 nm (10) with a specified BGC (confirmed by our observation under the specified conditions). These findings were contrary to the reported most sensitive line of 226.230 nm for tantalum (11). But the line suffers interferences from iron at levels >1 mg/mL which is similar to the 336.121-nm line for titanium, its second most sensitive line (12). The criteria adopted for the selection of the analytical lines is their freedom from interelement and concomitant interferences at the concentration levels studied, rather than the sensitivity for the respective lines.

Iron above the tolerance levels is removed by extraction with MIBK in an HCl medium (4–6M). The removal is imperative as iron elevates background levels, degrades the signal-to-noise ratio and the detection limits of the analyte, and changes the nebulization characteristics and excitation conditions (13).

Suppression of the analytical signals or hydrolysis of the peroxy complexes of the analytes (formed with H_2O_2 in the presence of H_2SO_4) was insignificant in the presence of HCl (4–6M). This is confirmed by the studies carried out with synthetic mixtures of the analyte at the 0.1–1.0-µg/mL levels (prepared from stock standard solutions) in the presence of HCl (4–6M). Since the CCR levels for uranium and thorium on the niobium and tantalum lines are low, they do require a correction for their unfavorable ratio to the analytes. However, the ratios hardly exceed the tolerance levels in the geological samples.

TABLE III
Critical Concentration Ratio (CCR) for Interferents at Proposed Analytical Lines Emitted by Niobium, Tantalum, and Titanium

Interferences	Critical Concentration Ratios		
	Nb (316.340 nm)	Ta (240.063 nm)	Ti (336.121 nm)
Fe	--	9995	9997
Nb	--	2588	113172
Ti	1250	9375	--
V	--	--	12680
Cr	--	--	8150
W	200	--	850
Mo	--	--	3074
Ta	585	--	2987
U	70	85	--
Th	100	1000	--

(--) No significant interference.

Interelement Interference and Correction

The CCR for Ta on the Nb(II) and Ti(II) lines was 585 and 2987, respectively; for Ti on the Ta(II) and Nb(II) lines it was 9375 and 1250, respectively; for Nb on the Ta(II) and Ti(II) lines it was 2588 and 113,172, respectively. The elements with moderate CCR positively influence the signal on a line at an unfavorable ratio with the analyte. The effect may be eliminated by applying suitable correction.

The ratio of tantalum to niobium in geological samples usually ranges from 1:15 to 35:1 (in tantalite) (3). The CCR for tantalum on the niobium and titanium lines is adequate to determine niobium and titanium in soil, rock, and mineral (not rich in tantalum) samples with accuracy (>98%). But a high ratio of tantalum to niobium in tantalite causes minor enhancements in niobium values, thus reducing the accuracy of the method (95%) as compared to gravimetry (98%) (14). However, the gravimetric method is a tedious and time-consuming method (usually 12–15 working days), involving multiple level separations in the hands of an expert. Besides, in this method niobium and titanium are separated together from tantalum and determined together gravimetrically (14) as combined oxide ($Nb_2O_5 + TiO_2$) - (a) due to difficulty in their separation from each other. Ti in the combined oxide is determined by visible spectrophotometry - (b) (15) and Nb is obtained from the difference between (a) & (b). Thus any error in titanium dioxide value is reflected in niobium value. The accuracy can be improved to 98% by applying a correction for tantalum. Tantalum is first determined by the proposed method (niobium present in tantalite does not interfere in the determination due to its low ratio with tantalum). The influence of tantalum may be calculated using the following formula:

$$\text{Ta influence} = \frac{\text{Concn of Ta } (\mu g/mL) \text{ in the final solution}}{\text{CCR}}$$

The correction is obtained by subtracting the Ta influence from the niobium value obtained in presence of tantalum. Similar corrections could be effected for inter-element influences wherever required.

Correction for Inter-element Interferences (other than proposed method)

The inter-element interferences (other than the proposed method) could be corrected by their separation from the analyte prior to determination. However, separation of niobium, tantalum, and titanium from each other is difficult due to the close similarity in their chemical properties. Niobium and titanium are separated together from tantalum with tri-butyl-n-phosphate (40% in kerosene) from HCl (2.2M) and the tartaric acid (1.5M) medium in the presence of 0.64M KHF_2 (16). Niobium and titanium are retained in the aqueous phase, while tantalum passes to the organic phase. Niobium and titanium are separated from each other by extracting niobium into try-iso-octyl amine (0.1M in CCl_4) from HF (13M) and HNO_3 (0.3M) medium (17). However, the separation process is tedious, time-consuming, and involves multi-level solvent extraction from media with appreciable concentration of hydrofluoric acid.

Validation of Proposed Method

The efficacy of the method is validated by the determination of niobium, tantalum, and titanium in in-house geological samples such as discrete or mixed minerals rich in the elements (columbite, tantalite, ilmenite, ilmenorutile), other minerals and rock (monazite and carbonatite), soil samples, and international geostandards IGS-33, IGS-34, SY-2, and SY-3. The values obtained are in good agreement with the gravimetric, spectrophotometric, and certified values, respectively (Tables IV and V). Chemical data of calcium and the total iron concentration of some of the in-house and SY-2 and SY-3 samples containing analytes at trace levels are included in Table V. Niobium, tantalum, and titanium are determined at the 10 µg/g levels with RSDs of 1.3%, 1.7%, and 0.8%, respectively.

CONCLUSION

This study describes a simple method for the decomposition of geological samples (without flux), utilizing the stability of peroxy complexes of niobium, tantalum, and titanium (in sulfuric acid medium) in order to prevent their hydrolysis and polymerization in aqueous medium. This avoids the need for removal of bulk of salts by dilution (which cuases significantly poor confidence levels of the elements at trace levels). Niobium, tantalum, and titanium are determined in their discrete or mixed minerals, as well as in other minerals, rock and soil samples down to the 10 µg/g level at the recommended emission lines with specified background correction resulting in RSDs of 1.3%, 1.7%, and 0.8%, respectively. The proposed method is far superior in operational ease, simplicity, and rapidity to conventional gravimetric (for high levels) and spectrophotometric (for trace levels) methods which require multilevel separations.

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TABLE IV
Niobium, Tantalum, and Titanium Values (%, average of three determinations with %RSD*) in Respective In-House Samples (IHS) (rich in one or more analytes) and International Geochemical Reference Samples (IGS)

Sample No.	Sample	ICP – OES			Other Methods		
		Nb_2O_5	Ta_2O_5	TiO_2	Nb_2O_5[a]	Ta_2O_5[b]	TiO_2[c]
1.	IHS-1	66.02 (0.3)	11.14 (0.9)	1.69 (0.3)	66.0	11.0	1.6
2.	IHS-2	64.81 (0.3)	11.31 (0.9)	1.73 (0.3)	65.0	10.9	1.7
3.	IHS-3	57.32 (0.4)	14.50 (0.8)	4.24 (0.3)	57.1	14.4	4.1
4.	IHS-4	59.84 (0.3)	14.27 (0.9)	2.01 (0.3)	59.4	14.2	2.1
5.	IHS-5	37.91 (0.6)	36.43 (0.7)	1.72 (0.4)	38.1	36.2	1.8
6.	IHS-6	32.00 (0.7)	33.81 (0.8)	1.72 (0.4)	31.8	33.4	1.7
7.	IHS-7	0.15 (1.0)	-- –	52.34 (0.1)	0.12	--	51.9
8.	IGS-33	68.81 (0.2)	5.44 (1.1)	1.79 (0.3)	68.79[d]	5.46[d]	1.80[d]
9.	IGS-34	27.41 (0.8)	49.07 (0.7)	1.28 (0.3)	27.45[d]	49.05[d]	1.27[d]

* RSD in parentheses.

[a] Value obtained by difference in values of combined niobium and titanium oxide (gravimetry) and titanium dioxide in the combined oxide (spectrophotometry).

[b] Gravimetry (References 14, 16).

[c] Spectrophotometric value (Reference 15).

[d] British Geological Survey, BGS, Geochemistry Directorate (re-evaluated 1985)..

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TABLE V
Determination of Niobium, Tantalum, and Titanium Values in Geochemical Samples

S.No.	Samples[a]	ICP – OES Nb Conc	Nb RSD	Ta Conc	Ta RSD	Ti Conc	Ti RSD	Other Methods Nb Conc	Ta Conc[d]	Ti Conc
1.	Monazite	75 µg/g	1.0%	<10 µg/g		1.18%	0.2%	71 µg/g[c]	<40 µg/g[d]	1.14%[e]
2.	Carbonatite (CaO 18.2%, Fe_2O_3 6.3%)	171 µg/g	0.9%	<10 µg/g		0.13%	0.6%	173 µg/g[c]	<40 µg/g[d]	0.13%[e]
3.	Soil-1 (CaO 18.2%, Fe_2O_3 6.3%)	19 µg/g	1.3%	10 µg/g	1.7%	0.28%	0.6%	18 µg/g[c]	<40 µg/g[d]	0.29%[e]
4.	Soil-2 (CaO 18.2%, Fe_2O_3 6.3%)	46 µg/g	1.1%	23 µg/g	1.5%	0.73%	0.3%	49 µg/g[c]	<40 µg/g[d]	0.71%[e]
5.	Soil-2[b]	47 µg/g	1.2%	65 µg/g	1.4%	0.73%	0.3%	48 µg/g[c]	67 µg/g[d]	0.71%[e]
6.	SY – 2	31 µg/g	1.2%	<10 µg/g		846 µg/g	0.7%	29 µg/g[f]	<40 µg/g[d]	900 µg/g[f]
7.	SY – 3	143 µg/g	1.0%	28 µg/g		912 µg/g	0.7%	147 µg/g[f]	<40 µg/g[d]	900 µg/g[f]

[a] Samples No. 1–5 are in-house samples and samples No. 6–7 are international geochemical reference samples.
[b] Spiked with Ta_2O_5, 50 ppm (Ta, 40 ppm).
[c] Spectrophotometric method using potassium thiocyanate (18).
[d] Spectrophotometric method using malachite green (19).
[e] Spectrophotometric method using hydrogen peroxide (15).
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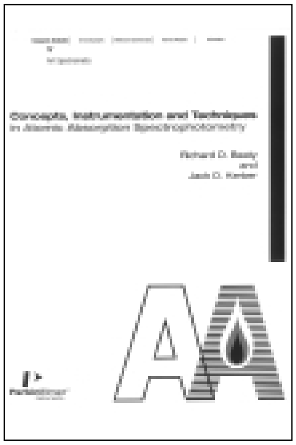
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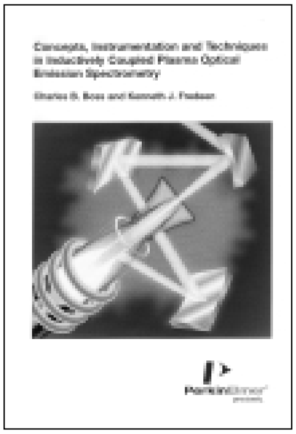
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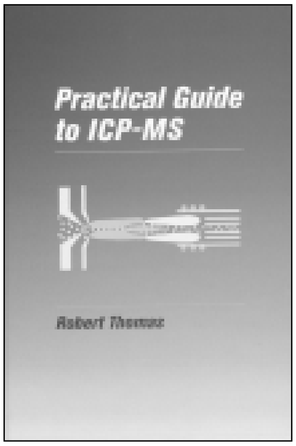
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