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Multielemental Analysis of Geological and Biological Samples using Laser Ablation ICP-SFMS

Mikael D. Axelsson

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Multielemental analysis of geological and biological samples using laser ablation ICP-SFMS

Mikael D. Axelsson

Department of Environmental Engineering
Division of applied Geology
Luleå University of Technology
S-971 87 Luleå, Sweden

Luleå 2000

Abstract

The analytical performance of laser ablation (LA) for multielemental determination of geological and biological samples has been investigated. In the present study, LA has been used for sample introduction in inductively coupled plasma sector field mass spectrometry (ICP-SFMS). Although LA can provide semi-quantitative results rapidly and easily, the calibration process still remains the "Achilles heel" of the technique. The major goal of this study has been to investigate the capabilities of LA-ICP-SFMS for qualitative and quantitative analysis of various solid materials. LA was used for analyses of coal were calibration was performed by using coal powder doped with analyte elements. This was done by adding solution standards (including analyte and internal standard elements) to the coal, drying and finally homogenising, followed by pressing tablets. LA results were compared with data obtained by conventional solution nebulisation (SN) after preparation of coal samples using microwave (MW) digestion or fusion. In spite of a relatively poor agreement for elements such as As, Se, Sn, Re, Te, and Tl, accuracy obtained with LA in the present study is otherwise generally superior to previously reported data for LA and slurry nebulisation. For about 50 elements, results obtained with LA fall within 20 % of those obtained by SN. The study shows the potential of LA quantification, based on solution-doped powders. However, the necessity of sample grinding and homogenising results in loss of spatial distribution information and makes the approach more vulnerable to sample contamination. The possibilities of sulphide minerals analysis by ICP-SFMS have been investigated. Seven elements (Co, Fe, Cd, Ag, Mn, Cu and S) have been quantitatively determined in sphalerite samples from the Zinkgruvan mine, using Zn as internal standard (IS). A straightforward calibration procedure allows on-line correction for possible Fe impurities at percent levels. Consequently, the use of complimentary techniques for determination of actual Zn content in the samples is avoided. The LA-ICP-SFMS results were compared with data from conventional SN introduction of sample solutions following acid digestion. Good agreement was found between the methods. For homogeneously distributed elements the overall precision for LA was found to be better than 10% RSD. A method for total mineral dissolution of five sulphides (sphalerite, pyrite, galena, pyrrhotite and chalcopyrite) has been developed, followed by multielemental analysis by ICP-SFMS. By performing this mineral characterisation the intention was to determine whether the analysed bulk mineral samples could be used as in-house LA calibration standards. The use of LA was focused towards elucidating whether the observed deviations in results obtained by ICP-SFMS for the two reference material powders used were caused by sample inhomogeneity or by inefficient matrix dissolution. It was found that the reference materials showed lack of accuracy in recommended concentrations for many trace and ultra trace elements, as well as possible inhomogeneity when using 50 mg sample amounts. The sulphide minerals studied appears to be suitable as matrix matched calibration standards for the determination of about 20 trace and ultra trace elements by LA. Laser ablation was also used for analysing element to sulphur ratios in washed human nails. The element ratios were then used to display the effectiveness of the applied washing method applied prior to MW digestion and analysis by ICP-SFMS. Based on the LA analysis, it was found that, even after the applied nail washing procedure, many elements are enriched in the surface of the nail.

Key words: Laser ablation, ICP-SFMS, sulphide mineral, multi-elemental analysis, and calibration standards

Preface

This thesis is based on the following papers that are hereafter referred to by their Roman numerals.

I. Rodushkin I., Axelsson M.D. and Burman E., 2000. Multielement analysis of coal by ICP-techniques using solution nebulization and laser ablation. Talanta 51, 743-759.

II. Axelsson M.D. and Rodushkin, I., 2000. Determination of major and trace elements in sphalerite using laser ablation double focusing sector field ICP-MS. Accepted in Journal of Geochemical Exploration.

III. Axelsson M.D., Rodushkin I., Petrov, P., Burman E and Öhlander B., 2000. Multi-element analysis of sulphides by ICP techniques using solution nebulisation and laser ablation. Submitted to the second edition of Recent Research Developments In Pure & Applied Analytical Chemistry.

IV. Rodushkin I. and Axelsson M.D., 2000. Application of double focusing sector field ICP-MS for multielement characterization of human hair and nails. Part I. Analytical methodology. The Science of the Total Environment 250, 83-100.

Papers not included in this thesis

A. Rodushkin I. and Axelsson, M.D. 2000. Application of double focusing sector field ICP-MS for multielement characterization of human hair and nails. Part II. A study of the inhabitants of northern Sweden. The Science of the Total Environment 250, 83-100.

B. Olofsson R.S., Rodushkin I., Axelsson M.D., 2000. Performance characteristics of a tandem spray chamber arrangement in double focusing sector field ICP-MS. Journal of Analytical Atomic Spectrometry, 15, 727-729.

C. Rodushkin I., Ödman F., Olofsson R., Axelsson M.D., 2000. Determination of 60 elements in whole blood by sector field inductively coupled plasma mass spectrometry. Journal of Analytical Atomic Spectrometry, 15, 937-944.

Table of contents

Introduction

Multielemental ICP techniques

The choice of the appropriate technique for a specific multielemental problem requires a clear understanding of the capabilities and limitations of the different techniques available. Among the multielemental inductively coupled plasma (ICP) related techniques, optical emission spectrometry (OES) is suitable for determination of refractory elements because of the high temperatures reached in the plasma. Elements of interest can be detected either simultaneously or sequentially, thus making ICP-OES a fast multielement technique. The limitation of the ICP-OES technique mainly concerns the limits of detection (LOD). Since the first commercial ICP-mass spectrometry (ICP-MS) instrument was introduced at the market in 1983, the technique has gained rapid and wide acceptance in a variety of analytical applications, including geology. The main principle of ICP-MS is that ions, produced by a conventional ICP, are sampled through a differentially pumped interface linked to a mass spectrometer. The spectra produced in this way, which are remarkably simple compared to conventional ICP optical spectra, consist of a simple series of isotope peaks for each element present. These spectra are used for qualitative determination of the elements present in the sample and for the quantitative measurement of their amounts. Usually the latter are based upon calibration curves in which the ratio of the ion count for the analyte to the count for an internal standard is plotted as a function of concentration (Skoog et al., 1998).
An ICP-MS instrument is more expensive than that employed for ICP-OES, but combines the fast multielement features of the latter with the significantly lower detection limits. The two main instrumental configurations used with the ICP ion source are the quadrupole and the double focusing sector field-based mass spectrometers. Both methods are based on ICP sample ionisation and transport into the mass filters. The suitability of the ICP as an ion source has been reviewed by e.g. Montaser and Golightly (1987) and Moore (1989). When using a quadrupole-based mass spectrometer there will always be spectral interferences originating from the plasma gas (i.e. $^{40}Ar^{16}O^{+}$ on $^{56}Fe^{+}$), solvent related (i.e. $^{16}O_2{}^{+}$ on $^{32}S^{+}$ and $^{40}Ar^{14}N^{1}H^{+}$ on $^{55}Mn^{+}$) and matrix (i.e. $^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$, $^{40}Ar^{23}Na^{+}$ on $^{63}Cu^{+}$ and $^{32}S_2{}^{+}$ on $^{64}Zn^{+}$) to deal with. Evans and Giglio (1993) provided a review concerning interferences in Ar ICP-MS. To decrease or even exclude the effect of spectral interferences, the following approaches can be used:

- Matrix separation
- Mathematical interference correction
- Spectrally resolving the interferences by sector field ICP-MS

To realise the third approach, high resolution is needed, which can be obtained by double focusing sector field ICP-MS (ICP-SFMS) instruments (Bradshaw et al., 1989).
Generally, the double focusing mass analyser separates ions of different masses by passing the ion through the magnetic and electrostatic sectors (Figure 1). The detector registers the ion current. The computer than relates the ion current to mass-to-charge ratio and to the number of ions. The mass separation principle of a sector field instrument will now briefly be explained (Marriot et al., 1998 and Skoog et al., 1998). To begin with, there is the interface that couples the ICP torch, which operates at atmospheric pressure, with the mass

spectrometer that requires a pressure of less than 10^{-4} torr. The functions of the interface are to separate the inlet system from the residual analyser, extract the sample ions from the plasma torch and reduce the gas pressure in the first stage of a differential pumping system. The sampler and skimmer cones extract the plasma ions, and provide the volume for the first pressure reduction stage. The extraction lens is the first element in the ion optics system. It extracts the sample ions from the skimmer cone region and accelerates them in the direction of the analyser. As the ions leave the lens system they enter the flight tube, transporting them across the magnetic field. The flight tube follows the circular path of the ions in the magnetic field. It is connected to the detector section of the analyser and the electrostatic analyser (ESA). For a given field strength, the radius of the path increases with mass-to-charge ratio and acceleration voltage. When scanning the magnetic field, or the acceleration voltage, or both in a specific way, ions are swept over the optimum path radius in mass number order. The selected ions then pass through the exit slit and enter the ESA. The ESA sector is an ion optical focusing element. In combination with the magnetic sector it provides the double focusing capabilities of the mass spectrometer. The focusing properties of the ESA are angular focusing and energy focusing. The ion deflections resulting from small energy differences in the magnetic sector are corrected in the ESA by an exactly inverse deflection. Therefore, if very small slit apertures are used for the entrance and the exit slits, double focusing provides very high resolution. Further details about the ion separation method and the operating principle of the ICP-SFMS instrument can be found elsewhere (Marriot et al., 1998 and Skoog et al., 1998a). The actual order of the magnetic and electrostatic mass filters differ depending on the manufacturer.

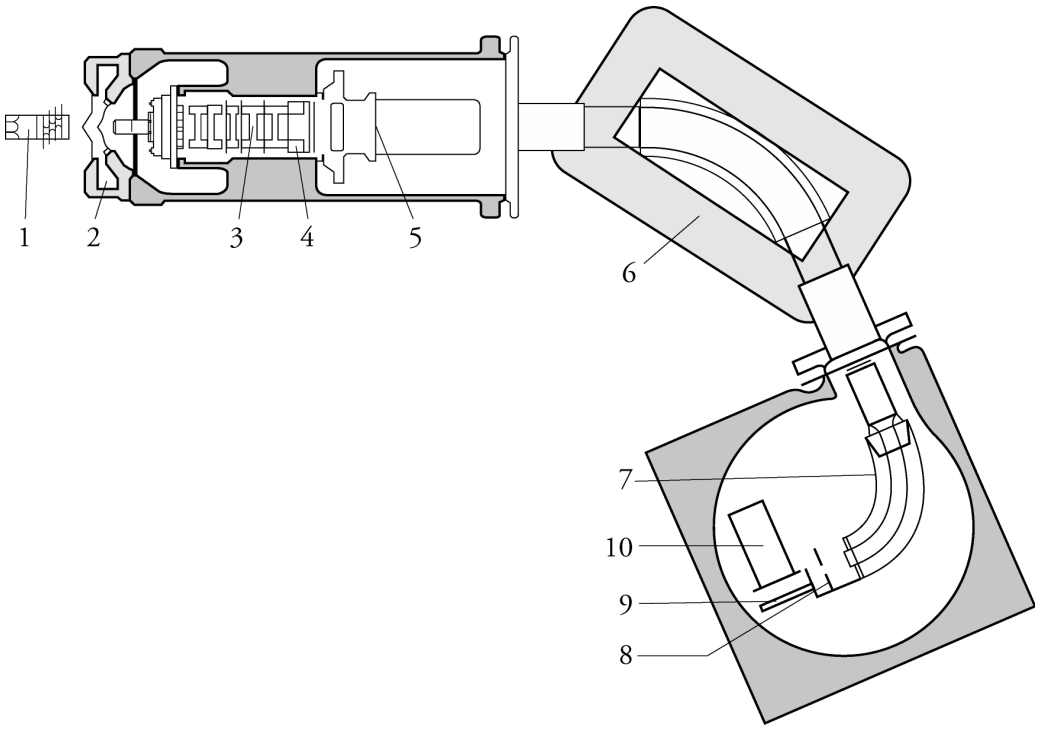

Figure 1. A schematic of a double focusing sector field ICP-MS instrument. 1, ICP, ion source; 2, interface, including sampler and skimmer cones; 3, transfer and focusing optics; 4, beam focusing lenses; 5, entrance slit; 6, electromagnet; 7 electric sector (ESA); 8, exit slit; 9, conversion dynode; 10, electron multiplier.

The advantages of using ICP-SFMS have been shown in many different applications to trace and ultra-trace elemental analysis in a variety of sample types such as iron meteorites

(Campbell and Humayun, 1999), alpine snow (Döring, 1997), high-purity process chemicals (Wildner, 1998), seawater (Rodushkin and Ruth, 1997, Garbe-Schönberg et al., 1998), body-fluids (Rodushkin et al., 2000; Begerow et al., 1997; Riondato et al., 1997), biological materials (Begerow et al., 2000; Rodushkin and Axelsson, 2000) and plant materials (Rodushkin et al., 1999). The common type of sample analysed by ICP-SFMS when using a solution nebulisation introduction system (SN) is that prepared by wet digestion or fusion. Wet chemical sample preparation has its limitations, such as incomplete sample digestion or losses during the heating process of fusion. These drawbacks result in incomplete recovery of some elements. There are, however, several examples of solid sampling techniques, for example glow discharge mass spectrometry and introducing a slurry to the ICP-MS. One of the recent innovations in further improving the analytical applicability of ICP-SFMS is to connect it with a laser ablation (LA) sampler. This system has all the benefits of a sector field instrument as well as the possibility to obtain spatial information on solid samples. The hardwere used throughout this thesis is an ICP-SFMS instrument, equipped with an UV LaserProbe LA system (both from Finnigan MAT, Bremen, Germany). This ICP-SFMS instrument can be operated in low- (LRM $m/\Delta m$ about 300), medium- (MRM $m/\Delta m$ about 4500) and high- (HRM $m/\Delta m$ about 9200) resolution modes.

Laser ablation

Laser ablation is one all-round solid sampling technique for ICP spectrometry and was first described by Thompson et al. (1981) and Gray (1985), for ICP-AES and ICP-MS, respectively. The LA sample introduction system is designed for solid sampling with only minimal sample preparation. In the LA unit, the pulsed laser beam is focused onto a point on the solid sample (10-500 µm in size), giving power densities as great as 10^{12} W/cm^2. Such high-intensity radiation rapidly vaporises most materials, even refractory ones. A flow of argon is used to transport the vaporised material to the ICP were atomisation and ionisation takes place. In Figure 2 a sketch of the LA set-up is shown (Skoog et al., 1998).

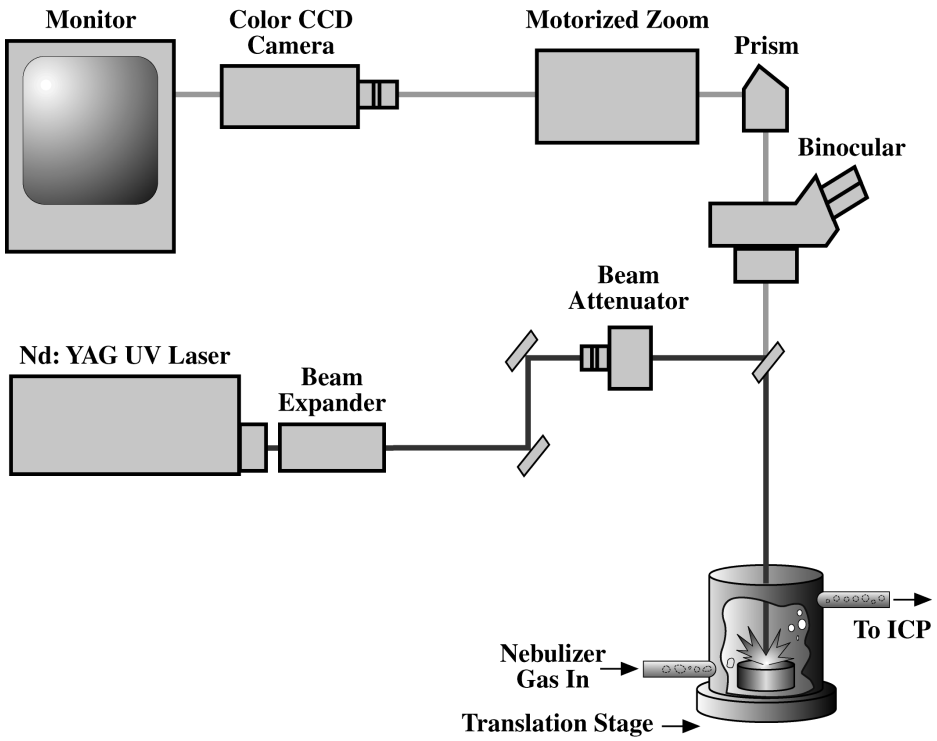

Figure 2. A schematic over the laser ablation sample introduction system used together with ICP-SFMS

Interest in LA comes from the ability to sample diverse materials ranging from conducting to non-conducting inorganic and organic compounds as solids or powders. The LA method also has the advantage over conventional bulk analysis, that the sampling of a small and well-defined surface area allows spatial information on the distribution of analysed elements to be acquired. The signal intensity obtained is directly proportional to the amount of ablated material transported to the plasma (Montaser, 1998b). The multi-elemental study of minerals is of particular concern for geologists, for whom spatial information often is of special importance (Nesbitt et al., 1997, Butler and Nesbitt, 1999, Devos et al., 2000). Chemical fractionation occurring during ablation and transport to the plasma has been reported by Jeffries et al. (1996). In a recent review by Russo et al. (1998), the current achievements and limitations in LA sampling for chemical analysis were summarised. Several current issues related to LA sampling are discussed, including calibration and optimisation, fractionation, sensitivity enhancements, mass loading, and particle transport. In this review the great potential and the variety of possible applications of LA-ICP-MS are illustrated.
Although valuable semi-quantitative data easily can be obtained by LA-ICP-SFMS, calibration, which is required for quantitative analysis, remains the "Achilles heel" of the technique. There are considerable problems involved in obtaining quantitative results by LA, mainly related to calibration and the lack of standard materials with well-characterised elemental concentrations (Longerich et al., 1996). The use of a simple dissolution method followed by ICP-MS or ICP-OES still is the most reliable solution, until matrix matched calibration materials for LA become available. The difficulties connected to each particular application of LA-ICP-MS demand careful development of the analytical procedure.

Aims

The major goal of this study has been to investigate the capabilities of LA-ICP-SFMS for qualitative and quantitative analysis of various solid materials. Owing to the lack of matrix matched calibration materials, different calibration approaches have been studied in order to realise quantitative analysis by LA sampling. The possibility to obtain spatial information by LA sampling has also been investigated.

Summary and discussion of results

When using LA sampling, the first problem to solve for each particular sample type lies in devising a calibration procedure and a way to determine the accuracy of the analysis. The calibration standard for LA needs to fulfil the following criteria: the levels of impurities have to be well above the LODs; the analysed elements have to be homogenously distributed in the material; and the ablation characteristics for the samples and the standard should be as similar as possible (Russo et al., 1998; Perkins et al., 1997). One way to obtain a standard meeting the aforementioned criteria is to prepare an in-house calibration standard. By spiking a powdered sample with standard solutions containing analyte and internal standard (IS) elements, it is possible to prepare such an in-house standard. This means to quantify material by LA has been investigated earlier for sulphide minerals (Perkins et al., 1997), carbonates (Perkins et al., 1991) and marine samples (Fuge et al., 1993). After drying and homogenisation the powdered material was pressed to form small disks. This approach was used for LA-ICP-SFMS analysis of coal samples and standards in **Paper I** of this thesis. The aim of the work was to quantitatively determine 70 elements in coal powder, using a combination of different microwave (MW) dissolution methods and fusion, as well as direct sampling by LA. In the past decade, MW assisted dissolution of coal has been developed as a rapid and safe sample preparation method, that requires smaller amounts of acids and that is less prone to

contamination than traditional hot-plate protocols. Various acids and acid mixtures, including HNO_3, HCl, HF, $HClO_4$, H_2SO_4, H_3BO_3 and H_2O_2 (Alvarado et al., 1990; Alvarado et al., 1998; Filey et al., 1990; Igarashi et al., 1991; Ikävalko et al., 1991; Nguyen et al., 1998), have been used for coal samples. Alternative techniques of sample pre-treatment that have been applied to ICP-AES and/or ICP-MS coal analysis include slurry nebulisation, electrothermal slurry vaporization, and LA. These techniques present several advantages, including simpler sample preparation with lower risks for contamination and analyte losses. Ebdon et al. (1988), obtained quantitative results for a large number of minor and trace constituents in coal by slurry nebulisation ICP-MS. However, poor results were obtained for Al, Se, Cd, Sb, U and some other elements. The dissolution methods evaluated together with the LA method in Paper I consisted of four different acid combinations and two different fusion methods.

The precision for the majority of elements was found to be in the range 10-20% for LA and in general better than 3-5% for all MW and fusion digestion procedures. In spite of this relatively poor precision common for LA, the method was still found to be ideally suited for rapid screening of element concentration ranges in coal, where 15–20% accuracy can be accepted. Possible reasons for such variations in result can be heterogeneous analyte distributions, including inhomogeneous mixing of coal powder with IS solution, caused by density differences between different points in the pressed coal tablets.

During the evaluation of the dissolution methods (including fusion), it was found that elemental recoveries obtained with a mixture of nitric and hydrofluoric acids with hydrogen peroxide were superior to those obtained with other mixtures. Recoveries for Si, Hf, W, Zr, REE and Nb were low. Hence, a combination of this procedure and lithium metaborate (LMB) fusion without ashing should be applied to coal analysis in order to obtain accurate data for as many elements as possible. It appears that the use of aqua regia provides no improvement in recovery and that hydrochloric acid must be avoided in coal digestion. As a final conclusion of the coal analysis work it can be said that, even when it was shown to be possible to evaluate accuracy for more than 50 elements, new coal reference materials with certified values for a larger number of elements are needed in order to facilitate method validation.

The limitation of the calibration method used in Paper I is the addition of standard solution to the coal powder, as this may result in a surface layer of added standard after drying. Furthermore, the spatial information is lost when a milled and pressed sample has to be used. By using LA sample introduction, the elemental composition of mineral grains can be determined *in situ*, with only minor sample preparation. Consequently, if a dissolved sample is needed, the minerals of interest should be separated from the host rock, prior to dissolution or fusion. Mineral separation is time consuming, and sample pre-treatment may result in incomplete recovery and/or analyte losses (Eggins et al., 1998). Moreover, the SN approach provides only bulk chemical data information.

Due to economic considerations it is important that contaminants, such as Co, Cd, Fe and Cu are low during the production of Zn ore concentrates. In **Paper II,** the potential of LA for the direct analysis of sphalerite using ICP-SFMS, was studied in order to measure impurities in sphalerite. The use of Zn for internal standardisation, together with correction for FeS impurities in sphalerite, allows straightforward quantification without using external methods for the determination of the actual Zn content. LA-ICP-SFMS intensities were normalised to intensity/concentration of the same isotope after conventional pneumatic nebulisation introduction to the ICP-SFMS.

It has been concluded previously (Watling et al., 1995) that direct quantification of the elemental composition of sulphide minerals (including sphalerite), using a 1064-nm Nd: YAG laser, is impossible. This is because of variations in sample matrices between minerals from varying deposits due to different surface textures, different degrees of crystallinity and

annealing. Though Perkins et al. (1997), obtained quantitative results using pressed mineral powders, the principal advantages of LA over SN, the freedom from mineral separation and minimal sample preparation are lost.

The ZnS fragments used were cut out from drill core samples, from the sphalerite-rich Zinkgruvan ore deposit. For LA, suitable sized (approximately 2 cm^2) fragments of the mineral were mounted in fast setting epoxy resin and ground to a flat surface. For sphalerite, Zn is a suitable IS choice as its concentration can be assumed to be relatively constant in the mineral. ^{66}Zn can therefore be utilised as an IS, and calibration then consists of establishing the relationship between the observed intensity ratio and the relative concentrations, analyte/IS. This is most conveniently performed by means of conventional nebulisation of aqueous standard solutions containing the elements under consideration.

The LA-ICP-SFMS results were compared with data obtained by conventional SN introduction of sample solutions following acid digestion. There was good agreement between the two methods for homogeneously distributed elements. For the majority of the elements under consideration, LA-ICP-SFMS precision was better than 10% RSD. The determination of accuracy could not be done when there was no available reference material having similar chemical and physical properties, and having not just the major elements certified. Limitations to this quantification approach may arise from possible changes in analyte/IS ratios between SN and LA (for example caused by changes in plasma temperature) and from element fractionation effects during ablation.

In Paper III, quantification of 69 elements in totally 27 samples of sphalerite (ZnS), pyrite (FeS_2), galena (PbS), pyrrhotite (FeS) and chalcopyrite ($CuFeS_2$) was performed by ICP-AES, ICP-SFMS and atomic fluorescence spectrometry (AFS) after mineral separation and dissolution. The aim of this paper was to quantify a wide range of elements in a set of in-house minerals standards for LA-ICP-SFMS. The analysis of the selected sulphides depended on acid MW digestion. Five different acid combinations were used as well as one fusion method. Further information regarding digestion techniques for the analysis of geological materials by ICP-AES and ICP-MS, can be found in recent reviews (Balaram, 1997 and Barefoot, 1998). The most successful digestion procedure tested in this work was a two-stage MW digestion with HNO_3 (or with aqua regia when the determination of platinum group elements is required), which is sufficiently rapid and efficient for dissolving all tested minerals. However, for the complete recovery of elements which are bound into refractory mineral impurities in the host minerals, the addition of HF or fusion is necessary.

The accuracy of the dissolutions and analysis was evaluated by comparing obtained results with certified/recommended concentrations for the reference materials (RMs). For the pyrite and galena RMs the differences between certified and found concentrations were insignificant for 15 out of 19 and 18 out of 20 elements, respectively. However, the agreement with the recommended values was not that good. Only eight out of 31 elements in pyrite RM and two out of 27 in the galena material fall inside a 20% range around the recommended values. For the elements Cd, Sn and Tl, results reported in this study for the pyrite RM were about 100 times lower than the recommended concentrations. The next step was to determine whether these discrepancies arose from inhomogeneities in the supplied RM or if there were some problems concerning the dissolution method. Five elements in the pyrite RM were determined by direct LA, including two in agreement (Ag and Bi) and three disagreeing (Cd, Sn and Tl) with certified or recommended values. Only coarse quantification was performed using normalisation to the intensity of the ^{123}Sb isotope, assuming the accuracy of the tabulated antimony concentration. In spite of relatively high uncertainty (1s), measured Ag and Bi concentrations compare well, both with results obtained after sample digestion, and with certified values. Thus an error of less than 50% can be expected while using this means of quantification. LA results for Cd (1.6±0.3µg g^{-1}), Sn (12±9 µg g^{-1}) and Tl (0.29±0.04 µg g^{-1})

in the pyrite RM are consistent with those obtained after sample digestion, thus suggesting poor accuracy for the recommended values for these elements.
It seems that results for PS-1 and GF-1 reference materials show lack of accuracy in recommended concentrations for many of the trace and ultra-trace elements, as well as possible inhomogeneity when using a 50 mg sample amount. It was also found that the selected minerals were suitable as matrix-matched standards for the determination of about 20 trace and ultra-trace elements by LA, providing the remaining untreated solid mineral fulfils certain characteristics for a solid standard material, set by the analyst (e.g., less than 10% deviation in concentration inside the mineral section, number of cracks inside the material should be low, material should be large enough to polish).

Laser applications outside geology

The use of LA for biological applications has been investigated, for example in teeth (Lee et al., 1999, Lochner et al., 1999, Ghazi et al., 2000) and marine animal skeletons (Craig et al., 2000). Analysis of clinical samples attracts quite a lot of attention, especially hair analysis due to the straightforward and painless sampling, even from small children. Hair can also be used to advantage for the evaluation of nutritional status, for diagnosing diseases and in forensic cases (e.g. Chatt et al., 1980; Passwater and Cranton, 1983; Katz and Chatt, 1988; Valkovic, 1988; Contiero and Folin, 1994; Batzevich, 1995; Bencjo, 1995; Borella et al., 1997). When the amount of hair sample is insufficient, nails can also be used (Gulson, 1996). The most frequently cited factors, which may jeopardise the usefulness of hair and nail analysis, include difficulties in differentiating between indigenous and exogenous deposition and concentration anomalies. In **Paper IV** ICP-SFMS was used for the multielemental analysis of hair and nails from human subjects. The method used to analyse the hair and nail samples consisted of a MW acid digestion with HNO_3 and H_2O_2, as well as the direct ablation of washed and unwashed nails. To evaluate the efficiency of the nail cleaning procedure, surface and interior ablation was performed. The method presented shows the capabilities to determine quantitatively 71 elements by ICP-SFMS in hair and nails. The most critical step when using such samples is to evaluate the origin of the sample surface impurities so they can be removed. Several cleaning procedures have been proposed in the literature, but there is still no standard procedure available. The final goal of the washing procedure should be to remove all loosely adhering metals associated with fat, sweat, and dirt without altering the indigenous content of elements in the samples (Caroli et al., 1992). When performing analyses of hair and nails both before and after washing it was seen that more than 10 elements were associated with surface contamination. Of this group of elements, Al, Bi, Hf, K, Na, Ti, Th and Zr had more than two times higher concentrations before the washing procedure. Even though cleaning seemed effective, further evaluation was provided by direct LA. The qualitative results obtained by LA were based on the ratio of the element of interest to ^{32}S, giving rapid spatial information from the nails. The ratio was used to correct for variations in ablation efficiency. In Figure 3 (paper IV) the spatial resolution for Mg, Zn and Ti is expressed in terms of the element to S intensity ratio along the nail. The results indicate that, even if the washed nail is ablated from the backside, there is visible contamination seen compared to the second ablation. The highest concentrations were found closest to the cut edges, probably due to the intimate contact with the skin, thereby being more difficult to clean using common hygienic washing. The ICP-SFMS method provides multielemental information from both hair and nails in this work. The method also shows the ability to resolve a significant part of the spectral interferences occurring in ICP-MS. The laser ablation experiment showed a potential for differentiating between indigenous and exogenous sources, as well as for determining short time fluctuations in the spatial distribution of elements in nails. This

analytical methodology was applied for a study of inhabitants in northern Sweden (Rodushkin and Axelsson, 2000).

Overall conclusions

This thesis describes several applications where the use of LA connected to the ICP-SFMS has proven to be a valuable and time saving approach. The use of LA has been shown to provide spatial information on the elemental composition of minerals and nails, but the lack of multi-elementally characterised reference materials has meant that a variety of calibration strategies have had to be used. In order to develop a new LA method, it is necessary to have, or present in direct connection to the method development, a quantification procedure for the unique matrix. This is needed to calibrate the data obtained. Using different forms of dissolution methods parallel to the laser experiments has been used in this work to assess the accuracy of the results. The different sample types have been dissolved, usually by a MW or fusion digestion method, then analysed by an available instrumental technique (ICP-SFMS, AFS, ICP-AES). LA has shown to be a convenient sampling instrument for sulphide mineral samples. The quantification procedure presented for sphalerite resulted in data in good agreement with results obtained by mineral dissolution experiments performed in parallel. The calibration strategy adopted for coal powder, using doping by standard solutions, was also successful for quantification by LA-ICP-SFMS. However, after several years on the market, LA method development is still restrained by the lack of matrix-matched standards.

Further studies

A major advantage with the LA sampling is that spatial distributions of the analysed elements in solid samples can easily be obtained. Further studies should be directed towards the development of methods for multielemental analyses with high spatial resolution. Al et al. (1997), used time of flight laser ionisation mass spectrometry to study adsorption of trace elements on the surface of pyrite grains in mine tailings rich in sulphide minerals. The possibilities to investigate surface adsorption on mineral grains by using LA-ICP-SFMS could be evaluated by determining the surface contribution and comparing this with results obtained from the interior of the mineral. This could be achieved by repeating the ablation sequence on a defined area, thereby obtaining concentration depth profiles for various elements. Method development for obtaining multielemental concentration profiles with high resolution in sample types such as finely laminated sediments, where redox boundaries are of particular interest, and Fe-Mn concretions represents a priority area. The possibilities of using LA sampling for isotope geochronology of titanite grains by ICP-SFMS are also worth pursuing.

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Rodushkin I., Axelsson M.D. and Burman E.

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Multielement analysis of coal by ICP techniques using solution nebulization and laser ablation

Ilia Rodushkin [a,*], Mikael D. Axelsson [b], Erik Burman [a]

[a] *SGAB Analytica, Luleå University of Technology, S-971 87 Luleå, Sweden*
[b] *Division of Applied Geology, Luleå University of Technology, S-971 87 Luleå, Sweden*

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Abstract

The combination of inductively coupled plasma atomic emission spectrometry and high resolution inductively coupled plasma mass spectrometry for the determination of 70 elements in coal were studied. Four microwave-assisted digestion procedures with different dissolution mixtures (nitric and hydrofluoric acids, aqua regia and hydrogen peroxide), lithium metaborate fusion with and without previous sample ashing as well as direct sampling by laser ablation (LA) have been tested. Examples of spectral interferences are given and different correction procedures are discussed. Detection limits in the low ng g^{-1} range were obtained for most of the elements investigated by using high-purity reagents and by taking special care to prevent sample contamination during preparation. The precision was assessed from replicate analysis (including sample preparation) of coal samples and was found to be, as average values far all elements, 4–5% RSD and 10–15% RSD for procedures including sample digestion and LA sampling, respectively. The accuracy of the overall analytical procedures was estimated by analysis of certified reference materials and of a coal sample obtained from the Interlab Trace round robin test. Among the dissolution mixtures tested, the combination of nitric and hydrofluoric acids with hydrogen peroxide provide the best agreement with certified, recommended, literature-compiled or consensus values, though fusion is necessary to obtain quantitative recoveries for Si, Cr, Hf, W, Zr, Y. In general, results obtained by LA fall within $\pm 20\%$ of those obtained after digestion.

Keywords: Coal; Laser ablation; High resolution inductively coupled plasma mass spectrometry; Multielement analysis

1. Introduction

Complete chemical characterization of coal is of primary importance in a variety of ecological, industrial and geological applications. The coal mining industry, as well as the combustion of coal for energy production, are well recognised sources of environmental pollution [1,2]. Element flows between coal, bottom ash, fly ash and flue gases are under study with the aim to refine coal combustion technology. The inorganic chemical composition of coal yields information about the

* Corresponding author. Tel.: +46-920-72489; fax: +46-920-72490.
E-mail address: ilia.rodushkin@sgab.se (I. Rodushkin)

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depositional environment, as well as the sources and differential fixation of elements during coalification processes [3].

Among analytical techniques for the determination of coal-associated elements, inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are interesting due to the combination of multielement capability, wide dynamic range and low instrumental detection limits. Both techniques require sample preparation, the type of which depends mainly on the sample introduction system available. Solution nebulization, which is the most commonly adopted tech-

Table 1
HR-ICP-MS and LA operating conditions and measurement parameters

Rf power/W	1400
Sample uptake rate/ml min^{-1}	0.3 (solution nebulization only)
Argon gas flow rates/l min^{-1}	
Coolant	15
Auxiliary	0.85
Nebulizer	1.15–1.30
Ion sampling depth/mm	9
Ion lens settings	Adjusted to obtain maximum signal intensity
Torch	Demountable with sapphire injector
Nebulizer	Microflow PFE
Spray chamber	Scott type PFE (double-pass)
Sample cone	Nickel, 1.1 mm orifice diameter
Skimmer	Nickel, 0.8 mm orifice diameter
Isotopes	
Low resolution mode	^{7}Li, ^{9}Be, ^{11}B, ^{23}Na, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{98}Mo, ^{101}Ru, ^{103}Rh, ^{105,108}Pd, ^{107,109}Ag, ^{111,114}Cd, ^{115}In[b], ^{120}Sn, ^{121}Sb, ^{126,128}Te, ^{127}I, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{143}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{173}Yb, ^{175}Lu[b], ^{178}Hf, ^{181}Ta, ^{184}W, ^{185,187}Re, ^{191,193}Ir, ^{194,195}Pt, ^{197}Au, ^{201,202}Hg, ^{205}Tl, ^{206,207,208}Pb, ^{209}Bi, ^{232}Th, ^{238}U
Medium resolution mode	^{26}Mg, ^{27}Al, ^{28}Si, ^{31}P, ^{32}S, ^{39}K, ^{44}Ca, ^{45}Sc, ^{47,49}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{62}Ni, ^{63}Cu, ^{64}Zn, ^{69,71}Ga, ^{72,74}Ge, ^{79}Br, ^{115}In[b]
High resolution mode	^{75}As, ^{78}Se, ^{115}In[b]
Acquisition mode	E-scan
No. of scans	15 for each resolution
Acquisition window/%[a]	50 in LRM; 120 in MRM and HRM
Search window/%[a]	50 in LRM; 80 in MRM and HRM
Integration window/%[a]	50 in LRM; 60 in MRM and HRM
Dwell time per sample/ms	10 in LRM; 20 in MRM, 40 in HRM
No. of samples per nuclide	30 in LRM, 25 in MRM and HRM
Laser (Nd:YAG)	
Wavelength/nm	266
Pulse width/ns	3
Pulse energy/mJ	2
Ablation diameter/μm	50
Repetition rate/Hz	20
Number of shots per point	50
Sample scan mode	Zigzag line scan across rectangular area
Distance between points/mm	0.1

[a] Percent of peak width.
[b] Internal standard.

Table 2
Mathematical correction for non-resolved interferences

Isotope	Interference	Mean degree of correction[a] for NIST SRM 1635 and Interlab samples
^{101}Ru	^{89}RbO	2.8
^{103}Rh	^{87}SrO, ^{87}RbO	2.4
^{105}Pd	^{89}YO	8.0
^{108}Pd	^{108}Cd, ^{92}ZrO, ^{92}MoO	6.5
^{107}Ag	^{91}ZrO	1.5
^{109}Ag	^{93}NbO	1.4
^{111}Cd	^{95}MoO	<1.01
^{114}Cd	^{114}Sn, ^{98}Mo	1.02
^{151}Eu	^{135}BaO	1.15
^{157}Gd	^{141}PrO	1.3
^{159}Tb	^{143}NdO	<1.01
^{163}Dy	^{147}SmO	<1.01
^{165}Ho	^{149}SmO	<1.01
^{167}Er	^{151}EuO	<1.01
^{169}Tm	^{153}EuO	<1.01
^{173}Yb	^{157}GdO	<1.01
^{175}Lu	^{159}TbO	1.06
^{178}Hf	^{162}DyO	<1.01
^{181}Ta	^{165}HoO	<1.01
^{185}Re	^{169}TmO	1.15
^{187}Re	^{171}YbO	<1.01
^{191}Ir	^{175}LuO	4.0
^{193}Ir	^{177}HfO	2.6
^{194}Pt	^{178}HfO	3.9
^{195}Pt	^{179}HfO	2.2
^{197}Au	^{181}TaO	4.2
^{202}Hg	^{184}WO	1.1

[a] Ratio uncorrected/corrected concentration.

nique, requires transfer of analytes from the solid phase into solution by either acid dissolution or fusion. In the past decade, microwave (MW) assisted dissolution of coal has been developed as a rapid and safe sample preparation method, that requires smaller amounts of acids and that is less prone to contamination than traditional hot-plate protocols. Various acids and acid mixtures, including HNO_3, HCl, HF, $HClO_4$, H_2SO_4, H_3BO_3 and H_2O_2 [2,4–8], have been used for coal samples. Important restrictions may arise from safety considerations ($HClO_4$ and HF), negative effects on instrument parts (HF and H_2SO_4), matrix effects (H_2SO_4 and H_3BO_3) and spectral interferences in ICP-MS (H_2SO_4, $HClO_4$ and HCl). The limitation of acid-based sample preparation is incomplete digestion while the fusion method enables resistant samples to be dissolved more easily after they have been fused [9]. Using lithium metaborate (LMB) as flux, more than 50 elements were successfully determined in coal ash by Bettinelli and Baroni [10]. However, a significant number of volatile elements, such as Hg, Se, Sb, Cd, Ge, Pb, As, Tl and S, can be completely or partially lost during ashing or fusion. Other problems that are present both in acid digestion and fusion include hydrolysis of refractory elements (e.g. Ta and W) if HF is not used and the low solubilities of the fluoride salts of Y, Pb, Ca, U and Th [11,12].

Alternative techniques of sample pre-treatment that have been applied to ICP-AES and/or ICP-MS coal analysis include slurry nebulization, electrothermal slurry vaporization, and laser ablation (LA). These techniques present several advantages, including simpler sample preparation with lower risks for contamination and analyte losses. Ebdon et al. [13] obtained quantitative results for a large number of minor and trace constituents in coal by slurry nebulization ICP-MS. However, poor results were obtained for Al, Se, Cd, Sb, U and some other elements. Moreover, sample grinding depends on coal type (bituminous or sub-bituminous) and the time necessary to reduce the size of the coal particles to $<5–10$ μm can be as long as 24 h [10].

Coal analysis by ultrasonic slurry electrothermal vaporization ICP-MS has been reported by Gregoire et al. [14] and Fonseca and Miller-Ihli [15]. Only a few elements (V, Mn, Ni, Cu, Pb, Cr and Co) have been determined in these studies and it was shown that both the addition of palladium and the oxygen ashing are necessary to improve accuracy.

Chenery et al. [16] reported quantitative determination of 14 trace elements by LA-ICP-MS. Sample preparation was restricted to the polishing of coal blocks and calibration was based on introduction into the ICP of a mixture of ablated material and a nebulized solution, produced in the mixing chamber. A questionable part of this method is the accuracy validation that is obtained by determining trace element contents in a glass reference material.

Table 3
Method detection limits (μg g^{-1}, based on HR-ICP-MS determination)

Element	Procedure A1	Procedure A2	Procedure A3	Procedure A4	Procedures B	Laser ablation
Si	2.4	5.4	3.2	6.3	24	14000
Al	0.27	0.66	0.23	0.95	2.30	1.80
Ti	0.37	0.47	0.56	0.64	0.57	0.05
Fe	0.32	0.36	0.29	0.36	1.20	0.50
Na	5.7	6.9	11.2	9.5	14	11.0
Ca	4.1	3.9	5.1	4.8	9.6	9.00
Mg	1.8	2.7	2.1	3.6	7.5	17
K	5.2	4.6	7.0	6.2	16	60
S	16	25	23	30	28	26
Ag	0.0038	0.0019	0.0014	0.0019	0.0048	0.001
As	0.032	0.022	0.048	0.052	0.095	0.008
Au	0.0003	0.0005	0.0012	0.0011	0.0002	0.001
B	0.19	0.15	0.19	0.11	Nd	8
Ba	0.013	0.017	0.012	0.022	0.12	0.028
Be	0.0029	0.0015	0.0068	0.0020	0.0016	0.024
Bi	0.0006	0.0001	0.0016	0.0021	0.0004	0.001
Br	9.4	8.4	7.8	6.2	6.6	17
Cd	0.0007	0.0007	0.0016	0.0012	0.0029	0.011
Co	0.015	0.012	0.015	0.021	0.033	0.022
Cr	0.022	0.017	0.019	0.013	0.053	0.001
Cs	0.0003	0.0001	0.0016	0.0011	0.0010	0.0004
Cu	0.031	0.041	0.026	0.034	0.26	0.140
Ga	0.0031	0.0030	0.0057	0.0062	0.055	0.008
Ge	0.007	0.005	0.044	0.076	0.016	0.039
Hf	0.0001	0.0062	0.0007	0.0067	0.0031	0.003
Hg	0.013	0.008	0.014	0.027	0.011	0.060
I	0.11	0.41	0.15	0.16	0.16	0.370
Ir	0.00007	0.00004	0.00009	0.00018	0.00005	ND
Li	0.010	0.028	0.014	0.047	Nd	12
Mn	0.029	0.033	0.045	0.077	0.094	1.200
Mo	0.014	0.024	0.009	0.018	0.009	0.018
Nb	0.0008	0.0012	0.0012	0.0023	0.0039	0.004
Ni	0.073	0.074	0.037	0.083	0.077	0.620
P	0.40	0.37	0.63	0.49	0.44	1.500
Pb	0.0035	0.0090	0.0053	0.0082	0.0056	0.002
Pd	0.0016	0.0033	0.0043	0.0020	0.0024	0.003
Pt	0.0002	0.0004	0.0007	0.0008	0.0007	0.002
Rb	0.005	0.007	0.012	0.013	0.019	0.010
Re	0.00002	0.00002	0.00009	0.00004	0.00005	0.001
Rh	0.00005	0.00009	0.00008	0.00011	0.00020	ND
Ru	0.0002	0.0003	0.0004	0.0003	0.0002	0.004
Sb	0.0019	0.0013	0.0030	0.0012	0.0017	0.007
Sc	0.0003	0.0005	0.0014	0.0026	0.0019	0.003
Se	0.16	0.19	0.22	0.26	0.16	0.111
Sn	0.019	0.034	0.015	0.035	0.015	0.019
Sr	0.004	0.013	0.013	0.025	0.011	0.045
Ta	0.0001	0.0008	0.0002	0.0016	0.0002	0.003
Te	0.0044	0.0047	0.0030	0.0051	0.0054	0.018
Th	0.0007	0.0017	0.0017	0.0043	0.0018	0.001
Tl	0.0006	0.0006	0.0008	0.0007	0.0002	0.004

Table 3 (*Continued*)

Element	Procedure A1	Procedure A2	Procedure A3	Procedure A4	Procedures B	Laser ablation
U	0.0006	0.0005	0.0007	0.0004	0.0007	0.000
V	0.004	0.016	0.006	0.006	0.035	0.005
W	0.0033	0.0054	0.0017	0.0015	0.0018	0.001
Y	0.0012	0.0012	0.0007	0.0010	0.0025	0.006
Zn	0.12	0.15	0.24	0.19	0.48	0.146
Zr	0.008	0.018	0.003	0.017	0.220	0.016
La	0.002	0.001	0.001	0.001	0.016	0.006
Ce	0.008	0.004	0.003	0.012	0.061	0.003
Pr	0.0008	0.0002	0.0004	0.0002	0.0029	0.002
Nd	0.003	0.002	0.004	0.007	0.011	0.005
Sm	0.0007	0.0003	0.0006	0.0002	0.0012	0.003
Eu	0.0002	0.0001	0.0002	0.0002	0.0008	0.003
Gd	0.0006	0.0002	0.0003	0.0004	0.0013	0.014
Tb	0.0001	0.0001	0.0001	0.0001	0.0002	0.001
Dy	0.0002	0.0002	0.0001	0.0002	0.0003	0.003
Ho	0.00005	0.00002	0.00012	0.00003	0.00010	0.0005
Er	0.0002	0.0001	0.0002	0.0002	0.0003	0.002
Tm	0.00002	0.00003	0.00009	0.00003	0.00004	0.000
Yb	0.0002	0.0001	0.0003	0.0002	0.0002	0.006
Lu	0.00005	0.00006	0.00016	0.00006	0.00012	0.002

In another study [17], about 50 elements were determined by LA-ICP-MS after a sample preparation based on the mixing of powdered coal with a binder material (1/1 graphite and cellulose mixture) in a ratio of 1/10 and pressing into a pellet. The results of coal reference materials were, as a rule, within a factor of 5 or better than the reference values. Poor accuracy is the main limitation of this method for multielement analysis of coal.

The present work was undertaken in order to compare different sample dissolution procedures to the determination of about 70 major, minor, trace and ultratrace elements in coal samples, with varying content of bituminous components, by the combination of ICP-AES and double-focusing sector-field ICP-MS. The latter technique, also known as high resolution ICP-MS (HR-ICP-MS), resolves many spectral interferences and provides improved instrumental detection limits in comparison of conventional ICP-MS instruments equipped with quadrupole mass filters (ICP-QMS) [18]. The use of a combination of different analytical techniques permits to obtain, for many elements, two values and this can help to reveal analytical errors.

In this study, two coal reference materials were analysed both after MW dissolution, with different mixtures of HNO_3, aqua regia, HF and H_2O_2 or after LMB fusion, with and without ashing of the samples, and by LA on coal pellets.

2. Instrumental

2.1. Instrumentation

An ARL 3580 (Applied Research Laboratories SA, Ecubilens, Switzerland) ICP-AES instrument was used with a Gilson 100 sample changer. The device has 40 channels for simultaneous multielement detection. Instrument configuration and general experimental conditions are reported elsewhere [19].

The HR-ICP-MS instrument used was an element, equipped with an UV LaserProbe LA system (both from Finnigan MAT, Bremen, Germany). It can be operated in low resolution mode (LRM, $m/\Delta m$ about 300), medium (MRM, $m/\Delta m = 4500$) and high resolution mode (HRM, $m/\Delta m = 9200$). Details of instrumental operating conditions and measuring parameters are given in Table 1.

Table 4
Results for NIST SRM 1635 and comparison with certified and published data

Reference		Found						
		Procedure A1	Procedure A2	Procedure A3	Procedure A4	Procedure B1	Procedure B2	Laser ablation
Macroelements (%)								
Si	0.65[c]	0.022 (0.004)	0.502 (0.012)	0.120 (0.005)	0.507 (0.008)	0.708 (0.014)	0.715 (0.009)	ND
Al	0.32[b], 0.195[d]	0.122 (0.003)	0.296 (0.004)	0.247 (0.018)	0.314 (0.008)	0.319 (0.006)	0.309 (0.008)	0.261 (0.028)
Ti	0.02[b], 0.0205[d]	0.018 (0.001)	0.021 (0.001)	0.017 (0.001)	0.020 (0.001)	0.021 (0.001)	0.021 (0.001)	0.019 (0.002)
Fe	0.239 (0.005)[a], 0.221[d]	0.216 (0.006)	0.225 (0.004)	0.219 (0.006)	0.218 (0.003)	0.231 (0.005)	0.226 (0.009)	0.190 (0.004)
Na	0.24[b]	0.244 (0.002)	0.242 (0.004)	0.236 (0.008)	0.242 (0.004)	0.239 (0.002)	0.235 (0.005)	0.240 (0.030)
Ca	0.54[c]	0.493 (0.007)	0.493 (0.003)	0.507 (0.022)	0.526 (0.009)	0.537 (0.015)	0.526 (0.009)	0.420 (0.061)
Mg	0.1[c], 0.082[d]	0.084 (0.001)	0.086 (0.004)	0.088 (0.003)	0.087 (0.002)	0.091 (0.005)	0.090 (0.004)	0.095 (0.009)
K	0.012[c]	0.008 (0.001)	0.011 (0.001)	0.013 (0.001)	0.013 (0.001)	0.012 (0.001)	0.011 (0.001)	0.007 (0.002)
S	0.33 (0.03)[a]	0.330 (0.010)	0.336 (0.013)	0.271 (0.024)	0.278 (0.018)	0.004 (0.001)	0.042 (0.006)	0.390 (0.030)
Trace elements (μg g^{-1})								
Ag		0.0159 (0.0026)	0.0148 (0.012)	0.0156 (0.0008)	0.0176 (0.0012)	<0.0048	0.0053 (0.0041)	0.0281 (0.0094)
As	0.42 (0.15)[a], 0.6[d]	0.419 (0.027)	0.449 (0.016)	0.411 (0.031)	0.426 (0.012)	0.123 (0.019)	0.403 (0.012)	0.45 (0.09)
Au	<0.006[c]	<0.0011	<0.0015	<0.0011	<0.0013	<0.0027	<0.0045	ND
B	105[c]	128 (3)	126 (1)	134 (15)	130 (7)	ND	ND	119 (12)
Ba	84[c], 75[d]	81.5 (7.1)	84.9 (6.6)	83.2 (6.4)	84.2 (1.8)	84.7 (2.2)	83.1 (5.4)	86 (17)
Be	0.5[d]	0.582 (0.051)	0.552 (0.012)	0.558 (0.033)	0.563 (0.010)	0.572 (0.011)	0.552 (0.006)	0.680 (0.005)
Bi		0.0771 (0.0029)	0.0701 (0.024)	0.0682 (0.0025)	0.0724 (0.0023)	<0.0004	0.0043 (0.0009)	0.085 (0.006)
Br	1.6[c]	13.2 (15.4)	15.3 (6.3)	<7.8	<6.2	<6.6	<6.6	<17
Cd	0.03 (0.01)[a], 10.6[d]	0.0253 (0.0037)	0.0281 (0.0041)	0.0317 (0.0011)	0.0312 (0.0029)	0.0032 (0.0002)	0.0137 (0.0007)	0.033 (0.003)
Co	0.65[b], 1.3[d]	0.649 (0.021)	0.649 (0.034)	0.631 (0.027)	0.667 (0.027)	0.656 (0.01)	0.621 (0.032)	0.62 (0.06)
Cr	2.5 (0.3)[a], 6.7[d]	2.19 (0.04)	2.55 (0.03)	2.05 (0.06)	2.32 (0.11)	2.68 (0.12)	2.62 (0.09)	2.8 (0.4)
Cs	0.053[c], 0.08[d]	0.048 (0.002)	0.060 (0.001)	0.054 (0.003)	0.059 (0.002)	0.058 (0.002)	0.055 (0.001)	0.104 (0.024)
Cu	3.6 (0.3)[b]	3.43 (0.06)	3.45 (0.04)	3.28 (0.04)	3.42 (0.09)	3.28 (0.05)	3.17 (0.18)	4.1 (0.9)
Ga	1.05[b], 7.9[d]	0.879 (0.010)	0.979 (0.016)	0.846 (0.028)	0.878 (0.015)	1.02 (0.04)	1.01 (0.02)	1.0 (0.1)
Ge	2.5[d]	0.241 (0.005)	0.289 (0.020)	0.754 (0.055)	0.821 (0.072)	0.269 (0.051)	0.289 (0.014)	0.73 (0.41)
Hf	0.29[a]	0.148 (0.001)	0.193 (0.02)	0.092 (0.014)	0.163 (0.003)	0.276 (0.009)	0.268 (0.011)	0.26 (0.04)
Hg	0.02[a]	0.028 (0.008)	0.019 (0.001)	0.029 (0.004)	0.028 (0.002)	<0.011	<0.011	0.018 (0.015)
I	0.6[c]	1.60 (0.02)	1.45 (0.06)	1.72 (0.46)	1.66 (0.17)	<0.16	0.31 (0.02)	1.72 (0.02)
Ir		<0.0002	<0.0002	<0.0002	<0.0002	<0.0003	<0.0004	IS[e]
Li	0.83[c], 2.6[d]	1.04 (0.13)	1.44 (0.11)	1.39 (0.12)	1.69 (0.16)	ND	ND	<11
Mn	21.4 (1.5)[a], 21.4[d]	21.5 (0.3)	21.8 (0.3)	21.1 (0.6)	21 (0.2)	20.9 (0.4)	21.3 (0.9)	19.8 (1.5)
Mo	0.27[c], 0.5[d]	0.351 (0.019)	0.352 (0.015)	0.327 (0.008)	0.357 (0.012)	0.367 (0.003)	0.349 (0.013)	0.41 (0.03)
Nb	0.9[d]	0.648 (0.014)	0.723 (0.006)	0.616 (0.065)	0.768 (0.025)	0.742 (0.013)	0.713 (0.018)	1.09 (0.06)
Ni	1.74 (0.10)[a], 4.9[d]	1.72 (0.02)	1.71 (0.03)	1.83 (0.09)	1.86 (0.14)	1.85 (0.14)	1.83 (0.06)	1.6 (0.1)
P	60[c]	61.4 (1.8)	66.1 (1.9)	67.3 (1.2)	66.6 (2.7)	63.5 (1.1)	61.6 (0.9)	83 (26)
Pb	1.9 (0.2)[a], 2.1[d]	1.96 (0.015)	1.91 (0.12)	1.84 (0.04)	1.88 (0.03)	0.128 (0.011)	0.313 (0.024)	1.86 (0.24)
Pd		<0.045	<0.056	<0.037	<0.052	<0.047	<0.051	ND
Pt		<0.0013	<0.0011	<0.0016	<0.0018	<0.0015	<0.0018	ND
Rb	0.7[d]	0.309 (0.023)	0.635 (0.027)	0.484 (0.061)	0.667 (0.017)	0.626 (0.013)	0.618 (0.022)	0.44 (0.05)

Table 4 (*Continued*)

Reference		Found						
		Procedure A1	Procedure A2	Procedure A3	Procedure A4	Procedure B1	Procedure B2	Laser ablation
Re		0.00083 (0.00006)	0.00079 (0.00007)	0.0007 (0.0002)	0.0008 (0.0001)	0.0002 (0.0001)	0.0006 (0.0001)	0.0065 (0.0045)
Rh		<0.0112	<0.0137	<0.0149	<0.0147	<0.0139	<0.0129	IS[e]
Ru		<0.0014	<0.0018	<0.0014	<0.0016	<0.0015	<0.0012	Nd
Sb	0.14[b], 0.20[d]	0.118 (0.003)	0.121 (0.002)	0.129 (0.005)	0.139 (0.006)	0.086 (0.008)	0.136 (0.012)	0.12 (0.01)
Sc	0.63[b]	0.585 (0.007)	0.635 (0.012)	0.567 (0.022)	0.596 (0.009)	0.626 (0.013)	0.614 (0.012)	0.56 (0.08)
Se	0.9 (0.3)[a], 4.0[d]	0.751 (0.101)	0.826 (0.059)	0.871 (0.052)	0.935 (0.068)	<0.16	0.326 (0.031)	0.93 (0.05)
Sn	0.2[d]	0.096 (0.008)	0.086 (0.005)	0.088 (0.004)	0.097 (0.010)	<0.015	<0.015	0.40 (0.08)
Sr	135[c], 110[d]	130 (4)	133 (4)	136 (3)	138 (3)	141 (3)	134 (3)	105 (11)
Ta	0.049[c]	0.0331 (0.0009)	0.0491 (0.0010)	0.0170 (0.0032)	0.0497 (0.0016)	0.0463 (0.0026)	0.0507 (0.0011)	0.074 (0.011)
Te		0.0227 (0.0025)	0.0223 (0.0005)	0.0262 (0.0035)	0.0274 (0.0009)	<0.005	<0.005	0.065 (0.016)
Th	0.62 (0.04)[a], 3.3[d]	0.570 (0.006)	0.640 (0.012)	0.498 (0.035)	0.567 (0.036)	0.628 (0.017)	0.641 (0.028)	0.68 (0.09)
Tl		0.0147 (0.0007)	0.0153 (0.0008)	0.0150 (0.0004)	0.0160 (0.0016)	<0.0002	<0.0002	0.036 (0.011)
U	0.24 (0.02)[a], 1.4[d]	0.242 (0.018)	0.232 (0.006)	0.178 (0.003)	0.211 (0.003)	0.225 (0.003)	0.228 (0.006)	0.27 (0.03)
V	5.2 (0.5)[a], 3.8[d]	4.96 (0.02)	5.37 (0.21)	4.47 (0.15)	5.07 (0.32)	5.38 (0.09)	4.94 (0.34)	4.2 (0.6)
W	<0.9[c]	0.155 (0.004)	0.201 (0.003)	0.157 (0.010)	0.178 (0.005)	0.358 (0.021)	0.339 (0.024)	0.36 (0.04)
Y	12.2[d]	1.82 (0.01)	1.93 (0.04)	1.78 (0.14)	1.89 (0.02)	2.13 (0.11)	2.14 (0.02)	2.5 (0.3)
Zn	4.7 (0.5)[a], 8.8[d]	4.08 (0.26)	4.69 (0.07)	4.95 (0.16)	4.74 (0.3)	4.13 (0.19)	4.13 (0.05)	4.6 (0.5)
Zr	16[c]	4.32 (0.11)	5.61 (0.03)	3.15 (0.50)	5.42 (0.09)	6.26 (0.19)	6.12 (0.35)	8.1 (2.2)
Rare-earth elements (μg g^{-1})								
La	2.1[c]	1.82 (0.02)	1.98 (0.04)	1.77 (0.14)	1.91 (0.07)	1.95 (0.04)	1.95 (0.03)	2.23 (0.37)
Ce	3.6[b], 4.2[d]	3.27 (0.07)	3.63 (0.08)	3.11 (0.24)	3.43 (0.10)	3.54 (0.09)	3.51 (0.02)	3.39 (0.53)
Pr		0.384 (0.015)	0.411 (0.009)	0.365 (0.030)	0.395 (0.006)	0.393 (0.006)	0.387 (0.002)	0.36 (0.07)
Nd	1.4[c]	1.44 (0.04)	1.56 (0.043)	1.34 (0.09)	1.47 (0.05)	1.49 (0.05)	1.45 (0.03)	1.3 (0.1)
Sm	0.25[c], 0.5[d]	0.286 (0.006)	0.298 (0.007)	0.259 (0.021)	0.279 (0.005)	0.286 (0.010)	0.278 (0.008)	0.30 (0.04)
Eu	0.06[b], 0.15[d]	0.0618 (0.0023)	0.0680 (0.0037)	0.0567 (0.0047)	0.0623 (0.0016)	0.0662 (0.0031)	0.0658 (0.0006)	0.078 (0.012)
Gd	0.23[c]	0.243 (0.002)	0.264 (0.005)	0.236 (0.017)	0.247 (0.006)	0.262 (0.009)	0.274 (0.005)	0.298 (0.023)
Tb	0.045[c], 0.17[d]	0.0436 (0.0006)	0.0450 (0.0014)	0.0357 (0.0029)	0.0391 (0.0012)	0.0468 (0.0011)	0.0471 (0.0012)	0.052 (0.008)
Dy	0.31[c]	0.260 (0.005)	0.280 (0.008)	0.229 (0.016)	0.250 (0.007)	0.282 (0.010)	0.286 (0.005)	0.312 (0.028)
Ho		0.0561 (0.0011)	0.0621 (0.0016)	0.0493 (0.0034)	0.0549 (0.0008)	0.0618 (0.0006)	0.0583 (0.0013)	0.066 (0.007)
Er		0.159 (0.02)	0.173 (0.002)	0.140 (0.012)	0.153 (0.005)	0.174 (0.005)	0.168 (0.004)	0.179 (0.024)
Tm		0.0231 (0.0004)	0.0271 (0.0009)	0.0205 (0.0010)	0.0232 (0.0005)	0.0271 (0.0003)	0.0258 (0.0007)	0.033 (0.006)
Yb	0.14[c]	0.135 (0.001)	0.152 (0.004)	0.152 (0.012)	0.160 (0.002)	0.152 (0.006)	0.161 (0.004)	0.178 (0.019)
Lu	0.027[c]	0.0202 (0.0004)	0.0228 (0.0003)	0.0191 (0.0014)	0.0209 (0.0003)	0.0229 (0.0006)	0.0215 (0.0005)	0.031 (0.006)

[a] From NIST certificate (certified values).
[b] From NIST certificate (recommended values).
[c] From references[26–29].
[d] From reference [13].
[e] Element used as internal standard.

Table 5
Results for Interlab coal sample

Reference[a]		Found						
		Procedure A1	Procedure A2	Procedure A3	Procedure A4	Procedure B1	Procedure B2	Laser ablation
Macroelements (%)								
Si		0.040 (0.032)	1.33 (0.06)	0.290 (0.030)	1.18 (0.05)	2.13 (0.07)	2.03 (0.05)	ND
Al		0.147 (0.013)	0.940 (0.090)	0.721 (0.065)	0.961 (0.042)	0.933 (0.022)	0.944 (0.040)	0.97 (0.04)
Ti		0.035 (0.01)	0.049 (0.002)	0.035 (0.002)	0.050 (0.002)	0.050 (0.001)	0.051 (0.001)	0.052 (0.004)
Fe		1.64 (0.03)	1.69 (0.06)	1.63 (0.03)	1.67 (0.05)	1.63 (0.03)	1.65 (0.03)	1.4 (0.1)
Na		0.014 (0.001)	0.020 (0.001)	0.019 (0.002)	0.021 (0.001)	0.020 (0.001)	0.020 (0.001)	0.022 (0.002)
Ca		0.236 (0.002)	0.236 (0.001)	0.246 (0.002)	0.246 (0.006)	0.246 (0.007)	0.240 (0.012)	0.193 (0.018)
Mg		0.073 (0.002)	0.097 (0.002)	0.095 (0.003)	0.102 (0.002)	0.097 (0.002)	0.098 (0.003)	0.090 (0.009)
K		0.068 (0.006)	0.169 (0.005)	0.148 (0.012)	0.166 (0.004)	0.173 (0.002)	0.166 (0.004)	0.14 (0.01)
S		2.70 (0.050)	2.68 (0.050)	2.19 (0.100)	2.15 (0.050)	0.020 (0.008)	0.250 (0.020)	3.5 (0.2)
Trace elements ($\mu g\ g^{-1}$)								
Ag		0.0536 (0.0045)	0.0491 (0.0039)	0.0559 (0.0056)	0.0497 (0.0024)	0.0133 (0.0016)	0.0224 (0.0020)	0.055 (0.005)
As	4.5	4.44 (0.11)	4.49 (0.09)	4.28 (0.19)	4.35 (0.12)	1.54 (0.05)	3.67 (0.01)	3.3 (0.3)
Au		<0.0013	<0.0015	<0.0018	<0.0027	<0.0032	<0.0036	0.011 (0.006)
B		25.9 (1.5)	29.6 (0.5)	24.5 (2.0)	32.8 (1.4)	ND	ND	26 (4)
Ba		15.1 (3.2)	30.7 (1.9)	26.1 (4.8)	30.1 (0.9)	32.1 (1.6)	31.1 (1.4)	30 (1)
Be	1.98	2.12 (0.07)	2.23 (0.15)	2.19 (0.13)	2.19 (0.18)	2.01 (0.05)	1.95 (0.07)	2.9 (0.2)
Bi		0.0670 (0.0029)	0.0651 (0.0004)	0.0700 (0.0031)	0.0679 (0.0011)	0.0041 (0.0001)	0.0161 (0.0018)	0.067 (0.012)
Br		59.5 (0.2)	56.6 (3.5)	15.0 (1.0)	15.2 (2.1)	<6.6	<6.6	42 (20)
Cd	1.5	1.54 (0.13)	1.62 (0.12)	1.53 (0.04)	1.59 (0.07)	0.16 (0.01)	0.27 (0.02)	1.3 (0.04)
Co	3.45	4.77 (0.21)	4.62 (0.37)	3.83 (0.09)	4.01 (0.15)	4.26 (0.1)	4.23 (0.12)	4.6 (0.3)
Cr	15.7	8.8 (0.3)	12.9 (0.9)	11.0 (1.3)	11.7 (0.7)	16.6 (0.6)	15.9 (0.6)	13.1 (0.5)
Cs		0.708 (0.041)	0.974 (0.015)	0.896 (0.013)	0.965 (0.031)	0.954 (0.023)	0.929 (0.026)	0.94 (0.12)
Cu	8.7	7.74 (0.26)	7.62 (0.07)	7.95 (0.31)	7.71 (0.28)	7.74 (0.41)	7.46 (0.23)	6.2 (0.5)
Ga		1.56 (0.07)	2.51 (0.07)	2.37 (0.08)	2.68 (0.04)	2.84 (0.08)	2.68 (0.03)	2.6 (0.1)
Ge		0.25 (0.03)	2.28 (0.14)	1.61 (0.1)	2.94 (0.27)	1.85 (0.09)	1.99 (0.05)	9.0 (2.5)
Hf		0.217 (0.007)	0.385 (0.011)	0.192 (0.045)	0.355 (0.019)	0.677 (0.013)	0.739 (0.019)	0.72 (0.09)
Hg	0.09	0.118 (0.009)	0.117 (0.009)	0.101 (0.016)	0.099 (0.009)	<0.011	0.012 (0.005)	0.19 (0.05)
I		20.2 (1.2)	22.3 (1.2)	19.0 (1.2)	20.6 (0.9)	0.22 (0.04)	0.42 (0.02)	18.9 (0.4)
Ir		<0.0006	<0.0006	<0.0005	<0.0005	<0.0006	<0.0008	IS[b]
Li		3.4 (0.7)	11.2 (0.3)	9.6 (0.7)	11.4 (0.5)	ND	ND	<17
Mn	34.6	35.2 (0.5)	35 (1.4)	35.4 (1.6)	35.6 (0.9)	35.9 (1.1)	34.6 (0.6)	34 (3)
Mo	9.65	6.91 (0.29)	7.17 (0.13)	6.86 (0.19)	6.99 (0.23)	7.09 (0.16)	6.81 (0.26)	5.2 (0.3)
Nb		1.47 (0.05)	1.81 (0.02)	1.24 (0.37)	1.66 (0.12)	1.55 (0.02)	1.46 (0.03)	3.5 (0.4)
Ni	19	17.5 (0.5)	19.1 (1.6)	19.1 (1.1)	19.1 (0.8)	18.7 (0.6)	18.3 (0.3)	24 (2)
P		63.1 (6.2)	65.8 (3)	67.5 (1.3)	65.5 (3.2)	64.9 (2.6)	64.1 (1.9)	81 (14)
Pb	47	51.3 (1.8)	49.1 (0.8)	49.4 (1.2)	50.6 (1.4)	9.6 (1.1)	14.7 (1.3)	53 (2)
Pd		<0.082	<0.097	<0.054	<0.084	<0.124	<0.166	ND
Pt		<0.0021	<0.0027	<0.0022	<0.0025	<0.0023	<0.0034	ND
Rb		7.3 (0.5)	13.3 (0.4)	12.7 (0.5)	13.4 (0.5)	13.2 (0.7)	12.8 (0.5)	12 (1)
Re		0.0138 (0.0005)	0.0137 (0.0004)	0.0137 (0.0006)	0.0130 (0.0009)	0.0009 (0.0001)	0.0086 (0.0004)	0.0148 (0.0035)
Rh		<0.0041	<0.0045	<0.0033	<0.0039	<0.0027	<0.0035	IS[b]
Ru		<0.0017	<0.0035	<0.0025	<0.0044	<0.0019	<0.0028	ND
Sb	0.84	0.138 (0.011)	0.438 (0.004)	0.414 (0.012)	0.453 (0.018)	0.263 (0.005)	0.417 (0.014)	0.49 (0.06)
Sc		1.83 (0.05)	1.98 (0.09)	1.69 (0.20)	1.68 (0.08)	2.08 (0.05)	1.97 (0.04)	2.2 (0.3)
Se	2.3	1.77 (0.21)	1.94 (0.16)	2.31 (0.16)	2.55 (0.17)	0.32 (0.02)	0.56 (0.02)	4.0 (0.7)
Sn		0.151 (0.021)	0.356 (0.008)	0.314 (0.026)	0.347 (0.016)	<0.015	0.080 (0.002)	0.49 (0.07)
Sr		34.0 (1.8)	38.9 (0.4)	37.1 (2.8)	38.2 (0.9)	38.6 (0.7)	37.6 (0.6)	33 (1)

Table 5 (*Continued*)

Reference[a]		Found						
		Procedure A1	Procedure A2	Procedure A3	Procedure A4	Procedure B1	Procedure B2	Laser ablation
Ta		0.005 (0.003)	0.121 (0.002)	0.002 (0.001)	0.124 (0.006)	0.131 (0.003)	0.142 (0.012)	0.26 (0.04)
Te		0.0169 (0.0027)	0.0181 (0.0015)	0.0270 (0.0010)	0.0259 (0.0022)	<0.0054	<0.0054	0.086 (0.017)
Th		1.46 (0.01)	1.75 (0.02)	1.36 (0.16)	1.44 (0.09)	1.70 (0.05)	1.79 (0.03)	1.9 (0.2)
Tl		0.676 (0.027)	0.704 (0.016)	0.642 (0.016)	0.682 (0.019)	0.185 (0.007)	0.272 (0.003)	0.63 (0.08)
U		2.19 (0.09)	2.25 (0.18)	2.18 (0.17)	2.27 (0.008)	2.18 (0.08)	2.16 (0.03)	2.8 (0.4)
V	37.7	33.5 (0.07)	38.1 (2.3)	33.8 (0.8)	35.8 (1.6)	38.1 (0.6)	36.1 (2.4)	33 (5)
W		0.252 (0.037)	0.743 (0.167)	0.567 (0.072)	0.730 (0.082)	0.817 (0.028)	0.902 (0.079)	0.95 (0.14)
Y		4.85 (0.04)	5.18 (0.06)	3.81 (0.32)	4.25 (0.14)	6.12 (0.11)	5.85 (0.28)	6.3 (0.3)
Zn	284	273 (22)	289 (29)	272 (16)	283 (21)	226 (8)	233 (11)	240 (20)
Zr		8.7 (0.3)	13.6 (0.3)	7.3 (2.1)	12.5 (0.6)	13.1 (0.1)	13.7 (1.2)	20 (4)
Rare-earth elements (μg g^{-1})								
La		4.55 (0.16)	6.39 (0.14)	5.99 (0.37)	5.76 (0.21)	6.38 (0.27)	6.47 (0.34)	6.3 (0.8)
Ce		11.7 (0.3)	14.8 (0.4)	14.1 (0.7)	13.5 (0.5)	14.8 (0.1)	15.3 (0.9)	15 (1)
Pr		1.47 (0.05)	1.81 (0.05)	1.71 (0.10)	1.61 (0.08)	1.78 (0.05)	1.77 (0.02)	2.2 (0.3)
Nd		6.00 (0.20)	7.17 (0.30)	6.86 (0.35)	6.47 (0.18)	7.15 (0.11)	7.12 (0.28)	7.5 (0.8)
Sm		1.40 (0.04)	1.55 (0.02)	1.43 (0.09)	1.33 (0.04)	1.51 (0.02)	1.50 (0.03)	1.3 (0.1)
Eu		0.256 (0.005)	0.280 (0.002)	0.289 (0.024)	0.270 (0.011)	0.281 (0.008)	0.273 (0.008)	0.248 (0.017)
Gd		1.18 (0.05)	1.16 (0.02)	0.94 (0.09)	0.87 (0.03)	1.17 (0.02)	1.13 (0.06)	1.4 (0.1)
Tb		0.180 (0.003)	0.188 (0.002)	0.150 (0.022)	0.148 (0.007)	0.188 (0.011)	0.191 (0.013)	0.20 (0.01)
Dy		0.98 (0.02)	1.06 (0.01)	0.83 (0.12)	0.89 (0.03)	1.07 (0.04)	1.06 (0.04)	1.1 (0.1)
Ho		0.193 (0.009)	0.211 (0.002)	0.161 (0.026)	0.152 (0.009)	0.213 (0.004)	0.216 (0.009)	0.22 (0.02)
Er		0.510 (0.012)	0.570 (0.008)	0.419 (0.080)	0.407 (0.016)	0.575 (0.009)	0.581 (0.026)	0.68 (0.13)
Tm		0.0749 (0.0015)	0.0855 (0.0017)	0.0618 (0.0111)	0.0600 (0.0022)	0.0865 (0.0023)	0.0868 (0.0002)	0.10 (0.01)
Yb		0.415 (0.012)	0.471 (0.003)	0.369 (0.068)	0.368 (0.013)	0.468 (0.010)	0.475 (0.016)	0.56 (0.02)
Lu		0.0568 (0.0010)	0.0673 (0.0017)	0.0489 (0.0095)	0.0495 (0.0034)	0.0667 (0.0026)	0.0677 (0.0028)	0.081 (0.006)

[a] Median results from Interlab Trace program.
[b] Element used as internal standard.

HR-ICP-MS optimization and mass calibration was carried out using solution nebulization, as reported previously [20]. System optimization for solid sampling was performed for ^{115}In signal intensity during continuous ablation of pressed coal powder doped with In at 100 μg g^{-1}. The only ICP parameter that has to be changed when shifting from liquid to solid introduction is sample gas flow (the optimum for LA being about 0.2 l min^{-1} higher than for conventional nebulization).

The major laser parameters that have to be optimized are energy and sampling (i.e. ablation crater) diameter. Generally, higher energy results in enhanced signal intensity, but it produces a noise, resulting from the release of large fragments of the solid to the plasma. This effect can, to some extent, be overcome by using a defocused laser beam (i.e. larger sampling diameter). The optimum signal to noise ratio was found with 2 mJ laser energy and 50 μm sampling diameter. Signal stability is further improved by including a Scott type double pass spray chamber between the ablation chamber and the ICP torch [21]. The use of a spray chamber facilitates some control of the particle size of ablated material and results in more uniform particle size distribution, thereby improving precision and preventing deposition of material in the torch injector and on the sampling cone [22].

For MW dissolution a microwave system (MDS-2000, CEM, Matthews, USA), equipped with 12 perfluoroalcoxy (PFA) vessels with safety rupture membranes (maximum operating pressure 1380 kPa), was used. The vessels are located on a rotating turntable to ensure even sample heating.

Before use and between each batch of samples, PFA utensils were thoroughly acid cleaned and then rinsed with deionized water.

2.2. Reagents

All calibration and internal standard solutions used were prepared by diluting 1 mg ml^{-1} single-element standard solutions (SPEX Plasma Standards, Edison, NJ), taking into account inter-element compatibility. Concentrations in the calibration standards were checked using quality control samples prepared by diluting 10 mg l^{-1} multi-element standard solutions (PE Pure Plus Atomic Spectroscopy Standard, Norwalk, USA).

Analytical grade nitric acid (65%, Merck, Darmstadt, Germany) was used after additional purification by sub-boiling distillation in a quartz still (Heraeus, Karlsruhe, Germany). Suprapure grade hydrochloric (37%) and hydrofluoric (40%) acids,

Table 6
Results for NIST SRM 1633b and comparison with certified and recommended data

Reference		Found		Reference		Found	
		Procedure A2	Procedure B2			Procedure A	Procedure B
Macroelements				Pb	68.2 (1.1)	68.8 (1.4)	19.8 (2.1)
Si	23.02 (0.08)	5.53 (0.71)	22.8 (0.4)	Pd		<0.142	<0.078
Al	15.05 (0.27)	6.36 (0.27)	15.0 (0.4)	Pt		<0.016	<0.021
Ti	0.791 (0.014)	0.782 (0.009)	0.781 (0.016)	Rb	140	136 (6)	134 (4)
Fe	7.78 (0.23)	6.59 (0.20)	7.83 (0.26)	Re		0.0040 (0.0004)	0.0032 (0.0004)
Na	0.201 (0.003)	0.196 (0.005)	0.209 (0.006)	Rh		<0.028	<0.042
Ca	1.51 (0.06)	1.49 (0.04)	1.54 (0.05)	Ru		<0.061	<0.087
Mg	0.482 (0.008)	0.210 (0.015)	0.479 (0.022)	Sb	6	5.42 (0.21)	3.49 (0.45)
K	1.95 (0.03)	1.92 (0.03)	1.94 (0.06)	Sc	41	16.1 (1.1)	37.8 (1.5)
S	0.208 (0.001)	0.200 (0.04)	0.012 (0.003)	Se	10.26 (0.17)	10.9 (1.0)	<0.16
Trace elements				Sn		6.13 (0.34)	0.89 (0.13)
Ag		0.754 (0.027)	0.238 (0.034)	Sr	1041 (14)	1050 (10)	1020 (20)
As	136.2 (2.6)	135 (6)	108 (8)	Ta	1.8	1.52 (0.12)	1.88 (0.15)
Au		<0.012	<0.015	Te		0.214 (0.005)	<0.054
B		87.8 (7.0)	ND	Th	25.7 (1.3)	14.9 (0.8)	24.3 (0.9)
Ba	709 (27)	709 (31)	689 (21)	Tl	5.9	6.07 (0.12)	0.22 (0.04)
Be		13.4 (0.3)	12.9 (0.5)	U	8.79 (0.36)	8.87 (0.08)	8.71 (0.14)
Bi		1.29 (0.03)	0.09 (0.02)	V	295.7 (3.6)	294 (6)	287 (9)
Br	2.9	<8.4	<6.6	W	5.6	4.92 (0.31)	6.21 (0.45)
Cd	0.784 (0.006)	0.793 (0.023)	0.141 (0.029)	Y		34.3 (2.3)	79.9 (3.8)
Co	50	46.2 (1.7)	44.9 (2.1)	Zn	210	192 (3)	162 (10)
Cr	198.2 (4.7)	198 (7)	205 (5)	Zr		185 (8)	212 (9)
Cs	11	10.9 (0.4)	10.8 (0.4)	La	94	60.2 (0.34)	84.8 (2.1)
Cu	112.8 (2.6)	111 (3)	56.2 (5.2)	Ce	190	149 (6)	181 (4)
Ga		58.3 (1.4)	56.4 (2.6)	Pr		15.2 (1.4)	19.8 (1.1)
Ge		16.1 (0.7)	29.7 (1.3)	Nd	85	57.1 (3.1)	81.8 (1.6)
Hf	6.8	5.63 (0.49)	6.74 (0.31)	Sm	20	13.7 (1.0)	18.8 (0.6)
Hg	0.141 (0.019)	0.153 (0.023)	<0.011	Eu	4.1	3.12 (0.23)	3.87 (0.18)
I		0.848 (0.123)	<0.16	Gd	13	9.53 (0.83)	12.1 (0.34)
Ir		<0.0043	<0.0075	Tb	2.6	1.95 (0.09)	2.39 (0.16)
Li		64.1 (3.7)	ND	Dy	17	11.5 (0.3)	16.5 (0.7)
Mn	131.8 (1.7)	131 (3)	136 (6)	Ho	3.5	2.25 (0.16)	3.24 (0.14)
Mo		20.7 (0.9)	19.2 (1.1)	Er		5.73 (0.31)	7.79 (0.16)
Nb		21.3 (1.6)	25.9 (1.9)	Tm	2.1	1.27 (0.07)	1.81 (0.11)
Ni	120.6 (1.8)	119 (1)	96.9 (4.7)	Yb	7.6	4.60 (0.32)	7.29 (0.33)
P	2300	2240 (130)	2230 (90)	Lu	1.2	0.778 (0.064)	1.05 (0.07)

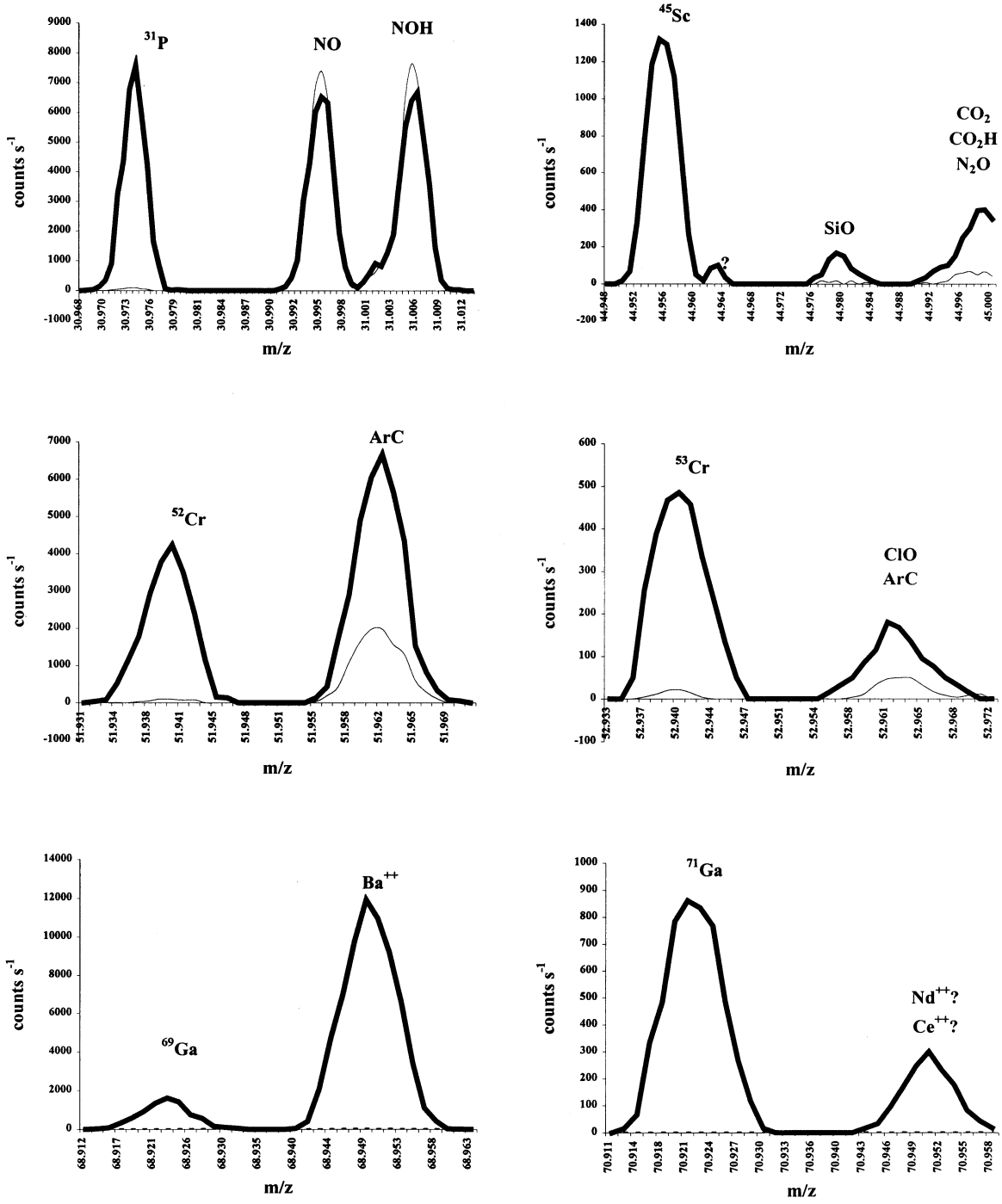

Fig. 1. Medium resolution ICP mass spectra obtained for NIST SRM 1635 (bold line) and for blank prepared according to procedure A2.

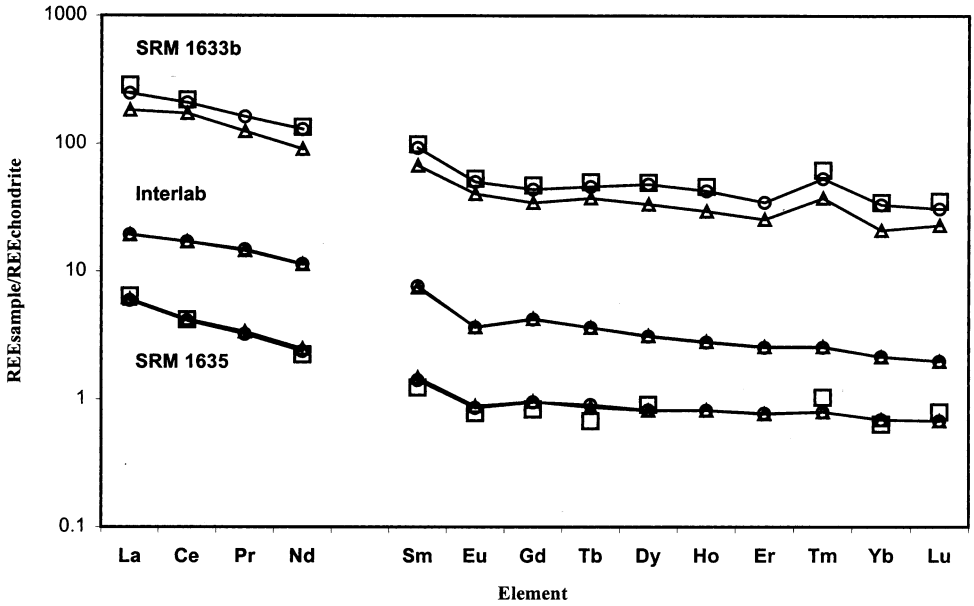

Fig. 2. Chondrite-normalized REE patterns for coal and coal fly ash samples. (squares, recommended or published values; circles, HR-ICP-MS results after LMB fusion; triangles, HR-ICP-MS results after A2 MW treatment).

as well as analytical grade hydrogen peroxide (30%) and tartaric acid (all from Merck), were used without additional purification. Lithium metaborate (J.T. Baker B.V., Deventer, Holland) was of analytical grade.

Deionized 'Milli-Q water' (Millipore Milli-Q, Bedford, USA) was additionally purified by sub-boiling distillation in a Teflon still (Savillex Corp., Minnetonka, Minnesota, USA).

2.3. Samples and standards

Two coal samples were used in the present study, namely, the certified reference material SRM 1635 (sub-bituminous coal, NIST, Gaithersburg, USA) and a bituminous coal sample supplied for a round robin test by the Interlab Trace program (Ashland, USA). NIST SRM 1633b (coal fly ash) was used for testing selected preparation procedures on ashed coal matrix. For HR-ICP-MS optimization and calibration using LA, a set of three in-house carbon standards was prepared from active carbon (intended for medical use, Pharmasorb, Perm, Russia), by doping 0.5 g sub-samples with internal standard solution (Rh, In and Ir) together with PE Pure Plus Atomic Spectroscopy Standard and SPEX standard solutions, followed by drying at 50°C for 12 h and homogenization. One sub-sample was not doped with analyte elements, as it is necessary to correct for the elemental content of the carbon. For the highest standard, this doping procedure results in an increase from the initial concentration by 5 μg g^{-1} for trace elements, and by up to 5000 μg g^{-1} for major elements. Internal standard (IS) elements (Rh, In, Ir) were added to all three sub-samples at 100 μg g^{-1} levels. It appears that the host matrix contained significant concentrations of Ba, Rb and Cr, resulting in poor linearity of calibration graphs for these elements.

2.4. Description of analytical procedures

2.4.1. MW dissolution

For MW dissolution, a sample weight of about 0.1 g and reagent volumes in the range from 5 to 6 ml were used. In preliminary experiments it appeared that the increasing sample weight while maintaining a constant sample/reagent ratio, may cause overpressure during the MW dissolution.

The increased sample/reagent ratio results in poor recoveries for some elements, as well as in difficulties when pouring the solutions from the MW vessel. The coal is weighed and transferred to MW vessels and reagent mixture is added. The vessels are then closed, mounted in sleeves (outer vessels) and heated in the MW oven at 325 W power for 1 h. The vessels are carefully vented in a fume hood after cooling to room temperature. The solution is then transferred to an acid-cleaned (hot mixture of HNO_3/HCl followed by soaking in 10% HNO_3 overnight) 10 ml polystyrene test tube (Nalge Nunc International, Rochester, NY). Four different reagent mixtures were used for MW assisted treatment: 5 ml HNO_3 + 1 ml H_2O_2 (procedure A1); 5 ml HNO_3 + 1 ml H_2O_2 + 0.1 ml HF (procedure A2); 5 ml aqua regia (procedure A3); 5 ml aqua regia + 0.1 ml HF (procedure A4). The choice of the volume of HF is based on Ikävalko et al. [8] findings. They showed that addition of HF to the sample in a ratio of about 1:1 (v/w) is sufficient for the dissolution of the silicates in coal samples. It should be noted that a significant part of the coal matrix remains unaffected by any of the reagent mixtures tested. Hence, this sample preparation results in leaching rather than in complete dissolution and, consequently, in significant losses. After sedimentation of undigested particles to the bottom of the tube, two particle-free aliquots of the solutions were diluted with ultrapure water, resulting in dilution factors of 500 and 2000 for ICP-AES and HR-ICP-MS determinations, respectively. Though it is advisable to use acid evaporation or addition of H_3BO_3 when applying acid mixtures containing HF for sample dissolution [3,8], these procedures were avoided in the present study as they are likely to cause losses of some analytes (evaporation), to increase matrix effects (H_3BO_3) as well as to introduce additional contamination. In HR-ICP-MS, using an acid-resistant sample introduction system eliminated negative effects caused by HF. After the sample dilution, the remaining of HF traces ($<0.2\%$) caused only moderate increases in ICP-AES blanks for Si.

2.4.2. LMB fusion

Two slightly different LMB fusion procedures were applied to the coal samples following, in general, the method described by Ödman et al. [23]. In the first procedure (B1), 1 g of coal is weighed and placed in a porcelain combustion crucible (LECO, Upplands Väsby, Sweden), which is then heated in a furnace at 550°C overnight. The ash is weighed with 0.1 mg resolution. An amount of LMB double with respect to ash is added and carefully mixed with the ash. The mixed sample/LMB powder is then transferred to a carbon crucible (Schunk, Lenhouda, Sweden) and heated in a furnace at 1000°C for 30 min. After cooling the bead is transferred from the crucible to a 10-ml acid-cleaned polystyrene test tube and 10 ml of a nitric/tartaric acid mixture (5% /1% v/v in ultrapure water) is added to the tubes. The tubes are placed on a laboratory shaker overnight till complete dissolution. Two aliquots of the resulting solution are diluted using 5% HNO_3 for ICP-AES and 2% HNO_3 for HR-ICP-MS. For ICP-AES the concentration of LMB in the final solution should be 2% w/v (this enables the use of B as an internal standard in the instrumental detection step). For HR-ICP-MS the dilution factor is approximately 2000 relative to the coal mass before ashing.

The ashing step is excluded in the second fusion procedure (B2). Approximately 1 g of coal powder is mixed with LMB, followed by fusion. Otherwise, this procedure is similar to that described above. Together with significantly shorter preparation time, the second fusion procedure eliminates losses of volatile elements during ashing. The presence of fluxing agent stabilizes some, but not all, of the more volatile elements during high temperature treatment. The need for greater sample dilution prior to analysis by ICP-AES (owing to the higher amount of LMB used) is the major drawback of the B2 procedure.

Coal samples were prepared in triplicate together with six preparation blanks for each procedure. The final solutions for HR-ICP-MS were spiked with IS solution (In) to 25 $\mu g\ l^{-1}$. Sample and blank solutions from each preparation procedure were separately analysed by ICP-AES and HR-ICP-MS using synthetic blanks and standards matching sample solutions in terms of reagents mixture and acid strength. All sample handling and analyses were performed in clean (class 1000) laboratory.

Results were corrected for moisture content which was determined on separate 0.2 mg sub-sam-

ples (being 15.5% and 0.6% for SRM 1635 and Interlab samples, respectively).

2.4.3. Laser ablation

Sample preparation for LA was restricted to doping to 100 μg g^{-1} 0.5 g coal powder with IS following the same procedure as described for in-house carbon standards (see Section 2.3). Coal and carbon powders so prepared were pressed into pellets (12 mm in diameter and 2–3 mm thick) at a total thrust of 10 t in a press Herzog TP20 (Osnabruck, Germany) designed for sample preparation for IR spectroscopy. All sample manipulations were performed using plastic gloves and plastic tweezers.

The samples and standards were placed in the ablation cell and the sequence started with analysis of the carrier gas without LA (gas blank). The laser had been programmed to perform continuous ablation for about 15 min on six areas for each pellet in sequence on samples and standards. A 30 s delay, after the ablation start was included before commencing HR-ICP-MS data acquisition, so that the analyte can reach the plasma and the signal can stabilize. Raw intensity data were transferred to a personal computer and subsequent data manipulation was performed off-line using statistical software. At the beginning, the intensities of analytes were corrected for the variations in ablation efficiency and plasma instability, using intensities for IS. For each isotope the IS that is closest in mass was used. The corrected intensities were summarized for each ablation area and within-pellet mean intensity and standard deviation were calculated. Calibration performed by means of carbon standards resulted in linear calibration graphs for the majority of elements with correlation coefficients better than 0.98.

2.5. Spectral interferences

For the ICP-AES data, mathematical corrections for spectral overlaps were carried out by the instrument software. These calculations are based on measured intensities for interfering elements, and provide both corrected results and correction factors which enable the detection of potentially inaccurate results for which the degree of correction is unacceptably high.

During analysis of complicated matrices by ICP-MS, spectral interferences are known to present one of the major obstacles to achieve accurate results [24]. As a result, several matrix elements (Si, P, S, K, Ca and Fe) are considered as 'problematic' in ICP-QMS. Due to high mass resolution capability, HR-ICP-MS allows accurate determination of many elements even in such a complicated matrix as seawater [20]. In the present study, MRM was used for 20 elements (Mg, Al, Si, P, S, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, and Br) while the determination of As and Se required HRM. Examples of spectra recorded in MRM for selected isotopes in NIST SRM 1635 digest (procedure A2) are presented in Fig. 1. Though it may appear that interferences on P originating from NO^+ and NOH^+ can be overcome by blank subtraction when applying ICP-QMS, this will actually result in erroneously low P concentrations. This is because lower levels of interfering signals are observed in the sample matrix when compared to the blank solution, owing to evaporative losses of nitrogen species from the former during digestion. Another monoisotopic element, Sc, is affected by numerous interferences, especially of carbon-containing molecules. These data are opposite to those of Fadda et al. [3] who stated that the determination of Sc did not suffer from increased carbon content in the sample solution. The spectra nearby Cr and Ga isotopes represent two examples where a minor isotope appears to be less affected by spectral interferences than the major isotope.

When performing MW dissolution, the use of HCl in the digestion mixture results in severe interferences on V, Cr, Ga, Ge, As, Se and Yb isotopes. Though it is possible to overcome the majority of spectral interferences using a resolution that is sufficient to isolate the analyte signals from interfering peaks in the mass range from 24 to 81 amu, a significant number of interferences originating from oxides in the higher mass region can not be resolved, even in HRM. Moreover, an increase in resolution is joined to a decrease in sensitivity owing to the reduced ion transmission. In order to assess the severity of these interfer-

ences, the oxide formation ratios for potentially interfering elements were determined by analyzing a set of single-element standards in LRM (solution nebulization) and these data were used for mathematical correction. The mean degree of correction (i.e. the ratio uncorrected/corrected concentration) values for selected isotopes in the NIST and Interlab coal samples are presented in Table 2. For ten elements the degree of correction was less than 1.05, and for them the contribution from oxide peaks on the analyte signal was assumed to be negligible. For the remainder, the results were corrected mathematically using oxide formation ratios that were determined experimentally on a daily basis. For the most severely affected isotopes (degree of correction higher than 2), small variations in oxide formation owing to changes in plasma parameters during the analytical procedure are expected to yield inaccurate results. Hence, results for such elements (Ru, Rh, Pd, Ir, Pt and Au) are reported as less than the uncorrected value.

It must be noted that the mathematical corrections discussed here ignore interferences originating from hydroxide and chloride species. The former is neglected as it was shown [25] that hydroxide formation is about 10-fold lower than oxide formation. Correction for chloride interferences is complicated as, for example, correction for BaCl interferences on Tm and Yb isotopes depends on the contents of both Cl and Ba in the sample solution.

Oxide formation while using LA is significantly lower if compared to the solution nebulization, owing to the reduced amount of oxygen that reaches the ICP as water vapour and aerosol. For example, the ratio UO/U decreases from about 0.03 (solution nebulization) to less than 0.01 (LA). Hence, no corrections for oxide interferences were performed for LA-ICP-MS, though the results for elements that might be severely affected (Ru, Pd and Au) were excluded from evaluations.

For both solution nebulization and LA, isobaric interferences such as from ^{114}Sn on ^{114}Cd were corrected mathematically using the intensity of an alternative isotope for the interfering element and its relative abundance.

3. Results and discussion

Detection limits, calculated as three times the standard deviation for preparation blanks (gas blanks for LA) for each procedure, are given in Table 3. For major elements they are in the low $\mu g\ g^{-1}$ range, except for Si if using LA. High values caused by a large and unstable Si blank are probably due to torch overheating when switching it to a dry plasma. Poor detection limits for Li and B with LA are attributed to the high instrumental blank levels of these elements caused by the contamination from previous analyses of fusion solutions containing large quantities of LMB. Cleaning or replacement of the sample introduction system (including tubing, nebulizer, spray chamber, torch and cones) do not eliminate these high blanks completely. It seems that deposition of LMB on the internal parts of the instrument is responsible for long-lasting memory effects. Detection limits are below 10 $ng\ g^{-1}$ for about 40 minor and trace elements in all procedures, though blank levels for fusion were significantly higher for elements such as Al, Ag, Ba, Cu, V and Ce, reflecting more extensive sample handling and possibly impurities in the LMB.

Results for NIST SRM 1635 and Interlab coals obtained by different approaches are summarized in Tables 4 and 5, respectively. As differences between ICP-AES and HR-ICP-MS results were, as a rule, insignificant (when not limited by instrumental detection limits in the former technique), the more precise data are reported. The accuracy of the results for NIST SRM 1635 can be evaluated by comparison with certified and recommended values, which are available for 25 elements for this material. Concentrations of 31 additional elements in this coal sample have been previously reported [17,23–25], but the significance of differences between found concentrations and literature values are difficult to evaluate. For the Interlab sample, median concentrations based on results received from all participants in the Interlab Trace program are available for 15 elements. These consensus values are to be treated with caution because of their great scatter, for some elements covering five orders of magnitude. This variability in the reported values is, however,

not unusual in trace element determinations with different analytical techniques. For the others elements, no independent check of accuracy is possible and applied procedures can be compared only with respect to relative recovery.

From the data obtained with different MW dissolutions, it appears that the recovery of Fe, Na, Ca, Mg, Ag, Be, Cu, Mn, Mo, Ni, P, B, Bi, Pb, Sb and Tl is independent of the acid mixture and that results for these elements fall within $\pm 10\%$ of certified/recommended values, where available. Recovery of the other elements are influenced by both the acid mixtures and the coal types. The addition of a minor amount of HF to $HNO_3 + H_2O_2$ or aqua regia results in higher recovery for many elements that are associated with siliceous materials in coal. Generally, procedure A2 provides the best accuracy (good agreement for 22 out of 25 elements for NIST SRM 1635 and for 13 out of 15 elements for Interlab, for which certified or recommended values are available). It should also be noted that, when applying procedure A2, good agreement with literature data was found for Ca, Mg, Ba, Cs and Sr. Poor recoveries for these elements when using HF in MW dissolution have been reported previously [10].

LMB fusion results in further improvement for the recovery of elements such as Si, Hf, Cr, W, Zr, Y, accompanied, however, by obvious losses for Ag, As, Cd, Cu, Bi, Hg, I, Se, Sn, Tl, Pb, Re, Te, S and Zn. Though it is possible to improve the recovery of selected elements, by excluding sample ashing from the fusion procedure (B2), results for the majority of volatile elements are still significantly lower if compared to MW dissolution.

Complete recovery of As, Cu and Zn in the LMB fusion of coal ash has been reported previously [10]. An explanation for this discrepancy might be that retention of volatile elements in coal is dependent upon the exact mineral matter composition.

Though no single sample preparation method can provide accurate results for all the elements under consideration, by using a combination of the A2 and B2 procedures, one can avoid negative effects related to acid-resistant mineral phases as well as to losses of volatile elements. In order to evaluate the suitability of these two sample preparation methods for other sample types, they have been applied to SRM 1633b coal fly ash (Table 6). Although recoveries in the MW procedure for elements such as Sc, Th and the REE were lower compared to coal samples (Fig. 2), accurate results were obtained for 46 out of 47 elements for which certified or recommended values are available. Smooth chondrite-normalized patterns in Fig. 2 also reflect internal consistency in REE results.

The precision, as determined by the analysis of coal samples prepared in triplicate, was generally better than 3–5% for all MW and fusion procedures. It was, however, significantly worse for LA, being in the range 10–20% of RSD for most of the elements. Possible reasons for this variation, other than the obvious problem of heterogeneous analyte distributions, include inhomogeneous mixing of coal powder with IS solution or density differences between different points in the pressed coal tablets. For about 50 elements, results obtained with LA fall within 20% of those obtained by MW digestion or fusion. In spite of relatively poor agreement for elements such as As, Se, Sn, Re, Te and Tl, accuracy obtained with LA in the present study is superior to that reported for this technique in other studies [16,17], as well as for slurry nebulization [13].

4. Conclusions

The combination of ICP-AES and HR-ICP-MS is an useful approach to the simultaneous determination of a wide range of major, minor, and trace elements in coal. Even if a significant number of elements affected by spectral interferences can be accurately determined by HR-ICP-MS, unresolved interferences caused by oxide species are still the major obstacle for quantification of Rh, Ru, Pd, Pt, Ir and Au. Accurate results for these elements at low ng g^{-1} levels can be obtained only after chemical separation of interfering elements or by minimizing oxide formation by using aerosol desolvation. For elements such as Ca, Fe, Ti, Mg, Cu, Be, Mn, Ba, Sr, Ni, B, Mo,

Sn, Bi and P, recovery is over 90% independent of the acid mixture used in MW dissolution. Extraction efficiency for certain elements is strongly dependent on the applied leaching mixture and varies among different coal types. Though elemental recoveries obtained with a mixture of nitric and hydrofluoric acids with hydrogen peroxide were superior to those obtained with other mixtures, recoveries for Si, Hf, W, Zr, REE and Nb were low. Hence, a combination of this procedure and LMB fusion without ashing should be applied to coal analysis in order to obtain accurate data for as many elements as possible. It appears that the use of aqua regia provides no improvement in recovery and that hydrochloric acid must be avoided in coal digestion.

LA is ideally suited for rapid screening of element concentration ranges in coal if a 15–20% accuracy is acceptable. Though it was possible to evaluate accuracy for more than 50 elements, new coal reference materials with certified values for a larger number of elements are needed in order to facilitate method validation.

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II

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Axelsson M.D. and Rodushkin, I.

Determination of major and trace elements in sphalerite using laser ablation double focusing sector field ICP-MS

Mikael D. Axelsson [a] and Ilia Rodushkin [b]
[a] Division of Applied Geology, Luleå University of Technology, S-971 87 Luleå, Sweden
[b] SGAB Analytica, Luleå University of Technology, S-971 87 Luleå, Sweden

Abstract
The analytical performance of laser ablation (LA) for the determination of Co, Fe, Cd, Ag, Mn, Cu and S in sphalerite was evaluated using double focusing sector field inductively coupled plasma mass spectrometry (ICP-SFMS). Samples were collected from Zinkgruvan, situated in the south central Sweden. The use of Zn for internal standardisation, together with correction for FeS impurities in sphalerite, allows straightforward quantification without using external methods for the determination of the actual Zn content. LA-ICP-SFMS results were compared with data obtained by conventional pneumatic nebulization introduction of sample solutions following acid digestion. Good agreement between the two methods was obtained for homogeneously distributed elements. For the majority of the elements under consideration, LA-ICP-SFMS precision was better than 10% RSD.

Keywords. Laser ablation, high resolution ICP-MS, mineral analysis, sphalerite, trace elements

Introduction
Zinkgruvan is the largest zinc mine in Sweden, situated in the south central part of the country. The ore system consists of c. 1.9 Ga old stratiform lenses rich in sphalerite (ZnS with some Fe) and containing some galena (PbS), occurring in a volcano-sedimentary environment (Hedström et al. 1989). The suitability of the ore for production of zinc concentrate is limited by the elemental composition due to economic considerations. For example, the Co content in the Zn concentrate produced in the concentrating plant has usually been < 100 μg g^{-1}. In recent years, however, when mining operations have started in new areas of the ore system, the Co content in the Zn concentrate has tended to increase. Values up to 250 μg g^{-1} have been found. An increased level of Co in the Zn concentrate result in decreased economic value of the mining product. Chemical analyses of 300 whole rock drill core samples distributed over the ore system have shown that the Co content and the Pb/Zn ratio both vary considerably between different areas (Hedström, 1999). The highest observed Co content in the region is 0.2 %. Minor amounts of cobaltite have been found, but not enough to explain the Co concentrations of whole rock samples. Two questions arise, firstly whether Co to some extent, are structure-bound in the sphalerite, and secondly, how the Co concentration in the sphalerite varies between different areas of the ore system.
Together with the Co concentration, impurities of Fe, Mn, Cd, Ag and other elements, ranging from low μg g^{-1} to percent levels in the sphalerite, are of interest. The need for multielement

analysis in geological materials has encouraged an increased interest in analytical techniques such as inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). The instrumentation, traditionally equipped with solution nebulization (SN) sample introduction systems, requires transfer of analytes from the solid phase into solution. Consequently, minerals of interest should be separated from the host rock, prior to dissolution or fusion. Mineral separation is time consuming, and sample pre-treatment may result in incomplete recovery and/or analyte losses (Eggins et al. 1998). Moreover, the SN approach provides only bulk chemical data. By using laser ablation (LA) sample introduction, the elemental composition of mineral grains can be determined *in situ*, with minor sample preparation. Although successful applications of LA-ICP-OES and LA-ICP-MS for geochemical studies have been extensively reported in the literature, serious problem may arise from difficulties in the quantification of analyte signals generated by LA. In fact, it has been concluded (Watling et al., 1995) that direct quantification of the elemental composition of sulphide minerals (including sphalerite), using a 1064-nm Nd: YAG laser, is impossible. This is because of variations in sample matrices between mineral from varying deposits due to different surface textures, different degrees of crystallinity and annealing. Perkins et al., 1997 describe calibration methods for sulphide minerals, with the attempt to produce quantitative results by using spiked sulphide powders and certified metal material as standards. Though quantitative results were obtained in the same work, using pressed mineral powders, the principal advantage of LA over SN, is the freedom from of mineral separation and the minimal sample preparation. On the other hand, accurate results for 10 minor and trace elements in sphalerite certified material were obtained by LA-ICP-OES using liquid-solid calibration in another study (Moenke-Blankenburg et al., 1994).

This study was carried out to evaluate the potential of LA for the direct analysis of sphalerite using double focusing sector field ICP-MS (ICP-SFMS). The ability to resolve spectral interferences as well as higher sensitivity and lower background levels is obtained by using the latter compared with quadrupole-based mass spectrometer systems. Some of the benefits of ICP-SFMS were recently demonstrated by the determination of platinum group elements in iron meteorites (Campbell and Humayun, 1999). The high-resolution capability of the ICP-SFMS also improves accuracy for many spectrally interfered isotopes (e.g. $^{16}O_2$ on ^{32}S, $^{40}Ar^{16}O$ on ^{56}Fe, $^{40}Ar^{14}N^{1}H$ on ^{55}Mn, $^{32}S_2$ on ^{64}Zn).

Materials and methods

1.1 Instrumentation

The ICP-SFMS instrument used was the ELEMENT equipped with an UV Laser Probe laser ablation system (both from Finnigan MAT, Bremen, Germany). The device can be operated in low (LRM, $m/\Delta m$ about 300), medium (MRM, $m/\Delta m$=4500) and high-resolution mode (HRM, $m/\Delta m$=9200). Only MRM was used in this work because this was sufficient to overcome the spectral interferences affecting analytes under consideration in LRM (e.g. $^{40}Ar^{16}O^{+}$ interference on the ^{56}Fe isotope, $^{32}S_2$ on ^{64}Zn). A disadvantage of using MRM compared to LRM is that the count rates decrease by a factor of approximately 15, which may affect the ability to determine ultra-trace elements. Details on instrumental operating conditions and measuring parameters are given in Table 1. ICP-SFMS optimisation and mass calibration was carried out using solution nebulization as reported previously (Rodushkin and Ruth, 1997). System optimisation for solid sampling was performed for the ^{66}Zn signal intensity during continuous ablation of a large sphalerite grain. The only ICP parameter that has to be changed when shifting from liquid to solid introduction is the sample gas flow rate (the optimum flow for LA is about 0.2 L min^{-1} higher than for conventional nebulization).

Table 1 ICP-SFMS and LA operating conditions and measurement parameters

Rf power/W	1400
Sample uptake rate/ml min^{-1}	0.3 (solution nebulization only)
Gas flow rates/l min^{-1}	
Coolant	15
Auxiliary	0.85
Nebulizer	1.15-1.30
Ion sampling depth/mm	9
Ion lens settings	Adjusted to obtain maximum signal intensity
Torch	Demountable with sapphire injector
Nebulizer	Microflow PFE
Spray chamber	Scott type PFE (double-pass)
Sample cone	nickel, 1.1 mm orifice diameter
Skimmer	nickel, 0.8 mm orifice diameter
Isotopes	^{32}S, ^{56}Fe, ^{55}Mn, ^{59}Co, ^{63}Cu, ^{64}Zn[b], $^{111,114}Cd$, ^{107}Ag, ^{115}In[c]
Acquisition mode	E-scan
No. of scans	15
Acquisition window/%[a]	120
Search window/%[a]	80
Integration window/%[a]	60
Dwell time per sample/ms	20
No. of samples per nuclide	25
Laser (Nd:YAG)	
Wavelength/nm	266
Pulse width/ns	3
Pulse energy/mJ	1.5
Ablation diameter/μm	40
Distance between points/mm	0.1
Repetition rate/Hz	20
Number of shots per point	50
Sample scan mode	Zigzag line scan across rectangular area (0.5 to 1.5 mm^2)
Time delay/s	0.1

[a] Percent of peak width
[b] Internal standard LA
[c] Internal standard nebulization ICP-SFMS

The major laser parameters that have to be optimised are laser energy and sampling (i.e. ablation crater) diameter. Generally, higher energy results in higher signal intensity. However, higher laser power produces a noisy signal resulting from the release of large solid fragments to the plasma. This effect can, to some extent, be overcome by using a defocused laser beam (i.e. larger sampling diameter). The optimum signal to noise ratio was found with 1.5 mJ laser energy and 40 μm sampling diameter. Signal stability was further improved by including a Scott type double pass spray chamber between the ablation chamber and the ICP torch (Campbell and Humayun, 1999). The use of a spray chamber allows the particle size of the ablated material to be controlled, achieving a more uniform particle size distribution, thereby improving precision and preventing deposition of material in the torch injector and on the sampling cone (Coedo et al., 1995).

1.2 Sample preparation and analysis procedure

The sphalerite originated from the ore deposits of Zinkgruvan. The fragments were cut out from core samples, taken from locations in the sphalerite rich mining region. For LA, suitable sized (approximately 2 cm^2) fragments of the mineral were mounted in fast setting epoxy resin and ground to a flat surface using SiC followed by aluminium oxide paste, and finally polished with diamond paste. The surface was thoroughly cleaned with ethanol to remove traces of polishing agents, followed by rinsing with high-purity Milli-Q water (Millipore Milli-Q, Bedford, USA). The samples were placed in the ablation cell one by one, and the sequence started with the analysis of the carrier gas without LA (argon gas blank). Gas blanks were measured repeatedly to determine the detection limit, based on the 3σ criterion. The detection limit was in the low or sub $\mu g\ g^{-1}$ range for all elements except Cu, due to a high blank level caused by previous analyses. The laser was then programmed to perform continuous raster ablation on four to six areas (0.5 to 1.5 mm^2 each) in sequence during approximately 15 min for each sample, in order to detect possibly inhomogeneous distributions of the impurities in the samples. Extreme care was taken to ensure that the areas were chosen in predominantly monomineralic parts of the samples. A 30 s delay after beginning the ablation was included before commencing ICP-SFMS data acquisition, allowing analyte material to reach the plasma and the signal to stabilise.

For SN, sphalerite grains from five drilling core fragments (remaining from sample preparation for LA) were first separated by hand, then a Frantz isodynamic magnet separator was used for final separation. Before dissolving the acquired concentrate, a rough inspection using microscopy was used to provide qualitative indications about the efficiency of the separation. This was mostly done to ascertain whether some further separation was necessary. The sphalerite thus separated (approximately 10 mg per fragment) was treated with concentrated nitric acid (Merck, Darmstadt, Germany) using a Grant BT3 wet digestion system (Grant Instruments Ltd., Cambridge, UK) and diluted to 2 % acid content with Milli-Q water. After addition of an internal standard (In), these solutions were analysed by SN-ICP-SFMS using external calibration with a standard that was prepared by diluting 1 $mg\ ml^{-1}$ single-element standard solutions (SPEX Plasma Standards, Edison, NJ, USA).

1.3 Quantification for LA-ICP-SFMS

The difficulties involved in calibration and quantification represent the major problems hindering the wider application of LA-ICP-MS, and are largely ascribable to the currently limited quantity of commercially available matrix-matched reference materials.

In LA-ICP-MS analysis, normalisation of the response for the analyte to that of an internal standard (IS, usually an isotope of a major element) is frequently used (Pearce et al., 1997), with the major element determined by an external method or from mineral stoichiometry. Electron probe micro-analysis (EPMA) has been used as a complimentary technique for determination of candidate elements in IS (Pearce et al., 1997, Perkins et al., 1997, and Pearce et al., 1992).

For sphalerite, Zn is a suitable choice as its concentration can be assumed to be relatively constant in the mineral. ^{66}Zn can therefore be utilised as an IS, and calibration then consists of establishing the relationship between the observed intensity ratio and the relative concentrations, analyte/IS. This is most conveniently performed by means of conventional nebulization of aqueous standard solutions containing the elements under consideration. However, if the Zn concentration was taken from sphalerite stoichiometry, a significant error may be introduced due to FeS impurities in the mineral. Fe concentrations from 0.1 to 12% have been reported in sphalerite by Moenke-Blankenburg et al. (1994) and by Watling et al. (1995). In order to decrease the error, the actual Fe content in the samples has to be taken into consideration.

The slope (b) of the Fe calibration curve is given by the instrumental response divided by the known Fe concentration ($b(\mathrm{Fe})_{solution}$). The ratio of the slopes for Fe and the internal standard

Zn, can then be calculated, $b(\mathrm{Fe})_{solution}/b(\mathrm{Zn})_{solution}$, to yield a normalisation factor between the isotopes. By dividing the measured LA-ICP-SFMS response (R) of Fe by this factor, a response normalised to Zn is obtained ($R(\mathrm{Fe})_{LA,norm}$).
By considering the mass relationship between FeS and ZnS in the solid, in terms of the normalised and observed LA-ICP-SFMS intensities for Fe and Zn, respectively, the following equation is obtained:

$$\frac{R(\mathrm{Fe})_{LA,norm}}{R(\mathrm{Zn})_{LA}} = k \cdot \frac{C_{FeS}}{C_{ZnS}} = k \frac{M_{Fe}}{M_{Zn}} \cdot \frac{M_{ZnS}}{M_{FeS}} = \frac{55.84}{65.39} \cdot \frac{97.456}{87.906} = 0.9467 \qquad (1)$$

where C denotes the mass fraction in the sample and M is the relative atomic or molecular mass, each referring to the species in question. Thus, k represents a conversion factor from elemental to sulphide concentration ratios. The mass fraction of ZnS in the mineral can then be calculated by making an assumption regarding the bulk composition of the material:

$$C_{\mathrm{ZnS}} + C_{\mathrm{FeS}} = 0.99 \Rightarrow C_{\mathrm{FeS}} = 0.99 - C_{\mathrm{ZnS}} \qquad (2)$$

The above assumption (eqn 2) was made because, although, it is reasonable that the samples contain elements on impurity levels the main components in sphalerite is Zn, S and Fe. Substitution of eqn (2) into eqn (1) and rearrangement yields an expression for the mass fraction of ZnS present:

$$C_{ZnS} = 0.9370 \Big/ \left(0.9467 + \frac{R(\mathrm{Fe})_{LA,norm}}{R(\mathrm{Zn})_{LA}} \right) \qquad (3)$$

In a similar fashion to that used to compute k and C_{ZnS}, the mass fraction of Zn present in the mineral can also be calculated:

$$C_{Zn} = 0.6287 \Big/ \left(0.9467 + \frac{R(\mathrm{Fe})_{LA,norm}}{R(\mathrm{Zn})_{LA}} \right) \qquad (4)$$

Using this estimate of the minerals Zn content as a starting point, the concentration of any element, X, in the sample can then be determined:

$$C_x = C_{Zn} \cdot \frac{R(\mathrm{X})_{LA}}{R(\mathrm{Zn})_{LA}} \cdot \frac{b(\mathrm{Zn})_{solution}}{b(\mathrm{X})_{solution}} \qquad (5)$$

Limitations of this quantification approach may arise from possible changes in analyte/IS ratios between SN and LA (for example caused by changes in plasma temperature) and from element fractionation effects during ablation.

Results and discussion

The results obtained using LA-ICP-SFMS and SN-ICP-SFMS for five sphalerite samples are given in Table 2. When evaluating the accuracy of the LA-ICP-SFMS results by comparison with SN-ICP-SFMS data, two important facts should be kept in mind. Firstly, the concentrates obtained for sphalerite digestion may not be fully separated from other minerals with similar separation properties. The mineral separation technique used ensures only about 95% sample enrichment in sphalerite. Secondly, SN provides only the bulk concentrations, while LA data can be affected by internal chemical zoning within samples. Fig. 1 demonstrates two examples of different elemental distributions within the samples. As follows from these data, sample A is

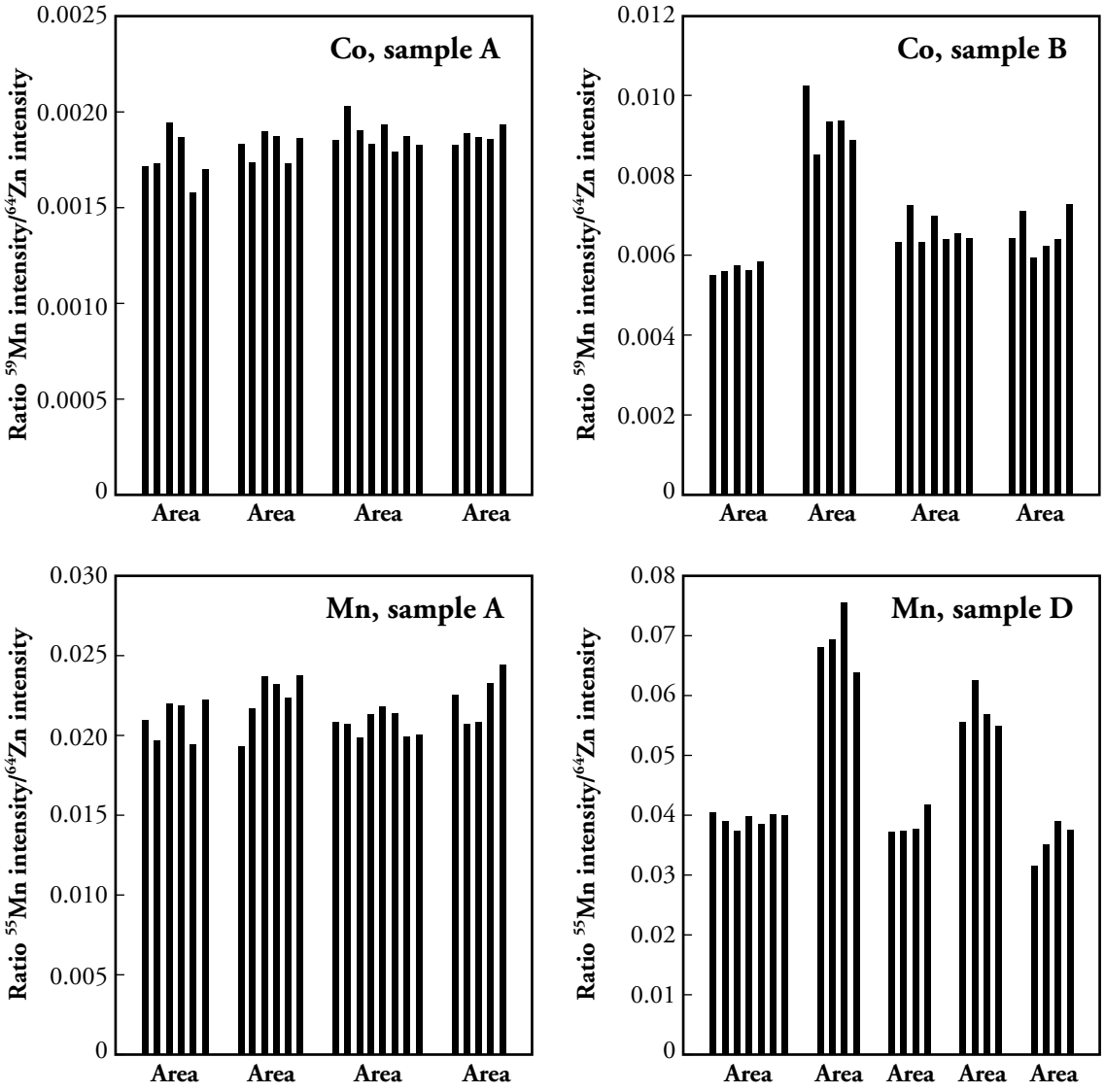

Fig. 1 Ratios (analyte/Zn) in profiles from different ablation areas for Co (A) and Mn (A) in one homogeneous sphalerite sample. Ratios for Co (B) and Mn (D) in two different inhomogeneous sphalerite samples analysed by LA-ICP-SFMS.

Table 2 Comparison of results obtained for five sphalerite samples by LA-ICP-SFMS and SN-ICP-SFMS

	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
	LA-ICP-SFMS[a]	SN-ICP-SFMS[b]	LA-ICP-SFMS[a]	SN-ICP-SFMS[b]	LA-ICP-SFMS[a]	SN-ICP-SFMS[b]	LA-ICP-SFMS[a]	SN-ICP-SFMS[b]	LA-ICP-SFMS[a]	SN-ICP-SFMS[b]
Zn, %	56.0(0.6)	51.9 (1.9)	57.5(0.3)	58.1(0.6)	54.9(1.1)	57.1(1.5)	61.0(0.2)	59.7(0.6)	61.1(3.1)	51.4(1.2)
S, %	28.2(0.8)	26.1(0.3)	29.9(0.3)	30.5(0.2)	32.2(2.5)	32.2(0.3)	33.1(0.7)	36.7(0.4)	33.0(2.4)	39.0(0.2)
Fe, %	9.91(0.55)	9.86(0.17)	8.47(0.27)	8.83(0.23)	10.9(0.9)	9.83(0.1)	5.16(0.20)	5.08(0.03)	5.06(2.97)	3.75(0.03)
Mn, %	0.169(0.013)	0.163(0.002)	0.231(0.007)	0.225(0.006)	0.577(0.192)	0.189(0.002)	0.128(0.004)	0.113(0.001)	0.034(0.003)	0.027(0.001)
Cd, µg g^{-1}	945(18)	963(5)	341(16)	361(17)	632(28)	842(8)	757(21)	813(2)	753(50)	805(1)
Co, µg g^{-1}	179(5)	164(2)	124(3)	128(6)	442(45)	489(7)	89(2)	92(1)	469(34)	456(4)
Cu, µg g^{-1}	66(42)	123(15)	86(40)	63(1)	87(14)	55(2)	42(14)	22(1)	47000(42000)	21600(130)
Ag, µg g^{-1}	5.7(1.2)	4.3(0.4)	9.9(4.6)	5.5(0.7)	4.4(1.1)	3.7(0.2)	10.9(3.3)	10.3(0.5)	10.4(3.0)	3.3(0.3)
Total, %	94.4	88.2	96.1	97.7	98.7	99.5	99.5	101.7	103.9	96.5

[a]Standard deviation for results obtained for different ablation areas within the samples (n=4-6)
[b]Standard deviation for replicate analysis (n=3)

homogeneous regarding both Co and Mn. On the contrary, significant differences in concentrations are evident between different areas of samples B and D. As a result of this inhomogeneity, the spread of LA-ICP-SFMS results significantly increases for such samples. Among the five samples analysed by both techniques (Table 2), results for two were affected by this phenomenon: sample 3 (for Mn and Co) and 5 (Fe, Co and Cu). In sample 1, 2 and 5 some problems to analyse the sulphur content can be seen. The theoretical composition of monosulphides should be in the 32-34% range, the inaccuracy occurring for sulphur for both for SN and for LA determinations need special evaluation when accuracy better than just a few percent is needed. It should also be noted that the Cu concentration in sample 5 is higher than in the other samples by about three orders of magnitude and shows very large differences between ablated areas within the sample. A probable explanation for this behaviour is the "chalcopyrite disease in sphalerite", which is well-known to result in high concentration Cu inclusions the sphalerite. These inclusions are clearly a result of the replacement of the original Fe-bearing sphalerite by an aggregate of chalcopyrite ($CuFeS_2$) and low-Fe sphalerite as an integral part of the mineralization process (Barton and Bethke, 1987). It should be noted that the presence of percent level impurities in sphalerite from elements other than Fe will introduce additional errors for all analytes because of the inaccuracy in calculating the IS (Zn) concentration. The presence of zones with different element concentrations within 2 cm^2 sphalerite samples highlights the need for analysing a few areas on each sample if the bulk chemical composition is of interest. Though the sub-mm spatial resolution of the LA allows study of the internal chemical zoning in sphalerite grains, it was outside the scope of this work.

With reservation for the aforementioned examples, close agreement between the LA and SN results for S, Mn, Fe, Cd, and Co is obvious, as differences between the two data sets are generally less than 10%. The close correlation between results obtained by the two techniques (Fig. 2) affirms that these elements are probably incorporated in the sphalerite structure and not occurring in separate mineral inclusions. The slope values systematically and significantly is less than unity. This error (6-10%) can be addressed to sample inhomogeneity and ablation fractionation caused by the laser. Poor LA-ICP-SFMS results for Cu are attributed to problems with high instrumental blank levels caused by contamination from previous analyses. The Ag sensitivity when using LA-ICP-SFMS in MRM is only about 100 counts s^{-1} per $\mu g\ g^{-1}$, which is responsible for the relatively high discrepancies between results for this element. An additional indication of the accuracy of the LA results for major elements is that the total concentration is close to 100% (being in the range 94.4% - 103.9%).

The spread of results obtained within one sampling area is generally within 10% RSD, reflecting the homogeneity of sphalerite grains on the mm scale. When sample inhomogeneity on the cm scale is not a limiting factor, precision for LA expressed as RSD for results for different areas within one sample are as a rule, better than 5% for all elements under consideration except for Cu and Ag (Table 2).

Application of LA-ICP-SFMS for the analysis of sphalerite grains in drill core samples from Zinkgruvan reveals significant variations in Co and Cu concentrations in the ore system.

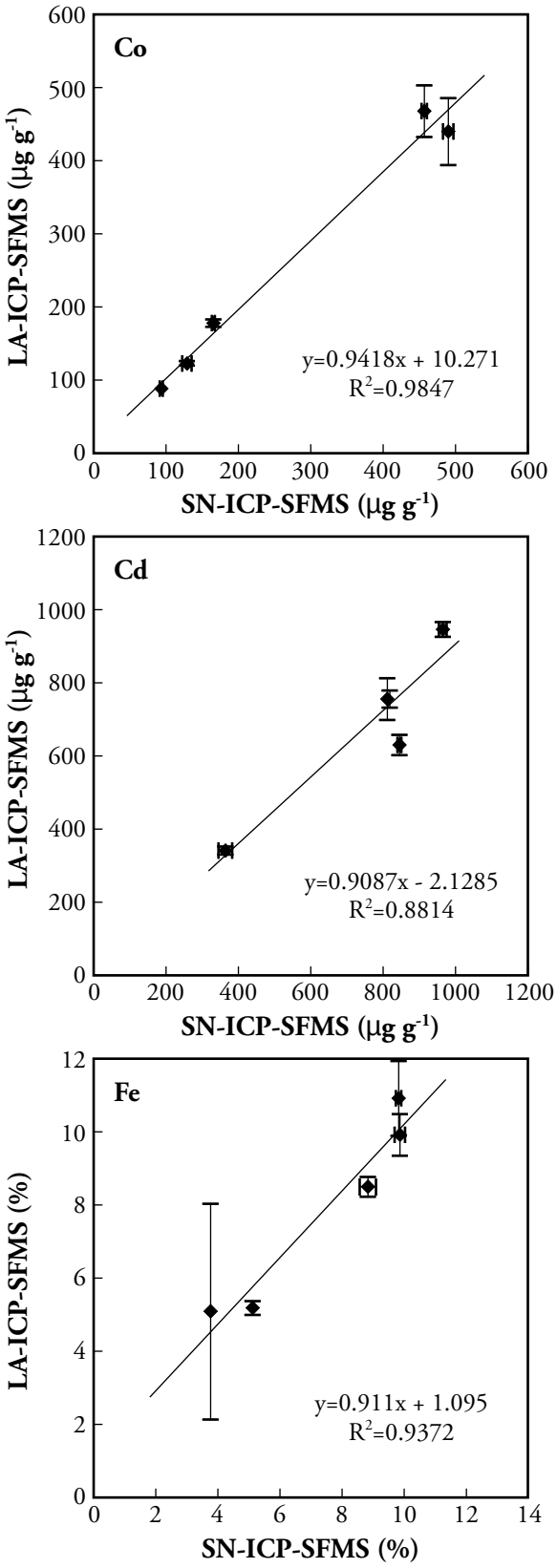

Fig. 2 Correlation between LA and SN-ICP-SFMS results for Co, Cd and Fe in five samples using two methods. Error bars included denote one standard deviation.

Conclusions

LA-ICP-SFMS is a useful tool for the rapid analysis of sphalerite with minor sample preparation. The results presented show that element fractionation during ablation and transport does not present a first order problem. By using the ^{66}Zn isotope as internal standard and correction for FeS content, accurate data can be obtained for elements ranging from tens of $\mu g\ g^{-1}$ to tens of per cent levels in the sphalerite. For the determination of low-abundance elements, such as Ag, that are present in the mineral at low and sub-$\mu g\ g^{-1}$ levels, LRM should be used. Though sub-mm resolution can be achieved with the technique, analysis of different grains is mandatory in order to gain information of the bulk concentrations in the samples. Due to the minimal amount of material needed for analysis by LA-ICP-SFMS, in-house solid mineral standards of cut sphalerite mineral can be produced by a combination of quantitative analysis of sample digests by SN-ICP-SFMS and checking for within sample homogeneity by LA.

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III

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Axelsson M.D., Rodushkin I., Petrov, P., Burman E and Öhlander B.

Multi-element analysis of sulphides by ICP techniques using solution nebulisation and laser ablation

Mikael D. Axelsson [*a], Ilia Rodushkin [b] Paraskev P. Petrov [c], Erik Burman [b] and Björn Öhlander [a]

[*a] Division of Applied Geology, Luleå University of Technology, S-971 87 Luleå, Sweden. E-mail: Mikael.Axelsson@sb.luth.se
[a] Division of Applied Geology, Luleå University of Technology, S-971 87 Luleå, Sweden. E-mail: Bjorn.Ohlander@sb.luth.se
[b] SGAB Analytica, Luleå University of Technology, S-971 87 Luleå, Sweden. E-Mail: ilia.rodushkin@sgab.se
[c] Economic Geology dept, GGF 15, Tzar Osvoboditel bd., Sofia 1000, Bulgaria. E-Mail: parp@gea.uni-sofia.bg

ABSTRACT

The combination of inductively coupled plasma atomic emission spectrometry, inductively coupled plasma mass spectrometry and atomic fluorescence spectrometry was used for the determination of 69 elements in various sulphide minerals. Alternative sample preparation procedures, including a two-stage microwave-assisted digestion with different acid mixtures and lithium metaborate fusion, were compared. Method detection limits in the sub-$\mu g\ g^{-1}$ range were obtained for some trace elements by taking extra care to prevent contamination during sample preparation. The relative analyte recoveries were compared for different preparation procedures. The accuracy of the methods was validated using two reference materials (pyrite, PS-1 and galena, GF-1). Obtained results were within the certified ranges for 15 out of 19 elements and for 18 out of 20 elements in PS-1 and GF-1, respectively. Compared to recommended values, significantly lower concentrations were found for a number of trace and ultra-trace elements, probably reflecting poor accuracy of the recommended data. The method precision was generally better than 5% relative standard deviation. More than 25 sulphide minerals from different ore deposits were analysed and found concentration ranges are reported for sphalerite, pyrite, galena, pyrrhotite and chalcopyrite.

KEYWORDS: Sulphide minerals, Digestion, Inductively coupled plasma sector field mass spectrometry, Laser ablation, Multi-element analysis

INTRODUCTION

The multi-elemental study of sulphides is of particular concern for geologists, were spatial information also is of importance [1, 2, 3]. In addition, there are industrial and economical interests. The elemental information gained from this kind of study may also be used for fingerprinting the origin of a unique sulphide deposit. The potential for the direct analysis of solid samples with high spatial resolution and minimal sample preparation makes laser ablation (LA), coupled either to inductively coupled plasma atomic emission spectrometry (ICP-AES) or to inductively coupled plasma mass spectrometry (ICP-MS), a useful technique for geological applications [2,4].

Although valuable semi-quantitative data can easily be obtained by LA-ICP-MS, calibration, which is required for quantitative analysis, remains the "Achilles heel" of the technique. There are considerable problems involved in obtaining quantitative results by LA. The use of a simple dissolution method followed by ICP-MS or ICP-AES still is the most reliable solution, until matrix matched calibration materials for LA become available. In the present study, quantification of 69 elements in totally 27 samples of sphalerite (ZnS), pyrite (FeS_2), galena (PbS), pyrrhotite ($Fe_{(1-x)}S$, $x<0{,}125$ hereafter referred to as FeS) and chalcopyrite ($CuFeS_2$) was performed by ICP-AES, sector field ICP-MS (ICP-SFMS) and atomic fluorescence spectrometry (AFS) after mineral separation and dissolution. Both ICP-AES and ICP-SFMS possess multi-element capabilities and wide dynamic ranges. The former is a well-recognised technique for the precise and accurate determination of analytes that are present in geological materials at relatively high concentrations. The latter provides extremely low instrumental detection limits and is less affected by spectral interferences compared to quadrupole-based ICP-MS instruments [5, 6]. The use of AFS allows Hg and Se determination at ultra-trace concentrations. Application of a combination of different techniques permits the acquisition, for many elements, of two analytical values and this can help to reveal instrumental errors [7]. Although many sample dissolution methods have been proposed for sulphide minerals, when aiming for wide elemental coverage no standard procedure can be prescribed in general. In the literature the use of a HNO_3-HCl-HF-$HClO_4$ mixture and a microwave-assisted (MW) digestion with aqua regia-HF in a high-pressure MW vessel has been described for the dissolution of geological

material with mixed success for the determination of the platinum-group elements (PGEs) [8]. Depending on the sample mineral composition, the described methods sometimes resulted in complete digestion, whereas, in other cases, an insoluble residue remained. For the latter, an alternative digestion method was also presented, where the residue was fused with a small quantity of 1:1 Na_2O_2+Na_2CO_3 before dissolving in diluted HCl [8]. It was concluded that the combination of MW digestion with aqua regia-HF and minifusion yields fully quantitative data for samples containing refractory minerals, and this method was also used by Jarvis et al. [9]. Further information regarding digestion techniques for the analysis of geological materials by ICP-AES and ICP-MS, can be found in recent reviews [10, 11].

Both MW digestions using different acid mixtures and lithium metaborate (LMB) fusion have been tested for the preparation of sulphide minerals in this work. Performance of sample preparation and analysis stages was evaluated using powdered pyrite and galena reference materials (PS-1 and GF-1, respectively).

EXPERIMENTAL

INSTRUMENTATION

The ICP-SFMS instrument used was the ELEMENT equipped with both a standard solution nebulisation introduction system and a laser ablation UV LaserProbe unit (both from Finnigan MAT, Bremen, Germany). The instrument can be operated in low (LRM, $m/\Delta m$ about 300), medium (MRM, $m/\Delta m \approx$ 4500) and high-resolution (HRM, $m/\Delta m \approx$ 9200) modes. In this work, only LRM and MRM have been used. An ARL 3580 (Applied Research Laboratories SA, Ecubilens, Switzerland) ICP-AES instrument was used with a Gilson 100 sample changer. The device has 40 channels for simultaneous multi-element detection. Instrument configuration and general experimental conditions for both techniques are reported elsewhere [12]. The AFS instrument used was a PSA Excalibur (PSA, Kent, UK). A microwave system MDS-2000 (CEM, Matthews, USA), equipped with 12 low-volume perfluoroalkoxy (PFA) lined vessels (ACV 50) with safety rupture membranes (maximum operating pressure 1380 kPa), was used for MW dissolution. A mechanical press, Herzog TP20 (Osnabruck, Germany) designed for sample preparation for IR spectroscopy, was used for the preparation of pressed pellets for LA.

SAMPLES AND STANDARDS

Samples of five sulphide minerals (FeS, FeS_2, $FeCuS_2$, ZnS and PbS, four to seven examples of each mineral) were obtained from the geological collection of the Division of Applied Geology, Luleå University of Technology, representing different ore deposits from Australia, Germany, Hungary, Norway, Spain, Sweden and the USA. Wide geographical distribution of sampling locations was chosen to ensure variations in the content of impurities. Only mineral sections determined visually to be mono mineralic were chosen from the selected bulk samples.

Two powdered sulphide mineral reference materials (RMs), PS-1 (pyrite) and GF-1 (galena), were supplied by the Mountain Academy of Freiberg in Germany, Department of Geosciences [13]. These RMs were chosen due to the availability of certified and recommended concentrations for more than 45 elements. It should be noted that, for the majority of commercially available sulphide mineral RMs, concentrations of only a few (often the major) elements are certified.

REAGENTS

Deionised "Milli-Q water"18 MΩ (Millipore Milli-Q, Bedford, USA) was used for sample and standard dilution. All calibration and internal standard solutions used were prepared by dilution of 1 mg ml^{-1} single-element standard solutions (SPEX Plasma Standards, Edison, NJ). Analytical grade nitric acid (65%, Merck, Darmstadt, Germany) was used after additional purification by sub-boiling distillation in a quartz still (Heraeus, Karlsruhe, Germany). The hydrofluoric (40%, Merck, "Suprapur" grade), hydrochloric (30%, Fluka, Steinheim, Germany, "PA+" grade) and tartaric (Merck, analytical grade) acids were used without additional purification. Lithium metaborate was of analytical grade (J. T. Baker B. V., Deventer, The Netherlands).

ANALYTICAL PROCEDURES

For multielement characterisation, a small amount (about 100 mg) of the selected sulphide minerals was carefully taken from different parts of the large mineral section to ensure a representative sub-sample. The sub-samples were ground to a grain size <50 µm. Sulphide mineral RMs were used as supplied.

An open-vessel hot-plate digestion with diluted HNO_3, HCl or aqua regia has been frequently applied to different sulphide minerals including the RMs. In preliminary experiments with 4-h open-vessel digestion, it appeared that none of these acids or acid mixtures provided complete dissolution of all minerals tested. The formation of yellow-grey residue, which is likely to be elemental sulphur, was especially pronounced for pyrite and sphalerite. When HCl or aqua regia is used for galena dissolution, a precipitation of white needle-shaped crystals ($PbCl_2$) appears, as has also been reported by Dolezal et al. [14]. After dilution of the digest solutions with water,

which results in 5-10% acid concentration, a significant part (though not all) of these residues was re-dissolved during a few days of storage. Digestion of both RMs leaves noticeable siliceous residue. As the completeness of dissolution is the major requirement, it was decided to develop a method based on MW digestion. Together with a shorter preparation time, digestion in closed vessels requires less reagents and runs lower contamination risks [15]. The following two-stage MW procedure was adopted in this study: a sample amount of about 50 mg was first digested with 2.5 ml of concentrated acid (HNO_3 or aqua regia) at 300W power for 30 min, followed by dilution with Milli-Q water and a second digestion stage using the same parameters. The second stage was aimed at re-dissolution of precipitates formed during the first digestion. The use of diluted acids in the first stage resulted in incomplete digestion for some sulphide minerals, whereas the two-stage procedure results in complete dissolution of the sulphide matrix with both HNO_3 and aqua regia. As both sulphide RMs used in this study are not mono-mineralic but contain impurities of other minerals, including refractory ones, an undigested residue was present for both these samples. Three different approaches were tested for complete dissolution of the RMs: Firstly, undigested residue was separated by centrifugation and re-digested with 0.2 ml concentrated HF. After evaporation of the HF, 0.5 ml of HNO_3 was added and after evaporation to approximately 0.1 ml it was recombined with the supernatant. Secondly, 0.1 ml of HF was added to HNO_3 or aqua regia prior to the first MW digestion stage. Thirdly, 125 mg quantities of the RMs were fused with 375 mg of LMB in a carbon crucible (Schunk, Lenhounda, Sweden) at 1000°C for 30 min. After cooling, the bead was dissolved in a 25 ml HNO_3/tartaric acid mixture (5%/1% v/v in Milli-Q water).

Digests obtained by each of the preparation methods have been analysed either directly (by ICP-AES) or after an additional dilution with 1% HNO_3, which results in a final dilution factor of about 10 000. This high dilution factor was chosen in order to prevent the ICP-SFMS and AFS instruments from being severely contaminated by major matrix elements (Fe, Zn, Pb and Cu) from the samples. In order to maintain low method detection limits (DL), the use of pure reagents as well as strict control of contamination during all analytical stages is mandatory. Each sample was prepared by different digestion procedures in triplicate together with a set of a minimum of three preparation blanks. Quantification by external calibration was used for all techniques. Monitoring of the ^{115}In isotope added as internal standard was used for correction of ICP-SFMS results.

The pyrite RM was additionally analysed for selected elements by LA-ICP-SFMS using 800 mg of material pressed into tablets (12 mm in diameter and about 2 mm thick) at a total thrust of 10 t during two minutes. Details of the LA procedure are reported elsewhere [7].

RESULTS AND DISCUSSION

Detection limits for the MW method, defined as three times the standard deviation for preparation blanks (n>3), are about the same for different acid mixtures and vary from the sub-µg g^{-1} level (Ir, Tb, Tm and Re) to a few µg g^{-1} (major elements). The highest detection limits are for S (about 1000 µg g^{-1}), owing to carryover contamination from previous samples. Detection limits were significantly higher for samples subjected to LMB fusion, as only ICP-AES was used for analysis after this preparation. Extremely high Li and B concentrations preclude analysis by ICP-SFMS in dissolved fusion samples. During the LA-ICP-SFMS experiments, the detection limit was in the low or sub µg g^{-1} range for detected elements except Cu, Fe, S, due to high blank levels caused by preceding samples.

RELATIVE RECOVERY

Analytical results obtained for the PS-1 RM after different sample preparations are summarised in Table 1. When discrepancies between the results obtained by different techniques were statistically insignificant, results with lower instrumental uncertainties were selected. In the case of significant differences, the lower concentrations were accepted. Results for elements, known to be severely affected by losses during fusion (Ag, Cd, Pb, Sb, etc) [15], were excluded from consideration. Regarding relative analyte recovery, for Ag, As, Au, B, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, I, Mg, Mn, Mo, Na, Ni, Pb, Re, S, Sb, Sr, Te, Tl, Zn and heavy rare-earth elements (REEs), no statistically significant differences were found between the MW preparations tested. The use of aqua regia provides higher recoveries for Ir, Pd, Pt, Rh and Ru. The addition of HF to the digestion mixture, as well as re-digestion of residue remaining after MW digestion, results in a noticeable improvement of Al, Ba, Be, Ga, Ge, Hf, K, Li, Nb, Rb, Sc, Si, Sn, Ta, Tb, Th, Ti, U, W, V, Y, and Zr recoveries. From the substantial recovery increase, it can be concluded that Al, Hf, Nb, Si, Ta, Ti, and Zr in this RM are mainly present in the refractory residue. Both HF-based digestions and LMB fusion provide similar recoveries for Ba, K, Sn, Ti, Y and Zr, while better recoveries of Al and Si were found with the latter approach. In GF-1 RM, similar trends were found for all elements, except for Cr. The fusion results showed about a 10-fold higher recovery for this element compared to MW

digestions, in spite of the use of HF. From Table 2 and forward, only results obtained using the preparation procedure providing the highest recovery for any given element will be considered.

ACCURACY

The accuracy of the overall analytical procedure was evaluated by comparing obtained results with certified / recommended concentrations for the RMs. For PS-1, the differences between certified and found concentrations were statistically insignificant for 15 (Ag, Al, As, Au, Bi, Ca, Cu, Hg, K, Mn, Ni, Pb, Sb, Si and Ti) out of 19 elements. Found concentrations were lower by 3% to 5% for Fe and S; and by about 20% for Mg and Co. For GF-1 (Table 2), good agreement was found for 18 (Ag, Al, As, Au, Bi, Ca, Cd, Cr, Cu, Fe, Hg, Mg, Mn, Pb, Sb, Si, Sn and Ti) out of 20 certified elements, with Zn and S results being within 10% of certified values. However, the agreement with recommended values was significantly poorer. Found concentrations fall inside a 20% range around recommended values for eight (Dy, Er, Ho, La, Na, Nd, Pr, and Tb) out of 31 elements in PS-1 and only for two (Er and P) out of 27 elements in GF-1. For elements such as Cd, Sn and Tl, results reported in this study for PS-1 RM were about 100 times lower than the recommended concentrations. As for the majority of these elements both ICP-AES and ICP-SFMS results were available, the errors during the instrumental analysis stage can be excluded. Assuming the recommended values to be correct, incomplete recoveries or losses of such analytes during preparation should be considered. To verify this, direct analysis of the PS-1 RM pressed into a pellet was performed by LA-ICP-SFMS. By using laser ablation sampling, fractionation depending on dissolution efficiency is avoided.

Five elements were determined by LA-ICP-SFMS, including a selection of those in agreement (Ag and Bi) and disagreement (Cd, Sn and Tl) with certified or recommended values. Coarse quantification was performed using normalisation to the intensity for the ^{123}Sb isotope assuming the accuracy of the tabulated antimony concentration. In spite of relatively high uncertainty (1s), measured Ag and Bi concentrations (17 ± 9 µg g^{-1} and 11.8 ± 1.3 µg g^{-1}) compare well, both with results obtained after sample digestion, and with certified values. Thus an error of less than 50% can be expected while using this means of quantification. LA results for Cd (1.6 ± 0.3µg g^{-1}), Sn (12 ± 9 µg g^{-1}) and Tl (0.29 ± 0.04 µg g^{-1}) are consistent with those obtained after sample digestion, thus suggesting poor accuracy for the recommended values for these elements. It should be noted that a Cd concentration of about 200 µg g^{-1} has been determined in the same RM by LA and spark ablation ICP-AES [16]. It seems that Cd determination by ICP-AES suffers from spectral interferences, presumably from Zn as especially large differences between ICP-AES and ICP-SFMS results for this element were found in sphalerite. Analytical difficulties in the determination of trace and ultra-trace elements at the time when these RMs were issued, may be responsible for the poorer accuracy of recommended values compared to the certified.

PRECISION

When not limited by detection power, the precision of the method, determined by the analysis of sulphide minerals prepared in triplicate, was generally better than 5% RSD for all preparation procedures. It was, however, significantly poorer for Ag and Sn, being in the range 15-50% RSD. It should be noted that poorer precision for these analytes, compared to elements such as Bi, Cd and Tl, was also obtained for LA analysis of PS-1 RM (see Accuracy section). Heterogeneous distributions of these analytes in sulphide minerals constitute the most probable reason for such variations. For many elements, relative standard deviations of mean concentrations obtained by each different MW digestion procedures are below the 5% level, thus proving good reproducibility for the methods.

RESULTS FOR THE 27 SULPHIDE MINERAL SAMPLES

The concentration ranges found for the sulphide materials tested are presented in Table 3. As thorough mineral separation has been made for these samples, no noticeable residues were observed after MW digestion. Consequently, sample preparations including re-digestion with HF or fusion were avoided. As an additional test for the accuracy of major element determinations, the total mass budget was calculated as the sum of obtained concentrations. Major element concentrations were in the range 99-101% of the total mass budget for PbS and FeS_2, 95-100% for ZnS and 94-98% for FeS and $CuFeS_2$. It appears that the concentrations of all analytes, other than the major elements, in these samples are significantly lower compared to the tested RMs. The galena samples analysed were almost without trace elements independent of mining location. Another problem associated with galena is the powerful loading of lead to the instrument, leading to severe memory effects for this element.

Table 1. Results for the PS-1 RM and comparison with certified and recommended concentrations (µg g^{-1}).

PS-1	Found (s)**						Reference
	MW (HNO_3)	MW (Aqua regia)	MW (HNO_3 + HF)	MW (Aqua regia) + HF	MW (HNO_3) redigestion with HF	Fusion	
Ag	24.6 (10.1)	22.9 (10.8)	27.1 (11.2)	32.2 (21.4)	24.8 (9.6)		28 (6)
Al	420 (27)	450 (14)	790 (30)	780 (6)	740 (35)	1230 (60)	1850 (740)
As	2790 (90)	2720 (60)	2830 (80)	2750 (50)	2800 (110)		2650 (302)
Au	0.045 (0.005)	0.049 (0.023)	0.049 (0.005)	0.048 (0.007)	0.047 (0.011)		0.041 (0.019)
B	24.2 (4.6)	25.0 (7.3)	24.2 (1.1)	26.2 (6.7)	22.2 (3.6)		
Ba	4.38 (0.16)	4.02 (0.23)	6.38 (0.22)	5.34 (0-36)	5.62 (0.27)	4.4 (1.7)	9.6
Be	0.142 (0.014)	0.138 (0.006)	0.174 (0.011)	0.177 (0.021)	0.184 (0.015)		
Bi	7.82 (0.27)	7.37 (0.18)	7.72 (0.37)	7.87 (0.05)	7.93 (0.32)		7.9 (4.4)
Ca*	1.96 (0.04)	1.97 (0.03)	1.94 (0.02)	1.93 (0.02)	1.96 (0.05)	1.96 (0.04)	2.03 (0.30)
Cd	1.11 (0.06)	1.06 (0.02)	1.13 (0.07)	1.05 (0.05)	1.12 (0.06)		192
Ce	3.99 (0.14)	3.66 (0.23)	4.70 (0.19)	4.77 (0.19)	4.06 (0.15)		6.8
Co	74.5 (1.4)	74.0 (2.1)	75.4 (0.7)	74.6 (1.0)	74.7 (1.6)	15.2 (1.1)	89 (5)
Cr	7.41 (0.51)	7.63 (0.50)	8.05 (0.25)	7.90 (0.07)	7.55 (0.64)	7.52 (0.55)	14
Cs	0.634 (0.040)	0.627 (0.007)	0.690 (0.020)	0.674 (0.015)	0.698 (0.037)		3
Cu	1020 (50)	995 (15)	1010 (10)	1020 (30)	1080 (60)	760 (50)	1058 (75)
Dy	0.731 (0.033)	0.677 (0.023)	0.705 (0.031)	0.711 (0.017)	0.748 (0.019)		0.8
Er	0.270 (0.010)	0.263 (0.006)	0.280 (0.013)	0.286 (0.009)	0.283 (0.014)		0.3
Eu	0.368 (0.011)	0.359 (0.008)	0.371 (0.011)	0.356 (0.012)	0.379 (0.012)		0.7
Fe*	38.9 (0.6)	38.5 (0.2)	38.3 (0.3)	38.6 (0.5)	39.0 (0.6)	36.0 (1.2)	40.4 (0.7)
Ga	0.402 (0.077)	0.371 (0.040)	0.677 (0.146)	0.530 (0.026)	0.525 (0.082)		3.6
Gd	0.672 (0.030)	0.637 (0.033)	0.674 (0.027)	0.668 (0.022)	0.697 (0.027)		
Ge	0.201 (0.082)	0.326 (0.056)	0.395 (0.085)	0.463 (0.195)	0.458 (0.102)		40
Hf	0.055 (0.011)	0.043 (0.010)	0.309 (0.039)	0.318 (0.023)	0.342 (0.037)		
Hg	0.160 (0.004)	0.149 (0.007)	0.145 (0.006)	0.152 (0.009)	0.163 (0.022)		0.208 (0.055)
Ho	0.125 (0.006)	0.119 (0.005)	0.127 (0.003)	0.127 (0.006)	0.129 (0.006)		0.120
I	<0.35	0.418 (0.202)	0.455 (0.132)	0.450 (0.205)	0.372 (0.092)		0.2
Ir	<0.0005	0.0024 (0.0010)	<0.0005	0.0013 (0.0001)	<0.0005		
K	223 (11)	441 (26)	460 (20)	472 (52)	300 (15)	456 (85)	620 (380)
La	2.01 (0.27)	1.73 (0.06)	2.27 (0.06)	2.29 (0.08)	2.06 (0.19)		2.6
Li	13.5 (0.3)	13.4 (0.4)	18.6 (0.6)	19.8 (0.3)	19.2 (0.5)		
Lu	0.024 (0.001)	0.024 (0.002)	0.030 (0.003)	0.035 (0.007)	0.028 (0.002)		
Mg	680 (23)	674 (25)	681 (10)	687 (11)	692 (17)	712 (30)	933 (155)
Mn	2810 (130)	2720 (80)	2820 (40)	2790 (50)	2820 (150)	2820 (120)	2600 (150)
Mo	1.06 (0.03)	1.10 (0.05)	1.14 (0.04)	1.15 (0.03)	1.11 (0.05)		4.2
Na	109 (8)	103 (9)	113 (6)	119 (12)	126 (15)	138 (32)	93
Nb	0.490 (0.059)	0.691 (0.023)	2.75 (1.05)	2.68 (0.83)	2.40 (0.11)		0.8
Nd	1.99 (0.07)	1.81 (0.07)	2.16 (0.11)	2.12 (0.06)	2.01 (0.09)		2.3
Ni	162 (3)	162 (6)	162 (4)	163 (3)	164 (8)	132 (19)	190 (52)
P	4.04 (1.81)	5.36 (1.47)	5.88 (1.37)	4.51 (1.32)	4.42 (0.85)	5.10 (1.6)	
Pb	250 (5)	240 (4)	249 (1)	245 (18)	253 (2)		345 (145)
Pd	<0.010	0.031 (0.016)	<0.010	0.034 (0.003)	<0.010		
Pr	0.491 (0.022)	0.445 (0.023)	0.548 (0.024)	0.552 (0.014)	0.497 (0.019)		0.5
Pt	0.023 (0.008)	0.366 (0.229)	0.031 (0.009)	0.178 (0.125)	0.025 (0.006)		
Rb	16.6 (0.4)	16.3 (0.5)	17.8 (0.1)	17.7 (0.3)	18.1 (1.4)		62
Re	0.006 (0.001)	0.006 (0.001)	0.006 (0.001)	0.006 (0.001)	0.006 (0.001)		
Rh	<0.005	0.292 (0.159)	<0.005	0.161 (0.143)	<0.005		
Ru	<0.004	0.015 (0.004)	<0.004	0.012 (0.004)	<0.004		
S*	40.2 (0.4)	39.8 (0.4)	40.1 (0.6)	40.1 (0.2)	40.2 (0.3)		42.9 (1.9)
Sb	66.3 (0.7)	67.8 (1.3)	68.8 (1.5)	70.6 (1.6)	68.8 (2.4)		62 (20)
Sc	0.202 (0.028)	0.206 (0.018)	0.291 (0.019)	0.280 (0.029)	0.252 (0.030)		
Se	37.5 (1.9)	31.8 (1.5)	33.1 (1.5)	29.7 (1.0)	30.9 (1.7)		76
Si*	0.092 (0.025)	0.173 (0.033)	1.76 (0.04)	1.70 (0.04)	2.60 (0.09)	3.13 (0.09)	3.19 (0.37)
Sm	0.529 (0.017)	0.488 (0.023)	0.517 (0.032)	0.525 (0.041)	0.533 (0.021)		
Sn	2.66 (0.65)	2.43 (0.44)	3.89 (0.22)	3.38 (0.22)	3.82 (0.41)	3.26 (0.74)	125
Sr	16.0 (0.5)	15.9 (0.4)	16.8 (0.5)	16.4 (0.3)	16.5 (0.7)	16.7 (1.3)	54
Ta	0.042 (0.006)	0.082 (0.009)	0.371 (0.056)	0.357 (0.046)	0.313 (0.022)		2.4
Tb	0.112 (0.005)	0.102 (0.005)	0.109 (0.004)	0.105 (0.003)	0.113 (0.005)		0.09
Te	0.030 (0.004)	0.024 (0.012)	0.021 (0.013)	0.033 (0.007)	0.031 (0.003)		
Th	0.380 (0.049)	0.327 (0.061)	0.483 (0.018)	0.439 (0.011)	0.415 (0.033)		0.675
Ti	4.72 (0.21)	4.61 (1.00)	9.60 (0.58)	9.57 (0.75)	11.1 (1.3)	10.0 (1.6)	21 (11)
Tl	0.246 (0.013)	0.238 (0.009)	0.235 (0.013)	0.242 (0.009)	0.258 (0.015)		120
Tm	0.037 (0.002)	0.037 (0.001)	0.041 (0.002)	0.042 (0.004)	0.041 (0.003)		
U	0.147 (0.013)	0.151 (0.008)	0.215 (0.020)	0.213 (0.028)	0.199 (0.015)		0.795
W	2.66 (0.18)	2.87 (0.09)	3.13 (0.42)	3.15 (0.06)	3.23 (0.24)		
V	0.567 (0.073)	0.578 (0.068)	0.742 (0.009)	0.713 (0.030)	0.730 (0.063)		14
Y	4.19(0.14)	4.16 (0.06)	4.35 (0.14)	4.42 (0.07)	4.28 (0.08)	4.29 (0.31)	8.5
Yb	0.198 (0.006)	0.198 (0.004)	0.239 (0.015)	0.237 (0.028)	0.228 (0.021)		
Zn	32.5 (3.0)	33.4 (2.0)	35.9 (2.4)	34.4 (1.9)	33.3 (0.9)		203
Zr	0.392 (0.170)	0.250 (0.037)	3.98 (0.74)	4.01 (1.67)	3.28 (0.25)	3.10 (0.9)	10

*Element concentrations in percent

**Uncertainties expressed as one standard deviation (N>3).

Table 2. Results for the GF-1 RM and comparison with certified and recommended concentrations (µg g^{-1}).

GF-1	Found (s) **	Reference	GF-1	Found (s) **	Reference
	MW (HNO_3) and fusion			MW (HNO_3) and fusion	
Ag	1310 (620)	2000 (275)	Nb	0.010 (0.003)	0.040
Al	578 (35)	670 (330)	Nd	0.081 (0.021)	
As	505 (15)	580 (160)	Ni	1.65 (0.23)	7
Au	0.013 (0.003)	0.014 (0.006)	P	1.04 (0.09)	1.1
B	<7		Pb*	86.4 (0.8)	87.9 (0.5)
Ba	44.2 (2.5)	109	Pd	<0.010	
Be	0.010 (0.004)		Pr	0.023 (0.005)	0.17
Bi	87.2 (1.6)	154 (66)	Pt	<0.004	
Ca	565 (15)	578 (330)	Rb	0.414 (0.027)	3.4
Cd	194 (5)	245 (50)	Re	<0.0002	
Ce	0.146 (0.031)	0.5	Rh	<11***	
Co	1.46 (0.21)	23	Ru	<0.004	
Cr	309 (11)	372 (135)	S*	13.0 (0.1)	14.3 (0.5)
Cs	0.043 (0.003)	0.8	Sb	1750 (140)	1800 (275)
Cu	1050 (35)	1150 (252)	Sc	0.020 (0.005)	
Dy	0.027 (0.004)	0.5	Se	8.48 (0.64)	32
Er	0.015 (0.004)	<0.09	Si	2810 (90)	2970 (630)
Eu	0.007 (0.001)	0.4	Sm	0.054 (0.018)	2.5
Fe	6080 (80)	6100 (550)	Sn	1600 (190)	2500 (660)
Ga	0.544 (0.054)		Sr	2.07 (0.10)	5
Gd	0.024 (0.005)	0.6	Ta	0.006 (0.001)	2
Ge	0.430 (0.216)	6.5	Tb	0.004 (0.001)	
Hf	0.015 (0.002)		Te	0.457 (0.065)	
Hg	0.116 (0.014)	0.205 (0.090)	Th	0.018 (0.002)	0.7
Ho	0.005 (0.001)	0.06	Ti	6.0 (0.7)	10.8 (3.5)
I	<0.35		Tl	3.35 (0.10)	100
Ir	<0.0002		Tm	0.002 (0.001)	
K	257 (31)	164	U	0.044 (0.004)	0.31
La	0.153 (0.026)	39	W	0.133 (0.010)	
Li	1.57 (0.07)		V	0.170 (0.012)	2
Lu	0.003 (0.001)	0.1	Y	0.180 (0.020)	
Mg	217 (14)	240 (80)	Yb	0.015 (0.004)	0.7
Mn	145 (4)	180 (60)	Zn*	1.12 (0.01)	1.26 (0.01)
Mo	0.960 (0.064)	4.8	Zr	0.291 (0.016)	1
Na	72 (3)	61			

*Element concentrations in percent

**Uncertainties expressed as one standard deviation (N>3).

***Element determination restricted by severe spectral interference, thereby the uncorrected value is reported as an upper limit.

Table 3. Concentration ranges for five different sulphide minerals (µg g^{-1}), each with different geographical and geological origin.

	FeS	PbS	FeS_2	$CuFeS_2$	ZnS
Ag	0.8 - 7.0	37 - 7100	<0.3 - 3.1	16 - 330	1 - 120
Al	<4 - 160	<4 - 15	16 - 900	<4 - 900	<4 - 120
As	1.8 - 3.1	2.6 - 4.1	3.7 - 1500	3.4 - 7.1	0.6 - 22
Au	<0.005 - 0.006	<0.005 - 0.042	0.005 - 0.3	<0.005 - 0.027	<0.005 - 0.028
B	<7	19 - 71	<7	<7	<7
Ba	<0.08 - 8.9	<0.08 - 0.09	0.2 - 11	0.8 - 7.2	<0.08 - 4.0
Be	<0.04 - 0.07	<0.04	<0.04 - 1.7	<0.04 - 0.09	<0.04
Bi	0.14 - 3.6	13 - 7000	0.58 - 930	0.28 - 21	0.03 - 16
Ca	15 - 270	<11 - 140	19 - 9300	<11 - 180	<11 - 380
Cd	0.08 - 5.2	1.9 - 83	0.05 - 1.8	3.2 - 19	860 - 5400
Ce	0.02 - 0.31	<0.003 - 0.021	0.08 - 26	0.006 - 0.21	0.006 - 4.3
Co	95 - 1530	<0.1 - 1.0	22 - 14000	0.58 - 40	
Cr	<0.2 - 36	<0.2	<0.2 - 1.5	<0.2 - 0.5	<0.2 - 0.7
Cs	<0.003 - 0.021	<0.003	0.004 - 0.12	<0.003 - 0.061	<0.003 - 0.16
Cu	170 - 35000	10 - 600	19 - 4500	330000 - 350000	8 - 1700
Dy	<0.001 - 0.015	<0.001 - 0.002	0.003 - 2.1	<0.001 - 0.011	<0.001 - 0.83
Er	<0.001 - 0.004	<0.001	<0.001 - 0.78	<0.001 - 0.007	<0.001 - 0.46
Eu	<0.001 - 0.098	<0.001	0.002 - 0.33	<0.001 - 0.004	0.002 - 0.070
Fe	600000 - 650000	15 - 700	450000 - 480000	310000 - 320000	2800 - 170000
Ga	<0.007 - 0.047	<0.007 - 0.049	<0.007 - 0.46	0.021 - 1.0	1.6 - 32
Gd	<0.002 - 0.035	<0.002 - 0.004	0.004 - 3.2	<0.002 - 0.015	<0.002 - 0.59
Ge	<0.3 - 0.54	<0.3 - 0.57	<0.3	<0.3 - 1.7	<0.3 - 1.8
Hf	<0.001 - 0.009	<0.001 - 0.005	0.008 - 0.064	<0.001 - 0.004	0.002 - 0.13
Hg	0.01 – 0.25	0.06 – 0.33	0.04 - 0.28	0.04 – 2.6	1.1 - 49
Ho	<0.001 - 0.002	<0.001	<0.001 - 0.35	<0.001 - 0.002	<0.001 - 0.19
I	<0.4 - 11	<0.4 - 3.6	<0.4	<0.4 - 7.7	<0.4 - 4.0
Ir	<0.0005	<0.0005	<0.0005 - 0.004	<0.0005	<0.0005
K	<80	<80	<80 - 560	<80 - 280	140 - 460
La	0.02 - 0.21	0.02 - 0.39	0.05 - 21	0.002 - 0.12	0.004 - 2.5
Li	1.8 - 2.1	<0.1 - 0.21	0.69 - 1.9	1.8 - 2.6	0.29 - 1.1
Lu	<0.001	<0.001 - 0.008	<0.001 - 0.069	<0.001	<0.001 - 0.051
Mg	4.7 - 140	<1.8 - 5.5	16 - 1200	<1.8 - 660	<1.8 - 190
Mn	6.5 - 250	<0.4 - 26	1.7 - 15	0.6 - 39	690 - 17000
Mo	1.7 - 17	<0.03 - 0.06	1.1 - 140	<0.03 - 1.6	<0.03 - 0.44
Na	77 - 110	<30 - 500	45 - 74	58 - 120	<30 - 140
Nb	<0.007 - 0.019	<0.007	<0.007 - 0.17	<0.007 - 0.026	<0.007 - 1.0
Nd	0.006 - 0.15	<0.003 - 0.011	0.021 - 12	<0.003 - 0.094	<0.003 - 2.1
Ni	120 - 23000	<0.4 - 0.9	0.9 - 200	<0.4 - 12	<0.4 - 2.8
P	<3 - 120	<3 - 4	<3 - 37	<3 - 77	<3 - 15
Pb	60 - 3600	850000 - 870000	5.9 - 600	6.1 - 510	3.1 - 5400
Pd	<0.01 - 0.21	<0.01	<0.01	<0.01	<0.01
Pr	<0.005 - 0.036	<0.005	0.008 - 3.2	<0.005 - 0.023	<0.005 - 0.52
Pt	<0.004	0.013 - 0.023	<0.004	<0.004	<0.004
Rb	0.03 - 0.04	<0.01 - 0.12	0.03 - 3.6	<0.01 - 0.79	0.13 - 1.5
Re	0.001 - 0.22	<0.0002	<0.0002 - 0.19	<0.0002 - 0.0012	<0.0002 - 0.0014
Rh	<0.004 - 0.54	ND**	<0.004	<0.004	<0.004
Ru	<0.004 - 0.048	<0.004	<0.004	<0.004	<0.004
S*	30.4 - 32.1	12.9 - 13.4	51.6 - 53.9	28.3 - 30.5	22.8 - 32.5
Sb	0.07 - 3.1	310 - 7100	0.1 - 3.3	0.1 - 0.6	1.1 - 600
Sc	<0.001 - 0.005	<0.001 - 0.018	<0.001 - 0.067	<0.001 - 0.13	0.003 - 0.12
Se	2.3 - 87	<1.5 - 6.7	2.4 - 97	10 - 130	<1.5 - 3.3
Si	240 - 720	<19 - 23	230 - 1100	<19 - 610	<19 - 160
Sm	0.001 - 0.026	0.007 - 0.184	0.002 - 2.8	0.001 - 0.029	0.001 - 0.44
Sn	<0.1 - 0.3	<0.1 - 28	<0.1 - 0.6	<0.1 - 86	0.2 - 2.7
Sr	<0.04 - 0.98	<0.04 - 0.07	0.05 - 32	<0.04 - 0.39	0.05 - 0.64
Ta	<0.001	<0.001	<0.001 - 0.006	<0.001	<0.001 -0.031
Tb	<0.0005 - 0.003	<0.0005	<0.0005 - 0.36	<0.0003 - 0.002	<0.0005 - 0.10
Te	0.01 - 2.0	<0.01 - 37	<0.01 - 5.4	0.02 - 2.9	0.01 - 2.3
Th	0.01 - 0.02	<0.006 - 0.013	0.034 - 0.77	<0.006 - 0.028	0.007 - 0.76
Ti	<0.4 - 1.9	<0.4 - 0.86	0.47 - 14	<0.4 - 9.8	<0.4 - 13
Tl	<0.02 - 0.36	2.8 - 62	<0.02 - 42	<0.02 - 0.49	<0.02 - 0.35
Tm	<0.0003 - 0.001	<0.0003	<0.0003 - 0.10	<0.0003 - 0.001	<0.0003 - 0.069
U	<0.002 - 0.37	0.005 - 0.020	<0.002 - 0.26	<0.002 - 0.025	<0.002 - 1.8
W	0.20 - 0.26	<0.04	0.21 - 13	0.14 - 0.87	<0.04 - 1.5
V	<0.004 - 1.4	<0.04	0.06 - 1.8	<0.04 - 1.1	<0.04 - 0.30
Y	0.003 - 0.10	<0.003	0.014 - 12	0.007 - 0.096	0.016 - 8.5
Yb	<0.001	<0.001	<0.001 - 0.59	<0.001 - 0.006	<0.001 - 0.38
Zn	490 - 1400	13 - 3100	6 - 130	560 - 1800	480000 - 670000
Zr	0.05 - 0.09	0.02 - 0.10	0.12 - 1.1	0.02 - 0.05	0.07 - 2.1

*Element concentrations in percent
**Not determined

EVALUATION OF THE SUITABILITY OF THE ANALYSED MINERALS AS LA CALIBRATION STANDARDS

The method described here may be used for preparation of in-house standards for LA, if some further considerations during sample preparation are made. Only sufficiently large (> 2 cm^3) samples are adequate, as mono mineralic sections have to be sampled from the selected specimens. From each mono mineralic sample a few sub-samples are removed and analysed as suggested here. Then, after additional studying of the large sections' homogeneity, it will be possible to use the material as a solid calibration material. The LA results will be improved if the surface can be polished without substantial contamination. The possibility to use the 27 different mineral samples analysed here was evaluated by the following criteria: wide concentration range and easily detectable levels of impurities. For an element to be suitable for LA-ICP-SFMS determination at optimum concentration range, the abundance of each isotope and required resolution mode also has to be considered. For example, for ^{209}Bi (100% abundance, LRM) a low µg g^{-1} concentration can be sufficient but for ^{44}Ca (2.1% abundance, MRM) at least 100 µg g^{-1} is needed. Elements well suited for standard calibration in the FeS mineral are: Ag, Al, Ba, Bi, Cd, Co, Cr, Cu, Eu, Ge, Hg, Mg, Mn, Mo, Ni, Pb, Rh, Sb, Se, Si, Sr, Ti, Tl, U and Zn. Approximately the same list of elements can be detected by LA-ICP-SFMS in the other minerals, except for galena. There are also some elements not suitable for calibration in any of the materials, these being: Au, B, Dy, Cs, Er, Hf, Ho, I, Ir, Li, Lu, Nb, Pd, Pr, Pt, Re, Ru, Sc, Ta, Tb, Tm, Yb and Zr. Hence, out of the 69 elements determined, 23 are not suitable for LA, mainly as a result of the low concentrations present.

The homogeneity of these mineral standards has not been tested in this work. Though a standard homogeneous down to the sub-µm level would be most practical, there have been reported analyses of materials with the opposite characteristics. In one example, the analysis was performed using LA-ICP-MS on heterogeneous powdered soils, although the precision essentially depended on the sample homogeneity. A mathematical function was presented to determine the smallest amount of sample needed to obtain reliable information on the bulk composition of the heterogeneous samples [17].

CONCLUSION

The combination of ICP-AES, ICP-SFMS and AFS allows wide element coverage in sulphide minerals at concentrations varying from sub-µg g^{-1} to tens of percent. Erroneous results caused by, e. g., spectral interferences or matrix effects are more readily revealed compared to the use of a single analytical technique. The two-stage MW digestion with HNO_3 (or with aqua regia when the determination of platinum group elements is required) is sufficiently rapid and efficient for dissolving all tested minerals. However, for the complete recovery of elements which are bound into refractory mineral impurities in the host minerals, the addition of HF or fusion is necessary. Results obtained for PS-1 and GF-1 reference materials show the lack of accuracy in recommended concentrations for many trace and ultra-trace elements, as well as possible inhomogeneity when using a 50 mg sample amount. New reference materials with certified values for a larger number of elements are thus needed in order to facilitate method validation. In spite of the selection of minerals from different ore deposits with wide geographic distributions, it was impossible to find samples that contained sufficiently high concentrations of many trace analytes such as REEs and platinum group elements to be used for LA calibration purposes. However, it can be possible to use the selected minerals as matrix-matched standards for the determination of about 20 trace and ultra-trace elements by LA. That is providing the remaining untreated solid mineral fulfils certain characteristics for a solid standard material, set by the analyst (e.g., less then 10% deviation in concentration inside the mineral section, number of cracks inside the material should be low, material should be large enough to polish).

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IV

Application of double focusing sector field ICP-MS for multielement characterization of human hair and nails. Part I. Analytical methodology. The Science of the Total Environment, 2000, 250, 83-100.

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Application of double focusing sector field ICP-MS for multielemental characterization of human hair and nails. Part I. Analytical methodology

Ilia Rodushkin[a,*], Mikael D. Axelsson[b]

[a] *SGAB Analytica, Luleå University of Technology, S-971 87 Luleå, Sweden*
[b] *Division of Applied Geology, Luleå University of Technology, S-971 87 Luleå, Sweden*

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Abstract

The capabilities of double focusing sector field inductively coupled plasma mass spectrometry (ICP-SMS) for the determination of 71 elements in hair and nails were studied. A microwave-assisted digestion procedure with nitric acid and hydrogen peroxide as well as direct sampling of the nails by laser ablation (LA) have been tested. Examples of spectral interferences are given and different correction procedures are discussed. Method detection limits below ng g^{-1} were obtained for 39 elements investigated by using high-purity reagents and by taking special care to prevent contamination during preparation. However, these detection limits were insufficient for detection of some platinum group elements in the majority of the samples. The accuracy of the analytical procedure was estimated by analysis of the GBW07601 certified reference material as well as by participation in an interlaboratory comparison program. The reproducibility was assessed from replicate analysis (including sample preparation) and was found to be, as average values for all elements, 9–10% R.S.D. and 18–19% R.S.D. for hair and nails, respectively. Contribution from exogenous deposition was evaluated by analyzing samples before and after washing, as well as by studying spatial element distribution along hair and nails. It was found that even after sample washing, many elements are enriched in the surface of the nail.

Keywords: Hair; Nails; High resolution inductively coupled plasma mass spectrometry; Laser ablation; Multielement analysis

* Corresponding author. Tel: +46-920-724-89; fax: +46-920-724-90.
E-mail address: ilia.rodushkin@sgab.se (I. Rodushkin)

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1. Introduction

During the past three decades, hair analysis has been widely used for assessment of environmental and occupational exposure, for evaluation of the nutritional status, for diagnosing diseases and in forensic science (e.g. Chatt et al., 1980; Passwater and Cranton, 1983; Katz and Chatt, 1988; Valkovic, 1988; Contiero and Folin, 1994; Batzevich, 1995; Bencjo, 1995; Cho et al., 1998; Borella et al., 1997). When untreated hair is not available in sufficient quantity, nail analysis becomes a useful alternative (e.g. Suzuki, 1988; Wilhelm et al., 1991; Hayashi et al., 1993; Nowak, 1996; Nichols et al., 1998; Chen et al., 1999). Among the factors responsible for an increasing popularity of hair and nails as biopsy tissues or exposure biomarkers there is the possibility to monitor elements accumulated over a period from a few weeks to a few months, the simplicity with which they can be sampled, transported and handled, and generally higher element concentrations compared to other biological media (blood, urine). However, alongside numerous reports of positive findings from studies involving hair and nail analysis, there are several papers that emphasize the limitations of the approach and question the utility of determining element concentrations in these matrices, especially in clinical medicine (Hambidge, 1982; Riolin, 1983; Barrett, 1985; Klevay et al., 1987; Bencze, 1990a,b; Yoshinaga et al., 1990; Tracqui et al., 1995; Gulson, 1996). The most frequently cited factors which may jeopardize the usefulness of hair and nail analysis include difficulties in differentiating between endogenous and exogenous deposition, inconsistency of hair and nail concentration anomalies with nutritional status and clinical symptoms and with other biological indicators, and the absence of well defined reference concentration ranges. Also poor, if not definitely erroneous, analytical results obtained without proper quality control and assurance measures may be responsible for the divergent opinions on the validity of hair and nail analysis (Caroli et al., 1994; Miekeley et al., 1998).

Although the importance of using well-validated analytical techniques in the analysis of biological samples has long been recognized (Katz and Chatt, 1988; Bozsai, 1992; Herber and Stoeppler, 1994; Borella et al., 1996), there is still a general lack of information on figures of merit for many analytical procedures currently used in hair and nail analysis. A survey of approximately 40 papers on the determination of elemental composition in hair that have been published since 1991 shows that only eight of these studies provide method detection limits, five discuss analytical precision and 14 contain results for hair reference materials. In another six studies, the use of blood and plant reference materials, spike recovery test and comparison of results obtained by different methods have been applied as means of accuracy assessment. Approximately half of the papers do not describe any approach to evaluating accuracy in the results. Although no attempt has been made to quote all relevant publications, these figures demonstrate that the full incorporation of the principles of quality control and assurance in analytical steps is regretfully not the rule in this field.

In spite of claims that 'simultaneous measurement of several elements is likely to produce falsely positive results' (Klevay et al., 1987), fast and cost-effective multielemental analyses are now capable of producing the data necessary for studying antagonistic and synergistic effects (Caroli et al., 1992) as well as for explanation of co-occurrence of elements based on inter-element correlation (Nowak, 1998; Nowak and Kozlowski, 1998). Together with nuclear activation analysis methods, which have been used for determination of the elemental composition of hair for more than 30 years (Ryabukhin, 1980; Chatt et al., 1980; Zhuk and Kist, 1995; Cho et al., 1998), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) have become widely accepted techniques for multielemental analysis of hair and nails (Delves, 1988; Bortoli et al., 1992; Caroli et al., 1992; Durrant and Ward, 1994; Ward and Savage, 1994; Yoshinaga, 1994; Buseth et al., 1998; Chen et al., 1999;

LeBlanc et al., 1999). As has been shown recently (Miekeley et al., 1998), the moderate sensitivity of ICP-AES for certain elements is the main obstacle for wide coverage of trace and ultratrace elements in biological samples. Though the lower detection limits in ICP-MS permit the determination of several elements usually reported as being below the detection limits by ICP-AES users, the accuracy of results obtained by ICP-MS for biological samples may be severely affected by spectral interferences and matrix effects (Vanhoe et al., 1994; Dams et al., 1995). It should be noted that in contrast to other biological sample types, the importance of correction for spectral interferences in hair and nail analysis by ICP-MS has not been extensively discussed in the literature. This reaffirms the conclusion made by Caroli et al. (1994) that 'the availability today of sophisticated and extremely powerful analytical techniques further complicates this investigation area in that users are not always fully aware of the pitfalls and limitations posed by them, while at the same time they are dazzled by the ease and rapidity with which an enormous mass of experimental data can be generated'.

Sector-field ICP-MS (ICP-SMS), also known as high resolution ICP-MS (HR-ICP-MS), offers the ability to resolve many spectral interferences and provides improved instrumental detection limits and isotope ratio precision compared with conventional ICP-MS instruments equipped with quadrupole mass filters (ICP-QMS). During the past decade, the superiority of ICP-SMS over ICP-QMS when applying to biological matrices such as blood, urine and serum has been demonstrated in numerous publications (Moens et al., 1994; Begerow et al., 1997a,b; Riondato et al., 1997; Schramel and Wendler, 1997; Krachler et al., 1998; Townsend et al., 1998; Muniz et al., 1999; Rodushkin et al., 1999b).

This part of the study focuses on method validation for the determination of 71 elements in hair and nail samples by ICP-SMS after microwave assisted digestion with special attention to correction for spectral interferences and to accuracy assessment.

2. Materials and methods

2.1. Instrumentation

The ICP-SMS instrument used was the ELEMENT equipped with both a standard solution nebulization introduction system and laser ablation UV LaserProbe system (both from Finnigan MAT, Bremen, Germany). The instrument can be operated in low (LRM, $m/\Delta m$ approx. 300), medium (MRM, $m/\Delta m = 4500$) and high resolution mode (HRM, $m/\Delta m = 9200$). Details of instrumental operating conditions and measuring parameters are given in Table 1.

For MW treatment a microwave system (MDS-2000, CEM, Matthews, USA), equipped with 12 low-volume perfluoroalcoxy (PFA) lined vessels (ACV 50) with safety rupture membranes (maximum operating pressure, 1380 kPa), was used. The vessels are located on a rotating turntable to ensure even sample heating. Before use and between each batch of samples, the PFA utensils were thoroughly acid cleaned and then rinsed with deionized water.

2.2. Reagents

All calibration and internal standard solutions used were prepared by diluting single-element standard solutions (1 g l^{-1}, 5 g l^{-1} and 10 g l^{-1}, SPEX Plasma Standards, Edison, NJ, USA and Promochem AB, Ulricehamn, Sweden), taking into account inter-element compatibility. Concentrations of the elements in the calibration standards were in the range from 1 μg l^{-1} (Au, Pd, Pt, Ir, Re, Rh, Ru, Te, REE, etc.) to 250 mg l^{-1} (S) in order to match expected contencentrations in the samples and they were checked using quality control samples prepared by diluting 10 mg l^{-1} multi-element standard solutions (PE Pure Plus Atomic Spectroscopy Standard, Norwalk, USA).

Analytical grade nitric acid (65%, Merck, Darmstadt, Germany) was used after additional purification by sub-boiling distillation in a quartz still (Heraeus, Karlsruhe, Germany). Suprapure grade hydrofluoric (40%) acid, analytical grade

Table 1
ICP-SMS operating conditions and measurement parameters

RF power (W)	1500
Sample uptake rate (ml min^{-1})	0.2
Gas flow rates (l min^{-1})	
Coolant	13
Auxiliary	0.65
Nebulizer	0.95–1.15
Ion sampling depth (mm)	9
Ion lens settings	Adjusted to obtain maximum signal intensity
Torch	Fassel torch, 1.5 mm i.d.
Nebulizer	MicroMist AR40-1-F02
Spray chamber	Scott type (double-pass)
Sample cone	Nickel, 1.1 mm orifice diameter
Skimmer	Nickel, 0.8 mm orifice diameter
Laser (Nd:YAG)	
Wavelength (nm)	266
Pulse width (ns)	3
Pulse energy (mJ)	5
Ablation diameter (μm)	50
Repetition rate (Hz)	20
Number of shots per point	50
Distance between points (mm)	0.1
Low resolution mode	
Isotopes	^{7}Li, ^{9}Be, ^{11}B, ^{23}Na, ^{75}As, ^{77,82}Se, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{98}Mo, ^{99,101,102}Ru, ^{103}Rh, ^{105,106,108}Pd, ^{107,109}Ag, ^{111,114}Cd, ^{115}In[b], ^{120}Sn, ^{121}Sb, ^{125,126}Te, ^{133}Cs, ^{138}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{143,146}Nd, ^{147,149}Sm, ^{151,153}Eu, ^{157,160}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{171,173}Yb, ^{175}Lu, ^{178,180}Hf, ^{181}Ta, ^{183,186}W, ^{185,187}Re, ^{191,193}Ir, ^{194,195,196}Pt, ^{197}Au, ^{202}Hg, ^{205}Tl, ^{206,207,208}Pb, ^{209}Bi, ^{232}Th, ^{238}U
Acquisition mode	E-scan
No. of scans	21
Acquisition window (%)[a]	20 for Be; 30 for other elements
Search window (%)[a]	20 for Be; 30 for other elements
Integration window (%)[a]	20 for Be; 30 for other elements
Dwell time per sample (ms)	5 for Na, Ba, Pb, Sr and In; 10 for other elements
No. of samples per nuclide	30
Medium resolution mode	
Isotopes	^{26}Mg, ^{27}Al, ^{28}Si, ^{31}P, ^{32}S, ^{35}Cl, ^{39}K, ^{44}Ca, ^{45}Sc, ^{47,49}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{62}Ni, ^{63}Cu, ^{66}Zn, ^{69,71}Ga, ^{73,74}Ge, ^{115}In[b]
Acquisition mode	E-scan
No. of scans	21
Acquisition window (%)[a]	60 for K; 100 for other elements
Search window (%)[a]	60
Integration window (%)[a]	60
Dwell time per sample (ms)	10 for Mg, Si, P, S, K, Ca, Fe, Cu, Zn and In, 20 for other elements
No. of samples per nuclide	25

[a] Percent of peak width.
[b] Internal standard.

hydrogen peroxide (30%), Triton X-100 detergent and ammonia solution (25%) (all from Merck) were used without additional purification.

Deionized 'Milli-Q water' (Millipore Milli-Q, Bedford, USA) was additionally purified by subboiling distillation in a Teflon still (Savillex Corp., Minnetonka, MN, USA).

2.3. Samples

Scalp hair and fingernail samples used for the method validation were obtained from a number of volunteers (age 3–33 years) living in Luleå, Sweden. Although scalp hair is more prone to contamination from the environment and from cosmetic treatments, it is still preferable to hair from other body parts since it is less affected by natural excretions (Caroli et al., 1992). Approximately 0.5–1 g of hair was collected from the nape of the neck using stainless steel scissors. Except for the study of elemental distribution along the length of the hair, the 2–3-cm hair segments closest to the scalp were used. Fingernails were clipped with a stainless steel cutting instrument providing samples ranging in mass from 15 to 100 mg. Human hair powder GBW07601, certified reference material from the Institute of Geophysical and Geochemical Exploration (Langfang, China), was used for accuracy evaluation.

2.4. Washing procedures and sample digestion

Many washing procedures for removing exogenous trace elements from hair and nail samples have been proposed (Assarian and Oberleas, 1977; Raghupathy et al., 1988; Herber and Stoeppler, 1994; Borella et al., 1996; Chen et al., 1999), but still no standard procedure can be prescribed in general. The ultimate goal of the chemical and physical treatments should be the complete removal of loosely adhering metals associated with fat, sweat, and dirt without altering the endogenous content of elements in the samples (Caroli et al., 1992). Because of latter requirement, mineral acids (Gulson, 1996) or strong complexing agents such as EDTA (Caroli et al., 1992), should be used with the greatest care or avoided. The washing procedure used in this study involved thorough stirring of the samples with different solvents in sequence: acetone, deionized water and 0.5% Triton X-100 solution using ultrasonic bath and laboratory shaker, followed by repeated rinsing with ultrapure water and air drying in a Class 100 clean room. The stirring time for each solvent was a few minutes for the hair and 1 h for the nail samples.

For microwave assisted digestion, approximately 50 mg of the sample (or all available material when the nail sample amount was lower) was weighed and transferred to PFA vessels followed by addition of 0.5 ml of HNO_3 and 0.5 ml of H_2O_2. The vessels were then closed, mounted in sleeves (outer vessels) and heated in the microwave oven at 325 W power for 30 min. After cooling to room temperature, the vessels were carefully vented in a fume hood and 9 ml of ultrapure water was added to each, resulting in a dilution factor of approximately 200. The solutions were then transferred to acid-cleaned (hot mixture of HNO_3/HCl followed by soaking in 10% HNO_3 overnight) 10-ml polystyrene test tubes (Nalge Nunc International, Rochester, NY, USA). The procedure resulted in complete digestion of all samples except for the hair reference material. Incomplete decomposition of this reference material using nitric acid and hydrogen peroxide was noted by Buseth et al. (1998). For this sample, undigested residue was separated by centrifugation and re-digested with 0.5 ml HF at 70°C on a water bath. After evaporation of the HF, 0.5 ml of HNO_3 was added and after evaporation to approximately 0.1 ml it was recombined with the filtrate. For the majority of elements the contribution from the undigested residue was negligible, though this additional procedure was found to be necessary as it significantly improves recovery for Al, Ti, Cr, Fe, U, Th, REE, Ga, Zr and Hf. It seems that the residue represents exogenous deposition rather than the hair itself. The final solutions were spiked with an internal standard solution (In) to 25 $\mu g\ l^{-1}$. All sample handling and analysis were performed in clean (class 1000 or lower) laboratory areas. At least one preparation blank was prepared for each batch of samples.

2.5. Analysis

The samples were analyzed by ICP-SMS using external calibration and correction for instrumental instability and matrix effects by means of internal standardization. It should be mentioned that practical problems might arise from analyte carry-over in the ICP-MS sample introduction system. The most severe memory effects were found after aspiration of calibration standards containing Au, Th, Zr, Hf, W, Ir, Pd, Br and I. As has been shown previously (Rodushkin et al., 1999b), even after an extended washing time, a fraction of these analytes remain in the sample introduction system resulting in erroneously high and unstable signals in the first samples following the standard. This effect was eliminated by analyzing calibration standards for these elements at the end of the analytical sequence, followed by prolonged washing of the introduction system with 0.1% EDTA solution. For the other elements, 5-min wash time was sufficient for the signals to return to previous blank levels. Hence, as an additional quality control measure for these elements, a check standard (equal to a calibration standard) was included repeatedly in the analytical run after each set of 12 samples (results for these standards being within $\pm 10\%$ of the initial value).

3. Results and discussion

3.1. Detection limits

A review of published concentration ranges for hair (Katz and Chatt, 1988; Valkovic, 1988; Caroli et al., 1992, 1994; Miekeley et al., 1998) shows that sub-$\mu g\ g^{-1}$ concentrations have been reported for all elements except for Ca, Cl, Fe, K, Mg, P, S, Si and Zn. The knowledge on concentrations in hair for elements such as Pt, Pd and Ir

Table 2
Method detection limits ($\mu g\ g^{-1}$)

Element	Detection limit	Element	Detection limit	Element	Detection limit
Ag	0.0006	Hf	0.00007	Ru	0.00003
Al	0.13	Hg	0.004	S	8
As	0.006	Ho	0.000007	Sb	0.0007
Au	0.0001	I	0.032	Sc	0.00008
B	0.02	Ir	0.00001	Se	0.025
Ba	0.031	K	3.1	Si	4.6
Be	0.0002	La	0.0002	Sm	0.00005
Bi	0.0004	Li	0.003	Sn	0.003
Br	1.3	Lu	0.000005	Sr	0.002
Ca	1.4	Mg	0.22	Ta	0.002
Cd	0.0002	Mn	0.006	Tb	0.000007
Ce	0.0007	Mo	0.001	Te	0.00007
Cl	580	Na	0.62	Th	0.00007
Co	0.0003	Nb	0.0004	Ti	0.027
Cr	0.012	Nd	0.0002	Tl	0.0001
Cs	0.00002	Ni	0.019	Tm	0.000006
Cu	0.034	P	0.11	U	0.0001
Dy	0.00004	Pb	0.005	W	0.0009
Er	0.00002	Pd	0.00006	V	0.0005
Eu	0.00001	Pr	0.00009	Y	0.0001
Fe	0.13	Pt	0.00001	Yb	0.00002
Ga	0.00007	Rb	0.001	Zn	0.07
Gd	0.00005	Re	0.000005	Zr	0.001
Ge	0.002	Rh	0.00001		

is still limited by the detection limits of the techniques applied. Hence, an analytical method intended for multielemental characterization of human hair and nails should enable detection limits for trace and ultratrace elements in the ng g^{-1} range or lower. Instrumental detection limits for ICP-SMS for non-interfered isotopes can be as low as pg l^{-1} even without using shielded torch or special introduction systems such as ultrasonic nebulizers (Rodushkin et al. 1999a). However, method detection limits for hair and nails are not limited by instrumental capabilities, but mainly by blanks and spectral interferences. Method detection limits were calculated as three times the standard deviation for digestion blanks ($n = 12$) and are expressed as equivalent concentration in the sample (Table 2). Detection limits lower than 10 ng g^{-1} were obtained for 51 elements and for 39 of these, detection limits in the sub-ng g^{-1} range were achieved. Poor detection limits for Cl is attributed to high instrumental blank levels caused by contamination from previous analyses of solutions containing 5% HCl. For all elements, except Pb, the method detection limits reported here are superior to those recently obtained by Miekeley et al. (1998) using ICP-QMS. It is not clear if these authors report the instrumental or method detection limits. Although method detection limits for Ir, Pd, Pt, Rh and Ru were in the low pg g^{-1} range, these elements were not detected in a significant number of samples.

3.2. Spectral interferences

Several examples of spectral interferences actually present when analyzing hair digest by ICP-MS are given in Fig. 1, which shows spectra around selected analyte isotopes in MRM. It should be noted that for Ti, Cr, Ni and Cu, the least affected isotopes are shown. In MRM, interferences are also detectable near the Mg, Al, K, Ca, Mn, Fe, Co, Zn, Ga, Ge and Br isotopes. Consequently, reliable results for these elements are difficult to obtain if LRM (or ICP-QMS) is used since for many isotopes the magnitude of the interfering peak(s) are comparable with that of the analyte peak. With ICP-SMS operated in MRM, isotopes of all above-mentioned elements except for K can be resolved from interfering peaks thus allowing accurate determination. The interference from O^{2+} on Be can be eliminated by using a narrow acquisition window in LRM (Table 1). In spite of the fact that in the higher mass region spectral interferences originating from the major matrix elements are less severe, trace and ultratrace elements give rise to many additional interferences (mainly from formation of oxide, hydroxide and double charged ions) which, as a rule, are not resolved even in HRM. The influence of these interferences on the determination of platinum-group (PGE) and rare-earth elements (REE) was discussed previously in relation to the analysis of blood, urine and other biological matrices (Begerow and Dunemann, 1996; Prohaska et al., 1998). Though interferences on K, Se and As can be resolved in HRM, an increase in resolution is accompanied by a significant decrease in sensitivity and calls for frequent mass calibration. The tail from $^{38}ArH^{+}$ results in an apparent blank level for K of approximately 15 μg l^{-1} that can be corrected for by blank subtraction. In order to assess the severity of the interferences, ratios of formation for interfering species were calculated. Detailed information on the procedure used can be found elsewhere (Rodushkin et al., 1999b). Table 3 lists some of the interferences studied, together with apparent concentrations caused by them (calculated using ratios of formation and published concentrations for trace and ultratrace elements in hair). Since concentrations of elements such as Cu, Zn and Pb have been reported to be higher in nails than in hair (Benischek-Huber and Beniscek, 1985), one can expect more severe interferences in the former matrix. Although isotopes of elements such as Cd, Ag, Bi, etc. can be also affected, apparent concentrations for these elements are significantly lower than expected levels in hair and nails so correction for these isotopes can be omitted. Mathematical correction has been applied on remaining isotopes, taking into account intensities for interfering elements and measured ratios of formation. It should be noted that matrix-induced changes in plasma parameters might lead to changes in the degree of formation of interfering species, resulting in poor cor-

Table 3
Apparent concentrations of some trace and ultra-trace elements caused by spectral interferences from a hair matrix in ICP-MS

Isotope (abundance, %)	Major interferences	Apparent concentration, (ng g^{-1})
^{75}As (100)	$^{40}Ar^{35}Cl$	180
^{82}Se (9)	^{82}Kr, $^{66}Zn^{16}O$, ^{81}BrH	600
^{99}Ru (13)	^{98}MoH, $^{40}Ar^{59}Co$	0.003
^{101}Ru (17)	$^{84}Sr^{16}OH$, $^{85}Rb^{16}O$	0.009
^{102}Ru (32)	^{102}Pd, $^{86}Sr^{16}O$, $^{36}Ar^{66}Zn$	0.08
^{103}Rh (100)	$^{40}Ar^{63}Cu$, $^{87}Sr^{16}O$, $^{87}Rb^{16}O$, $^{206}Pb^{++}$	0.21
^{105}Pd (22)	$^{88}Sr^{16}OH$, $^{89}Y^{16}O$, $^{40}Ar^{65}Cu$	1.9
^{106}Pd (27)	^{106}Cd, $^{40}Ar^{66}Zn$, $^{90}Zr^{16}O$, $^{89}Y^{16}OH$	5.2
^{108}Pd (27)	^{108}Cd, $^{40}Ar^{68}Zn$, $^{92}Zr^{16}O$, $^{92}Mo^{16}O$	3.2
^{151}Eu (48)	$^{135}Ba^{16}O$	0.08
^{153}Eu (52)	$^{137}Ba^{16}O$	0.15
^{157}Gd (16)	$^{141}Pr^{16}O$	0.35
^{160}Gd (22)	^{160}Dy, $^{144}Nd^{16}O$	0.36
^{159}Tb (100)	$^{143}Nd^{16}O$	0.03
^{191}Ir (37)	$^{175}Lu^{16}O$	0.002
^{193}Ir (63)	$^{177}Hf^{16}O$	0.02
^{194}Pt (33)	$^{178}Hf^{16}O$	0.07
^{195}Pt (33)	$^{179}Hf^{16}O$	0.04
^{195}Pt (25)	$^{180}Hf^{16}O$	0.11

rection. In this study, UO^+/U^+ and Ba^{2+}/Ba^+ ratios were repeatedly measured in order to control possible changes in plasma conditions. During this study these ratios were fluctuating in the range from 0.017 to 0.019 and from 0.015 to 0.019, respectively. No difference in formation of oxide and double charged ions was found between synthetic matrix (5% HNO_3) and sample digest. Together with low long-term variation in internal standard intensity (better than 10% R.S.D.) this confirms that matrix effects are negligible; thus accurate mathematical correction is possible. For elements having more than one isotope, results were assumed to be correct if evaluation (including mathematical corrections) for two different isotopes yield comparable results.

3.3. Accuracy and precision

The most straightforward and reliable approach for assessment of accuracy in hair analysis can be applied to those elements for which reference values are available in the same matrix. Results obtained for GBW07601 human hair are presented in Table 4.

As follows from these data, results obtained by ICP-SMS fall within certified ranges for 26 elements (Ag, As, Ba, Bi, Ca, Cd, Ce, Co, Cu, Hg, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Sr, Ti, Y, and Zn). Fe result is slightly outside the certified range, the Se result was approximately 20% higher than the certified value and very low recoveries were found for Cr and Si. In the case of the latter element, the losses during the additional digestion with HF will account for the low recovery. In the case of Se, a result obtained by atomic fluorescence spectrometry for the same digests was significantly closer to the target value. It seems that some additional interferences (i.e. $^{12}C^{35}Cl_2$) affect ^{82}Se. A comparison of results from these two different techniques for randomly selected hair and nail samples reveals that systematically higher (by 10–15%) results were obtained by ICP-SMS. Though 'reference values in brackets' and information values are available for another 31 elements in this reference material, these data may not be as accurate as certified values. ICP-SMS results were inside 20% from information values for Au, B, Gd, Hf, K, Nd, Sn, and Tl. Using chondrite (meteorite) normaliza-

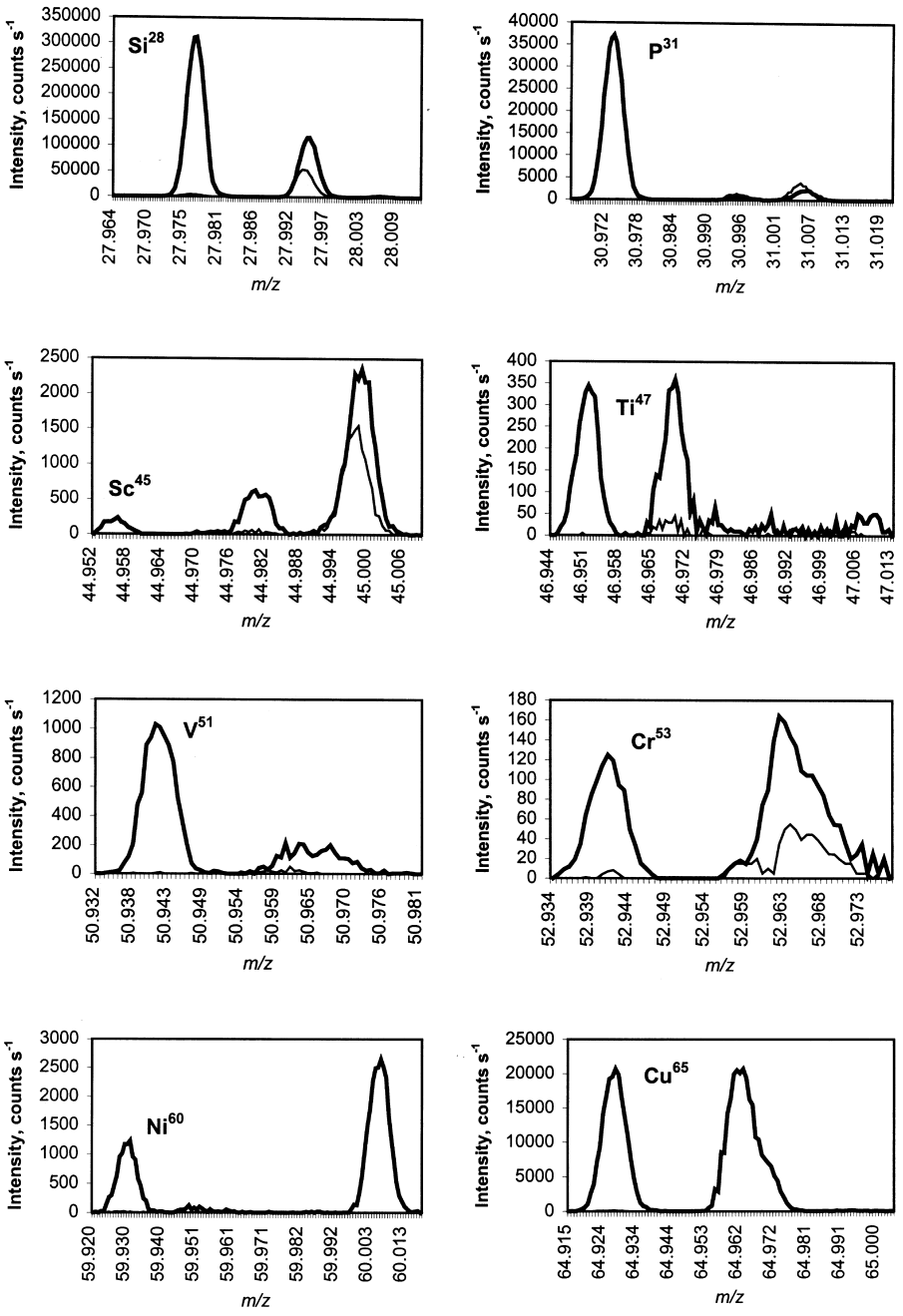

Fig. 1. Medium resolution ICP mass spectra obtained for GBW07601 reference material (bold line) and for preparation blank.

tion for REE (Rollinson, 1993), it is possible to evaluate internal consistency of the data for these elements (Prohaska et al., 1998). The smooth curve obtained for ICP-SMS results (Fig. 2) as well as the good agreement with previously reported values for Ce, Sm and Dy (Buseth et al., 1998) probably illustrates the poor accuracy in the information values for Pr, Sm, Eu, Tb, Dy, Ho,

Table 4
ICP-SMS results for CRM GBW07601 Human hair powder (μg g^{-1}, dry wt.)

Element	Found(s)[a]	Certified(s)	Element	Found(s)[a]	Certified(s)
Ag	0.034 (0.001)	0.029 (0.006)	Na	156 (3)	152 (10)
Al	9100 (450)	–	Nb	0.016 (0.001)	0.03[b]
As	0.274 (0.009)	0.28 (0.04)	Nd	0.039 (0.002)	0.04[b]
Au	0.0022 (0.0001)	0.0025	Ni	0.79 (0.03)	0.83 (0.15)
B	1.41 (0.05)	1.3	P	169 (3)	170 (7)
Ba	16.4 (0.2)	17 (1)	Pb	8.7 (0.2)	8.8 (0.9)
Be	0.061 (0.003)	0.063 (0.015)	Pd	< 0.00006	–
Bi	0.333 (0.009)	0.34 (0.02)	Pr	0.0099 (0.0005)	0.008[b]
Br	4.46 (0.37)	0.36	Pt	< 0.00001	–
Ca	2800 (90)	2900 (200)	Rb	0.051 (0.004)	0.15[b]
Cd	0.108 (0.003)	0.11 (0.02)	Re	0.00005 (0.00001)	–
Ce	0.093 (0.003)	0.12 (0.03)	Rh	< 0.00001	–
Cl	< 580	35[b]	Ru	< 0.00003	–
Co	0.065 (0.002)	0.071 (0.008)	S	45 000 (1000)	43 000 (2000)
Cr	0.177 (0.014)	0.37 (0.05)	Sb	0.092 (0.003)	0.095 (0.012)
Cs	0.0020 (0.0001)	0.009[b]	Sc	0.0077 (0.0003)	0.008 (0.001)
Cu	10.5 (0.4)	10.6 (0.7)	Se	0.73 (0.05)	0.60 (0.03)
Dy	0.0129 (0.0005)	0.017	Si	510 (30)	870 (70)
Er	0.0059 (0.0004)	0.014b	Sm	0.0092 (0.0003)	0.012
Eu	0.0018 (0.0001)	0.006	Sn	0.24 (0.01)	0.23[b]
Fe	46 (2)	54 (6)	Sr	23.7 (0.5)	24 (1)
Ga	3.4 (0.2)	1.2[b]	Ta	0.0029 (0.0003)	–
Gd	0.0109 (0.0005)	0.01[b]	Tb	0.0021 (0.0002)	0.003[b]
Ge	0.024 (0.003)	–	Te	0.0011 (0.0001)	–
Hf	0.0072 (0.0005)	0.006b	Th	0.0092 (0.0004)	0.012[b]
Hg	0.351 (0.009)	0.36 (0.05)	Ti	3.1 (0.2)	2.7 (0.4)
Ho	0.0024 (0.0002)	0.008[b]	Tl	0.0125 (0.0003)	0.014[b]
I	2.9 (0.2)	0.8[b]	Tm	0.00072 (0.00004)	0.002[b]
Ir	< 0.00001	–	U	0.061 (0.002)	0.09[b]
K	20.4 (0.6)	20	W	0.037 (0.002)	–
La	0.045 (0.002)	0.049 (0.008)	V	0.25 (0.01)	0.03[b]
Li	2.2 (0.1)	2.0 (0.1)	Y	0.091 (0.008)	0.084 (0.016)
Lu	0.0006 (0.0001)	0.003[b]	Yb	0.0044 (0.0002)	0.009[b]
Mg	360 (30)	360 (30)	Zn	185 (7)	190 (5)
Mn	6.2 (0.2)	6.3 (0.5)	Zr	0.21 (0.01)	0.16[b]
Mo	0.073 (0.002)	0.073 (0.012)			

[a] Standard deviation from between-batch determination ($n = 12$).
[b] Information values.

Er, Tm, Yb and Lu. This can also be the case for Cs, Nb, Rb, Th, V, U and Zr, which are present at sub-μg g^{-1} levels. The largest differences between found and information values were found for Br and I. It is known that the behavior of these elements in ICP-MS using solution nebulization of acidic media strongly depends on chemical form, and that the use of calibration standards with the elements in a different chemical form may result in inaccurate data (Takaku et al., 1995). This effect may be overcome by making the acidic digestion solution alkaline (Cho et al., 1990). However, for this hair reference material results obtained in acidic and alkaline media (using ammonia solution for sample dilution) were the same within measurement uncertainty. Assuming the information values to be correct, the presence of unresolved spectral interferences remains the most probable explanation for this discrepancy and results for these elements obtained by ICP-MS should be treated with caution.

External accuracy assessment was accom-

plished by participation in a specific ICP-MS Interlaboratory Comparison Program for trace metals in biological materials (Le Centre de toxicologie du Quebec, Canada), which included, among other biological materials, human scalp hair samples. More than 20 laboratories participate in the program, a majority of which uses ICP-QMS. Mean concentrations based on results received from all participants are available for 24 elements. These consensus values should be treated with caution because of great scatter in the results for most parameters, for some elements covering four orders of magnitude. This variability in the reported values is, however, not unusual in trace element determinations even when similar techniques are applied to well-homogenized sample. The ICP-SMS results from two rounds of the program during 1997–1999 are presented in Table 5 together with mean values and reported ranges. As follows from the data, there is generally good agreement between our data and mean values for As, Cd, Co, Cu, Mn, Pb, Sb, Se, and Zn. For other elements results presented by this laboratory are on the low edge of the reported ranges. These discrepancies for ultratrace elements seem to emphasize the need for strict contamination control and/or proper interference correction.

For Ge, Ta, Re and PGE, no independent check of accuracy is possible, which reflects the lack of reference materials with certified values for these elements. This can partially be explained by insufficient detection power of the majority of analytical techniques. Concentrations of PGE in GBW07601, for example, are lower than the method detection limits obtained in the present study.

The precision of the ICP-SMS results for a homogenous hair sample was evaluated by including several digests of the reference material in a number of analytical runs for hair and nail samples. The results indicate (Table 4), that for the 48 out of 65 elements that are present in the sample at detectable levels, between-batch precision is better than 5% R.S.D. and only for Ge and Re it is worse than 10% R.S.D. Cl, Ir, Pd, Pt, Rh and Ru were not detected in the sample, so the precision for these elements could not be evaluated. Although evaluation of precision by using homogenous sample is useful for evaluation of reproducibility of digestion and analysis stages, it has limited value in application to unpooled hair and nail samples because of the inhomogeneous nature of samples. In order to assess reproducibility of the complete procedure (including sampling), duplicate analysis of washed hair and nail

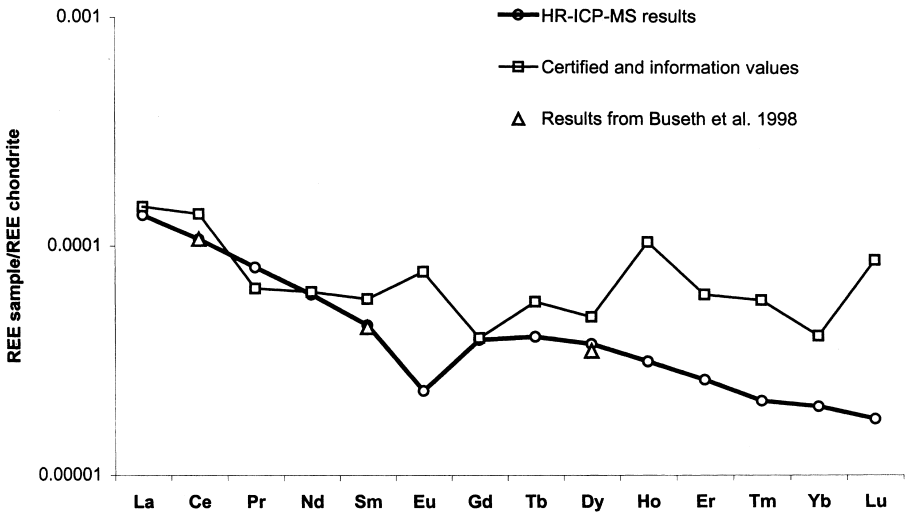

Fig. 2. Chondrite-normalized REE patterns for GBW07601 reference material.

Table 5
ICP-SMS results from participation in the Le Centre de toxicologie du Quebec ICP-MS Comparison Program ($\mu g\ g^{-1}$)

Element	Run 1997–2 ICP-SMS This lab.	All results Mean[a] (range)	Run 1999–2 ICP-SMS This lab.	All results Mean[a] (range)
Ag	–	–	0.076	0.07 (0.03–9.9)
Al	8.6	79 (7–225)	25.4	26.5 (0.07–535)
As	1.24	1 (0.8–16)	0.027	0.10 (0.02–0.38)
Be	0.006	0.2 (0.006–0.6)	0.003	0.01 (0.003–0.1)
Bi	0.09	0.16 (< 0.01–18)	0.036	0.04 (0.03–0.10)
Cd	0.95	0.9 (0.5–6.9)	0.41	0.40 (0.36–3.0)
Co	0.11	0.1 (< 0.01–1.1)	0.67	0.70 (0.50–7.0)
Cr	1.5	2.4 (< 0.5–19)	0.25	0.43 (0.20–9.0)
Cu	61	70 (61–1140)	31	32 (27–190)
Hg	–	–	0.24	0.29 (0.1–8.0)
Mn	12	12 (9–112)	8.6	9.3 (8.2–97)
Mo	0.06	0.16 (0.04–7.8)	0.045	0.10 (0.04–2.0)
Ni	2.3	3.3 (2.1–19.6)	3.3	3.8 (2.9–37)
Pb	74	79 (70–585)	7.0	8.0 (6.6–66)
Sb	0.07	0.08 (0.005–9.5)	0.11	0.11 (0.04–0.21)
Se	8.3	7 (2.5–77)	0.79	0.60 (0.24–5.0)
Sn	0.67	0.9 (0.15–51)	1.5	1.5 (1.3–76)
Te	0.0009	1 (0.0009–7.2)	0.0002	0.01 (0.0002–0.01)
Ti	0.62	1 (0.6–39)	–	–
Tl	0.0026	0.05 (0.0026–0.2)	0.0002	0.01 (0.0002–0.01)
U	–	–	0.014	0.02 (0.01–0.03)
W	0.02	0.09 (0.01–0.3)	–	–
V	0.03	0.51 (0.03–9.6)	0.055	0.08 (0.05–9.0)
Zn	159	163 (95–1096)	530	544 (359–2400)
Zr	0.56	1.1 (0.56–10.8)	0.27	0.32 (0.27–0.39)

[a]Only results obtained by ICP-MS after exclusion of outliers were included.

sub-samples (resulting from sample division) from 10 subjects was performed (Table 6). For hair samples, uncertainties (expressed as mean R.S.D. of the results) were better than 5% R.S.D. for 19 elements, and in the range from 5 to 10% R.S.D. for 21 elements. Though these figures are worse than for the reference material (Table 4) they still allow to discriminate between donors since between sub-samples differences as a rule are lower than between sample differences. Only for Pd the uncertainty was worse than 20% R.S.D. Significantly larger differences between results were found for nail sub-samples. Uncertainties were better than 10% R.S.D. only for As, Ca, Cd, Cu, Hg, Pb, S, Se and Zn, and worse than 20% R.S.D. for 24 elements. These differences in nail concentrations for the same person are likely to be explained by remaining exogenous contamination.

3.4. Effect of sample washing

Differences between hair and nail samples in the degree of surface contamination (or in the effectiveness of the washing procedure) are obvious from a comparison of results before and after washing (Table 7). In this table, hair and nail elements were grouped in accordance with the degree of concentration decrease after washing. For hair, 23 elements show insignificant contribution from surface contamination, while for 12 elements this contribution was higher than 50% of the total concentration. For nails, these numbers were 15 and 20, respectively. Interestingly, little if any U was removed by the washing procedure from the hair, though the major portion of the element were removed from the nails. No contamination of the samples in the washing procedure was found.

Table 6
Uncertainties expressed as mean relative standard deviation of results from duplicate sampling and ICP-SMS analysis of hair and nail samples ($n = 10$)

Element	Mean R.S.D., %		Element	Mean R.S.D., %		Element	Mean R.S.D., %	
	Hair	Nails		Hair	Nails		Hair	Nails
Ag	4	12	Hf	18	21	Ru	–	–
Al	12	21	Hg	4	9	S	2	3
As	5	8	Ho	7	17	Sb	11	18
Au	12	32	I	7	15	Sc	9	21
B	5	18	Ir	–	–	Se	3	9
Ba	9	10	K	10	12	Si	9	38
Be	9	19	La	10	22	Sm	11	18
Bi	5	10	Li	13	21	Sn	7	29
Br	9	16	Lu	5	14	Sr	3	10
Ca	4	8	Mg	3	12	Ta	19	27
Cd	4	8	Mn	3	11	Tb	11	14
Ce	7	19	Mo	4	15	Te	16	17
Cl	6	14	Na	11	14	Th	9	10
Co	8	19	Nb	20	20	Ti	13	34
Cr	8	18	Nd	9	22	Tl	12	25
Cs	5	12	Ni	9	21	Tm	9	13
Cu	5	9	P	2	12	U	10	16
Dy	8	15	Pb	6	9	W	15	31
Er	8	14	Pd	26	51	V	12	25
Eu	12	16	Pr	11	20	Y	6	16
Fe	5	20	Pt	17	43	Yb	10	14
Ga	16	26	Rb	11	15	Zn	3	6
Gd	8	24	Re	16	24	Zr	15	18
Ge	19	42	Rh	–	–			

It is possible to check for remaining nail surface contamination by performing laser ablation sampling from different sub-layers of the nail. An assessment of the utility of this approach for nail analysis is the subject of an ongoing study. At this stage, it is possible to conclude that the possibility for quantitative analysis by laser ablation is limited by the absence of matrix-matched calibration standards, but information on spatial distribution can be easily obtained by using the ^{32}S isotope for correction for variation in ablation efficiency. In this experiment, the back surface of a washed nail was studied. The upper 10–20-μm layer of the nail was removed during the first ablation sequence, so the second ablation was performed on an inner layer of the nail. No significant differences (intensity ratio in the range 0.7–1.3) were found between outer and inner layers for I, P, Hg,

Table 7
Effect of sample washing on element concentration expressed as mean ratio (concentration before washing)/(concentration after washing) for hair and nail samples ($n = 6$)

Ratio	Hair	Nail
0.9–1.2	As, Ba, Ca, Cl, Cs, Cu, Ge, Hg, I, Mg, Mo, P, Pb, Re, S, Se, Sb, Sn, Sr, Ta, Te, U, Zn	As, Ag, Ca, Cs, Hg, I, Mg, Mo, P, Re, S, Se, Ta, Te, Zn
1.2–1.5	Ag, Be, Cd, Co, Fe, Li, Mn, Ni, Pt, Tl	Co, Cu, Fe, Mn, Pd, Pt, Cl, Li, Nb, Rb,
1.5–2.0	Au, B, Br, Cr, Ga, Nb, REE, Sc, Si, Y	Au, Be, Br, Cr, Ge, Sb, Si, Sr, W
< 2.0	Al, Bi, Hf, K, Na, Pd, Rb, Ti, Th, W, V, Zr	Al, B, Ba, Bi, Cd, Hf, Ga, K, Na, Ni, Pb, REE, Sc, Sn, Ti, Th, V, U, Y, Zr

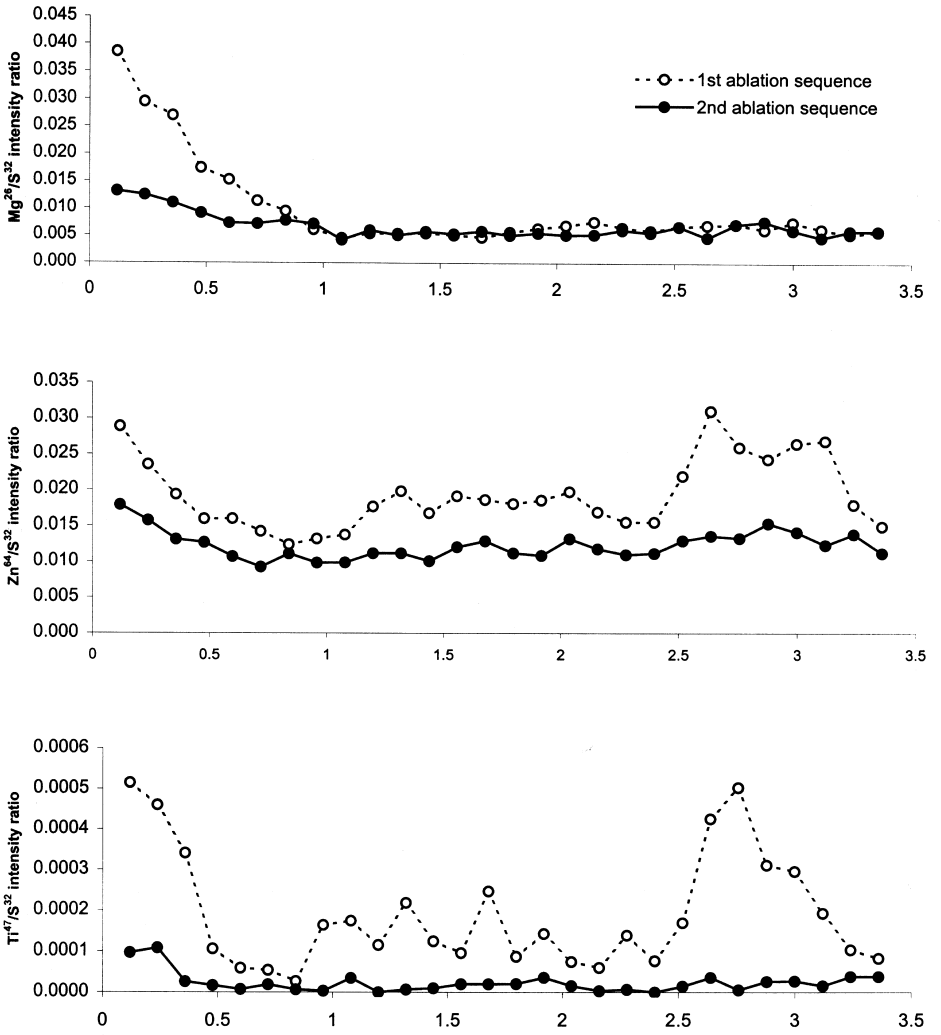

Fig. 3. Spatial distribution of Mg, Zn and Ti along nail (expressed as element to S intensity ratios).

Se, Cu, Br, Cl, Na, Li, Nb, Pd and Bi. The concentrations of Zn, Ca, Mg, K, Cs, Rb, Mo, Cd, Pb, Al, Ga, V, and Be exhibit a moderate increase in the surface layer (ratio being in the range 1.3–2.0). For the rest of the elements, concentrations in the surface of the nail were more than twofold higher than in the inner layer, and for Ti, U, Th, W, Zr and Hf more than fivefold. Spatial distributions of Mg, Zn, and Ti along the length of the nail are shown in Fig. 3. From the data, the highest concentrations of these elements were found near the cut edge of the nail. Because of the close contact of this nail area with the skin, it is not effectively washed during common hygienic procedures; thus higher surface contamination can be expected there.

3.5. Element distribution along the length of a hair

The variation in element content along the length of a hair was studied using hair samples of three young subjects (two 12-year-old girls and one 3-year-old boy, hair length > 10 cm). None of the subjects used hair dyes or bleaches. Three

2-cm hair sections were taken at different distances from the scalp prior to the washing procedure. After digestion, they were analyzed as separate samples. The results show that the majority of the elements may be separated into three different groups according to their distribution pattern (Fig. 4). Elements such as Se, S, Zn, P, Cu, Mo, Mg, Fe, Li, Si, As, Co, and Cr are uniformly distributed along the hair strands in all three samples, which may reflect steady-state endogenous deposition. Concentrations of Ag, Au, Ba, Be, Ca, Cs, Ga, Ni, Pb, Pt, Rb, Sc, Sn, Sr, Ti, V, Zr, Hf and REE increase from the proximal to the distal end of the hair. The magnitude of the increase differs between different elements as well as between samples. As a rule, the highest concentrations were found at the longest distance from the scalp (approx. 40 cm). As the distal part of the hair has been exposed to the external environment for the longest time, an exogenous deposition may be the responsible for this distribution pattern (Valkovic, 1988). Elements such as Br, Cl, I, K, Na, Re, Te, Tl and U show the opposite trend. It was proposed that repeated washing continuously remove labile elements from the hair (Valkovic, 1988). However, the appearance in this group of elements such as Re, Te, Tl and U is quite surprising. The distribution patterns for the remaining elements including Al, Cd, Hg, Mn, Sb, Th, W, etc., differ between the subjects, probably reflecting dietary fluctuations and/or variation in environmental exposure.

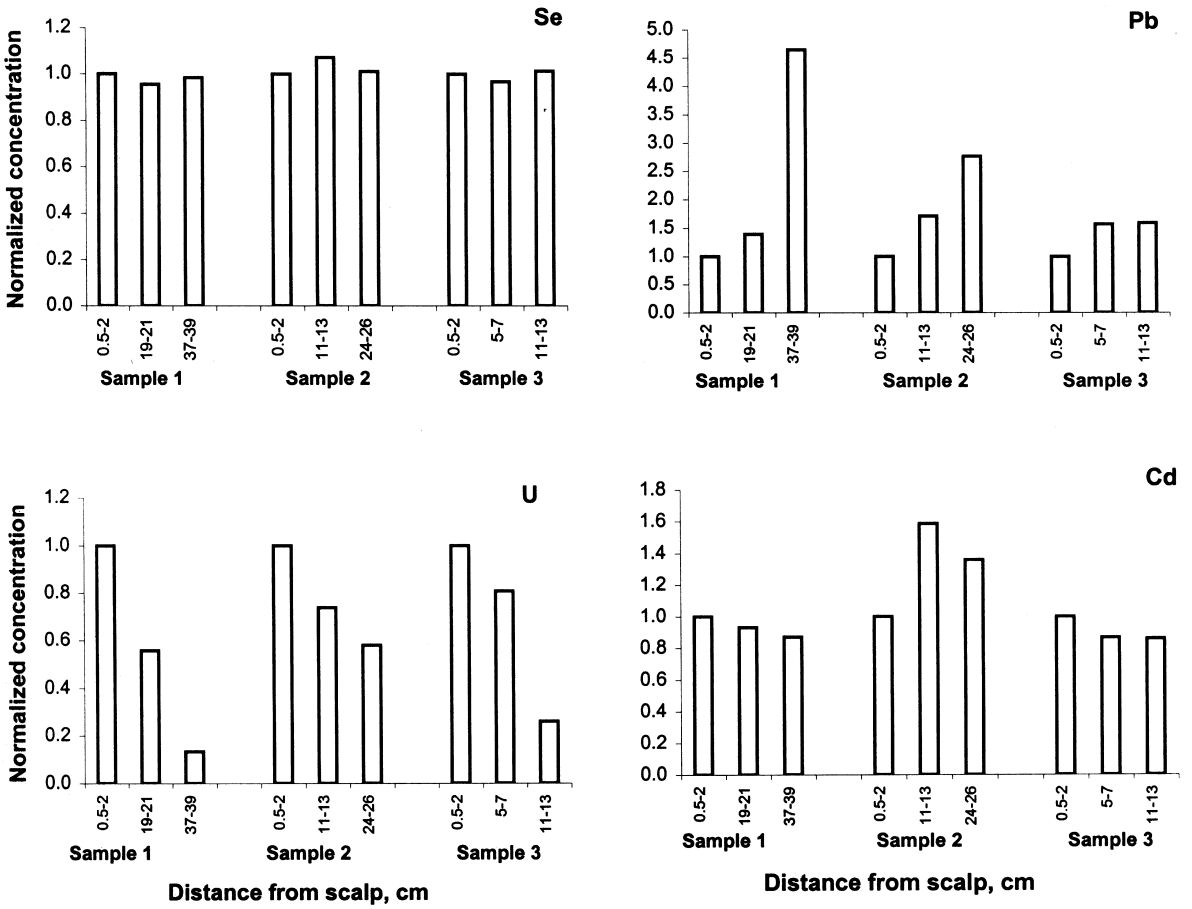

Fig. 4. Normalized concentrations of Se, Pb, U and Cd in hair as a function of distance from the scalp (samples 1 and 2 taken from 12-year-old girls, sample 3 taken from a 3-year-old boy).

4. Conclusions

ICP-SMS is a useful tool for multielement analysis of hair and nail samples that provides wide elemental coverage, low detection limits and the ability to resolve a significant part of the spectral interferences occurring in ICP-MS. However, mathematical corrections have to be used for the accurate determination of many of the heavier elements. Insignificant matrix effects and stable plasma conditions make these corrections more easy to perform in comparison with other biological matrices. Though it was possible to assess the accuracy of the method for more than 40 elements, the lack of certified values for Br, I, Re, Ta and PGE makes such evaluations difficult for these elements. Though precision better than 5% R.S.D. can be obtained for powdered reference material, the reproducibility of the results is limited by non-homogeneity of real samples. In spite of the fact that part of the surface contamination is removed by washing, results for hair segments taken at different distances from the scalp as well as from mapping element content in different sub-layers of the nail by laser ablation may be interpreted as showing remaining contributions from exogenous sources. The latter technique possesses a potential for differentiating between endogenous and exogenous deposition in nails as well as for measuring short-distance fluctuations in the spatial distribution of elements. This potential has to be further investigated. The application of ICP-SMS for multielement analysis of hair and nail samples collected from inhabitants of northern Sweden will be discussed in a second part of the study.

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