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Mass Spectrometry Element Analysis-Advances and New Perspectives in a Modern Analytical Method

Klaus G. Heumann[a]
[a] Institut für Anorganische Chemie der Universität Regensburg, Regensburg, Federal Republic of Germany

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Mass Spectrometric Element Analysis—Advances and New Perspectives in a Modern Analytical Method

Mass spectrometry is an extremely sensitive method for the determination of elements down to the sub-pg level. The different ionization methods used for mono- and multi-element analyses are discussed. Spark source mass spectrometry has been the most commonly multi-element technique in the past. However, inductively coupled plasma and glow-discharge mass spectrometry will probably replace spark source mass spectrometry in the future. Accurate trace element determinations can only be obtained with isotope dilution mass spectrometry. Because of a lack of accurate methods, isotope dilution is one of the few definitive calibration techniques that can be used for trace element analyses. The formation of negative and positive thermal ions on a hot metal surface is the most frequently applied ionization method in isotope dilution mass spectrometry. All elements which can be analyzed by this method are listed. A selected number of trace determinations with thermal ionization isotope dilution mass spectrometry are discussed, e.g., the analysis of ultra-low amounts of heavy metals in Antarctic snow, of halide traces in geochemical materials, and of nitrite and nitrate in food samples. Determinations of element species with the isotope dilution technique will become more and more important in the future.

INTRODUCTION

The determination of trace and micro amounts of elements is an important requirement in many fields of natural science and applied science. The field of inorganic analytical chemistry makes it possible to determine extremely low traces in many different substances. For example, it is used in the analysis of traces in electronic materials and other substances used in high technology or to an-

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TABLE I

Comparison of detection limits of a selection of instrumental methods in trace element analysis

Method	Detection Limit Analyzable Amount [g]	Element and Matrix Dependence
X-ray fluorescence	10^{-9}	strong
Emission spectroscopy (ICP)	10^{-10}	moderate
Inverse polarography	10^{-12}	strong
Electrothermal AAS	10^{-13}	moderate
Chelate GC	10^{-13}	strong
Neutron activation analysis	10^{-14}	strong
Mass spectrometry	10^{-14}	moderate
Radionuclide techniques	10^{-18}	moderate

alyze heavy metals found in very low concentrations in the environment but which are partially of toxic character.

Mass spectrometry is an extremely sensitive method for the determination of elements down to the sub-pg ($<10^{-12}$ g) level. Therefore, one of the main goals in inorganic mass spectrometry is the analysis of extremely low element concentrations. The fact that mass spectrometry is one of the most powerful analytical methods with respect to the detection limit in element analyses can be seen by reviewing the selected instrumental methods presented in Table I. The order of magnitude of detection limits is listed in the second column of Table I. Following the principles of mass spectrometry, analyses cannot be carried out without destruction of the sample material. If a nondestructive method is required, methods such as x-ray fluorescence spectroscopy or neutron activation analysis must be applied. The chemical preparation of the sample depends on the ionization method used in mass spectrometry. However, it is common experience in trace analysis that the most precise and accurate analytical results can usually be obtained by methods where a selective chemical separation of the element(s) is carried out before the instrumental measurement takes place.

IONIZATION METHODS AND INSTRUMENTATION

The ionization methods currently used in inorganic mass spectrometry are listed in Table II. Included are remarks about the preferred mass analyzer systems used with the instrumentation as well as comments about the elements that can be successfully analyzed using these ionization methods. The ionization methods listed in Table II are divided into two groups. Mono- or oligo-element determinations can be carried out with the first group of ionization methods whereas multi-element determinations are possible with the second group. Therefore, one has to select the most suitable type of ionization method that leads to optimum results with respect to the analytical problem to be solved. As will be discussed later, a multi-element method is not the best analytical procedure in all cases. Many people—especially non-analysts—do not take into account that a method that has the advantage of multi-element determinations also brings with it a number of dis-

TABLE II

Ionization methods in inorganic mass spectrometry

Ionization Method	Preferred Analyzer System	Preferred Elements Analyzed
Mono- and oligo-element determinations:		
Thermal ionization:		
—Positive ions	Magnetic field	Metals with low first ionization potential
—Negative ions	Magnetic field	Nonmetals with high electron affinity
Electron impact	Magnetic field	Noble gases, H, C, N, O, S; elements after chelation and GC-separation
Field-desorption	Magnetic field	Alkali and alkaline earths
Multi-element determinations:		
Spark source	Magnetic and electric field	All elements
Plasma sources:		
—ICP, MIP	Quadrupole	All metals and semimetals
—Glow-discharge	Magnetic and electric field	All metals and semimetals
Laser	Time of flight	All elements (microanalysis)
Secondary ion source	Magnetic field	All elements (surface and microanalysis)

advantages. For example, the results of a multi-element method are commonly less precise and accurate than those obtained with a mono- or oligo-element method (see Fig. 3). In addition, the technical expenditure for a multi-element determination is generally much higher than for the analysis of a few elements. Therefore, one must decide whether a multi-element determination is really necessary or not.

The first group of ionization methods includes thermal ionization, electron impact, and field-desorption mass spectrometry. In the first technique, the ionization process takes place at the surface of a hot metal filament. Inorganic salts are used as samples. High yields of single-charged positive ions are available from metals with low ionization potentials (first ionization potential <7 eV) which can be attributed to the physical background of this ionization process.[1,2] Therefore, sufficiently high positive thermal ion beams are produced from the alkalis, the alkaline earths, the lanthanides, and the actinides. Nevertheless, a sufficiently high ion yield can also be obtained for elements with higher first ionization potentials (e.g., for the important trace metals lead and cadmium) using special techniques which increase the formation of positive thermal ions. Those techniques include the silica gel technique[3-5] or the resin bead technique,[6,7] respectively. High negative thermal ion beams can be obtained from nonmetals and nonmetal compounds with high electron affinities.[8,9] The analyzer system currently preferred for thermal ionization instruments is a magnetic sector field. The principle of a thermal ionization mass spectrometer is shown in Fig. 1; here a double-filament ion source (evaporation and ionization processes of the sample are locally divided into two steps) and a Faraday cup are used for the detection of the ion current.

Electron impact ionization is the preferred method if determinations of the noble gases and of the nonmetals hydrogen, carbon, nitrogen, oxygen, and sulphur have to be carried out. The chemical form of samples in electron impact ionization mass spectrometry is usually carbon dioxide for carbon and oxygen analyses and sulphur dioxide for sulphur measurements. The other elements are measured in their atomic or biatomic form. The analysis of these compounds is advantageous because gaseous substances can be continuously introduced into the ion source of the mass spectrometer. The electron impact ionization technique is also used for

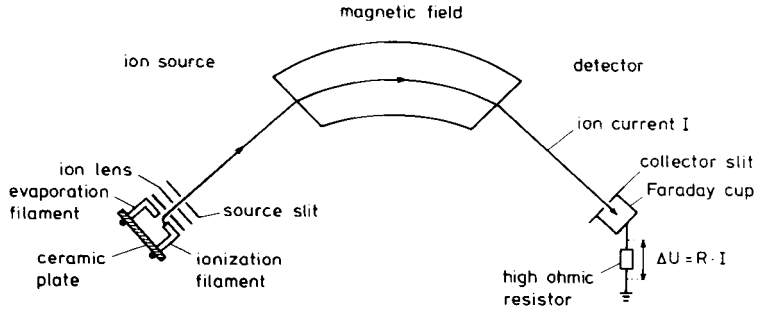

FIGURE 1 The principles of a thermal ionization mass spectrometer with a magnetic sector field analyzer.

element analyses after converting an element into a chelate compound and separating this compound by gas chromatography. One of the few elements which has been analyzed successfully by this method is selenium.[10]

Field-desorption mass spectrometry, which is usually used for the analysis of organic compounds, is also applicable for the determination of metals, as has been shown in particular by Schulten and co-workers during the past few years.[11,12] The preparation of the field-desorption emitter for metal analyses and the deposition of samples as an inorganic metal salt solution are similar to those for organic compounds. One can also make use of electrodeposition of the metal at the emitter surface. The desorption of ions is carried out by direct heating of the emitter with an electric current in the high electric field of the ion source. The emitter can be heated up to 1400°C without influencing its activity. Under these conditions sufficiently high ion currents can be obtained for a number of elements, especially for the alkalis and alkaline earths. If higher temperatures are necessary for the ionization process, additional indirect heating with a laser can be applied.[12]

The three ionization methods described for mono- or oligo-element analyses are usually applied after a chemical separation of the element(s) to be determined. There is no doubt that electron impact ionization is the best technique for analyzing the noble gases and, after the conversion of hydrogen, carbon, nitrogen, oxygen, and sulphur into the compounds mentioned above, it proves to be the best technique for these elements as well (see also Fig.

6). The precision of the analytical results from thermal ionization mass spectrometry is usually better than that obtained by the field-desorption technique. Furthermore, the ion currents produced in a thermal ion source are higher and no commercial field-desorption mass spectrometer with a laser heating system is available at the moment. Therefore, a thermal ionization instrument is preferred for the determination of most of the other elements not determined by the electron impact technique (see Fig. 6). However, one particular advantage of field-desorption mass spectrometry is that it allows successive analyses of organic compounds and metal traces in the same sample. For example, the organic part of chlorophyll can be detected by using a low laser power. Afterwards, magnesium can be measured by increasing the laser power.[12]

Mass spectrometric multi-element determinations can be carried out with spark source instruments[13] and mass spectrometers which have plasma sources, e.g., an inductively coupled plasma (ICP),[14] a microwave induced plasma (MIP)[15] or a plasma produced by a glow discharge.[16] These techniques are preferred for bulk analyses. In analyzing metals or electrical conducting materials, samples can be used in a spark source or glow-discharge mass spectrometer without any chemical pretreatment: the sample only has to be prepared as an electrode (see Fig. 2). In the case of nonconducting sample materials, the pulverized sample must be mixed with graphite powder or a metal powder, e.g., gold powder. This mixture is then compressed into an electrode which can be used in the spark or glow-discharge source. Because of the high energetic inhomogeneity of the ions produced in a spark source, a double-focusing mass spectrometer (a combination of an electric and magnetic sector field) must be used. A schematic diagram of such a spark source mass spectrometer with Mattauch–Herzog geometry and a photoplate as well as an electrical detection system is shown in Fig. 2. The only glow-discharge mass spectrometer commercially available today also includes a double-focusing system.[17] The major advantages of a glow-discharge plasma source as compared to a spark source are the more stable ion currents and the fact that only a small number of multiple-charged ions are produced.

In contrast to the analyzer systems used in spark source mass spectrometry, a quadrupole mass filter is applied in ICP-MS and MIP-MS. For element analyses with ICP-MS and MIP-MS the

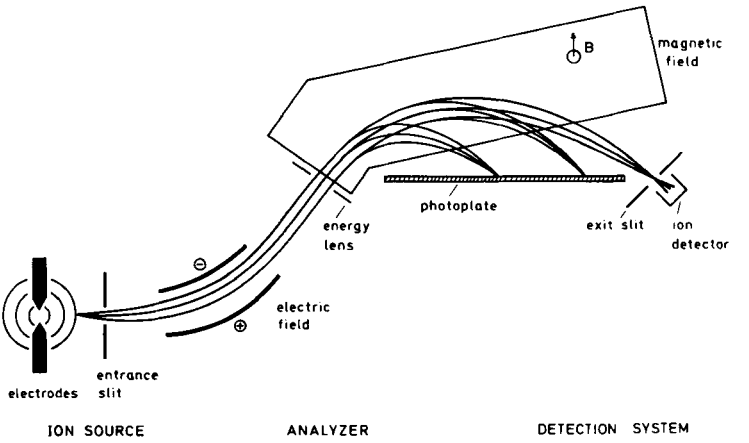

FIGURE 2 Schematic diagram of a spark source mass spectrometer with photoplate and electrical detection.

sample must be dissolved before introducing the solution into the plasma with a nebulizer system. The most abundant ions in ICP-MS are the single-charged ions, and only a few double-charged ions with low abundances can be observed. This makes the multi-element spectrum much simpler than it is for spark source mass spectrometry where a greater number of multiple-charged ions and cluster ions can be observed. An ICP mass spectrum also shows cluster ions which can usually be attributed to the plasma gas, e.g., argon, or the solvent, e.g., water.

Laser mass spectrometry (LAMMA = laser microprobe mass analyzer) and secondary ion mass spectrometry (SIMS) are methods which have been extensively used for microprobe and surface analyses.[18–20] Table III includes a comparison of SIMS and LAMMA with two other frequently used spectroscopic methods for surface analyses, Auger (AES) and ESCA spectroscopy. It can be seen that SIMS, AES, and ESCA are able to analyze only a few monolayers, whereas the analytical information obtained by LAMMA comes from a depth down to approximately 100 nm. From that it follows that laser mass spectrometry is an ideal method to analyze surface layers in the range of a few hundred nanometers thickness with a lateral resolution of 1–2 μm. Depth profiles of substances can be determined with SIMS and LAMMA by bombardments

TABLE III

Comparison of analytical data for SIMS and LAMMA with Auger and ESCA spectroscopy

Method	Analyzable Elements	Depth of Analytical Information [nm]	Detection Limit [μg/g]
SIMS	All elements	1	0.1
LAMMA	All elements	100	1
AES	$Z > 2$	3	10^3
ESCA	$Z > 1$	3	10^4

with a continuous current of secondary ions and with repeated laser pulses, respectively. The use of laser pulses in a LAMMA instrument enables one to apply a time-of-flight mass analyzer which has several advantages due to its relatively simple construction.

The principal ion detectors usually used in inorganic mass spectrometry for the thermal ionization, electron impact, and field-desorption technique are electrical detection systems with a Faraday cup or an electron multiplier. Faraday cups are preferred when ion currents of more than 10^{-15} A are available on the detector side. To detect lower ion currents, secondary electron multipliers are employed. The amount of ionized substance, which corresponds to an ion current of 10^{-15} A for one minute, is 6×10^{-19} mol. This illustrates the high sensitivity of mass spectrometry if an ionization process with sufficient efficiency and an instrument with a good ion transmission from the ion source to the detector system are used. In a few cases, especially for multi-element determinations with spark source mass spectrometry, photoplate detection is also used (see Fig. 2). However, photoplate detection is usually less precise than electrical detection. An electron multiplier together with a multichannel analyzer can be used for single ion detection, which is the detection mode applied in ICP-MS and laser mass spectrometry.

QUANTITATIVE DETERMINATIONS IN INORGANIC MASS SPECTROMETRY

The different techniques used for quantitative determinations of elements in connection with different mass spectrometric ionization methods are listed in Table IV. In the first group of mono- and oligo-element methods (see also Table II) application of the isotope dilution technique is preferred, whereas the second group of multi-element methods uses relative sensitivity factors (RSF) for a quantitative analysis. The most frequently used technique in ICP-MS involves quantitative determination by calibration curves obtained from solutions with known element concentrations.

Isotope dilution mass spectrometry (IDMS) is a definitive analytical method which yields results of high accuracy and preci-

TABLE IV

Techniques for quantitative determinations of elements with mass spectrometry

Ionization Method	Technique
Thermal ionization, field desorption	Isotope dilution
Electron impact	Isotope dilution, calibration gas (double-gas inlet system)
ICP, MIP	Calibration curves, standard addition method, isotope dilution
Spark source	RSF[a] (range: 1–3), isotope dilution
Glow discharge	RSF (range: 1–10)
Laser	RSF (range: 1–50)
Secondary ion source	RSF (range: 1–1000)

[a]RSF = relative sensitivity factor.

sion.[2,21] A definitive method can be defined as a method which, after exhaustive investigation, is found to have no known source of inaccuracy or ambiguity.[22] It is commonly accepted that IDMS is one of the most accurate methods in trace analysis of the elements. Using relative sensitivity factors for calibration, one has to take into account that RSF values strongly depend on the element to be determined and on the matrix material in which the trace element is distributed. The normal range of RSF values for different ionization methods is listed in Table IV. In general it can be pointed out that the higher the possible variations of the RSF values, the more difficult it is to produce an accurate and precise analysis. With respect to the range of RSF values given in Table IV, this means that acceptable quantitative results should be obtained with spark source and glow-discharge mass spectrometry as well as with laser mass spectrometry. However, the SIMS method is preferred for quantitative and semiquantitative analyses.

The problem of obtaining accurate analyses results in element trace analysis can be seen in Fig. 3. In this diagram the variation

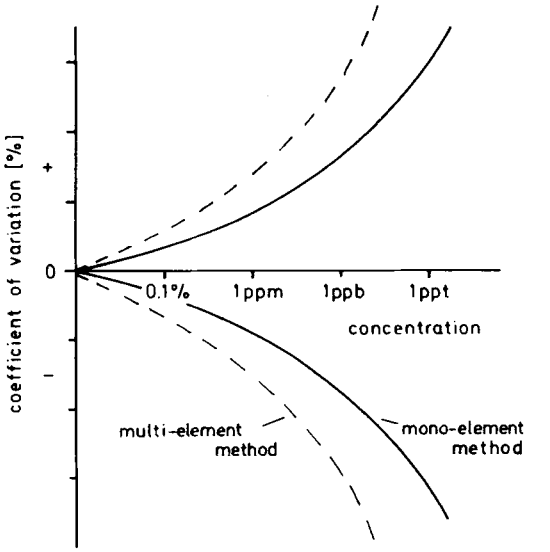

FIGURE 3 Variation of results for trace element analyses in interlaboratory studies (Ref. 23).

of analytical results obtained by different laboratories is shown to depend on the concentration range of the element to be determined. The variation in the analytical results increases exponentially with lower concentration of the elements. Normally, the coefficient of variation is higher for multi-element methods than for mono- or oligo-element methods. When different laboratories employ the same analytical method, a disparity in the results can also occur. This depends on the reliability of the applied method with respect to systematic and statistical errors. To show this effect on mass spectrometric methods, Fig. 4 represents the results of eight laboratories that used spark source mass spectrometry for the determination of 12 elements in the concentration range of 7–62 ppm in an iron standard material.[13] Table V lists the results of our laboratory[24–26] (lab 1) and of other laboratories[27] (lab 2) that employed thermal ionization IDMS for lead trace determinations

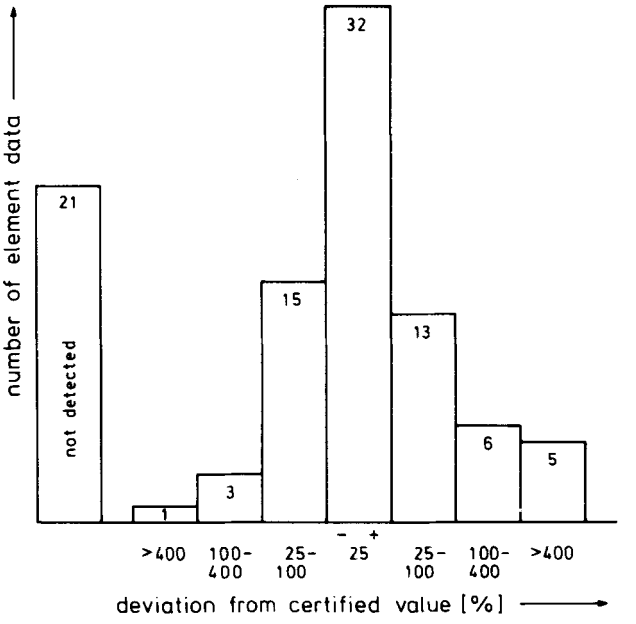

FIGURE 4 Accuracy of spark source mass spectrometry obtained for the analysis of 12 elements in an iron standard reference material by eight laboratories (Refs. 13 and 21).

TABLE V

Determination of lead in different standard reference materials with thermal ionization IDMS (Refs. 24–27)

Sample	Lead Concentration [μg/g] Lab. 1	Lab. 2	Certified Value
Sewage sludge (BCR 144)	483.7 ± 4.8	485.2 ± 2.0	495 ± 19
Aquatic moss (BCR 61)	61.1 ± 0.3	61.1 ± 1.6	64.4 ± 3.5
Sandy soil (BCR 142)	37.6 ± 0.8	36.7 ± 0.4	37.8 ± 1.9
Olive leaves (BCR 62)	26.9 ± 1.2	26.4 ± 0.5	25.0 ± 1.5
Milk powder (BCR 150)	0.96 ± 0.01	0.95 ± 0.01	1.00 ± 0.04

in different standard reference materials of the Community Bureau of Reference (BCR) of the European Communities. The advantages and disadvantages of spark source mass spectrometry using RSF values for the quantitative analysis and of thermal ionization IDMS are clearly demonstrated by the results in Fig. 4 and Table V: With spark source mass spectrometry, up to 12 elements have been analyzed at the same time, whereas with thermal ionization IDMS, it was only possible to analyze a few elements other than lead at the same time, e.g., cadmium and thallium.[24] But the results of spark source mass spectrometry are much less accurate than those obtained with the isotope dilution technique. The results listed in Table V show that excellent agreement is obtained between the analyses of different laboratories using thermal ionization IDMS and that all IDMS values agree within the limits of error with the certified values of the standard reference materials. Generally, the uncertainties in the certified values, which are a result of analyses by different selected methods and laboratories, are higher than those obtained with IDMS. In selecting one of the two mass spectrometric methods one must choose the correct method according to the analytical necessity, e.g., whether as many elements as possible are to be analyzed at one time or whether the analysis results should be as accurate as possible. In other words, a multi-element method usually cannot produce results with the highest accuracy and an oligo-element method cannot be applied in multi-element analyses.

Due to the great importance of accurate trace analyses, the basic principle of IDMS will be explained next. Figure 5 illustrates this principle by using the example of a lead analysis. A known quantity of a spike isotope must be added to the sample. The spike substance is enriched in at least one isotope compared with its natural isotopic composition, e.g., in ^{206}Pb for lead analyses (see Fig. 5). After the spike addition, the sample and the spike must be completely mixed. This means that a solid sample must be chemically decomposed. The spike isotope addition can be understood as an isotope dilution of the sample with natural isotopic composition. The analytical technique receives its name from this process. Part of the isotopically diluted element (it need not be quantified) is then isolated. Conventional separation methods can be used for isolating elements, e.g., ion exchange chromatography, electrolytic deposition,

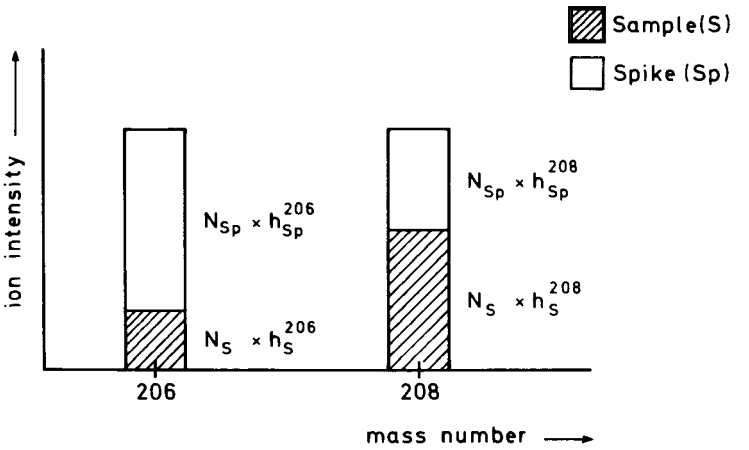

FIGURE 5 The principle of IDMS illustrated by a schematic mass spectrum of a lead analysis (Ref. 2).

and extraction. After the element is isolated, the isotope ratio R of the isotopically diluted sample is measured in the mass spectrometer. For lead analyses, where a ^{206}Pb spike is used, the $^{208}Pb/^{206}Pb$ ratio is selected for the mass spectrometric measurement. This is because ^{208}Pb has the highest natural isotope abundance. From the schematic diagram of Fig. 5 it follows:

$$R = \frac{^{208}Pb}{^{206}Pb} = \frac{N_S \times h_S^{208} + N_{Sp} \times h_{Sp}^{208}}{N_S \times h_S^{206} + N_{Sp} \times h_{Sp}^{206}} \quad (1)$$

where N is number of atoms, h is isotope abundance [%], S is sample, Sp is spike, 206 is ^{206}Pb isotope, 208 is ^{208}Pb isotope.

If the isotope abundances of the sample and of the spike are known, the unknown amount of the element in the sample ($=N_S$) can be determined simply by measuring the change in an isotope ratio which is caused by the isotope dilution process. For further details concerning IDMS, see other publications.[2,9,21,23]

One important advantage in using IDMS is that the element to be determined need not be isolated quantitatively after isotope dilution. Thus, loss of substance during chemical isolation steps will not influence the result. Quantitative isolation of μg or sub-μg amounts of an element—or the exact determination of the

corresponding isolation yield—is a great problem in other trace analysis methods. The use of an enriched isotope is also the best form of an internal standardization for element analyses. These are the major reasons why IDMS can be used successfully as a definitive method in trace element analyses.

As mentioned before, low detection limits are a general advantage of mass spectrometric methods. The detection limits of spark source mass spectrometry are given in Table VI for a selection of elements in metallurgical silicon.[28] The detection limits given in atomic ppm units (ppma) are valid for the analysis of solid silicon samples. As can be seen, many elements can be analyzed using spark source mass spectrometry within a concentration range of a few parts per billion without any chemical pretreatment of the sample. The detection limits obtained by ICP-MS for a representative selection of elements are given in Table VII together with the comparable results of ICP atomic emission spectroscopy (ICP-AES) and flame atomic absorption spectroscopy (FAAS).[29] These detection limits all correspond to concentrations in an aqueous solution. Except for a few cases, e.g., Li and Zn, ICP-MS has the lowest detection limits. For many elements the detection limit for ICP-AES is a factor of 3–20 higher than for ICP-MS. This is due to the smaller number of lines in the mass spectrum than in the atomic emission spectrum and to the high sensitivity of the ioni-

TABLE VI

Detection limits with spark source mass spectrometry for a selection of elements in metallurgical silicon (Ref. 28)

Element	Detection Limit [ppma]
Li	0.002
B	0.01
F	0.04
S	0.04
Cl	0.3
Cr	0.03
Fe	0.4
Cu	0.02
As	0.03
Ba	0.5
Pb	0.08

TABLE VII

Detection limits of elements analyzed with ICP-MS compared with those obtained by ICP-AES and FAAS (Ref. 29)

Element	Detection Limit [ng/ml] ICP-MS	ICP-AES	FAAS
Li	3	1.9	2
B	1	3.2	1000
Cr	0.2	4.1	3
Mn	0.8	0.9	3
Zn	3	1.2	0.6
As	7	35	100
Se	15	50	100
Cd	0.5	1.7	1
Ba	0.3	0.9	20
Hg	0.4	17	200
Pb	0.3	28	20
U	0.4	170	7000

zation process in the plasma gas. Compared with FAAS, the detection limit of ICP-MS is usually better by a factor of 15–100. In some special cases, e.g., uranium, there is a tremendous improvement in the detection limit when using the ICP-MS method.

Table VIII shows the detection limits of a selected number of trace elements and inorganic trace anions which have been determined in our laboratory by thermal ionization IDMS. The detection limits listed are for the whole analytical procedure that includes the decomposition of the sample (if necessary), the isolation process, and the mass spectrometric measurement. The detection limit is usually limited by the variation of the blank. The detection limit of most of the species in water samples is in the sub-ng/g level. In the case of Pb and Cu it is a few pg/g, and for Cd it is less than 1 pg/g ($<10^{-12}$ g Cd/g water). These extremely low detection limits of thermal ionization IDMS are much better than the comparable results obtained by ICP-MS (see Table VIII). However, contrary to ICP-MS, only a few elements can be analyzed at the same time when using thermal ionization IDMS. In the negative thermal ionization mode of IDMS,[9] a number of semimetals and nonmetal species, e.g., boron, selenium, halides, and nitrate, can be analyzed in different matrices with sufficiently low detection limits. Whereas in ICP-MS—and also in some cases in

TABLE VIII

Detection limits of trace elements and inorganic anions in different matrices analyzed by thermal ionization IDMS

Element or Anion	Matrix	Detection Limit [ng/g]	Reference No.
Pb	Water	5×10^{-3}	30
	Soil, sewage sludge etc.	3	24
	Food samples	1.2	31
Cd	Water	2×10^{-4}	30
	Soil, sewage sludge etc.	6	24
	Food samples	0.8	31
Cu	Water	1.5×10^{-2}	30
	Soil, sewage sludge etc.	2	24
	Food samples	9	31
B	Water	0.2	32
	Metals	40	33
Se	Water	8×10^{-2}	34
Cl^-	Water	13	35
	Geological samples	1.5×10^3	36
Br^-	Water	0.4	35
	Geological samples	15	36
I^-	Water	0.9	35
	Geological samples	6	37
	Food samples	18	38
NO_3^-	Water	0.9	39
	Food samples	2×10^2	40

spark source mass spectrometry—it is difficult to obtain low detection limits for semimetals and nonmetals, the species analysis is not possible with ICP-MS and spark source mass spectrometry.

SELECTED EXAMPLES OF ELEMENT ANALYSES WITH THERMAL IONIZATION IDMS

Because of the great importance of accurate trace analyses in all fields of natural and applied science, a selected number of element determinations are presented in the following, which have been carried out by IDMS in our laboratory using the positive or negative thermal ionization technique. Thermal ionization and electron impact ionization mass spectrometry are the most common techniques used for IDMS of elements. Figure 6 shows all elements in the periodic table which are amenable to these two ionization methods. In principle, it is also possible to analyze all marked elements by spark source IDMS. Those elements which can only be determined by a long-lived radioactive spike isotope, because

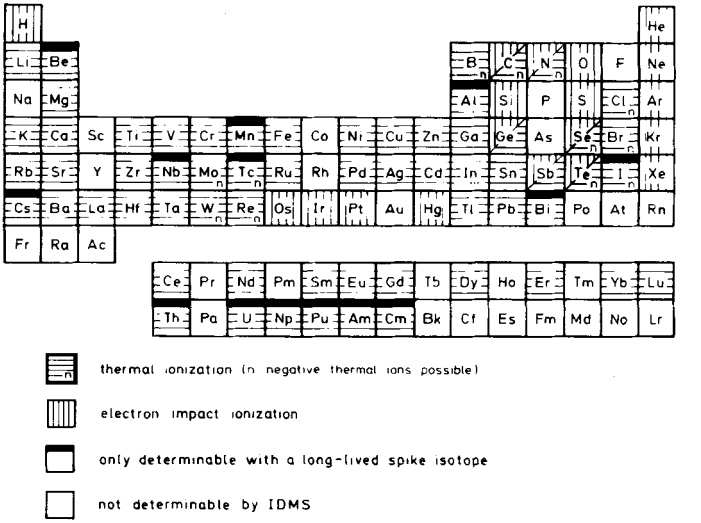

FIGURE 6 Elements determinable with thermal ionization or electron impact IDMS (Refs. 2 and 21).

TABLE IX

Average concentration of heavy metals analyzed with thermal ionization IDMS in 20 Antarctic ice samples from the Ekström ice shelf (Ref. 30)

Heavy Metal	Concentration [pg/g]
Tl	1.4
Cd	4.9
Cr	10.6
Pb	20.0
Ni	38.3
Cu	123.9

no stable spike isotope exists, are characterized by a black bar at the top of the element box. The great power of IDMS as a definitive method in element analysis is demonstrated by the fact that only a few elements in the periodic table are not marked.

The first set of analyses shown using IDMS is the determination of extremely low heavy metal concentrations in Antarctic ice samples. The results are given in Table IX and show the average concentration of six heavy metals which were analyzed in 20 Antarctic ice samples from the Ekström ice shelf.[30] The German Antarctic station, Georg-von-Neumayer, is located at the Ekström ice shelf. The samples were collected at different points on the ice surface and at depths of up to 1 m below the surface during the Antarctic summer, January/February 1985. The sample treatment and the isolation of the elements by electrode-position were carried out under clean-room conditions and in extremely carefully cleaned vessels to prevent contamination of the samples. The isotopically diluted elements were measured in a single-filament thermal ionization mass spectrometer with the silica gel technique. As one can see from the results in Table IX, the average concentration of the analyzed heavy metals is in the range of a few pg/g. In other words, a few atoms of Cu, Ni, Cr, Pb and less than one atom of Cd and Tl have been determined in one trillion molecules of Antarctic ice. There are not many other analytical methods known which are able to analyze such extremely low concentrations. As can be seen from the detection limits listed in Table VIII, the average concentrations of the analyzed ice samples are still distinctly higher than the corresponding detection limits for Pb, Cd,

and Cu in a water matrix. The major aims of analyzing heavy metals in the Antarctic ice are the determination of the actual trace element concentration and to follow the trend of the concentration with time which can be influenced by natural or anthropogenic processes. Information about events which occurred in the Southern Hemisphere in previous centuries, e.g., about volcanic activities, can be obtained from analyzing trace element concentrations in a depth profile of the Antarctic ice shield.

In contrast to the determination of metals, where a number of different methods are available for trace analyses, only a few alternative methods can usually be applied to the trace determination of nonmetals and some semimetals. For example, the only methods that have been frequently applied—in some cases with only limited success—for iodine and selenium trace analyses in solid samples is neutron activation analysis for both elements and the Ce(IV)/As(III) catalytic method for iodine and hydride atomic absorption spectrometry for selenium, respectively. Because of the deficiency of alternative methods for nonmetals and a number of semimetals, it is of particular importance that IDMS methods have been developed for many of these elements using the formation of negative thermal ions.[9] These elements include boron, carbon, nitrogen, selenium, tellurium, chlorine, bromine, and iodine (see Fig. 6). The main advantage of using negative thermal ionization—as compared with other analytical methods, as well as with other ionization techniques in inorganic mass spectrometry (see Table II)—is the selective ionization method for nonmetals and semimetals with sufficiently high electron affinities ($\gtrsim$2 eV). The analytical sensitivity is very good for most of these elements because of the high ionization efficiency in the ion source and the fact that there are usually no problems with interferences or with background peaks. In the following, an investigation of halide trace analyses in geochemical samples is presented as an example of nonmetal analyses by IDMS.

Results of chloride, bromide, and iodide analyses are presented in Table X for three different geochemical standard reference materials from the Centre de Recherches Pétrographiques et Géochimiques in Nancy, which are not certified with regard to the three halides. The halide analyses using IDMS could be carried out simultaneously by isolating the three halides as AgX and meas-

TABLE X

Halide trace analyses in geochemical standard reference materials with thermal ionization IDMS (Ref. 36)

Sample	Concentration [μg/g] Chloride IDMS	Chloride Other Methods	Bromide IDMS	Bromide Other Methods	Iodide IDMS	Iodide Other Methods
Granite GS-N	442 ± 3	47 - 830	2.18 ± 0.02	3	0.038 ± 0.004	–
Granite GH	60.5 ± 0.6	58 - 503	0.094 ± 0.003	2	0.020 ± 0.001	0.15 - 114
Bauxite BX-N	27.7 ± 0.3	45	0.98 ± 0.01	1	2.52 ± 0.05	–

uring the isotope ratio from the same isolated sample by a successive increase in the filament temperature of the thermal ion source.[36] As far as they are available, the results of other laboratories using other different methods are included in this table for comparison. If a range of results is listed, the first value represents the lowest and the second value the highest analyzed concentration. As can be seen, it is possible to simultaneously determine chloride traces down to the low μg/g level, bromide and iodide traces down to the ng/g level in geochemical materials with negative thermal IDMS. The problem of accurate halide trace analyses in geological samples using other methods becomes evident from the broad variation in the results (factor of 18 and 9 for chloride analyses in Granite GS-N and Granite GH; factor of 760 for iodide analyses in Granite GH) and by the significant deviation of single results from the result of the definitive method IDMS. Up to now, chloride, bromide, and iodide contents have not been able to be certified in geochemical standard reference materials, but IDMS offers a good chance for such a certification in the future.

In principle, species analyses are also possible with the IDMS technique if a selective chemical separation of the different element species is carried out before the mass spectrometric measurement takes place. This chemical separation is necessary because a thermal ionization mass spectrometer is not able to differentiate between different element species. This is the same reason why most of the other ionization methods used in inorganic mass spectrometry, e.g., spark source or ICP, are not suited for analyzing element species. One precondition in the application of IDMS for species analyses is that no isotopic exchange takes place between the element species during the chemical treatment of the sample. Species analyses in inorganic chemistry are especially important for anion forming nonmetals. Up to now, our laboratory has developed analytical procedures with IDMS to determine the element species pairs NO_2^-/NO_3^-, SeO_3^{2-}/SeO_4^{2-}, and I^-/IO_3^-.[34,35,40]

The results of nitrite and nitrate analyses with IDMS in plant materials and food samples are listed in Table XI.[40] This species analysis was carried out using a $^{15}NO_2^-$ and $^{15}NO_3^-$ spike, respectively, and by separating the two isotopically diluted species in the sample with an anion exchange resin. No isotopic exchange of nitrogen exists between NO_2^- and NO_3^- for pH values of ≥ 4,

TABLE XI

Nitrate and nitrite species analyses with thermal ionization IDMS (Ref. 40)

Sample	Concentration [μg/g]	
	NO_3^-	NO_2^-
Spinach (NBS 1570)[a]	$(16.08 \pm 0.03) \times 10^3$	39.4 ± 0.9
Aquatic plant (BCR 61)[a]	$(4.41 \pm 0.05) \times 10^3$	1.86 ± 0.11
Smoked cut of lean pork	165 ± 4	18.0 ± 0.5
Raw ham	61 ± 3	28.0 ± 0.6
Creek water	39.2 ± 0.2	0.65 ± 0.03

[a]Standard reference materials not certified for NO_3^- and NO_2^-.

which was taken into consideration during the sample treatment. As one can see from the results in Table XI, it is possible to analyze nitrite and nitrate in plant materials and food samples with relative standard deviations in the range of 0.6–6% using negative thermal IDMS. Here the nitrate concentration can exceed the nitrite trace content by a factor of a thousand. The difficulties in obtaining accurate nitrate results in food samples became obvious in the past, e.g., in an interlaboratory study where nitrate traces in the range of 3–150 μg/g were to be analyzed in milk powder samples. This interlaboratory comparison was organized by the Community Bureau of Reference (BCR) of the European Communities in 1983. The results of the participating laboratories using various analytical methods differ as much as 45% in the 150 μg/g level, and as much as several hundred percent in the 3 μg/g level.[41] These results illustrate the problem of obtaining an accurate trace analysis of a well-known inorganic anion, although the knowledge of the exact concentration of nitrate in food samples is of essential importance because of the toxic effect of this species in the human body. Mass spectrometry in combination with the isotope dilution technique offers the possibility of obtaining more precise and accurate results even in this important analytical question.

FUTURE TRENDS

One future trend regarding mass spectrometric instrumentation will be the use of simpler and more cost-efficient equipment which will open the way to a much broader use of mass spectrometry in element analysis. For example, only magnetic sector field instruments have been used for analyses with the thermal ionization technique in the past. As the application of a recently constructed—and now commercially available—quadrupole thermal ionization mass spectrometer has shown, this type of cost-efficient instrument, which is not much more complicated to handle than an atomic absorption spectrometer, leads to results in IDMS that are identical to those obtained by large magnetic sector field instruments.[9] The quadrupole analyzer used in ICP-MS has also demonstrated that this type of simple mass-separation system can be applied in combination with plasma ion sources. Therefore, the modern trend in glow-discharge mass spectrometry goes in the

same direction as recent developments have shown,[42] although the only commercially available instrument today with this ion source uses the double-focusing system.[17] However, in multi-element analyses, spark source mass spectrometry will be replaced by glow-discharge, laser, and ICP-MS. If the excitation of the sample in the ion source is carried out by a laser or a primary ion beam using a pulse mode, more and more time-of-flight analyzer systems will be employed.

Because of the increasing necessity of accurate trace analysis results, an increased application of the isotope dilution technique will occur in the future. In addition, this technique, although traditionally used in thermal and electron impact ionization mass spectrometry, will also be transferred to other ionization methods, e.g., to ICP and glow-discharge mass spectrometry. The ideal internal standardization reached by using an enriched spike isotope has lead to the fact that no other analytical method can compete with IDMS as a definitive method in the analysis of such a great number of elements. However, the essential or toxic effects of many trace elements cannot be attributed only to the absolute amount of the element, but also to the chemical form in which the element exists in the particular system. Therefore, an increasing number of methods for species analyses must be developed in mass spectrometry as well.

Another trend in thermal ionization IDMS is to expand the method (usually used as a mono-element method in the past) for oligo-element determinations. In this case, groups of elements are combined that can be successively ionized from the same sample by increasing the filament temperature. Fortunately, elements of similar analytical interest and those which can be combined with regard to their ionization behavior in the ion source are very often identical. For example, the toxic heavy metals lead, cadmium, and thallium can be determined in the same sample with the positive thermal ionization technique,[24] whereas chloride, bromide, and iodide can be analyzed with negative thermal ionization mass spectrometry (see Table X).[36]

KLAUS G. HEUMANN
Institut für Anorganische Chemie
der Universität Regensburg,
D-8400 Regensburg,
Federal Republic of Germany

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