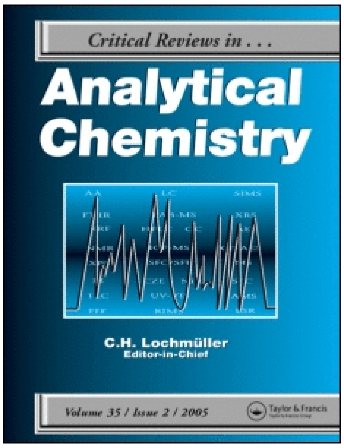

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A Critical Review of Inductively Coupled Plasma-Mass Spectrometry for Geoanalysis, Geochemistry, and Hydrology. Part I. Analytical Performance

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A Critical Review of Inductively Coupled Plasma-Mass Spectrometry for Geoanalysis, Geochemistry, and Hydrology. Part I. Analytical Performance*

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ABSTRACT: Present-day inductively coupled plasma-mass spectrometry (ICP-MS) instrumentation is described briefly. Emphasis is placed on performance characteristics for geoanalysis, geochemistry, and hydrology. Applications where ICP-MS would be indispensable are indicated. Determination of geochemically diagnostic trace elements (such as the rare earth elements [REE], U and Th), of isotope ratios for fingerprinting, tracer and other geo-isotope applications, and benchmark isotope dilution determinations are considered to be typical priority applications for ICP-MS. It is concluded that ICP-MS furnishes unique geoanalytical and environmental data that are not readily provided by conventional spectroscopic (emission and absorption) techniques.

KEY WORDS: inductively coupled plasma-mass spectrometry, inductively coupled plasma emission spectrometry, geochemistry, geoanalysis, trace elements.

I. INTRODUCTION

In recent years attention has been drawn to the development and steady introduction of inductively coupled plasma-mass spectrometry (ICP-MS) into the field of geoanalysis. The performance characteristics, including detection capability and the potential for determining isotope ratios, are considered to be important for geological, environmental chemistry, and water quality applications. The initial problems in instrument design have been overcome, and there is currently an upsurge of interest in the geosciences.

Current instrumentation for widespread elemental analysis of geological and environmental materials, based on flame and graphite-furnace atomic absorption spectrometry, is continually growing less suitable because of the limitations of single-element detection capability, inadequate sensitivity and limits of detection (LODs) of the flame, and the low sample throughput, elemental scope, and potential interferences of graphite-furnace atomization. Although inductively coupled plasma-atomic emission spectrometry (ICP-AES) is now a well-established method for multielement trace analyses of geological, water, and related environmental materials, there are several limitations:

1. The LODs of ICP-AES (Table 1), in solution, presented to the instrument for analysis (10 to 100 μg/l) allows a concentration range of 1 to 10 mg/kg to be determined with adequate accuracy in solid geological samples (prior to sample dissolution). Consequently, data on the distribution of trace metals in geological and environmental materials cannot be readily obtained without resorting to tedious and contamination-prone preconcentration and matrix separation procedures. Although the limits of detection of graphite-furnace atomic absorption spectrometry (GFAAS) are superior for many elements, with the exception of the refractory elements and the metalloids, the single-element analysis

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* Use of tradenames does not imply endorsement by U.S. Geological Survey.

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TABLE 1
Comparison of Detection Limits for ICP-AES Using Ultrasonic Nebulization and ICP-MS and GF-AAS

Element	GFAAS	ICP-AES	ICP-MS	ICP-AES-USN
Ag	0.005	1	0.04	0.3
Al	0.04	4	0.1	0.2
As	0.2	20	0.05	0.4
B	20	2	0.1	0.1
Ba	0.1	0.1	0.02	0.1
Be	0.01	0.06	0.1	0.02
Bi	0.1	20	0.04	1
Cd	0.003	1	0.02	0.01
Co	0.01	2	0.02	0.2
C	0.01	2	0.02	0.1
Cu	0.02	0.9	0.03	0.05
Fe	0.02	1	1	0.05
Hg	1	20	0.03	1.5
Li	0.05	0.9	0.1	0.3
Mn	0.01	0.4	0.04	0.02
Mo	0.04	5	0.08	0.3
Ni	0.1	4	0.03	0.2
Pb	0.25	10	0.2	1
Sb	0.2	20	0.02	1
Se	0.2	20	0.5	2
Si	0.4	3	10	0.4
Sn	0.2	20	0.03	0.8
Sr	0.02	0.05	0.02	0.04
Ti	1	0.5	0.06	0.2
Tl	0.1	20	0.02	0.5
U	—	10	0.01	—
V	2	0.5	—	—
Zn	0.01	1	0.08	0.09

Note: All data in milligrams per liter.

capabilities and potential interference effects place serious constraints on the sample analysis throughput time and routine operational procedures for multielement analysis.

2. Limited simultaneous multielement capability of ICP-AES is due, not so much to the technique, but to the limitations of state-of-the-art commercial instrumentation. In geochemistry, there is often the demand to obtain the maximum amount of data on any particular sample. This is not possible employing conventional single-channel photomultiplier-based detection instruments. Furthermore, the possibility of accumulating elemental data in a computerized database for subsequent reference and interpretation is not currently available.
3. Neither ICP-AES nor GFAAS can be readily employed to determine the mode of occurrence of elements in a particular sample. In environmental studies, there is a growing requirement to provide not only data on the abundance of an element in a sample, but on its form and how it is associated with other elements. In the environment, particularly surface waters and effluents, some metals can be found in anomalous concentrations due to enhanced transport and concentration in the form of colloidal materials, organometallic compounds, and absorption on submicrometer-diameter clay particles[1,2] (Table 2).
4. With the growing improvement of instrumentation capabilities, the application of ICP-MS as a geoisotopic tool is expanding. Such information can only be obtained by alternative thermal-ionization mass spectrometry (TIMS), which exhibits substantially better accuracy but

TABLE 2
Mode of Occurence of Trace Elements in Environmental Systems[a]

Mode of Occurrence	Pathways
Resistant mineral phases	Metals in silicate minerals not readily released unless intense weathering occurs
Absorbed on clay and silt fractions	May be liberated and occur in the free ionic form
Incorporated in Fe and Mn hydroxides	May be liberated and occur in the free ionic form
Can exist as colloids associated with submicron clay particles.	
Incorporated in biological materials	May be liberated and occur in the free ionic form
Occurrence in the solute form	
Role of redox processes	A means of sorption, transportation and release of metals within water entities and sediments
Gravitational settling	Larger solid particles (clay aggregates, organic matter — excretion and unassimilated material) in lakes
Bacteriological and diagenetic processes	Phase transformations due to pH and Eh changes
Preferential accumulation in biota	Direct bonding to organic molecules within biota

[a] Depending on the physicochemical conditions in the environment.

is extremely slow and tedious, resulting in low sample throughput.

5. Lack of capability for localized direct analysis of solid geological materials (including liquid inclusions) at trace concentration levels and for isotope abundance information.

The above limitations of ICP-AES create serious problems for performing modern comprehensive geoanalysis and geochemical studies.

II. CURRENT STATUS OF ICP-MS INSTRUMENTATION

Inductively coupled plasma-mass spectrometry (ICP-MS) combines the well-accepted high-energy inductively coupled radiofrequency plasma source with a quadrupole mass spectrometer to produce both an elemental and isotopic analyzer in the same instrument. This technique has become a competitive tool with the previously described trace elemental analysis methods, especially for the determination of trace metals in the part per billion and sub-part per billion range[3,4] (over 90% of the elements can be determined with LODs in the 0.1 to 0.001 μg/l range in aqueous solutions). The possibility of applying isotope dilution protocols,[4] rapid determination of isotope ratios, and the potentiality of interfacing to element preconcentration and sample introduction devices for speciation and sensitive detection studies makes ICP-MS a powerful analytical tool for the evaluation of metal pollution in the environment. An additional merit of ICP-MS is the capability of determining isotope compositions for screening patterns, fingerprinting both ancient and modern geological processes, and for stable isotope tracers to evaluate metal migration in the environment.[5]

The configuration of the instrument consists of three components: (1) a conventional argon ICP operating at temperatures of 6000 to 9000° K, (2) a conventional quadrupole mass spectrometer, and (3) the critically important interface. At this temperature chemical interference effects are insignificant, and essentially all atoms are ionized to a very large extent.

For conventional analysis of solutions, the sample is introduced into the central region of the plasma at *atmospheric pressure*, where the sample is sequentially dissociated into atoms, and elements with a first ionization potential of <10 to 12 eV are dissociated and ionized. The torch is mounted horizontally within 1 cm of the sampling orifice of the interface to the high vacuum mass spectrometer.

The major innovation in the design of ICP-MS analyzers is the interface between the mass spectrometer and the ICP.[6,7] Here ions produced in the plasma are transported at atmospheric pressure into the quadrupole. Current designs have minimized the interference effects from space charges effecting ion transport, that were observed in the early stages of development, between the high-temperature plasma and the modest vacuum (10^{-5} torr) of the analyzer region of the quadrupole mass spectrometer. The state-of-the-art interface consists of a series of orifices that separate the plasma from the ion optics of the mass spectrometer.

There are two regions in the interface:

1. The region behind the outer "sampling cone" (a water-cooled orifice 1 mm in diameter) is maintained at a pressure of 1 torr. It should be emphasized that the outer orifice is open to the atmospheric pressure plasma but is continuously pumped by the mechanical vacuum pumps. The outer orifice-sampler is immersed in the "analytical zone" of the ICP. Positive ions produced in the argon plasma are transported through this narrow aperture, which is not tolerant of solutions containing high salt and acid concentrations.
2. The second region is called the "zone of silence." Here the plasma beam expands at supersonic speeds and is sampled by the "skimmer" cone. The ions and plasma gas pass into the higher vacuum region. In the vacuum chamber, ion lenses focus the ions to the quadrupole mass filter for analysis according to their mass-to-charge ratio. After mass isolation, the filtered ions pass into an electron multiplier detector that generates a signal for every ion impinging upon its surface.

III. ANALYTICAL BENEFITS AND PERFORMANCE CAPABILITIES OF ICP-MS FOR GEOANALYSIS AND GEOCHEMISTRY

A. Limits of Detection

One of the main advantages of ICP-MS lies in its very high sensitivities that generally cannot be obtained by conventional ICP-AES LODs are listed in Table 1. Here detection limits for ICP-MS are compared with those obtained for ICP-AES, with and without ultrasonic nebulization (USN). Data for ICP-AES-USN are from Brenner and co-workers,[8] all other data are from Reference 9. It is evident that LODs are generally enhanced by factors varying from 100 to 1000 in comparison to those obtained by ICP-AES. Thus, the application of ICP-AES for the direct determination of ultratrace element concentrations (e.g., As, Bi, Cd, Cr, Co, Pb, Mo, Se, Ag, Sn, Hg, V, etc.) in waters and geological samples has been limited due to inadequate sensitivity. The sensitivity of ICP-AES can be improved with the use of USN, and flow injection analysis (FIA) and column preconcentration (see below).

Detection limits in the ranges tabulated for ICP-MS in Table 1 are readily attainable for more than 70 elements using conventional sample introduction systems. The LODs of selected elements by GFAAS are also in the same range but with considerable interference effects and small sample throughput due to the single-element capability. Thus, the superior LODs, operational simplicity, large dynamic concentration range, and multielement detection capability, and the greater convenience and speed of ultratrace multielement analysis by ICP-MS is attractive, because environmentally important elements may be determined without the need to preconcentrate,[10,11] a time-consuming process prone to contamination.

The technique also permits determination of the REEs and other rare trace elements (Th, U, Os, Ir, W, Nb) that are important indicators of geological environments and petrogenetic processes. Consequently, the number of elements that can be determined is extended and the sample throughput increased.

Although by ICP-MS it is not feasible to directly analyze brines containing 10 to 20% by weight salt concentrations, a 100 to 200-fold dilution frequently allows determination of many of the heavy metals.

B. Multielement Analysis

Element determinations can be considered to be performed nearly simultaneously due to the very rapid scanning rates obtainable with quadrupole spectrometers. Several computer-controlled measurement modes are available.

C. Extended Dynamic Range of Measurement

The development of instrumental capabilities for extending the dynamic range of the measurement system over six orders of magnitude permits the analysis of a wide range of elemental concentrations. This capability allows trace and major concentration elements to be determined on the same sample aliquot. Although the focus of ICP-MS is on trace element determinations, the range of concentrations that can be measured is significantly extended with the above detection systems. This capability overcomes the necessity of diluting the solutions or attenuating the ion beam. The systems claim to have a linear range of eight orders of magnitude, permitting trace and major elements to be determined in the same solution.

D. Modes of Quantification

In ICP-MS there are three methods of quantification, each yielding different levels of accuracy and precision.

1. Semiquantitative Analysis

For the rapid determination of the approximate concentrations of elements in a sample, SEMIQUANT routines are used with an accuracy of ~10 to 20%.[12] More than 80 elements are typically determined in about 5 min using a standard containing only a few surrogate elements. This approach is based on the predicted instrument response across the mass range. This multielement capability is very useful for semiquantitative reconnaissance or assessment analysis, particularly in regional environmental and geochemical surveys, where a maximum amount of information with a minimum cost and effort is required.

The application of SEMIQUANT routines allows rapid prescreening of water samples, producing data to permit selection of elements for more quantitative subsequent determinations. This technique is also useful for developing preliminary data prior to the design of conditions for isotope dilution experiments. The analysis of the National Institute of Standards and Technology (NIST) 1643a, in Table 3, compares favorably with published values.

It should be pointed out that As is easily determined at the parts per billion level. This element is normally determined by an individual hydride-generation atomic absorption spectrometric method.

2. Isotope Ratio Measurements

A major advantage of ICP-MS is its capability of rapidly determining stable isotope ratios; however, the precision of determination is poorer than that obtained by TIMS. In recent measurements made in various laboratories using different instrumental measurement modes and optimized plasma and quadrupole operating conditions, isotope ratio measurement precisions varied from 0.1 to 1% relative standard deviation. In certain cases, this precision may be improved by utilizing internal references. Such isotope ratios are useful for screening samples for subsequent analysis by TIMS, for fingerprinting, and for scanning surveys.[5,13,14] With the use of ICP-MS, measurements on large numbers of samples can be made, in comparison to the very small number of samples that can be analyzed using TIMS for the same time period. Also, a very small quantity of sample is required for the determination, and multiple element isotope ratios can be acquired on the same sample, simultaneously. The ICP-MS technique has been demonstrated to be

TABLE 3.
Semiquantitative Analysis (SQ) of Trace Elements in NIST 1643a Standard Reference Material (ng/ml)

Element	Certified value	ICP-MS (SQ)
Ag	2.8	3
As	76	85
Ba	46	49
Be	19	15
Cd	10	18
Co	19	22
Cr	17	19
Cu	18	24
Fe	88	85
Mn	21	18
Mo	96	102
Ni	55	60
Pb	27	31
Sr	239	242
V	53	58
Zn	69	62

capable of determining the ratios of the isotopes of Sr, Nd, Sm, Os, Pb, B, and Br.[5] In certain cases the precision of ICP-MS was sufficient for some geochronologic applications.

ICP-MS technology can play an important role in tracing contaminant flows and metal influx in hydrological systems, waste disposal depositories, aquifers, and soil horizons. Trace element content and the enrichment of stable isotope composition enable the monitoring of water salinization and contaminant migration and can provide criteria for characterizing natural sources and man-made pollution. It is also feasible to add unique stable isotopes into a sedimentation environment and monitor rates of deposition using ICP-MS. There is little doubt that isotope ratio criteria can be found that will allow the discrimination of water and sediment entities.

3. Isotope Dilution Analysis (IDA)

Isotope dilution is an absolute quantitative method of analysis based on altering the natural relative abundance of two stable isotopes by adding a known spike of a pure enriched isotope of the element to be determined to the sample. Measurement of this altered ratio allows very accurate quantification, of 0.1 to 0.5%. This is due to the added enriched isotope acting analogous to an ideal internal standard. Using the isotope dilution approach, ICP-MS is capable of rapidly providing accurate analytical results for the determination of trace metals in a number of sample types, including natural waters, with a minimum of sample preparation. The scope of the technique is limited only by the presence in the spectrum of two uninterferred isotopes and the availability of one of these isotopes in the enriched form. The technique has been shown to be suitable for the determination of trace elements in the multielement analysis mode.[15]

IV. DISADVANTAGES OF ICP-MS AND THEIR RESOLUTION

The advantages of ICP-MS over atomic absorption spectrometry (AAS) and ICP-AES in geological and environmental applications are very real and have been discussed previously. However, the following are several disadvantages that have been investigated in detail.[6,16,17]

A. Matrix-Induced Signal Depression (Nonspectroscopic Interferences)

These interferences have been attributed to space-charge effects within the skimmer, plasma ionization, vaporization processes, and atom-electron collisions. These processes occur prominently in the presence of high dissolved solid concentrations and result in a general decrease in ion intensity. This signal suppression can be compensated by matrix matching calibration procedures, standard addition methods, internal standards, and by matrix exclusion techniques. For these reasons, ICP-MS is limited to solutions containing about 0.1 to 0.5% total solids for continous sampling. When the solids content of the sample solution exceeds 0.5%, salt condensation can occur on and in the sampling orifice and aperture blocking may eventually occur. Many of these difficulties have been overcome when using large apertures of 1 mm and a skimmer of about 0.8 mm. With the dramatic increase in sensitivity of ICP-MS, resulting in an improvement in the LODs, a 10-fold dilution of the original sample solution will allow trace elements to be determined at indigenous concentration levels in geological samples in spite of the resulting high dissolved solids solutions.

B. Isobaric Overlaps

The position of the occurrence of an isotope of an element may be directly coincident with the position of the occurrence of the isotope of another analyte or matrix element. These occurrences are called isobaric overlaps. In many cases either an alternate isotope can be used or a spectral interference correction can be made. Interferences from the ICP gases (Ar), entrained air (O and N), and sample solvent (O and H) are also prevalent, for example, the interference of $^{40}Ar^+$ on $^{40}K^+$ can preclude its determination.

C. Matrix- and Solvent-Induced Ions

Because of the ionization potential of Ar, most elements are observed as single, positively charged monoatomic ions yielding a relatively simple mass spectrum.[18] Spectral interferences due to doubly charged ions are occasionally observed, especially for elements such as barium and strontium that have relatively low second ionization potentials. Molecular products of the sample, solvent, and decomposition reagents ("polyatomic ions") also are observed frequently due to ion-molecule reactions, recombination, or clustering. Of all the interferences, these can be quite severe in geochemical applications. For example, CaO^+ interferes with both Co^+ and Ni^+; $^{51}ClO^+$ interferes with $^{51}V^+$. The low-abundance $^{74}Se^+$ ion cannot be measured without severe interference of high-intensity species of Ar-Cl combinations. Due to the interference of $^{40}Ar^{35}Cl^+$ on $^{75}As^+$, it cannot be readily determined in natural waters containing high Cl concentrations and in geological materials digested with HCl and $HClO_4$. These types of interferences have serious implications in samples using sample preparation and preservation schemes involving HCl or perchloric acid.

Formation of molecular species with oxygen in the plasma-interface region have been studied by Horlick and co-workers.[19,20] Fortunately, the oxide intensities are usually low and can be diminished by manipulation of ICP operating conditions (power and gas flows), by spray chamber cooling, and by the use of mixed plasma gases. Alternatively, "dry sample" introduction systems can be employed (e.g., electrothermal vaporization (ETV)).

V. SAMPLE INTRODUCTION - IMPLICATIONS AND APPLICATIONS

In addition to pneumatic nebulization of conventional aqueous and nonaqueous solutions, other types of samples can be introduced into the plasma for atomization. Recently, several advanced methods of sample introduction into the ICP have been reported for the analysis of environmental materials.[10,11,21–29]

A. Conventional Direct Introduction of Solutions

Analytical geochemists were the first group of users who recognized the great value of ICP-MS. Date[3] described the applications of ICP-MS in a special issue of *Spectrochimica Acta Reviews* devoted to geoanalysis. He cited numerous examples where geological sample solutions were injected directly into the ICP-MS. Among the typical applications described are analysis of all types of geological materials for REE, Th, As, Sb, Ni, Co, PGMs (Pt, Au, Ir, Pd), etc. Several papers have appeared recently in the analytical and geochemical literature demonstrating the power of ICP-MS for the direct determination of these elements in geological materials.[11,30–33] As a result of the enhanced LODs, preconcentration using exchange columns is not necessary (e.g., in the determination of the REEs). This is an important application, because the ratio of low- to high- atomic-number REEs (LREE/HREE) is a unique indicator of fractionation and other petrogenetic processes. Papers have also appeared on the application of ICP-MS for the direct determination of trace elements in marine sediments.[33]

B. Direct Analysis of Suspensions

In general, the analysis of geological materials involve dissolution of the solid material, which is time consuming and may introduce considerable metal contamination from the decomposition reagents. Slurry nebulization (SN) with both pneumatic and ultrasonic nebulizers (USN) and ICP-MS has been demonstrated to be capable of providing quantitative results when the particle size of the materials is <0.2 µm in diameter.[24,25,28]

Finely ground materials (<10 µm) have been injected successfully into the ICP-MS. Ebdon et al.[34] described the performance for the multielement analysis of coal slurries, and Jarvis[31] used the direct introduction for REE determinations in geological materials. Results were satisfactory in both cases. The advantage of this technique is the avoidance of time-consuming and potentially contamination-prone sample decomposition procedures that could result in additional polyatomic interferences (i.e., chloride molecular species).

River and stream suspended sediments have been analyzed by a similar approach using sedimentation field-flow fractionation coupled directly to the ICP-MS for the direct chemical characterization of submicrometer-diameter particulates.[35,36] Sedimentation field-flow fractionation (SdFFF) is used to separate particulates by size and density in a manner analogous to a chromatographic procedure. The effluent from the SdFFF is directly injected into the ICP-MS for elemental analysis. This technique is useful for the characterization of clay minerals and for the study of surface adsorbed contaminants on the suspended particulates.

C. Laser Ablation

This technique is used for direct solids analysis and localized spatial determinations of sample surfaces. Larger surfaces can be analyzed by beam rastering techniques, while small localized areas (approximately 10 mm^2) can be investigated by stationary beam focusing. Viewing microscopes and video detectors allow visual placement of the beam prior to analysis. For rastering a large area, the laser beam is motor driven in an X-Y direction under computer control. In this application a Nd-YAG laser is used to ablate a small amount of solid material (ablated spot ~50 µm^2) for the spatial determination of trace, major, and isotope compositions.[37] The laser beam produces a cloud of microparticulate material that is dynamically transported to the ICP by a flow of argon gas. The microparticulates are decomposed in the plasma, atomized, and ionized prior to being mass-analyzed, with detection limits in the parts-per-billion concentration range. With this device, liquid and mineral inclusions can be analyzed for their trace and isotope compositions. When using the moving stage and ablating a mineral specimen, spatial elemental and isotopic distributions are obtained. Bulk analysis can also be made on glasses or on pressed powders.

Quantitative protocols for the application of laser ablation are still in the development stage.

D. Analysis of Small Volumes of Solution Using Electrothermal Vaporizers

Another innovation in ICP-MS is the development of fast electronics capable of scanning the entire mass range in 100 ms. This facility enables measurement of fast analytical transient signals essential for use with electrothermal vaporizers and laser ablation. Although ETV has several limitations (single element capability, matrix effects, and low sample throughput), the enhanced limits of detection and capability of analyzing small volume samples is an advantage for the present work.[26,27]

Extremely high sensitivity has been obtained, permitting the determination of PGMs in water and vegetation for geochemical exploration[38] purposes, screening of acids in the microelectronics industry, and for the analysis of microliter quantities of biological samples. In certain cases traditional fire assay Pb cupellation is performed with a NiS collection and subsequent analysis by ETV-ICP-MS.

In utilizing ETV for ICP-AES and ICP-MS, the following parameters should be studied in order to optimize the system for multielement analysis:

1. Effect of matrix modification and halogenation
2. Carrier gas flow and its composition
3. Geometry of the graphite sample cup or filament
4. Volatilization rates of the matrix and the analytes

VI. GEOLOGICAL APPLICATIONS

The following are examples of some geological applications.

A. Isotope Ratio Measurements

As mentioned previously, ICP-MS has the capability of rapidly determining isotope ratios. However, the precision of determination is poorer than that obtained by conventional TIMS techniques. In recent measurements made in various laboratories, using different measurement modes and optimized plasma and quadrupole operating conditions, the precisions varied from 0.1 to 1%. Such ratios are useful for screening samples for subsequent analysis by TIMS, fingerprinting, and scanning surveys.

With the use of ICP-MS numerous measurements can be made in comparison to the very small number of samples that can be analyzed using TIMS. The ICP-MS technique has been demonstrated to be useful in determining the ratios of the isotopes of Sr, Nd, Sm, Os, Pb, B, and Br. In certain cases the precision of ICP-MS was sufficient for geochronology.[5]

1. Rb/Sr, and U/Pb Geochronology

For these systems, precisions of one to two orders of magnitude better than that routinely obtainable by ICP-MS are required. However, because of the large isotope variations found in Rb/Sr and U/Pb systems, ICP-MS can be used as a rapid screening technique for preselection of samples prior to TIMS analysis.

2. Re/Os Geochronology

The interest in Os ratios is due to the radioactive decay of ^{187}Re to ^{187}Os, with a half-life of approximately 5×10^{10} years. When ICP-MS is used, osmium is separated by oxidation and volatilization as the tetroxide. Using this technique, Os ages have been determined that are in good agreement with U/Pb dates. It is now recognized that ICP-MS is a method superior to TIMS because of the much higher degree of ionization of Os in the ICP than is obtained thermally from a rhenium filament; precisions of 0.1 to 0.4% are attainable. Os ratios have been used as an indicator of the origin of Pt group metals in argillaceous rocks.

3. The Ir Anomaly of the CT Boundary

The Cretaceous-Tertiary boundary (CT) is considered to represent a period of mass extinction that occurred as the result of the impact on Earth of a huge meteorite. Anomalously high concentration levels of Ir from this meteorite were disseminated across the Earth's surface. The concentration of Ir has been determined by ICP-MS in sediments associated with this zone. The Os content (50 ppb) and the Os ratios in a CT clay indicated noncrustal abundance signatures, implying either meteoric or primary mantle origins. The CT boundary in Spain was identified using laser ablation ICP-MS.

4. Pb Isotopes

The variation of isotope ratios of Pb is due to the decay of ^{238}U, ^{235}U, and ^{232}Th to ^{206}Pb, ^{207}Pb, and ^{208}Pb, respectively. Therefore, substantial variation is observed between the stable isotopes of Pb depending on the geological history of the radioactive isotopes of U and Th. A recent comparison between ICP-MS and TIMS for the determination of Pb ratios for exploration samples indicated that useful data can be produced rapidly by ICP-MS and usually without chemical separation or preconcentration. Various types of galena deposits have been discriminated using Pb ratios measured by ICP-MS. Isotope ratio data for Pb generated by ICP-MS have been used to typify Au deposits. In environmental studies, Pb isotope ratios have been used to trace the sources of human lead ingestion.

5. B and Br Ratios

Boron concentrations and B isotope ratios have been used to delineate crustal assimilation processes in basalt lavas. Both the isotopes of B and Br in brines have been used to invoke differentiation of marine and crustal origins.

B. Matrix Elimination Using On-Line Column Preconcentration and Flow Injection Analysis for the Analysis of Brines

In the case of the analysis of solutions containing high dissolved solids concentrations, such as saline springs and soil and rock digestions (TDS >1 to 2%), both ICP-AES and ICP-MS are constrained due to several interference processes. In a high salt matrix the high concentrations of Na, K, Ca, Mg, and Cl, combined with the very low trace transition metal concentrations, make direct analysis by plasma spectrometry problematic. As discussed previously, in ICP-MS the determination of low trace metal concentrations, in the presence of high concentrations of concomitants, is often mitigated by a wide range of interference effects. Most of these effects can be attributed to phenomena occurring in the interface region between the ICP and the primary and secondary skimmer of the quadrupole mass spectrometer. The presence of high salt causes orifice blockage, resulting in a variable change of sensitivity. The introduction of solutions containing salt concentrations >1% into an ICP-AES results in interferences in the sample transport system and in the plasma. This phenomenon has an adverse effect on detection limits and analytical precision. Transport effects and nebulizer blockage can be minimized by using high salt nebulizers specifically designed for high dissolved solids samples.[21,22] The interferences in the plasma are attributed to high concentrations of easily ionized elements (Na, K, Li, Ca, Mg) that distort the normal distribution of excited ion and atom species in the plasma zone used for multielement analysis.[39,40]

As a result of these shortcomings, there are essentially two approaches when analyzing samples containing high dissolved solids for trace element concentrations: dilution and/or matrix separation. In ICP-AES little can be achieved by sample dilution because the detection limits are not sufficient to allow meaningful measurement of indigenous concentration levels of trace elements.

Preconcentration and separation techniques for ICP-AES and -MS were recently reviewed by Horvath and co-workers.[41] In this publication the current status of these techniques are described in great detail. One of the most popular preconcentration techniques for the analysis of environmental materials uses ammonium pyrrolidine dithiocarbamate (APDC) to complex the trace elements followed by extraction into methyl isobutyl ketone (MIBK). This approach has several disadvantages. Concentration factors conveniently attainable by the APDC-MIBK technique (20- to 30-fold) are insufficient for the determination of trace transition metals in most natural waters. Also, the solvent extraction approach is time consuming and increases the potential for contamination. Other chemical preconcentration procedures such as coprecipitation have similar potential problems.

Both in ICP-AES and ICP-MS the matrix can be excluded and the analytes of interest concentrated using on-line preconcentration columns containing immobilized (adsorbed or chemically bonded) chelates. Chelex 100, a commercial chelating resin, has been used for the isolation and up to 100-fold concentration of heavy trace metals from seawaters.[42-44] According to the proposed procedure alkali and alkali earth elements were eluted completely from the resin with 1 *M* ammonium acetate. The resin-sequestered trace metals were then eluted with 2.5 *M* nitric acid. The simplicity of this procedure encouraged numerous analysts to apply the technique to the determination of trace metals in different types of natural water. However, significant tailing of the elution curves and recovery deficiencies for several trace transition metals were observed.[44] Volume changes of the resin were also reported when it was converted from the NH_4^+ form into the H^+ form, which resulted in erratic column flow rates. Van Berkel and colleagues[44] made a fresh reexamination of Chelex 100 for off-line preenrichment of heavy metals (Cd, Co, Cu, Mn, Pb, and Zn) from seawater and analysis by ICP-AES. They concluded that provided pH, column washing, and quantity of resin are critically controlled, quantitative recoveries from seawater can be obtained.

Berman et al.[45] and Sturgeon and co-workers[46,47] developed a new and more efficient method involving complexation of the metal ions with immobilized 8-hydroxyquinoline (I-8-HOQ) on C18 chemically bonded silica gel. Subsequently, this technique was used by Watanabe and co-workers[48] for ICP-AES. A concentration factor of 200 was obtained.

Recently, several workers described the adaption of these off-line methodologies for the on-line separation and preconcentration of trace metals using flow injection analysis (FIA).[23,29] The application of these techniques for trace metal analysis of seawater using a microcolumn and FIA was described by a number of authors.[23,29,49–52] Hirata et al.[51] and Hartenstein et al.[50] made an evaluation of chelating resins, the former using Muroumac A-1 (MA-1), the latter Chelex 100. Hirata et al. concluded that acidic conditions for MA-1 as opposed to high pH operation for Chelex has several advantages: in the latter numerous ions are unstable. Nakashima et al.[52] described the adaption of Sturgeon's off-line methodology for the on-line separation and preconcentration of trace metals in seawater using a microcolumn of I-8-HOQ and determination using GFAAS. The recoveries for the heavy metals were approximately 90%. Recently, analytical protocols have been developed for the analysis of high dissolved solids solutions (seawater) using FIA and column-enrichment techniques. Part per trillion (pg/g) trace metal concentrations in seawater have been determined by ICP-MS with preconcentration and matrix exclusion.[49]

According to Tyson[29] and Fang,[23] FIA is an efficient method of sample manipulation where gas-liquid, liquid-liquid, solid-liquid transfer and even more complicated on-line sample treatments can be performed. However, it is evident that the acceptance for routine preconcentration techniques using ICP-AES and ICP-MS depends on the development of fully automated on-line flow injection sample transport systems.

C. Speciation

The combination of liquid chromatography with ICP-AES and ICP-MS can be used for the determination of the form of the metal. There is little doubt that there is a growing interest in the speciation of metals in environmental materials. Metal speciation in marine sediments, organisms and waters has been determined using on-line chromatographic FIA systems.[29,34,42,53–57] However, such column devices are not generally commercially available and are rarely integrated into the spectrometric instrument system.

In this technique, effluent is automatically injected into an ICP-MS, which acts as a detector. McLoed[56] reported the use of activated alumina as a novel material for cation and anion separation and speciation depending on pH. The oxidation states of Cr (Cr^{3+} and Cr^{6+}) were separated by this procedure and measured using ICP-AES.

Liu and Ingle[55] used two columns in series, the first Chelex 100, the second a macroporous anion exchange resin (AG MP-1) for the study of the speciation of Cu, Cd, and Zn in natural water. Three sample fractions were collected — the first was a fraction not retained by either column (considered to be inert or positively charged complexes or metal associated with large colloidal particles). The second fraction retained by the anion exchange column (negatively charged species, including humic acid complexes) and the third fraction, retained on the Chelex 100 column, consisted of labile metal complexes.

The application of liquid chromatography (LC) and ICP-AES and -MS was reviewed within the framework of a broader review on LC-metal speciation by Robards and co-workers.[57] Beauchemin and co-workers[53,54] and others have demonstrated that in-column chemical reactions and hyphenated HPLC-ICP-MS has the potential of producing quantitative data on speciation. The speciation of Cr, As, and Sn in environmental materials has been determined in a variety of substrates using column enrichment and ICP-MS.

VII. WATER QUALITY APPLICATIONS

The determination of trace metals in natural and polluted waters to assess environmental water quality depends on the ability to make measurements at indigenous concentration levels (i.e., milligrams per liter and lower levels). The use of ICP-MS provides an ideal measurement technique, especially at ultratrace levels.

A. Sampling

The quality and representativeness of a water sample is directly affected by the sampling procedure utilized. The significance and interpretation of results is dependent on the integrity of the sample and how well it represents the original population sampled. The degree of representativeness is directly related to the homogeneity of the population sampled, the techniques for collection of the sample, and the magnitude of the individual sample size.

The strategy used for investigating the chemical quality in rivers and streams usually involves collecting a single sample or a series of samples simultaneously that are representative of the entire flow at the sampling location for that specific instant in time. In addition, frequent collections over a fixed period of time may be used to define transient changes in concentrations of the constituents being measured. Vertical and horizontal stratification dictates that many subsamples be collected at prescribed locations either across channel, at depth, or both, followed by compositing, to obtain a single sample representative of the sampling location.

The hydrodynamic factors that result in substantial mixing of rivers and streams are much less significant in groundwater systems, resulting in more complex chemical distributions. Therefore, because of the cost and difficulty in sampling groundwater systems, sampling strategies are more complex and often more difficult to interpret.

B. Sample Preparation

Samples must be filtered in the field to remove suspended particulate matter. Precleaned membrane filters are used for sample filtration into precleaned inert containers such as polytetrafluoroethane or polyethylene bottles. Preservation is accomplished by adding a sufficient quantity of ultra-high-purity acid to lower the pH to <2. This precludes precipitation from occurring during transport to the laboratory and inhibits adsorption of metals to active sites on the walls of the sample bottle. Preservation acids must be contamination free and nitric acid is recommended to avoid interferences from molecular ions, such as chloride species.

C. Analysis

The determination of multiple trace elements is usually performed directly on the filtered water samples as received in the laboratory. Depending on the specific elements to be determined and the concentration levels expected, USN or preconcentration steps may be required prior to analysis. However, one of the most desirable characteristics of ICP-MS is its high inherent sensitivity, resulting in detection limits rivaling those attainable in the single element mode by GFAAS (Table 1). This high sensitivity precludes the need for preconcentration in most water analysis situations. Internal standard elements are often added to both samples and standards to improve the stability and accuracy of results. Specialized techniques such as standard additions or isotope dilution may be employed to achieve specific analysis objectives.

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