Atomic Spectroscopy

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Review Contents

Atomic spectrometry remains one of the most powerful methods for the determination of the elements and their compounds in a wide variety of types of samples and in widely differing concentrations. Innovation in the optical methods atomic absorption, atomic fluorescence, and atomic emission spectrometry mainly with plasma sources as well as in the use of the same sources as ion sources for elemental mass spectrometry continued to be discussed worldwide in well-known international conferences such as the Colloquium Spectroscopicum Internationale held in Antwerp, Belgium, in 2005, the Winter Conference on Plasma Spectrochemistry in Fort Lauderdale, FL, in 2004, the European Winter Conference on Plasma Spectrochemistry, held in Budapest, Hungary, in 2005, and the annual FACCS and PitCon Meetings in the United States. The results communicated are the best proof that for elemental determination and for speciation work through hyphenation with chromatography atomic spectrometry is a very strong tool, as discussed, for example, in ref *1*. Another trend in atomic spectrometry certainly is the increased use of chemometric methods, as discussed in ref *2*. In this biannual review, papers published in the journals *Analytical Chemistry, Analytica Chimica*

Acta, Analytical and Bioanalytical Chemistry, Applied Spectroscopy, International Journal of Environmental Analytical Chemistry, Journal of Analytical Atomic Spectrometry, in which the regularly occurring Atomic Spectrometry Reviews for selected fields are a prominent feature, Journal of Environmental Monitoring, Microchemical Journal, Microchimica Acta, Spectrochimica Acta, Part B, and some other special journals as indicated in the respective chapters have been considered. The limited selection is determined by the volume allowed for the review, so that more trends than complete covering of the literature have been aimed at. These trends will subsequently be discussed for the different optical and mass spectrometric methods. It further is to be mentioned that the new developments in atomic spectrometry discussed here also have been taken up in the second edition of the monograph *Analytical Atomic Spectrometry with Flames and Plasma Sources,* published in 2005 (*3*).

ATOMIC ABSORPTION SPECTROMETRY

Flame Atomic Absorption Spectrometry. Though a standard method since the 1960s, there is still considerable innovation especially with respect to sample introduction. through the use of high-efficiency nebulization systems such as thermal spray after on-line preconcentration; for example, Cd can be determined down to the microgram per liter level (*4*). Here a large variety of preconcentration techniques, such as C18 columns or fullerenes (*5*), can be used. Even subcritical liquid carbon dioxide can be used as carrier in combination with a gas pressure pump (*6*). Through the use of small CCD spectrometers, flame AAS can be really be made very compact, as required for field use and capable, for example, of determining Ca and Mg in water (*7*).

Diode Laser Atomic Absorption Spectrometry. Semiconductor laser diodes have been recognized to be very useful as primary radiation sources for AAS. They are low-cost versus hollow cathodes and make use of a monochromator superfluous, thus simplifying the instrumentation considerably. As shown in a review, laser diodes can be used successfully when AAS is used for element-specific detection, as well as for performing Doppler-free spectroscopy and for including background correction to wavelength-tuning of the diode-emitted line radiation (*8*). However, the general breakthrough is hampered by the lack of diodes for the important UV wavelength area where most metals have their resonant wavelengths. Despite this, applications of diode laser graphite furnace AAS, where femtogram detection limits are realized, e.g., by using the double modulation technique (*9*), and sub-parts-per-quadrillion graphite furnace AAS based on laser mixing (*10*) have been described.

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Continuum Source Atomic Absorption Spectrometry. The monoelement character of atomic absorption spectrometry and the need to make use of many different hollow cathode lamps when the variety of analytes is large can be circumvented by the use of continuum sources as primary sources in combination with high-resolution spectrometry, enabling it to isolate narrow-bandwidth primary radiation, necessary to make full use of the high power of detection of AAS. This way, which has been followed through decades in various research groups, now has led to commercial instrumentation and a very practicable method of analysis, as shown by both the theory and practice in a monograph by the ISAS group in Berlin and Welz (*11*). The basics of the method, as shown in ref *12* go back to Fraunhofer. The primary source and the atomizer can even be the same tungsten filament source, and then with a CCD spectrometer, detection limits in the picogram range for simultaneous determinations of many metals can be realized. A xenon or deuterium lamp is used as primary source, and then with a tungsten coil atomizer, Cd, Zn, Cu, Yb, Sr, and Co can be determined with detection limits of 8, 40, 1, 4, 1, and 4 ng/mL, respectively, when 25-μL sample liquid aliquots are used (*13*). With a graphite furnace atomizer, Th could be determined in coal with the use of Ru as matrix modifier with a detection limit of 0.01 μg/g (*14*), and background correction was easy as no separate D_2 lamp is necessary. Also, for flame AAS, the approach is very valuable, as demonstrated by the determination of S in wine (*15*).

On-Line Preconcentration. To enhance the power of detection, especially of flame AAS methods, on-line preconcentration techniques are very valuable and their development is a continued field of innovation. Here advanced principles such as cloud point extraction in the presence of electrolyte, as shown for the case of Cd (*16*) or Sn (*17*), are very valuable. Metal ion preconcentration for flame AAS can be realized by reagentless coacervate phase separation–extraction into lamellar vesicles as shown for the case of Cd and Zn in natural waters (*18*). Through automated sequential injection and separations on microcolumns, metal fractionation schemes for environmental solid samples can be realized (*19*). Also, continuous ultrasound-assisted extraction from vegetable samples coupled to flow injection flame AAS was shown to be very useful for the determination of Cd (*20*). A further useful way for pre-enrichment makes use of the deposition of complexes on the inner walls of a knotted reactor, as shown for the determination of As in seawater by graphite furnace AAS using the formation of As(III)–pyrrolidine dithiocarbamate complexes (*21*). Ion-pair adsorption can also be used as shown for the case of Pd (*22*), as well as flow injection, as shown for Pt (*23*). Octadecyl immobilized surfaces for precipitate collection with a renewable microcolumn in a lab-on-a-valve coupled to graphite furnace AAS for the determination of Cd was described (*24*).

Graphite Furnace Atomic Absorption Methodology. For graphite furnace AAS, many basic studies are still reported. In the standard graphite furnace, phenomena on a platform for example, require in-depth studies, as reported by Castro et al. (*25*), who performed X-ray spectrometric and electron microprobe studies as well as IR measurements of condensed-phase zirconium species produced during the evaporation. The transversally heated furnace, just as it enables isothermic vaporization, is the subject of many studies. Through shadow spectral imaging of absorbing layers, the dynamics of formation and dissipation of analyte layers could be studied for the case of transversally heated furnaces with and without platform and the effect of internal gas flows studied both for atomic (*26*) and molecular (*27*) species. In various papers, Katskov et al. described the usefulness of a transversally heated filter furnace atomizer, for example, for the determination of Cd and Pb in oil (*28*) and for the determination of Pb and Cd in blood (*29*). For enhancing the power of detection of graphite furnace AAS, electrochemical separation in a microcell (*30*) or electrostatic deposition on a platform in a graphite furnace AAS (*31*) has been described as useful.

For graphite furnace AAS, the use of thermochemically acting substances under the name of "matrix modifiers" remains an important field of research and analytical method development. This is reflected by a review by Volynsky (*32*) on the efficacy of Pt group metal modifiers in electrothermal AAS. Typical examples are the use of Pd as chemical modifier for the stabilization of volatile Ni and V compounds in crude oil analysis (*33*) or the use of W compounds in the determination of Pb, Cr, Mn, and Zn in slurries of botanical and biological samples (*34*).

A further important application of graphite furnace AAS is the possibility of direct solids sampling. This has been shown for the direct determination of Hg in soils (*35*). An interesting approach to studying the binding forms of Hg in biological matrixes is the use of thermolysis coupled with AAS (*36*). In direct solids analysis, background correction as done with Zeeman AAS is most important as shown for direct trace determinations in ZrO_2 powders (*37*).

Vapor Generation Techniques. For Hg, much research still is done on the refinement and use of the cold vapor technique for well-defined applications mainly in environmental health studies. A novel vapor generation system has been described by Lalor et al. (*38*). In the case of biological samples, digestion with tetramethylammonium hydroxide has been shown to be powerful by Barbosa et al. (*39*). For the determination of methylmercury electrothermal AAS, using headspace single-drop microextraction with in situ reduction with $NaBH_4$ has been shown to be a viable way as well (*40*).

In the field of hydride generation, many studies have been reported. For the study of Se species, for example, ion-pairing liquid chromatography-microwave-assisted hydride generation-atomic fluorescence spectrometry has been described (*41*). For Sb, preconcentration of the stibine in a quartz flame atomizer has been proposed (*42*). For electrothermal trapping, the use of a Mo foil strip electrothermal device (*43*) or collection in the cavity in a graphite rod (*44*) have been described. Further, the use of radiometric methods for the study of the efficiency of electrochemical hydride generation is interesting (*45*). Also, for the less conventional volatile hydride-forming elements, progress has been realized. For the determination of Pb, flow injection using tetraborate immobilized on an anion-exchange resin has been reported (*46*).

Much progress has been made in the study of volatile compound formation for a series of metals. For the noble methods, the mechanisms of volatile compound formation in the case of organoboron compounds have been studied especially in the Sturgeon group (see, e.g., ref *47*). For Au, trapping in heated graphite tubes was shown to be feasible for additional enhance-

ments in power of detection (*48*). Further, especially for Cd, studies have been undertaken and even multimode sample introduction systems for overcoming bubbling by using concentrated reagent solutions and the use of interference suppressing substance has been studied (*49*). Also, gas-phase sampling for the case of Cd determinations in polyethylene have been reported (*50*).

Element-Specific Detection for Speciation. Hydride generation has also been combined on-line with chromatographic studies for speciation work. Many results were published in a special issue on As in *Microchimica Acta*, as introduced by Mattusch and Wennrich (*51*). Further studies in this area were made for Se compound determinations (see, e.g., ref *52*). For this aim, more and more use is made of miniaturized systems. Here, automated AAS determinations of Hg with a lab-on-valve system (*53*) have been reported. A further novelty especially important for real sample analysis are advanced oxidation principles, such as the use of photooxidation in the speciation of organoarsenicals in seafood by hydride generation after cation-exchange chromatography (*54*). UV radiation can even be used for the generation of volatile species itself, as shown by Guo and Sturgeon (*55*) for many metals, and its efficiency can be increased by the use of TiO_2 as a photocatalyst (*56*).

Flame and furnace AAS themselves remain important detection methods in speciation. This has been shown for the case of the speciation of Cr compounds in industrial wastewater (*57*). In the case of flame AAS, the use of vesicular liquid coacervate extraction can be used to realize speciation in water samples (*58*), where as also for solids such as cements, selective extraction can be used (*59*). Also, for hyphenated techniques, lab-on-valve approaches have been shown to be useful (*60*).

ATOMIC EMISSION SPECTROMETRY

Arc and Spark Sources. Classical atomic emission spectrometry with arcs and sparks remains important for production and product control in industry. For the direct analysis of solids, however, laser-induced breakdown spectrometry is a valuable alternative, as shown for the case of aluminum alloys (*61*). Studies on dc plasmas included the use of oscillating magnetic fields for improving aerosol sample introduction (*62*). Dc plasmas also have been shown to be useful for the monitoring of alkali metals in gas flows, as required in the case of flue gases (*63*).

Microwave Plasma Sources. Many papers dealing with the description of a new type of microwave plasma discharge for spectrochemical analysis, their diagnostics, or their application for element-specific detection have been published (for a review, see, e.g., ref *64*).

Ivković et al. (*65*) reported on the measurement of electron number densities in microwave discharges and Christova et al. (*66*) on the measurement of electron number densities and gas temperatures as determined from line broadening measurements for the case of an argon surface wave sustained discharge at atmospheric pressure. Both for the surfatron and the "torche à injection axiale", such measurements for an argon plasma have been reported by Garcia et al. (*67*). From the same group, Alvarez et al. (*68*) reported on the radial distribution of gas temperatures and air species in a helium microwave discharge at atmospheric pressure. 2D Thompson scattering was used for high-resolution

electron number density and temperature mapping of a microwave plasma torch (*69*).

The microwave plasma according to Beenakker remained of use for elemental speciation work as reviewed by Wuilloud et al. (*70*) and this both when used as radiation source for OES and as ion source for mass spectrometry. Koch et al. (*71*) extended the use of this source to elements emitting their most sensitive lines in the near-infrared through the use of a suitable Echelle optical spectrometer. It further was shown that the GC-MIP-AED system is a powerful method for the determination of selenite in selenized yeast, when used after derivatization and solid-phase microextraction (*72*). Together with GC/MS, GC-AED has been shown to be useful for the evaluation of the byproducts of solar photo-Fenton degradation of methyl terbutyl ether in wastewater (*73*).

The microwave plasma torch continued to be used as a low-cost but robust alternative to the inductively coupled plasma (ICP) for work where dry analyte vapors were generated. Özmen et al. (*74*) used the torch for the determination of As both by chemical and by electrochemical hydride generation, and Matsumoto used a similar source for the simultaneous determination of Bi and Te in steels with the aid of hydride generation (*75*). Also, for the direct introduction of powders with an argon carrier, medium-power MIPs were shown to be useful (*76*). For powder analysis by MIP-OES, slurry sample introduction for the case of the determination of main and trace elements in biological samples was shown to be useful by Matysiewicz and Golik (*77*). In the case of biological substances, the use of tetramethylammonium hydroxide has been shown to be useful for the solubilization of major and trace elements in biological substances prior to their analysis with MIP-OES (*78*). Also, with high loads of ethanol a high-power nitrogen−oxygen mixed gas microwave-induced plasma has been shown to be useful (*79*). For determinations with aqueous solutions, however, the capacitively coupled plasma was shown to be more stable than the microwave-induced plasma. This was reflected by the use of the first for the determination of Al in water samples (*80*). Studies on the spectra of uranium in the case of a low-power MIP also have been reported (*81*). A miniaturized simultaneous microwave plasma torch spectrometer, being of use for elemental detection in chromatography, has been described as well (*82*).

Microplasmas. The development of dc and radio frequency (rf) as well as microwave microplasmas has attracted much attention in the last years. This has been shown by several reviews on microplasmas (*83−85*) in general and ultrahigh-frequency microplasmas (*86*), especially. For these sources, stability studies and diagnostic studies are very important, as shown for a low-power argon capacitively coupled plasma (*87*) Such source is ideally suitable for elemental detection in gas chromatography, as shown, for example, by Guchardi and Hauser (*88*). In the case of a microwave microplasma, the suitability of the source for OES for atomic and molecular species detection could be much improved by having it sorting freely in air out of the carrying substrate (*89*). The same and similar microplasmas of course also are potential ion sources for mass spectrometry, as shown by initial work of Miclea et al. (*90*).

Inductively Coupled Plasmas. A lot of innovation still was published on ICP-OES, for which Mermet in a perspective showed

that its development should not yet be considered as completed (*91*).

With respect to the excitation mechanisms, Chan and Hieftje (*92*) through matrix effects studies could show that charge transfer plays a role and that this is even state-selective (*93*). Studies on the selection of emission lines and plasma operating conditions for efficient internal standardization in ICP-OES have been performed (*94*). Further fundamental studies were made on the influence of the operating conditions and of the optical transmission on nonspectral matrix effects (*95*). As a special application, the use of diode laser-induced fluorescence spectrometry in an ICP for the determination of Li has been described. (*96*). A novel bottom-viewed ICP has been shown to be very useful for the determination of the alkali and earth alkaline elements (*97*).

Much work in ICP spectrometry is still done in the field of sample introduction. Jorabchi et al. (*98*) reported on the in situ visualization and characterization of aerosol droplets in an ICP for the case of a direct injection, high-efficiency (DIHEN) and a MicroFlow PFA nebulizer. For microconcentric nebulizers, Kahen et al. (*99*) proposed modified Nukijama-Tanasawa and Rizk-Lefebvre models to predict droplet sizes for microconcentric nebulizers with aqueous and organic solutions. Several of the now available types were evaluated with respect to their performance for ICP-AES and MS by Maestre et al. (*100*). In the case of radially measured analyte signal intensities, fundamental plasma parameters and nonspectral interferences for a direct injection nebulizer (Vulkan DIN) and a microconcentric glass nebulizer both coupled to a cyclonic spray chamber were studied. (*101*). Direct injection using a commercially available micronebulizer in a reduced length torch was also described (*102*). Microwave-assisted desolvation under the use of a TM_{010} cavity (*103*) was described, and studies on the mechanism of microwave-assisted desolvation were described (*104*). A new nebulizer with exchangeable aerosol generation mode was found useful to differentiate between the effects of the aerosol production and its following desolvation on the analytical performance of ICP-OES (*105*). Studies on the aerosol characterization and on the fundamental properties of aerosols generated by a flow-focusing pneumatic nebulizer were performed (*106*). Further, a new so-called pneumatic extension nozzle nebulizer with high efficiency and increased power of detection in ICP-OES was described (*107*).

On-line digestion and pre-enrichment methodology continues to be developed to improve the practical power of detection or the accuracy achievable with ICP-OES. On-line digestion for biological and environmental samples in a resistance heated flow digestion system has been described (*108*). For oil analysis, on-line emulsification has been shown to be very useful for enabling direct olive, sunflower, and corn oil analysis by ICP-OES (*109*). For speciation work, anion-exchange chromatography for Co was shown to enable both pre-enrichment and speciation (*110*). New developments in chromatography can very well be of use, also. Here the preconcentration for rare earths through preconcentration with multiwalled carbon nanotubes (*111*) is a nice example. For bioavailability studies, continuous-flow dialysis coupled to ICP-OES for the case of Ca, Mg, P, Fe, and Zn in milk has been applied (*112*). Further sedimentation field-flow fractionation coupled to ICP-OES has been shown to be a suitable approach for the size-based speciation for Al, Fe, and Ti in air particulates (*113*).

In the field of alternative sample introduction methodology for ICP-OES, many studies on the use of volatile compound formation, slurry sampling, and other direct solids sampling techniques and electrothermal vaporization have been reported.

For the hydride-forming elements, ICP-OES has the advantage over AAS to enable a simultaneous determination of many volatile hydride-forming elements such as As, Sb, Bi, Ge, Sn, Se, Te, and Hg, provided a careful optimization, as is possible by multivariate techniques (see, e.g., ref *114*), is done. The power of detection of vapor generation techniques can be increased by suitable trapping procedures. Here the use of lanthanum hydroxide has been shown to be effective in the determination of As and Sb in seawater by hydride generation ICP-OES after coprecipitation in a PTFE-knotted reactor (*115*). For Hg, on-line preconcentration by forming the APDC complexes and retaining them on the surface of hydrophobic PTFE turnings prior to reduction with $SnCl_2$ could be used successfully for determining Hg in digested urine, blood, and hair samples (*116*). Speciation by coupling chromatography to hydride generation ICP-OES also has been applied. Exemplarily, the use of capillary electrophoresis separations in the case of the As species (*117*) as well as their separation on yeast-immobilized columns prior to hydride generation (*118*) can be mentioned in this respect. Also, for other elements, volatile compound formation has been described. For the determination of I in milk, oxidation of dissolved ashes with hydrogen peroxide and ICP-OES could be applied (*119*). For the determination of nickel, volatile species could be formed in a flow system using the reaction of borohydride solutions with the acidified sample solutions (*120*), and for the determination of free and total sulfur dioxide in wines, vapor generation through acid addition in a flow system and ICP-OES using VUV lines was found to be useful (*121*).

Slurry nebulization remains an attractive way for the direct analysis of fine powders with ICP-OES. Wang et al. (*122*) here studied the stability of suspensions of aluminum nitride powders for which slurry nebulization ICP-OES is very useful. Also, for screening analyses of fly ash, slurry nebulization has been found to be feasible (*123*). Trace impurities in fine TiN powders are relevant for their use in ceramics production and could be well determined by ICP-OES using a V-groove Babington nebulizer (*124*). This also applied to trace determinations in cement, gypsum, and basic slag after adding emulsifiers and applying dispersion in an ultrasonic bath (*125*).

A most sensitive analysis can be performed by directly inserting the sample in the ICP, as was shown by the determination of Cd and Zn in nanoliter-volume aquatic organisms through rhenium cup in-torch vaporization (*126*). Laser ablation can be used for direct solids sampling, as shown by determinations in pharmaceutical tablets (*127*). Its effectiveness can be very much increased through the use of resonant laser radiation (*128*), and extremely low absolute detection limits can be achieved when performing in-torch laser ablation, as described in ref *129*.

Electrothermal vaporization has continued to be described both for enhancing the power of detection and for enabling direct solids sampling in ICP-OES. A key issue remains the transport of the analytes from the furnace unit to the radiation source, and transport studies were performed by Kantor et al. (*130*). An interesting analytical application described was the determination of P and S in environmental samples including the use of suitable

matrix modifiers for the case of water samples (*131*). As in ETV, the volatilization depends on the analyte species present; one easily can distinguish between species, as shown for a discrimination between boric acid and boron nitride (*132*). This also was shown for the case of V, the different species of which were preconcentrated and immobilized as thenoyltrifluoroacetonates on microcrystalline naphthalene prior to species-dependent volatilization. For direct solids digestion prior to on-line analysis, Hamier and Salin (*133*) described a continuously fed ohmically heated reactor. For the case of silicon carbide powders, it was shown that by ETV-ICP-OES reliable direct trace analyses could be performed (*134*) and that for Al a differentiation between its different species is possible (*135*). A direct determination of trace elements in human hair has been shown to be possible by using slurry sampling and PTFE as modifier in electrothermal vaporization ICP-OES (*136*), and direct solid sampling conductive heating for vaporization combined to ICP-OES could be shown to be of use for the direct determination of S in steel (*137*).

A further topic of continued studies in ICP-OES is the features of axial viewing versus radial viewing (*138*). In the treatment of the spectra, the features of wavelet smoothing have been studied (*139*), and as an alternative to spectrometers, the use of visible acoustooptic tunable filter hyperspectral imaging has been studied (*140*). The maturity of ICP-OES is well demonstrated by its use for the identification of metal concentration fluctuations in waste-to-energy plant flue gases (*141*).

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Developments in the field of elemental mass spectrometry are still driven by the increasing demand for high sample throughput, highest possible sensitivity, and precision combined with fast and preferably simultaneous multielemental detection capabilities. Remaining ionization source- and spectrometer-related shortcomings are still the major subjects of modern research. As a result, different mass spectrometric techniques in combination with various sample introduction techniques, as well as instrumental developments concerning time-of-flight, multicollector and sector field mass analyzers, were predominant focal points of the research conducted within the period covered by this review article, although most of the published material mainly deals with applications of inductively coupled plasma mass spectrometry (ICPMS). Different approaches for the introduction of liquids, through sample nebulization or in combination with chromatographic and electrophoretic separation techniques, were investigated. Most notably, the acceptance of laser ablation (LA) coupled to ICPMS as a technique for direct analysis of solid samples has increased substantially during the last two years. An ongoing activity on the development and application of collision and reaction cells for the specific removal or reduction of polyatomic ions was recognized, especially in the field of the analysis of biological material.

This section deals with new developments in ICPMS in the field of fundamental studies, instrumental developments, and applications. It should be mentioned that the selection of representative or significant papers was quite difficult, due to the increasing number of ICPMS publications. Therefore, only new applications, using new methodology, will be dealt with, since purely application papers are thoroughly treated in alternative review articles. In addition to the journals mentioned in the first section of this article, the following journals were considered for the selection of the papers: *Canadian Journal of Analytical Sciences and Spectroscopy*, *Journal of Chromatography A*, *Rapid Communications in Mass Spectrometry*, *Journal of the American Society for Mass Spectrometry*, *International Journal of Mass Spectrometry*, *European Journal of Mass Spectrometry*, and *TrAC−Trends in Analytical Chemistry*.

Very interesting review papers by Barnes and Hieftje (*142*) and Koppenaal et al. (*143*) discussed some of the relevant technologies that have been or could be applied to mass spectrometric ion detection. Although array detectors capable of determining the spatial distribution of particles have long existed, this technology has recently been applied to mass spectrometry for the simultaneous detection of multiple ions of differing mass-to-charge (m/z) values. When simultaneous detection is utilized in mass spectrometry, benefits such as improved detection limits and precision, reduced sample consumption and analysis time, and elimination of correlated noise sources are realized. In both articles, the authors classified different detector technologies, especially array detectors, according to detection method. The figures of merit of each system were discussed. High mass resolution and chemical resolution in a collision or dynamic reaction cell as powerful and versatile means to overcome spectral overlap was elucidated by Vanhaecke and Moens (*144*). The authors illustrated how the introduction of such cells has led to a substantial extension of the application range of ICPMS for isotope ratio applications, and in their opinion, high mass resolution is the most elegant and straightforward way to overcome the problem of spectral overlap. Offering the possibility to operate the MS at a higher mass resolution, while at the same time preserving the flat-topped or trapezoidal peak shape required for highly precise isotope ratio measurements, was a challenge for the manufacturers of ICPMS instrumentation. It was outlined how these apparently contradicting requirements can be fulfilled simultaneously, and an overview of the current situation was given. Chemical resolution in a collision or dynamic reaction cell is an alternative to high mass resolution for overcoming spectral overlap. Real-life examples were given to illustrate how this approach can also be used to advantage in isotope ratio work. Despite the greater flexibility and straightforwardness of high mass resolution, some situations were discussed where chemical resolution is to be preferred. Although LA-ICPMS is a highly accepted, widely used method for the determination of major, minor, and trace elements in solids, as well as isotope ratio measurements, it suffers from nonstoichiometric effects occurring during sampling, aerosol transport, vaporization, atomization, and ionization within the ICP, described as elemental fractionation. A review by Günther and Hattendorf (*145*) summarized recent developments in LA-ICPMS based on fundamental understanding of the LA process and particle formation but also pointed out the importance of the ICP and its operating conditions. Figures of merit and new trends in quantification were discussed in order to demonstrate the capabilities of this direct solid sampling technique. A few selected applications to underline why LA is a fast-expanding analytical technique were presented.

During the past few years, ICPMS has been increasingly used for precise and accurate determination of isotope ratios of long-

lived radionuclides at the trace and ultratrace level due to its excellent sensitivity, precision, and accuracy. At present, ICPMS and LA-ICPMS are applied as powerful analytical techniques in different fields such as the characterization of nuclear materials, in environmental monitoring and bioassay measurements, and in health control, geochemistry, and geochronology. Becker (146) published a review on the state of the art and the progress of ICPMS and LA-lCPMS for isotope ratio measurements of long-lived radionuclides in different sample types, especially in the before-mentioned predominant fields of application.

To gain an understanding of the function, toxicity, and distribution of trace elements, species-specific determination is of fundamental importance. For sensitive detection of compounds containing elements of interest, ICPMS is a popular method, and for identification of compounds via determination of molecular weight, electrospray ionization MS (ESI-MS) is gaining increasing use. ICPMS and ESI-MS, usually coupled to a separation technique such as chromatography or capillary electrophoresis, have already been applied to a large number of research problems in such diverse fields as environmental chemistry, nutritional science, and bioinorganic chemistry and were outlined in review articles by Hieftje et al. (147, 148). Furthermore, novel instrumentation, techniques, and strategies for ICPMS, microwave-induced plasma (MIP) mass spectrometry, and glow-discharge (GD) mass spectrometry, among others, were described. The use of ionization sources that provide tunable ionization, others that can be modulated between different sets of operating conditions, and others used in parallel were also examined.

One of the most accurate approaches to quantitative elemental determinations developed so far is the application of isotope dilution (ID) analysis. Critical reviews by Rodriguez-Gonzalez et al. (149) and Heumann (150) discussed the conditions under which ID-ICPMS is suitable as a routine method for trace element and element-speciation analysis. Recent developments in analytical techniques capable of providing information on the identity and quantity of heteroatom-containing biomolecules were critically discussed in a review by Szpunar (151). Particular attention was paid to the emerging areas of bioinorganic analysis including the following: (a) a comprehensive analysis of the entirety of metal and metalloid species within a cell or tissue type (metallomics), (b) the study of the part of the metallome involving the protein ligands (metalloproteomics), and (c) the use of a heteroelement, naturally present in a protein or introduced in a tag added by means of derivatization, for spotting and quantification of proteins (heteroatom-tagged proteomics). In the author's opinion, ICPMS, used as detector in chromatography and electrophoresis, and supported by ESI-MS and matrix-assisted laser desorbtion/ionization MS (MALDI-MS), appears as the most promising analytical technique for these emerging areas. Recent advances in ICPMS in biological speciation analysis including sensitive detection of nonmetals, especially of S and P, couplings to different separation techniques, LA-ICPMS detection of proteins in gel electrophoresis, and isotope dilution quantification of biomolecules were highlighted in this review.

Fundamental Studies. To evaluate the validity of data produced in spectrochemical analysis, Salin et al. (152) compared the results obtained by using four different calibration methods in ICPMS: external standards, standard additions, internal stan-

dards, and standard additions in combination with an internal standard. Y, Rh, Mg, Co, Cu, Ni, Ag, Tl, Mo, and Pb were analyzed in solutions of known composition with a 500 mg mL^{-1} Na matrix. Additionally, the Mg, Co, Y, Rh, and Pb signals were used as internal standards for the other elements in the same matrix. Severe drift effects were simulated by drastically altering the liquid sample uptake rate. The average errors for external standards varied from 23 to 41% while the average errors for internal standards ranged from 1 to 71%. The error for standard additions was 45%. The use of standard additions with an internal standard produced an average error of 0.7−5%, suggesting that this is a powerful calibration technique. Laborda et al. (153) investigated the quality of the quantitative results obtained from transient signals in HPLC−ICPMS and FI-ICPMS under multielement conditions, based on multiple-point calibration by simple and weighted linear regression, and double-point calibration. An uncertainty model, which includes the main sources of uncertainty, was developed to estimate peak area uncertainties and statistical weights used in weighted linear regression. The behavior of the ICPMS instrument was characterized in order to be considered in the model. Proper quantification by the three calibration methods was achieved when compared to reference materials. Relative expanded uncertainties ranged from 10 to 20% for concentrations around the LOQ to 5% for concentrations higher than 100 times the LOQ. A full uncertainty budget was used by Clough et al. (154) to compare the performance of species specific single and "approximate matching" double IDMS. Methylmercury, originating from two fish tissue reference materials, was separated from inorganic mercury by HPLC, which was coupled to MC-ICPMS via a cold vapor generation system for the measurement of isotope ratios. For each Certified Reference Material (CRM), the mass fraction of methylmercury determined by the two IDMS methods was not statistically different, within the limits of uncertainty, from the certified values. Double IDMS was found to be more precise than single IDMS when a full uncertainty budget was estimated; the converse applied when the method precision was estimated only by the standard deviation of replicate analysis. For single IDMS, the major uncertainty contribution was derived from the standard uncertainty of each analytical replicate. The between blend standard uncertainty was determined to be the major contributor to the expanded uncertainty for approximate matching double IDMS.

Different groups covered fundamental studies on liquid sample nebulization, aerosol generation, and comparison of various types of nebulizers. Yanes and Miller-Ihli (155) evaluated and compared four different low-flow parallel-path Mira Mist capillary electrophoresis (CE) nebulizers for the quantification of cobalamin species (vitamin B12) by CE-ICPMS. The nebulizer orientation as well as the effect of methanol on analytical response was the focus of the study. To characterize the nebulizer's performance, the signal response of a multielement solution containing elements with a variety of ionization potentials was used. The selection of elements with varying ionization energies and degrees of ionization was essential for a better understanding of observed increases in signal enhancement when methanol was used. The net result was that as much as a 30-fold increase in signal was observed for As and Mg when using a makeup solution of 20% methanol at a 15 μL min^{-1} flow rate, which is equivalent to a net volume of 3 μL

min⁻¹ pure methanol. Montaser and co-workers (*156*) investigated aerosol diagnostics data and analytical figures of merit for a demountable concentric nebulizer (DCN) in ICPMS, operating at conditions similar to a commercial pneumatic nebulizer but which is supposed to be "more easily fabricated and is considerably less expensive". The DCN was found to produce a better quality primary aerosol when using inner capillaries of smaller diameters. Under optimum conditions, detection limits, sensitivities, and precision for the DCN compared favorably with a commercially available cross-flow nebulizer. The accuracy and precision of the DCN in ICPMS measurements were demonstrated using two standard reference materials. In a similar study, the same group designed and evaluated a low-cost, demountable direct injection high-efficiency nebulizer (d-DIHEN), which not only reduces chances of accidental nebulizer tip meltdown but provides an adjustable solution capillary (*157*). Fundamental investigations to improve operational characteristics, aerosol properties, and analytical figures of merit in ICPMS were performed. Compared with the DIHEN, the d-DIHEN produces smaller droplets with narrower droplet distributions and lower mean droplet velocities, characteristics important for improved sample–plasma interaction. Sensitivity, detection limits, and precision are superior with the d-DIHEN compared to conventional nebulizer spray chamber arrangements and other direct injection nebulizers, especially at low solution uptake rates (<40 μL min⁻¹). Maestre et al. (*100*) reported on the characterization of the behavior of five pneumatic micronebulizers based on slightly different designs in ICP-OES and ICPMS. Two nebulizers were used as reference nebulizers, a high-efficiency nebulizer (HEN) and a micromist (MM). They were compared with a commercially available tetrafluoroethylene–perfluoroalkyl vinyl ether copolymer (PFA) nebulizer and with two new prototypes called the polymeric pneumatic concentric nebulizer (PMN) and the high-solids micronebulizer (HSM). Overall, the results indicated that the PFA and the HEN nebulizers provided the best results. These two nebulizers delivered a higher mass of analyte to the plasma and showed better sensities giving lower limits of detection than the PMN, HSM, and MM. Nebulizer design did not have a relevant effect on the recovery, which confirmed that the spray chamber plays an important role in terms of nonspectroscopic interferences. In combination with a heated spray chamber and a membrane desolvator, a HEN was used for liquid sample introduction in chemical reaction interface MS (CRIMS) by Jorabchi et al. (*158*). Compared to the conventional thermospray nebulizer operated at solvent flow rate of 1 mL min⁻¹, the HEN provided small droplets at lower flow rates, improving the desolvation and analyte transport efficiency. As a result, the sensitivity for carbon detection by CRIMS is improved by a factor of 4. The new arrangement offered an easy-to-use and robust interface, facilitating the availability of a variety of liquid chromatographic techniques to the CRIMS. Separation and detection of labeled peptides in a mixture of unlabeled biopolymers was illustrated at a solvent flow rate of 45 μL min⁻¹.

The efficiency of the formation of negative background and F⁻, Cl⁻, Br⁻, and I⁻ ions in ICP at temperatures ranging from 4000 to 9000 K was investigated by Pupyshev and Surikov (*159*) using thermodynamic simulation. The estimated total concentration of negative ions in ICP was found to be 4–5 orders of magnitude smaller than that of positive ions. The highest efficiency of negative ion formation should be observed for elements having high electron affinity, namely, Cl, F, Br, and I. However, the detection sensitivity in the negative ion detection mode may be increased slightly as compared with the positive ion detection mode only for fluorine in the temperature range 6000–7000 K. This was found to be in contradiction with experimental results and, in the authors' opinion, may be explained by the formation of negative ions behind the skimmer or smaller losses of negative ions in the ion beam at low ionic current.

Matrix effects during phosphorus determination with quadrupole ICPMS were studied by Kovacevic et al. (*160*). The influences of nitric acid and methanol on phosphorus determination were investigated using two different measuring methods at different plasma conditions: detection of phosphorus ions at m/z 31 and detection of phosphorus oxide ions at m/z 47. Nitric acid and methanol are shown to be the sources of polyatomic ions and therefore cause poorer detection limits. Better detection limits were achieved in such matrixes when phosphorus was detected as ³¹P⁺. The presence of methanol improves the system sensitivity toward phosphorus 7-fold; however, this positive effect is hindered by the high background signal due to carbon-based polyatomic ions.

Brenner and co-workers (*161*) evaluated the use of a Cu–Ni laminated sampler cone in ICPMS. The short-term sensitivities of this cone-type were about 30–40% lower, but Na-induced signal suppressions were distinctly smaller than in the case of the normal cone, resulting in superior long-term stability. Suppression was dependent on analyte mass and was considered to be mainly due to salt deposition on cones and not on shifts in ion–atom equilibrium. In the authors' opinion, the observed effects may be attributed to the smaller orifice diameter, resulting in a less prominent salt barrier, and it was concluded that the Cu–Ni laminated sampler cone is more robust than a conventional cone, especially for the analysis of geoenvironmental samples.

Spatial profiling of analyte signal intensities in ICPMS were determined by Holliday and Beauchemin (*162*). Axial profiling, which provided information on the energy and time needed to form a given ion, was found to be helpful when establishing the optimal operating conditions and can be used to assess whether a matrix induces earlier desolvation. The authors concluded that radial profiling can provide valuable insight into the predominant ionization mechanisms in the ICP, which can facilitate the selection of an efficient internal standard.

For LA-ICPMS analysis, the temporal intensity distribution was modeled by Gackle and Merten (*163*, *164*), comparing single-shot, scanning, and drilling modes. Signal equations basing on dispersion functions describing the measured temporal intensity distribution were developed. Variable ablation rates due to varying focusing conditions typical for drilling mode and due to the changes of physical and chemical properties in inhomogeneous samples as typically investigated in scanning mode were considered. The established model accounts for intermixing of the sample aerosol within the sampling chamber, the influence of transport in a cylindrical transport channel, and the fact that normally not the entire vapor generated and transported to the ICP can be observed. An algorithm was proposed by the authors providing the relative temporal distribution of any analyte with significantly higher temporal resolution than the measured

temporal intensity distribution itself. Furthermore, usage of dispersion functions for investigation of a given transport system, for explanation of typical signal deviations, for the proof of homogeneous regions in a heterogeneous sample, for examination of changes in ablation rate, and for investigation of fractionation effects was shown.

Coedo et al. (165) described a study designed to determine the possibility of using a dried aerosol solution for calibration in LA-ICPMS. The relative sensitivities of tested materials mobilized by laser ablation and by aqueous nebulization were established, and the experimentally determined relative sensitivity factors (RSFs, desolvated aerosol response/ablated solid response) were used in conjunction with aqueous calibration for the analysis of solid steel samples. The RSFs were close to 1 for the analytes Cr, Ni, Co, V, and W, about 1.3 for Mo, and 1.7 for As, P, and Mn. The analytical results were found to be in good agreement with the certified values of standard reference material, indicating that the applicability of dried aerosol solutions could be a good alternative calibration system for LA sampling. Russo and co-workers (166) compared the analytical performance of scanning versus single-spot sampling strategies in LA-ICPMS, employing a 213-nm laser system. A geological rock (Tuff) was quantitatively analyzed based on glass standard reference materials. Laser ablation data were compared to ICPMS analysis of the dissolved samples. The scan strategy (50 μm s^{-1}) produced a flat, steady temporal ICPMS response whereas the single-spot strategy produced a signal that decayed with time (after 60 s). Single-spot sampling provided better accuracy and precision than the scan strategy when the first 15 s of the sampling time was eliminated from the data analysis. In addition, the single-spot strategy was found to show less matrix dependence among the four glass standards. Additional studies were performed by the same group, focusing on the comparison of femtosecond and nanosecond lasers for ablating brass alloys (167, 168). The ablated aerosol vapor was collected on silicon substrates for particle size measurements or sent into an ICPMS. The diameters and size distribution of particulates were measured from scanning electron microscope (SEM) images of the collected ablated aerosol. SEM measurements showed that particles ablated using nanosecond pulses were single spherical entities ranging in diameter from several micrometers to several hundred nanometers. Primary particles ablated using femtosecond ablation were similar to 100 nm in diameter but formed large agglomerates. ICPMS showed enhanced signal intensity and stability using femtosecond compared to nanosecond LA. Furthermore, Russo et al. pointed out that double-pulse LA can be used to improve internal (temporal relative standard deviation, TRSD) and external (RSD) precision (169). In such a case, the first laser pulse was used to ablate a large quantity of mass from the sample surface. The second pulse was applied with a variable time delay after the first pulse to break the ablated mass into a finer aerosol, which was more readily transported to and digested in the ICPMS. A factor of 2 improvement in TRSD and factor of 5 in RSD were demonstrated. An in-line cascade impactor was used as a low-pass filter to study the effects of particles on ICPMS performance (170). The TRSD, which represents the short-term internal precision during repetitive ablation, was improved from 20 to 4% by removing large particles ablated from brass alloys. External precision for spot-to-spot measurements on a bulk sample was improved to ~2%. The ablated aerosol chemistry was particle size dependent: smaller particles were zinc rich while larger particles were copper rich.

In a similar study, Kuhn and Günther investigated elemental fractionation effects in LA-ICPMS (171). Laser-generated aerosols from glass samples were filter collected before entering the ICP to study their total and particle size-dependent composition. Furthermore, elemental concentrations in different particle size fractions on filters were compared with their response measured in the ICP. Results showed an enrichment of certain elements such as Cu, Zn, Ag, Tl, Pb, and Bi of up to 90% relative to Ca within the small particle size fraction of an aerosol in comparison with the total composition of the aerosol. The same elements were depleted in large aerosol particles measured from deposited particles within the ablation cell. However, the total transportable aerosols produced using different laser wavelengths (193/266 nm), and gas environments (He/Ar), which were also filtered and digested, showed no significant deviation in their overall stoichiometry from the original sample (except Be, Fe, and Cd for all lasers and gases) within the uncertainty of the measurements. Therefore, the composition of filter-collected aerosol of glass samples indicated that the elemental fractionation in LA-ICPMS, detected at the beginning of a 266-nm single hole ablation, is predominantly caused by incomplete vaporization of large particles within the ICP and is not dominated by nonstoichiometric ablation of the glass. The modification of the particle size distribution of laser-produced aerosols has been studied by Vaculovic et al. (172) based on heating a generated aerosol by means of an electro-thermal vaporizer (ETV) installed between an ablation cell and an ICP torch. The aim of this study was (a) to modify the particle size distribution toward reduced diameters, (b) to determine the elemental dependence of the vaporization process, and (c) to determine element-dependent laser-induced phase separation into different particle sizes. It was observed that the vaporization depended on melting points of metals, and the particle size distribution could be reduced for low-melting elements. Kuhn and Günther (173) evaluated the agglomeration state of nanosecond LA-generated aerosol particles entering the ICP. Such aerosols, generated under different ablation conditions, were collected on membrane filters. The particles and agglomerates were then visualized using SEM imaging. To determine variations between different sample matrixes, opaque and transparent glass, CaF$_2$, and brass samples were ablated using two different laser wavelengths, 193 and 266 nm. This study showed that the condensed nanoparticles (similar to 10 nm in diameter) formed by laser ablation reach the ICP as micrometer-sized agglomerates; this is apparent from filters that contain only a few well-separated particles and particle agglomerates. Ablation experiments on different metals and nonmetals show that the structure of the agglomerates is matrix-dependent. Laser aerosols generated from silicates and metals form linear agglomerates whereas particle agglomerates of ablated CaF$_2$ have cottonlike structures. Among other conditions, this study showed that the absorption characteristics of the sample and the laser wavelength determine the production of micrometer-sized spherical particles formed by liquid droplet ejection.

To study direct in torch laser ablation, an ICPMS was modified by Tanner and Günther (*174*). In this setup, a sample was placed at the tip of the injector tube where the ablation took place. The laser beam was focused orthogonally through the ICP torch onto the sample surface. The ablated material caused transient signals of a few milliseconds in duration in the quadrupole ICPMS system. The setup allows comparison with conventional LA-ICPMS where the sample is placed in an ablation cell and the aerosol is transferred to the ICP via plastic tubing. The same number of counts per laser shot were measured for both sample introduction systems. However, the limit of detection (LOD) for uranium in glass was improved by 2 orders of magnitude, which is caused by the significantly reduced dispersion of the aerosol entering the plasma.

Bleiner et al. (*175*) developed a method to overcome pulse mixing and signal tailing in LA-ICPMS, which are limiting depth profiling resolution during the aerosol transport. Raw signal processing procedures were developed for the minimization of shape line dispersion, deconvolution of pulse mixing, and more appropriate assessment of the profiles of implanted Si crystals. Shape line dispersion could be corrected for by determining the signal warning constant and implementing this information for a nonaffine alibi transformation of the LA-ICPMS signal traces. Pulse mixing deconvolution was attained with an algorithm that considered accumulated signal intensity due to pulse-on-pulse stacking, i.e., the latest pulse on top of all antecedent individual pulses' exponential tails proportionally. To minimize the dead volume in large cells for LA-ICPMS, thus improving the aerosol entrainment characteristics, a rotating gas inlet nozzle has been used by Bleiner and Altorfer (*176*). This allowed a wider volume to be swept than with the traditional static inlet nozzle approach. Therefore, sensitivity combined with site-to-site repeatability was found to improve by a factor of 2, together with minimization of aerosol loss within the cell and signal dispersion.

In an interesting study by Simpson et al. (*177*), octopole collision cell ICPMS was compared with double-focusing sector field ICPMS and an ICP-OES. Double-matched IDMS was employed for ICPMS techniques, and an exact matching bracketing technique using Sc as an internal standard was used for ICP-OES analysis. Medium-resolution mode was utilized for double-focusing sector field ICPMS analysis to resolve the dominant interferences on the $^{44}Ca/^{42}Ca$ isotope pair. H_2 reaction gas was employed to chemically resolve a number of polyatomic interferences predominantly through charge-transfer reactions in the octopole collision cell. Comparison data presented for NIST human serum analysis from all three techniques demonstrate highest accuracy (99.6%) and lowest uncertainty (1.1%) for octopole collision cell ICPMS. ICP-OES produced comparably accurate data and low uncertainties. The much higher total expanded uncertainties for double-focusing sector field ICPMS compared with octopole collision cell data were explained by lower precision on the measurement of the $^{44}Ca/^{42}Ca$ isotope ratio.

Spezia et al. compared quadrupole versus sector field ICPMS techniques for the determination of Pt in human urine (*178*). The two procedures were validated, and their expanded uncertainties were evaluated. The LODs, calculated by taking into account dilution factors, were 0.18 and 0.05 ng L^{-1} Pt for the quadrupole and sector field procedures, respectively. The median value

observed was 4.13 ng L^{-1} Pt in urine, while the relative combined uncertainty at 5 ng L^{-1} was below 20% with both ICPMS techniques. These data were in good agreement with those reported in the literature for similar studies.

Instrumental Developments and Applications. Rodushkin et al. (*179*) demonstrated that for many analytes the capabilities of ICP−SFMS significantly improves by virtue of enhanced sensitivity and reduction of polyatomic interferences if methane is added to the Ar plasma gas. A total of 100 isotopes of 70 elements were studied, and the parameters under consideration included instrumental background, analyte sensitivity, precision, and formation of spectral interferences as functions of methane flow. In contrast to quadrupole-based ICPMS, these gains in instrumental performance do not compromise multielement capabilities given that the amount of methane is carefully optimized. The accuracy of the results for the determination of 50 elements in water samples was evaluated using certified reference materials.

The geometry of the ICP induction coil is known to influence the ICPMS secondary discharge. Jorabchi and Montaser (*180*) therefore proposed several coil geometries for helium ICPMS using a crystal-controlled 40-MHz generator. The effectiveness of the proposed geometries in controlling the plasma potential was investigated by the Langmuir probe method and ion kinetic energy (IKE) measurements. The influence of rf power on plasma gas temperature T_g was investigated through measurements of ICPMS interface pressure and IKEs for new and conventional coil geometries. The authors found that trends in plasma potential and T_g are well correlated, revealing that T_g is elevated at high power levels mainly as a consequence of the interaction between the ICP and the grounded sampler. The reduction of the secondary discharge results in lower T_g values, necessitating the use of a membrane desolvator to remove water-related polyatomic interferences.

Alvarez-Llamas et al. (*181*) reported on the development and evaluation of an alternative CE−ICPMS interface based on volatile species generation (VSG) and compared this unit to conventional sample introduction systems via nebulization, using Cd−metallothionein species (MTs) in rabbit liver as a model. The separated Cd compounds were transformed into volatile species by $NaBH_4$ at the exit of the capillary and on-line detected by ICPMS. Detection limits for Cd−MTs turned out to be almost 1 order of magnitude better than those derived from using a conventional Babington nebulizer-based interface. Compared to a Micro Mist-based interface, detection limits were similar, but the observed peak height was eight times higher using the VSG interface, indicating the enhanced analyte transport efficiency derived from VSG sample introduction systems. In a similar approach, Richardson et al. (*182*) applied a developed hyphenated CE-HG-ICPMS technique to the separation and quantitation of common arsenic species. Three concentric tube designs were investigated, allowing alleviation of back pressure commonly observed in CE-HG-ICPMS. Quantitative analysis of As(III), As(V), monomethylarsonic acid, and dimethylarsinic acid was achieved. Optimization of CE separation and hydride generation conditions were performed, and the detection limits obtained for the arsenic species were less than 40 ng L^{-1} with a total analysis time of 9 min. Finally, the interface

was used for speciation analysis of arsenic in river and tap water samples.

An interesting approach to rapid elemental speciation was considered by Song and co-workers (183) by interfacing a microfluidic chip-based electrophoresis system with ICPMS. The chip had an 8-cm-long, 100-μm-wide, and 20-μm-deep separation channel etched in a serpentine pattern on the glass base plate. Hydrodynamic sample injection was accomplished by a flow injection mode through an externally controlled gravity pump and a three-way valve. With application of an electric field up to 500 V cm^{-1}, species such as Cr(III) and Cr(VI) and Cu(II) and Cu(EDTA)$^{2-}$ were separated in acidic solution within 30 s. The separation of As(III) and As(V) was achieved in an alkaline buffer system by using hydrodynamically modified electroosmotic flow to control the fluid. The quantification of these species was also reported.

Hann et al. (184) presented a novel separation method for highly sensitive speciation of cancerostatic platinum compounds (cisplatin, monoaquacisplatin, diaquacisplatin, carboplatin, oxaliplatin) in biological and environmental samples by HPLC−ICPMS. Chromatographic separation was achieved on pentafluorophenyl-propyl-functionalized silica gel. For cisplatin, carboplatin, and oxaliplatin, limits of detection of 0.09, 0.10, and 0.15 μg L^{-1}, respectively, were calculated at m/z 194, using aqueous standard solutions. The method was utilized for model experiments studying the stability of carboplatin and oxaliplatin at different chloride concentrations simulating wastewater and surface water conditions. It was found that a high fraction of carboplatin is stable in ultrapure water and in solutions containing 1.5 mol L^{-1} Cl$^-$, whereas oxaliplatin degradation was increased by increasing the chloride concentration. To support the assessment of oxaliplatin ecotoxicology, the method was tested for speciation of patient urine. The urine sample contained more than 17 different reaction products, which demonstrates the extensive biotransformation of the compound. In a second step of the study, the method was successfully evaluated for monitoring cancerostatic platinum compounds in hospital wastewater.

For the on-line removal of metal ions from the blank solution and an improvement of the detection limits in ICPMS, Hasan et al. (185) employed electrochemically modulated liquid chromatography (EMLC). The EMLC column contained glassy carbon particles held at an appropriate negative applied potential. The supporting electrolyte and reference electrode were outside the porous stainless steel column to minimize contamination of the blank flow stream. Various metal ions were retained at cathodic potential with an efficiency of 99% or better at liquid flow rates of 50−80 μL min^{-1}. Other metals are retained at a potential that is moderately positive with respect to their standard reduction potentials. The column was regenerated by stripping the deposited metal at high anodic potentials.

Li et al. (186) investigated the behavior of bacteria in the ICP with special reference to the atomization and production of atomic ions for MS, by monitoring metal incorporation into bacteria through combining perfusion chromatography (PC) and ICPMS. U$^+$ signals from U incorporated intrinsically in *Bacillus subtilis* were measured with 4-ms time resolution to investigate the behavior of individual cells in the ICP. When intact cells were introduced directly into the ICP, occasional U$^+$ spikes were observed. The positive U$^+$ spikes suggest that bacteria behave more like solid particles than wet droplets in the ICP, compared to previous studies of such transient effects in the ICP. Drying the bacterial aerosol did not eliminate the spikes. Lysing the bacteria by sonication increased the U$^+$ response by 30% compared to that from the untreated sample. PC results from a 10 ppb U standard and partially lysed and fully lysed bacteria samples showed that the intracellular U-bound species are released by sonication and are small in size. The atomization ionization efficiencies for different elements (U, Ca, Mg) from cells were found to differ somewhat. Reducing the aerosol gas flow rate by 0.1 L min^{-1} improved the relative U$^+$ response for unlysed bacteria to 85% of that for lysed cells, although the absolute U$^+$ signal was attenuated greatly.

1. ICPMS Applications. Some Trends. Wolf et al. (187) have developed a method for the quantification of 14 cosmochemically moderately volatile to highly volatile trace elements (Cu. Zn, Ga, Se, Rb, Ag, Cd, In, Sri, Sb, Te, Cs, Tl, Bi) in chondritic meteorites by ICPMS. The method utilizes internal standardization via addition of Be, Rh, Re, and U and multiple single-point matrix-matched external calibrations with Allende standard reference meteorite to provide drift-corrected calibration. The method's precision and accuracy was demonstrated, and a rapid and accurate determination of the cosmochemically important volatile trace elements in chondritic meteorites providing the means for an even more comprehensive elemental analysis of a single sample of chondritic material was performed.

Selenomethionine (SeMet) and methionine (Met), liberated by acid hydrolysis of selenium-enriched yeast, were quantified by McSheehy et al. (188) through liquid chromatography−mass spectrometry (LC/MS) using standard additions calibrations as well as ID based on species-specific ^{13}C-enriched spikes. LC−ICPMS was also employed for the quantification of SeMet, and ^{74}Se-enriched SeMet was used for ID calibration. The results were evaluated to ascertain the feasibility of using these methods in a campaign to certify selenized yeast. Good agreement was found between the different methods. Quantification by ID LC/MS and LC/ICPMS yields the most precise sets of results with relative standard deviations in the range 0.5−1.3% ($n = 6$). A total Se concentration of 2064.6 ± 45.4 μg/g was obtained for this yeast material. The extraction efficiency and a mass balance budget were determined. Acid hydrolysis liberated 81.0% of the total selenium present. SeMet comprised 79.0% of the extracted selenium and 63.9% of the total selenium present in the yeast.

The potential of quadrupole ICPMS was studied as an alternative to X-ray spectrometry for the measurement of ^{129}I in environmental samples by Bienvenu et al. (189). Although ICPMS exhibits attractive features for the measurement of this radionuclide, the occurrence of natural iodine ^{127}I at substantial levels in the solutions recovered after dissolution and extraction steps was shown to induce an interference on the ^{129}I signal, due to the formation of a polyatomic IH$_2$ species, as well as a substantial matrix effect for quantitative analyses. These difficulties were overcome by analyzing diluted solutions and using ^{133}Cs as internal standard. The use of ICPMS after sample pretreatment allowed detection limits for ^{129}I in the range of 10^{-4} Bq/g (10^{-11} g/g). The accuracy of the measurements was estimated in comparison with results obtained on the same samples by X-ray spectrometry.

Sturgeon and co-workers (190) described a method for the determination of U, Th, and Pu in natural water, biological materials, and urine samples by ETV-ICPMS. Carbide formation was minimized using sample vaporization from a tantalum surface for U and additional use of tetrafluoromethane (Freon-23) as a gaseous modifier for Th and Pu. A prior $Ca_3(PO_4)_2$ coprecipitation provided an enrichment factor of 50, yielding procedural detection limits of 0.013, 0.029, and 0.017 pg g^{-1} for Th, U, and Pu, respectively, and corresponding absolute values of 0.13, 0.29, and 0.17 fg. Recovery of spikes from urine was typically 80%, whereas those from seawater, river water, and biological materials averaged 99%. The accuracy of the method was validated by determination of U and Th in standard Oyster Tissue and U in a series of natural water certified reference materials. Precision of determination was better than 10% at concentrations of 0.1 ng mL^{-1}. In a short communication, Lafleur et al. (191) demonstrated that a single human hair strand can be analyzed for total mercury using an induction heating-electrothermal vaporizer in combination with ICPMS. A detection limit of 20 pg absolute, corresponding to 30 ng g^{-1} based on a 0.6-mg hair sample, was achieved.

Chu and Beauchemin (192) developed a quick and simple method to assess the maximum bioaccessibility of elements, i.e., the maximum amounts of elements that can be released from food into artificial gastrointestinal fluids. The method is based on leaching of the food sample by, successively, artificial saliva, gastric juice, and intestinal juice. It uses a single-line flow injection manifold to repeatedly inject 100-μL aliquots of a given reagent that is then pumped through a microcolumn of food (maintained at 37 °C in a thermostated water bath), which is connected to ICPMS through sample nebulization. This on-line leaching approach allows the continuous monitoring of the progressive release of elements by a given reagent. A proof of concept of this simple method was made using a microcolumn of a standard reference material of corn bran, and quantitation of the bioaccessible fraction of Zn and Pb was performed. Following consecutive leaching by the three reagents, total digestion of the sample remaining in the column was done to verify mass balance. In contrast to the batch method, the elements are continuously removed from the system, thereby driving the dissolution equilibrium to the right. As a result, the maximum amount of analyte that can be dissolved in a given reagent is measured, which allows a quick assessment (risk assessment) of the worst-case scenario in the case of toxic elements.

Lam and Salin used LA coupled to ICPOES and ICPMS for the analysis of pharmaceutical tablets (127). For spot analysis with LA-ICPOES, precision ranged from 12 to 31% RSD, but improved to 1−6% when ratios of signals were used. For continuous scanning, the precision ranged from 1 to 7% RSD. Weaker laser conditions required for ICPMS gave precisions of 47−61% RSD (29% when signal ratios were used). Under unoptimized conditions, the detection limits for LA-ICPOES of tablets were 70 μg g^{-1} for Al and 20 μg g^{-1} for Mg. The detection limits for LA-ICPMS were 40 μg g^{-1} for Al and 6 μg g^{-1} for Mg. These results suggest that LA-ICP spectroscopy may find application in tablet analysis. The same group briefly described the application of single-shot laser ablation ICPMS to the detection of Hg in single human hairs with a resolution corresponding to less than 1 day of growth and with a detection limit of ~0.2 μg g^{-1} (193). In a work described

by Vanhaecke and co-workers (194), LA-ICPMS was used for the fast and direct characterization of antique glazed ceramics manufactured in the Aragon area during the 14th−18th century. The samples were covered by a vitreous Pb-enriched layer (to ~100 μm of thickness) to which Co was added as coloring pigment. The goal of the work was to investigate the trace and major element composition of these thin layers, in an attempt to establish differences between samples originating from different ceramic workshops, but also to discover further information about the possible ores used as a source of Co and their location. The results confirmed the possibilities of the technique for obtaining spatially resolved information. It was feasible to achieve a controlled ablation of the glazed layers, ensuring minimum sample damage (spot size diameter 120 μm; sample consumption a few μg g per sample), while the sensitivity of the ICPMS device (LODs in the 0.1−1 μg g^{-1} range were obtained for most elements) permitted the monitoring of ~30 elements. The differences in the concentration levels of Cu, As, and Mn allowed the classification of the samples into three different categories, which was in good agreement with the results achieved by alternative and more laborious sample digestion and subsequent ICPOES analysis of the ceramic bodies. LA-ICPMS has been used by Rege et al. (195) to determine quantitatively the trace element composition of diamond. Experiments with different synthetic multielement carbon-based standards, various lasers, and a range of instrument conditions have shown that a 266-nm UV laser at 10 Hz provided the best sensitivity, and synthetic oil and a doped cellulose proved most suitable as external standards; ^{13}C was used as the internal standard. The precision and accuracy of the method, and the homogeneity of the cellulose multielement standard, were tested by multiple analyses. Artifacts resulting from polyatomic interferences were quantified by analysis of a pure synthetic diamond. Concentrations of 41 elements were determined for two fibrous diamonds, which have been analyzed previously by instrumental neutron activation analysis and proton microprobe. A comparison of these three analytical techniques showed that the use of the cellulose standard produces accurate and precise data for most elements. Typical detection limits for the rare earth elements are 5−20 ppb, and for transition elements, <500 ppb (10−30% RSD). Yang et al. (196) presented a discrete sample introduction approach based on LA-ICPMS for the quantitation of several trace metals in aqueous samples. Dried microdroplets of sample, previously mixed with a sodium acetate matrix, were quantitatively ablated from a polystyrene substrate. Calibration via the method of standard additions or isotope dilution provided accurate results for Ni, Cd, and Pb in drinking water and Se in yeast extract (off-line coupling of HPLC to dried-droplet isotope dilution LA-ICPMS (197)). Compared to conventional solution nebulization, LA sample introduction was found to provide a 2−7-fold enhancement in absolute sensitivity and transport efficiency of 2−14% for the elements examined, although estimated detection limits are 1−7-fold poorer for the dried-droplet LA technique, primarily a result of degraded precision arising from counting statistics limitations for discrete sample introduction. It was concluded that integration of the transient signal should eliminate contributions to elemental fractionation from the LA step and that dried-droplet LA-ICPMS should offer several advantages over ETV-ICPMS with respect to background intensity, throughput, and ease of desorption. Laser

ablation inductively coupled plasma isotope dilution mass spectrometry was applied by Boulyga and Heumann (*198*) to the direct and simultaneous determination of the platinum group elements (PGEs) Pt, Pd, Ru, and Ir in geological and environmental samples. A special laser ablation system with high ablation rates for bulk analysis (LINA-Spark-Atomiser) was used, along with sector field ICPMS. Special attention was paid to deriving the distributions of PGEs in the pulverized samples. No significant oxide ion interferences were determined, allowing the ICPMS to be run in its low mass resolution but high-sensitivity mode. The detection limits obtained for the geological samples were 0.16, 0.14, 0.08, 0.01, and 0.06 ng g^{-1} for Ru, Rh, Pd, Ir, and Pt, respectively. The same system was used for direct determinations of chlorine, bromine, and iodine in rock and sediment samples. Special attention was focused on possible interhalogen fractionations and analyte/spike isotope fractionations by using LA-ICPMS and LA-ICP-IDMS, respectively (*199*). It was found that at high laser power densities (>5.7 GW cm^{-2} for iodine and >4.0 GW cm^{-2} for bromine and chlorine) the corresponding measured isotope ratio of the isotope-diluted sample deviates significantly from the target value. Under optimized conditions, concentrations in the range of 30 to 16×10^3 μg g^{-1} for chlorine, $<2-140$ μg g^{-1} for bromine, and $<0.1-31$ μg g^{-1} for iodine were determined by LA-ICP-IDMS in two sediment reference materials and three rock reference samples, which have not been certified for these halogens. Detection limits of LA-ICP-IDMS are 8 μg g^{-1} for chlorine, 1.7 μg g^{-1} for bromine, and 0.1 μg g^{-1} for iodine were presented.

2. ICPMS Applications. Bioanalysis. The recent developments and trends in quantitative speciation analysis of endogenous trace element compounds in biological systems by isotope dilution ICPMS and the application of capillary electrophoresis as a high-resolution separation technique in metalloproteomics research are critically reviewed by Schaumlöffel and Lobinski (*200*) and Prange and Pröfrock (*201*). Application of CE as a high-resolution separation technique in metalloproteomics research is critically reviewed. The focus is on the requirements and challenges involved in coupling CE to sensitive element- and molecule-specific detection techniques such as ICPMS or ESI-MS. The complementary application of both ICPMS and ESI-MS techniques to the structural and functional characterization of metal-binding proteins and their structural metal-binding moieties is emphasized. Beneficial aspects and limitations of the different techniques are discussed, on the basis of the literature published in this field over the past decade. Recent metalloproteomics applications are reviewed to demonstrate its potential and limitations in modern biochemical speciation analysis and to indicate future directions of this technique.

Boulyga et al. (*202*) used size exclusion chromatography (SEC) coupled on-line to ICPMS for speciation study of trace metals in cancerous thyroid tissues in comparison to healthy thyroids aimed toward estimation of changes in metalloprotein speciation in pathological tissue. The study showed the presence of species binding Cu, Zn, Cd, and Pb in healthy thyroid tissue with good reproducibility of chromatographic results, whereas the same species could not be detected in cancerous tissues. Thus, remarkable differences with respect to metal-binding species were revealed between healthy and pathological thyroid samples,

pointing out a completely different distribution of trace metals in cancerous tissues. Although the metal-binding species could not be identified in the frame of this work because of a lack of appropriate standards, the obtained results confirmed the suitability of SEC–ICPMS for monitoring changes in trace metal distribution in cancerous tissue.

Cd-bound phytochelatins (Cd–PCs) were used by Loreti et al. (*203*) as model substances to develop and optimize ion-pair chromatography coupled to ICPMS for analysis of Cd–PCs. Subsequent analysis of samples taken from *Silene vulgaris* plants cultivated under heavy metal stress conditions revealed Cd signals but no Cd–PC signals. By use of isotopically enriched ^{116}Cd–PCs, the sample preparation steps were verified to determine the stability of the analytes. Species transformation between Cd–PCs and other unidentified Cd complexes was observed, suggesting that the kinetic and thermodynamic labilities of Cd–PCs are decisive factors in their detection.

The potential for developing improved procedures for phosphate measurement through combinations of gel electrophoresis and quadrupole-based ICPMS utilizing $^{47}PO^+$ was investigated by Elliott et al. (*204*). Although it has capabilities for direct analysis, LA of gels is subject to high blanks due to P impurities in gels and associated reagents. The implementation of whole gel elution with FI-ICPMS based on conventional solution nebulization following gel electrophoresis permitted quantitation at the submicrogram per liter level, and microcolumn processing was effective at rejecting phosphate contamination. The potential for S-induced molecular ion interference at mass 47 was also demonstrated. On a similar topic, Warnken et al. (*205*) have demonstrated a quantitative method to analyze polyacrylamide gels for trace metals (Co, Ni, Cu, Zn, Cd, Pb) using the method of diffusive gradients in thin films (DGT) and LA-ICPMS. Internal standardization was carried out using ^{115}In, which was preloaded into a second layer of gel and dried together, with the analyte gel layer, as a dual-layer DGT gel standard. It was determined that drying the gels prior to ablation resulted in robust plasma conditions with minimal oxide (CeO^+) and doubly charged (Ba^{2+}) ion interferences. Laser defocus was used to maximize analyte sensitivity-to-background ratios for both the single-layer and dual-layer gels. Matrix-matched calibration standards, containing the analytes of interest, showed a linear response between analyte signal intensity and mass.

Knispel et al. (*206, 207*) performed the analysis of Ni species in cytosols of normal and malignant human colonic tissues using two-dimensional liquid chromatography, gel electrophoresis, and sector field ICPMS detection. The developed method allowed comparison of Ni species in healthy and neoplastic tissues from cancer subjects. Seven nickel species in tissue extracts were resolved, which can be considered as fingerprints of nickel speciation. A qualitative difference in Ni-binding biomolecules between cytosols of normal and malignant colon tissues was not found. In a later study (*207*), different sample preparation strategies were studied to find a suitable method for the isolation and characterization of Ni species previously found in cytosols from normal and malignant tissues of the human colon. The total Ni concentrations of the cytosols were determined as well as the total protein content. A Ni-containing protein was isolated from cytosols of malignant human colonic tissues using SEC with

ICPMS for element-specific detection. Ni-containing species in the molecular mass range from 10 000 to 20 000 Da were found and preconcentrated. The determination of the molecular mass of the species was performed through on-line coupling of reversed-phase chromatography with electrospray ionization quadrupole time-of-flight MS. Using identical chromatographic conditions and ICPMS, the detected protein was shown to contain Ni.

Becker et al. (*208*) measured the distribution of Cu, Zn, P, and S in thin section of rat brain tissues by LA-ICPMS and evaluated the methods possibilities for small-sized tumors analysis. Ion intensities of $^{63}Cu^+$, $^{64}Zn^+$, $^{31}P^+$, and $^{32}S^+$ in the rat brain section containing the local tumor and control area were measured by scanning with a 50-μm focused laser beam and laser power density of 3×10^9 W cm^{-2}, in a cooled laser ablation chamber coupled to a double-focusing sector field ICPMS. The quantitative determination of element distribution in a thin slice of the rat brain tissue was carried out using matrix-matched laboratory standards. After separating protein mixtures originating from human brain by 2D gel electrophoresis, the Becker group determined P, S, Si, and metals in such samples by LA-ICPMS of the single protein spots in the gels (*209*, *210*). Relative ion intensities for P, Si, and metals with respect to sulfur in protein spots were determined. The detection limits for P and S in protein spots with a silver staining procedure on the 2D gels were compared with alternative staining techniques. In a different study, the formation of proteins containing Cu, Zn, and Fe in a human brain sample (*211*) was investigated. Therefore, isotopic-enriched tracers (^{54}Fe, ^{65}Cu, ^{67}Zn) were doped to 2D gels of separated Alzheimer-diseased brain proteins after 2D gel electrophoresis. The protein spots were screened systematically by LA-ICPMS with respect to these metal ion intensities. $^{54}Fe/^{56}Fe$, $^{65}Cu/^{63}Cu$, and $^{67}Zn/^{64}Zn$ isotope ratios in metal-containing proteins were measured directly by LA-ICPMS. The isotope ratio measurements obtained by LA-ICPMS indicated certain protein spots with a natural isotope composition of Cu, Zn, and/or Fe. These proteins already contained the metal investigated in the original proteins and are stable enough to survive the reducing conditions during gel electrophoresis. On the other hand, proteins with a changed isotope ratio of metals in comparison to the isotope ratio in nature demonstrate the accumulation of tracers within the protein complexes during the tracer experiments in 2D gels. The identification of singular protein spots from Alzheimer-diseased brain separated by 2D gel electrophoresis was attempted by biopolymer mass spectrometry using MALDI-FTICR-MS after excision from the 2D gel and tryptic digestion.

Through interfacing reversed-phase nanoHPLC with collision cell ICPMS and on-line isotope dilution analysis, Giusti et al. (*212*) achieved accurate quantification of Se-containing peptides in nanoliter volumes of protein tryptic digests. This method allowed the stable introduction into an ICP of mobile phases containing up to 90% acetonitrile at flow rates of less than 500 nL min^{-1}. The on-line postcolumn addition of an isotopically enriched spike at flow rates of less than 4 mL min^{-1} enabled isotope dilution quantification of heteroatom-containing analytes while the consumption of the labeled isotope was low. The absolute detection limit was 40 fg for ^{80}Se, a factor of 2 less than ever reported for a capillary HPLC−ICPMS coupling. The Se recovery was found to be $103 \pm 4\%$. Since the tryptic peptides, miscleaved or oxidized peptides, incompletely digested protein, and undigested protein were determined in one run, the method allowed the precise evaluation of the efficiency and quality of tryptic digestion using several nanoliters of sample only. Bergmann et al. (*213*) developed a fast and sensitive method for the determination of the absolute configuration of selenomethionine. Its enantiomers were converted into diastereomeric isoindole derivatives. The authors described this method as an "easy-to-handle" reaction, which should proceed quantitatively in a few minutes at room temperature. Separation and detection of the diastereomers was achieved by a C18-based reversed-phase HPLC coupled to ICPMS. Detection limits of ~4 μg L^{-1} were obtained. The method was applied to the determination of the configuration of selenomethionine extracted from antarctic krill, which turned out to possess the L-configuration. The determination of selenomethionine in selenized yeast by HPLC−ICPMS has been revisited by Polatajko et al. (*214*) with the focus on recovery of this amino acid during the proteolytic digestion and chromatography steps. Recovery of the extracted selenium from an anion-exchange column was found to be 100%, but selenomethionine quantified by the method of standard additions accounted only for 67% of the Se injected. Analysis of the eluate collected before and after the selenomethionine peak showed the presence of oxidized selenomethionine and selenomethionine likely to be unspecifically associated with the biological matrix continuum. This finding was validated by two-dimensional LC−ICPMS using a different elution order. The approach developed enabled demonstration that more than 80% of Se in the selenized yeast is actually present in the form of selenomethionine and suggests that many results reported elsewhere for the concentration of this vital amino acid in selenized yeast may be negatively biased.

It has been shown by the Feldmann group that in vitro incubation of *Laminaria digitata* extract, containing mainly As−sugar 1 and As−sugar 3, with liver cytosol, produced the same two arsenicals, as when *L. digitata* extract was treated with H$_2$S (*215*). By parallel use of HPLC−ICPMS and HPLC−ES-MS, the compounds displayed mainly m/z 345 and 409. A pure As−sugar 1 standard was obtained, and a standard of arsinothioyl−sugar 1 (m/z 345) was produced, by purging a solution of As−sugar 1 with gaseous H$_2$S. The identity of arsinothioyl−sugar 1 was characterized by ES-MS and 1D and 2D NMR. Arsinothioyl−sugar 1 showed the same chromatographic behavior and MS characteristics as one of the two arsenic-containing compounds (m/z 345) produced by incubation of *L. digitata* extracts with liver cytosol and as the product of the incubation of As−sugar 1 with liver cytosol. When assuming that As−sugar 3 reacts in a similar way to As−sugar 1 with H$_2$S, the authors considered it as most likely that the second unknown (m/z 409) is arsinothioyl−sugar 3. The degradation of As−sugar 1 in acidic solution was followed by ^{1}H NMR, and the relative slow degradation suggested that arsenosugars are taken up from the stomach in their original chemical form. In this study, arsinothioyl sugars were detected for the first time. The authors concluded that the in vitro formation of arsinothioyl−sugars in liver cytosol suggests the large biochemical and toxicological importance of arsinothioyls.

A new approach to measurement of Eu and Sm monoclonal antibody labels by FI-ICPMS following dual immunoassay for the prostate cancer markers, free prostate specific antigen (fPSA) and

total prostate specific antigen (tPSA), based on a sandwich-format immunoassay was described by Hutchinson et al. (216). Limits of detection were 0.01 μg L^{-1} (6.22 ng L^{-1} Eu) for fPSA and 0.02 μg L^{-1} (0.11 ng L^{-1} Sm) for tPSA, and precision ranged from 0.75 to 3.68% for fPSA (Eu) and from 1.04 to 5.47% for tPSA (Sm). In general, the approach was found to be competitive with the standard time-resolved fluorometric method as applied in clinical chemistry.

3. Collision and Reaction Cells. Collision and reaction cells are becoming very popular in the field of ICPMS to help solving analytical problems, e.g., isobaric interferences in both single-element and multielement determination modes. Correspondingly, a high number of publications in many different fields of applications has been reported in the literature during the time period covered by this review. The development and utilization of collision and reaction cells in atomic MS was outlined in a critical review article by Koppenaal et al. (217), focusing on the devices' capabilities to promote reactive and nonreactive collisions, with resultant benefits in interference reduction, isobar separation, and thermalization/focusing of ions in ICPMS. Marcus (218) discussed collision-induced dissociation for the removal of molecular isobars in ICP- and GD-MS and how former studies on this topic compare in practical terms with the current commercial implementation of chemical reactions.

Hattendorf and Günther (219) compared the efficiency of kinetic energy discrimination and band-pass tuning for the suppression of potentially interfering product ions, formed by ion−molecule reactions in a dynamic reaction cell of an ICPMS. Suppression of the oxide ions from Sc$^+$, Y$^+$, La$^+$, and Th$^+$, formed in reactions with oxygen impurities in nonreactive gases, have been used as test systems to determine the suppression efficiency of the in-cell generated ions in dependence of the operating parameters of a dynamic reaction cell. Kinetic energy discrimination was investigated by successively lowering the pole bias voltage of the reaction cell quadrupole below the pole bias of the analyzer quadrupole to create a potential barrier of increasing height. For band-pass tuning, the transmission window of the reaction cell quadrupole was successively narrowed to determine the cutoff m/z, where precursors of the product ions are rejected. The efficiency of interference suppression and the elemental sensitivity were found to decrease in all cases with m/z of the precursor ions. The authors state that both approaches allow the suppression of the in-cell generated ScO$^+$ and YO$^+$, while LaO$^+$ and to a greater extent ThO$^+$ cannot be fully eliminated without compromising elemental sensitivity significantly. LaO$^+$ and ThO$^+$ were observed at levels that are by a factor of 2 and 6 higher than in standard operation of the ICPMS. Elemental sensitivity was higher by a factor of ~5, and the abundance of the cell-produced ions was reduced more effectively with the band-pass tuning approach.

When H$_2$ is used as a reaction/collision gas, interference in the detection of Se in Br-containing samples, such as extracellular fluids, are produced. Ogra et al. (220) studied the use of D$_2$ as a reaction gas instead of H$_2$. Se concentrations in serum and urine were overestimated in the H$_2$ reaction mode but were determined accurately in the D$_2$ mode. In speciation analyses, the background counts at m/z 77, 78, and 80 were reduced and the signal-to-noise ratios were improved by either the H$_2$ or the D$_2$ reaction. The

^{79}Br^{1}H$^+$ and ^{81}Br^{1}H$^+$ interferences appearing at m/z 80 and 82, respectively, were decreased by changing from the H$_2$ reaction mode to the D$_2$ one. Thus, D$_2$ was found to be effective in dissociating polyatomic interferences and removing Br interferences during Se determination and speciation, suggesting that the D$_2$ reaction mode is useful for selenometallomics, particularly in samples containing Br, such as serum, urine. and cell culture medium.

For phosphorylation profiling of tryptic protein digests, Pröfrock et al. (221) described a comparison of different nebulizers for direct hyphenation of capillary and nanoliquid chromatography (Cap-LC, Nano-LC) and quadrupole-based collision cell ICPMS. He was used as cell gas, and specially tuned instrumental conditions were used to achieve background minimization at the mass of P, because of kinetic energy discrimination of the interfering polyatomic ions. The proposed setup is based on a modified CE interface and a low-volume spray chamber, enabling the use of gradient conditions with a highly concentrated organic mobile phase, without the need to apply membrane desolvation for removal of the organic phase or further background minimization. No significant signal suppression or other negative effects caused by the organic mobile phase occur, because of the low flow rates used in Cap-LC and the robust plasma conditions. A tryptic digest of β-casein was investigated as model compound to demonstrate the applicability of the proposed setup for phosphorylation profiling in protein analysis. Detection limits for phosphorylated peptides down to the subpicomole level were obtained.

In a different application of collision cell ICPMS, St. Remy et al. (222) reported on the analytical potential of a quadrupole ICPMS instrument equipped with an octopole reaction cell for the multielemental determination of essential (Cr, Mn, Fe, Co, Cu, Zn, Se, I) and toxic (Al, Cd, Pb) elements in whole premature breast human milk and premature infant formulas. Milk samples were microwave digested, and different parameters affecting the octopole reaction cell were optimized in order to minimize/remove polyatomic interferences caused by argide species from the ICP. The detection limits in a synthetic matrix obtained ranged from 0.5 to 11 ng g^{-1} for the elements under study. After validation, the method was applied to the multielemental analysis of premature human milk samples at three different lactating stages during the first month after birthday and to formula milks commercially available for premature newborns. Important differences between human and formula milk in their respective contents of essential elements were shown, and the nutritional significance of such differences was highlighted. The study was extended to multielemental speciation of several essential (P, S, Cr, Mn, Fe, Co, Cu, Zn, Br, Se, I) and toxic elements (such as Al) in the mentioned matrixes by size exclusion chromatography coupled to a quadrupole ICPMS instrument, equipped with an octopole reaction cell (223).

A dynamic reaction cell (DRC) ICPMS was evaluated by Nixon et al. (224) for the determination of As, Pb, Cd, Hg, and Tl in urine and whole blood. Reaction cell conditions, using 5% H$_2$ in Ar as reaction gas, were evaluated for suppression of ArCl$^+$ and CaCl$^+$ polyatomic interferences, while Pb, Cd, Hg, and Tl were determined with the reaction cell vented. A mixture of 2.5% *tert*-butyl alcohol, 0.5% HCl, and 2 mg L^{-1} Au plus Ga, Rh, and Bi internal standards was used to dilute whole blood and urine.

Calibration was achieved using aqueous acidic standards spiked into urine matrix. Urine and whole blood addition calibration curves were nearly identical for all five elements. DRC-ICPMS detection limits were found to be equivalent or better than conventional ICPMS. Mermet and co-workers (225) performed the quantification of Cr in whole blood by using a quadrupole ICPMS equipped with a DRC and NH_3 as reaction gas. The rejection parameter of the DRC and the NH_3 flow rate were optimized and set at 0.7 and 0.6 mL min^{-1}, respectively. The blood samples were diluted 1:51 (v/v) with an aqueous solution containing 0.1 mg L^{-1} NH$_4$OH, 0.1 g L^{-1} EDTA, 5 mg L^{-1} 1-butanol, and 0.01% Triton X-100. External calibration with blank and standard solutions prepared in purified water led to biased results for quality control samples. Standard addition calibration was therefore used and its validity verified. By comparing the slopes and calculating residues, the authors proved that the plot obtained with standard additions and the plot obtained from blood samples of different concentrations were aligned down to 0.05 μg L^{-1} after dilution.

Bandura et al. (226) investigated the possibilities of determining P and S as PO$^+$ and SO$^+$, produced by oxidation reactions with O_2 performed in the reaction cell of an DRC-ICPMS. Subnanogram per milliliter detection limits were achieved, allowing picomolar per milliliter detection of phosphoproteins, with S used as an internal standard. The method was applied to digests of in vitro tyrosine kinase assays, both as an evaluation of kinase autophosphorylation and phosphorylation of substrate. It was indicated that the detection the P/S ratio (via PO$^+$/SO$^+$) in cell cultures provides a distinguishable difference between malignant cell lines and primary cultures.

A reversed-phase ion-pairing HPLC method was developed by Sadi et al. (227) for the separation of two phosphorus herbicides, glufosinate and glyphosate, as well as aminomethylphosphonic acid, the major metabolite of glyphosate. On-line coupling to ICPMS allowed the detection of the herbicides through ^{31}P. An octopole reaction cell was utilized to minimize the isobaric polyatomic interferences and to obtain the highest signal-to-background ratio. While the detection limits were found to be in the low ppt range, the developed method was successfully applied to the analysis of water samples, spiked with standard compounds at a level of 20 μg L^{-1}.

Pröfrock et al. (228) described a sensitive and highly selective method for the determination of a wide range of pesticides, based on the simultaneous element-specific determination of P, S, Cl, Br, and I by GC hyphenated with octopole reaction cell ICPMS. The chromatographic system was optimized for separation efficiency and short run times and was coupled via a commercially available interface with the ICPMS. Instrumental settings were optimized with respect to high sensitivity for the target nuclides ^{31}P, ^{32}S, ^{35}Cl, ^{79}Br, and ^{127}I and minimized background levels especially for the ions most affected by interferences, such as ^{31}P and ^{32}S. He and N_2 were tested as additional plasma gases for possible sensitivity enhancement of the element-specific detection resulting from improved ionization processes within the plasma. Identification of the detected pesticides was carried out using their retention times, elemental compositions, and ratios present in each chromatographic peak. Detection limits down to the ppt−ppb level were obtained, and the average RSDs of the retention times and the peak areas were better than 0.8 and 8%, respectively. Quantita-

tive results have been obtained for pesticides of different fruit extracts by external calibration and by using a compound-independent calibration.

Izmer et al. (229) presented an improved method for the determination of ^{129}I in sediments by quadrupole collision cell ICPMS. The hot extraction of iodine from environmental samples and on-line introduction of analyte via the gas phase into the ICPMS was equipped with a cooling finger, which allowed intermediate iodine enrichment and improved the detection limits for ^{129}I down to 0.4 pg g^{-1} without additional sample preparation. A mixture of oxygen and helium as reaction gases in the hexapole collision cell was used for minimizing interferences caused by ^{129}Xe$^+$. The developed analytical method was applied for ^{129}I determination at the ultratrace level and for isotope ratio measurements of ^{129}I/^{127}I down to 10^{-7} in contaminated sediments and in Ocean Sediment reference material.

Due to recent regulations concerning low-sulfur gasoline, analytical methods are required to provide specific information on S-containing compounds present in petroleum products at the nanogram per gram range. Bouyssiere et al. (230) proposed a strategy, coupling of capillary GC with collision cell ICPMS for the speciation of S in hydrocarbon matrixes. An absolute detection limit of 0.5 pg for a 1-μL sample was presented, which is ∼2 orders of magnitude lower than such achievable through currently used techniques.

The determination of S-containing amino acids by CE hyphenated to dynamic reaction cell ICPMS and its application to urine and nutritive complement samples was outlined by Yeh et al. (231). L-Cysteine, L-cystine, DL-homocystine, and L-methionine were selected as model amino acids. The species studied were well separated using a 70 cm length × 75 μm i.d. fused-silica capillary while the applied voltage was set at +22 kV and a 10 mmol L^{-1} disodium tetraborate buffer (pH 9.8) containing 0.1 mmol L^{-1} EDTA and 0.5 mmol L^{-1} Triton X-100 was used as the electrophoretic buffer. The S-selective electropherogram was determined at m/z 48 (^{32}S^{16}O$^+$) by using its reaction with O_2 in the reaction cell, avoiding polyatomic isobaric interferences caused by ^{16}O^{16}O$^+$ and ^{14}N^{18}O$^+$ on ^{32}S$^+$. The detection limits of various species studied were in the range of 0.047−0.058 μg mL^{-1}, which correspond to the absolute detection limit of 1.3−1.6 pg of S based on the injection volume of 27 nL.

The simultaneous determination of Fe/S and Mn/S ratios on transient signals was performed by Hann et al. (232), employing SEC, hyphenated to DRC-ICPMS, to characterize metalloprotein samples by their metal/sulfur ratio. Oxygen was used as reaction gas for the generation of ^{32}S^{16}O$^+$, thus avoiding isobaric interferences at m/z 32. Using the same reaction gas conditions, Fe and Mn were measured at m/z 54, 56, and 55, respectively. Detection limits of 4.3, 0.4, 2, and 0.6 ng g^{-1} were assessed for ^{32}S^{16}O, ^{55}Mn, ^{54}Fe, and ^{56}Fe, respectively. Reference measurements were carried out by SEC coupled with sector field ICPMS, setting the mass resolution at 4500. LODs of 14, 0.5, and 0.4 ng g^{-1} were obtained for the same analyte ions. The metal/sulfur ratios of five commercially available metalloproteins were determined (myoglobin, hemoglobin, cytochrome c, arginase, Mn superoxide dismutase from *Escherichia coli*). Different calibrants (i.e., Fe^{3+}, Mn^{2+}, SO$_4^{2-}$, methionine, myoglobin) for the assessment of interelemental ratios have been employed. The authors found that calibration using

metalloprotein myoglobin is preferable to inorganic standards in terms of uncertainty of measurement. However, all metal/sulfur ratios of the investigated proteins obtained by the different methods agreed within their total combined uncertainty.

SEC hyphenated to collision cell ICPMS was also used by the Lobinski group for the analysis of the selenium species distribution in cow blood (233). The concentrations of selenized hemoglobin and free selenomethionine were estimated using the chromatogram. The method was applied to a study involving 15 control and 15 treated dairy cows at four different supplementation time points. The increase in the selenomethionine and selenized hemoglobin was a linear function of the total Se concentration. A threshold value of 600 ng mL^{-1} total Se was established beyond which selenomethionine could not be incorporated into the protein. No inorganic Se was found to be present, and the total Se in cow blood correlated well with that in milk. The authors reported that the Se supplementation did not change the protein distribution profiles for other essential elements (Cu, Fe, Mn, Zn).

Wallschläger and London used a sophisticated hyphenation of anion-exchange chromatography with hydride generation reaction cell ICPMS (AEC-HG-ICP-DRC-MS) for the determination of inorganic Se species in rain- and seawaters (234), achieiving detection limits of 0.15, 0.27, and 0.19 ng L^{-1} Se for selenite, selenate, and selenocyanate, respectively. Seawater had to be diluted 10-fold prior to analysis to overcome chromatographic interferences, so practical method detection limits for this matrix were ~2−3 ng L^{-1}. The species were separated by gradient elution with NaOH and converted to SeH$_2$ with iodide in HCl at 100 °C, followed by subsequent reaction with KBH$_4$, before the SeH$_2$ was introduced into the plasma after aerosol and water vapor removal. Quantification using ^{80}Se was possible by employing a mixture of two reaction gases: CH$_4$ for eliminating the ^{40}Ar$_2^+$ and NH$_3$ for eliminating a significant interference from HBr$^+$ caused by bromine present in the employed reagents. Oxidation of Se$^+$ to SeO$^+$ using O$_2$ as the reaction gas was also attempted, but was found to yield incomplete conversion. In addition, the HBr$^+$ interference was not eliminated by this approach, because the interfering molecular ion was also oxidized to HBrO$^+$. The optimized method was successfully applied to the determination of Se speciation in uncontaminated seawater and in rainwater. In rainwater, an unidentified species was detected, which is believed to be a monomethylated Se species.

Encinar et al. (235) reported on the accurate determination of selenoamino acids in human serum by HPLC−ICPMS, using species-specific isotope dilution. A serum sample was enzymatically digested with a mixture of lipase and protease after derivatization of the selenocysteine residues with iodoacetamide. The selenoamino acid fraction was isolated by SEC followed by the separation of selenomethionine and the carboxymethylated selenocysteine by capillary HPLC. The isotope-specific determination of ^{77}Se and ^{80}Se was achieved on-line by collision cell ICPMS. For quantification through isotope dilution, a ^{77}Se-labeled selenomethionine spike was used and the ^{77}Se/^{80}Se ratio in the cHPLC selenomethionine peak was calculated. The accurately determined selenomethionine was used as an internal standard for the selenocysteine determination from the same chromatogram. Absolute detection limits of 75 fg were achieved, which results in

a procedural detection limit below 0.5 ng g^{-1} for a 450-mg serum sample. The precision was less than 5% RSD, and the method was validated by the mass balance of Se.

The reaction of cisplatin with methionine was studied by Stefanka et al. (236) using high-performance ion chromatography coupled to ICPMS equipped with a dynamic reaction cell. Two different cisplatin concentrations were studied simulating chemotherapy conditions and wastewater levels. The reaction of cisplatin with methionine was monitored over a period of 16 h. Accurate quantification of all Pt-containing compounds was achieved via species unspecific on-line IDMS. LODs of 0.31, 0.25, 3.83, 1.07, 0.56, 0.82, and 2.38 μg L^{-1} were calculated at m/z 194 for cisplatin, monoaquacisplatin, diaquacisplatin, and four Pt-containing adducts, respectively. Stoichiometric Pt/S ratios were assessed to characterize these four adducts by employing O$_2$ as reaction gas. For an injected sample volume of 20 μL, the LOD for S was found to be 1.30 μg L^{-1}. The authors pointed out that, at high cisplatin levels typical in chemotherapy, adducts show different kinetic behavior depending on the two investigated chloride levels (1.5 and 150 mmol L^{-1}). Moreover, the reaction course depended on the concentration of the reactants, i.e., cisplatin and methionine. Experiments simulating possible reactions of the compounds in the aquatic environment revealed that at low micromole per liter levels no adduct formation occurred. Finally, the stability of the four adducts potentially formed during chemotherapy was investigated representing the dilution of patient urine via hospital wastewater. A considerable amount of highly active monoaquacisplatin was formed, indicating a reversal of detoxification reaction pathways of the human body. Kan and Tanner (237) reported on the development of an analytical method for the determination of low concentrations of Pt in digested roadside dust samples by employing ICP-DRC-MS and NH$_3$ as reaction gas for removing the interfering species HfO$^+$. Detection limits in the region of 8−10 ng g^{-1} for different Pt isotopes were achieved, and certified reference materials were used to monitor the recovery of Pt. Results showed that the conventional ICPMS empirical corrections for isobaric interferences of Pt may be inaccurate.

In a different work, Tanner et al. (238) studied the chemical resolution of Pu$^+$ from U$^+$ and Am$^+$ using a band-pass reaction cell ICPMS, since isobaric overlaps between the elements themselves and U usually necessitate time-consuming chemical separation of these elements. The reactions of U$^+$, ^{242}Pu$^+$, and ^{243}Am$^+$ with ethylene, carbon dioxide, and nitric oxide inside the reaction cell are reported. Since the net sensitivities to the isotopes of an element were found to be similar, chemical resolution was inferred when one isobaric element reacts rapidly with a given gas and the isobar is unreactive or slowly reactive. Chemical resolution of the m/z 238 isotopes of U and Pu was obtained using ethylene as a reaction gas, but little improvement in the resolution of the m/z 239 isobars was found. However, high efficiency of reaction of U$^+$ and UH$^+$ with CO$_2$, and nonreaction of Pu$^+$, allowed the sub-ppt determination of ^{239}Pu, ^{240}Pu, and ^{242}Pu (single ppt for ^{238}Pu) in the presence of 7 orders of magnitude excess U matrix without prior chemical separation. Similarly, oxidation of Pu$^+$ by NO, and nonreaction of Am$^+$, permitted chemical resolution of the isobars of Pu and Am over 2−3 orders of magnitude relative concentration. The method provided the potential for analysis of the actinides with reduced sample matrix separation. A rapid

technique for the determination of Pu in urine samples using flow injection (FI) on-line preconcentration, desolvation nebulization through a highly sensitive APEX device and dynamic reaction cell ICPMS was developed by Epov et al. (239), avoiding the chemical separation of Pu from U. Analyte preconcentration and matrix separation for urine samples was achieved using TRU resin as the ion exchanger resulting in a LOD for ^{242}Pu of 1.9 pg L^{-1} for raw, undigested urine samples using a 10-mL sample volume. The reproducibility of the method was demonstrated by recovery measurements performed on urine that had been collected from several nonexposed volunteers and spiked with Pu using ^{205}Tl and ^{175}Lu as an internal standard and yield tracer. The authors state that the method provides a rapid means of measuring Pu in urine at levels below the regulatory requirements for drinking water. An additional study aimed at the application of a method similar to the determination of Pu isotopes in leaves (240). The samples were microwave-digested and flow injection on-line preconcentration/matrix separation (anion-exchange resin) was performed prior to sample desolvation and introduction using an APEX unit connected to a dynamic reaction cell ICPMS. Detection limits were reported to be as low as 2.9 and 0.46 fg g^{-1} for ^{239}Pu and other Pu isotopes, respectively, for an Apple Leave matrix.

In the field of biochemical speciation analysis for studying V association to human serum proteins, Fernandes et al. (241) used an ICPMS with and without collision cell. The separation of human serum proteins was achieved on an anion-exchange column using an ammonium acetate gradient in the mobile phase. Proteins, initially incubated with V(III) or alternatively V(IV), were detected spectrophotometrically and the V detection was carried out on-line with a quadrupole ICPMS or an octopole collision/reaction cell ICPMS system. Both instruments proved to be adequate for V detection at basal levels in human serum. The results obtained confirmed that V(IV) and V(III) seem to be eventually associated preferentially to transferrin protein in normal human serum. The observed V distribution profile was found to be similar to that previously reported for Fe(III) and Al(III) associations to human serum transferrin. Intact protein analysis by MALDI-TOF had confirmed the molecular structure of transferrin as the protein associated to the V fraction.

4. Time-of-Flight Instruments. Since the commercialization of plasma source time-of-flight mass spectrometers (TOFMS) in the late 1990s, the research on ICP-TOFMS developments and applications has continued. In a short review article by Bings (242), the capabilities of ICP-TOFMS were outlined and recent applications and trends in this field were highlighted.

The modulation of the central-channel gas flow rate was explored by McClenathan and Hieftje (243) as a means to operate the ion source of an ICP-TOFMS as a switched source in order to achieve optimal performance for a greater range of elements and to alleviate certain isobaric overlaps. By rapidly switching between low and high central-channel flow rates, hot and cold plasma conditions were produced in an alternating fashion and LODs with this modulation strategy were found to be similar to those obtained under steady-state hot and cold plasma conditions. The authors concluded that because both plasma conditions were produced in a single analysis, this modulation technique should be particularly useful for multielemental analyses that employ

transient sampling methods such as chromatography, FIA, ETV, and LA.

The ability of a cooled Wu−Hieftje vertical-rotary spray chamber to reduce oxide species in ICP-TOFMS was investigated by Wetzel et al. (244). Cooling the spray chamber from 20 to 5 °C yielded a 20% reduction in the interfering oxide level of ^{140}Ce^{16}O^{+} on ^{156}Gd^{+} without compromising detection limits. A corresponding decrease in the background-equivalent concentrations of the interfering species was also observed. Additionally, $1/f$ noise present in plasma-derived signals was less when the temperature of the spray chamber was lowered.

The performance of ICP-TOFMS in comparison with quadrupole (Q) ICPMS with respect to isotope ratio precision from transient signals generated by FI was investigated by Beauchemin (245). Area ratios and point-to-point ratios were compared, too. With ICP-QMS, windows corresponding to FW at 80 and 60% peak maximum provided, respectively, the ^{68}Zn/^{64}Zn and ^{65}Cu/^{63}Cu ratios of best precision using either integration or point-to-point ratios. For the ^{57}Fe/^{56}Fe ratio, a FW at 10% peak maximum was found to be better with area ratios, but a FW at 90% peak height was best with point-to-point ratios. The best precision achieved by either method ranged from 0.2% for ^{65}Cu/^{63}Cu to 0.9% for ^{68}Zn/^{64}Zn. The precision was also independent of the data processing mode in ICP-TOFMS. A FW at 90−60% peak height provided the best precision for ratios exhibiting a large error. A FW at 40% peak height was reported to be best for ratios exhibiting errors similar to those observed in FI-ICP-QMS, yielding a RSD as low as 0.5%. Although with continuous nebulization in ICP-TOFMS, the precision obtained with point-by-point ratios was systematically better than that by using area ratios, this advantage vanished in the FI mode. In a similar study, the capabilities of ICP-TOFMS for measuring precise isotope ratios was performed by the Sturgeon group (246), comparing steady-state with transient signal detection mode. An HPLC pump was used to introduce microliter volumes of analyte solution into a carrier flow to generate precise and repeatable transient signals having a fwhm of ∼1 s. Analog and pseudopulse data processing modes were evaluated and found to obey Poisson statistics for prediction of isotope ratio performance. For transient signals, area measurements are superior to averaging point-to-point measurements across the peak for optimum ratio precision. Although the TOF system provides for simultaneous sampling of the extracted pulse, thereby permitting elimination of correlated noise through ratio techniques, detection remains sequential and noise components present in the detection system limit isotope ratio precision in this study to 0.04% RSD.

Ertas and Holcombe (247) described the optimization of ETV-ICP-TOFMS for the reduction of isobaric interferences due to the ETV's ability to temporally separate analyte elements in complex mixtures by differences in their vaporization temperatures. Isobaric overlaps among Zn, Ni, Se, Ge, Cd, In, and Sn were resolved. A Monte Carlo simulation that focused on particle motion from the ETV to the plasma source was employed to evaluate the roles of diameter of transport tubing and heating rate of the ETV on signal broadening. It was shown that laminar flow broadening was reduced by decreasing the transport tubing diameter and thus more closely reflected the generation function of the ETV. However, for some elements, a reduction in signal as much as a 75% from use of smaller i.d. tubing was reported. Lüdke et al.

(*248*) employed a novel ICP-TOFMS system in combination with an inductively heated vaporizer system (IHVS) to analyze the trace metal content in size-separated arctic aerosols in the mass range between [7]Li and [209]Bi. The sampling of aerosol particles was performed by cascade impaction of the particles on cleaned graphite targets. To analyze the metal content in the aerosol particles, the targets were rapidly heated to 2700 °C in the IHVS. The simultaneous extraction of the ions into the TOFMS allows one to obtain the full mass spectrum of the sample during the vaporization pulse without any limitation in the number of elements detected. For calibration, acidified reference solutions were pipetted onto the cleaned targets and LODs for the investigated elements ranged between 2 and 200 pg, except Na, Mg, and Cr, which were influenced by high background level.

Stefanka et al. (*249*) developed a FI method in combination with hydraulic high-pressure nebulization as a sample introduction system for ICP-TOFMS for the rapid and simultaneous determination of Ag, As, Ba, Cd, Co, Cu, Ga, In, Li, Mn, Mo, Pb, Sb, Se, Sn, Sr, Tl, V, and Zn. The operating conditions of the system were optimized, and the LODs were comparable or better than those resulting from ICP-TOFMS with alternative sample introduction techniques, e.g., conventional nebulization, flow injection chemical hydride generation. Absolute detection limits in the range of 2−750 pg and precision between 0.5 and 9.6% from five replicate measurements of 10 ng mL^{-1} multielemental sample solutions were achieved by using a 200-μL sample loop. Benkhedda et al. (*250*) combined FI with analyte preconcentration for the determination of total Pb and Pb isotope ratios in natural waters by ICP-TOFMS. A 20-fold enrichment compared to the direct FI determination was yielded, and improved isotope ratio precision was provided. It was found that Pb isotope ratio precision in transient signals in ion counting mode were affected by detector dead time and mass discrimination was evaluated for pairs of isotopes using an isotopic standard reference material. The precision obtained for [204]Pb/[206]Pb, [207]Pb/[206]Pb, and [208]Pb/[206]Pb ratios at a Pb concentration of 1 μg L^{-1} was 1.87, 0.7, and 0.28%, respectively, using ion counting mode, 1.0-s integration time, and full peak integration.

Multicapillary GC hyphenated to ICP-TOFMS was employed by Jitaru and Adams (*251, 252*) for speciation analysis of mercury at ultratrace levels on the basis of solid-phase microextraction using Carboxen/poly(dimethylsiloxane) fiber. Isothermal separation of the Hg species was achieved within a chromatographic run below 45 s without the introduction of spectral skew. Method detection limits were 0.027 pg g^{-1} (as metal) for MeHg and 0.27 pg g^{-1} for Hg^{2+}. The method accuracy for MeHg and total mercury was validated through the analysis of marine and estuarine sediment reference materials. A comparison of the sediment data with those obtained by a purge-and-trap injection method was also addressed.

Due to the ICP-TOFMS simultaneous fashion of measurement, this technique seems to be ideal for the analysis of increasingly smaller sized samples, especially in combination with direct sample introduction, such as LA. Scadding et al. (*253*) investigated the potential of LA-ICP-TOFMS in the field of forensic analysis of microdebris, as sample type, which is often limited in amount. The authors state that, traditionally, relatively large amounts of sample have been required to obtain a representative elemental fingerprint of the type of material being under investigation. However, this quantity of material is unlikely to be recovered from a persons of interest (POIs). The authors developed a new method for the analysis of oxyacetylene debris, left behind at a crime scene, and described the establishment of its coprovenance with single particles of equivalent debris found on the clothing of POIs. In this study, the resulting data, for debris as small as 70 μm in diameter, were unambiguously matched between a single spherule recovered from a POI and a spherule recovered from the scene of crime, based on an analytical procedure taking less than 5 min.

5. Multiple-Collector Instruments. In single-collector scanning-based ICPMS, the achievable precision for isotope ratio measurements is limited to ∼0.05−0.5%, mostly caused by the unstable nature of the ion source. Unfortunately, many analytical applications demand a much higher precision leading to the development and application of multiple-collector mass spectrometers (ICP-MCMS), which allow the simultaneous measurement of each isotope ion in a certain space array of detectors. Through calculating the ratio, the effect of multiplicative or flicker noise can be minimized, and much higher precision can be achieved while increasing both the duty cycle and measurement sensitivity.

In the area of instrumental development, Hieftje and co-workers described the design and analytical evaluation of a Mattauch− Herzog geometry mass spectrograph equipped with different new detector types in combination with an ICP as ionization source and various sample introduction techniques (*254−257*). Such detectors employ different-sized arrays of Au Faraday cups, each with its own charge-integrating circuit that allows the simultaneous detection of several m/z ratios. LODs in the tens to hundreds of parts per quadrillion regime and isotope ratio accuracy and precision of 5% error and 0.007% RSD, respectively, were presented.

In a fundamental work by Andren et al. (*258*). several factors were identified as contributing to the mass bias in ICP-MCMS. Analyses of the isotopic compositions of B deposited on sampler and skimmer cones revealed an enrichment of [10]B on the former and [11]B on the latter. Grounding the capacitive discharge system to enhance sensitivity also magnified the level of [11]B enrichment on the skimmer cone more than 4-fold. This supersonic expansion of the ion beam behind the sampler was confirmed to be an important source of mass bias, too. Isotopic analyses of the Fe, Zn, and Tl leached from used extraction lenses yielded a linear relationship between the levels of lighter isotope depletion and mass ratio. Although consistent with the space-charge effect, the fact that isotopically heavy deposits were found underlined that the ion beam diverges into a relatively wide solid angle in the field-free region behind the skimmer. This severely impairs transmission of the lighter isotopes. For a wide range of elements (Li, B, Fe, Ni, Cu, Sb, Ce, Hf, Re), the magnitude of the mass bias was found to be affected by the sample gas flow rate, as well as the distance between the sampler and the end of the torch. Mathematical analysis of the profiles of intensity variations as a function of these instrumental parameters revealed that the response had a maximum value closer to the torch for the heavier isotopes of all studied elements. The authors concluded, that owing to this spatial noncoincidence, tuning for maximum intensity on either isotope will result in sampling from a region where even slight plasma instabilities will be translated into substantial

variations in mass bias. Therefore, in-plasma processes also contribute to the degree and temporal stability of mass bias. Recommendations for optimizing multi-collector ICPMS with respect to obtaining the highest possible precision were given.

Quite a few studies outlined the application of ICP-MCMS to highly precise and accurate isotope ratio measurements in the lower parts per thousand range of, for example, $^{238}U/^{234}U$ and $^{232}Th/^{230}Th$ in silicate glasses and iron oxides, in combination with LA (259), of $^{87}Rb/^{85}Rb7$ in geologic materials (260), of $^{87}Sr/^{86}Sr$ in silicate reference materials (261), and of $^{44}Ca/^{43}Ca$, $^{44}Ca/^{42}Ca$, and $^{48}Ca/^{42}Ca$ in seawater and biogenic and nonbiogenic marine carbonates (262), while a systematic survey was performed by Krupp and Donard (263) to investigate the drift observed on Pb and Hg isotopes during short transient signals obtained from GC coupled to different MC-ICPMS systems. Neither changes in instrumental mass bias nor chromatographic fractionation effects were found to be the source of the observed isotope ratio drift. An influence of analyte concentration on the observed drift was as well excluded as a source, because the slope on isotope ratios showed the same values for different concentrations evaluated. In contrast, the peak width was found to influence the extent to which the isotope ratio drifts during peak elution. It was concluded that the relative intensity change per time is an important factor for measurements of transient signals with MC-ICPMS. Similar studies were undertaken by Günther-Leopold et al. (264) to investigate the origin of ratio drifts across transient signals with a time duration of 30−60 s, achieved by coupling HPLC to ICP-MCMS. Measurements with the same standard solutions were also carried out using a FI device for sample introduction. As a result of this application, it was concluded that the main source of the bias in the measured isotope ratios is within the ICPMS instead of fractionation effects on the chromatographic column material; i.e., a reverse fractionation effect was found compared with dry plasma conditions (GC sample introduction).

An interesting application of high-mass resolution ICP-MCMS combined with LA to the study of the isotopic composition of Fe in iron meteorites and iron sulfides was reported by Kosler et al. (265). The long-term reproducibility of the measurements was 0.16 and 0.21 ppt for *^{56}Fe and *^{57}Fe, respectively, i.e., a factor of similar to 2 worse than conventional solution analysis. LA-related instrumental mass discrimination and laser-induced fractionation of Fe isotopes were again found to be the major limitations of precision and accuracy. Two types of particles were found, coarse spherical and crystalline, as well as fine amorphous particles, and in the authors' opinion, differential transport of the two types to the ICP can compromise the accuracy of Fe isotope measurements. Despite lower precision compared with liquid sampling ICP-MCMS analysis, the LA technique was capable of resolving Fe isotopic variations between seafloor and sub-seafloor hydrothermal sulfides, and between kamacite and taenite alloys that are commonly present as thin lamellae in iron meteorites.

6. Sector-Field Instruments. Increased mass resolution through high-resolution sector field MS (ICP-SFMS) allows resolving several interferences caused by undesired polyatomic species, as documented by a wide variety of applications. Zoriy et al. (266) proposed an analytical procedure for the determination of precise U isotope ratios in a thin uranium layer on a biological surface by LA-ICP-SFMS using a Peltier-cooled LA chamber.

Additionally, the elemental distribution in thin cross sections of frozen tissues with a lateral resolution in the micrometer range was established. The precision and accuracy of isotope ratio measurements were significantly improved using the cooled ablation chamber, resulting in a precision in the range of 2.0−1.6% for $^{234}U/^{238}U$, 1.3−0.4% for $^{235}U/^{238}U$, and 2.1−1.0% for $^{236}U/^{238}U$ in selected uranium isotopic standards reference materials. The accuracy of $^{234}U/^{238}U$, $^{235}U/^{238}U$, and $^{236}U/^{238}U$ isotope ratio measurements varied in the range of 4.2−1.1, 2.4−0.5, and 4.8−1.1%, respectively, and was found to depend on the diameter of the laser beam.

In the field of Hg determination in polar snow and ice samples, various Hg isotopes, such as ^{199}Hg, ^{200}Hg, ^{201}Hg, and ^{202}Hg, appeared to be free of polyatomic interferences, which allowed Planchon et al. (267) to make the ICP-SFMS measurements in low-resolution mode, leading to high sensitivity. Ultralow concentration Hg standards (from 1.5 to 20 pg g^{-1}) were used for calibration purposes, and a ^{202}Hg LOD as low as 0.18 pg g^{-1} was achieved. Ultraclean procedures used from field sampling to final laboratory analysis showed no significant blank contributions and appeared suitable for the reliable determination of Hg at ultralow concentrations. A high variability in Hg concentration (1.2−32.0 pg g^{-1}) of the snow samples collected in the Canadian Arctic was revealed.

In an interesting application by Schultheis et al. (268), LA-ICP-SFMS was used for the characterization of ancient and art nouveau glass samples by Pb isotope ratios with minimum total combined uncertainty. By employing this microanalytical technique, minimum sample damage was ensured. No significant laser-induced mass bias effects was observed by comparing LA-ICPMS with pneumatic nebulization ICPMS. Iridescent Art Nouveau lead crystal glass samples were analyzed, and the authors proved that the material of the single layers originates from different glass sources. Although the analysis of ancient glass fragments revealed only a low concentration of Pb, successful differentiation of the investigated samples via the Pb isotope ratios was possible whereas multielement pattern did not allow grouping of the data. Boulyga et al. (269, 270) used isotope dilution LA-ICP-SFMS for the direct determination of trace elements (Fe, Cu, Pb, Zn, Pu) in powdered samples. The results, achieved with a special LA system with high ablation rates (LINA-Spark-Atomiser) for bulk analyses of solid samples, were compared with those obtained by a commonly used NewWave UP213 system. Using different reference materials for validation, it was demonstrated that the accuracy of isotope dilution LA-ICP-SFMS determinations of elements such as Fe, Cu, Pb, and Zn by both systems was comparable in the concentration range of 10^{-2}−10^{-6} g g^{-1}, but the LINA-Spark also provided accurate results in the submicrogram per gram range. The higher ablation rate of the LINA-Spark resulted in better precisions and a ∼2 orders of magnitude higher sensitivity compared with the UP213 system. The authors concluded that the LINA-Spark is more suitable for precise analyses of less homogeneous samples.

Medium-resolution ICP-SFMS was applied by both groups, Helfrich and Bettmer (271), to resolve the $^{31}P^+$ signal from the interfering cluster ions in order to determine phytic acid and its degradation products through coupling the MS with ion-pair chromatography, and by Sarmiento-Gonzalez et al. (272) for the

multielemental determination of traces of metals (Ti, V, Cr, Co, Ni, Mo) potentially released from dental implants and articular prostheses in human urine and whole blood. Bruchert and Bettmer (273) described the on-line coupling of gel electrophoresis with medium-resolution ICP-SFMS for the separation of large biomolecules combined with sensitive $^{31}P^+$ detection. This coupling has been achieved by means of gels housed in glass tubes and an on-line transfer of the analytes to the nebulizer of the ICPMS. The authors outlined the analysis of commercially available standard solutions.

In the field of ultratrace determinations of radionuclide, Benkhedda et al. (274) reported on the development and validation of a sensitive and efficient FI preconcentration and matrix separation technique coupled to ICP-SFMS for simultaneous determination of ultralow levels of U and Th in human urine. The described method is based on selective retention of the analytes from a urine matrix, after microwave digestion, on an extraction chromatographic resin and their subsequent elution with ammonium oxalate. Using a 10-mL sample, the limits of detection achieved for ^{238}U and ^{232}Th were 0.02 and 0.03 ng L^{-1}, respectively. Levels of U and Th in human urine were found to be in the ranges 1.86−5.50 and 0.176−2.35 ng L^{-1}, respectively, well in agreement with levels considered normal for nonoccupationally exposed persons. The precision obtained for five replicate measurements of a urine sample was 2 and 3% for U and Th, respectively. An approach using nanovolume FI without analyte preconcentration, thus injecting 54 nL of sample into a continuous flow of carrier liquid at 7 μL min^{-1} prior to ICP-SFMS, was outlined by Schaumlöffel et al. (275) for the ultratrace determination of U and Pu. Absolute detection limits were found to be 9.1 × 10^{-17} and 1.5 × 10^{-17} g for U and Pu, respectively. The method was validated for the determination of the U isotope ratios. Additionally, the authors described the determination of Pu at subfemtomole levels in water with a detection limit down to 6 × 10^{-18} g mL^{-1}.

GLOW DISCHARGE ATOMIC EMISSION AND MASS SPECTROMETRY

Glow discharge spectrometry (GDS) has become a well-established analytical method for both bulk and depth profiling analysis of conducting and nonconducting samples. The majority of developments and applications are for GD sources in combination with mass spectrometry (GDMS) or optical emission spectroscopy (GD-OES). This has been the subject of a number of reviews in the last two years.

Jakubowski et al. wrote a chapter on glow discharges in emission and mass spectrometry in the recent book, *Atomic Spectroscopy in Elemental Analysis* (276). This chapter included basic principles of glow discharges (i.e., most important plasma species and collision processes in the plasma and at the walls), as well as methodological developments and analytical applications of both GDMS and GD-OES. It was concluded that analytical GDS is now well accepted as a powerful technique for the direct analysis of both conducting and nonconducting samples, as well as for depth profiling analysis. It has the ability to fulfill the new challenges coming from the material sciences. Furthermore, it was demonstrated that rf sources are gaining increasing importance, but novel matching units are needed, which allow the measurement of the applied voltage and the real current passing the plasma only.

An interesting review paper by Hoffmann et al. discussed the history, present situation, and future of GDMS (277). Over the past 20 years, GDMS has become the industry standard for the analysis of trace elements in metals and semiconductors. Other applications, such as depth-resolved measurements and analysis of nonconductors, are also overviewed. Quantification aspects and the use of relative sensitivity factors are described. The effect of physical properties of the analyte materials, such as temperature and secondary electron emission coefficients, are discussed. Finally, latest developments in the field of "fast flow" sources and pulsed glow discharges are presented.

Betti published a review on the applications of GDMS and secondary ion mass spectrometry (SIMS) on isotope ratio measurements in several matrixes (278). Emphasis was placed to new research fields, such as solar system studies, medicine, biology, and environmental and nuclear forensics. Both techniques have the capability of depth profiling, but GDMS can perform with a deeper penetration of the surface, whereas SIMS can carry out surface profiling with micrometer lateral resolution. Used in combination, GDMS and SIMS can give a complete characterization of the sample, with respect to isotope ratios as well as quantitative analysis at the solid state.

In another interesting review paper, Betti et al. reported on the application of GDS to characterize nuclear samples as well as to determine radionuclides in environmental samples (279). The use of instrumentation for dc GDMS and rf GD-OES, installed inside a glovebox for the handling of radioactive samples, is described in detail. Procedures for quantitative determination of major, minor, and trace elements in conductive samples are reported. For nonconductive samples, three different approaches are described, i.e.: (i) the use of rf sources, (ii) the mixing of the sample with a binder conducting host matrix, and (iii) the use of a secondary cathode. The analytical capabilities of GDMS are compared with ICPMS in terms of accuracy, precision, and detection limits for the determination of trace elements in uranium oxide specimens. For the determination of isotopic composition, GDMS was found to be competitive with thermal ionization mass spectrometry (TIMS). Applications of GDMS to the determination of radioisotopes in environmental samples, as well as for depth profiling of trace elements in oxide layers, are discussed.

The use of GDMS for isotope ratio measurements, in comparison with other techniques, was discussed by Becker in a review paper on methodological and instrumental developments, as well as novel approaches and applications in isotope ratio measurements, using different mass spectrometric techniques, such as ICPMS, LA-ICPMS, TIMS, accelerator mass spectrometry, resonance ionization mass spectrometry, SIMS, and GDMS (280).

Although GDS with dc sources is widely used in routine applications for the analysis of conducting samples, it cannot directly be applied for nonconducting samples, because of charging-up effects. For this application, rf sources are more suitable, because they can directly be used without sample preparation steps. Winchester and Payling published a very interesting and complete review on rf GDS (281). The historical foundations as well as current knowledge of the fundamental physics of analytical rf GDs are discussed. Additionally, instrumentation, methodologies, and applications of rf GD-OES and GDMS are reviewed. Finally, the review also provides explanations of some develop-

ments that are needed for further progress in the field of analytical rf GDS.

Another review on the state of the art of rf GD, coupled to AAS, OES, and MS for direct solid analysis, is presented in ref 282. A description of the principles and operation of the rf GD and attempts to model these discharges are also given. Rf GD instrumentation, both developed at research laboratories and commercially available, is described. Further, several practical examples are given, demonstrating the capabilities of these techniques for bulk and depth profile analysis. Finally, the research gaps to be filled for full implementation of rf GD spectrometric techniques in industry and research centers are discussed.

Besides dc and rf GDS, pulsed GDs, with millisecond or microsecond pulse duration, are also gaining increasing interest in recent years, especially in combination with TOFMS. In a recent A-page article in *Analytical Chemistry*, Hieftje and co-workers discuss, among other items, the coupling of such a pulsed GD to TOFMS (283). Because the ionization mechanisms vary substantially during the lifetime of the pulsed plasma, a succession of elemental, molecular, and structural information can be generated from a single pulse event, and the different types of spectra can be accessed by the appropriate choice of delay time between initiation of the GD pulse and extraction of ions into the TOFMS system. Moreover, coupling a pulsed GD with a separation method can provide an additional dimension of information.

Besides review papers, several new developments in GDS were published in the last two years, both in the field of fundamental studies and methodological work and (novel) applications.

Fundamental Studies. Since GDS is very important for depth profiling analysis, as will be discussed below, the study of crater shapes as a result of GD sputtering is of fundamental importance, because for good depth resolution, the crater should be as flat as possible. In ref 284, the influence of crater shape on depth resolution in rf GD-OES was investigated. Three different effects were shown to play a role: (i) the so-called "crater edge effect" (i.e., the crater is deeper at the sides than in the center), (ii) the roughening of the crater bottom, and (iii) the redeposition of material at the crater wall. The importance of these effects was tested on multilayer stacks consisting of alternating Cr and Ti layers, with individual thicknesses of >500 nm. Moreover, this study was also extended to the case of thinner layers (layer thickness <150 nm) (285). An increased degradation of the compositional depth profiles was observed, due to the continuous change in crater shape after each interface, which induces a higher mixing of the thin layers.

In ref 286, crater profiles were calculated by means of numerical modeling of the GD. A comparison was made between calculated and measured crater profiles, under exactly the same conditions and GD source geometry, for a wide range of current–voltage conditions. Good agreement was reached, demonstrating that the model takes into account the correct underlying mechanisms responsible for the crater shape and that it can be used to predict optimum conditions for flat crater profiles. It is concluded from the model that the characteristic crater shape is determined by the electrical potential distributions in front of the cathode, the radial distribution of fluxes and energies of the species bombarding the cathode, and the redeposition of sputtered atoms at the cathode surface.

Another comparison between model predictions and measurements in a dc GD was performed in refs 287 and 288. In ref 287, a laser-scattering based instrument was applied to determine the gas kinetic temperature via Rayleigh scattering, whereas the electron number density, electron temperature, and shape of the electron energy distribution function were determined by Thomson scattering. Axial profiles of these parameters were obtained for different values of electrical current, voltage and pressure. In ref 288, the profiles of gas temperature, electron density, electron energy distribution function, and average electron energy were calculated with a two-dimensional model, for the same values of current, voltage, and pressure as in the Thomson and Rayleigh experiments. The gas temperature distribution and electron density profiles were found to be in reasonable agreement with the experiments. As far as the electron energy was concerned, the experiment was able to detect only the thermal and low-energy electrons, whereas the model focuses mainly on the high-energy electrons. Hence, model and experiment were found to give complementary information.

The gas temperature and electron number density were also determined experimentally by Niemax and co-workers, in a microhollow cathode discharge operated in Ar and He at various pressures, by means of absorption and emission spectroscopy (289). Furthermore, the discharge was also coupled to emission and mass spectrometry for analytical applications, more specifically for organometallic compounds. The high electron number density implies a high ionization degree of the plasma, which favors the coupling to a mass spectrometer. The high gas temperature helps in efficient dissociation, while the high electron number density is responsible for the excitation of the analytes introduced. It is concluded that these microplasmas can substitute other analytical instruments in specific areas. In particular, they are good detectors for gases, delivering excellent detection limits.

The effect of reactive gases in dc and pulsed GDs was investigated by Harrison and co-workers, by gradually replacing Ar by N_2 or O_2, until a discharge is obtained that is completely sustained in these reactive gases (290). A common trend with N_2 or O_2 addition was the significant loss of the Ar^+ and ArH^+ ion signals. The O_2^+ ion signal increases, whereas the N_2^+ ion did not exhibit the same trend. The results have shown that both dc and pulsed discharges are stable in reactive environments, which suggests a range of new GD possibilities.

The effects of adding H_2 to Ar GDs was also studied in a number of papers. Mason and co-workers investigated the addition of H_2 to an Ar plasma, with "fast flow" (ff) GDMS (291). Changes in steel and copper cathode ion intensities from the afterglow of a ff dc GD have been studied as a function of the amount of H_2 added downstream from the active discharge region. The signals from the majority of different elements increased, although some analytes were actually quenched. This behavior was explained by a mechanism based on the Rydberg gas model of this kind of flowing plasma, developed earlier by these authors.

Weiss and co-workers reported on the effect of hydrogen, either originating from the sample or added at a low concentration to the discharge gas, on the intensities of many Zn lines in a Grimm-type GD, by means of a CCD camera and a Fourier transform spectrometer (292). Hydrogen was found to increase the emission yields of all observed Zn lines, but the enhancement

factors were different for different kinds of lines. Furthermore, the excitation of Zn in pure Ar discharges was also investigated, analyzing Zn−Cu and Zn−Al alloys, and suppression or enhancement of the ZnI and ZnII lines by Cu or Al was determined. These effects can be corrected for by certain multiplicative corrections, as is described in the paper.

Sanz-Medel and co-workers studied the addition of hydrogen (at contents of 0.5, 1, and 10%) to a dc GD coupled to a TOFMS, at constant voltage and pressure (293). It is found that hydrogen addition gives rise to significant changes in the slope of the current−voltage relationship, indicating that the electrical resistance of the discharge increases with hydrogen addition to pure argon. Furthermore, a drop in the sputtering rates was observed upon hydrogen addition, but the analytical ion signals observed for discharge voltages above 900 V turned out to be higher in a 0.5% H_2/Ar discharge than in pure Ar. Finally, the effect of H_2 addition on the in-depth profile of a tin plate has also been investigated. A higher sensitivity for major and minor components of the coating were observed, compared to a pure Ar discharge, without loss of the relative depth resolution.

Finally, calculations were performed by Bogaerts and Gijbels on the cathode (sample) temperature (294). It is generally known that the cathode of glow discharges can become quite hot, when no or inappropriate cooling is applied, as a result of the bombardment of energetic ions and atoms from the plasma. The cathode temperature has an important effect on both the plasma behavior (e.g., on the gas temperature and hence on the electrical characteristics) and on the analytical performance, but the exact value is very difficult to measure. Therefore, the temperature of the cathode (sample) in analytical glow discharges was calculated as a function of depth in the sample, by means of a one-dimensional heat conduction equation. The energy input was determined by the energetic ions and atoms bombarding the cathode. Calculations were performed for various cathode materials, for a range of different voltages, pressures, and currents, and under conditions ranging from perfect cooling to the limit of no cooling. It was found that the efficiency of cooling has a very important effect on the cathode surface temperature. Moreover, different cathode materials can give rise to great differences in the cathode surface temperature, due to differences in the thermal conductivities. Since the cathode surface temperature determines the gas temperature, and hence the current−voltage−pressure relations, this can explain why different cathode materials exhibit different electrical characteristics.

Methodological Developments. Fundamental studies, as described above, can lead to new insights in the GD behavior, which can then be useful for further methodological developments. Some research groups have reported on special ion or emission sources. Mason et al. have described an ion source for use in low-power GDMS, using fast-flowing argon as the discharge gas, and attached to a quadrupole analyzer (295). The argon flow carries the plasma downstream onto an ion exit sampling cone. Based on studies of the physical and chemical properties of the plasma, it was suggested that such a ff GD contains large quantities of high n Rydberg atoms of both the discharge gas and the sputtered cathode.

In ref 296, a compact, small-volume dc GD lamp for GD-OES was presented. The design aspects, fundamental characteristics, and analytical performance (process optimization for Cu and brass solid samples) were described in detail. Wagatsuma and co-workers have reported on the combination of an rf GD lamp with a Nd:YAG laser as emission excitation source (297). In this system, sample atoms ablated by the laser irradiation are introduced into the GD lamp chamber and subsequently excited by the He GD plasma. The pulsed operation of the laser can produce a cyclic variation in the emission intensities of the sample atoms, whereas the plasma gas species emit the radiation continuously. By phase-selective detection, the laser modulation signal can be separated from the continuous background emission. Hence, the emission intensity of the laser ablated atoms can be measured, free from the interference of other species present in the plasma. Furthermore, a voltage modulation technique was applied by Wagatsuma et al. for the precise and accurate determination of manganese in steels in dc GD-OES (298). Emission signals from the GD source were modulated by a cyclic variation of the discharge voltage, so that only the desired signals can be detected at very low noise levels by using a lock-in amplifier.

A special GD, using a solution as the cathode, also called ELCAD (i.e., electrolyte-as-cathode discharge) by the inventors more than a decade ago, was recently investigated in detail by Hieftje and co-workers (299). Spectroscopic and electrical studies were carried out to gain a better understanding of the operating mechanism and characteristics of such systems. The effects of the discharge gap size, the pH and conductivity of the solution, the applied current, and the solution flow rate were studied. Detection limits were in the range of tens of ppb. This system shows promise as a sensitive and inexpensive technique for the elemental analysis of liquids. It is suggested that better signal-to-noise ratios can be achieved for certain elements if emission were collected only from certain areas. However, the variations among the emission distribution of different elements limit the feasibility of this approach, if the ELCAD is to be used as a multielemental technique. Collecting emission from all but the zone 0.5 mm closest to the anode might offer a good compromise. Finally, it was suggested that a significant fraction of the emission for many elements is not from atoms ejected by sputtering from the solution, but from metals desolvated and atomized some distance above the solution.

Several research groups have also reported on methodological developments for rf sources. Wagatsuma investigated the effect of dc bias current on an rf GD plasma, by measuring a large number of Ni emission lines, with and without the bias current introduction (300). Emission intensities of Ni atomic lines, especially with an excitation energy of ∼5 eV, were predominantly elevated by the bias current. This could be explained by the additional excitation through collisions with the introduced electrons, having kinetic energies favorable for the excitation of such Ni atomic lines. This additional excitation mechanism was, however, less effective for excited states of Ni ions, argon atoms, and ions, because of their much higher excitation energies.

Anfone and Marcus have evaluated three modes of calibration and quantification in rf GD-OES for the determination of Al, C, Fe, P, and Si in various NIST reference materials (i.e., normal calibration, with internal standards, and based on sputtering rate) (301). The incorporation of the dc bias potential correction in the

normal and sputtering rate modes of calibration was also investigated. The internal standard mode, using the intensity of the Ar(I) 404.44-nm transition as the internal standard, performed better than the normal and sputtering rate modes. Using the dc bias potential correction in the latter two modes provided enhanced performance. The accuracy was typically ≤5−7% error, and the best precision was reached with a 1.3−7.7% RSD range.

Payling et al. presented two methods for dealing with variable background signals in rf-GD-OES, to improve elemental analysis at trace levels, both in bulk analysis and in depth profiling, without having to measure background signals during analysis (*302*). The background signals were measured away from the analytical emission lines of interest during calibration only and for each material type of interest. The methods yield significantly better results than with a constant background, as tested for bulk analysis of a tool steel and for two depth profiles (TiO$_2$ coating on Si, and TiN-coated tool steel).

Finally, Wilken and co-workers explained in ref *303* that, for quantification of rf GD-OES, two independent electrical signals are required. These are provided in real time by the GD source with integrated voltage and current sensors, by means of a plasma equivalent circuit. It is shown that the cathode voltage and the active cathode current describe the sputtering and excitation well. Further investigations in ref *304* were related to the use of this new GD source for quantitative rf GD-OES measurements at insulators or insulating layers on conductors. When sputtering insulating samples, the voltage over the discharge is not directly measurable. The coupling capacity of the sample is required in order to calculate the discharge voltage. A procedure was outlined where the coupling capacity is determined using an electrical measurement without discharge. The calculated time-dependent discharge voltage and current were evaluated using a plasma equivalent circuit. When using this method for sputtering an insulating sample at constant voltage and current, the emission yield of an Al line was found to be comparable to that of a conducting reference material.

With respect to pulsed GDs, King and co-workers presented a very interesting study of a millisecond pulsed rf GD for TOF-MS, making use of a so-called "thermometer molecule", i.e., tungsten hexacarbonyl (W(CO)$_6$) (*305*). Vapor of W(CO)$_6$ is introduced in the plasma and subjected to various ionization and excitation processes. The resultant molecular and fragment ions are monitored using a TOFMS, to determine the internal energy distributions in the plasma. Three different temporal regimes were distinguished, i.e.: (i) the prepeak period, characterized by high energy and hence a large amount of fragmentation, producing mainly atomic ions, (ii) the plateau region with lower energy, yielding mainly structural information, and (iii) the afterpeak period, characterized by the lowest amount of energy, resulting in soft ionization, and hence the intact molecular ions. These observations suggest that the pulsed GD affords excellent energy tunability that can be used to perform selective ionization and fragmentation for molecular, structural, and elemental information.

In a paper by Hieftje and co-workers, a microsecond pulsed GD has been coupled with a miniature Mattauch−Herzog double-focusing mass spectrograph (*306*). Several well-established advantages have been realized with the pulsed GD, such as a higher instantaneous power, reduced sample heating, and the ability to temporally resolve spectra of analyte and support gas ions. The latter advantage is demonstrated by the determination of ^{40}Ca$^+$ and ^{39}K$^+$ concentrations in an Ar GD. In another paper by the Hieftje group (*307*), several absolute quantification strategies have been evaluated for multielemental analysis in dc GDMS with a time-of-flight mass analyzer. A method for standardless analysis was described that offers accuracy within 1 order of magnitude, without relying on any calibration factors or internal standards. The accuracy of this method was further improved by 2−4-fold, through use of relative sensitivity factors, which were fairly independent of the matrix. When RSFs were employed, experimental results were determined with a mean accuracy of 5−12% for analyte concentrations greater than 1%.

An interesting instrumental development for GDMS was published in ref *308*. To improve the sensitivity for low-abundance ions in glow discharge Fourier transform ion cyclotron resonance mass spectrometry, an external octopole ion guide was applied. The latter functions as a high-pass mass filter to destabilize the trajectories of the low-mass, high-abundance ions and hence to remove them, prior to introduction of the remaining (low abundance) ions from the source into the FT-ICR analyzer cell. An increase in detection sensitivity for high-mass, low-abundance Pb and Sn ions in a steel sample was observed.

Finally, Marcus and co-workers have reported on the development of a Microsoft Windows-based software program, for rapid routine data analysis, to be used for GD-TOFMS. Software functions include algorithms for calibration, isotope ratio determination, resolution, and ion dynamics. Description of this software program is explained in ref *309*, and the electronic files of the program are archived on the homepage of *Spectrochimica Acta Electronica*.

Applications. 1. Bulk and Depth Profiling Analysis of Conducting Samples. GDS is one of the standard methods for bulk and depth profiling analysis of conducting materials; hence, most of the application-oriented publications are related to these topics. Especially in the field of thin-film and depth profiling analysis, several new developments are reported every year. In refs *310*−*312*, GDMS was applied to determine trace impurity concentrations in Cu films, deposited by the non-mass-separated ion beam deposition method. Because GDMS had some difficulty to apply to thin films deposited on a nonconducting substrate, an aluminum foil was used in ref *310* to cover the edge of the Cu film, to make an electrical contact. Furthermore, to obtain the depth profile of the trace impurities in the film, a Cu bulk sample was used in advance, to provide the optimum conditions for depth profile analysis, so that no loss of the film surface was reached prior to the actual analysis. Furthermore, in ref *311*, it was shown that the Cu film deposited at a substrate bias voltage of −50 V was characterized by lower impurity contents than the Cu film deposited without the substrate bias voltage, and some reasons for this purification effects were given. In a subsequent study (*312*), a combination of GDMS and SIMS was used to determine the impurity concentrations, and it was found that the dominant impurities with great influence on the film purity were H, C, N, and O.

More than GDMS, in particular, GD-OES has become the standard method for depth profiling analysis, either with dc or (most often) with rf sources. A very interesting paper was written

by Shimizu et al., where the first example of depth profiling analysis of a layer of subnanometer thickness by rf GD-OES was presented (*313*). It concerns a monolayer of thiourea adsorbed on a mirror-polished copper substrate. The adsorbed layer was disclosed clearly in the depth profile as narrow peaks, above the Cu substrate, of C, H, N, and S. Furthermore, the positions of peaks were separated and located in the order that is expected from the orientation of the thiourea molecules adsorbed on the Cu substrate. This new achievement greatly extends the power of rf GD-OES and may open entirely new areas of its application in surface analysis, such as the study of adsorbed molecules or monolayers. In fact, it was concluded that rf GD-OES is the only technique that allows depth profiling analysis of surface regions, both conducting and nonconducting, from the first atomic layer to depths of several tens of micrometers, readily and rapidly, with excellent sensitivities (~ppm), for most of the elements in the Periodic Table.

Luesaiwong and Marcus performed a parametric evaluation of the discharge conditions that affect the quality of rf GD-OES depth profiles of Ni–P plated Al hard disks (*314*). The optimal discharge operating parameters were determined to be an rf power of 40 W and an argon gas pressure of 6 Torr. Optimized discharge conditions were employed to profile hard disks extracted from two commercial drives of different technological generations. Distinct compositional differences were observed that correlate with improvements in the base technology over the years 1992–1998.

In ref *315*, rf GD-OES was used to study the elemental composition of the surface and near-surface regions of hot-rolled Al alloys, before and after annealing treatments. The GD-OES depth profiles suggested enrichment of some and depletion of other alloying elements, as well as the introduction of impurity elements within the disturbed surface layer of the alloy.

Michler et al. applied rf GD-OES for the depth profiling of thin oxide films (*316*). Dc bias voltage, hydrogen, and density corrections were applied, which allow the combination of samples with different electrical characteristics in a single calibration, and the obtaining of depth profiles of coatings, even in the presence of significant amounts of hydrogen in the coating. More or less the same group of authors presented a calibration procedure for depth profiling by GD-OES, based on the well-established relative or internal standard method (*317*). It allows reduction of the number of CRMs with known sputtering rates to a strict minimum, while still using a large number of CRMs for establishing the analytical curves. Hence, this new calibration method allows the uncertainty in the calculation of the chemical composition to be separated from the uncertainties of sputtering rate measurements.

In ref *318*, the capability of GD-OES to provide a fast and quantitatively reliable way of obtaining depth profiles of more than 150 μm with a time consumption no longer than 2 h was demonstrated. The performances of rf and dc sources were compared, and results were presented for dc and rf GD-OES of industrial surface treatments, such as chemical vapor deposition, physical vapor deposition, and ion implantation. In ref *319*, GD-OES was applied, together with STEM and glancing angle X-ray diffraction, to measure the composition and structure of thin deposits of Zn–Ni on Cu and Fe substrates, obtained by Zn–Ni electrodeposition. The influence of substrate material on composi-

tion of the deposits was demonstrated by GD-OES. Another application was presented in ref *320*, where rf GD-OES was used, together with carrier gas hot extraction to investigate the behavior of organic impurities adsorbed on and incorporated into electroplated Cu layers. GD-OES depth profiles showed that the majority of organic impurities have to leave the Cu before an accelerated abnormal grain growth can start. Furthermore, in ref *321*, GD-OES was used to measure depth profiles in the oxide scales on Fe–Cr alloys. The obtained depth profiles were consistent with SIMS results, with some differences in minor elements. Three zones were identified from surface to internal oxides: a Mn- and Fe-rich layer, a Cr-rich layer, and a Si-rich layer.

Finally, Djulgerova reported on a hollow cathode discharge (HCD) operating in neon, used to investigate the depth profile analysis of a $SnO_2/SiO_2/Si$ structure (*322*). The depth behavior of the elements Sn, N, C, and Si in this structure was deduced from the temporal variations of their emission spectra. The results confirmed the sensitivity of the HCD as a spectroscopic source as well as its flexibility and usefulness when applied to modern analytical problems.

2. Analysis of Nonconducting Samples. As mentioned above, the analysis of nonconducting samples is mostly carried out by rf GD sources. Sanz-Medel and co-workers have developed an rf GD-TOF-MS system for direct analysis of nonconducting samples (*323*). Several different instrumental configurations of the rf GD source, such as the optional use of a sampler cone, and the possibility of allowing electrical floating of the discharge, were first evaluated with a conducting sample. Higher ion signals were obtained when the GD was electrically floating and no sampler cone was used. Subsequently, a homogeneous glass was analyzed, and analyte signals were found to be systematically higher without the use of a sampler cone. The analytical capability of the proposed rf GD-TOF-MS system, in terms of sensitivity, isotope ratio accuracy, and mass resolving power, has been investigated for the analysis of thick glasses, up to 6 mm. Isotope ratio accuracies of ~±1% and mass resolving powers of ~700 were observed.

The same research group has also investigated the direct solid quantitative analysis of glass by rf GD-OES, and the effect of sample thickness was studied (*324*). The quantification scheme used is based on the "constant emission yield" concept, in which the measured analytical signals were corrected for thickness differences. Furthermore, in ref *325*. the same authors have evaluated the effect of thin conductive gold layers (10 and 50 nm thick) on glass samples of different thicknesses (in the range 1.8–4.8 mm) measured by rf GD-OES. As the glass becomes thicker, a drop in sputtering rates was obtained, and this effect was more serious for homogeneous glasses than for those coated with gold. It was found that the coated glasses exhibit an intermediate behavior between insulating glasses and conducting materials. Higher analytical signals were obtained for coated glasses than for the insulating glasses, and the differences were more noticeable for the thicker glasses. The emission yields of Si and Ca, on the other hand, were found to be virtually independent of the insulator thickness and the presence of a conductive coating. Finally, in ref *326*, the use of dc and rf GD-OES for the quantitative analysis of metallurgical-grade Si was presented. Samples of different thickness, between 1.6 and 4 mm, were evaluated. It was found that for samples thinner than 2 mm, the behavior was

similar to that of conductors, but for thicker samples, the observed behavior resembled that of an insulator. The dc measurement yielded poor sensitivity, because soft electrical conditions had to be selected to avoid instabilities. The rf measurements showed a higher performance, and it was demonstrated that rf GD-OES is a useful technique for the rapid and convenient analysis of metallurgic-grade Si in industry.

3. Analysis of Gaseous or Liquid Samples. Besides the analysis of solid materials, for which GDS has almost become a routine method, several attempts have been published in the last two years, for the analysis of gaseous or liquid samples, where GDMS or GD-OES is then used as detector for gas or liquid chromatography. Newman and Mason applied their so-called ff GD ion source for the detection of halogenated hydrocarbons, using GC as the sampling introduction technique (*327*). A simple and robust interface design enabled direct coupling of the ion source to a common gas chromatograph. The source operating conditions could be "tuned" to obtain different information, allowing both sensitive elemental detection and structure elucidation using a single instrument, with subpicogram detection limits. The source pressure, power, and discharge gas flow rate appeared to have significant influence on the relative fragment ions detected. In ref *328*, the same combination of ff GDMS coupled to GC was evaluated for the speciation of tetramethyl-, tetraethyl-, triethyl-, and tributyltin compounds. Because the sample is introduced into the flowing afterglow, and not in the active discharge region, the rapid flow of Ar gas carries the analyte toward the sampling cone, reducing diffusional losses. The technique demonstrated excellent linearity (response indices 0.98−1.01) with a dynamic range of 3−4 orders of magnitude. By varying the ion extraction voltage, controllable fragmentation could be obtained without affecting the primary discharge. From measurements of the relative ion kinetic energies, the observed fragmentation has been attributed to dissociation by electron bombardment in the ion extraction field. Because this ff GDMS technique combines sensitive and selective detection with low cost and simplicity (relative to other MS methods), it has potential applications in routine monitoring and identification of unknown organotin compounds in the environment.

Marcus and co-workers applied their so-called particle beam (PB)-GDMS setup to detect a mixture of organic and inorganic arsenic compounds using ion-exchange LC separation (*329*). The particle beam interface makes use of nebulization and momentum separation to deliver a stream of dry analyte particles to the GD source, from the LC output. The analyte particles are then vaporized and ionized in the GD, and the ions are subsequently analyzed with a quadrupole mass spectrometer. The results show that PB-GDMS has a high potential as a comprehensive (inorganic/ organic) detector for both biological and environmental speciation work.

A similar approach is the so-called particle beam/hollow cathode optical emission spectroscopy (PB/HC-OES), also developed by Marcus and co-workers. In refs *330* and *331*, this technique was applied for total protein determinations. In ref *330*, a range of nonvolatile inorganic salts (i.e., chloride salts with different cations, and potassium salts with different anions) and a more typical volatile organic carrier agent were investigated for their potential "carrier" capabilities. The analyte response curves

of samples with KCl added as the sample injection matrix showed a higher sensitivity, better linearity, and lower detection limits in comparison with those obtained with water, HCl, KNO$_3$, or ammonium acetate as carrier matrixes. Similarly, in ref *331*, the effect of silica microparticles as possible carrier agents for enhanced particle transport was investigated. Parametric optimizations for sample treatment, including silica product type, silica concentration, sample incubation temperature and time, sonication time, and solvent pH, were performed. The analytical results showed clear improvements, in comparison with the use of simple aqueous solvent as the sample injection matrix. In the future, a promising application of the PB/HC-OES might be as a diagnostic tool for protein-binding studies to a wide variety of materials. In such studies, the particles in question would themselves serve as the carriers. Binding to inorganic, polymeric, and metallic microparticles of different composition could then be evaluated with high sensitivity in a relatively straightforward fashion. Finally, in ref *332*, the PB/HC-OES was applied as an element-specific detector for nucleotide determinations. Use of the PB interface to remove latent solvent species facilitates the sample preparation procedure and enhances the feasibility of interfacing liquid chromatography to the system. It was observed that high current densities and modest He gas pressures are favorable for the detection of P. As also reported in ref *55*, with the addition of KCl as a carrier salt, significant improvements in the sensitivity were observed.

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