Anal. Chem. **2004,** *76,* 3313−3336

Atomic Spectroscopy

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Review Contents

Methodological developments in atomic spectrometry are related to new techniques in optical spectrometry as well as in elemental mass spectrometry especially, as the sources used in atomic spectrometry are prominent sources of electromagnetic radiation, absorption reservoirs for atomic absorption, and ion sources for elemental mass spectrometry. Developments in the field are related to the sources themselves and their improvement and optimization as well as with the different types of spectrometers and detectors and the different ways for optimal sampling of the analytes.

Improvements in the different fields have regularly been published in the journals *Analytical Chemistry*, *Analytical and Bioanalytical Chemistry*, *Analytical Sciences*, *Analyst*, *Analytica Chimica Acta*, *Applied Spectroscopy*, *Journal of Analytical Atomic Spectrometry*, *Mikrochimica Acta*, *Spectrochimica Acta*, *Part B*, and *Talanta* as well as to a lesser extent in a number of other journals. These progress reports published have been considered for noting the trends of development in the fields mentioned, at the hand of a selection of the papers published in the journals named in the period January 2002 to December 2003 for the case of atomic absorption and atomic emission work, whereas for inductively coupled plasma mass spectrometry and for glow discharge atomic emission and mass spectrometry, the selection of the papers considered the journals as indicated in the respective chapters.

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Results in the field of atomic spectrometry in the last biannual period also were reported on the following important conferences: Winter Conference on Plasma Spectrochemistry, Scottsdale, AZ (2002), the International Conference on Atomic Spectroscopy (ICAS), Tokyo (2002), the Colloquium Spectroscopicum Internationale, Granada (2003), the European Winter Conference on Plasma Spectrochemistry, Garmisch Partenkirchen (2003), and the annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, in Nashville, TN (2002) and Fort Lauderdale, FL (2003) as well as in many other meetings.

Progress made in the field of atomic spectrometry is discussed for the following fields: optical atomic spectrometry (atomic absorption and atomic emission spectrometry with sparks, arcs, and plasma sources at atmospheric pressure including laser plasmas); plasma mass spectrometry and optical atomic and mass spectrometry with glow discharge sources.

ATOMIC ABSORPTION SPECTROMETRY

Innovation in atomic absorption spectrometry (AAS) both from the instrumental and from the methodological side is related to the primary sources, atom reservoirs, sample introduction, and analytical figures of merit so as to be able to solve challenging analytical problems in a wide variety of fields in science and technology.

AAS from its principle is well known, but in the primary sources especially there is considerable potential for development as a result of emerging technologies.

With respect to the primary sources, research on boosted hollow cathode lamps is still progressing (*1*). Here the radiant output of the sources is improved and also the "sharpening" of the resonance lines. Radio frequency (rf)-powered lamps with a high radiance at low-UV wavelengths (*2*) have been described. Further, the availability of diode lasers enables realization of the whole selectivity of AAS in the primary source and makes the monochromator superfluent, but it also creates a new tool for source diagnostics. The analytical possibilities of diode laser AAS including modulation techniques have been discussed by Koch et al. (*3*), whereas Gustafsson et al. (*4*) treated the possibilities of wavelength modulation in diode laser AAS especially in the case of graphite furnace atomization. The features of diode laser AAS for isotope analysis were shown by Liu et al. (*5*), who found that for $^{235}U/^{238}U$ both high accuracy (<5%) and reasonable precision (∼17% RSD) can be achieved at 0.2−0.7% (w/w) ^{235}U in the ^{238}U level.

Flame Atomic Absorption Spectrometry. Despite the maturity of flame atomic absorption spectrometry and its wide use in analytical routines, there are still interesting developments in the method itself.

10.1021/ac040052x CCC: $27.50
Published on Web 04/23/2004

In calibration, instrumental provisions for automated standard addition are to be named as well as the use of derivative methods, e.g., through the coupling of double microcolumns with a cation exchanger for the determination of Cr(III) and total chromium with flame AAS (*6*). In many papers, the use of flow injection technology is used to enable an on-line preconcentration of the analytes as well as removal of the matrix elements in an automated way, as shown for the determination of cadmium in seawater (*7*). This approach, as well as selective extraction methodology and lately especially microwave-assisted selective leaching, is useful for speciation work as well.

A further way to improve the power of detection, being the weak point of flame AAS for environmental work and for the analysis of biological samples, is the use of atom trapping. The revolatilization of analytes from silica traps, e.g., for the elements Bi, Au, Mn, Cd, and Pb, has been studied by Korkmaz et al. (*8*). A special approach for preconcentration of trace elements is selective cloud point extraction, which for Ag has been shown by Manzooni and Karim-Nezhad (*9*).

An interesting approach for an integral analysis of biological samples is possible in high-temperature/high-pressure flow digestion coupled on-line with flame AAS, as shown by Jacob and Berndt (*10*). They were able to determine Cd, Pb, Cu, Mn, and Zn down to the microgram per gram level in suspensions of powdered plant and animal tissue samples.

Direct solids sampling was shown to be successful in the case of flame AAS for volatile elements such as Cd, which could be determined down to 0.25 μg/g in 1-mg samples of sediments (*11*). Flame AAS also enables one to perform highly precise determinations, as was shown for the analysis of Li1 + *y*Co2 materials analyzed by flame AAS and automated potentiometric titration (*12*).

Graphite Furnace Atomic Absorption Spectrometry. In methodological studies, the different processes occurring in the graphite furnace were further investigated.

Sadagoff and Dedina (*13*) compared calculated and measured diffusion coefficients for various types of furnaces whereas Ozcan et al. (*14*) studied the vertical spatial distribution of Sn in the graphite furnace in the presence of HCl and different salts including Pd as matrix modifier.

Further, especially the use of isothermal systems was studied. This principle can be realized with the tranversally heated graphite furnace, for which, for example, Ortner et al. (*15*) studied corrosion through the replicate introduction of Fe and La compounds. Graphite furnace AAS with a transversally heated furnace was shown by Ngobeni et al. (*16*) to be of use for direct determinations of Pb and Cd in complex samples such as urine. As a second approach for isothermal heating, the L'vov platform now is of routine use. For example, Pereiro-Filho et al. (*17*) used the L'vov platform technique together with so-called permanent (Zr) and conventional (Mg or Mg,Pd compound mixtures) chemical modifiers and studied elemental distributions for P, S, Ca, Ti, Fe, Zr, Hf, and Pd by synchrotron X-ray fluorescence spectrometry. Tsalev et al. (*18*) studied the use of platforms charged with permanent modifiers such as Zr or W to reduce the amount of phosphate modifier required, as the latter may introduce contamination in the case of Pb and Cd.

The use of tungsten furnaces has been further investigated, as they have advantages in the case of carbide-forming elements and as their heat capacity generally is low. Queiroz et al. (*19*) studied the electrothermal behavior of Na, K, Ca, and Mg in a tungsten coil atomizer, and Amin et al. (*20*) used a preconcentration of Sb in water on a tungsten wire to be inserted in the tungsten furnace.

An interesting furnace enabling integrated preconcentration is the filter furnace described by Anselmi et al. (*21*). With this device—which through transversal heating is isothermal—Cd, Cr, Cu, Pb, and Ni can be directly determined in automotive fuels without need for use of a chemical modifier.

Chemical modifiers themselves remain an important field of research in graphite furnace AAS. Here both Pd, W, Rh, Ir, Nb, Ni, Zr, and Mg salts or binary mixtures of them can be used to retain the analytes while evaporating the matrix elements. In efforts to clarify the mechanisms of these modifiers, Rohr et al. (*22*) investigated whether intercalation of Pd in the graphite occurs with the aid of valence bond X-ray spectrometry. Maia et al. (*23*) investigated the use of a permanently modified graphite tube surface to eliminate interferences in coal analysis, whereas Fischer (*24*) studied the electrothermal atomization of Pd-stabilized Se in the presence of phosphate. Cabon (*25*) studied the use of hydrofluoric acid as chemical modifier in the determination of Cu and Mn, whereas Kopyść et al. (*26*) used noble metal modifiers in the simultaneous determination of As, Sb, and Bi.

Though historically and through its limited dynamic range, a monoelement method, graphite furnace AAS, through the use of continuum sources well enables simultaneous determinations. Here xenon lamps and especially high-resolution Echelle spectrometers are instrumental for realizing high elemental selectivity, as shown by Welz et al. (*27*). The features of the Echelle spectrometers now available, especially in the case of high-quality CCDs, have been described by Becker-Ross et al. (*28*). They also enable background evaluation. For background correction, apart from the well-known D_2 lamp and Zeeman methods, self-reversal of lines still is a very practical approach, as described by Oppermann et al. (*29*). Simultaneous determinations in real samples were shown for the case of As, Cd, Cr, and Pb in soil extracts (*30*).

Direct solids analysis for a number of analytes and types of samples remains an important field of research in graphite furnace AAS. Sahuquillo et al. (*31*) determined total and leachable As in sediments to test the potential for remobilization of As in sediments, and Resano et al. (*32*) showed the potential for various types of solid samples such as a polymer, a pharmaceutical drug, and a used autocatalyst reference material. Particularly, slurry sampling is an interesting approach in direct solids AAS. Dong and Krivan (*33*) determined Si in titanium and used Pd−$Mg(NO_3)_2$ as a modifier. In a simultaneous determination of Pb, Ni, Sn, and Cu in aluminum-base alloys, colloidal metallic slurries as obtained with an electrical discharge were analyzed (*34*).

To improve the power of detection of flame AAS, a flame-heated furnace was used as atomizer, in which the sample can be entered as a liquid jet produced with the aid of a peristaltic pump (*35*) or by a thermospray produced in a ceramic capillary being heated in the flame (*36*). In such a setup, powder samples can also be fed as slurries and digested in a flow-through system before being nebulized, as shown by Pereira-Filho et al. (*37*). Such systems are very similar to flow injection microwave-assisted digestion, as applied by Burguera et al. (*38*) for blood analysis by graphite

furnace AAS.

Graphite furnace AAS is now of paramount importance for speciation work due to its high power of detection. Approaches used include microwave-assisted leaching and extraction or liquid chromatography coupled on-line with AAS but also direct techniques, as shown in the case of Cr by the volatilization of Cr(III)−thenoyltrifluoroacetonate from the graphite furnace (*39*) and by the speciation of Cr in airborne dust on a weak anion-exchange diethylamine fast-monolithic chromatographic disk (*40*). Also for Se, numerous applications are mentioned in the literature.

Graphite furnace AAS continues to be a powerful method for the determination of trace elements in biological samples (blood, serum, hair), for water analysis (also for ultratrace species such as *t*-Bu−Sn), for soil micronutrient determinations, and for analyses in the case of food as well as art objects. Often on-line preenrichment is used to attain the required detection limits or to avoid interferences. Here column chromatography, as well as (often micelle assisted) extraction and coprecipitation, is of use during which the avoidance of contamination and analyte losses must have highest priority.

Hydride Generation Atomic Absorption Spectrometry. Hydride generation since the mid-1960s has been introduced as a powerful approach for the determination of elements that have volatile hydrides such as As, Se, Bi, etc. As these hydrides thus allow it to transfer the analytes practically quantitatively in the atom reservoir, they enable it to realize the highest power of detection for a number of ecotoxicologically relevant elements. The approach, though powerful, needs careful optimization and progress in its development.

For atomization in the flame, the form and size of the quartz tube atomizers is to be optimized and interesting viewpoints in this respect, such as the multiple microflame quartz tube atomizer (*41*), have been investigated.

Apart from flame atomization, combined hot-trapping in a graphite furnace together with graphite furnace atomization is very useful, due to its high power of detection. Bulska et al. (*42*) studied the use of modifiers for increasing the trapping efficiency with the aid of secundary ion mass spectrometry. Different flow systems and in-atomizer trapping techniques for the determination of Cd after vapor generation were studied by Lampugnani et al. (*43*). For hydride generation itself, flow injection analysis is now used as the standard and it even can be combined with on-line sample digestion, as in a microwave-heated flow-through system (*44*). For speciation purposes, pervaporation can be used to achieve derivatization of various species, as shown by Caballo-López and Luque de Castro (*45*). As an alternative to chemical hydride generation, electrochemical hydride generation has been shown for the case of Se, for which, in combination with in situ trapping in a graphite tube atomizer, absolute detection limits of 50 pg can be obtained (*46*). It also has been shown that hydride generation not only can be applied in the case of solutions but that for the determination of As in slurry samples reliable results can also be obtained, as shown by Matusiewicz and Mroczkowska (*47*).

The hydride technique has been developed into a routine method for the determination of volatile hydride-forming elements. This is shown by its use for the speciation of As in urine through coupling of HPLC and hydride generation AAS (*48*), through studies on the mechanisms and interferences in the on-line atomization of selenium hydride in graphite furnaces by Matousek et al. (*49*), and by the determination of Sb in pharmaceuticals using Fourier transform infrared spectrometry (*50*).

A similar reduction of Hg in compounds to metallic Hg by the mercury cold vapor technique still is one of the most sensitive methods for the determination of Hg. Due to its high power of detection, the technique is very useful for the speciation of Hg as, for example, shown by Segade and Tyson (*51*) by the use of flow injection Hg speciation analysis in fish tissue samples by slurry sampling cold vapor AAS. Due to the easy amalgamation of Au, the absolute power of detection of the mercury cold vapor technique can be increased enormously by trapping the Hg vapor on an Au gauze, as shown by the determination of Hg in cigarette smoke (*52*). Through the application of precipitation as mercury iodide, the mercury cold vapor technique can also be used for the determination of iodine (*53*).

Innovation in the vapor generation method also stems from the use of aminoboranes and cyanotrihydroborate(III) reagents as an alternative to $NaBH_4$. They allow avoidance of interference by Fe(III), Ni(II), Co(II), and Cu(II) (*54*). Further novelties are related to the generation of volatile species of a whole series of other metals. Volatile species of Au also can be obtained as a result of reduction with $NaBH_4$ and trapping in a graphite furnace (*55*). Also, for Ag, volatile species were found to occur; however, they are assumed to be the result of multistep reactions (*56*). Further, Feng et al. (*57*) also reported on the generation of volatile atomic and molecular Cd species from aqueous media as a result of the reaction with $NaBH_4$.

ATOMIC FLUORESCENCE SPECTROMETRY

Atomic fluorescence spectrometry (AFS) in its variations has long been used and has been continuously refined.

In resonance fluorescence, one uses laser radiation to excite the analyte vapor which can, for example, be contained in a discharge. Pixley et al. (*58*) reported an improved sensitivity for the case of Cs through the use of Doppler-free two-photon excitation with two properly aligned lasers with suitable wavelengths. Laser-excited AFS with atomization in a graphite furnace still is one of the most sensitive methods, as shown by the example of the determination of Al in seawater, reported by Le Bihan et al. (*59*). When using hollow cathode primary radiation and an inductively coupled plasma (ICP) as the atom reservoir, Young et al. (*60*) could show that axial viewing of the fluorescence signals in the ICP leads to an increase of the power of detection as compared to radial viewing. Also, in AFS, direct solids analysis is possible, as shown by the determination of Hg in minerals by combustion/trap/atomic fluorescence spectrometry (*61*).

Further, hydride generation combined with a suitable atomization was found to be extremely useful as an atomization technique for AFS. This was shown for the case of Se, where hydride generation through reduction with a solution of $NaBH_4$ is coupled on-line with flame AFS using a hollow cathode as primary radiation source. Here a detection limit of 1 $\mu g \cdot L^{-1}$ for Se is obtained (*62*). When combining the technique with HPLC, the determination of Sb(V), Sb(III), and Me_3SbBr_2 in water below 0.3 $\mu g.L^{-1}$ is possible (*63*). The determination of Ge after preconcentration by on-line coprecipitation as hydroxide after addition of Ni^{2+} was possible with a detection limit of 0.11 $\mu g \cdot L^{-1}$ (*64*). Zn could be determined by volatile species generation by

the use of surfactant-based organized media and AFS as well (*65*).

As a related method, laser-enhanced ionization was shown to be useful for the determination of ultratraces of As down to the subpicogram per milliliter level in environmental and biological samples by Simeonsson et al. (*66*).

ATOMIC EMISSION SPECTROMETRY

Atomic emission spectrometry dates back in its origins to the work of Bunsen and Kirchhoff in the mid-19th century. But considerable innovation is still possible with related developments in detector technology, source development, and sampling techniques.

All branches of optical atomic spectrometry benefited from the availability of high-quality CCD detector technology. The noise characteristics and implications as to their use in atomic spectrometry were investigated (*67*). The optimum adaption of Echelle spectrometers to high-quality CCDs was described by Haisch and Becker-Ross (*68*).

The main developments in atomic emission spectrometry are related to the different radiation sources.

Arcs and Sparks. Dc arc sources still are attractive tools in solutions analysis, as shown by the studies on interrupted arcs by Kuzmanovič et al. (*69*).

Spark sources are a working horse in the laboratories of the steel industry. Novelties are the direct analysis of inclusions in steels, for which different spark emission spectrometric techniques are described (*70*), and the direct determination of ultralow carbon and nitrogen contents in steels, which up to now were the domain of combustion analysis but more and more can be taken over by less time-consuming spark emission spectrometry (*71*).

Microwave Plasmas. Microwave plasma discharges have been described since the 1950s and still are an area of innovative research, as they can be operated with different gases among which are nitrogen and air, and this at relatively low power.

Filament-type argon microwave-induced plasmas (MIPs) have been investigated with respect to easily ionized element interferences in solution analysis using ultrasonic nebulization without desolvation (*72*). Similar investigations for the case of a high-power nitrogen plasma have been reported by Zhang and Wagatsuma (*73*); these authors also compared the analytical features of high-power MIPs at atmospheric pressure in air and with nitrogen as working gases (*74*).

Further research on microwave plasmas is related to sample introduction. A 20-μL sampling into a conventional Meinhard-type concentric glass nebulizer has been described by Matusiewicz (*75*). Further, the determination of carbon in aqueous solutions, as required in TOC measurements, by a conventional low-power MIP, was possible under a calibration with carbonates and the use of gas-phase sample introduction of the CO_2 generated (*76*). Especially hydride generation has been used for sample introduction in MIPs, as the gaseous products can be excited in a low-power discharge and as helium can be used as working gas, which is beneficial for elements with high excitation potentials such as As, Se, Bi, etc. Both the plasma parameters and the analytical figures of merit in such hydride-generation MIP systems have been investigated by Wlodarczyk and Zyrnicki (*77*). Here hot trapping of the hydrides is a feasible way to further increase the power of detection (*78*). MIP atomic emission spectrometry as an element-specific detector for gas chromatography has been used extensively in environmental analysis, especially for speciation work. Its features are shown by the determination of methylmercury and butyltin compounds in marine samples using microwave-assisted extraction, solid-phase microextraction, and gas chromatography MIP atomic emission spectrometric detection (*79*). As microwave plasmas can be operated with air, they are most suitable for monitoring metal concentrations in stack gases as required in environmental pollution control (*80*).

Inductively Coupled Plasmas. ICP atomic emission spectrometry (ICP-AES) is now a widely available method in most routine analytical laboratories. However, in many aspects, methodological developments in ICP-AES still take place.

With respect to excitation processes, measurements of the plasma parameters with refined techniques were published. Warner and Hieftje (*81*) described the possibilities of Thomson scattering for the diagnostics of analytical plasmas. van de Sande et al. (*82*) used Thomson scattering to study the relation between the so-called internal (electron temperature, gas temperature, electron number densities) and external parameters (power, gas flows) of a spectrochemical ICP, and Lehn and Hieftje (*83*) discussed the excitation mechanisms from their measurements of Thomson and Rayleigh scattering. The noise characteristics of the ICP have been studied for different nebulizers and in terms of the use of a peristaltic pump (*84*).

With respect to the instrumentation, improvements in torch design regularly were reported. Yabuta et al. (*85*) described a dual-inlet ICP torch for low gas consumption that is suitable for the use of argon as well as of helium as working gas. An interesting novelty is the use of in-torch vaporization from a Rh foil, which allowed it to obtain detection limits down to the femtogram level for Be and Ca (*86*). In the case of low-volume sampling of liquids, a torch integrated nebulization chamber with a conventional pneumatic nebulizer also proved to deliver a stable nebulization with high efficiency, as shown by Todoli and Mermet (*87*).

With respect to the spectral characteristics, the choice of axial or radial observation is discussed by several authors, for example, by Sun et al. (*88*). Here especially, the easily ionized element interferences and the possibilities to correct for them with the aid of internal standardization were discussed. As a further topic, background correction has been addressed.

A technique for the estimation of the background continuum emission intensity for the correction of fast-changing background in ICP-AES has been proposed by Chan and Chan (*89*). Miller et al. (*90*) proposed the use of acoustooptical filters for background correction in ICP-AES. Also, the use of Kalman filtering remains an interesting approach for trace element determinations in samples with a complex matrix composition, as shown by Ni et al. (*91*) for determination of Ca in rare-earth samples. Through the availability of complete spectra in the digitized form in CCD-based spectrometers, single-element spectra can be combined to simulate spectra of analytical samples, as shown for steel samples by Poussel and Mermet (*92*), allowing studies of matrix effects. Matrix effects stemming from influences of sample matrix elements such as Li, Cu, and Zn on Ca, Sr, and Ba as analytes were shown to be related to the influence on the fundamental plasma parameters by Lehn et al. (*93*).

Also in ICP-AES, sample introduction remains an important point of innovation.

For pneumatic nebulization of solutions with the direct injection nebulizer (DIN), matrix effects in the case of ICP-AES using axial and radial viewing were compared by O'Brien et al. (*94*). Isoyama et al. (*95*) described the use of a modified Babington nebulizer in conjunction with a cyclone chamber for ICP-AES and reported a short wash-out and a good nebulization of matrix-loaded solutions. Several groups studied drop size distributions, as did Gras et al. (*96*) for various pneumatic nebulizers. Horner et al. (*97*) developed computer simulations for the aerosol droplet desolvation in an inductively coupled plasma and performed calculations for a wide variety of plasma working conditions. Benson et al. (*98*) performed Monte Carlo simulations for droplet coalescence along with transport, heating, and desolvation in an argon ICP and derived optimum conditions for a direct-injection high-efficiency nebulizer (DIHEN). The latter type of nebulizer is used especially for hyphenation with HPLC, as shown in a study of the hydrolysis of trialkoxysilane by Kozerski et al. (*99*). Nebulization effects in the case of pneumatic nebulization still are an important topic of research. Cano et al. (*100*) studied the influence of the sodium content of the sample solutions on the aerosol characteristics of a V-groove nebulizer and two pneumatic concentric nebulizers designed for work with saline solutions. Maestre et al. (*101*) studied the influence of the type of spray chamber on nebulization effects caused by Na and Ca. Schaldach et al. (*102*) applied computational fluid dynamics to the characterization and optimization of a cyclonic spray chamber for ICP-AES (*103*) and in several other publications used this software for spray chamber optimization work.

Apart from pneumatic nebulization, ultrasonic nebulization remains of interest, as shown by its use in the simultaneous determination of As(III) and As(V) by flow injection ICP-AES (*103*). Thermospray systems also were shown to be useful for coupling ICP-AES to chromatography, as used in work on the direct speciation of Cr through a deposition of Cr(III) as Cr_2O_3 in the thermospray, a reaction for which mechanistic studies were performed by Zhang and Koropchak (*104*).

For direct solids analysis, laser ablation coupled to ICP atomic spectrometry is very useful. Aerosol transport from the ablation cell to the ICP remains a peculiar point, as studied, for example, by Koch et al. (*105*). Aeschliman et al. (*106*) recorded photographs of laser-ablated particles and dried solution aerosols from a microconcentric nebulizer and found that, for Y as Y_2O_3, YO bands could be found with laser ablation but not, however, in the case of the solutions. To ablate inhomogeneous samples, such as pellets of WC/Co powders, the so-called LINA system (laser-induced argon spark ablation) is very useful, as a larger surface is ablated and fair analysis results can be obtained (*107*). As a further direct solids approach, direct powder introduction is useful and—as shown by Vacher and André (*108*)—the analysis of CuO powder is possible without external calibration.

Electrothermal sample vaporization (ETV) of metal chelates, preconcentrated on a microcolumn and released with methanol into a heated atomizer, allows the determination of heavy metals at the picogram per milliliter level (*109*). In ETV coupled to atomic spectrometry, the aerosol transport efficiencies can be studied with in-line electrostatic precipitation, as reported by Ertas and Holcombe (*110*). Kantor and de Loos-Vollebregt (*111*) investigated the carrier gas optimization for an end-on type of electrothermal vaporizer in plasma spectrometry, and Wende and Broekaert (*112*) used a commercial boat-sampling graphite tube furnace for sampling refractory powders of different graininess and performing ETV-ICP-AES analyses of Al_2O_3. Salin and Ren (*113*) applied inductively heated electrothermal vaporization to analyze loaded air filters and reported mass detection limits for Pb of 20 ng and for Zn of 0.5 ng.

Chemical vapor generation systems for sample introduction in ICP-AES were used for the determination of Sb(III) in soils through a reaction with bromide (*114*). Hydride generation was shown to be useful for metals such as Ag, Au, Cd, Co, Cu, Ni, Sn, and Zn as well, but care must be taken because of the often limited stability of the gaseous species and because of possible interferences, as reported for steel samples (*115*). In the case of continuous-flow hydride generation ICP-AES for As, Bi, Sb, Se, and Sn, the elimination of chemical interferences through the use of various complexing agents has been studied as well (*116*). Also for Ir, Os, Rh, and Ru, the reduction with $NaBH_4$ was shown to lead to the formation of volatile species (*117*). For the case of Ni vapor generation, ICP-AES was shown to be possible in the case of a reduction with $NaBH_4$ in acid solution as well (*118*).

ICP-AES now is a routine method of analysis for many applications, reported in the respective literature but is not a topic of this review. These applications range from the analysis of biological samples (animal tissue, plant materials, serum) over water, eventually with on-line preconcentration, to the analysis of metals and their alloys, crystal dopant determinations, and analyses of glasses and hard materials. Nevertheless, it is interesting to mention that work is being done on some challenging applications, such as the determination of metals in flue gases in waste incineration plants (*119*), determination of the exact stoichiometry of superconductor materials such as YNi_2B_2C with In as internal standard and CCD-based ICP-AES (*120*), and direct determination of Ca, Cl, K, Mg, Na, and P in biodiesel with the aid of an argon−oxygen mixed-gas ICP (*121*).

Laser-Induced Plasmas. Laser-induced plasmas have become increasingly important as sources for atomic spectrometry, the method being known as laser-induced breakdown spectrometry (LIBS).

A review of the field of laser ablation by Russo et al. (*122*) explores the possibilities and limitations of this approach for direct solids analysis.

The development of LIBS of course depends on laser development with respect to all variables such as wavelength, pulse duration, etc. Horn et al. (*123*) reported on the evaluation and the design of a solid-state OPO−Nd:YAG laser ablation system for in situ microanalyses of solids in chemistry and earth sciences. Margetic et al. (*124*) reported on the hydrodynamic expansion of a femtosecond laser-produced plasma under argon, which could be studied with fluorescence spectroscopy, and discussed the influence of the laser power. The sampling statistics and considerations for single-shot analysis using LIBS were discussed by Carranza and Hahn (*125*), who studied the threshold irradiance for plasma ignition, plasma absorption, and many other aspects of the method. Beddows et al. (*126*) discussed the feasibilities of the ablation of samples submerged in water while providing a buffer gas flow to the sample surface and using a single-fiber light delivery system, and they performed steel analysis. Also, background correction approaches for LIBS have been reported (*127*), and temporal as well as spatial evolution of the laser-induced

plasma for the case of a steel target was studied to get optimal plasma homogeneity (*128*).

Applications of LIBS were described for many fields. Palanco et al. (*129*) described the features of a portable LIBS system incorporating a Nd:YAG laser and a 0.125-m iCCD spectrometer with fiber optics, with which steel scrap sorting is possible. Smith et al. (*130*) reported on the determination of $^{239}Pu/^{240}Pu$ isotope ratios using high-resolution emission spectroscopy with a 2-m double-pass spectrometer with an intensified CCD detector in a laser-induced plasma. A further challenging application is the remote analysis of a mineral melt under real conditions with the aid of a customized mobile laser-induced plasma spectrometer, based on a Nd:YAG laser for plasma ignition and an Echelle spectrometer with an intensified charge-coupled device, as reported by Panne et al. (*131*). A similar approach was described by Kraushaar et al. (*132*) for the analysis of slag samples in a steel plant, where for the main analytes CaO, SiO_2, and Fe a good agreement of the values with X-ray fluorescence values and RSDs of 1% were obtained. Also for the direct analysis of ceramics, LIBS is suitable, as shown by the determination of Mg, Al, Ca, Fe, and Ti with a system operated at a pressure of 200 Torr (*133*). Understandably, the remote character of laser energy production is very advantageous in controlling the composition of a potentially highly radioactive glass melt as is present in nuclear waste vitrification processes (*134*). LIBS, due to its high lateral local resolution, also has great potential for the mapping of inclusions, as it is important in the quality control of steels (*135*). Further prospective fields of application include the classification of biological aerosols, with the potential to discriminate biological agents from background aerosols on the basis of the Ca, Mg, and Na contents (*136*), and the determination of metals in flue gases on a continuous monitoring basis. Here it was reported that transient occurrences of Be and Cr by the method could be detected whereas integral measuring systems fail (*137*).

Microplasmas. Microplasmas operated at lowest power and gas flows become of growing importance with respect to the miniaturization of analytical systems according to the lab-on-a-chip principle. They are used for atomic emission work, but also for atomic absorption, and they even have potential for mass spectrometry.

Reviews on recent achievements in the field of microplasmas for analytical spectrometry were made by Franzke et al. (*138*) and by Broekaert (*139*). An ICP operated at a frequency of 490 MHz at a power less than 4 W could be produced with a planar, spiral-shaped inductor, however, under reduced pressure. The system could be shown to have potential for the detection of SO_2 with the aid of its molecular spectra (*140*) and therewith is in line of earlier work on dc plasmas by the Manz group (see earlier references in refs *138* and *139*). Microstrip microwave-induced plasma at atmospheric pressure could be further improved, in a way that the discharge exits from the wafer structure, by which space angle limitations in the case of atomic emission spectrometry vanish (*141*). The figures of merit for Hg vapor are similar to those of formerly described sources. A capacitively coupled high-frequency microplasma could also be sustained in a capillary of 250-μm internal diameter around which two electrodes are placed and at a power of 8 W only, as described by Guchardi and Hauser (*142*). They used the device to monitor organics using C_2 band emission. A similar microplasma was also used by Quan et al. (*143*) as an atomic emission detector for chlorinated organic compounds in gas chromatographic effluents. A barrier layer discharge plasma could be obtained in a borosilicate glass wrapped by two copper electrodes of which one was earthed and the other was powered with rf high voltage (98 kHz, 3.2 kV). The system could be used for the detection of F, Cl, Br, and I, as reported by Watanabe et al. (*144*). It can be expected that the sources described first will get importance for coupling with gas chromatography as well as all vapor generating devices and are a viable way to come to small dedicated analytical systems, especially when making use of miniaturized spectrometers.

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Inductively coupled plasma mass spectrometry (ICPMS) has continued to rapidly expand in the past few years and is therefore viewed by many as a mature and routine technique. But in comparison, ICPMS has still not gained as much popularity as other atomic spectrometry techniques, such as FAAS, GFAAS, or ICPOES, and thus, remaining ionization source- and spectrometer-related problems and shortcomings are subject to modern research. The ongoing demand for high sensitivity in combination with fast and preferably simultaneous multielemental detection capabilities has led to further developments in the field of plasma mass spectrometry. Interestingly, mixed gas ICPs as alternative ionization sources gained some interest in the last years, with regard to diagnostic measurements and mathematical modelations of the corresponding ion profiles. Noise characteristics and the resulting analytical precision of such plasmas in combination with various sample introduction techniques, as well as instrumental developments concerning time-of-flight, multicollector, and sector field mass analyzers, were other focal points of the research conducted within the period covered by this review article. Nevertheless, most of the published material mainly deals with applications of ICPMS and different sample introduction techniques. An ongoing activity on the development and application of collision and reaction cells for the specific removal or reduction of polyatomic ions was recognized.

This chapter focuses on new developments in inductively coupled plasma mass spectrometry 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 high 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*, *International Journal of Environmental Analytical Chemistry*, *Journal of Chromatography A*, *Rapid Communications in Mass Spectrometry*, and *Journal of the American Society for Mass Spectrometry*.

Fundamental Studies. The validity of data produced in chemical analysis must be properly guaranteed for their quality as analytical results are far from being accurate. There is a growing pressure to improve the overall quality of analytical information and to make it consistent with general metrological principles. Adams and co-workers (*145*) evaluated plasma spectrochemical methods for their ability to increase the accuracy of analysis, to

serve eventually as definite methods of analysis, and to assist in the elaboration of certified reference materials. Possibilities reside in the application of isotope dilution mass spectrometry and in increasing knowledge of the fundamental processes governing ion and photon formation so that they become able to describe fully the processes that link analytical signals with concentration. Cold plasma sources are known to aid in the determination of elements that commonly suffer from interference from background argon species. Likewise, plasmas with nitrogen introduced into the nebulizer flow can be used to minimize interferences from $ArCl^+$ and $ArNa^+$. Holiday and Beauchemin (*146*, *147*) examined radial distribution of analyte and background ions in cold plasmas and mixed-gas plasmas with nitrogen introduced into the nebulizer gas in ICPMS. Profiles in the presence of matrix elements were also obtained. The two plasma sources show very similar patterns, and it appears that, as postulated for the cold plasma, ionization in the center of the central channel of the mixed-gas plasma may be partly due to charge transfer with NO^+.

The achievable analytical precision in ICPMS influenced by noise characteristics of the peristaltic pump, a DIHEN, and a microconcentric nebulizer combined with a double-pass or cyclone spray chamber for sample introduction was described by Björn et al. (*84*, *148*), using noise power spectra to visualize the relationship between precision and different noise components. Steady-state signals and steady-state isotope ratio measurements were chosen for the investigation. For background and shot noise limited precision, the DIHEN was found to give better precision than the double-pass spray chamber system due to higher sensitivity. For flicker noise limited precision, it was found that white noise and pump interference noise were higher, and $1/f$ noise and main power interference noise were lower, for the DIHEN compared to the spray chamber systems. For the isotope ratio measurements, due to the high white noise level, the DIHEN generally gave poorer precision compared to the double-pass spray chamber system. The origin of background ions in ICPMS was determined by Carter et al. (*149*) through ion stopping experiments using a triple grid placed between the ion extraction and collector lenses of a modified lens stack. Controlled contamination of the ion extraction interface was performed, and the stopping voltage for Be^+ ions contributing to the subsequent background signal was determined to be between 1.5 and 5.9 V. This suggests that these ions originated downstream of the ion sampling interface, possibly due to deposition of Be on the skimmer cone, which was subsequently revolatilized. The low stopping voltage of these ions meant that they would be prevented from entering the quadrupole by applying a small retarding potential on one of the lens elements, while still admitting those ions with higher energies, which were extracted from the plasma.

A tremendous number of papers have been published on using ICPMS as a sensitive detector for separation techniques in elemental speciation studies. It is well known that the various heavy metal species have different toxicological impacts and therefore regulating elemental species, for example, in drinking waters, is a reasonable objective. However, developing robust and sensitive speciation methods is mandatory prior to any such regulations since the question of robustness or ruggedness for a regulatory method has not been fully explored. Caruso and coworkers (*150*) illustrated the use of anion-exchange chromatography coupled to ICPMS with a commercially available "speciation kit" option. The samples analyzed, provided by the U.S. EPA, were taken from water utilities in different areas of the United States, and the analytical performance characteristics studied proved the suitability of the method to fulfill the current regulation. The data suggest the speciation setup performs to U.S. EPA specifications, but sample treatment and chemistry are also important factors for achieving good recoveries for samples spiked with, in this case, As(III) as arsenite and As(V) as arsenate.

A significant number of publications were devoted to the speciation of metal-containing biomolecules, and the potential of the developed methods for proteomics was described. Sanz-Medel and co-workers (*151*) investigated the chemical association of trace elements to such molecules and their importance in the bioinorganic and clinical fields by stressing the complexity of the speciation of metal−biomolecule associations in various biological fluids. Analytical strategies to tackle speciation analysis and the state of the art of the instrumentation employed for this purpose are critically reviewed, including size-exclusion, ion-exchange, reversed-phase chromatography and capillary electrophoresis in combination with different types of mass analyzers (*152*). An effort is made to assess the potential of present trace element speciation knowledge and techniques for "heteroatom-tagged" proteomics. Hyphenated techniques based on the combination of (electro)-chromatography with ICPMS have become a routine tool for the analysis of metallospecies present in biological tissues, but finer analytical information on the true (down to individual species) speciation of trace elements in living organisms can be obtained by adding additional dimensions to the separation and detection steps, consisting of a sequential use of different HPLC separation mechanisms and capillary electrophoresis at the separation level, and of the use of electrospray MS, including collision-induced dissociation MS, on the detection level. Such multidimensional approaches in biochemical speciation analysis were performed by Szpunar et al. (*153*, *154*), who illustrate, that the value of the instrumental analytical data is decisively enhanced by the complementary use of molecular biology approaches involving gene identification, cloning, and in vitro reproduction of the metal-controlled processes. The authors present a brief summary of the recent progress in biochemical speciation analysis in the context of the latest research carried out in their laboratories. Selenium speciation analysis became a more dominant area of research in analytical chemistry within the past years. One reason for that might be that various plants can accumulate Se up to the thousands of ppm and therefore have potential to remediate areas contaminated with this metalloid. To date, few studies have been done for Se speciation with most studies reporting total Se concentration in various parts of the plant. Montes-Bayon investigated "Indian mustard" in terms of the Se metabolic pathway and summarized some studies dealing with employed extraction of Se species, cleaning procedures, separation methodologies, and mass spectrometric techniques (*155*). Some of the species produced by the plant, such as Se−methylselenocysteine or Se−methylselenomethionine were identified at ppb levels by RP-HPLC-ICPMS, while others needed to be further characterized by ES-MS. The coupling of GC−ICPMS using solid-phase microextraction as sample preparation system was also evaluated.

A review of "real-life applications" in the field of electrothermal vaporization in combination with ICPMS (ETV-ICPMS) for the determination and speciation of trace elements in solid samples

was published by Vanhaecke et al. (*156*). In almost all instances, accurate results were obtained via external calibration or single standard addition using an aqueous standard solution. The presented applications aim at trace element determination in industrial (different types of plastics) and environmental (plant material, animal tissue, sediments) materials. Additionally, Se speciation in biomolecules was performed by separation of Se-containing proteins using polyacrylamide gel electrophoresis prior to quantification of the Se content in the protein spots using ETV-ICPMS. Another application documented the direct speciation of different Hg species using ETV-ICPMS. The volatilization of methylmercury and inorganic Hg originating from a fish tissue sample could be separated from one another with respect to time.

Russo et al. (*157*, *158*) and Hattendorf et al. (*159*) thoroughly reviewed the principles and instrumentation of laser ablation ICPMS (LA-ICPMS) and concluded that this technique is becoming a dominant technology for direct solid sampling in analytical chemistry. They describe recent research to understand and utilize laser ablation for direct solid sampling, with emphasis on sample introduction to an ICP. Current research related to contemporary experimental systems, calibration and optimization, and fractionation is discussed, with a summary of applications in several areas. Elemental fractionation during LA was studied by Kuhn and Günther (*160*), and it was shown that in the case of brass samples preferential vaporization of zinc occurs, leading to limited possibilities for non-matrix-matched calibration. Cu and Zn were found to be not homogeneously distributed within the laser-produced aerosol: Cu was enriched up to 100% in particles larger than 100 nm and zinc was enriched by over 40% in the particles smaller than the lowest measurable particle size. Within this study, different sources of elemental fractionation were distinguished and described: (A) The ablation process leads to no measurable copper enrichment at the ablation crater rim. (B) Zinc deposition between the ablation site and the aerosol collection on filters leads to an up to 37% higher Cu/Zn ratio on the filter in comparison to the certified value. (C) On-line laser ablation aerosols measured within the ICPMS lead to significantly lower Cu/Zn ratios in comparison to the certified value. (D) Combination of the various studied sources of fractionation can finally lead to an agreement between measured and certified values due to inverse overlapping of various fractionation sources. Another factor controlling the extent of elemental fractionation in LA-ICPMS analysis is the composition of sample carrier gas in the sample cell. In an additional study, the laser pulse energy influence on the $^{65}Cu/^{63}Cu$ isotope ratio of an ablated Cu sample was investigated (*161*). It was shown, that at low laser pulse energies (3 J cm^{-2}), the resulting aerosol possessed a ratio that deviated by more than 12 parts per 10 000 from that of the sample. At high pulse energies (9 J cm^{-2} and above), near isotopically stoichiometric ablation generally occurred. However, even at high pulse energies, Cu isotope ratios showed large biases from the target sample, whereas filtered aerosols always yielded isotopic values that were closer to the true value than unfiltered aerosols, but it was concluded that volatilization and ionization of particles in the ICP was incomplete, because filtering was accompanied by a reduction in signal that was generally much smaller than the associated reduction in volume transport. The authors underline, while significant isotopic fractionation occurred at the ablation site at low laser fluence, the dominant source of isotopic fractionation at high laser fluence was the preferential volatilization of ^{63}Cu during incomplete vaporization and ionization in the ICP of particles greater than $\sim 0.5\ \mu m$ in diameter. Similarly, Guillong and Günther et al. (*162*) investigated the effect of particle size distribution on ICP-induced fractionation in LA-ICPMS. Signals related to the ablated volume show that the larger particle fractions are not completely vaporized and ionized in the ICP. These studies indicate that the secondary effect of incomplete aerosol or particle ionization within the ICP is the dominant process influencing elemental fractionation during LA-ICPMS. The effect was observed to be different for individual ICP sources, and therefore, the requirement for matrix-matched quantification in LA-ICPMS remains instrument-dependent. As shown by Houk and co-workers (*163*), high-speed photographs and videos of an ICP can be helpful to examine the fates of solid particles produced by LA in an ICP. The trajectories, lifetimes, and emission behavior of particles traversing the plasma are studied under a variety of conditions. Desolvated particles from a nebulized Y solution and particles ablated from a Y_2O_3 pellet are mixed and introduced simultaneously into an ICP. The plasma behavior of particles generated by a 266-nm and a 193-nm laser are compared, and either Ar or He is used as the transport gas through the ablation cell. It was concluded that the desolvated particles from the nebulized solution atomize and ionize like the small dry particulates from laser ablation. However, many large ablated particulates are observed to fly through the plasma intact, possibly contributing to signal noise, deposition on the sampler and skimmer cones, and elemental fractionation. A study by Kosler et al. (*164*) demonstrates that the presence of small amounts of oxygen in the He carrier gas has a significant effect on elemental fractionation during the ablation of silicate and sulfide samples. This indicates that an oxidation reaction takes place in the laser plasma plume, which can affect the particle size distribution during laser sampling and hence change the extent of elemental fractionation.

Since one of the primary factors limiting precision in LA-ICPMS measurements is the instrument fluctuation, different methods for internal standardization in LA-ICPMS are still subject to optimization and revision (*165*, *166*). New approaches are reported for the normalization of LA-ICPMS measurements, based on multiple internal standards. The novelty of the approach is that it (a) takes into account the measurement uncertainties, (b) generates uncertainty bounds on the normalized measurements, and (c) allows one to check and dismiss the mass dependency of the normalization procedure. As a result, it is shown that the improvement in the normalization factor increases proportionally to the square root of the number of internal standards. The use of two internal standards leads to a decrease of the standard deviation by 30%, three to 42%, and four up to 50% compared with the classical normalization. Panne et al. (*167*) investigated different normalization procedures with internal and extrinsic standards and established a quantitative determination of Al, Ti, Zn, Ni, and V in coal by LA-ICPMS with measurement uncertainties below 10% and Fe, Si, and Sn with uncertainties below 20%.

Russo and co-workers (*168*) compared different ablation wavelengths (193, 213, and 266 nm) from individual LA systems, whereas Günther (*123*, *169*) used a single solid-state laser source (1064-nm Nd:YAG) for harmonic generation together with sum frequency mixing and optical parametric oscillation to achieve the same laser wavelengths. NIST glasses were ablated to test the

effects of these wavelengths on fractionation and transport efficiency. Crater geometry and volume were measured. Particle size distributions for all three wavelengths increased in the order 193 < 213 < 266 nm. This effect is related to the absorption behavior of the sample opaque < transparent at each wavelength. A smaller number of particles with diameters of > 150 nm are produced in comparison to longer wavelengths when ablating with 193 nm. Due to the decreased amount of particles above 0.15 μm, vaporization-induced elemental fractionation within the ICP, especially for more transparent samples, is reduced. This study shows that the wavelengths in the first instance are responsible for particle size distribution and that their distribution leads to enhanced vaporization, atomization, and ionization effects within the ICP. Until now, only 193-nm-produced particle sizes can be stoichiometrically converted into ions using common ICPMS instruments.

The phonon relaxation time in a solid is of the order of 100 fs, which is the same as the laser pulse duration. For such excitation, there should be little time for the matrix to experience a "temperature" during the laser pulse. If the surface explodes before the photon energy is dissipated as heat in the lattice, the ablation process should produce stoichiometric vapor (elemental fractionation should be negligible). Based on this hypothesis, Russo et al. (*170*) ablated NIST glasses using 100-fs laser pulses at 800 nm in combination with ICPMS and concluded that fluence (laser energy/spot area) has a significant influence on the amount of mass ablated and on the degree of fractionation. Margetic et al. (*171*) used a femtosecond-LA system in combination with a plasma time-of-flight mass spectrometer (ICP-TOFMS) for in-depth multilayer analysis of semiconductor and metal samples and showed that this technique is capable of resolving 56−150-nm depth profiles. Although poor precision was achieved, which was related to pulse-to-pulse stability of the current laser system, it was concluded, that fs-LA-ICP-TOFMS is a promising technique for rapid in-depth profiling with a good lateral resolution of various multilayer thin-film samples.

LA combined with a chemical evaporation reaction was developed by Hirata (*172*) for elemental ratio analysis of solid samples by ICPMS. Using the chemically assisted LA technique, analytical repeatability of the Pb/U ratio measurement in zircon samples was successively improved. 1,1,1,2-Tetrafluoroethane was introduced into the laser cell as a fluorination reactant, which reacts with the ablated sample U, and refractory U compounds are converted to volatile UF_6 under the high-temperature condition at the ablation site. This avoids the redeposition of U around the ablation pits and improves its transmission efficiency. Since the observed Pb/U ratio is relatively insensitive to laser power and ablation time, the author concluded that the optimization of ablation conditions or acquisition parameters no longer needs to be performed on a sample-to-sample basis.

To date, the exact mechanisms of laser ablation are not yet fully understood. This mainly concerns phenomena like the mechanisms of particle formation or thermal versus mechanical effects during and after the interaction of laser light with the sample surface. To obtain a better understanding of such mechanisms and to improve analytical applications, numerical modeling is used by different groups. St-Onge investigated a mathematical model relevant to studies of depth profile analysis utilizing pulsed LA (*173*). The main focus of the model is on the influence of the laser beam radial energy distribution on the depth profiles. Accordingly, super-Gaussian (top hat) and Gaussian laser beams were modeled. Although the model can be used to simulate depth profiles in samples where the analyte concentration varies continuously as a function of depth, a particular emphasis of this paper is on multilayer samples. The model is tested in relation to LIBS studies of galvannealed coatings on steel that use a Gaussian Nd:YAG laser beam at 1064 nm. The simulated depth profiles are found to correctly reproduce the shape of an experimental depth profile of the zinc signal, and the influence of specific model parameters is investigated. Another important parameter for high-irradiance LA is the ablation crater depth. Russo and co-workers (*174*) found that this depth in the case of single-crystal Si shows a dramatic increase at a laser intensity threshold of $\sim 2 \times 10^{10}$ W cm^{-2}, above which, large (micrometer-sized) particulates were observed to eject from the target. An analysis of this threshold phenomenon is demonstrated, and the thermal diffusion and subsequent explosive boiling after the completion of the laser pulse is presented as a possible mechanism for the observed dramatic increase of the ablation depth. Calculations based on this delayed phase explosion model provided a satisfactory estimate of the measurements, and the shielding of an expanding mass plasma during laser irradiation was found to have a profound effect on this threshold phenomenon. Further studies were concerned with the formation of a laser-induced plasma in a cavity, the effects of a cavity on the ablation process, and the use of an adiabatic expansion model for simulation (*175*). Cavities were fabricated in fused silica with equal depths and variable diameters to provide different aspect ratios. The temperature and electron number density of the pulsed laser-induced plasma in the cavities were determined from spectroscopic measurements. Reflection and confinement effects by the cavity walls and plasma shielding were discussed to explain increased temperature and electron number density with increasing cavity aspect ratio. The authors found that the selected model was not suitable for the laser-induced plasma in the cavity because plasma−wall interactions were not included. Bogaerts et al. (*176*) reviewed the different analytical application fields of LA and gave an overview of various modeling approaches available for this technique. The laser-evaporated plume expansion in a vacuum or in a background gas, as well as the different mechanisms for particle formation in the laser ablation process, are discussed. A model is presented that describes the interaction of a nanosecond-pulsed laser with a Cu target, as well as the resulting plume expansion and plasma formation. The results are presented as a function of time during and after the laser pulse and as a function of position in the target or in the plume and include the temperature distribution in the target, the melting and evaporation of the target, the vapor density, velocity, and temperature distribution in the evaporated plume, and the ionization degree and the density profiles of Cu^0 atoms, Cu^+, and Cu^{2+} ions and electrons in the plume, as well as the resulting plasma shielding of the incoming laser beam. The influence of the target reflection coefficient on the above calculation results was considered, too, as well as the effect of the laser pulse fluence on the target heating, melting, and vaporization, and on the plume characteristics and plasma formation. The model was found to be in reasonable agreement with calculated and measured data from the literature.

Instrumental Developments and Applications. A tandem calibration methodology (TCM) based on a dual-nebulizer system for sample introduction in ICPMS was developed by Salin and co-workers (*177*). It involves simultaneous introduction of sample and standard into the plasma by two nebulizers operated in parallel. Classical standard addition verified the validity of the TCM, and the two methods were shown to be statistically equivalent. The precision of the results obtained was limited by the noise of the sample introduction device (∼4% RSD on difficult samples versus roughly 1% on clean standards), while the accuracy was only slightly limited by the short- and long-term stability of the arrangement, typically ∼2% relative error.

Silica and polymer capillaries were used by Hoang et al. (*178*) to modify an oscillating capillary nebulizer (OCN). The performance of four modified OCNs was compared to that of the original OCN design and also to a Meinhard high-efficiency nebulizer (HEN), using an identical single-pass cylindrical spray chamber for all the nebulizers. It was shown that an OCN fabricated with PEEK gas capillary, with either a thicker capillary wall or a larger inner diameter liquid capillary tube, performed better than the original OCN design. The optimal improvement of analytical signal of 3−4 times, corresponding to a 2.5−3.0 times improvement in analyte transport efficiency was found, compared to the original OCN design and also to a standard Meinhard HEN.

Tanner and co-workers developed a novel reaction cell for ICPMS with an electric field provided inside the quadrupole along its axis (*179*). The field is implemented via a dc bias applied to additional auxiliary electrodes inserted between the rods of the quadrupole and reduces the settling time of the pressurized quadrupole when its mass band-pass is dynamically tuned. It also improves the transmission of analyte ions. It is shown that, for the pressurized cell with the field activated, the recovery time for a change in quadrupole operating parameters is reduced to <4 ms, which allows fast tuning of the mass band pass in concert with and at the speed of the analyzing quadrupole.

The capabilities to use modified anionic capillaries for the on-line removal of chloride in ICPMS determination of As, which causes spectral interference due to formation of $^{40}Ar^{35}Cl^+$, were investigated by Malik et al. (*180*). The results indicate that arsenic at a concentration higher than 1 μg L^{-1} in a matrix with a chloride content up to 600 mg L^{-1} can be accurately determined using a (3-aminopropyl)trimethoxysilane-modified capillary connected to a microconcentric nebulizer. The interference level of chloride is considerably reduced due to its retention in the capillary. The method has been successfully applied and validated for wastewater and by recovery tests for urine samples.

When high current (1−10 A cm^{-2}) is applied between two conductive samples in aqueous solution, electroerosion occurs on the surface as a result of electrolysis and possibly collisions of dissolved ions with the metal surface. Electroerosion of steel and brass in aqueous solution was investigated by Goltz et al. (*181*), both for rapid sample dissolution and as a solid sampling approach for ICPMS. Some of the electroerosion properties described in this paper include rates of erosion as a function of the gap between the conductive samples and solution conductivity. Those rates decrease as the gap is increased from 2 to 5 mm. They also increase significantly as the conductivity of the electroerosion solution increases from 0.01 to 0.05 M NaCl. Interfacing the electroerosion apparatus to an ICPMS is described to be straightforward, as no special equipment was required. The authors conclude that the developed system can be used for rapid on-line sample dissolution prior to introduction into an ICP.

The analytical results in LA-ICPMS can be significantly influenced by the sizes of the particles produced during the ablation process. To minimize the particle size-related incomplete conversion of the sample to ions in the ICP a particle separation device was developed by Günther and co-workers (*182*), which allows effective particle separation using centrifugal forces in a thin coiled tube. In this device, the particle cutoff size is varied by changing the number of turns in the coil, as well as by changing the gas flow and the tube diameter. Various sample materials were investigated in this study to demonstrate the applicability of the device and its potential for the reduction of ICP-induced elemental fractionation.

(1) Inductively Coupled Plasma. The use of a Ne ICP for LA-ICPMS was investigated by Petibon et al. (*183*). The potential for this plasma to reduce the formation of argides, both in the background and from sample-induced interferences, is demonstrated and the reduction of the interferences of $^{63}Cu^{40}Ar^+$ and $^{65}Cu^{40}Ar^+$ on $^{103}Rh^+$ and $^{105}Pd^+$ in a Cu_2S sample, as well as the reduction of the interferences of $^{58}Ni^{40}Ar^+$ and $^{60}Ni^{40}Ar^+$ on $^{98}Ru^+$ and $^{100}Ru^+$ in a NiS sample, is shown, although the sensitivity of the Ne ICP is in general lower than that obtained for the Ar ICP.

The effect of an ICPMS sampler interface on electron temperature, electron number density, gas kinetic temperature, and analyte emission intensity upstream in the plasma was investigated by Lehn et al. (*184*) through Thomson scattering, Rayleigh scattering, and line-of-sight emission intensities of Ca ion and Sr ion from the ICP in the presence and in the absence of an interface. The experimental results suggest that both the electron temperature (T_e) and the gas kinetic temperature (T_g) dropped in the presence of the sampler interface, with the change in T_g was seemingly greater than that in T_e, suggesting a faster cooling process for the heavy particles. In contrast, electron number density (n_e) seemed to be generally increased in the outer regions of the discharge but went down in the central channel, a reflection that n_e is possibly dominated by ambipolar diffusion, which becomes less efficient as T_e drops. Assuming these results, the plasma decays more gradually above the load coil and deviates from local thermodynamic equilibrium even more significantly in the presence of the sampler interface.

Speciated isotope dilution with GC−ICPMS was used by Donard and co-workers (*185*) to determine and unravel the artificial formation of monomethylmercury (MMHg) in certified reference sediments during analysis. Different spiking and derivatization procedures were tested. The amount of inorganic mercury initially present in the sample was found to be the critical factor that should be known and carefully controlled. A simple solvent extraction technique involving no critical cleanup steps was applied in order to reduce high Hg^{2+} amounts. The limitations of applicability of the proposed method to the determination of MMHg in sediment reference material are evaluated as related to inorganic mercury, organic carbon, and sulfur contents. The results obtained confirmed that available sediment reference materials are adequate to achieve traceable mercury speciation analysis and to detect potential sources of MMHg artifact formation. In a different application (*186*), isotope dilution ICPMS was used in combination with GC for the determination of butyltin

compounds in environmental samples. Different spikes containing the isotopically labeled butyltin species have been synthesized in the laboratory, and the isotopic compositions of the Sn species in the different spike solutions were determined by GC−ICPMS after derivatization. Reverse isotope dilution analysis was used for quantitation of the spike solutions. Good agreement of the different speciation results obtained by use of the different spikes was found and indicates good precision, accuracy, and reliability, which can be achieved by using isotope dilution analysis for trace metal speciation. Application of a double spike enabled evaluation of the conditions resulting in quantitative extraction of the species from the solid matrix, in combination with possible alterations depending on the different extraction procedures used. Mathematical equations were used for this purpose and computed the correct species concentrations directly and, additionally, the decomposition factors after precise measurement of the Sn isotope ratios for all butyltin species by GC−ICPMS.

The determination of so-called "memory-prone elements", such as mercury, iodine, and boron, can be problematic, when using conventional sample introduction systems incorporating spray chambers or desolvation devices owing to their large surface area and hence long washout characteristics. The use of direct injection sample introduction systems can help to overcome these problems, since spray chambers can be eliminated, reducing dead volumes (and memory effects) to a few microliters. In a study by Montaser and co-workers (*187*) a DIHEN and a large-bore DIHEN were investigated for the determination of such elements. Wash-in and washout times were reduced to less than 10 s for mercury, iodine, and boron at a concentration of 100 ng mL^{-1}. The effectiveness of the DIHEN-ICPMS technique is documented in the determination of mercury and iodine in an alternative remedy medicine and boron in rodent liver samples. Similar direct introduction nebulizers (DIHEN and DIN) were used by Björn et al. (*188*) and Botto (*189*) for the trace elemental determination of As, Na, Pb, Hg, P, and V by ICPMS in high carbon content solvents, e.g., ethanol, hexane, toluene, and gas condensates. In the authors' opinion, DIN-ICPMS has proved to be a rapid analysis technique for petroleum samples, offering a sensitivity sufficient for the determination of trace elemental concentrations being harmful to petrochemical processes for ethylene production, since detection limits were at the low part-per-billion level and analyses were performed using simple sample dilution.

Moens and co-workers used solid sampling ETV-ICPMS for the fast direct determination of trace amounts of silicon in polyamides (*190*). For all Si isotopes, the occurrence of spectral interferences was studied as a function of the vaporization temperature and Pd was investigated as chemical modifier. The developed method showed the ability to use aqueous standard solutions for calibration, low sample consumption, high sample throughput, low limit of detection, and reduced risk of analyte losses and of contamination. This is especially advantageous when analyzing minute amounts of samples, exemplified by the same group for the quantification of Se in proteins by means of gel electrophoretic separation and ETV-ICPMS detection (*191*). External standardization with the use of an internal reference was applied, and a detection limit of ∼40 pg of Se/band of the gel and a recovery of ∼98% were obtained. A single measurement is accomplished in less than 4 min, and thus, a gel lane after a separation of ∼1.5 h can be entirely analyzed with ETV-ICPMS in 3.5 h. The analysis is directly carried out on the stained gel, without blotting. The method was applied to the fractionation of proteins from a selenium−yeast candidate reference material. The authors conclude as major advantages of this method the high resolution of the protein fractionation and the straightforward quantification of Se. For similar applications, speciation analysis of selenoproteins in Se-contaminated wildlife (*192*), the detection and characterization of Zn- and Cd-binding proteins in *Escherichia coli* (*193*), and the determination of protein phosphorylation (*194*, *195*) gel electrophoretic separation was performed prior to the direct laser ablation of the gels (blots (*194*)) in combination with ICPMS detection. A solution-based calibration strategy in LA-ICPMS was proposed by Becker et al. (*195*) for the quantification procedure using an ultrasonic nebulizer for introduction of calibration standard solutions coupled to the laser ablation chamber. Co was used as an internal standard element and was added to the gel at a defined concentration. In this application, the quality of P determination was ascertained with P-casein as reference material (*195*).

In a different field, paints and coatings are frequently encountered as types of materials that are submitted to forensic science laboratories as a result of trace evidence transfers, Hobbs and Almirall (*196*) developed a LA-ICPMS-based method to complement the commonly used techniques in a forensic laboratory in order to better characterize these samples for forensic purposes. Matrix-matched standards were successfully incorporated into the analysis scheme for quantification of Pb in the solid paint samples, and the elemental composition was used to associate/discriminate such samples. Resano et al. (*197*) evaluated the performance of LA-ICPMS for the fingerprinting of diamonds of different deposits. It was shown that a homogenized 193-nm excimer laser with a flat-top beam profile is capable of controlled ablation of the diamonds and the sensitivity of the ICPMS device suffices for the detection of more than 10 elements. A total of 31 diamonds originating from four different mines were the subjects of the study. Every diamond was ablated on eight different spots for 30 s, and the median of the eight integrated signals was considered as the representative value for subsequent statistical analysis. The total mass of material removed from a single diamond was ∼16 μg. Al, Hg, Na, Ni, Pb, Sb, Sn, Ti, and Zn were selected for fingerprinting purposes, and different pattern recognition techniques were used in order to classify the data. Reinhardt et al. (*198*) developed a cryogenic sample chamber for LA to determine elemental signatures in polar ice core samples from Greenland by LA-ICPMS directly from the solid (frozen) state with a spatial resolution of 4 mm along the core axis. This resolution is necessary to detect seasonal variations of element concentration in thin annual layers of deep ice. Calibration of the system was performed with frozen multielement standard solutions along a special preparation procedure. Detection limits for the tracers Na, Mg, Al, and Zn were 0.1−1 μg kg^{-1}, but best detection limits in the range of 0.001−0.01 μg kg^{-1} were reached for Co, Pb, and all rare earth elements. The spatially resolved 2D mapping of element concentrations showed strong inhomogeneities along the core axis, which was concluded to be due to seasonal variations of element deposition.

Beauchemin et al. (*199*) developed a new on-line leaching technique to assess the mobility and site of specific elements in complex natural materials such as rocks. The concentration

profiles during leaching were obtained by pumping suitable reagents, either continuously or with flow injection, through a microcolumn of sample while continuously monitoring analyte signals by ICPMS. It was concluded that the investigated technique involves minimal sample preparation and reduced contamination since the leaching is performed in a closed system. Whether in the continuous or flow injection modes, the proposed approach provided real-time data on what phases were reacting with the sample and what metals were released. It can therefore be used to design effective leaching strategies and to trace isotopic compositions. The resulting spectra were complex, and high-resolution ICPMS was suggested for correct determination of some elements.

High-performance liquid chromatography (HPLC) hyphenated to ICPMS is commonly used in the field of speciation analysis. Feldmann and co-workers reported dimethylarsinoyl acetate (DMAA) as a new arsenic metabolite found in sheep's urine after arsenosugar ingestion identified by the parallel use of HPLC−ICPMS and HPLC−ESI-MS (*200*). The two methods together were found to provide an excellent tool for identification of novel arsenic compounds in body fluids and extracts. The pH-dependent retention behavior of all three arsenic compounds, the major arsenic metabolite dimethylarsinic acid, the minor dimethylarsinoylethanol, and the second most abundant metabolite DMAA, was studied on an anion-exchange column in the pH range 3−8.5. The speciation of diverse elements in salmon egg cell cytoplasm was performed by Matsuura et al. (*201*) using a surfactant-mediated HPLC−ICPMS system, allowing separation of large and small molecules within 10 min; large molecules, such as proteins, were eluted within 2.5 min, while small molecules were eluted afterward (<10 min.). Fe, Cu, and Zn in egg cell cytoplasm were observed mostly in species with large molecular weights, indicating that these elements are contained as metalloproteins or metalloenzymes in egg cell cytoplasm. On the contrary, it was found that P, Mo, Cl, and Br were contained as PO_4^{3-}, MoO_4^{2-}, Cl^-, and Br^-, respectively.

Capillary electrophoresis (CE), with its high-resolution capability, is well suited for the investigation of metal-containing proteins, too, especially in hyphenation with ICPMS. But electropherograms of proteins in body fluids are difficult to compare, and the peak identification is uncertain because of the effects of different sample matrix composition. The migration time of proteins varies significantly, depending on the nature of the matrix. A study by Wolf et al. (*202*) investigated a technique for obtaining electropherograms that can be used for comparison purposes by correction of the data with the aid of five different time markers. All electropherograms were normalized to a reference run by recalculation of the time axis using those markers, and the method was applied to the analysis of human brain cytosols. Casiot et al. (*203*) developed a CE−ICPMS system for the simultaneous determination of metalloid species in environmental samples. Arsenite, arsenate, monomethylarsonic acid, dimethylarsinic acid, selenite, selenate, selenomethionine, selenocystine, antimonite, tellurite, and tellurate species were separated using either a chromate or a phosphate electrolyte. Different nebulizers were tested for sample introduction into the ICP, and special attention is given to the position of the capillary inside the nebulizer. It was found that different nebulizer gas and liquid sheath flow rates hardly affected electrophoretic resolution and peak width. Best detection limits were found to range between 6 and 58 $\mu g\ L^{-1}$ with the MicroMist nebulizer depending on the species investigated. The application to the analysis of soil extracts was documented. A hyphenation of miniaturized analysis systems with ICPMS was communicated by McCreedy and co-workers (*204*). Although the microchip-based electrophoresis system provided rapid elemental speciation capabilities, its resolving power needs to be improved through the application of higher voltages, the optimization of the carrier electrolyte, and the composition of the sample solution. Nonetheless, the principal feasibility of this method for elemental speciation was demonstrated by the on-line electrophoretic separation of Cr(III) and Cr(VI) within 30 s using an 8-cm-long separation channel etched in a glass base.

(2) Collision and Reaction Cells. An overview relating to the history, design, operation, and application of linear radio frequency-driven multipole collision cells and reaction cells in combination with ICPMS was summarized by Tanner et al. (*205*). The available material is supplemented with original experimental data that demonstrates the principles presented. The relation of these devices to collision cells for organic mass spectrometry and to the three-dimensional ion trap is discussed in its historical context. A general tutorial on the fundamentals of ion collision and reaction, including thermochemistry, energy transfer, and reaction kinetics, is given as well as consideration to some of the fundamental aspects of operation and design of linear rf devices. Furthermore, special attention is paid to the thermal characteristics of the ions in the cell, as this has important implications for the application of the available databases of thermochemical and thermal kinetic data to the development of analytical methods. Different effects of ion energy in collision/reaction cell ICPMS were investigated by Sharp and co-workers (*206*). It was demonstrated that the input ion energy is a key determinant of cell reactivity, and this was termed the ion kinetic energy effect (IKEE). The authors varied the ion kinetic energy by alteration of the potential difference between the plasma and the hexapole cell, while kinetic energy discrimination (KED) is shown to be a different effect. It can be used to change the relative levels of polyatomic ions arriving at the detector. The IKEE can be used to influence the reactive attenuation of argide ions and the production of MO^+ in the cell. whereas KED is shown to preferentially reject cell-formed MO^+ from the mass analyzer.

In the opinion of Jackson et al. (*207*), quadrupole ion traps can be used to selectively attenuate strongly bound diatomic ions occurring at the same nominal mass as an analyte ion of interest. Dissociation rates for TaO^+ were found to be at least 1 order of magnitude larger (sufficient for its selective removal) than the loss rate of Au^+ due to scattering under "slow-heating" resonance excitation conditions when Ne was used as the bath gas. The authors underlined that collision-induced dissociation can be accomplished in concert with a slow mass analysis scan, thereby providing a means of (1) eliminating polyatomic ions (formed in the plasma or reaction cell) over an extended mass range, (2) recovering metal ion signal from the metal-containing polyatomic ions, and (3) minimizing deleterious secondary reactions of product ions. The effect of adventitious water in hexapole collision cell ICPMS was investigated by Dexter et al. (*208*). Studies with H_2O and D_2O, employed both as samples and as impurities in the cell gas, were used to investigate the origins of the polyatomic ions. It was found that no new species were formed in the cell as

water from the plasma provides the basic reactive components; however, some were greatly enhanced when the cell gas was deliberately wetted. The reactivity of the H_2O/D_2O dominated the cell chemistry when an unreactive gas such as helium was used, indicating a need for careful control of water content, but the effects were greatly reduced when a reactive gas such as hydrogen was also employed. It was concluded that water could be a useful reagent molecule, if its partial pressure can be adequately controlled. Vais et al. found that condensation reactions in the band-pass reaction cell can improve the sensitivity for the ICPMS detection of U, Th, Nd, and Pr (*209*). These elements react with oxygen reagent gas in the dynamic reaction cell to give mono, dioxo, or both cationic species. Increasing the oxygen flow rate in the dynamic reaction cell leads to the rapid decrease of the singly charged metal ions accompanied by the fast increase in the intensity of the oxide ion. Estimated detection limits obtained in this work for U, Th, Nd, and Pr were found to be 0.022, 1.0, 0.045, and 0.10 ng L^{-1}, respectively. Different strategies for method development for an ICPMS for the determination of selenium and SeO^+ using a band-pass reaction cell with various reaction gases were outlined by Hattendorf and Günther (*210*). Methane was found to provide the highest reaction efficiency for determination of Se. Nitrous oxide and oxygen also very efficiently suppressed the Ar_2^+ interference, but reaction or scattering losses of Se^+ and SeO^+ were significant. Hydrogen is the least efficient gas for Ar_2^+ reduction, but little scattering or reactive loss was observed. Using a natural water sample, very good agreement was obtained using methane or hydrogen for analysis of $^{80}Se^+$ at the microgram per liter level. Limits of detection were lowest (2 ng/L) when methane was used to suppress the Ar_2^+ ion and when $^{80}Se^+$ was used for analysis. The fundamental mechanisms for reducing isobaric interference in octopole collision cell ICPMS were investigated by Yamada et al. (*211*) in view of the effects of cell gas impurities and kinetic energy discrimination, along with the consideration of the ion−molecule reactions involved. The cell was operated under nonthermalized conditions, where kinetic energies of the analyte ions were maintained above thermal energies after collisions. The in-cell product ions were attenuated efficiently by energy discrimination, which was also found to reduce interfering polyatomic ions that do not react with the cell gas or with any other species in the cell. The mechanism for this reduction was explained by the experimental results that showed lower kinetic energies of polyatomic ions than monatomic ions, after a number of collisions with the cell gas. Chakrabarti and co-workers (*212*) found that NH_3 used in a DRC is effective in reducing or eliminating carbon-based interfering polyatomic ions in electrothermal vaporization ICPMS on both Cr and Mg isotope ions but less effective for Si and unsuitable for the determination of $^{30}Si^+$. However, the limits of detection for $^{28}Si^+$ and $^{29}Si^+$ were improved over conventional ICPMS. Similarly, Liu and Jiang (*213*) reduced the intensity of potentially interfering ions $^{12}C^{16}O^+$ and $^{14}N_2^+$ at $^{28}Si^+$ for the determination of Si in steel through the use of NH_3. The signal-to-background ratio was improved more than 1 order of magnitude and the accuracy was better than 3% for all the determinations, while the detection limit for Si was in the range of 0.2 ng mL^{-1}, which corresponds to 2 μg g^{-1} in the original sample. Ammonia was as well used as reaction gas for the direct determination of several transition elements in seawater by reaction cell ICPMS. A study by Louie (*214*) showed significant improvement of the described method over standard quadrupole ICPMS performance, comparable to high-resolution ICPMS. Molecular ion interferences were reduced significantly but not completely for ^{58}Ni and ^{63}Cu, giving rise to a positive bias typically no more than 0.3 μg L^{-1}. Detection limits in the undiluted seawater range from 0.02 μg L^{-1} for Cr to 0.3 μg L^{-1} for Cu.

The addition of Xe to the collision cell can be helpful for the determination of Cd, Cu, Zn, and S in metallothionein-like proteins and P in phosphorylated deoxyribonucleotides using CE and HPLC hyphenated to ICPMS with an octopole reaction cell, as shown by Prange et al. (*215*, *216*). Detection limits down to 1.3 (^{34}S) and 3.2 μg L^{-1} (^{32}S) were derived. For the other trace elements determined simultaneously, detection limits ranging from 300 (^{58}Ni) to 500 ng L^{-1} (^{66}Zn, ^{55}Mn) were achieved. For quantification of S and Cd in a commercially available metallothionein preparation under hyphenated conditions, the use of external calibration was suggested.

(3) Time-of-Flight Instruments. Time-of-flight mass analyzers (TOFMS) have been known since the 1950s, but ICP-TOFMS for elemental analysis became commercially available only in the late 1990s. Since those years, extensive research on ICP-TOFMS developments and applications has been performed. A brief overview of the applications of (ICP-)TOFMS for analytical purposes is presented in a review article by Balcerzak (*217*), and the performance of such systems is described, especially in comparison with quadrupole mass filters for multielemental analysis of fast transient signals. A new type of ICP-TOFMS was constructed, built up, and described by Hoffmann et al. (*218*). For fast signal counting, an application-specific integrated circuit was developed, which permits a time resolution of 1 ns. The analytical performance of the instrument was investigated in terms of resolution, ion extraction rate, detection limits, and dynamic range. The determination of $^{39}K^+$ and $^{40}Ca^+$ at trace level were realized under cool plasma conditions only with a small interference by $^{40}Ar^+$. Detection limits of 23 elements were measured with typical values in the lower nanogram per liter range. The ion extraction rates, measured for a sample mass of 1 ng in terms of counts per second divided by the relative isotope abundance, were 1 order of magnitude higher than those obtained with a quadrupole-based instrument.

Sanz-Medel and co-workers (*219*) evaluated and critically compared ICP-TOFMS with conventional quadrupole ICPMS and found that the best precisions (less than or equal to 1%) were achieved using an ICP-TOF-MS for more than 15 isotopes at concentration levels over 10 μg L^{-1} to be measured in transient signals of less than 5 s. However, when less than seven isotopes had to be measured, even for very short transient signals, the measured precision was always similar or even better using a quadrupole MS. The detection limits obtained, even for very short integration times, were always favorable to the quadrupole ICPMS, while ICP-TOFMS demonstrated similar or better accuracy for isotope ratio measurements. The achievable precision in Pb and Rb isotope ratio measurements using an ICP-TOFMS for transient and steady-state signals was investigated by Carrion et al. (*220*). The best possible precision for isotopic ratios was 0.08% (as RSD) for $^{85}Rb/^{87}Rb$, 0.04% for $^{207}Pb/^{206}Pb$, 0.49% for $^{204}Pb/^{206}Pb$, and 0.07% for $^{208}Pb/^{206}Pb$, using the analogue detection mode. In transient mode, the corresponding precisions were 0.2, 0.3, 1.0, and 0.3% RSD, respectively. It was found that calculation of ratio and

precision performed on the whole peak profile for nonunity ratios resulted in deteriorated precision compared with calculations performed at peak apex on a minimum of five data points. As the peak intensity increases or decreases over the transient peak profile, a slight change in the ratios close to the rims of the transient peak could be observed. As expected, the quality of the measurements improved for longer integration times and higher concentrations and with transient peak profiles that reached a steady-state level. The use of a DIHEN as a microliter solution introduction system for ICP-TOFMS was first investigated by Montaser and co-workers (*221*). An increased secondary discharge at 27 MHz compared to 40 MHz generator frequency for the DIHEN compared to conventional solution introduction was indirectly observed. Analytical figures of merit achieved using DIHEN-ICP-TOFMS are superior in both normal and cool plasma conditions to those obtained with a conventional nebulizer spray chamber arrangement. Using the DIHEN system, typical precision is less than 0.6% for an integration time of 10 s, the signal intensity is nearly a factor of 2 higher compared to the conventional arrangement, and isotope ratio precision closely approximates values predicted by Poisson counting statistics for both steady-state and transient signals.

A flow injection system (FI) was combined on-line with ultrasonic nebulization ICP-TOFMS for the determination of Pt, Rh, and Pd in urine, blood serum, and road dust by Benkhedda et al. (*222*), using simultaneous and selective preconcentration of the analytes by sorption of their complexes formed on-line with diethylthiourea on the inner walls of a PTFE knotted reactor. The detection limits obtained were in the lower nanogram per liter range, and the RSD was less than or equal to 3%. Using a preconcentration time of 120 s and a sample flow rate of 5 mL min^{-1}, enrichment factors of 55, 5, and 2 for Pd, Pt, and Rh, respectively, were obtained in comparison with direct determination by ICPMS without preconcentration. Special attention was paid to the study of the adverse effects of potentially interfering species present in the matrix on the preconcentration and the mass spectrometric determination of the analytes. Chemical and electrochemical (EcHG) hydride generation in combination with FI-ICP-TOFMS was studied in detail by Abranko et al. (*223*) and Bings et al. (*224*) for rapid and simultaneous determination of hydride forming elements. In the latter case, a novel low-volume electrolysis cell especially suited for FI experiments was designed and the instrumental operating conditions for simultaneous EcHG/detection of 12 isotopes were optimized. By using a 200-μL sample loop, absolute detection limits in the range of 10−160 pg for As, Bi, Ge, Hg, and Sb and 1.1 ng for Se and a precision of 4−8% were achieved.

The same group investigated a low-volume tungsten filament electrothermal vaporizer as a sample introduction system for ICP-TOFMS for rapid and simultaneous determination of Cr, Cu, Li, and Pb in human whole blood and serum samples (*225*). Absolute detection limits in the range of 0.007−11 pg and a precision of 2−6% were achieved. Except for the addition of a phosphate-based matrix modifier, followed by appropriate dilution, no additional sample pretreatment was necessary. Internal standardization using multielemental solutions was used for calibration. Good agreement with the certified values was observed, and the filament had a lifetime of more than 350 firings. In a different study, Bings et al. used direct laser ablation in combination with ICP-TOFMS for rapid multielemental analysis of fresh and used lubricating oil samples (*226*). This method was found to offer the advantage of a simplified sample preparation technique without the need for sample decomposition or sample dilution with organic solvents, although dealing with a relatively complex matrix. Two different calibration strategies (external calibration based on the use of different standard oils and aqueous solution-based calibration) were investigated and showed good agreement. Detection limits were in the range of 0.5 (Pb) to 28 ng g^{-1} (Cr), and the precision was typically ∼6% RSD. It was concluded that direct LA-ICP−TOFMS is a rapid and powerful tool for the analysis of trace and wear metals in lubricating oils. The temporal width of a single-shot LA analyte transient is inversely related to the best achievable signal-to-noise ratio. Thus, production of fast transient signals is an important consideration in single-shot LA analyses. Leach and Hieftje investigated the factors affecting the production of such signals in LA-ICPMS (*227*) and developed a novel method for the rapid identification of alloys using single shot LA-ICP-TOFMS (*228*). Minimization of ablation cell volume and the length and diameter of the transfer tube was found to dramatically decrease the peak widths of transient signals. However, use of He gas to sweep analyte particles from the ablation cell was found to significantly reduce the effect of cell volume on transient width. A cell volume of 0.70 cm^3 produced a transient sample pulse 85 ms in duration and limits of detection in the tens of femotgram range for single-shot LA events. In the case of alloy samples, this technique provides good accuracy for elemental concentrations greater than 0.1% by mass from samples with a range of different matrix compositions. Through the simultaneous measurement of all elements present within a cloud of ablated particles, relative composition values are measured that can be directly compared with certified concentrations. Cluster analysis has been used to successfully classify 33 metal alloys based on the measurement of 15 elements. Several alloys investigated in this study were less than 500 mm in length at their largest dimension and weighed less than 1 μg.

The potential of the ICP-TOFMS for detection of fast transient signals with peak widths significantly shorter than 1 s with high temporal fidelity and ultratrace sensitivity was demonstrated by Adams and co-workers (*229*) through the coupling with capillary GC for the speciation analysis of inorganic and methylmercury in environmental and biological samples. Absolute detection limits of 20 fg and 1.5 pg and relative detection limits of 2 and 150 pg L^{-1} for methylmercury and inorganic Hg, respectively, were achieved, and application to ultratrace speciation analysis of organomercury compounds in ice from the French Alps has been addressed. When replacing the conventional GC capillary by a multicapillary and using purge-and-trap injection, after in situ derivatization of the ionic mercury species with sodium tetraethylborate, a baseline separation of $MeHg^+$ and Hg^{2+} was achieved within a chromatographic run of <35 s (*230*). The resulting detection limits were found to be 16 and 257 fg g^{-1}, for $MeHg^+$ (as Hg) and Hg^{2+}, respectively.

Size exclusion high-performance liquid chromatography in combination with ICP-TOFMS was investigated by Infante et al. (*231*) for the isotope dilution-based quantitative speciation of Cu, Zn, and Cd in carp and eel cytosols. Quantitative information on the distribution of essential and toxic metals between the different molecular weight fractions in kidney cytosols of control and Cd-

exposed carp was obtained with species-unspecific spiking by postcolumn addition of the enriched isotopes ^{65}Cu, ^{67}Zn, and ^{106}Cd. Speciation differences were encountered between control and Cd-stressed carp, indicating that quantitative speciation studies might be useful for ecotoxicological and biomonitoring purposes. Application of this methodology to quantitation of metals associated with metallothioneins was also addressed.

(4) Multiple-Collector Instruments. Due to the unstable nature of an ICP, the achievable precision for isotope ratio measurements with scanning single-collector ICPMS is limited to approximately 0.05−0.5%. Multiple-collector ICPMS (MC-ICPMS) performs the simultaneous measurement of each isotope ion in a certain space array of detectors, thus providing a mechanism to reduce the effect of multiplicative or flicker noise prevalent in plasma sources. Through this technique, much higher precision can be achieved, as demanded by many analytical applications. The duty cycle is increased, which leads to enhanced sensitivity, detection limits are improved, and the analysis time can be reduced. An additional benefit of simultaneous detection is superior analysis of short-lived transient signals.

Solyom and Hieftje (*232*) presented a theoretical comparison between simultaneous/continuous multichannel acquisition and single-channel scanning acquisition. Reported sensitivity, single-channel precision, and background values for commercial ICP sector-field MS (ICP-SFMS) were used to generate theoretical figures of merit for both acquisition methods. The instruments were compared on the basis of detection limits, precision, and analysis time, particularly for multielement or multiisotope analysis. A study by Chu et al. (*233*) indicates that the presently accepted abundances of the Yb isotopes are not appropriate. The investigation was performed by measuring mixed solutions of Yb and Hf on two MC-ICPMS instruments; a series of REE fractionation experiments using a thermal ionization mass spectrometer (TIMS) was undertaken, too. New values for Yb isotopic abundances based on the TIMS and MC-ICPMS results were calculated. Using the newly defined Yb values, it was concluded that Yb and Hf have similar levels of mass bias in plasma ionization instruments and that Hf isotope ratios can be used to correct Yb mass bias before subsequent correction of isobaric interference. Ingle et al. (*234*) considered instrument response functions, mass bias, and matrix effects as important parameters in isotope ratio measurements and semiquantitative analysis, when using single-collector and multicollector ICPMS and proposed a new approach to the estimation and correction of mass bias, based on modeling the underlying instrument response function. The common mass bias correction models were shown to be directly derivable from assumptions about the nature of the instrument response function. When the true instrument response function was investigated using a multielement solution, a second-order polynomial was found to provide the best fit to the data. The mass bias correction expression derived from such a model was used to calculate corrected Cd isotope ratios that were closer to the natural values than those obtained from the commonly used correction expressions.

A substantial number of publications focused on the application of MC-ICPMS for the precise determination of isotope ratios of various elements, mostly in comparison with scanning-based mass analyzers. In such studies, some fields of interest were, for example, the determination of Hg isotopes in cinnabar ores (*235*), Li isotopic determinations of igneous rock samples (*236*), the investigation of the chemical bias from alkali matrix on the determination of Ge isotope ratio variations (*237*), low-level Pu isotope analysis (*238*), and Os isotopic compositions of different geological and environmental samples using vapor-phase sample introduction (*239*). In all cases, the suitability of multiple-collector instruments and the advantages over conventional MS for high-precision measurements were documented.

Hirata et al. (*240*) investigated the time profile of ^{65}Cu/^{63}Cu and ^{56}Fe/^{54}Fe isotopic ratios originating from metal reference materials during LA-MC-ICPMS. They found that ^{65}Cu/^{63}Cu ratios increased systematically (1−2%) with prolonged ablation, suggestive of isotopic fractionation during the LA or ionization process in the ICP. However, systematic increase in the measured ^{65}Cu/^{63}Cu ratio was minimized down to <1% level when a newly developed correction technique for slow response of a Faraday preamplifier (0.2−1 s) was applied. The resulting precision or repeatability of the isotopic ratio measurements was improved to the 0.7% level, which was almost half the level achieved by the conventional measurements. The validity of this correction technique was also demonstrated by the ^{56}Fe/^{54}Fe isotopic ratio measurement for metal Fe. For isotope ratio measurements of the transient signal from trimethylstibine, Feldmann and coworkers (*241*) used GC coupled to both MC-ICPMS and ICP-TOFMS with a simultaneous aspiration of aqueous samples creating wet plasma conditions. The influence of different mathematical models on the precision of the isotope ratio determination of transient signals was studied. The trapezium integration of full or half peak gave precisions of 0.08 and 0.02% using the MC-ICPMS, whereas the ICP-TOFMS gave values of ∼0.2%. The multicollector ICPMS used as a detector showed a chromatographic isotope fractionation of trimethylstibine. $(CH_3)_3{}^{123}Sb$ eluted earlier than $(CH_3)_3{}^{121}Sb$, with a shift of the 123/121 ratio of ∼2%.

(5) Sector-Field Instruments. Through increased mass resolution, as achieved by (high-resolution) sector-field MS (ICP-SFMS), several interferences from polyatomic species can be resolved. For instance, a resolution of $R = 7500$ is required to resolve ^{75}As from ^{40}Ar^{35}Cl, whereas a medium resolution of $R = 3000$ is already adequate to resolve, for example, ^{52}Cr from ^{40}Ar^{12}C, ^{51}V from ^{35}Cl^{16}O, ^{27}Al from ^{12}C^{14}N^{1}H, and Mn, Fe, Cu, Zn, etc., from other polyatomic ions. This enables the direct determination and speciation of different elements at trace levels in complex matrixes with minimum sample preparation requirements. Simple sample dilution was shown to be less prone to contamination and resulted in better precision than preconcentration procedures. However, for the direct determination of Pu isotopes at ultratrace levels in seawater by ICP-SFMS, solid-phase extraction combined with on-line sequential injection was necessary, as shown by Kim and Kim (*242*). The precision of the measurement for the ^{239}Pu and ^{240}Pu was less than 3.4 and 5% for 5 L of seawater, while the detection limits for ^{239}Pu and ^{240}Pu were found to be 0.64 and 0.19 fg mL^{-1}, respectively. Yang et al. (*243*) documented the application of ICP-SFMS to the determination of vanadium in biological fluids, such as urine and serum. Samples were diluted 20-fold in 0.3% HNO_3, and quantitation was achieved by standard addition using standards prepared in a pooled urine or serum sample. A detection limit of 10 pg mL^{-1} was estimated for V in reconstituted urine and serum samples, and vanadium concentrations in the range of 10−1500 (urine) and <10−760 pg

mL^{-1} (serum) were determined. Similarly, Przybylski and co-workers (*244*) used a sector-field instrument for the determination of phosphorus in small amounts of protein samples after decomposition in HNO_3 and H_2O_2 by closed-microvessel microwave digestion and flow injection of the digest. The authors discuss the developed method with reference to real protein digests after protein separation using 2D gel electrophoresis. Resulting detection limits were found to be at the nanogram per gram level. A new approach to the characterization and quantification of metallothionein (MT) isoforms using CE-ICP-SFMS was reported by Schaumlöffel et al. (*245*). MT isoforms were separated by CE, and the elements Cu, Zn, Cd, and S were detected simultaneously in the medium resolution mode. On-line isotope dilution is performed by continuous introduction of an isotopically enriched, species-unspecific spike solution after the separation step. MT from rabbit liver and a further purified MT-1 isoform were quantified by determination of S, and the stoichiometric compositions of the metalloprotein complexes are characterized by determination of their sulfur-to-metal ratios. The employed quantification method was found to be limited to proteins such as MT, where the sulfur stoichiometry is known. The authors conclude that for unknown compounds additional structural information, which can be obtained, for example, from electrospray tandem mass spectrometry, is necessary.

For in situ determination of Ni concentrations in tissues that have been exposed to nickel wire, Ghazi et al. (*246*) used LA-ICP-SFMS, studying the diffusion of Ni with time and its spatial distribution around Ni-containing implants in vivo. Pure Ni wires were implanted subcutaneously into rats, and later the tissues were analyzed for Ni and degree of inflammation away from the implants using ^{24}Mg and ^{60}Ni isotopes. Quantification was performed by assuming a uniform nominal magnesium concentration value of 97 $\mu g\ g^{-1}$ in untreated tissue and using ^{24}Mg intensity for internal calibration. The precision of measurements for ^{24}Mg for the tissue samples was within 3.2−4.5%. A significant penetration of Ni ions into tissues exposed to nickel wire implants was found, reaching concentration values as high as 60 $\mu g\ g^{-1}$ near the implants, falling exponentially to undetectable levels 3−4 mm from the implants.

Becker and co-workers applied ICP-SFMS to the determination of long-lived radionuclides at ultratrace levels. In recent work, they have focused on the isotopic analysis of uranium and transuranium elements in contaminated environmental samples (*247*) and depleted uranium ammunition (*248*). The detection limit for ^{236}U and ^{239}Pu after chemical extraction was 0.2 pg L^{-1} in aqueous solution and 0.04 pg g^{-1} in soil, respectively. $^{235}U/^{238}U$, $^{236}U/^{238}U$, and $^{240}Pu/^{239}Pu$ isotope ratios were measured in soil samples collected within the 30-km zone around the Chernobyl nuclear power plant. The average $^{240}Pu/^{239}Pu$ isotope ratio in contaminated surface soil was 0.396 ± 0.014. The burn-up grade and the portion of spent uranium in the spent uranium/natural uranium mixture in soil were calculated. A slight variation in the burn-up grade of spent reactor uranium was revealed by analyzing $^{235}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios, and a relationship between the $^{240}Pu/^{239}Pu$ isotope ratio and burn-up of spent uranium was observed.

In an interesting application in the field of forensic analysis of commercially available adhesive packaging tapes, Dobney et al. (*249*) employed ICP-SFMS to minimize the effect of polyatomic interferences originating from the acids used for sample digestion. The developed method was applied to nine tape rolls purchased from three different shops of three different chain stores. The authors were able to discriminate both between brands and within brand for all three brands. In the case of one brand, for rolls originating from the same product line but from different production batches, it was shown that the "between batch" difference is detectable while there is no statistically significant difference within rolls from the same production batch. This combination of "between batch" differences and "within batch" consistency may provide the forensic scientist with the means to discriminate between tape rolls even if they come from the same product line. However, in real forensic cases, the surface area free from contamination (e.g., dirt, blood, tissue, soil, hair) and hence amenable to this type of analysis will be smaller than that referred to by the authors, and therefore, the need to measure surface areas of 1 cm^2 or less will have to be addressed in the future.

GLOW DISCHARGE ATOMIC EMISSION AND MASS SPECTROMETRY

A large number of papers have been published in 2002 and 2003 in the field of glow discharge atomic spectrometry, including fundamental studies, methodological work, and applications, of both glow discharge mass spectrometry (GDMS) and glow discharge optical emission spectrometry (GD-OES). In 2003, there have been two special issues on glow discharge spectrometry (GDS). In *Journal of Analytical Atomic Spectrometry*, the June issue (No. 6) of 2003 (Vol. 18) was entirely devoted to glow discharge spectroscopy, with N. Jakubowski, V. Hoffmann, and A. Bogaerts as guest editors, and with 19 scientific papers, one technical note, and two review articles. Furthermore, the July issue (No. 7) of 2003 (Vol. 35) of *Surface and Interface Analysis* was a special issue containing the papers presented at the International Symposium on GDOES for Surface Analysis, in Japan. This issue contained 10 papers, and K. Shimizu was the guest editor. State of the art and further outlooks of glow discharges as sources for atomic emission and mass spectrometry are treated in a book edited by Marcus and Broekaert (*250*).

In the following, we will give an overview of the new developments on glow discharge spectrometry in 2002 and 2003, in the fields of fundamental studies, methodological work, and novel applications.

Fundamental Studies. To understand the basic plasma processes occurring in analytical glow discharges, both measurements in the plasma and theoretical modeling have been carried out.

(1) Plasma Diagnostics. A laser scattering instrument is developed in the group of Hieftje, to perform fundamental studies on GD plasmas (*251*). The electron number density, electron temperature, and shape of the electron energy distribution function (EEDF) can be obtained from Thomson scattering. It was observed that several groups of electrons contribute to the Thomson scattering spectrum, and the existence of a non-Maxwellian EEDF was confirmed. In addition, Rayleigh scattering was used to obtain the argon gas kinetic temperature.

Wagatsuma (*252*) estimated the excitation temperature from Boltzmann plots obtained for some chromium atomic lines in a rf GD. It was found that Boltzmann plots are well fitted to a straight line at frequencies of 3.56 and 6.78 MHz, but departures from a linear relationship were observed when the driving frequency exceeds 10 MHz. Similarly, deviations from a linear relationship

are noticed when the argon pressure is reduced. It seems that the deviation is mainly due to the behavior of Cr I lines having excitation energies in the range of 4.1−4.2 eV, suggesting a potentially selective excitation of the 4.1-eV chromium lines.

In the same group, a comparison was also made between variations in signal intensities with varying discharge parameters (current, voltage, pressure) for GDMS and GD-OES (*253*). It is found that the ion signals and optical emission intensities behave differently when varying pressure and current (at constant voltage), but they behave similarly when varying voltage and current (at constant pressure). These results suggest that the pressure determines the different behavior of ion signals and emission intensities, and this indicates that the transport process of analyte ions plays an important role in determining the ion intensities in GDMS.

(2) Effect of Cathode Sputtering. Kasik et al. investigated the effect of the sample (cathode) temperature on the current−voltage characteristics in the VG9000 GDMS system (*254*). Two sets of measurements were performed: (i) for steady-state conditions and (ii) immediately after discharge reignition, which corresponds to a cold cathode temperature. It is found that the cathode temperature has a strong influence on the electrical properties in GDMS.

In ref *255*, a simple model is developed for estimating the mass loss due to evaporation of zinc, as cathode material in GD-OES. The model is used to calculate the net evaporated flux versus surface temperature. It is concluded that for zinc, which has a high vapor pressure in the solid phase, evaporation can contribute significantly to the mass loss of the cathode, if the cathode surface temperature is high.

Guillot et al. (*256*) determined Paschen curves for several materials (copper, iron, nickel, titanium) in GD-OES. From this work, effective secondary electron emission coefficients have been calculated versus the reduced electric field for each sample.

Payling et al. presented a detailed theory for relative sputtering rates in GD-OES (*257*). The theory suggests that sputtering rates are nearly independent of plasma conditions, and this was supported by experimental results.

Some more fundamental work on cathode sputtering was carried out by the group of Hoffmann (*258*, *259*). A new instrument, based on a laser interferometer, was developed to measure the depth during sputtering in a Grimm-type GD (*258*). Using a mathematical model, the signal disturbance during thermal expansion of the GD source and sample surface is corrected for. Further, a modern optical profilometer was used to measure 3D crater profiles, and the crater volume, erosion, and sputtering rates are calculated (*259*). A plot of the reduced sputtering rates versus voltage proves the validity of the so-called Boumans equation, which was formulated a long time ago.

Bogaerts et al., who have gradually built up a comprehensive modeling network for analytical glow discharges over the past decade, have applied this model to predict crater profiles and erosion rates due to sputtering, as well as implantation profiles, optical emission intensities, and other characteristics that are revelant for glow discharge spectrometry (*260*). This modeling network normally assumes a static background gas density, which is justified when the gas flow is low. However, when GD sources with high gas flows are developed (see below), the effect of the gas flow should be taken into account. This was accomplished in ref *261*, by combining the plasma modeling network with a computational fluid dynamics model. It was found that the argon gas flow had only minor effect on the density distributions of the plasma species, but their fluxes were significantly affected.

(3) Effect of Gas Mixtures. The modeling network for an argon glow discharge was also extended to take into account the effect of small amounts of hydrogen (*262*, *263*). The species described in the model (*262*) are as follows: electrons, Ar^+ ions, and fast Ar atoms, ArH^+, H^+, H_2^+, and H_3^+ ions, H atoms, and H_2 molecules, as well as Ar metastable atoms, sputtered Cu atoms, and the corresponding Cu^+ ions. The effect of hydrogen addition on the electrical characteristics, the density of the plasma species and their flux energy distribution functions, the relative contribution to production and loss processes for the various species, the sputtering rate, and the ionization of copper, is investigated (*262*, *263*).

The effect of hydrogen addition, as well as other gases such as nitrogen and oxygen, is also studied in a number of experimental works. Mason et al. (*264*) studied the positive-column plasma of a fast-flow GDMS system, with and without the addition of small concentrations of hydrogen gas. It was suggested that the ions detected in the mass spectrum were the field-ionized Rydberg species and that the flowing plasma can be considered as mainly a neutral Rydberg atom gas, rather than a conventional ion−electron plasma.

Hodoroaba et al. (*265*) discuss how the effects of hydrogen in GD-OES can be exploited to improve analytical figures of merit, such as analytical sensitivity, detection limits, and depth resolution. On the other hand, problems caused by the presence of hydrogen, e.g., the occurrence of hydride bands, are also discussed.

In the group of Sanz-Medel (*266*), the effect of controlled addition of hydrogen to direct current (dc) GD TOFMS was investigated in terms of changes in the mass spectral features, the signal intensities of argon, hydrogen species and sputtered analytes, the sputtering rates, and the observed crater shapes. It was found that the Ar^{2+} signals were significantly increased when 0.5% v/v hydrogen was added. A strong line at $m/z = 3$ was also observed, corresponding to H_3^+. Further, the hydrogen addition yielded a drop in sputter rates but, in most cases, enhancements in analyte ion signals.

The same authors also investigated the influence of controlled addition of hydrogen, nitrogen, or oxygen to an argon rf GD-OES system, in terms of analyte emission intensities, sputtering rates, and analyte emission yields (*267*). Both conducting and insulating sample types have been used. It was observed that the addition of the molecular gases gives rise to a decrease of the sputtering rates. For the emission yields, selective enhancements (i.e., for some lines) were obtained with the addition of hydrogen or nitrogen, whereas the addition of oxygen yielded a systematic increase of emission yields for all lines. Further, the effect of hydrogen, nitrogen, or oxygen addition was also investigated for depth profile analysis by rf-GD-OES (*268*). Changes in dc bias voltage, crater shape, and depth resolution were reported. The results suggest that plasma gas mixtures might offer great potential to improve the depth resolution.

The effect of nitrogen on GD-OES was also investigated with a high-resolution Fourier transform spectrometer (*269*). Controlled amounts of nitrogen were added to the working gas. Intensities and line profiles of emission lines (of sample, argon,

and nitrogen—both atomic and molecular bands) were recorded. It was found, among others, that the self-reversal for the ArI 811.5- and ArI 763.5-nm resonance lines was reduced by the addition of nitrogen, implying a reduction in the population of argon metastable atoms.

(4) Electrical Characterization of rf GD Plasmas. Some fundamental research was also carried out for electrical characterization of rf GD plasmas. Belenguer et al. (*270*) used a simple analytical approach to estimate the different components of the total discharge current in an rf GD. Also the sheath and plasma region were electrically characterized. From this, information was obtained on the electric field on the sample, the sheath length, the ion density in the sheath, and the plasma density.

Payling et al. (*271*) combined an equivalent model of an asymmetric rf GD, with an equivalent circuit of the stray cell capacitance, coaxial cable connection, matching box, and power generator, to provide an electrical model of the impedance-matched rf source used for GD-OES.

Marshall presented a new design for an rf GD power supply (*272*). A lot of attention was paid to correcting for possible power losses. With this new rf design, comparison was made between dc and rf GD-OES. The similarity of the dc and rf results with respect to operating pressures, sputter rates, and emission intensities indicates that the power losses in rf-GD have indeed been properly corrected for.

Wilken et al. (*273*) developed an rf GD source with integrated voltage and current probes, for accurate measurements of the current−voltage characteristics in rf-GDOES. The main source feature is the small disturbance of the current signal by displacement currents and the independence of the current signal from leak currents of the water cooling. With this new technique, current−voltage characteristics can even be measured for samples with insulating layers. A new procedure allows the determination of the plasma bias voltage for insulating samples. The current−voltage time profiles, measured with this new technique, were also compared with results from a numerical model by Bogaerts et al., for an rf Grimm-type GD (*274*). Beside the time profiles of current and voltage, the rf voltage, dc bias voltage, electrical power, and peak-to-peak current were compared, and good agreement was reached between measurements and modeling results.

(5) Study of Pulsed GD Sources. Finally, several fundamental studies were devoted to millisecond-pulsed GD sources. The group of King investigated the excitation and ionization mechanisms in millisecond-pulsed GD, based on temporal optical emission characteristics (*275*). During the pulse, electron, ion, and atom excitation, as well as asymmetric charge-transfer and Penning ionization, are found to be significant. Upon power termination, thermal electron−ion recombination, yielding excited atoms and argon metastable species, becomes most important. Comparison is made between millisecond pulses of rf and dc power, but the two power sources yielded very similar results.

In a related paper (*276*), the authors investigated the spatial and temporal characteristics of a millisecond-pulsed GD. Interpretation of emission data provided insight into the nature of the plasma at each instant of a typical pulse cycle and at each position in space. It is found that the plasma is highly ionizing in nature at the time of pulse breakdown. The plateau region is also ionizing. The postpulse period, on the other hand, typically displays recombining behavior. Moreover, it is reported that the sputtered analyte atom emissions closely mimic those of the plasma gas, except that their emissions persevere for a longer time in the recombining afterpeak period than the discharge gas species.

Another paper by the same authors (*277*) reports about the addition of nitrogen to a millisecond-pulsed GD and its effect on the ion signals and optical emission intensities. The nitrogen was found to have significant effect on both the argon and sputtered analyte signals. The influence was different for different types of signals (e.g., ion signals, emission intensities) and for the plateau and afterpeak periods. This work demonstrates that nitrogen addition can be used to investigate the excitation and ionization processes in pulsed GDs.

Based on the experimental results obtained by King and coworkers, a modeling network was developed by Bogaerts et al. for a millisecond-pulsed GD (*278*). Special attention was paid to the mechanisms giving rise to the afterpeak, which is attributed to electron−ion recombination to the highest excitation levels, followed by radiative decay to lower levels. It is expected that the electron temperature decreases drastically upon pulse termination, resulting in a significant rise in electron density, making electron−ion recombination more plausible. Another, simple model for a pulsed GD in a thin-walled metallic hollow cathode was developed by Potapov et al. (*279*), and the atomization and ionization processes were investigated with atomic absorption and mass spectrometry.

Methodological Developments. The methodological developments for GDS can be classified into (i) GD source design, (ii) developments for the mass spectrometer, and (iii) for the OES system.

(1) GD Source: dc, rf, and Pulsed Operation Modes. To enhance the ion signals in the MS, Beyer et al. (*280*) developed a Grimm-type GD ion source with high gas flow rates (up to 240 mL/min), which was coupled to a mass spectrometer with high mass resolution. Analytical characterization of the source, using steel standards, showed that limits of detection at nanogram per gram levels could be obtained.

In the group of Harrison, a special sample holder was developed for a Grimm-type GD source that allows pin−sample analysis (*281*). In this way, rapid pin and flat sample analysis without additional sample preparation steps can be carried out. The analytical characteristics, such as detection limits and isotope precision, were found to be comparable to normal Grimm-type and diode GD sources. Also depth profiling for pin samples is shown in this work.

In a number of papers from the group of Sanz-Medel, the coupling of a dc GD source with a TOFMS is reported (e.g., refs *282* and *283*). The GD source is designed to be easily and quickly exchanged with an ICP source. One of the most important parameters was the actual design of the channels introducing the plasma gas into the GD. It was found that the sensitivity could be improved by 1 order of magnitude by using two opposite gas inlets into the chamber (*282*). This source was also evaluated for depth profile analysis, in terms of crater shape, sputtering rates, sensitivity, and mass resolving power. It was found that good crater shapes were obtained provided a “sampler cone” is placed in the interface between GD chamber and TOF (*283*).

A number of efforts have also been reported for better electrical characterization of rf GD sources (*271*−*273*), as was discussed

already above (see Electrical Characterization of rf GD Plasmas).

Finally, some methodological work has been devoted to pulsed GD sources. A double-pulsed GD was developed in Harrison's laboratory and compared to the single-pulsed mode, as ion source for mass spectrometry (*284*). The second pulse was applied during the time window between the first applied pulse and signal collection. The results show that the double-pulse GD increases the ion signals, provided that appropriate pulsing delays and gas flow rates are applied. Jackson et al. (*285*) developed a new pulsed GD source, with enhanced ion extraction for small nonconductive samples (in submilligram quantities). The same GD can also be tuned into an atmospheric sampling glow discharge, where a metal capillary is used in place of the rod, which normally is used as the cathode.

(2) Mass Spectrometry. Jackson et al. reported the coupling of a pulsed dc GD with a quadrupole ion trap (*207*). It is shown that strongly bound diatomic ions, occurring at the same nominal mass as an analyte ion of interest, can be selectively attenuated, by collision-induced dissociation.

In the Hieftje group, a Mattauch−Herzog mass spectrograph was coupled to a GD source (*286*, *287*). The Mattauch−Herzog geometry produces a linear focal plane, in contrast to the curved focal region of most sector instruments. Placing an array detector along this focal plane allows simultaneous and continuous acquisition of data over an entire mass range. Detection limits with this new MS system were reported in the nanogram per gram range, the isotope ratio accuracy and precision were better than 5% error and 0.2% RSD, and a linear dynamic range of at least 6 orders of magnitude was obtained (*286*). The combination of this MS with a microsecond-pulsed GD is also investigated. Since the pulsed GD produces analyte and bulk plasma ions at different periods within the pulse cycle, the combination with gated ion optics enhances the determination of species with m/z near bulk plasma ions (*287*).

(3) Optical Emission Spectrometry. In ref *288*, a GD-OES device has been designed for glovebox adaptation, to analyze C, H, N, and O at low concentrations in nuclear materials. To avoid optical interferences with matrix emission lines, the vacuum ultraviolet region of the spectrum (between 120 and 160 nm) was chosen for the light element analysis. For this purpose, two different systems of collection have been developed: a first based on two focusing lenses and a second having an optical interface based on mirrors. It is stated that these systems allow an increase in the number of photons transmitted from the source to the analyzer.

The other methodological work reported for GD-OES in the period of this review was related to the development of methods for more accurate analysis. Weiss (*289*) reported on multimatrix analysis by GD-OES, using spectrometers with solid-state detectors. By using a set of emission lines for each element, the accuracy of the analysis can be improved. Payling (*290*) reviewed several quantification algorithms, such as corrections for emission yield, self-absorption, spectral interferences, and relative sputtering rates, for rf-GD-OES calibration and analysis. Finally, in ref *291*, the use of the simplex method is described for optimization of lamp control parameters in GD-OES, for the analysis of copper−titanium−zinc alloys. It was stated that this approach substantially reduces the required number of experiments.

Applications of GDMS and GD-OES. (1) Bulk Analysis of Solid Conducting Materials. The major application of GDMS and GD-OES, i.e., the bulk analysis of solid conducting materials, is in a stage of maturity and is mainly used for routine analysis, e.g., in industrial laboratories. Consequently, there are not many scientific papers in the literature reporting about this application, and the few papers that have been published are purely application papers, and are therefore somewhat outside the scope of this review, which focuses mainly on novel applications and developments. We want to mention, however, a few papers, which are interesting and give novel information, for one or another reason.

Bengtson (*292*) reported on an international standard ISO 14707:2000, which was prepared by technical committee ISO/TC201, to give guidelines for the use of GD-OES for bulk and depth profile analysis of rigid solids.

Xhoffer and Dillen (*293*) describe the use of GD-OES for a wide variety of coated and uncoated steel products and show some interesting examples of off-line production assistance or customer support. The examples demonstrate the ease of the GD-OES technique to solve problems where other techniques would be much more time-consuming, more expensive, or would even fail. However, in most case studies, the combination of GD-OES with complementary techniques is required.

Finally, in ref *294*, a round robin analysis was carried out for copper samples, by 10 different laboratories, with 11 different instrument setups, including both GDMS and GD-OES, to investigate the analytical performance and quantification methods for these techniques. Two grades of pure Cu samples were used. GD-OES was employed in the study of the sample with high impurities only, whereas the GDMS results were evaluated for the trace element concentrations in both samples.

(2) Analysis of Nonconducting Materials. As mentioned above, dc GDs are very suitable for the analysis of solid conducting materials, but nonconducting materials would be charged up, due to the continuous sputter bombardment of positive ions. Therefore, in dc GDS, the nonconducting material must be either mixed with a conducting binding power (after grinding) or a secondary cathode needs to be applied. In ref *295*, both techniques were used simultaneously for neptunium determination in marine sediment samples, by dc-GDMS.

The most common technique for the analysis of nonconducting materials is, however, the use of an rf GD. In ref *296*, rf-GD-OES is used for the characterization of glass surfaces, including physical heterogeneities such as discrete layers and continuous interphases, and the distribution of elements in glass materials. It is shown that rf-GD-OES offers good spatial depth resolution and elemental sensitivity for several applications, such as the characterization of interfaces or interphases, and the determination of chemical gradients in glasses.

King and colleagues report on the use of pulsed rf GDMS for the determination of bromine in flame-retardant plastics (*297*). Both atomic and molecular species were produced, allowing elemental identification and molecular characterization. However, quantitative results for these species could not be achieved by direct analysis of the bulk plastic samples, because of the low signal intensities, which are probably correlated to the reduced sputter rates for some polymers. Analysis of samples compacted with a silver binder, on the other hand, provided intense analyte signals, allowing quantitative analysis.

The last application, which is worthwhile to mention here, is the use of rf-GD-OES for the analysis of particulate matter, by the so-called sol−gel technique, as developed by Marcus and coworkers (*298*). A thin film, suitable for sputter sampling into the GD, is generated by dispersion of the particles in a sol−gel sample matrix. The use of sol−gels as sample matrixes allows for background subtraction, through the use of analytical blanks. Detection limits were determined in the range of 1−10 μg/g or slightly higher.

(3) Depth Profiling Analysis. Depth profiling analysis is undoubtedly the application of GDS (mainly GD-OES) on which most papers are published in the literature. Indeed, it is already widely used, but there are still a lot of scientific challenges, such as accurate quantification, increase of depth resolution, extension of the layer thickness from thick to ultrathin layers, etc.

Shimizu et al. have described in two interesting review papers (*299*, *300*) the use of rf-GD-OES for depth profiling analysis, for film thicknesses ranging from several tens of microns thick, to ultrathin films of less than 10 nm thick. The significant features of rf-GD-OES enabling such analysis arise from the nature of rf GD sputtering, where both conducting and nonconducting samples are sputtered very stably with Ar^+ ions of low energies (<50 eV) and high current fluxes (order of 100 mA/cm^2). The low Ar^+ energy ensures that film sputtering proceeds without significant formation of altered layers, which is a prerequisite for successful depth profiling analysis of ultrathin films with high depth resolution. The high current fluxes allow sputtering to proceed at very high rates, >1 μm/min, thereby extending the limit to film thicknesses of 100 μm.

Angeli et al. have pointed out the special needs and requirements for thin-film analysis by GD-OES (*301*). State of the art is presented in terms of measurement technique, GD source control and design, effect of traces of molecular gases, correction and quantification procedures, modeling techniques, and reference materials.

Bengtson (*302*) has reported on dc-GD-OES for depth profiling of organic coatings on low-alloy steel sheets. Special attention is paid to the effect of molecular emission, originating from diatomic molecules CH, OH, NH, and probably CO. The observed molecular bands overlap with several atomic emission lines, causing line interferences. The effect of voltage and current on these molecular emission intensities is investigated, to understand better and minimize the interferences.

A comparison of GD-OES with other depth profiling techniques is carried out in ref *303*, for thin films with thicknesses in the nanometer range. It is concluded that GD-OES is characterized by very fast measurements and easy data interpretation; however, quantification is rather poor, mainly due to crater shape effects.

Several other papers report on the application of (rf-)GD-OES for depth profiling analysis (see, for example, the special issue in *Surface and Interface Analysis*, mentioned above), but they cannot all be mentioned here, because of limitations in number of references for this review paper.

(4) Liquids Analysis. In recent years, the application field of GDS is widened from solid analysis (based on cathode sputtering), toward liquids and gas analysis.

A number of setups are reported in the literature, which use the liquid directly as the cathode of the GD. Jenkings and Manz (*304*) describe a miniaturized GD for optical emission detection in aqueous analytes. To attain sufficient transport of sample into the discharge region, acidification of the liquid sample was required. However, a number of stability issues will need to be resolved to allow further optimization.

A review on the electrolyte-as-cathode glow discharge (ELCAD), which was already developed several years ago, is presented in ref *305*. Its use for on-line determination of trace heavy metals in waste and drinking waters, as well as in other liquid samples, is discussed.

A capillary version of the ELCAD cell is described by Cserfalvi and Mezei (*306*), which could act as a multimetal detector for chromatographic or flow injection analysis applications. The cathode flow system consists of a glass capillary of 1-mm inner diameter. The new cell has a volume of 15 μL and requires only 3.5 mL/min flow.

In ref *307*, an atmospheric sampling glow discharge ionization soure is used for the direct analysis of liquid-phase samples. Electrospray is utilized for nebulizing and transporting intact sample molecules into the glow discharge.

The group of Marcus is also very active in developing GD sources for liquid analysis. In ref *308*, a liquid sampling atmospheric pressure glow discharge (LS-APGD) is used as optical emission detector for low-flow separations, such as capillary flow liquid chromatography and electrophoresis. A concentric sheath gas is employed to stabilize the solution delivery. The LS-APGD is demonstrated to operate with a variety of electrolyte species and under conditions where the analyte solution acts as either powered or grounded, cathode, or anode.

A particle beam glow discharge (PB-GD) source for MS (*309*) and a particle beam hollow cathode (PB-HC) GD source for OES (*310*, *311*) are also developed in the Marcus group for liquids analysis. The PB-GDMS combination can be operated in a flow injection mode, wherein the analyte is injected directly into the solvent flow, or it can be coupled to a HPLC system. In ref *309*, it was utilized for the mass spectrometric determination of nucleic acid bases, nucleosides, and nucleotides. Use of this combination of sample introduction and ion source decouples the vaporization and ionization steps, leading to very simple spectral structure, with clearly identified molecular ions and fragmentation patterns.

The PB-HC-GD-OES system was used, for instance, in ref *310* as a detector for liquid chromatography, for the separation and speciation of organic and inorganic selenium compounds. The PB interface includes a thermoconcentric nebulizer, to generate a finely dispersed aerosol, a heated metal spray chamber for desolvation, and a two-stage momentum separator, which removes solvent vapor. The resulting beam of dry analyte particles is then introduced into a heated (∼250 °C) hollow cathode, where they are vaporized, atomized, and excited within the plasma. In ref *311*, it was applied for quantitative total protein determinations. The reported advantages of the technique include ease of operation, exclusion of labor-intensive sample pretreatment processes, rapid analysis, high sensitivity, and low detection limits. The method can also be adapted to be integrated to microfluidics devices.

(5) Gas Analysis. Lewis et al. have described the use of a millisecond-pulsed glow discharge, coupled to TOF-MS, as detector for gas chromatography, for the determination of aromatic and halogenated hydrocarbons (*312*, *313*). Depending on the sampling distance and time, either elemental information or structural or molecular weight information could be obtained. In general,

elemental information was obtained during the first 0.015 ms after the plasma onset and structural information was obtained during the plateau time regime, whereas molecular ions were obtained during the afterpeak time regime (*312*).

In the Hieftje group (*314*), a gas sampling glow discharge (GSGD) coupled to a TOFMS, was successfully applied for the determination of arsenic by hydride generation. Several discharge gases (helium, neon, hydrogen, argon) were investigated. The He GSGD appeared to be the most attractive source, due to the lower detection limit (0.6 ppb, which is almost comparable to the ICP), higher sensitivity, and greater stability.

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AC040052X