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Atomic Spectroscopy

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Review Contents

ATOMIC SPECTROSCOPY

Atomic spectrometric methods make use of flames and furnaces as atom reservoirs for atomic absorption and mainly plasma sources at reduced or ambient pressure as radiation and/or ion sources for emission and elemental mass spectrometry, respectively. Whereas applications deal with almost every area of science and technology, a lot of methodic innovation took place, as reflected in the literature published in the period between November 2005 and October 2007. As in the recent issues of this review series (*1–3*), a representative part of the papers published in the journals *Analytical Chemistry, Analytical Sciences, Analytical and Bioanalytical Chemistry, Applied Spectroscopy, International Journal of Environmental Analytical Chemistry, Journal of Analytical Atomic Spectrometry, Journal of Environmental Monitoring, Microchimica Acta, Microchemical Journal*, and *Spectrochimica Acta, Part B* is discussed and at the hand of these papers trends of development show up. Of course the number of journals covered as well as the number of citations does not allow a complete overview of the area but nevertheless allow it to draw up the great lines of development in atomic spectrometry. Within the period covered a number of important scientific meetings such as the *Winter Conferences on Plasma Spectrochemistry* in the U.S.A. (January 8−14, 2006, Tucson, AZ), Europe (February 18−23, 2007, Taormina, Italy), and Asia (November 26−December 2, 2006, Bangkok, Thailand), the *Colloquium Spectroscopicum Internationale* (September 4−9, 2005, Antwerp, Belgium) (*4*) or the *International Congress on Analytical Sciences* (June 20−30, 2006, Moscow, Russia) (*5*) took place or the proceedings were published. Further, special issues of the above-mentioned journals occurred, where actual topics like new plasma discharges for atomic spectrometry (*6*) or the use of vapor generation for analytical atomic spectrometry (*7*) was treated. Also reviews dealing with topics like atmospheric plasma discharges for atomic spectrometry, in which both the principles as well as a number of prominent applications were discussed (*8*), have been published.

ATOMIC ABSORPTION SPECTROMETRY

Flame Atomic Absorption Spectrometry. Flame atomic absorption spectrometry (AAS) is a standard method, which is of use in any analytical laboratory where elemental determinations are made. Apart from the optimization of the commercial systems with respect to the burner and the nebulization system, novelties deal with special sampling techniques especially. Here, e.g., work with slurries for the direct determination of volatile compound-forming elements in chocolate powder are to be mentioned (*9*). A further interesting area is the use of furnaces heated by flames as atom reservoir. Here, the residence times of the analyte are increased with a positive influence on the power of detection achievable. Ribeira et al. (*10*) made use of the ultrasonic nebulization of solutions and determined Ag, Bi, Cd, Cr, Cu, Mn, Pb, Sb, Sb, Se, Tl, and Zn with a gain of sensitivity of up to 39. Petrucelli et al. (*11*) used a thermospray system for aerosol generation and nickel tube furnaces. With high-speed imaging, Brancalion et al. (*12*) studied the formation of the vapor cloud and its diffusion in the atomizer. With a thermal spray furnace in the flame system, online preconcentration made it possible to directly determine Cd in vegetal samples with a detection limit in the solutions of 8 ng L^{-1} (*13*). Also, determinations of Cu after preconcentration on polyurethane foam have been reported (*14*). Further, cloud point extraction combined with flame quartz furnace atomic absorption has been described for the determination of Cd in waters and urine (*15*), where a detection limit of 0.04 $\mu g\ L^{-1}$ was obtained.

Furnace Atomic Absorption Spectrometry. Furnace AAS is a method for ultratrace determinations "par excellence". Systematic errors and traceability of the data here have to deal with every step in the analytical process from sampling to analysis, as shown in a tutorial paper of Duta et al. (*16*). The process of electrothermal vaporization still is the topic of many theoretical studies. With the aid of Monte-Carlo simulations, the transport of the analyte vapor from the furnace could effectively be studied, which seemed to be of great use when employing the furnace as

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a sampling cell in plasma spectrometry (*17*). When using it as atomizer in AAS, the nonuniform heating of the furnace and platforms may cause vapor transport inside the furnace which influences the interferences, as it was studied by Gilmutdinov et al. (*18*). Apart from dry solution residue sampling, work with microemulsions is also possible, which is of considerable use for determinations in diesel, gasoline, and naphta (*19*). Also slurries can be easily dispensed with automated systems into the graphite furnace, which after all is an important approach for determinations in all types of biological samples, which can be transformed into powders. This is shown as an example of the determination of Pb in marine plankton (*20*). A continuous homogenization by ultrasonic energy and the use of matrix modifiers may improve the accuracy of the method as shown by Muñoz and Aller (*21*). The possibilities of online electrothermal AAS configurations were discussed by Burguera and Burguera (*22*). When combined with suitable extraction procedures, graphite furnace AAS through its high power of detection also is a method of choice as detection in elemental speciation, as shown for the speciation of Cr in wastewaters by Meluka et al. (*23*). Here also the use of microsequential bead injection lab-on-valve technology may be useful, as also shown for the speciation of Cr incorporating online chemical reduction (*24*).

The study and the application of volatilization aids remains an important topic in graphite furnace AAS work. Here gases promoting the formation of volatile analyte compounds are very useful. Freon has been investigated, e.g., to promote the volatilization of Cr, Mo, Ti, and V in multielement AAS, but the efficiency seemed only to be high when Ar−H_2 mixtures were used as protection gases for the furnace (*25*). With a 1% addition of $CHClF_2$ and an atomization temperature of 2550 °C, the limits of detection of 0.05, 0.2, 2.3, and 0.5 $\mu g\ L^{-1}$ for Cr, Mo, Ti, and V were obtained, and even in dissolved silicon nitride and boron carbide powders determinations were possible. Katskov et al. (*26*) studied the release of transition metals from the graphite filter furnace. Ta or W lined tubes with Ar and He as internal gases were used, and results for Cd, Zn, Cu, and Ag are presented. In a large series of papers, the use of different matrix modifiers in the case of real samples was studied. Damin et al. (*27*) , e.g., reported on the use of Pd as a chemical modifier for the stabilization of Ni and V compounds for determinations in crude oil samples and demonstrated the increase of the accuracy at the hand of the analysis of standard reference materials. Further Castro et al. (*28*) performed electron microscopic and diffuse reflection IR measurements to clear the influence of Th and Pd based modifiers in graphite furnace AAS analyses of complex samples. They could show that spatial variations in the residues along the furnace occurred and that added Si could act as an internal modifier for As.

Further methodological studies in graphite furnace AAS dealt with the use of electrodeposition combined with in situ stripping for the analysis of samples with high concentrations of NaCl. Here the detection limits for Pb and Cd in a solution containing up to 30 $g\ L^{-1}$ of NaCl were 8.5 and 2.3 pg, respectively (*29*). The procedure was found to be well suited for the determination of Au, with which subsequently to deposition on a graphite ridge probe (*30*) and under the use of Pd as a modifier, determinations of Au in river water down to the nanogram per liter level are possible. For the element B, the isotopic ratio of $^{10}B/^{11}B$ could be determined by Zeeman effect background-corrected graphite furnace AAS and the results found were in good agreement with those of quadrupole ICPMS (*31*). Katskov (*32*) showed that graphite filter atomizers for the case of high and medium volatility elements in matrixes associated with strong spectral and chemical interferences have advantages over commonly used electrothermal vaporizers and atomizers, tube and platform furnaces at the hand of analytical applications using organic liquids and slurries, biosamples, and food samples. Trenin et al. (*33*, *34*) studied the use of an electrothermal vaporization unit with axially focusing convection upstream and the influence of modifiers. Transport efficiencies for Cu, Fe, Mn, Ni, and Pb were studied and coherent forward scattering measurements performed. Further modeling of the condensation process was dealt with as well.

Vapor Generation AAS. For all elements, which can be brought with a high efficiency in the gas phase, the sensitivity of AAS can be much increased as compared to pneumatic nebulization of solutions. This has been recognized already in the 1960s for elements such as As, Se, etc., forming volatile hydrides but through the use of many different techniques this approach can be expanded to many elements. Pohl and Prusisz (*35*) treated the use of tetrahydroborate for the chemical vapor generation of noble metals and dealt with the instrumentation required for this work. Matoušek (*36*) especially studied the efficiency of chemical vapor generation of transition and noble metals. He stated that the true efficiencies obtained did not surpass 30% and that overestimates often occur from determinations of the residual analyte concentrations in the effluent. Laborda et al. (*37*) reviewed the use of electrochemical hydride generation as a sample-introduction technique for atomic spectrometry in general and especially treated the fundamentals, the interferences, and the applications of this technique for the analysis of real samples. Kratzer and Dědina (*38*) described a novel quartz device to be used as an atomizer in connection with arsine and selenium hydride generation. The system includes a trapping system and uses a microflame, and collection and volatilization efficiencies of 50 and 70%, respectively, were obtained. D'Ulivo et al. (*39*) performed gas chromatography/mass spectrometry studies of the hydrogen−deuterium exchange reaction of volatile hydrides of As, Sb, Bi, Ge, and Sn in aqueous media to estimate the relative abundances of each species formed following the H−D exchange process. They concluded that the H−D exchange in the already formed hydrides can be the source of interference and could show that no H−D exchange was detected in the pH intervals where no interferences occurred. Apart from the noble metals and the commonly known volatile-hydride forming elements, also for Pb hydride generation were studied (*40*) and analytical applications were reported. Furthermore, Cd volatile compound formation was described and the technique applied for the determination of Cd in foodstuffs and water down to the 0.021 $\mu g\ L^{-1}$ level (*41*). For Pd, cold atom solution atomic absorption was also described to be possible (*42*) when gas phase atoms are trapped in bubbles, which could be promoted by the use of surfactants. With this approach, limits of detection for Pd of ~100 $mg\ L^{-1}$ can be obtained. For the case of S, indirect determinations at the ultratrace level in natural water can be performed by flow-injection online sorption in a knotted reactor coupled with hydride generation atomic fluorescence spectrometry (*43*). Here, a detection limit of 0.05 μg L^{-1} can be obtained and a sample throughput of 20 samples/h realized.

Photochemical vapor generation has also been found to be of use for the generation of volatile metal species. Here photocatalytic reduction is used, and the mechanisms therefore were discussed for a wide variety of nonvolatile precursors (*44*). An analytical procedure for the determination of Se could be developed, where the Se was sequestered in an aqueous microdrop containing Pd(II) and then brought into the graphite furnace for AAS measurements (*45*). Several organic acids, such as formic, oxalic, acetic, citric, and ethylenediaminetetraacetic acid, were tested for the photoreduction of Se(IV) into volatile Se species under the use of UV radiation. Vieira et al. (*46*) described the determination of total Hg and methylmercury in biological samples by photochemical vapor generation. They digested the tissues in formic acid or tetramethylammoniumhydroxide and determined the total Hg by exposure of the solution to UV irradiation. The results were found to be in good agreement with those of the conventional Hg cold vapor technique. In a further step, sono-induced cold vapor generation was also used for the determination of Hg (*47*). Here the released Hg can be trapped on a noble metal-pretreated platform (Pd, Pt, or Rh), which is inserted into the graphite furnace atomizer, and a limit of detection of 0.03 μg L^{-1} is obtained.

In situ trapping indeed is a very important possibility in vapor generation techniques, so as to preconcentrate the analyte and to remove any interferences in the AAS determination step. This has been shown for the determination of Te by Matusiewicz and Krawczyk (*48*), who reported a detection limit of 0.9 μg L^{-1} for a 2 min preconcentration time. Similar approaches were followed by Krejči et al. (*49*) for the determination of Sb and Bi, where a Mo foil strip in the presence of Pt, Ir, and Rh as a modifier was used to trap the hydrides, and then they brought them into a miniature hydrogen flame atomizer. Ajtony et al. (*50*) determined Se in cereals and bakery products by flow injection hydride generation graphite furnace atomic absorption spectrometry with in situ trapping on iridium-treated graphite platforms, and they could determine Se in the range of 7.7−68 ng g^{-1}. The samples were dissolved in a mixture of HNO_3 and H_2O_2 solutions using microwave-assisted digestion, and a transversally heated graphite atomizer was used. Rivaro et al. (*51*) described the speciation of Hg in environmental samples by cold vapor atomic absorption spectrometry with in situ trapping on a gold trap. They differentiated between organic and total Hg after selective extraction of the organomercury compounds. Trapping was also used in the determination of Au in geological samples, where interferences of Fe in the vapor generation technique were studied (*52*). Here a quartz tube furnace was used as the atomizer. For the Hg cold vapor generation, it has been shown to be possible to use a $NaBH_4$ solution layer on an inert carrier to reduce the Hg compounds. The system could be miniaturized by using lab-on-valve technology, and limits of detection of 0.06−0.005 mg L^{-1} could be obtained in the case of atomic fluorescence detection (*53*). Determinations of As in urine by batch hydride generation AAS have been described to enable observations on toxicologically relevant As in adult offspring of families with Balkan endemic nephropathy (*54*). Here, the limit of detection of 0.25 μg L^{-1} in 10 mL of 1 + 4 v/v diluted urine and the 2−6% RSD at the 1.0 μg L^{-1} As level were adequate for the study.

High-Resolution Continuum Source AAS. Through the availability of high-intensity continuum radiation sources such as Xenon arcs and W-X-lamps on one side and of high-resolution Echelle spectrometers using CCD detection on the other side, multielement atomic absorption with integrated background measurement and correction possibilities now are available. Becker-Ross et al. (*55*) discussed the present state of development of continuum source AAS and the appropriateness of detector technologies for the development of simultaneous and sequential continuum source AAS. The essential role of a number of aspects of detector performance is elucidated. Welz et al. (*56*) used a continuum source Echelle spectrometer for diagnostic purposes in analytical AAS and could show by a visualization of the spectral environment around the P 312.6 nm line that the absorption signal in the absence of a modifier is mostly due to the PO molecule and not to atomic phosphorus. Heitmann et al. (*57*) discussed the determination of nonmetals via molecular absorption using continuum source AAS and graphite furnace atomization. Here the limited accessibility of resonance atomic lines for these elements can be avoided. Through the addition of an excess of Ga, the elements F and Cl can be converted into GaF and GaCl, S can be converted through the presence of C into CS, and P into PO. With these molecular bands, detection limits for these elements in the low nanogram to high picogram range for these elements can be obtained. Huang et al. (*58*) described the determination of the halogens via molecules in the air−acetylene flame using high-resolution continuum source AAS. For F again, the GaF bands were used, which are at the 211−214 nm spectral range. With the strongest absorption band head at 211.248 nm, a detection limit of 1 mg L^{-1} for F is obtained when Ga is added up to a concentration of 10 g L^{-1}. In the case of filter atomization, known from the work of Katskov, it could be shown that the external tube in conventional AAS and temperatures of 2800 °C for up to 55 cycles is more corroded than the filter and the collector in the case of filter atomization (*59*). For the determination of Al in serum, the use of Zeeman and continuum background correction were compared (*60*). The characteristic mass for Al was found to be 12.1 ± 0.6 pg in the case of continuum background correction and 16.1 ± 0.7 pg in the case of the Zeeman technique; however, the detection limits were practically the same. As discussed by Van et al. (*61*) , both continuum- and line source AAS are very useful for speciation analysis of butyl- and phenyltin compounds through a coupling of gas chromatography and quartz-tube atomization. The continuum source instrumental detection limits were found to be 5−10 times better than in line source AAS after an application of background correction.

Direct Solid Sampling AAS. For the case of powder samples, direct solid sampling in many cases is very favorable especially as in furnace AAS slurries can be dispensed very reproducibly into the furnace, and in many cases a calibration through the addition of synthetic analyte solutions can easily be done and a good accuracy achieved as well. The approach is attractive as sample dissolution is a time-consuming task, which introduces risks for both losses and contamination. Further, the lack of standard samples can be circumvented by the calibration with synthetic solutions, which are easy to prepare.

Huang and Krivan (*62*) described the determination of Si in biological samples, such as pork liver, bovine liver SRMs, and pure cellulose. The organic matrix was destroyed and expelled from the graphite furnace during pyrolysis between 160 and 1200 °C, and a limit of detection of 30 ng g^{-1} for an amount of sample of 6 mg was obtained. The results of analysis were found to be in good agreement with those of graphite furnace AAS subsequent to sample digestion with acids, wavelength-dispersive X-ray fluorescence spectrometry, and radiochemical neutron activation analysis. Dočekal and Vojtkova (*63*) described the use of direct solid sampling graphite furnace AAS for trace determinations in TiO_2 powders. They applied Zeeman background correction, determined As, Cd, Hg, Pb, Sb, and Zn, and used a sample boat technique. Detection limits at the ng g^{-1} range were obtained, and when using the boat at temperatures below 2000 °C, it could survive over 1000 runs and the results were found to be in good agreement with those of analyses subsequent to sample dissolution. For the determination of F, the formation of AlF in the presence of Al could be made use of. For the case of coal or alumina samples, a detection limit of 0.17 μg g^{-1} for the determination of F with direct solid sampling graphite furnace AAS could be obtained (*64*). The direct solid sampling approach could also be used for the direct determination of Pb in blood samples transmitted to and dried on filter papers. Here a detection limit of 2.5 μg L^{-1} could be obtained, so that for children the level of concern (100 μg L^{-1}) can be well controlled with a minimally invasive paper test (*65*). Zeeman based background correction is very useful for obtaining accurate results, as shown by the results of the determinations of Hg, Cd, Mn, Pb, and Sn in seafood with direct solid sampling graphite furnace AAS and a calibration with standard addition of solutions (*66*). For direct solid sampling graphite furnace AAS, a two-step atomizer including a transversally heated graphite atomization tube and a moveable vaporizer graphite cup was described by Friese et al. (*67*). Here the atomizer is placed between the poles of an electromagnetic field providing longitudinal Zeeman-effect background correction capabilities, and both tube and cup are heated by independent power supplies. High-resolution continuum source graphite furnace AAS was used for the determination of Pb in coal, as described by Borges et al. (*68*). Here interference-free calbrations could be made by calibration with aqueous standard solutions in 0.5% v/v HNO_3.

A direct determination of Hg in soils by direct solid sampling graphite furnace AAS is possible with a detection limit of 25 ng g^{-1}. Here $KMnO_4$ was used as the chemical modifier, and the procedure was found useful for a semiquantitative screening (*69*).

ATOMIC EMISSION SPECTROMETRY

Atomic emission spectrometry with various radiation sources now is of routine use in many fields of application. However, methodological developments take place especially with respect to the radiation sources, whereas CCD detection now became the standard in practically any line of spectrometers. For atomic emission spectrometry, monochromatic imaging spectrometers, through the availability of high-density CCDs with sufficiently high resolution and dimensions, now can be used. They allow it to achieve spatial resolution in the source of 0.1 mm × 0.3 mm with a magnification of 0.52 (*70*). Also the read-noise of focal plane array detectors through mean-variance analysis can be well characterized, improving the quality of low-level intensity measurements with these devices (*71*).

Arc and Spark Sources. Arc and spark sources have been used since long, especially as routine devices for metals analysis. However, some innovative developments still take place.

Spark ablation was, e.g., applied for the dissolution of precious metals and alloys, as described by Goltz et al. (*72*). Here suspensions can be obtained, which often can be dissolved in concentrated acids (e.g., 16 M HNO_3), and the craters formed as well as the amounts of material ablated were found to widely depend on the type of metal and alloy as well as on the sparking parameters. Direct current arc emission spectrometry was found to be a powerful technique for the direct analyses of boron carbide powders, especially when the suitable gas atmosphere and chemical modifiers are used (*73*). Under the addition of graphite powder and CaF_2, detection limits for Al, Ca, Cr, Cu, Fe, Mg, Mn, and Si were 0.3−9 μg g^{-1} and for Ti, W, and Zr 18−39 μg g^{-1}. For B, the best values were found when O_2 is present. The magnetically stabilized arc proved to take up wet aerosols quite well, and as a function of the field, considerable enhancements of analyte signals could be obtained (*74*). The use of a wall-stabilized arc for the determination of As, Se, Sb, and Sn after volatile hydride generation was described by Eid et al. (*75*). In the case of sodiumtetrahydroborate, high-resolution monochromator detection limits of 3.9, 6.8, 9.8, and 13.2 μg L^{-1} for As, Se, Sb, and Sn, respectively, were obtained and the procedure could be well used for the determination of As in lake sediment samples.

Tungsten coil emission spectrometry, as described by Rust et al. (*76*) , was shown to allow the determination of a wide range of elements in aqueous solutions after drying them on a tungsten coil and applying 150 W. The coils could be used for up to 265 heating cycles, and detection limits of 0.02 ng of Al, 0.7 ng of Co, 0.003 ng of Cr, 0.01 ng of Dy, 0.7 ng of Ga, 0.3 ng of K, 0.04 ng of Mn, 10 ng of Pb, 0.07 ng of Rb, 1 ng of Sc, and 0.003 ng of Yb were obtained.

Inductively Coupled Plasma Emission Spectrometry. In inductively coupled plasma emission spectrometry (ICP-OES), innovation took part with respect especially to sample introduction, but also optimization and control of the excitation processes and developments such as axial viewing or the use of VUV lines were found to still considerably enlarge its possibilities.

Pneumatic Nebulizers. In the rule, conventional pneumatic nebulizers are used for sample introduction in ICP-OES. Here Lagomarsino et al. (*77*) described the necessity to use a sheathing gas when injecting the aerosol generated by a high-efficiency pneumatic nebulizer in a single-pass spray chamber. Different types of nebulizers such as the PFA micronebulizer and a HEN nebulizer as well as spray chambers like the Cinnabar low inner volume cyclonic spray chamber as well as the so-called torch integrated sample introduction system (TISIS) were used, and the results indicated that the sheathing gas effect depends on the cavity inner volume and on the delivery liquid volume as shown in terms of the sensitivity and matrix effects for the case of Al, As, Ba, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Sb, Se, St, V, and Zn. Olesik and Kinzer (*78*) measured monodisperse droplet desolvation in the ICP using droplet size dependent peaks in Mie scattering. The desolvation rates were found to be independent of the addition of 0.1 M NaCl to the sample solutions. The droplet sizes, however, were found to be higher than those obtained with other techniques. Jorabchi et al. (*79*) used interferometric droplet imaging for in situ aerosol characterization in the ICP as well. Through a combination with particle tracking velocimetry, they could follow the droplet diameter changes for the case of a demountable direct injection high-efficiency nebulizer for droplets in the range of 3−30 μm diameter traveling at 15−70 m s^{-1} in the analytical zones of the ICP. The measured evaporation rates are in good agreement with the values expected for a 3000 K Ar environment.

Dual-nebulizer sample introduction by several authors has been described recently. Gómez et al. (*80*) used a dual nebulizer sample introduction system for the simultaneous determination of volatile hydride forming elements and other elements. Here radial viewing of the plasma was applied, and the plasma operating conditions as well as the nebulizer working conditions were optimized for the determination of As, Hg, Sb, and Se. The analytical performance realized was superior to the one of conventional nebulization systems, and the excess of gases released during hydride generation was found to have no influence on the plasma stability. Maldonado et al. (*81*) evaluated the use of a dual-micronebulizer sample introduction system. The system essentially is a modified cyclonic spray chamber that allows the simultaneous operation of two micronebulizers. Advantages of the systems were shown to lie in the use of tandem calibration approaches and the use of the system for hydride generation even with submilliliter volumes of sample. The nonspectroscopic interferences commonly known to be higher at lower solution uptake rates could be well compensated for by the tandem calibration technique. Bauer and Broekaert (*82*) described a pneumatic cross-flow nebulizer with dual solution loading and used this system for the correction of matrix effects caused by 40 mmol L^{-1} of Na, K, Rb, and Ba in elemental determinations of Cd, Co, Cr, Cu, Fe, Mn, Ni, and Pb as analytes at the 300 μg L^{-1} level. Calibration by standard addition in the case of such a nebulizer has been shown to be possible without preparing additional solutions. This has been shown to deliver highly accurate results for the determination of Cr, Cu and Ni as minor elements in steel and of traces of Ca, Fe, Ga, Li, Mg, Mn, Na, Si and Zn in a reference alumina powder sample.

Almagro et al. (*83*) described a flow focusing pneumatic nebulizer and compared its performance in ICP-OES with the one of several micronebulizers. It was found that as a result of the filtering action of the cyclonic spray chamber used in all cases, the flow focusing nebulizer produces a finer primary aerosol than the tertiary aerosol and also the detection limits were found to be similar to those of other nebulizers. For the case of organic solutions, Grindlay et al. (*84*) used microwave assisted desolvation. They obtained an increase of the signals by a factor of 7−17, and the matrix effects could be substantially reduced. For determinations in crude oil, the use of detergentless microemulsions was shown to be possible. de Souza et al. (*85*) used propan-1-ol as a cosolvent and added water as well as concentrated nitric acid. With a 6% sample containing solution, they could obtain detection limits for Mo, Zn, Cd, Ti, Ni, V, Fe, Mn, Cr, and Co at the nanogram per gram range, and the results of the analysis agreed well with those obtained with sample dissolution and analysis of aqueous solutions. Slurry nebulization was shown by Schwarzer et al. (*86*) to be a good approach for the analysis of platinum concentrate. The slurries consisted of 0.05 m/v % of sample, 0.5 m/v of Triton X-100, and 5% v/v HCl. Allowing for a grinding time of 30 min, the analysis took 90 min and results for Ag, Au, Cu, Fe, Ir, Ni, Pb, Pd, Pt, Rh, Ru, and Te were found to be within the 95% confidence level compared to those obtained with the Carius tubes technique. For As, Bi, and Se, crystal inclusions in the ground sample may have falsified the results and Al as well as Si could not be determined because of the mill materials. Purawatt et al. (*87*) showed that flow field-fractionation ICP-OES was suitable for the investigation of the size-based distribution of Fe complexed to phytic and tannic acids in a food suspension. Investigations were performed at a pH of 2 as present in the stomach, 5.0 as found in the upper part of the duodenum, and 7.0 as in the small intestine, so as to study the binding of Fe by the acids and its presence in several high-molecular weight fractions.

Evaporation Systems. Greib and Karanassios (*88*) used the introduction of particulate matter into the ICP for programmable delivery of small amounts of diluted powdered samples to the ICP and reported stable operation of the plasma. It was possible to enter nanometer- and micrometer-sized materials and to determine refractory elements such as W, of which the signals were shown to increase by the addition of SF_6 to the ICP working gas.

Electrothermal evaporation was widely used as the sampling technique. Davis et al. (*89*) used chelation of Cd with ammonium pyrrolidine dithio-carbamate prior to its determination by tungsten-coil ICP-OES. For urine samples, the complex was extracted with methyl isobutyl ketone, Bi was added as an internal standard, and 20 μL aliquots are brought to the tungsten coil. The detection limit was 0.04 μg L^{-1}, and an accuracy of 98% was obtained in the case of a standard reference material. Okamoto et al. (*90*) made use of electrothermal vaporization for the direct determination of Zn in steel samples and used a tungsten boat evaporation unit. By calibration with dry solution residues of an Fe, Zn, and ammonium dihydrogenphosphate containing solution, a good accuracy at the 10−40 mg kg^{-1} level could be obtained. Barth et al. (*91*) described the determination of trace impurities in boron nitride by graphite furnace AAS and electrothermal vaporization ICP-OES using solid sampling. Al, Ca, Cr, Cu, Fe, Mg, Mn, Si, Ti, and Zn could be determined at concentration levels of 1−23,54−735, 0.05−21, 0.005−1.3, 1.6−112, 4.5−20, 0.03−1.8, 6−46, 38−170, and 0.4−2.3 mg g^{-1}, respectively. In both cases, analyte/matrix separation was applied, and the calibration was performed with calibration curves obtained with aqueous standard solutions. In AAS, the platform was covered with graphite powder and for the determination of Si, $Pd/Mg(NO_3)_2$ modifier was used. In the ETV-ICP-OES measurements, Freon R12 was added to the argon carrier gas and the achievable detection limits for the AAS and ETV-ICP-OES procedures were within 5 (Cu)-130(Si) ng g^{-1} and 8(Cu)-200(Si) ng g^{-1}, respectively. Matschat et al. (*92*) used ETV-ICP-OES and dc arc OES for multielement trace determinations in SiC powders within the frame of an international interlaboratory comparative study. Here calibrations were done with solutions or oxides.

Vapor Generation. Also in ICP-OES, hydride generation has been used for the determination of volatile hydride forming elements and also applied for real sample analysis. Suárez and Giné (*93*) used capillary electrophoresis combined to hydride generation ICP-OES for the speciation of As. With a dedicated reactor/phase separation system, they could realize a peak increase by a factor of 40 for the As(III) and As(V) species. Peña-

Vázquez et al. (*94*) used lanthanum hydroxide as a trapping agent in the determination of hydrides by hydride generation ICP-OES. For the determination of As and Sb in seawater they applied a prereduction with thiourea and a preconcentration by coprecipitation with lanthanum in a PTFE knotted reactor, resulting in detection limits of 0.17 and 0.27 μg L^{-1} for Sb and As, respectively. For standard reference materials, an agreement at the 2 μg L^{-1} level for As and 14 μg L^{-1} level for Sb was achieved. Peña-Vázquez et al. (*95*) extended the vapor generation ICP-OES method to the determination of metals such as Ag, Au, Cd, Cu, Ni, and Zn by using sodium tetrahydroborate as the reducing agent and adding constant concentrations of 8-hydroxyquinoline and Co to all standards in order to increase the efficiency of the reaction. After a thorough optimization of all working parameters, detection limits for the elements mentioned were found to be below 10 μg L^{-1}. Grotti et al. (*96*) applied chemical hydride generation for the simultaneous determination of As, Sb, Bi, Ge, Sn, Se, Te, and Hg by ICP-OES and performed a multivariate optimization. They studied differences in the hydride generation from one element to another and used Pb II and Pb I line intensities for diagnostic purposes. dos Santos et al. (*97*) determined Pb in sediments and sewage sludge by online hydride-generation and axial-view ICP-OES using slurry sampling. After a multiparameter optimization, external calibration against aqueous standard solution in the concentration range 10−100 μg L^{-1} could be used for the analysis of three marine sediments, one river sediment, and two sewage sludges as reference materials and a good agreement for the Pb and Sn values could be obtained, despite Pb was only partially extracted into the liquid phase.

Inductively Coupled Plasma Sources. The information capacity of ICPs is now much better made use of, as now spectrometers are available with which measurements down to the low VUV can be made. Herewith, e.g., the halogens can be determined with a number of analytical lines being relatively free of interferences as shown as the example of the determination of I in algae by Niedobová et al. (*98*).

Further, basic studies on the excitation mechanisms in analytical ICPs have been performed. Chan and Hieftje (*99*) described the probing of potential charge-transfer reactions with nonargon gaseous species in a mixed-gas ICP by means of two different experimental strategies, namely, the plasma-related matrix-effect approach and the relative-intensity technique. The foreign gases introduced one by one into the central channel were oxygen, hydrogen, nitrogen, krypton, methane, and carbon dioxide at volumetric concentrations of 15%, 10%, 5%, 100%, 3%, and 3%, respectively, and both matrix effects and relative intensities showed no change in behavior for emission lines with excitation energies in the vicinity of the ionization potential of the foreign gases. This suggests that the charge-transfer contribution from the foreign gas is not important to the overall analyte ionization and excitation at the foreign gas concentrations used. Elements with a low second ionization potential were found to cause more plasma-related matrix effects. Especially with the presence of low-lying energy levels, the doubly-charged matrix ion could be responsible and therefore the Penning ionization by argon metastables is proposed as the dominant mechanism for both analyte excitation and matrix effects (*100*). Also the topic of internal standardization in ICP-OES was addressed, and methodology to enlarge the pool of potential internal standards for axially viewed ICP-OES has been developed and evaluated. Here Pan and Tyson (*101*) proposed to use composite spectral lines created by combining real spectral lines in such a way as to integrate their characteristic behavior. Further Tognoni et al. (*102*) described the use of the ionic-to-atomic line intensity ratio from two test elements for the determination of the plasma temperature and the electron number density in the ICP as an alternative to the ionic-to-atomic line intensity ratio from the same element, as it is known for the MgII(280.270 nm)/MgI(285.213 nm) line pair. The approach is proposed as an effective diagnostic tool for the multielemental low temperature LTE in a plasma of unknown composition.

The alternative use of axial and radial viewing of the ICP was investigated in detail by several groups. Sengoku and Wagatsuma (*103*) compared the spectrochemical characteristics of various emission lines as viewed from the axial direction and the direction radial to the long axis of the plasma. It was stated that emission intensities from the axial direction were more affected by easily ionized elements whereas the radial direction leads to somewhat higher detection limits in general. This was supported by measurements of excitation temperatures, emission intensities, and measurements of the degrees of ionization. Grotti et al. (*104*) performed studies with the introduction of different amounts of wet aerosols as well as partially desolvated aerosols and dry vapors. Under robust conditions (1.5 kW and 0.7−0.8 L min^{-1} carrier gas flow), an increase of the water loading was found to improve the plasma excitation conditions whereas desolvation leads to its deterioration, which was the inverse under so-called nonrobust conditions. In the case of hydride generation, the introduction of the excess of hydrogen in both cases on the contrary was found to improve the excitation conditions. Griffiths et al. (*105*) proposed the application of piecewise direct standardization with variable selection to the correction of the drift in ICP-OES as a procedure to keep the workload involved with recalibration over a large dynamic range reasonable.

ICP-OES through its high multielement capacity and high power of detection is very powerful for the determination of the distribution of ecotoxicologically relevant elements such as Cd, Pb, Sb, etc. over the different sizes of size classified airborne particulate matter, as shown by Furuta et al. (*106*) in a long-term air pollution study in Tokyo. A further strong application line of ICP-OES is its use in process analytical chemistry and real-time environmental monitoring, as shown by Poole et al. (*107*) for the continuous analysis of emissions from a biofuel gasifier.

Microwave Plasma Atomic Spectrometry. Microwave induced plasmas (MIP) produced in a resonator or at the end of a coaxial conductor offer many possibilities as radiation sources for optical emission spectrometry of varying robustness and analytical performance in terms of power of detection and achievable freedom of interferences. One of the most powerful sources is the microwave plasma torch (MPT) operated with Ar or He at about 100 W. van der Mullen et al. (*108*) used single-shot Thomson scattering to reveal the nature of the discharge and concluded that the MPT discharge consists of tiny filaments which rotate on the mantle of a virtual cone and that the plasma is not diffusive in nature. Jankowska and Jackowska (*109*) performed measurements at a mixed Ar + He MIP and compared the spatial emission profiles and radial distributions of electron number densities with those of pure Ar and He plasmas. The mixed gases plasma was found to be able to excite lines with energies in the range of 6−10 eV more efficient than the Ar plasma, and the addition of He increased the excitation and rotation temperatures. At an addition of 20% of He, the line intensities for many metals were maximum. Matusiewicz et al. (*110*) investigated the use of various conventional pneumatic and micronebulizers together with the same cyclonic spray chamber for sample introduction into MIPs. The flow focusing pneumatic nebulizer was found to give slightly lower detection limits. Matusiewicz and Ślachciński (*111*) also could determine several volatile-hydrides forming (As, Bi, Ge, Sb, Se, and Sn) and nonhydride forming elements (Ca, Fe, Mg, Mn, and Zn) in sonicated slurries by MIP-OES using a dual-mode sample introduction system and could analyze environmental reference samples such as coal fly ash, lake sediments, sewage sludge, etc. MIP-OES is a very powerful tool for compound-independent calibration and partial molecular formula determinations when used for element-specific detection in gas chromatography, as shown by Juillet et al. (*112*) for organophosphorus and organosulfur warfare compounds.

Microplasmas. The use of smaller plasmas always has drawn the attention so as to obtain lower instrument and operation costs and to enhance field use potential and the setup of dedicated instrumentation. Efforts to realize a static ICP centered on ways for the introduction of wet aerosols, as described by Scheffer et al. (*113*). Here in a low-flow argon plasma (0.3−0.5 L min^{-1}) with cross-flow, Meinhard and low-flow PFA nebulizers mounted in a cyclonic spray chamber aerosols could be brought into the ICP and detection limits in the low microgram per liter range realized. Engelhard et al. (*114*) used infrared thermography to monitor the wall temperatures in the case of conventional and low-flow gas consumption ICPs and registered, after calibration of the system, temperatures at the 1500 and 700 K level for the low-flow ICP and the conventional ICP, respectively.

Miniaturized plasmas down to plasmas on a chip are a challenging field of research. Here, considerable advances have been made from the design of the according devices to their application for real sample analysis. This was shown in a review paper authored by Franzke and Miclea (*115*), who dealt with developments from low-pressure to atmospheric pressure plasma sources using dc, high-frequency, and microwave energy and especially the use of these plasmas as sources for atomic emission and atomic absorption spectrometry.

Hopwood et al. (*116*) described a microfabricated atmospheric-pressure microplasma source operated in air at several 100 MHz and used cell phone technology power supplies. Zhu et al. (*117*) used an atmospheric pressure dielectric barrier discharge plasma for the determination of Se, Sb, and Sn with atomic absorption spectrometry. They applied chemical hydride generation and obtained detection limits of 13, 0.6, and 10.6 μg L^{-1} for Sb, Se and Sn, respectively. Jiménez Zapata et al. (*118*) used argon and helium microstrip plasmas for the determination of Hg by optical emission spectrometry, and in the case of a plasma operated inside the discharge channel, one obtains a detection limit of 0.6 μg L^{-1} in the case of the argon plasma. Hg could reliably be determined in dissolved sewage sludge samples. Pohl et al. (*119*) also could determine As and Sb by hydride generation coupled to the microstrip microwave plasma operated inside the capillary channel in a sapphire wafer with detection limits of 18 and 31 μg L^{-1} for As and Sb, respectively. Also determinations in galvanic baths and dissolved coal fly ash samples could be performed. Karanassios et al. (*120*) described various planar-geometry, atmospheric-pressure, battery-operated microplasma devices and used an electrothermal, mini-in-torch vaporization dry sample-introduction system for them. Herewith down to 2 pg of K and 25 ng of Pb could be determined. For element-specific detection in gas chromatography, Miclea et al. (*121*) reviewed the possibilities of the different microplasmas described in the literature.

LASER-INDUCED BREAKDOWN SPECTROSCOPY

Laser-induced breakdown spectroscopy (LIBS), also referred to as laser-induced plasma spectroscopy (LIPS), has emerged in the recent years as a promising tool for spectrochemical elemental analysis of various types of materials. Because of significant advances in laser source and detector technology in the 1980s, considerable research effort demonstrated the potential of LIBS in a broad field of routine and specialized applications, including process control, environmental and waste monitoring, and geochemical analysis, which triggered the development of commercial LIBS technology. In this section, a brief overview on the recent developments and applications in the field of LIBS will be given.

An interesting review by Giakoumaki et al. (*122*) describes in brief the basic principles and technological aspects of LIBS and discusses several test cases that demonstrate the applicability and prospects of LIBS in the field of archeological science. A review of recent results obtained by double-pulse (DP) LIBS was presented by Babushok (*123*). This configuration was indeed suggested recently to overcome sensitivity limitations of the conventional single-pulse (SP) LIBS technique. An overview was given of the different DP-LIBS configurations (i.e., collinear, orthogonal prespark or preheating, and dual pulse crossed beam modes), as well as the combinations of laser pulses with different wavelengths, energies, and durations. The effect of interpulse delay time on different types of enhancements was discussed, and several suggestions have been proposed to explain the mechanism of DP enhancement.

The emission enhancement mechanisms in DP-LIBS was reviewd by Scaffidi et al. (*124*). It was mentioned that the enhancements are clear, but the mechanisms behind it are still not so well understood. There exist several explanations, depending on the interpulse delay time, such as an increased pulse-plasma coupling (reflected in the higher plasma temperature and electron densities), an increased sample heating, yielding more ablation, and ambient gas rarefaction.

De Giacomo et al. (*125*) have presented a review article and additional work (*126*) on the developments of LIBS under water, i.e., for the elemental analysis of aqueous solutions and submerged solid samples. The limitations of SP-LIBS were discussed, based on plasma emission spectroscopy observations, and the fundamental improvements obtained by means of DP-LIBS was reported, from both an experimental and theoretical point of view. Also a detailed description of laser−water interaction and laser-induced bubble formation was presented. Fang and Ahmad (*127*) have tested two sample presentation configurations for LIBS in aqueous media, namely, plasma excitation within water bulk and on the surface in a water jet for direct and quantitative comparison.

Spectral data recorded under optimum detection gating conditions showed that the signal-to-noise ratio (S/N) for excitation in the water jet configuration is approximately 10 times higher than that in the bulk excitation, the actual values of enhancement being dependent on the element type. It was found that for better sensitivity of detection, a simple water jet sample presentation configuration could be designed and implemented for cost-effective commercial use of this technique for elemental analysis in a water environment.

Another review paper by Sallé et al. (*128*) focused on recent results of stand-off LIBS analysis and applications. This is particularly interesting for the elemental analysis of materials located in environments where any physical access was not possible but optical access could be envisaged. A process optimization and control system has been developed by Hubmer et al. (*129*) that uses LIBS to quasi-continuously chemically analyze liquid high-alloy steel under pressure. The laser beam, located on safe ground, was guided by a mirror system to a process tuyere below bath level. Passing through an approximately 1.5 m long tuyere, the beam was then focused onto the steel bath. Light emitted from the induced plasma passed back through the tuyere, which was coupled to a fiber optic cable that carried the information over a distance of approximately 10 m back to an Echelle spectrometer located beside the laser. Harmon et al. (*130*) presented a concept of utilizing LIBS technology for landmine detection and discrimination using both laboratory LIBS and a prototype man-portable LIBS systems. LIBS spectra were collected for a suite of landmine casings, nonmine plastic materials, and "clutter-type" objects likely to be present in the soil of a (former) conflict area. Landmine casings examined included a broad selection of antipersonnel and antitank mines from different countries of manufacture. Other materials analyzed included rocks and soil, metal objects, cellulose materials, and different types of plastics. With the use of a linear correlation approach, "mine/no mine" determinations were correctly made for more than 90% of the samples in both tests. A similar test using a prototype man-portable LIBS system yielded an analogous result, validating the concept of using LIBS for landmine detection and discrimination. Statistical analysis of ambient air particle monitoring was suggested by Hettinger et al. (*131*, *132*) to elucidate the correlations between LIBS-based speciated aerosol monitoring and nonspeciated aerosol monitoring (i.e., total particle counts). LIBS was used in a real-time, conditional-processing mode to identify individual aerosol particles containing detectable quantities of either calcium or sodium, as based on the resulting atomic emission signals. With the use of this technique, real-time measurements of speciated aerosol particle concentrations and analyte mass concentrations were evaluated for a total of 60 1 h sampling periods. For aerosol particles in the 500 nm to 2.5 μm size range, significant correlations were found between the two sampling methods, resulting in correlation coefficients r^2 ranging from 0.22 to 0.93. In a fundamental study, Fichet et al. (*133*) investigated the ability of LIBS to analyze remotely complex aqueous solutions. The importance of parameters influencing the quantitative results of LIBS such as multispecies analysis, sheath gas, use of an internal standard, and temporal parameters for analysis was described, and the quantitative data were compared with results from ICP-OES measurements. The same group gave an insight into the potentials and the limitations of the DP-LIBS for analytical purpose so that the materials could be classified in terms of effectiveness of the double-pulse approach (*134*).

Balzer et al. suggested using LIBS as an online method of characterizing galvanized coatings on sheet steel moving through a production line (*135*). The traversing sheet steel was irradiated with a series of single laser bursts, each at a different position on the sheet steel. An ablation depth in the same range as the coating thickness (10 μm) was achieved by using a laser in collinear double-pulse mode. The coating thickness was determined from the ratio of the intensities of an Fe line and a Zn line measured at a burst energy high enough to penetrate the coating with a single burst. A temperature correction was applied, because the parameters of the plasma change with burst energy, and the influence of this on the thickness resolution was discussed. The ambient atmosphere present was found to have an influence on the thickness resolution. At optimum conditions, a depth resolution of better than 150 nm was obtained.

A comparative analysis of the discriminating power of LIBS and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS), each coupled with refractive index (RI) measurements, was presented by Bridge et al. (*136*) for a study of 23 samples of automobile float glass. Elemental emission intensity ratios (LIBS) and elemental concentration ratios (LA-ICPMS) and their associated confidence intervals were calculated for each float glass sample. The ratios and confidence intervals were used to determine the discrimination power of each analytical method. It was possible to discriminate 83% of the glass samples with 99% confidence based on LIBS spectra alone, and 96−99% of the samples could be discriminated based on LIBS spectra taken in conjunction with RI data at the same confidence level. LA-ICPMS data allowed for 100% discrimination of the samples without the need for RI data. The results provide evidence to support the use of LIBS combined with RI for forensic analysis of float glass in laboratories that do not have access to LA-ICPMS.

Yaroshchyk et al. (*137*) reported on the development of a model to simulate LIBS emission spectra and predict sample composition using a proposed calibration-free algorithm. The model uses a database of atomic emission lines to create a theoretical emission spectrum for selected elements using defined plasma parameters. The resulting theoretical spectrum was fitted to experimental data obtained from a LIBS instrument comprising of four compact spectrometers that image the plasma emission. Elemental concentrations were obtained by comparing observed and predicted spectra while varying the plasma temperature and relative elemental concentrations. The use of the model for analysis of major elements in bauxites, brass and mineral samples, as well as the analysis of laboratory air was demonstrated, and for the majority of elements investigated, agreement with certified values within 25% was achieved.

For studying the plumes obtained in the double pulse orthogonal LIBS in the preablation configuration, Cristoforetti et al. (*138*) used both spectroscopic and shadowgraphic approaches. Single and double pulse LIBS experiments were carried out on a brass sample in air. Both the distance of the air plasma from the target surface and the interpulse delay were varied, revealing a significant variation of the plasma emission and of the plume-shock wave dynamical expansion in different cases. The intensity of both atomic and ionized Zn lines was measured in all the cases, allowing the calculation of the spatially averaged temperature and electron density and an estimation of the ablated mass. The line intensities and the thermodynamic parameters obtained by the spectroscopic measurements were discussed bearing in mind the dynamical expansion characteristics obtained from the shadowgraphic approach. The authors concluded that, in agreement with a model, the line enhancement is mainly attributed to the ambient gas rarefaction produced by the first laser pulse, which causes a less effective shielding of the second laser pulse. Shaikh et al. (*139*) compared the Zn and Cd plasma parameters produced by LA. The excitation temperature has been determined from the Boltzmann plot method, whereas the electron number density was estimated from the Stark broadened profile of several spectral lines. Also the temporal evolution of the plasma has been investigated. The experiments were performed in air but also in He, Ne, and Ar atmosphere to study the effects of the ambient gas environment on the emission intensity of the atomic and ionic lines and on the plasma parameters. A spectral processing method toward calibration-free LIBS was described by Tognoni et al. (*140*) using a model based on LTE, homogeneous and optically thin plasma. A systematic study was made of errors and biasing factors affecting the calculations in calibration-free LIBS.

GLOW DISCHARGE OPTICAL EMISSION AND MASS SPECTROMETRY

Research activities on glow discharge optical emission and glow discharge mass spectrometry (GD-OES, GDMS) cover a wide range, including instrumental developments, fundamental studies for a better understanding, pulsed discharges, as well as novel GD sources for gaseous or liquid analysis. Jakubowski et al. (*141*) published an interesting perspective paper on these current trends in glow discharge spectroscopy. Moreover, some information was given in this paper on two new large EC projects on GD spectrometry, which both started in 2007, and which certainly give a new boost in GD research. In the following, a literature overview is given on the recent developments, in the fields of (i) fundamental studies, (ii) applications of the more mature techniques of GD-OES and GDMS, and (iii) new GD sources for more novel applications.

Fundamental Studies. A review of the fundamental studies that have been carried out for analytical glow discharges has recently been published by Bogaerts (*142*). A critical discussion is given on the various plasma diagnostics that can be used, illustrating their strong and weak points. The major part of the paper is, however, on numerical modeling techniques. An overview is given of the different possible modeling approaches, again with their advantages and disadvantages, to point out the advantages of hybrid modeling. Typical calculation results of the latter are illustrated, for direct current (dc), radio frequency (rf), and pulsed discharges. It is concluded that dc glow discharges are nowadays well described by numerical modeling. Radio frequency discharges are found to be more complicated to model, but the most important aspects of rf discharges are also correctly predicted. Finally, for pulsed discharges, some questions remain unanswered, mainly related to the so-called afterpeak behavior. Hence, this will need further attention in the future, both by modeling and experimental studies (see also below).

Finally, the general conclusion of this review paper was that the accuracy of the model predictions critically depends on the availability (or unavailability) of rate constant data used for the various plasma processes. For some processes, like asymmetric charge transfer between argon ions and sputtered metal atoms, the rate constants are simply not known. In ref 143 it was suggested that differences in asymmetric charge transfer rate coefficients for different elements might be responsible for variations in relative sensitivity factors (RSFs) in GDMS. Therefore, an attempt was made to calculate the rate coefficients for these elements, based on a semiclassical approach. The latter allowed to predict RSFs in reasonable agreement with experiment. The only weak point was, however, that an adjustment factor had to be applied for the charge transfer rate coefficients of Ar^+ ions with Fe and Cr atoms. Therefore, it would be interesting if these rate coefficients could be calculated more accurately by a quantum-mechanical approach and/or measured experimentally. The latter is in fact planned in the experimental program of the EC Marie Curie Research Training Network on Analytical Glow Discharges (GLADNET).

A more qualitative study on the importance of asymmetric charge transfer was carried out by Zhao and Horlick (*144*). They performed a spectral study of several ion emission lines in the GD, to reveal the unique and specific excitation pathways of various analyte ions. By comparison of the emission lines in different filler gases (Ar, Ne, He), the role of Penning ionization and asymmetric charge transfer could be identified. In a subsequent paper (*145*), Zhao and Horlick presented detailed spectra of Cu, Zn, Ag, and Cd atomic lines in a glow discharge. Many lines originating from highly excited atomic energy levels were observed, and it was suggested that ion−electron recombination, followed by stepwise de-excitation and radiative decay is a key mechanism in setting the spectral character of neutral atom emission in a glow discharge.

The latter process has also been the subject of fundamental research on pulsed discharges (for many years already). King and co-workers examined the energy transfer processes (excitation and ionization) at different locations within the afterpeak regime of a millisecond pulsed glow discharge, by means of a power perturbation method (*146*). Responses of several transitions to the power perturbations were measured via atomic emission and absorption spectroscopy. Although the enhancement of the large population of metastable Ar atoms is again confirmed, the mechanism responsible for this enhancement remains unclear. The most likely possibility involves some form of ion−electron recombination followed by radiative relaxation of the resulting species. The metastable Ar atoms subsequently ionize the sputtered Cu atoms by Penning ionization, and the latter undergo a similar electron−ion recombination process, yielding various degrees of observable afterpeak emission for Cu atom transitions. However, it was noted that the exact identity of the ion−electron recombination process remains unclear. The experiments also revealed valuable information regarding the kinetics of the plasma processes. More specifically, the electron thermalization time allowing for recombination with ions was found to be $\sim 25\ \mu s$ after the discharge power termination.

Detailed measurements inside the GD plasma of fundamental plasma quantities, such as the electron number density and temperature, are difficult to carry out because of the small dimensions of GD cells and possible disturbance of the plasma. Only the Hieftje group has dedicated instrumentation to perform such measurements, by means of Thomson and Rayleigh scattering. In ref 147, these techniques were applied by Gamez et al. to a millisecond-pulsed glow discharge to measure spatial and temporal profiles of the electron number density and temperature and the gas temperature. The electron number density and temperature were found to decline monotonically after pulse termination, but the maximum electron density in the afterglow shifts further away from the cathode. The latter is related to the argon metastable population, which exhibits the same behavior, and suggests that the electrons are produced in the afterglow by argon metastables. Nevertheless, the decreasing electron number densities upon pulse termination bring into question the significance of the Ar^+ ion−electron recombination mechanism as production process for the argon excited levels and the subsequent afterglow peaks in optical emission intensities.

The latter, so-called "afterglow mystery" is also discussed by Bogaerts in ref 148. Indeed, the widely accepted idea that electron−Ar^+ ion recombination is responsible for the afterpeaks in optical emission intensities could up to now not yet be confirmed quantitatively by numerical modeling, because of too low electron and Ar^+ ion number densities and recombination rate coefficients. Therefore, it is suggested in ref 148 that dissociative recombination between electrons and Ar_2^+ ions might be responsible for this afterpeak behavior. However, further experimental studies will be needed, e.g., on the densities of Ar_2^+ ions and the partition function over various vibrationally excited levels, as well as on other cluster ions, to validate these model predictions.

There have been some more fundamental studies on pulsed discharges, which illustrates the interest in this operation mode. Surmeian et al. (*149*) suggested that beside atomic metastables also ionic metastables play a role in ionization in the afterglow of pulsed hollow cathode discharges.

Martin et al. (*150*) coupled a microsecond-pulsed dc GD to a TOFMS and studied the effects of pulse parameters on mass spectra, craters shapes, and sputtering rates. By comparison with dc GDs, a strong reduction (3−6 times, depending on the matrix) of the sputtering process was observed for the pulsed mode. This is associated to the low average power available in each period. On the other hand, the high voltage reached in the pulse enhances the ion generation, allowing for a sensitivity increase (about 50-fold) compared with dc operation.

Voronov and Hoffmann (*151*) investigated a fast flow GD source for MS in both dc and pulsed mode. The dynamics of ions extracted from the discharge was measured, and the processes of sample sputtering, ionization, and transportation were investigated. It is demonstrated that most of the detected ions are generated in a secondary discharge behind the sampler orifice.

Finally, Nelis et al. (*152*) studied the excitation characteristics of pulsed rf GD-OES. Enhancements in the emission yields through rf-power pulsing were observed, which were attributed to a temporal reduction of the self-absorption. Furthermore, the possibility of analyzing heat-sensitive nonconductive materials and layers was demonstrated.

Regarding rf discharges, fundamental studies were focused on the electrical parameters (voltage, current, power). An extensive review on the electrical measurement techniques in rf-GD-OES was published by Wilken et al. (*153*). Indeed, it was argued that reproducible electrical measurements are important for accurate quantitative chemical measurements. The fundamentals of rf discharges and a plasma equivalent circuit describing the electrical behavior of rf discharges were presented. The benefit of a GD source with integrated voltage and current probes was demonstrated for the start-up phase of an rf discharge and for a microsecond-pulsed rf discharge. The dependence of sputtering rate and optical emission on rf discharge voltage and current was described, and the techniques to measure both thick and thin insulating layers with rf-GD-OES were discussed (*153*).

Nelis et al. (*154*) also reported on a new method for determining plasma power in rf-GD-OES, based on the effective resistance located in the inductive coil of the impedance matching. The new correction method is experimentally evaluated and compared with the integral plasma power calculation. Finally, the effect of applying the rf voltage to the back of the sample was investigated by Thérèse et al. (*155*). They reported an improved voltage transfer coefficient (which means the ratio between the peak voltage in front of the sample, i.e., facing the plasma, and the peak voltage applied to the back of the sample). Increasing this voltage transfer coefficient permits higher power deposition in the plasma.

There is also increasing interest for the effects of gas mixtures (and/or impurity gases) in Ar GDs, not only from application point of view, but certainly also for more fundamental reasons, to understand the underlying physical processes. Martin et al. (*156*) gave an overview of the effects produced by the presence of H_2 in an Ar (or Ne) GD, more specifically the influence on electrical current or dc bias voltage, on crater shapes and sputtering rates, as well as on the analytical signals measured by OES and MS. The authors have stressed the general increase of analyte ionization yields, achieved by the external addition of H_2 to the Ar plasma, a critical feature for GDMS applications. This was also reported by the same research group for the analysis of both conducting and insulating materials by rf-GDMS (*157*). On the other hand, the influence of hydrogen present in the sample matrix on measured GDMS signals has not yet been fully approached experimentally. Therefore, the authors foresee an important niche of basic research on this topic for further work (*156*).

A very interesting effect of H_2 addition on the optical emission intensities was reported by Steers et al. (*158*). Indeed, the authors have demonstrated that asymmetric charge transfer involving H^+ ions is a very important selective excitation mechanism for spectral lines with a total excitation energy close to 13.6 eV (i.e., the ionization potential of H). The magnitude of the effect varies for different elements and spectral lines, but in general, this study illustrates that ionic lines with a total excitation energy between 12.5 and 14 eV should be avoided if possible when selecting lines suitable for analytical use.

Beside effects of H_2 addition, which has been studied already for several years now, there is more recently also increasing interest in the effects of N_2 impurities. Sanz-Medel and co-workers (*159*) studied the effect of N_2 in the calibration curves of various emission lines in GD-OES. Also the molecular bands recorded in the spectra when N_2 is present were investigated, and the resulting interferences were determined.

Similarly, Tsukiji and Wagatsuma investigated the sputtering and emission characteristics of a He GD with N_2 additions (*160*). The authors observed an increase in sputtering rate upon addition of N_2, because the N_2^+ ions are much more efficient in sputtering than the He^+ ions. Also the analyte atomic emission lines were enhanced, but for the ionic lines a maximum was reached at a certain N_2 pressure. The latter behavior was explained because excitation of these lines is caused by He metastables and He^+ ions, and these species are quenched through collisions with N_2 molecules. The same group investigated also the sputtering and emission characteristics of a Ne−Ar mixed GD plasma (*161*). Again it was observed that the addition of small amounts of Ar to a Ne plasma increases the sputtering rate and consequently the emission intensities of analyte atomic lines. The ionic lines again showed a different behavior, which was explained because some lines were excited by charge transfer with Ne^+ ions whereas other lines by charge transfer with Ar^+ ions. Finally, it was found that the crater bottoms became more flat upon Ar addition, resulting in a better depth resolution.

To conclude this section on fundamental studies, an interesting new approach to calculate sputtering rates in glow discharges needs to be mentioned. This approach is based on a new crater volume evaluation method and was presented by Martin et al. (*162*). The crater volume was determined based on a computer software, which calculates the crater volume from a 2D profile. Excellent agreement was obtained with experimental crater volumes, obtained with an optical profilometer. This work is important for the accurate determination of sputtering rates, which is crucial for accurate quantification procedures where calibrations are based on the emission yields.

Applications of GD-OES and GDMS. GD-OES and GDMS are used already for many decades for the analysis of solid materials, for bulk and especially for depth profiling analysis. A major topic of research is the quantitative analysis and the corresponding calibration procedures, including correct description of matrix effects, for GD-OES. Weiss (*163*) published a review paper on the so-called standard model, which is a semiempirical calibration model describing the signal response in GD-OES. The assumptions of the model are discussed in detail, illustrating that this semiempirical model is, however, based on the real physical processes occurring in the plasma. Furthermore, the implementation of this model and practical use as a calibration model in analytical applications is also described. In ref 164, the same author has investigated deviations from this so-called standard model, such as matrix effects, in the analysis of Zn−Al−Cu alloys. Most observed deviations from the standard model can be explained by variations in the discharge gas ion densities, caused by asymmetric charge transfer reactions with the matrix element. It is shown which lines are free of matrix effects and suitable for highly accurate analysis of Zn−Al−Cu alloys by GD-OES and how to optimize the calibration model. A similar study was carried out by the same author in ref 165, where an explanation for the matrix effects encountered in the GD-OES spectrum of Zn was provided. More specifically, it was observed that the emission yields of Zn(II) lines are higher for Zn−Al alloys than for Zn−Cu alloys. This matrix effect is again explained by variations in the Ar ionization degree with the analyzed matrix. These variations are caused by asymmetric charge transfer for the Ar^+ ions with Cu and Zn, because the latter process is much more efficient with Zn than with Cu. It was concluded that matrix effects of this type probably also occur for other elements, and therefore, attention should be paid if ionic lines of such elements are used in analytical applications of GD-OES (*165*).

Bengtson and Nelis (*166*) have also described the evolution of the quantification procedures for compositional depth profiling in GD-OES, based on the constant emission yield concept, which have nowadays become routine work.

Because quantitative GD-OES of nitride and oxide materials is limited by the lack of certified standards containing known amounts of nitrogen and/or oxygen, Escobar Galindo et al. (*167*) have proposed an alternative method for nitrogen quantification, using as calibration samples a series of deposited nitride coatings whose compositions are pre-established by absolute quantitative measurements with Rutherford backscattering spectrometry. The authors conclude that this approach could enlarge the application of GD-OES to a wider range of practical applications. It should, however, be mentioned that a critical comment on this approach was recently published (in 2008) in *J. Anal. At. Spectrom.* by Hoffmann, doubting the elaborateness in this paper and the validity of the conclusions.

The same research group (*168*) also identified different factors determining the depth resolution of rf-GD-OES for thin and ultrathin multilayer coatings, such as the roughening induced during the sputtering, the resulting crater geometry, and sputtering of material redeposited on the crater wall. Nevertheless, the authors demonstrated the excellent capabilities of rf-GD-OES for compositional depth profiling of thin (i.e., down to the nanometer range) multilayer coatings. This nanometric resolution was also demonstrated for the GD-OES depth profiling of metal nitride multilayers (*169*). In order to discriminate and identify artifacts in the GD-OES depth profile due to the sputtering process, the authors verified the layered structures by Rutherford backscattering spectrometry and scanning electron microscopy. As a consequence of the crater shape, a linear degradation of the depth resolution with a depth approximately 40 nm μm^{-1} was observed. The ultimate GD-OES depth resolution at the near surface region was estimated to be of 4−6 nm (*169*).

Several other groups reported on GD-OES bulk analysis or depth profiling applications for a variety of different sample types. Stangle et al. (*170*) applied rf-GD-OES for the detection of C and H, as indicators for hydrocarbon impurities in thin electroplated Cu metallizations. Yasuhara et al. (*171*) compared dc and rf GD-OES for the rapid analysis of C in steel. The dc mode was observed to be more effective than the rf mode for the analysis of C, because higher sputtering rates could be obtained. However, for the rapid and high precision simultaneous multielements analysis, the rf mode appeared to give better results, by applying a bias current conduction as a preburn discharge. Baunack et al. (*172*) attempted the quantitative nitrogen analysis by GD-OES and Auger electron spectrometry for various nitride samples. In the case of a Cr−N sample, a nonlinear calibration curve was observed, probably caused by self-absorption of the Cr line. Schwaller et al. (*173*) applied pulsed GD-OES for the rapid depth profiling analysis of lead zirconate titanate (PZT) thin films. The surface roughness of coatings was measured using GD-OES depth profiling analysis by Biao and Meng (*174*). The principle of the method was explained in this paper, and an example of electrodeposited Zn coating on a Cu substrate was illustrated. A round robin exercise, organized by Hodoroaba et al. (*175*) , has been carried out for selected coated materials, with the aim of finding the optimal conditions for the analysis of nitride layers with GD-OES. This work is of interest for the production of nitride layers as certified reference materials.

Marcus and co-workers applied rf-GD-OES for the determination of particulate matter in a sol−gel matrix (*176*). Analytical blanks were obtained by use of an undoped sol−gel. Detection limits were found in the microgram per gram range, which corresponds to single-nanogram absolute detection limits. In another paper (*177*), they applied rf-GD-OES for the nonmetal element detection in organic analyte species (such as nucleic acids) immobilized in a sol−gel matrix. Absolute subnanogram detection limits were achieved for all the elements studied.

Sanz-Medel and co-workers have also been particularly active in applications of rf-GD-OES for various sample types. In ref 178, they applied rf-GD-OES for the direct analysis of the main components in glass samples. An internal standard calibration method was evaluated, using glasses of very different compositions and thickness. The concentrations of the oxides of the different elements were used instead of the elemental concentrations. The authors found good agreement with the certified values. In ref 179, the authors applied rf-GD-OES as an assessment tool in the control of cleaning processes developed to remove oil residues covering the surface of low alloy steels. Both qualitative and quantitative rf-GD-OES results have been used to control the carbon-based impurities present on the surface of the steel sheet. Furthermore, also the rf-GD-OES depth profiling analysis of arrays of Ni nanowires in nanoporous alumina and titania membranes (*180*), the (qualitative and quantitative) depth profiling analysis of thin films deposited on nonconducting glasses (*181*), and the rf-GD-OES quantification of bromine in flame-retardant coatings (*182*) have been reported by this research group.

Finally, a very interesting application of GD-OES was demonstrated by Webb, Hoffmann, and Hieftje (*183*). They applied GD-OES for mapping the elemental surface distributions, more specifically to image an inhomogeneity in the elemental distribution. An example was shown for a Cu inclusion in a Ni−Cr alloy. The spatial resolution was greatly improved compared to measurements with dc power by pulsing the glow discharge. Also the pulse frequency, pulse width, applied voltage, pressure, and gas flow appeared to have significant effect on the spatial resolution, which could be related to atomic transport in the glow discharge plasma. The authors suggest that this technique, in combination with gated detection, could be used to examine analyte transport in a glow discharge (*183*). The performance of this technique was also demonstrated for etched Cu circuits on fiber−glass substrates, as well as for nonconductive sample types, such as photographic film and glass (*184*). The capabilities for the 3D elemental analysis of proteins on blotting substrates are demonstrated. The present lateral resolution is only on the order of hundreds of micrometers, but the authors reported that this resolution can still be improved by instrumental modifications and by improving the discharge stability (*184*).

Beside GD-OES, which is being used for compositional depth profiling for many years, GDMS is also gaining increasing interest for this type of application in recent years. Nelis and Pallosi (*185*) reviewed the analytical capabilities of both GD-OES and GDMS for compositional depth profiling as a tool for surface and interface analysis. Some examples of applications from recent literature and from the authors' laboratories are presented, ranging from computer hard disks to molecular monolayers on Cu substrates, to illustrate the excellent depth resolution that can be achieved with GD spectrometry. Also Pisonero presented some examples of depth-profiling analysis of thin and ultrathin films using GDs in combination with either OES or MS (*186*, *187*). These examples show that there is an important niche of applications in surface analysis for GD spectrometry. A clear trend is the evolution from micrometer to subnanometer layers (*187*).

Hohl et al. (*188*) presented a new pulsed-rf GD-TOFMS system as a successful combination of a commercial high-end GD instrument and an extremely fast and high-resolution TOFMS system. The new instrument was applied to the fast surface and interface analysis of conductive and nonconductive materials.

A new quadrupole-based GDMS system was designed by Konarski et al. (*189*) , and preliminary results of the elemental analysis of steel and alloys were compared with results of SIMS. The GDMS results allowed one to find RSFs for SIMS for the analyzed materials. Quadrupole-based GDMS was also applied by Yu et al. for multielement determination of stainless steel (*190*). Mass interferences were investigated, and correction formulas were established.

The use of Ar_2^+ ions as the internal standard in GDMS was explored by Xing et al. (*191*). It was observed that the Ar internal standard and the matrix internal standard have the same corrective effect on sample analysis. The use of Ar as the internal standard proved to reduce the effect of differences in samples and fluctuations of discharge conditions on the analytical results. This method seems to yield satisfactory results when the matrix content is unknown.

Matschat et al. (*192*) also proposed a new approach for quantitative calibrations in GDMS, based on doping powders with varying concentrations of analytes. They exemplified the approach for the multielement ultratrace determination in ultrahigh-purity Cu and Ir samples. The same research group also reported on enhancements of intensities in GDMS by using mixtures of Ar and He as plasma gases (*193*). Indeed, it is known that elements with an ionization potential close to or higher than that of Ar, such as C, Cl, F, N, P, O, and S, are ionized with small efficiency only. With the use of Ar/He gas mixtures, these elements can be ionized by Penning ionization from the He metastable atoms, resulting in pronounced signal enhancements.

Finally, GDMS was also compared with other solid sampling techniques for particular types of samples. Betti et al. gave an overview of several mass spectrometric techniques, including GDMS, for the determination of transuranium elements (*194*), and Vanhaecke and co-workers compared three solid sampling techniques, i.e., LA-ICPMS, GDMS, and spark-OES, for the determination of Pt-group metals (*195*). They concluded that this working scheme allows for a reliable analysis.

New GD Sources for Novel Applications. In August 2007, a special issue on "New Plasma Discharges for Atomic Spectrometry" appeared in *Analytical and Bioanalytical Chemistry*, with Broekaert and Jakubowski as the guest editors. Indeed, whereas GD spectrometry used to be associated mainly with solid bulk and depth profiling analysis, in recent years there is undoubtedly an increasing interest for more novel applications for liquids and gaseous analysis. The latter is catalyzed by the development of new types of plasma sources, often working at atmospheric pressure and/or with reduced dimensions (so-called microplasmas). Indeed, miniaturizing discharges for atomic spectrometry leads to less expensive, smaller, and even portable instrumentation and allows them to be integrated more easily with separation instrumentation, such as chromatographs.

With respect to liquids analysis, the so-called electrolyte cathode atmospheric glow discharge (ELCAD) was developed several years ago by Mezei and Czerfalvi. In ref 196, the authors presented a review on this system, going back to its invention in 1992. The main operating parameters, mechanisms, and analytical performance were discussed in detail. It is shown that this optical emission source has upcoming applications in the field of environmental protection, as an outstanding instrument for monitoring the toxic heavy metal content of waters and wastewaters (*196*). A diagnostic study on a capillary ELCAD was performed in ref 197 by the same authors, by means of a CCD camera. The current density and the cathode dark space length were measured, and the gas temperature in the cathode surface−dark space boundary layer was estimated. The current density was found to be significantly higher than in a normal ELCAD glow, the cathode dark space length was smaller, and the gas temperature was higher, as a result of this higher current density.

In recent years, Hieftje and co-workers have adopted (and modified) this concept of the ELCAD. In ref 198, Webb et al. reported on the spectroscopic characterization of the ELCAD. With the use of the Stark broadening of the hydrogen β line, electron number densities were measured in the negative glow and the positive column of the discharge. The electron density was surprisingly insensitive to the electrical current, in contrast to the behavior found in low-pressure glow discharges. The relatively high electron number density suggests that calibration curves obtained using the source should not be subject to nonlinearities from concentration-dependent degrees of ionization. Also the ionization temperatures were determined from the relative strengths of Mg neutral and ionic lines, and the degrees of ionization were estimated. Calculations based on the degree of ionization and the excitation in the source show that the ELCAD provides a good compromise between ideal conditions for detection of easily and less easily ionized elements but that somewhat higher temperatures would give an even better compromise (*198*). In ref 199, the ELCAD was explored for the analysis of complex samples. Remedies to various interferences were proposed and evaluated. The response of the ELCAD to the various interferences provides insight into the possible mechanism, in which droplet formation and desolvation are both enhanced by the strong electric field of the cathode fall and in which the discharge temperature is altered. It is finally concluded that previous literature about interferences in flames serves as a useful preliminary guide to gauging similar effects in the ELCAD (*199*).

Recently, Webb et al. presented a new design of a solution-cathode GD (*200*). The liquid sample to be analyzed acts again as one of the electrodes, most typically the cathode. The present source has a smaller volume (approximately 2 mm^3) and a corresponding increase in power density, compared to the previous (ELCAD-like) source designs, such as refs 198 and 199. Consequently the detection limits are greatly improved, being now mostly in the subppb range. In ref 200, this miniaturized ELCAD was evaluated for elemental analysis of continuously sampled aqueous solutions. However, for some applications, transient analysis is desirable, such as for chromatographic separations, small-volume sampling, high-throughput sampling, and online preconcentration. Therefore, in ref 201, the miniaturized ELCAD was applied for transient analysis, illustrating two benefits of this approach, i.e., high-throughput analysis and small volume sampling.

Finally, another type of a small scale plasma, maintained in atmospheric pressure He, between a tubular cathode and a rod-shaped anode, i.e., the so-called annual GD, was also developed by Webb et al. (*202*). An aerosol is introduced in the plasma through the cathode, and atomic emission is observed in the near-cathode region. The effects of solvent addition on the plasma were investigated in terms of its electrical and spectroscopic characteristics. Although the discharge is affected by the presence of an aerosol, the authors report that it still remains stable even with significant solvent loading (*202*).

Marcus and co-workers were also particularly active in the field of liquid sampling for GD sources. In ref 203, they determined the susceptibility of a liquid sampling-atmospheric pressure glow discharge (LS-APGD) atomic emission source to easily ionizable element effects. The voltage drop across the plasma was monitored as a function of the pH to ascertain whether or not the conductivity of the liquid eluent alters the plasma energetics and subsequently the analyte signal strength. It was found that altering the pH (from 0 to 2) in the sample matrix did not significantly change the discharge voltage. On the basis of emission signal intensities of atomic and ionic lines it was concluded that the easily ionized elements in the matrix did not affect the plasma energetics to a large extent. This was explained by the electrolytic nature of the eluent, acting as an ionic (and perhaps spectrochemical) buffer.

In ref 204, Marcus and co-workers presented a review paper on the use of the particle beam (PB) sample introduction system for liquid samples into GD plasmas. Emphasis was put on the coupling of the PB interface with liquid chromatography (LC). Some fundamental aspects of the PB system, such as solvent removal and analyte delivery, were highlighted. The combination of PB with hollow cathode optical emission spectrometry (PB/HC-OES) and with GDMS (PB/GDMS) was discussed, in terms of their potential for speciation analysis of organic compounds, organometallics, and small biomolecules (*204*). The abilities of LC-PB/HC-OES as well as LC-ICP-OES for the quantitative determination of free iron and bound iron in metalloproteins was further demonstrated in refs 205 and 206. Both techniques showed detection limits on the nanogram level. Parametric optimization of sample introduction, nebulization, and HC source conditions was carried out for the PB/HC-OES system in ref 206. In addition, in ref 205, a reversed-phase separation of the same analyte mixture was carried out by PB/HC-OES, demonstrating the compatibility of PB/HC-OES with a wide range of solvent polarities and its ability to detect nonmetals and act as a protein specific detector for liquid chromatography of proteins. Finally, in ref 207, an LC-PB/MS system with interchangeable electron impact and GD ionization sources was evaluated for the application in analysis of botanical extracts. The approach was illustrated for the analysis of green tea tincture.

For gaseous analysis, Hieftje and co-workers reported on a novel, versatile dc atmospheric pressure GD (APGD) in He, interfaced with a TOFMS system (*208*). A very stable APGD could be maintained between a rod-shaped cathode and anode, separated by 1 cm distance. The anode was characterized by a conical end, which appeared to be essential to stabilize the discharge in the high-pressure regime. This APGD was further characterized in ref 209 by means of electrical and spectroscopic measurements. The diffuse and extremely stable discharge is typically operated within a voltage range of 300−900 V and at currents ranging over tens to hundreds of milliamperes. It could be deduced from the presence of He^+ ions in the MS that a significant amount of energy is available for the ionization of gaseous analyte species. When this detection system is coupled with hydride generation, the analytical performance of the hydride generation APGD is comparable to that of an ICP source. Detection down to 10 ppt could be realized (*208*).

An atmospheric pressure GD, with two glass plates (dielectrics) covering the electrodes, commonly called dielectric barrier discharge (DBD) was applied by Zhu et al. (*210*) for the determination of Se, Sb, and Sn with atomic absorption spectrometry. The elements were first converted to volatile hydrides through the reaction with $NaBH_4$. Subsequently, the hydrides were atomized in the DBD and detected with AAS. Compared with other hydride atomization methods, the proposed atomizer shows (i) smaller size, which is preferable for the miniaturization of the total analytical system, (ii) lower temperature, and (iii) low power consumption, which would be helpful for further improvements in the compactness of the system. The paper shows that this approach is a promising technique for hydride detection. In ref 211, the same technique was applied to arsenic speciation with AAS.

A DBD in He, used as a microchip plasma source for analytical spectrometry, was also studied theoretically by Martens et al. (*212*, *213*). Typical calculation results, obtained with a fluid model, include the potential distribution inside the plasma and across the dielectrics, the electrical current and gap voltage as a function of time, the spatial and temporal number density profiles of the different plasma species, and the relative role of their production and loss mechanisms (*212*). The effect of the gas pressure on the calculated plasma species densities and reaction rates was investigated in the range between 25 mbar and 1.1 bar (*214*). It was found that the plasma activity, expressed in terms of discharge current and species densities, is remarkably higher in the range between 50 and 140 mbar. This is in good agreement with the typical operation conditions (between 10 and 180 mbar) used in experiments (*213*).

Some other researchers also reported on the analysis of gases or vapors by GD spectrometry. Newman and Mason (*214*) introduced organic vapors into the flowing afterglow of a low power dc GD coupled to a quadrupole mass spectrometer. With dependence on whether a positive or a negative bias was applied to the ion sampling orifice, either molecular mass spectra or fragmentation of the analyte was observed. The authors conclude that the fast flowing (FF) GDMS technique, when combined with chromatographic separation, could be used for chemical speciation studies at the subpicogram level. Moreover, Fliegel et al. (*215*) evaluated the use of a pulsed GD-TOFMS system as a detector for gas chromatography analysis. It was found that varying the GD source parameters, such as capillary distance, cathode−anode spacing, and gas pressure, had a severe influence on the ratio of elemental, structural, and parent molecular information in chemical speciation analysis (*215*).

Finally, a last paper which the authors would like to mention here, although it has nothing to do with solution or gaseous analysis, is the combination of laser induced plasma spectrometry (LIPS) with a GD, presented by Laserna and co-workers (*216*), as it can also be seen as a novel spectroscopic source. The authors reported that the dual GD-LIPS scheme provides significant enhancements (up to 75×) compared to LIPS or GD under identical conditions. All the material ablated by the laser appears to be efficiently excited. Furthermore, it is suggested that it is possible to lower the laser energies needed for the excitation/ionization thresholds of materials to those required solely for ablation of the sample, thus creating the possibility of improving lateral and depth resolutions in the spatial characterization of material (*216*).

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

The increasing demand for high sample throughput in routine analysis and the need for highest possible sensitivity and precision combined with fast and preferably simultaneous multielemental detection capabilities are still the driving forces for developments in the field of elemental mass spectrometry. Remaining ionization source- and spectrometer-related shortcomings are the major subjects of modern research. As a result, different mass spectrometric techniques in combination with various sample introduction techniques as well as instrumental developments concerning multicollector, sector field, and time-of-flight mass analyzers were predominant focal points of the research conducted within the period covered by this review article, although most of the published material mainly deals with applications of inductively coupled plasma mass spectrometry (ICPMS). Different approaches for the introduction of liquids, through sample nebulization or in combination with chromatographic and electrophoretic separation techniques, were investigated. Most notably, the acceptance of laser ablation (LA) coupled to ICPMS as a technique for direct analysis of solid samples has continued to increase substantially during the last 2 years. Furthermore, an ongoing activity on the development and application of collision and reaction cells for the specific removal or reduction of polyatomic ions was recognized, especially in the field of the analysis of biological material and environmental samples.

This chapter deals with new developments in ICPMS in the field of fundamental studies, instrumental developments, and applications that have been reported since the last update (*3*). It should be mentioned that the selection of representative or significant papers was quite difficult, due to the increasing number of ICPMS publications. Therefore, only new applications, using new methodology, will be dealt with, since papers exclusively dealing with application of ICPMS 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*, *Rapid Communications in Mass Spectrometry*, *International Journal of Mass Spectrometry*, and *TRAC, Trends in Analytical Chemistry*.

In an interesting review paper, Ammann (*217*) discussed some of the relevant technologies that have been or could be applied to mass spectrometric ion detection. The principles and advantages of ICPMS were stressed by giving examples from recently published investigations in diverse research fields such as earth, environmental, life, and forensic sciences and in food, material, chemical, semiconductor, and nuclear industries. Outstanding properties such as high sensitivity (ppt−ppq), relative salt tolerance, compound-independent element response, and highest quantitation accuracy lead to the unchallenged performance of ICPMS in efficiently detecting, identifying, and reliably quantifying trace elements. The increasing availability of relevant reference compounds and high separation selectivity extend the molecular identification capability of ICPMS hyphenated to species-specific separation techniques. In a monograph titled “Inorganic Mass Spectrometry: Principles and Applications” (*218*) published in 2007, Becker gives an insight into state-of-the-art mass spectrometry by highlighting various challenging tasks and recent developments. The book is concerned with the theoretical and experimental conditions of different types of mass spectrometers and gives an overview of new methodological developments and trends for analytical work and modern applications, especially in survey, (ultra)trace, surface, and isotope analysis, thus providing students and scientists interested in the field of analytical chemistry with basic knowledge of inorganic mass spectrometry.

In the field of ICPMS using a dynamic reaction cell (ICP-DRC-MS) to overcome isobaric overlaps, Bandura et al. (*219*) presented a thorough overview on results for the separations of such overlaps via cation reactions. Ion−molecule reactions that can be used for resolution of spectral overlaps of long-lived or stable atomic isobars on the long-lived radioisotopes in MS were considered, and an overview of potential and reported reactions for separation of 35 isobars was given. The effect of instrumental parameters on reactivity as well as the relevance of this work to accelerator mass spectrometry was discussed. In mass spectrometry, several advantages can be derived when multiple mass-to-charge values are detected simultaneously and continuously. One such advantage is an improved duty cycle, which leads to superior limits of detection, better precision, shorter analysis times, and reduced sample sizes. A second advantage is the ability to reduce correlated noise by taking the ratio of two or more simultaneously collected signals, enabling greatly enhanced isotope ratio data. A final advantage is the elimination of spectral skew, leading to more accurate transient signal analysis. To achieve simultaneous acquisition of a range of mass-to-charge ratios, Hieftje and co-workers (*220*, *221*) coupled a second-generation Faraday-strip array detector to an ICP Mattauch−Herzog geometry mass spectrograph. This device incorporates narrower, more closely spaced collectors than the earlier system. Furthermore, the new camera can acquire signal on all collectors at a frequency greater than 2 kHz and has the ability to independently adjust the gain level of each collector, allowing one to obtain limits of detection of about 0.01 pg L^{-1} for metals in solution. Some additional features, such as a broader linear dynamic range, greater resolving power, and improved isotope ratio accuracy were attained. In addition, isotope ratio precision as low as 0.018% RSD was achieved.

Fundamental Studies. Scheffer et al. (*222*) described the use of a novel static high sensitivity inductively coupled plasma (SHIP) for inorganic MS, which is based on a similar torch design previously described by Busher et al. (*223*). The SHIP-torch, including the external air cooling system, was modified in order to allow its application as an ion source in a conventional ICP mass spectrometer. While the torch geometry was adjusted for its use in connection with the sampling interface, the principal shape of the torch remained the same as in the recently developed SHIP-OES system. The plasma discharge was operated at 0.65 kW rf power with a total plasma gas flow rate of 1.95 L min^{-1} and the mass spectrum was investigated. Limits of detection for aqueous samples were presented and compared to those achieved with the conventional ICPMS setting. A fundamental study on the analytical characteristics of a 27.12 MHz and a 40.68 MHz time-of-flight ICPMS were evaluated by McClenathan et al. (*224*) under both hot and cool plasma conditions. The study was both direct and unambiguous because the same power supply, impedance-matching unit, load coil, and ICP torch were used at both operating frequencies. Although the authors reported on significant differences in the figures of merit between hot and cool plasma conditions, the performances at 27 and 40 MHz were comparable. Under hot plasma conditions, measured ion energies and the plasma offset potential were nearly independent of the generator frequency. Higher ion energies and a greater plasma offset potential were apparent at 27 MHz under cold plasma conditions than at 40 MHz; however, this result may be an artifact of the difference in the optimal nebulizer flow rate rather than of frequency. Experimentally determined gas-kinetic and ionization temperatures did not demonstrate a significant frequency dependence.

Warburton and Goenaga-Infante (*225*) described the possibility to improve the power of detection for Se in speciation analysis of food-type samples by ICPMS down to low nanogram per kilogram (0.35 and 0.49) for selenate and selenomethionine, respectively. The effect of carbon load to the ICP was thoroughly investigated. The addition of methane gas yielded an improvement in sensitivity by approximately a factor of 9, in comparison with the conventional Ar plasma. Moreover, the combined addition of 2% of methanol to the anion-exchange HPLC mobile phase and methane gas resulted in a 11-fold sensitivity enhancement of Se ICPMS detection.

In a fundamental study on aerosol transport processes, Holcombe and Ertas (*17*) developed Monte Carlo simulations to elucidate the time and spatial distribution of analyte during the transport from an electrothermal vaporizer (ETV) to ICP. A time-of-flight ICPMS was employed to collect experimental data that was compared with the simulated transient signals. Consideration was given to analyte transport as gaseous species as well as aerosol particles. In the case of aerosols, the simulation assumed formation of 5 nm particles and used the Einstein−Stokes equation to estimate the aerosol's diffusion coefficient, which was approximately 1% of the value for free atom diffusion. Desorption conditions for Cu that had been previously elucidated for electrothermal atomic absorption spectrometry were employed for the release processes from the ETV. The primary distinguishing feature in the output signal to differentiate between gas and aerosol transport was found to be a pronounced, long-lived signal after the transient peak if aerosols were transported. Time and spatial distributions of particles within the transport system were presented.

In the case of liquid sample nebulization, various groups focused on the comparison, optimization, and development of alternative nebulizer systems. Brennan et al. (*226*) described the use of a demountable direct injection high efficiency nebulizer as an interface to couple nano-HPLC with ICPMS, to reduce sample and mobile phase consumption, minimize organic waste generation, decrease analysis time, and enhance separation efficiency. A HPLC column (50 mm × 0.3 mm i.d.), packed with 3.5 μm C-18 material, was explored for chromatographic separation of five As species. A fast chromatographic separation of theses species was achieved in less than 12 min at a solution flow rate of 0.9 μL min^{-1} using a 50 nL sample injection. The HPLC-ICPMS interface was found to provide well defined flow injection profiles at various concentrations, giving a correlation coefficient of 0.999 for each individual As species calibration curve. Precision values for peak height and area ranged from 0.5 to 6.5% RSD, and absolute detection limits were within 0.4 to 5.4 pg of As, comparable to previously reported data at higher solution uptake rates and larger sample injection volumes. A novel nebulizer (nDS-200) working at sample uptake rates of less than 500 nL min^{-1} for a sheathless interfacing of nano-HPLC with ICPMS was developed by Giusti et al. (*227*). This nebulizer is based on a hollow fused-silica needle of which the tip (i.d. 10 μm, o.d. 20 μm) centered in a 254 μm i.d. sapphire orifice. The system, equipped with a 3 cm^3 drain-free vaporization chamber, enabled a stable introduction into an ICP of aqueous mobile phases containing up to 95% acetonitrile at eluent flow rates between 50 and 450 nL min^{-1}. The low dead volume of the interface resulted in a peak width of 1.3 s (at half-height) and the entirely preserved chromatographic resolution. Goitom and Bjorn (*228*) characterized noise and precision of ion count rate measurements for ICPMS using a Vulkan direct injection nebulizer (Vulkan DIN) for sample introduction. For comparison, experiments were also carried out using a DIHEN. The Vulkan DIN was found to give considerably higher relative white noise compared with the DIHEN (−40.3 and −45.8 dB), caused by a broader size distribution and larger mean size of droplets for the Vulkan DIN. Compared with the DIHEN, interference noise from a peristaltic pump was very small with the Vulkan DIN because at the liquid flow rate giving maximum sensitivity, the analyte signal intensity was not much affected by changes in the liquid flow rate. Although this had a positive effect on precision, the authors concluded that the plasma is cooled by large droplets that do not positively contribute to the analyte signal intensity. For analytical precision data, it was evident that with the Vulkan DIN, precision was limited by the high white noise in the frequency range 0.4−500 Hz, but for the DIHEN there were relatively large contributions from $1/f$ and/or interference noise to the observed precision. When integration times of 1000 ms or longer were used, the DIHEN appeared to give slightly better precision for most of the isotopes tested.

The fundamental parameters of an ICP in the sampler/skimmer MS-interface region were measured by different groups, using various spectrometric approaches. Gamez et al. (*229*, *230*) used Thomson and Rayleigh scattering to study interface-related changes in electron number density, electron temperature, and gas-kinetic temperature (T_g) upstream from the mass spectrometer sampler, while the central-gas flow rate, the MS interface sampling depth, and the applied rf power were varied. T_g was found to decline at greater central-gas flow rates, an effect that was elevated in the presence of the MS interface. As the MS interface was brought closer to the ICP load coil, decreases in upstream plasma T_g ensued. Overall, changes in the upstream fundamental parameters caused by the presence of the MS interface were found to depend on operating conditions, such as applied rf power and the pressure at the back of the sampling interface. Furthermore, the changes caused by matrix interferents were found to be different in the presence and in the absence of the interface. The effects of collisions on the composition of the plasma passing through the vacuum stage of an ICPMS were monitored by Farnsworth and co-workers in different sets of experiments (*231*–*233*). For example, rates of collisional quenching of an excited state in the neutral calcium atom were estimated from changes in experimental fluorescence lifetimes. Intensities from collisionally assisted fluorescence provided evidence of energy transfer between excited states. Changes in analyte number density along the axis of the supersonic expansion in the first vacuum stage provided evidence that ion−electron recombination occurs to a significant extent during the expansion. In the authors' opinions, the results create a picture of the vacuum interface region in which collisions play an important role in shaping the composition of the plasma that is ultimately delivered to the mass analyzer. The same group investigated the density distribution of ground-state Ba atoms, ground-state Ba ions, and excited-state Ba ions in the region between the load coil and the sampling cone of an ICPMS by using planar laser-induced fluorescence (*234*). The effects of power, nebulizer gas flow rate, and the addition of Li to the sample were studied. The maps revealed that the radial distributions of atomic species across the diameter of the plasma are compressed as the plasma is drawn into the sampling orifice and that as a result of that compression, the distribution of ions across the diameter of the sampling orifice is nonuniform. The distribution changes as conditions in the plasma change, and it was found that the overall efficiency with which ions are transmitted through the vacuum interface varies as conditions in the plasma change. The distribution of elemental ions in the plasma of an ICPMS was investigated by Wang et al. (*235*) using laser ablation (LA) for sampling of silicate materials, while scanning the ICP vertically across the sampler orifice of the MS at four different sampling depths. The distributions were found to, e.g., show a wider radial spread for all ions when He was used as the carrier gas instead of Ar and when the fraction of large particles in the aerosol was small, which is a result of faster vaporization of the aerosol and higher mobility of vapor and ions when He was present in the central channel of the ICP. This caused the axial distribution to become smaller because the ions distributed over the ICP more rapidly. Mass dependencies were pronounced in the radial profiles, especially at short sampling depth and for incompletely vaporized aerosols. Lighter ions showed generally a wider radial spread, in accordance to their greater mobility, while the axial profiles showed no pronounced dependency on mass.

Ferguson and Houk (*236*) as well as Hieftje and co-workers (*237*, *238*) provided information about the origins of polyatomic background ions in ICPMS, often necessitating the use of high-resolution instruments, and indicated possible locations for their formation and strategies for their removal. Methods for making accurate mass measurements and correcting for mass bias were discussed (*236*). The effects of sampler and skimmer cone composition and extraction voltage on polyatomic ion formation were explored too. The authors estimated neutral species densities at several locations in the extraction interface, and the corresponding effects of the kinetic gas temperature were calculated. A new method for reducing oxide interferences in ICPMS utilizes careful manipulation of the central-channel gas flow to impart distinguishable frequency-specific behavior to analyte and oxide species (*237*). Subsequently, application of a Fourier transform permits contributions from the analyte and oxide superimposed at a given mass to be unraveled. The authors reported on the elimination of a greater than 10-fold error at m/z 156 caused by the interference of $^{140}Ce^{16}O^+$ on $^{156}Gd^+$ through application of this correction method, which was shown to be well suited for overcoming multiple analyte−oxide interferences in a simultaneous manner. Although the authors utilized a time-of-flight mass analyzer, this correction method is in the authors' opinions well suited also for implementation with scan-based systems. Additionally, a mathematical correlation between an interference-compromised analyte response and an internal standard may be used to efficiently eliminate errors from troublesome interferences, allowing one to address multiple analyte−oxide interferences without sacrificing analyte sensitivity (*238*).

Accurate calibration in LA-ICPMS still is a difficult task, since it is hampered by elemental fractionation and the lack of available standard reference materials. Kuhn and Günther (*239*) presented a quantification strategy based on simultaneous measurements of LA-ICPMS signal intensities and aerosol particle size distributions. Together with the bulk density of the sample ablated, this allowed assessment of the relative mass of the particles introduced into the ICPMS. This mass was reduced by the particles larger than the ionization size limit of the ICP and was used to correct for variations in sample ablation and aerosol transport, allowing nonmatrix-matched calibration without using an internal standard element. A constant fraction of the aerosol (1%) was separated and diluted, and particle size distributions were measured by light scattering measurements in the diluted aerosol using an optical particle counter, while the remaining part of the aerosol (99%) was used for ICPMS measurements. Results using an external standard showed deviations of less than 10% compared with internal standardization for various sample matrixes. Pickhardt et al. (*240*) proposed an online solution-based calibration technique for LA-ICPMS by the insertion of a microflow nebulizer into the ablation chamber. This arrangement was found to allow an easy, accurate, and precise quantification by online isotope dilution using a defined standard solution with an isotope enriched tracer nebulized to the laser-ablated sample material. The figures of merit of this arrangement and applications of online isotope dilution in LA-ICPMS were presented.

Instrumental Developments and Applications. Trace elemental speciation in complex, real-world matrixes is a daunting task because of the low concentration of metals/metalloids and the correspondingly high molecular chemical noise. Sacks et al. (*241*) developed a HPLC parallel elemental and molecular mass spectrometry (PEMMS) system and evaluated the use of peak elution profiles to identify trace molecular species containing specific heteroatoms, in the case of Se in yeast. Elemental peak profiles were used to identify candidate ions with matching peak profiles in the molecular MS data. Proof of principle was demonstrated by C-18 separation of three Se-amino acid standards. Retention time and peak width were found to correlate well between the two MS systems, and correction factors for differences in flow path length and peak broadening were required. The normalized correction factors were species and concentration independent and were stable from run to run. Overall, the authors demonstrated that correlated information in peak shape between parallel detectors can facilitate detection of trace elemental species in complex matrixes. Stefanka et al. (*242*) reported on stepwise downscaling of narrowbore HPLC to capillary HPLC employing 2.1, 1, and 0.32 mm i.d. separation columns. Provided that each column was operated at optimum chromatographic conditions and provided that the system connection was optimal, the authors succeeded to investigate the influence of different HPLC-ICPMS interfaces on extra column dispersion. Several pneumatic nebulizers were tested, and it was shown that the contribution to extra column dispersion is minimal for the DIHEN interface. As a major advantage, most of the microbore and capillary hyphenations were not prone to signal suppression due to organic solvents. The 1 mm i.d. microbore setup employing flow rates of 60 μL min^{-1} was presented as the best compromise in terms of sensitivity, peak dispersion, resolution, peak asymmetry, and compatibility with organic solvent. Bouyssiere et al. (*243*) modified and optimized a total consumption micronebulizer working at a flow rate of 30 μL min^{-1} and fitted with a singlepass spray chamber for the determination of Hg in gas condensates by high-throughput flow-injection ICPMS. This low flow rate and the addition of 70 mL min^{-1} O_2 assured the plasma stability and reduced the carbon buildup on the interface and on ion lenses. A limit of detection of 0.5 ng g^{-1} was obtained owing to the reduction of dead volume and sample dispersion in the liquid pass of the nebulizer. A sample introduction system specifically designed for interfacing laboratory-on-a-chip devices with ICPMS was introduced by Pearson and Greenway (*244*). This system uses a microcross-flow nebulizer (MCFN) sited directly at the liquid exit of the chip. An evaporation chamber has been incorporated into the interface, allowing the entire sample aerosol to enter the plasma. The optimized system achieved a sensitivity of 13 500 cps for 10 μg L^{-1} In at 5 μL min^{-1}, allowing the analysis of sample volumes as low as 440 nL. The stability of the sample introduction over 10 min was 2.6%, and no sample recondensation was observed in the evaporation chamber at flow rates up to 20 μL min^{-1}.

For assessing metal mobilities and geochemical associations in soil compartments, a continuous-flow system comprising a novel, custom-built extraction module hyphenated to ICPMS was proposed by Buanuam et al. (*245*) using a three step BCR sequential extraction scheme. Alternate directional flows of the extractants were used to overcome compression of the solid particles within the extraction unit to ensure a steady partitioning flow rate and thus to maintain constant operationally defined extraction conditions. The proposed flow setup was proven to allow handling of soil samples up to 1 g and flow rates up to 10 mL min^{-1}. The method was found to be suitable for online monitoring of major and trace elements released when applying the various extracting reagents as addressed in the BCR scheme. As a result of the enhanced temporal resolution of the ongoing extraction, insights into the breaking down of phases and into the kinetics of the metal release were obtained.

Nakazato and Tao (*246*) and Sun et al. (*247*) reported on the development of photooxidation reactors in combination with hydride generation (HG) ICPMS for speciation analysis. The HPLC postcolumn reactor (*246*) revealed remarkably high efficiency for organic arsenicals and urinary As species after ion-exchange chromatography (*247*). The photocatalytic oxidation efficiency of the analyte species was optimized, and a rapid online prereduction process for converting the oxidized species into As(III) prior to HG-ICPMS determination was developed. Under the optimized conditions for the nano-TiO_2-catalyzed photooxidation, monomethylarsenoic acid and dimethylarseinic acid can be converted quantitatively into As(V). To attain maximal hydride generation efficiency, 0.5% $Na_2S_2O_4$ solution was added as a prereductant prior to performing the HG step (*247*). Because of the absence of broadening and dilution of the LC-separated peaks caused by mixing with the oxidant solution (*246*), the detection limits for 10 As species ranged from 2.3 to 18 ng L^{-1} of As, which were about $^1/_{10}$th as low as those by HPLC-ICPMS. The proposed method revealed, for the first time, the occurrence of 20 As species, including unknown trace species, which were formerly not detected through HPLC-ICPMS and HPLC-HG-ICPMS in human urine.

Through the simultaneous introduction of an aerosol from a nebulizer and vapor formed by $NaBH_4$ reaction, Asfaw and Wibetoe (*248*) performed simultaneous ICPMS determination of As, Bi, Cd, Co, Cu, Ni, Pb, Sb, and Zn. Effects of HNO_3, $NaBH_4$, and thiourea plus flow rates of sample and $NaBH_4$ were evaluated, and the most significant of the parameters were optimized. The factors of sensitivity increase for As, Bi, and Sb were 77, 33, and 56, respectively, compared to pneumatic nebulization. For the other elements (Cd, Co, Cu, Ni, and Zn), that are also known to react with $NaBH_4$ forming volatile species, no significant change in sensitivity was observed. The limits of detection obtained for As, Bi, and Sb using dual mode sample introduction were 7, 15, and 10 pg mL^{-1}, respectively. Similarly, Colon et al. (*249*) investigated the possibility to determine reduced sulfur species at the microgram per liter level through H_2S vapor formation after reaction with HCl in a commercial vapor generator coupled to ICPMS equipped with a reaction cell, thus avoiding polyatomic isobaric interferences at m/z 32 caused by $^{16}O_2{}^+$ and $^{14}N^{18}O^+$ through the elimination of the aqueous matrix. The new method was evaluated by comparison to the standard potentiometric method and was applied to the analysis of reduced sulfur species in natural waters and acid volatile sulfides in sea sediments.

An interesting application of solid sampling ETV-ICPMS was presented by Vanhaecke and co-workers (*250*) for the direct multielemental analysis of two different perfluorosulfonic acid/TFE copolymer samples, which were selected in order to test the potential of this technique for routine control of fluorocarbon polymers. Careful selection of the most suitable isotopes permitted the reliable monitoring of the analytes of interest: Cr, Cu, Fe, K, Mn, Pb, and Zn. The use of Pd as a chemical modifier allowed stabilization of all of these analytes during the pyrolysis step, enabling adequate matrix removal, while the use of a high vaporization temperature was required for the efficient simultaneous vaporization of these elements. The $^{105}Pd^+$ signal was used as an internal standard, correcting for possible sensitivity drifts. A straightforward calibration with aqueous standard solutions was feasible for all of the elements investigated. Detection limits in the nanogram per gram range and precision values usually in the 7−12% range were achieved for most elements combined with the absence of any sample pretreatment, with the subsequent lower risk of analyte losses or contamination. The method was found to offer a promising alternative for the laborious procedures currently in use for analysis of such complex samples. Goltz et al. (*251*) used ETV-ICPMS for the analysis of inorganic pigments in paint, which were sampled using a dry cotton bud that was contacted lightly with the surface of painted objects to remove <1 μg of sample material followed by pigment extraction from the cotton with concentrated HNO_3. The application of both GFAAS and ICPMS was described for determining the identity of the metals in different pigments of two cultural objects, which had darkened over time. Raman spectroscopy was used for confirming the identity of a darkened red pigment as Pb_3O_4. In an interesting radiotracer study, Peschel at al (*252*). used neutron-activated Al_2O_3 powder containing the γ-radiation emitting radionuclides ^{51}Cr, ^{59}Fe, ^{60}Co, and ^{65}Zn to investigate the influence of thermochemical reagents on the volatilization and transport efficiency for these trace elements in ETV-ICPMS of Al_2O_3 powders. γ-Spectra of the radiotracers revealed that less than 2% of the elements Cr, Fe, Co, and Zn remained in a graphite furnace from Al_2O_3 powders at 2200 °C even without addition of a thermochemical reagent, and the latter even was found to decrease the volatilization efficiencies. The recovery for the radiotracers on filters at the end of the transport tube, however, was found to increase in most cases when different modifiers were added at amounts generally used in ETV-ICPMS, while transport efficiencies considerably decrease again when adding higher amounts as stoichiometrically required for a complete halogenation of the sample matrix. A comparison of the modifier's influence on the transport efficiencies vs its influence on the measured signal was made and demonstrates the importance of transport efficiency changes for the effects of thermochemical reagents in ETV-ICPMS analysis.

The online coupling of gel electrophoresis (GE) and ICPMS was presented by Bettmer and co-workers for different purposes, such as DNA quantification (*253*), species-specific isotope dilution for iodide and iodate determination in aerosols (*254*), and determination of phosphorylation degrees in caseins (*255*). In all cases, GE conditions were chosen for optimized separations depending on the target analyte composition. The separated sample compounds were directly transported to the nebulizer system of the ICPMS. In the first reported application (*253*), a precisions lower than 3% was achieved but the accuracy of the developed method was not proven due to the lack of existing quantitative DNA reference material. For the analysis of marine aerosols (*254*), it was demonstrated that the use of ^{129}I-enriched iodide and iodate allows the correction of the impact of the matrix on both the electrophoretic migration and the detection sensitivity of the ICPMS. Iodide and iodate was found to be present at the (sub)nanogram per cubic meter level in the investigated aerosol samples, being in good agreement with other recent studies. Also, on the basis of simultaneous detection of $^{32}S^+$ and $^{31}P^+$, the application of online GE-ICPMS might eventually offer an alternative in the analysis of phosphorylated proteins (*255*). A similar system based on online GE-ICPMS was used by Anorbe et al. (*256*) to investigate the separation of Fe-containing proteins. The GE system has been operated with different conditions, e.g., using sodium dodecylsulfate for charging and denaturing proteins and using native conditions below and above the isoelectric point resulting in anodal and cathodal separations. Since quantification was hampered by the loss of Fe, the ratio of measured $^{56}Fe^+$ to $^{32}S^+$ was additionally given by the authors.

The hyphenation of gas chromatography (GC) with ICPMS was used by Gonzaez-Gago et al. (*257*) for the determination of trihalomethanes in drinking water using compound independent calibration with internal standard. The use of $CBrCl_3$ as an internal standard allowed the simultaneous determination of four compounds in one single injection by detecting chlorine at m/z 35 and bromine at m/z 79. For the determination of trihalomethanes (THMs) in drinking waters, the method required only the addition of a known amount of internal standard to 100 mL of sample, the extraction of the THMs using 4 mL of *n*-pentane and the direct injection of the extract in the GC system. Extraction recoveries were between 80 and 98%, reproducibility was below 3%, and method detection limits were below 0.01 ng mL^{-1} for all compounds, meeting the requirements of international legislation for the routine determination of THMs in drinking waters.

Lobinski and co-workers (*258*) used a modified total consumption micronebulizer in combination with a μ-flow-injection collision cell ICPMS for the determination of Mo, Ni, and V in petroleum samples. The increase in the nebulizer capillary diameter and the elimination of the internal connections reduced the problem of clogging, pressure instability, and memory effects. The xylene carrier could be introduced for several hours, while the sample (2.5 μL) was injected into the carrier flow to produce peaks of 5 s at half-height, which allowed a throughput of approximately 100 h^{-1}. Calibration curves with good linearity over at least 3 orders of magnitude and detection limits at the subnanogram per milliliter levels were obtained. The use of a He-pressurized collision cell was essential to obtain good accuracy for Ni and V but was not required for Mo. The determination of Pb isotope ratios in crude oils using ICPMS and aqueous standard solution calibration was performed by Dreyfus et al. (*259*). Two introduction systems, an ultrasonic nebulizer and a Scott-type spray chamber, were fitted to a specifically designed dual inlet torch. This special configuration allowed simultaneous introduction of organic and aqueous solutions into the plasma and permitted mass bias correction of Pb isotope ratios using a certified Pb isotope standard. Crude oils diluted to total Pb concentrations ranging from 0.6 to 10 ng g^{-1} were analyzed for their Pb isotope ratios. Routine measurements of 10 replicate organic samples containing 10 ng g^{-1} of Pb provided precision better than 0.5% for the different isotope ratios. The isotopic measurements of crude oils of specific geochemical interest exhibited good accuracy and reproducibility.

Elemental Speciation and Analysis of Biological Samples. In recent years, a vast number of papers on Se and its role in health issues have been published. A review by Dumont et al. (*260*) gave a brief, critical overview of the recent main analytical findings and included a detailed image of the current state-of-the-art of Se speciation analysis in these food sources and in human tissues and body fluids. Of particular interest was the Se content in different food sources worldwide and the extent to which their consumption is reflected in the Se content of human tissues and body fluids. Several natural and Se-enriched food sources were discussed as to origin, characteristics, Se metabolism, and impact of their consumption on the human body. An up-to-date literature study on Se speciation analysis was given, illustrating how analytical chemistry in its different facets aids in the identification of Se compounds and provides insight into the complete metabolic pathway of Se throughout the human body. The analytical methodology for speciation of metals and metalloids associated with alkyl groups and biomacromolecules was critically reviewed by Hirner (*261*). It was outlined that because of the toxicological relevance of alkylated metals and metalloids present in trace to ultratrace concentrations, firm species identification and exact quantification are essential. While many instrumental techniques coupling chromatography with ICPMS are nowadays available for quantification, methods used for structural identification often suffer from inadequate sensitivity. Other problems encountered are sample derivatization artifacts, lack of suitable standards for quantification, lack of equilibrium between spikes and sample, and the integrity of metal−protein association during separation, in particular during SDS-PAGE. Selected application examples with respect to Hg and As speciation were critically discussed by the author.

Yang et al. (*262*) presented a method for the simultaneous determination of Cr(III) and Cr(VI) in yeast using species-specific double-spike isotope dilution (SSDSID) with anion-exchange liquid chromatography (LC) separation and sector field ICPMS detection. Samples were digested on a hot plate in an alkaline solution for the determination of Cr(III) and Cr(VI), whereas acidic microwave-assisted decomposition was used for the determination of total Cr. Despite the observed significant bidirectional redox transformation of the different Cr species during alkaline extraction and subsequent chromatographic separation at pH 7, quantitative recoveries for both Cr(III) and Cr(VI) were achieved using the SSDSID method. In addition, mass balance between total Cr and the sum of Cr(III) and Cr(VI) concentrations was achieved. Method detection limits of 0.3, 2, and 30 mg kg^{-1} were obtained for total Cr, Cr(VI), and Cr(III). Total determination and speciation analysis of Se in commercial and selenized Agaricus mushrooms have been performed by Sanz-Medel and co-workers (*263*) to investigate the Se species naturally occurring in nonenriched mushrooms as well as those present in specimens grown in a Se-enriched medium. Three complementary chromatographic separation mechanisms (size-exclusion, anion-exchange, and reversed-phase) were used and coupled to an ICPMS equipped with an octopole reaction system. Postcolumn isotope dilution analysis has been used online with the separations for quantification of the Se species eluted. Selenomethionine together with a number of unknown selenocompounds was detected in both investigated types of Agaricus mushrooms: free in commercial mushrooms and incorporated into proteins in selenized ones. Juresa et al. (*264*) reported on a HPLC−ICPMS study on the long-term stability of the major Se metabolite in human urine. Three separate experiments were performed of 4−28 weeks duration and incorporating various storage conditions: room temperature, 4 °C, −20 °C, −80 °C, lyophilization, deoxygenation, or addition of a bactericide (NaN_3). Triplicate spiked samples of urine or water, spiked with Selenosugar 1, were processed in each case. Selenosugar 1 was stable in water under all investigated conditions, and for the urine samples, no significant degradation (<2%) was observed after 17 weeks frozen storage at −80 °C or after lyophilization and frozen storage at −20 °C, whereas small quantities of degradation products (approximately 3%) were recorded for frozen storage of wet samples at −20 °C. At 4 °C, the Selenosugar was essentially unchanged after storage for up to 2 weeks, but clear losses were observed thereafter ranging up to 75% loss after 28 weeks. The work indicates that urine samples should be cooled immediately after collection and that they may be stored at 4 °C for up to 2 weeks before analysis with no appreciable loss of Selenosugar. For longer-term storage, urine samples should be kept at −80 °C or, when such facilities are not available, at −20 °C after lyophilization. The study has also revealed potential quantification problems in Se speciation analysis resulting from different responses for Se species during ICPMS analysis. A method based on the online combination of ion-pair reversed-phase HPLC with ICPMS and ESI-Q-TOFMS/MS was proposed by Infante et al. (*265*) for the identification of a number of Se-containing compounds in selenized yeast aqueous extracts without any pretreatment or fractionation of the water extract. The online combination of reversed phase HPLC using a gradient of up to 40% MeOH in 0.1% formic acid with ICPMS was used for detection of multiple Se-containing species within a single chromatographic run of the water extract. The methanol load to the plasma was reduced 2-fold by using postcolumn effluent dilution with ultrapure water, which allowed concentrations of up to 40% MeOH in the mobile phase to be well tolerated by the ICP system. Direct analysis of the water extracts by HPLC with online ESI-TOFMS allowed the accurate molecular mass determination of a range of Se compounds detected by HPLC-ICPMS. Two selenium compounds were identified as methyl Se-glutathione and a Se-glutathione species with a S−Se bridge between glutathione and Se-cysteinylgammaglutamylglycine (GS-SeG) in selenized yeast and were reported for the first time.

Busto et al. (*266*) proposed an isotope dilution ICPMS-based method for the quantification of transferrin isoforms once saturated with Fe and separated by anion-exchange chromatography. Species-specific and species-unspecific spikes have been explored. In the first part of the study, the use of postcolumn addition of isotopically enriched Fe permitted the quantification of individual sialoforms of transferrin in human serum samples of healthy individuals as well as alcoholic patients. Second, the species-specific spike method was performed by synthesizing an isotopically enriched standard of saturated transferring, which was used to quantify the individual isoforms in the same serum samples obtaining results comparative to those of postcolumn isotope dilution and to those previously published in the literature, demonstrating the suitability of both strategies for quantitative transferrin isoform determination in real samples. Hann et al. (*267*) presented the complementary use of LC-ESI-MS and LC-ICPMS for characterization of native and recombinant Cu proteins. SEC and IC separation protocols were implemented for hyphenated ICPMS analysis. The studies showed that validation of the methods addressing metal integration on a quantitative basis via metal to sulfur ratios demanded complementary determinations of molar mass. Reversed phase LC-ESI-TOFMS measurements showed point mutation for the investigated recombinant apoplastocyanin. Excellent precision ranging at 3 ppm was achieved for the determination of multiply charged ion patterns, while the precision of the molar mass determination after deconvolution ranged at 5−15 ppm. Additionally, IC-ICPMS measurements on isotopically enriched Cu proteins were accomplished showing the potential of hyphenated ICPMS analysis in future tracer studies. Lobinski and co-workers (*268*) established a method for selenopeptide mapping in a Se-yeast protein digest by parallel nanoHPLC-ICPMS and nanoHPLC-ESI-MS/MS after online preconcentration. The performance of the method was demonstrated for a comprehensive online characterization of a mixture of peptides in a tryptic digest of a Se-containing protein fraction isolated by size-exclusion chromatography from a selenium yeast extract. The method allowed the identification of a whole series of Se/S substitutions in individual peptides and, in some cases, sequencing of isomers differing in the position of selenomethionine residues in the amino acid sequence.

LA-ICPMS was used by Becker et al. (*269*) and Jackson et al. (*270*) for elemental mapping and quantitative imaging of thin sections of different kinds of tissue samples to study the bioavailability of selected elements, transport processes, distribution, contamination, and to monitor environmental risks using indicator organisms. Cu, Zn, P, and S were determined in sections of rat brain (*270*), and Se and metal distributions in longitudinal sections of entire slugs, which were fed with either a placebo or Se-containing solutions, were investigated (*269*). The authors found out that Se was enriched in the kidney and in the digestive gland of Se-treated animals. The highest Se concentrations were detected in the gut of Se-treated slugs, and additional Se occurred in the skin of these animals. Cu was enriched in the heart and the mucous ventral skin. The developed analytical technique allows the quantitative imaging of Se together with selected metals in thin sections of biological tissue with limits of detection at the submicrogram per gram range.

Different studies outlined the suitability of LA-ICPMS for the direct detection of metal-containing proteins in separated protein bands in one- and two-dimensional gels to investigate the binding of Cu and Zn on tau protein isoforms as a target protein in Alzheimer’s disease (*271*), to characterize and identify several human proteins from Alzheimer’s diseased brain through the distribution of P, Cu, Zn, and Fe (*272*), and for investigating new strategies for readout of microarray (*273*). The presented atomic and molecular mass spectrometry-based methods allowed one to characterize the human brain proteins with respect to their structure, sequence, phosphorylation state, and metal content. Lobinski and co-workers (*274*) reported on an improved LA-ICPMS method offering superior sensitivity for the detection of heteroatom-containing proteins in 1D polyacrylamide gels. A 2 mm wide lane was ablated by ultrafast (10 cm s^{-1}) back-and-forth movement of a 20 μm laser beam parallel to the protein bands while the gel advanced perpendicularly, resulting in a 40-fold increase in detection sensitivity, mainly because of the much larger amount of ablated material introduced into the plasma on the time scale of the dwell time of the mass spectrometer. The method was applied to the specific detection in the gel of formate dehydrogenase expressed in *Escherichia coli* and of selenoproteins in Desulfococcus multivorans with detection limits at the low femtomole levels. Venkatachalam et al. (*275*) used LA-ICPMS detection for the determination of the phosphorylation status of proteins through the detection of heteroelements on membranes after sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) and electroblotting, achieving good reproducibility with a standard deviation of 6.1%. Quantification of phosphoproteins was performed with dotting and SDS-PAGE separated and blotted standards to overcome protein losses during blotting. A linearity in the range from 20 to 500 pmol of phosphorus in proteins and an estimated limit of detection of 1.5 pmol for phosphorus in β-casein were presented.

Laser Ablation for Direct Solid Sampling. The number of applications of LA-ICPMS to the determination of major, minor, and trace elements as well as isotope-ratio measurements in various sample types has substantially increased during the last 2 years. A review by Mokgalaka and Gardea-Torresdey (*276*) gives a summary of both such applications, primarily in the field of environmental chemistry and fundamental studies on LA. Hergenröder (*277*) presented a review on the mechanisms for generation of aerosols by LA, for typical laser sampling conditions as used in LA-ICP spectrometry. Although there exists a general agreement that, independent of the sample type, two size fractions with different chemical composition are found, the author concludes that the mechanisms generating these different particle fractions are not yet so clear.

Fundamental studies on LA- and ICP-based isotopic fractionation were presented by Kuhn et al. (*278*) and Kroslakova and Günther (*279*). Results from respective studies on Cu samples (*278*) outlined that particles <200 μm transported in the aerosol are isotopically lighter by up to 0.7 ppt compared to the larger particles. The dependence of this isotopic fractionation on the ablation time, together with isotopic effects caused in the ICP during particle vaporization, was found to explain the variations of isotope ratios observed during LA-ICPMS. Large systematic within-run variations of up to several parts per thousand were observed depending on the ablation time and, correspondingly, as well as large offsets from solution data for the same sample when compared directly. Analysis of small particles generated by vapor condensation after the laser impact, and larger particles formed by ejection of liquid droplets from the crater, showed that the laser impact results in isotopic fractionation of $^{65}Cu^+/^{63}Cu^+$ between different aerosol particle size fractions of up to 0.7 ppt. The authors concluded that this fractionation cannot be overcome by removal of large particles from the aerosol that are not completely vaporized and ionized in the ICP source although it was found to significantly reduce within-run fractionation, as well as improving the accuracy relative to solution data. Temporal variations in the isotopic composition of particulate vapor condensate were explained by a crater effect that influences the residence time of large particles in the laser-generated plasma plume, leading to preferential vaporization of the lighter isotopes. To study mass load dependent matrix effects, different masses of aerosols from glass standard were generated using a 193 nm ArF excimer laser and a 266 nm Nd:YAG laser and introduced into an ICPMS (*279*). The different mass loads in the ICP were achieved using different crater diameters, the application of an aerosol dilutor, a tandem ablation setup, and mixing of a single element matrix with the laser generated aerosols. The comparison of results acquired using these different experimental setups supports the existence of a significant matrix effect dependent on the mass load of the ICP. It was shown that an increase of the mass load of the ICP by a factor of 16 leads to a decrease in certain intensity ratios up to 25%. In contrast, applying dilution up to a factor of 30 to the aerosols generated using different crater diameters leads to a stabilization of the intensity ratios to a constant value. The mass load enhanced matrix effect was found to be element dependent and most severe for elements with low melting points. The induction of matrix effects independently of the ablation process by adding various Rb concentrations to the laser aerosols indicated that elements previously described to be dominantly influenced by laser-induced elemental fractionation undergo significant ICP-induced matrix effects. The authors stated that these matrix effects are mass load dependent and for most elements exceed the contribution of laser-induced fractionation.

Hergenröder presented different models for LA, which identify possible sources for element-specific fractionation, such as the melting and subsequent resolidification of the heated sample area (*280*) and the impact transfer from the expanding plasma to the liquid melt layer and the subsequent generation of droplets of variable sizes (*281*). He also proposed a model for the generation of small particles from laser ablation products under a He or Ar atmosphere (*282*), explaining the size dependent chemical composition of the particles. The calculations were compared with preliminary brass ablation experiments and good agreement was found.

Bogaerts and co-workers investigated theoretically the effect of ambient pressure (*283*), kind of background gas (*284*), and kind of metal (*285*) on the laser ablation characteristics and the plume expansion dynamics. The ambient pressure has mainly an effect on the plume expansion dynamics, i.e., the vapor plume can expand much further in vacuum or low background gas pressure compared to 1 atm background gas pressure (*283*). Similarly, heavy background gases (such as Ar and Kr) result in slower expansion, or more confinement, of the vapor plume, compared to lighter gases (such as He and Ne) (*284*). Furthermore, the target evaporation depths were found to be slightly deeper for He than for Ne, Ar, and Kr, which was in reasonable agreement with crater depths measured in the case of these different background gases. Finally, by applying the model to several metals and comparing the calculation results with experimental crater profiles, information could be obtained on the relative role of surface vaporization and melt expulsion on the amount of target ablation (*285*).

Bleiner and Bogaerts provided experimental evidence for the processes of phase explosion and melt splashing being the mechanisms of large particulate creation in laser ablation of metal samples (*286*). The differences in ablation mechanisms across the irradiated region of the sample were attributed to the spatial distribution of the beam energy profile. Finally, they reported that the measured particle size distribution was composed of an abundant nanosized fraction, produced by vapor condensation, and a microsized fraction, created during melt expulsion (*286*).

With respect to the study of laser ablation cell design and transport efficiencies to the ICP, progress was made by Bleiner and Bogaerts by means of computational fluid dynamics modeling (*287*, *288*). In ref 287, the carrier gas flow characteristics and particle trajectories through the transport tube were calculated for several different tube designs. The carrier gas flow was in general found to be laminar, with nested velocity paraboloids. The particle transport efficiency appeared to be size-independent for Ar as the carrier gas, whereas He resulted in less efficient transport of the finer particles. Furthermore, also the temporal signal profiles were modeled, both for single shot and repeated shot analysis (*287*). In ref 288, the performance of various sample chambers (i.e., cylindrical, elliptical, different volumes, and with different inlet setups) was modeled. It was found that both the chamber geometry and size influence the gas velocity pattern and particle trajectories. Also the difference between He and Ar as the carrier gas was investigated (*288*).

Russo and co-workers have also performed very interesting work on the fundamentals of LA plume expansion, in a series of papers published by Wen et al. (*289–293*). In ref 289, an experimental and theoretical study was made of the cooling of the laser induced vapor plume in background air. The temperature and size variations of the vapor plume were determined from spectroscopic measurements during the first tens of microseconds after the laser pulse. The energy transport by thermal radiation from the vapor plume to the background gas and to the sample was formulated, and spectral line calculations were made. The calculations yielded good agreement with the experimental results for the decreasing vapor plume temperature. The study was focused on both optically thin and optically thick conditions of the vapor plume.

The gas dynamics of the expanding vapor plume was studied by means of integrated conservation equations of mass, momentum, and energy in ref 290. The effect of a counterpropagating internal shock wave was included. The incident laser energy transferred to the vapor plume and the background gas, as well as the vaporized sample mass, were used as input in the model. The latter were obtained by comparison of the calculated trajectories of the internal and external shock wave and the contact surface with experimental results, obtained in ref 291 for a range of different laser fluences and three different background gases. These measurements were performed by means of a series of synchronized shadowgraph and emission images. Finally, in ref 290, the interaction of the internal shock wave with the sample was identified as one of the mechanisms inducing liquid sample ejection during laser ablation. In ref 292, it was reported that the inclusion of ionization energy in the analysis leads to a change in the evolution of the pressure, mass density, electron number density, and temperature of the vapor plume. More specifically, it results in higher expansion speeds and temperatures for a longer time after the laser pulse. Finally, another paper by the same authors (*293*) describes the experimental and theoretical studies of particle generation after LA. The formation of small particles by condensation was studied by recording a series of light scattering images. The primary particle shape and size distributions were measured using a transmission electron microscope, a scanning electron microscope, and a differential mobility analyzer. The gas dynamics simulation included nucleation and coagulation in the vapor plume, heat and mass transfer from the vapor plume to the background gas, and heat transfer to the sample. The experiments and calculations showed the same trend for the spatial distribution of the condensed particles, both in He and Ar. Also the simulated particle size distribution agreed qualitatively with the experimental data.

Hirata and Miyazaki (*294*) employed a high-speed camera for imaging the ablation process of solid samples by an argon-fluoride excimer laser operated at 193 nm wavelength. The authors found out that the production of the sample aerosols was significantly delayed (similar to 4 μs) from the onset of the laser shot. The typical speed of particles released from the ablation pit was 100−200 m s^{-1}, which was significantly slower than the reported velocity of the plasma plume expansion. Since the initial measured speed of the sample particles was rather close to the speed of sound, the sample aerosols could be rapidly decelerated to the terminal velocity by a gas drag force with ambient He. It was found that the degree of sample redeposition around the ablation pit can be effectively minimized by evacuation of the sample cell down to 20 kPa. Although details of the mechanism of production and release of the sample aerosols from the ablation pit are not fully understood, the present imaging device for laser ablation was found to be helpful for further precise elemental and isotopic analyses using LA-ICPMS. The expansion of aerosols generated by near-infrared (NIR) nanosecond- and femtosecond-LA of metals at atmospheric pressures was explored by Koch et al. (*295*) through laser-induced scattering. It was shown that NIR-nanosecond-LA under quiescent Ar atmosphere provokes the formation of a dense aerosol confined within a radially propagating vortex ring. The expansion dynamics achieved under these conditions were found to be fairly slow whereas the degree of aerosol dispersion for NIR-nanosecond-LA using He drastically increased due to its lower viscosity. As a consequence, the maximum diameter of expansion differed by a factor of approximately 4. Analytical implications concerning, e.g., dispersion phenomena or the choice of the LA protocol and physical dimensions of future ablation cell designs were critically discussed by the authors.

Gurevich and Hergenröder (*296*) presented a novel concept of an ablation cell for LA-ICPMS, which is characterized by suppression of the turbulence in the flush gas flow in the ablation region to reduce the wash-out time of the aerosol. With this cell design, ICPMS pulse durations down to several tens of milliseconds have been achieved. It was demonstrated that such pulses become sharper, and the amplitude of the signal grows as the turbulence in the ablation cell is suppressed. Express in-depth profiling was demonstrated on examples of an Al−Zn multilayer structure and an industrial Mg−Zn coating. Pisonero et al. (*297*) developed a so-called "high efficiency aerosol dispersion" (HEAD) ablation cell, based on the use of a directed gas flow expansion of the laser generated aerosol at the ablation site and a venturi effect created by two nozzles to extract the aerosol into the main make up gas stream. The investigation of the capabilities of this type of aerosol extraction demonstrates that a laser-generated aerosol can be modified by shifting the original particle size distribution toward smaller particle sizes. In comparison with standard cell results, elemental ratios showed reduced elemental fractionation effects attributed to reduced agglomeration and, therefore, an improved vaporization of the aerosol within the ICP. Most importantly, stability and reproducibility of the ion signals were significantly improved without compromising sensitivity. For the imaging purpose of the elemental distribution in protein spots blotted onto membranes with a conventional size, Feldmann et al. (*298*) have investigated three different LA cell geometries to find a design of a cell showing constantly high signal intensity across the cell and offering short wash-out times. The optimized cell has a volume of about 11.3 cm^3 in which single shot signals are washed out in less than a second so that translation velocities of up to 1.5 mm s^{-1} can be applied to baseline separate structures with a distance of less than 2 mm.

Because of the fact that vapor generation, nucleation, condensation, and agglomeration take place within an extremely short period of time, ablation under atmospheric pressure might not allow influencing these processes; while under the reduced pressure condition, the cooling of the aerosol and therefore the condensation is expected to be slower. In a recent study, Fliegel and Günther (*299*) described a low-pressure LA cell for the generation of laser aerosols in ICPMS analysis and underlined the dependence of the size distribution and particle structure on the ablation cell pressure. A significant difference between the low pressure and ambient pressure ablated aerosol was observed, since the intensity ratios (U/Th) of the ablated sample moves closer to the bulk composition at lower pressures at the expense of sensitivity, suggesting increasing vapor deposition within the ablation cell walls.

The addition of 4−9 mL min^{-1} of H_2 to the He carrier gas flow in 193 nm excimer LA increases the sensitivity for a number of elements by a factor of 2−4, as reported by Guillong and Heinrich (*300*). The sensitivity enhancement for some elements, including Be, P, As, Pt, and Au was found to be 5−7-fold. This effect was explained by a higher electron temperature in the plasma. Interestingly, a correlation was observed between the enhancement factor and the first ionization energy of the respective elements. Limits of detection were improved for all elements except those with hydrogen based polyatomic interferences, such as Si, K, Ca, and Se, thus suggesting new applications in LA-ICPMS. A similar but weaker effect was found for the addition of CH_4, while almost no sensitivity enhancement was found for N_2 addition.

Becker et al. (*301*) showed a new way of nanometer scale analysis of elements on sample surfaces by near-field LA-ICPMS. This technique uses the near-field enhancement effect on the tip of a thin silver needle in a 532 nm laser beam on the sample surface. A small amount of sample material is ablated at atmospheric pressure by a single laser shot in the near-field of the silver tip in the defocused laser beam. Significant increase in signal intensity was observed in the case of single-shot analysis on 2-D gels and biological surfaces doped with U in the microgram per gram range in comparison with the background signal, while a lateral resolution in the nanometer scale was theoretically possible.

A compact simultaneous LIBS/LA-ICPMS setup was developed by Latkoczy and Ghislain (*302*) to determine the elemental distribution of major and trace elements in an industrial multiphase Mg-based alloy sample. Fundamental parameters of laser-induced plasmas, including the influence of different gas atmospheres together with the laser wavelength in the UV region, were studied and optimized. Multielement mappings of the sample surface were performed, and a calibration approach using the LA-ICPMS signal intensities for internal standardization of the LIBS data was investigated.

Guillong et al. (*303*) described the design and function of an α-box integrated LA system coupled to an ICPMS for the analysis of highly radioactive samples. The LA system was separated into beam generation and ablation and sample handling to avoid radiation induced defects of the hardware. The optical beam path was delivered through a window within the α-box. Isotope ratios were measured with a precision of 0.3%, and a spatial resolution down to 10 μm was achieved. The optimized parameters were applied to spent nuclear fuel samples.

In a study by Resano et al. (*304*) , several red-colored paintings of post-Paleolithic schematic style were sampled and subjected to analysis by means of LA-ICPMS, SEMEDX, and Raman spectroscopy to obtain meaningful information on the samples composition, in order to establish differences or similarities among them. LA-ICPMS was found to provide the most relevant data for fingerprinting purposes. Forty elements were determined in a wide concentration range with minimum sample consumption. The authors proposed the suitability of the method for discriminating between various paint pots, as demonstrated for the investigated samples.

Horvath et al. (*305*) developed a method for the direct determination of the fission gas products in microinclusions contained in nuclear fuels using LA-ICPMS. To determine the concentration of Xe in nuclear fuel, different calibration strategies were investigated. One strategy was based on the direct injection of a known quantity of a reference gas into the LA-ICPMS carrier gas system. Further, the ablation of a matrix-matched standard of a nonirradiated UO_2 sample, implanted with a known amount of ^{129}Xe was also applied, and quantitative LA-ICPMS measurements were performed on high burnup nuclear fuel. The study demonstrated that direct gas injection is most suitable for the quantification of fission gas in micrometer-sized inclusions.

Significant improvements in the processes responsible for fractionation effects have been recently observed with the use of ultrashort laser pulses. A critical review by Donard and co-workers (*306*) outlined the emerging potential of femtosecond-LA-ICPMS for the direct analysis of solid materials and aimed to summarize the main differences between the LA mechanisms of short (>1 ps) and ultrashort (<1 ps) laser pulses based on fundamental understanding of the LA process and the most relevant parameters governing the quality of analysis. A variety of examples for elemental and depth-profiling analysis of solid samples in biological, geological, and materials applications were presented. Horn and von Blanckenburg (*307*) described the use of femtosecond-LA and its effects on elemental and isotopic fractionation using the Pb/U system and stable Fe isotopes to illustrate elemental and isotopic fractionation, respectively. No elemental fractionation was observed beyond the precision of the multiple-collector inductively coupled plasma mass spectrometry (ICP-MC-MS) measurements. Without a matrix match between standard and sample, elemental fractionation was absent even when using different laser ablation protocols for standardization and samples. It was also found that LA-induced isotope ratio drifts, commonly observed during nanosecond-LA, are not detectable during ultraviolet femtosecond-LA, which carries, in the authors' opinions, the potential to solve some of the difficulties encountered during the 2 prior decades since the introduction of LA.

In a study on transport effects of near-infrared femtosecond-LA-generated aerosols, Garcia et al. (*308*) compared different ablation cells with short and long washout times. It was found that the transport efficiencies are independent of the cell used within the mutual experimental uncertainties. This finding was confirmed by additional measurements providing the absolute particle mass transport efficiencies of femtosecond-LA in He. Russo and co-workers (*309*) pointed out that femtosecond-LA sampling into the ICPMS improves the precision by reducing systematic errors related to the particle size distribution and resultant spikes on the signal intensity. Internal (precision within an ablation spot) and external repeatability (precision between ablation spots on the sample) were evaluated during repetitive 266 nm femtosecond- and nanosecond-LA-ICPMS.

The feasibility of using near-infrared femtosecond-LA-ICPMS for the analysis of solid samples with nonmatrix matched standard reference materials was studied by Bian et al. (*310*). Major and minor concentrations of Zn and Cu were measured in three sets of metallic and dielectric standards using He as the ablation cell gas and, with admixed Ar, for aerosol transportation from the cell into the ICPMS. The experimental Zn/Cu ratios of the brass and Al samples were found to be proportional to the certified ratios independent of the laser fluence applied. In contrast, the Zn/Cu ratio of an optical transparent glass sample was found to be strongly fluence dependent. With increasing fluence, the measured ratio asymptotically approached the experimentally expected ratio taking into account the results obtained from the brass and Al measurements.

The capabilities of ultraviolet femtosecond-LA-ICPMS for depth profile analysis of thin metal coatings (*311*) and polymer-coated steel samples (*312*) were evaluated by Pisonero et al. and Mateo et al., respectively. A standard sample consisting of a single Cr layer on a Ni substrate was used (*311*), and a fast washout was obtained by a high-efficiency aerosol dispersion ablation cell, which allowed single-shot analysis with increased depth resolution. A laser repetition rate of 1 Hz and low laser fluence were used, yielding very low ablation rates (<10 nm/pulse), which were determined by atomic force microscopy. The calculated depth resolution was smaller than 300 nm. The absolute amount of ablated material per laser pulse was similar to 1 pg, which corresponds to a detection limit of 180 μg g^{-1}. For different kinds of polymer coatings over galvanized steel substrates, the depth profiles obtained by LA-ICPMS were found to be in good agreement with those obtained by GD-OES, while LA-ICPMS achieved better depth resolution due to the better lateral resolution (*312*). The depth resolution obtained by LA-ICPMS was found to be 240 nm and 2.3 μm for a hot-dip galvanized steel and a polymer−polymer-coated steel sample, respectively, compared to the 2.2 and 4.5 μm achieved with GD-OES. Both groups agreed that femtosecond-LA-ICPMS represents a powerful combination of high lateral and depth resolution for the analysis of thin coatings.

Collision and Reaction Cells. ICPMS instruments that use ion−molecule reactions to overcome spectral overlaps are becoming more widely available. Strategies to develop methods that use ion−molecule reactions in a quadrupole reaction cell (RC) were systematically described by Olesik and Jones (*313*). Strategies to produce a new analyte-containing product ion at a higher mass where the background is low were discussed as an alternative to "conventional" ion−molecule reactions for spectral overlap removal. Considerations for each approach including selection of the reaction gas, adjustment of the reaction cell bandpass, and optimization of the gas flow rate were discussed. Examples were given with available kinetic rate constants, thermodynamic data, and experimental ICPMS measurements to illustrate each consideration in development of methods using ion−molecule reactions. Recent applications of collision cell (CC) and RC technology in isotope dilution MS were reviewed by Yip and Sham (*314*). Currently available instrumentation and potential areas for future development were also addressed.

Prohaska et al. (*315*) reported on the optimization of an ICPMS equipped with a dynamic reaction cell (ICP-DRC-MS) for the determination of ^{44}Ca/^{40}Ca isotope ratios in aqueous solutions with respect to repeatability, robustness, and stability, using NH_3 as the reaction gas. The effect of laboratory conditions as well as ICP-DRC-MS parameters such a nebulizer gas flow rate, rf power, lens potential, dwell time, or DRC parameters on precision and mass bias was studied. Precision of a single isotope ratio measurement of a 60 ng g^{-1} Ca solution was achieved in the range of 0.03−0.05%, which corresponded to the standard error of the mean value of 0.012−0.020%. These experimentally observed RSDs were close to theoretical precision values given by counting statistics. Accuracy of measured isotope ratios was assessed by comparative measurements of the same samples by ICP-DRC-MS and thermal ionization mass spectrometry (TIMS). The Δ^{44}Ca values measured by TIMS and ICP-DRC-MS coincided within the obtained precision.

As already mentioned in the chapter "*Elemental Speciation and Analysis of Biological Samples*", ICP-DRC/CC-MS has gained substantial attraction for the determination of metals and nonmetals in proteins and other biological samples, e.g., to contribute to the understanding of DNA−Cr interaction, which was extracted from metal-contaminated soil (*316*), to determine selenocompounds after HPLC separation of tryptic digest of spots obtained from 2-D gel electrophoresis of the water-soluble protein fraction of selenized yeast (*317*), and for the quantitative analysis of proteins via sulfur determination (*318*). Schaumlöffel et al. (*319*) developed a method for accurate Se determination in blood serum by isotope dilution ICPMS using an octopole reaction system with Xe as the collision gas to eliminate polyatomic interferences from Ar, Cl, P, and Br. The achieved detection limit of 3.3 μg L^{-1} was higher than with H_2 (0.4 μg L^{-1}) but sufficiently sensitive to determine Se in serum. Precise and accurate Se isotope ratios were determined without mathematical interference corrections. In contrast, these corrections were necessary when H_2 was used as the reaction gas. The presented Se recovery from human serum reference material was only 78.0 ± 0.4% when measured with H_2

but 96.7 ± 4.0% with Xe. McShane et al. (*320*) described an ICP-DRC-MS-based method for the routine determination of total As, total Se, and total Cr in urine by ICP-DRC-MS using Ar as the reaction cell gas. The proposed method uses the same diluted urine solutions prepared for conventional ICPMS toxic metal biomonitoring and chemical terrorism screening analysis with the same internal standards, and no creatinine corrections were necessary. The presented strategy was found to be useful for the analysis of approximately 100 urine samples per day of unexposed subjects and persons considered to be exposed to those elements through chemical terrorism, environmental, nutritional, or other pathways. A rapid method for the extraction and determination of ^{90}Sr in natural water, plant, and sediment samples was developed by Taylor et al. (*321*) using extraction chromatography and ICP-DRC-MS, with O_2 as a reaction gas. While isobaric interference from the stable isotope ^{90}Zr was efficiently removed by this method, interferences produced from in-cell reactions with Fe^+ and Ni^+ required suppression by tuneable bandpass. Method detection limits were given as 0.1 pg g^{-1} (0.5 Bq g^{-1}), 0.04 pg g^{-1} (0.2 Bq g^{-1}), and 3 pg L^{-1} (5 Bq L^{-1}) for sediments, plant, and water samples, respectively, and ^{90}Sr concentrations determined by ICPMS were in good agreement with activities determined by Cerenkov counting and with certified reference values. While mass spectrometric determination does not rival detection limits achievable by radiometric counting, radiometric determination of ^{90}Sr, a pure β-emitter, is hindered by long analysis times of several weeks; the comparatively fast analysis achieved via ICPMS enables same-day preparation and analysis of samples and was considered an important technique for the environmental monitoring of areas contaminated by radioactivity.

Time-of-Flight Instruments. Time-of-flight mass analyzers (TOFMS) have been known since the 1950s, but ICP-TOFMS became commercially available only in the late 1990s. Since those years, extensive research on ICP-TOFMS developments and applications has been performed, although the number of published manuscripts rather decreased slightly during the last 2 years.

Bauchemin and co-workers used such an instrument as a tool to study fundamental processes on ion abundances and ion distributions in the interface region of an ICPMS. Axial profiling of the plasma was done to investigate how a pre-evaporation extension interface (i.e., heated glass tube between the nebulizer and the torch) affects the signal from As and other analytes. A reproducible axial profile was observed for As^+ with a signal enhancement ratio (heated/unheated) of 1.55, while the axial profile showed a signal intensity ratio of 0.65 (*322*). No such difference in signal was observed for all the other analytes investigated, which are ionic in solution, in contrast to As and Se, which would be mostly in the neutral form in 1% HNO_3. For ionic analytes, the optimal signal upon heating was found to be similar or higher than that without heating with an inverse dependency on analyte mass. These observations were rationalized by changes in the number of Coulomb fission events occurring during pre-evaporation, which depend on the size and charge of droplets, as well as the identity and concentration of the matrix. The optimal axial position for various elements was found to shift closer to the load coil upon heating the pre-evaporation extension interface (*323*). In a different study, the radial profiles of some background ions and analytes spanning the mass range and with a wide range of first ionization potentials were investigated (*324*), and three different matrixes were considered to assess the effect of organic modifiers: 1% HNO_3, 1% HNO_3 with 2% v/v MeOH, and 1% HNO_3 with 0.2% m/v sodium dodecylsulfate (SDS). Although these concentrations of methanol and SDS induced the same sample transport increase (37%), neither of them resulted in a 37% increase in signal across the mass range. In fact, the change in analyte signal as a function of m/z followed opposite trends in these two matrixes. Although, the total carbon concentration was quite different in these two matrixes, it cannot account for the completely different radial profiles that they produced. However, a bimodal distribution, with maxima on either side of the central axis, resulted in the presence of 2% MeOH. This distribution was found to be similar to that of several C-based background ions, which further substantiates the suggestion that ionization then predominantly occurs through charge transfer with carbon-containing ions. In the authors' opinion, this bimodal distribution suggests that a volatile organic solvent such as MeOH quickly spreads into the surrounding area of the central channel upon sample introduction in the plasma.

The performance of an $Ar-N_2$ mixed-gas plasma was compared to an Ar plasma by Holcombe and co-workers (*325*) using electrothermal vaporization (ETV) as a sample introduction source to an orthogonal accelerating ICP-TOFMS. The effect of sample matrixes $NaNO_3$ and $Pd(NO_3)_2$ on a multielement solution was investigated in mass amounts ranging from 0.1 to 5 μg of the metal matrix. Addition of 2% N_2 to the outer plasma gas of an Ar plasma reduced signal suppressions observed in the presence of high concentrations of Na and Pd at the expense of a large reduction in analyte sensitivity (approximately 83%). Signal profiles indicated that suppression may be caused, in part, by space charge effects that are dependent on the ion density of analyte and matrix ions.

Tanner and Günther took advantage of the fast spectral repetition rate of an ICP-TOFMS and implemented in torch LA sampling to such a system (*326*). The achieved signal-to-noise ratios (S/N) for minor elements were found to be 2 times higher than the S/N ratios calculated from continuous signals of conventional 10 Hz LA in an ablation cell. The elemental signal intensity ratios during single spot analysis were the same for in torch and in cell LA and the authors concluded that the same particle size distributions are formed by the laser impact and consequently sampled into the ICP. Single shot in torch LA-ICPMS was found to exceed the figures of merit of continuous LA in an ablation cell and can provide 10 Hz LA analyses with single shot resolution. Duwe and Neff (*327*) used an ICP-TOFMS in combination with LA for the analysis of glaze-paint and slip of 161 White Mountain Red Ware ceramic samples (AD 1275-1325) from east-central Arizona to establish viability of the technique for measuring chemical compositions of glazes and slips and to establish a methodology for inferring this structured variability, specifically delineating the presence of specific pigment mixtures or "recipes" used by prehistoric potters. Cizdziel (*328*) evaluated LA-ICP-TOFMS as a tool for the determination of Pb in blood spotted onto specially designed filter paper (FP) for subsequent laboratory testing within the frame of a screening program for pediatric Pb poisoning. Some elements monitored along with Pb exhibited signal profiles conducive to potential quantitation (Ca, V, Fe, Cu, Zn), whereas others did not (Cr, Mn, Co, Ni, Cd, Hg, Tl, U). The method required no sample pretreatment and was found to be particularly suitable for rapidly screening of a large number of samples. Pb isotope ratios appeared to be effective for discerning contamination extraneous to the blood sample.

Adams and co-workers (*329*) developed a flow injection online sorption system for the separation and preconcentration of traces of Ag, Cd, Co, Ni, Pb, U, and Y from natural water samples with subsequent detection by ICP-TOFMS. Simultaneous preconcentration of the analytes was achieved by complexation with a chelating reagent immobilized on the inner walls of a PTFE knotted reactor. The detection limits varied from 0.3 ng L^{-1} for Y to 15.2 ng L^{-1} for Ni, and the precision was better than 4%. Enhancement factors of 3−14 were obtained for the different analytes in comparison with their direct determination by ICP-TOFMS with ultrasonic nebulization without preconcentration. Infante et al. (*330*) investigated for the first time the capability of postcolumn isotope dilution combined with anion-exchange HPLC-ICP-TOFMS for environmental quality assessment through metal speciation analysis of metallothionein (MT) isoforms in cytosols of gibel carp, used as biomarkers for environmental metal exposure. A full spectral scan of the biological sample using the instruments transient mode allowed fast multi-isotope screening of cytosolic metal-containing fractions and to investigate the presence of matrix-induced interferences. The presented work on gaining quantitative speciation information on the preferences of MT isoforms in different fish organs for sequestering heavy metals was found to be important to elucidate the role of isoform-specific induction of vertebrate fish MT in metal detoxification and the use of MT as a biomarker.

Lüdke et al. (*331*) combined a novel orthogonal accelerating ICP-TOFMS with an inductively heated vaporizer system (IHVS) for the analysis of trace metal content in size separated arctic aerosols, which were preciously sampled during a measurement campaign at Spitsbergen. Eight size classes between 0.35 and 16.6 μm aerodynamic diameters of ground-based aerosol particles were sampled by impaction of the particles on cleaned graphite targets through a cascade impactor. Subsequently, the targets were rapidly heated up to 2700 °C in an IHVS. With optimized experimental parameters, the element content of the particles was simultaneously determined by ICP-TOFMS in a mass range between ^{7}Li and ^{209}Bi. Acidified reference solutions, placed on the cleaned targets, were used for calibration, and the resulting absolute limits of detection ranged between 2 and 200 pg for the investigated elements.

High Resolution Instruments. During the last 2 years, the number of environmental applications of high resolution ICPMS (ICP-HRMS) has increased rapidly. Many factors contribute to make ICP-HRMS a very powerful tool, including extremely low achievable detection limits, high sensitivity, high mass resolution to overcome spectral interferences for the reliable determination of many trace elements, and the reasonable precision of isotope ratio measurements. External factors such as the stability of laboratory blanks are often the limiting factor in ICP-HRMS analysis rather than the detection power. A review by Krachler (*332*) aims to highlight the most recent applications of ICP-HRMS in the field of environmental analysis, focusing on matrixes and applications where the superior capabilities of the instrumental technique are most useful. Field et al. (*333*) proposed a rapid high-throughput method for the determination of trace P, V, Mn, As, Mo, Ba, and U in seawater with application to tracing ballast water exchange in ocean-going vessels. Direct flow injection and CH_4 addition were employed, and the method was found to be capable of 4700 continuous determinations of 10-fold diluted seawater samples in less than 30 h. The authors suggested expanding the method for its application to other problems in seawater analysis requiring high precision and sample throughput.

A method, based on sector field (SF) ICPMS coupled with a microflow nebulizer and a desolvation system, has been developed by Gabrielli et al. (*334*) for the direct determination of rare earth elements (REE) down to the subpicogram per gram level in molten Antarctic ice. Contamination problems were carefully taken into account by adopting ultraclean procedures during the sample pretreatment phases. Spectral interferences from oxide formation were greatly reduced due to the use of a desolvation system for sample introduction. Instrumental detection limits ranged from 0.001 pg g^{-1} for Ho, Tm, and Lu to 0.03 pg g^{-1} for Gd. The precision ranged from 2% for La, Ce, Pr, and Lu up to 10% for Er, Tm, and Yb. The presented method allowed the direct determination of REE in a 1 mL sample of ancient Antarctic ice with concentration ranges between 0.006 and 0.4 pg g^{-1} for Tm and 0.9−60 pg g^{-1} for Ce.

Rudolph et al. (*335*) demonstrated the use of isotope dilution ICP-SFMS for accurate online ultratrace analysis of Pd through cation-exchange chromatography combined with microconcentric nebulization and membrane desolvation. For solid samples, the limit of detection was found as 0.24 ng g^{-1} Pd, and the necessity of combining matrix separation and preconcentration for elimination of spectral interferences was demonstrated using soil samples. A study performed by Ovari et al. (*336*) focused on the determination of the Pt concentration in the urine of train drivers occupationally exposed to urban air with heavy traffic by ICP-SFMS. Samples were taken from respective individuals both before and after the shift, and the results for Pt were compared to those previously obtained by the same group. Interestingly, the values from train drivers in Budapest were about twice as high as those from Vienna.

Stefanka and co-workers (*337*) presented an interesting application of ICP-SFMS for the determination of Am and Pu. A sequential sample preparation method was employed using a coprecipitation step for preconcentration and a separation step applying extraction chromatographic resins. The average recovery of sample preparation calculated from the concentration of the tracer before and after sample treatment was better than 80%. The method development focused on the elimination of possible interferences in mass spectrometric analysis employing matrix separation and desolvation prior to ICP-SFMS analysis. The addition of 5 mL min^{-1} N_2 to the sample gas after the desolvation system yielded a 2-fold signal improvement. For ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{241}Am, limits of detection of 15, 9.2, 14, and 104 fg g^{-1} were achieved, while for all investigated actinides, the precision of the analysis was in the range 0.8−3%. The method was applied for analysis of environmental samples originated from Chernobyl and from the Mayak region. The possibility of the determination of the origin and date of pollution was demonstrated using isotopic data obtained by ICP-SFMS and alpha spectrometry.

A Mattauch−Herzog ICP-SFMS equipped with a novel array detector in combination with ETV was employed by Peschel et al. (*338*) for the analysis of solutions and slurries. The ability of this instrument to record the transient signals produced for a number of analytes in ETV-ICPMS was demonstrated. Detection limits for seven investigated elements were found to be in the range of 4−60 pg μL^{-1} for aqueous solutions and in the low microgram per gram range for the analysis of 10 mg mL^{-1} slurries of Al_2O_3 powders. The dynamic ranges measured for some of the investigated elements spanned 3−5 orders of magnitude when the detector was operated in the low-gain mode and appear to be limited by the ETV system. Trace amounts of Fe, Cu, and Ga could be directly determined in Al_2O_3 powders at the 2−270 μg g^{-1} level without the use of thermochemical reagents.

Boulyga et al. (*339*) reported on the optimization of a multicollector ICP-SFMS equipped with an ion deceleration filter for the determination of extremely low U isotope ratios applied for the first time to the analysis of ^{236}U/^{238}U isotope ratios in the 10^{-8} to 10^{-7} range in isotopic reference material IRMM-184, as well as in two unknown samples obtained in the frame of a round-robin exercise. The ion deceleration lens system reduced the peak tailing from ^{238}U^{+} ions at $m/z = 236$ down to 3×10^{-9}, whereas the absolute sensitivity for U was reduced by only about 30%. Thus, abundance sensitivity was improved by almost 2 orders of magnitude, and the minimum determinable ^{236}U/^{238}U ratio was improved by more than 1 order of magnitude compared with conventional sector-field ICPMS or TIMS. On the other hand, interference by ^{235}UH^{+} deteriorated the accuracy and increased the measurement uncertainty up to 48%, in particular in the case of samples enriched in ^{235}U.

An online Hg reduction technique using stannous chloride as the reductant was applied by Foucher and Hintelmann (*340*) for accurate and precise Hg isotope ratio determinations by cold-vapor multicollector ICP-SFMS to significantly detect the anticipated small differences in Hg isotope ratios in nature. Internal precision was better than 0.002% on all Hg ratios, and instrumental mass bias was corrected using ^{205}Tl/^{203}Tl correction coupled to a standard-sample bracketing approach. The authors concluded that analytical techniques have reached a level of long-term precision and accuracy that is sufficiently sensitive to detect even small differences in Hg isotope ratios that occur within one type of sample (e.g., between different sediments) and so far have unequivocally shown that Hg isotope ratios in sediments vary within approximately 5 ppt.

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