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Atomic Spectroscopy: A Review

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Review Contents

Developments in atomic spectrometry during the last two years have further centered on innovation in atomic absorption spectrometry with flames and furnaces and especially with volatile species generation, as well as in atomic fluorescence and atomic emission spectrometry with plasmas, especially in the direction of sample introduction and miniaturization, as well as in laser plasmas, glow discharges both at low and at atmospheric pressure, and plasma mass spectrometry. As in the former issues of this review series (*1–4*), the review aims to form a picture of the trends of development in the mentioned areas at the hand of a discussion of significant publications, especially in the field of methodological developments. Problem-oriented work is only cited where methodological innovation is involved, and due to the high volume of the literature dealing with atomic spectrometry, a choice on the publications cited had to be made, which certainly is arbitrary and does not claim any completeness in coverage either. For this aim, a number of papers published in the journals *Analytical Chemistry*, *Analytical and Bioanalytical Chemistry*, *Angewandte Chemie*, *Analytica Chimica Acta*, *International Journal of Environmental Analytical Chemistry*, *Journal of Analytical Atomic Spectrometry*, *Microchimica Acta*, *Talanta*, *Spectrochimica Acta, Part B*, *Spectroscopy Letters*, and *The Analyst*, which were published in the period of January 2008 to December 2009, were considered and discussed. It should be emphasized that in the respective period important international meetings took place, such as the *Winter Conference on Plasma Spectrochemistry*, Temecula (January 2008), the *European Winter Conference on Plasma Spectrochemistry*, Graz (February 2009), the *Asian Winter Conference on Plasma Spectrochemistry*, Tskukuba (December 2008), the *Rio Symposium*, Bahia (April 2009), the *XXXVI. Colloquium Spectroscopicum Internationale*, Budapest (September 2009), the *Nordic Conference on Plasma Spectrochemistry*, Loen (June 2008), and the *Euroanalysis*, Innsbruck (September 2009), of which in a number of cases the proceedings were published in one of the above-mentioned journals. This is, e.g., the case for the *10th Rio Symposium* held in Bahia (Brazil) (*5*).

Atomic spectrometry as a principle of analysis always makes use of a sampling unit, a source as a signal generation unit, a spectrometer to sort out the element-specific signal from the spectrum, and a detection system. Innovation takes part in all parts mentioned. As common to all atomic spectrometry methods, general topics remain of interest. Such general topics in atomic spectrometry include further research on the methodology for the practical determination of the limit of detection and decision in spectrochemical analysis (*6*) as well of the limit of quantification (*7*). Further, reviews on important approaches such as electrothermal vaporization, which are of interest for all methods of atomic spectrometry, were published (*8*). The greater part of research done deals with the different methods of atomic spectrometry themselves, as they were mentioned before, and this will be discussed below for the different methods.

ATOMIC ABSORPTION SPECTROMETRY

In atomic absorption spectrometry (AAS), both with the classical flame AAS and with furnace AAS innovation took place. Remarkable efforts, however, were made to use all types of methods allowing volatile species generation with metals.

Flame Atomic Absorption Spectrometry. Flame atomic absorption spectrometry (FAAS) is a mature analytical method, which is present in almost any analytical laboratory as a working horse for elemental determinations of metals. Innovation, however, is still going on with respect to the introduction of the sample into the atomizer and the increase of the analyte sampling efficiencies and residence times in the atomizer. By the so-called furnace in flame approach for volatile elements or volatile species forming elements especially, the sampling efficiency can be

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considerably increased as compared to conventional pneumatic nebulization with the possibility to considerably improve the power of detection for a number of elements. This especially could be shown for the case of Cd, where by pneumatic nebulization into a flame-heated furnace the limits of detection could be brought down to 15 ng mL^{-1} (*9*). The approach was also shown to be helpful for the analysis of samples with high salinity (*10*).

A further technique for sample introduction which remains to attract the interest is thermospray, with which the sampling efficiency and, accordingly, also the power of detection of FAAS can be improved, as shown for the case of Co and Mn (*11*). Further innovative work in FAAS deals with the use of cloud point extraction for isolating and pre-enriching heavy metals from complex samples, such as environmental samples (*12*). Also, the development of methods for online sample digestion in connection with FAAS is interesting (*13*).

Electrothermal Atomic Absorption Spectrometry. Electrothermal atomic absorption spectrometry, especially with graphite furnaces, has developed in the past decades to an unrivaled method for ultratrace analyses at an affordable price. Furnace atomic absorption spectrometry retained its original form stemming from L'vov and Massmann's work; however, in every part of the system, considerable innovation occurred.

In graphite furnace atomic absorption spectrometry (GFAAS), special attention has been paid to the thermochemical processes responsible for the atom cloud formation, as they are of crucial importance for the signal magnitude and form and, accordingly, for the accuracy and precision achievable.

The stabilized temperature platform principle by a number of groups has been shown to be very powerful to eliminate a number of volatilization interferences in GFAAS. Exemplarily, the use of L-tyrosine immobilized on multiwalled carbon nanotubes as a substrate for the separation and speciation of Tl using a stabilized temperature platform GFAAS can be cited (*14*).

A considerable amount of publications deal with the use of chemical modifiers and their use for improving the analytical figures of merit of GFAAS. For filter furnace atomizers in GFAAS, the use of different chemical modifiers for the determination of Pb in wine could be shown to be beneficial. The use of the filter furnace here was shown to have a 2−6 times higher sensitivity than the conventional furnace, both in the case of transversal heating (*15*). The relevant mechanisms in the use of chemical modifiers after all are not fully understood, and this still is a fruitful field of research. Here, it was shown that the use of Raman spectrometry changes in the structure of the graphite surface as a result of the use of chemical modifiers could play a role. The presence of Th, Zr, Pd, or nitric acid were shown to result in an increase in the content of sp^3-bonded carbon clusters on the platform (*16*). Mixtures of Pd salts and different organic acids also were found to be effective in the determination of Tl and Sn, especially when performing a background correction with the D_2-lamp technique (*17*). The use of sodium tungstate was shown to be an effective permanent chemical modifier for slurry sampling in the case of the determination of In in soils by GFAAS (*18*).

The background correction further remains a topic of methodological development in GFAAS. In the case of diode laser electrothermal atomization, both Zeeman- and wavelength-modulated atomic absorption could be shown to be valuable, and the detection limits obtained were shown to be at the same level as in coherent forward scattering in the case of crossed polarizers (*19*). With diode lasers in GFAAS, also, isotopic dilution could be applied for calibration, as Doppler-free measurements are possible (*20*).

Apart from graphite furnace, also, tungsten furnaces remain a topic of investigation. Though they do not have the advantages of graphite furnaces in the sense of a reduction of the analytes from the oxides to the elemental form nor do they have the precision as a result of a good sample uptake, they have the advantage of being cheaper, and no risks for stable carbide formation are present. The preconcentration of Mn through adsorption on a tungsten wire in the case of tungsten furnace AAS was shown to enable a detection limit at the pg·mL^{-1} range in water samples (*21*). For volatile and semivolatile elements such as Cd, Th, Ag, Pb, Zn, Hg, Cu, Sb, Bi, T, In, As, Se, Sn, and Au, tungsten coil AAS and thermospray FAAS were found to give similar detection limits (*22*). By the use of Zr as a modifier and atomization from a tungsten surface, even Be could be very well determined by electrothermal AAS (*23*).

Volatile Species Generation Atomic Absorption Spectrometry. It is well-known from FAAS that volatile species generation through the increase of the analyte sampling efficiency, as compared to pneumatic nebulization, is an effective means for improving the power of detection and that through the separation of the analytes from the sample matrix it is very useful for excluding a number of matrix interferences. Especially, however, when the released analyte species are trapped by cryotrapping or by hot trapping, which is possible as the volatile species often are destructed at a temperature below the volatilization temperatures of the elementary species, a considerable pre-enrichment allows it to further increase the power of detection. A review on these processes for the analytes As, Se, Pb, Bi, Cu, In, Tl, Te, Sn, and Hg is given in ref 24. As the volatile hydrides of the elements mentioned decompose at relatively low temperatures, a conduction of the analyte species into flame-heated quartz tubes is sufficient for atomization. The decomposition of the species, however, can be influenced by sample constituents, which in this way cause matrix effects. The ways to minimize these effects by the use of a multiple microflame quartz tube atomizer were described (*25*). The approach also was used in combined procedures, where for Sb the analyte was first preconcentrated by a headspace single drop microextraction. Then, detection limits of 25 pg mL^{-1} for Sb(III) were obtained, and determinations in water samples could be realized with a good accuracy (*26*).

Apart from the above-mentioned elements, also, a number of metals could be determined by suitable volatile species generation reactions. Here, much research during the last years was done to widen the circle of metals which could be determined in this way and to know more about the volatile species generation mechanisms. Volatile Co species could be generated by UV photoreduction, and it was attempted to identify them by gas chromatography coupled to mass spectrometry, which showed that one obtained carbonylated species (*27*). Room temperature ionic liquids further were found to enhance the chemical vapor generation of Cu, Ag, and Au following reduction in acidified aqueous solution with KBH_4 (*28*). By radiotracer studies, it could

be shown that volatile Ag species also were generated in the flow injection arrangement from the nitric acid environment in the presence of surfactants (Triton X-100 and Antifoam B) and permanent Pd deposits as the reaction modifiers with efficiencies of 23% (*29*). Trapping requires careful optimization of the working conditions as shown for stibine in a quartz atomizer, not only with respect to the trapping efficiency but also with respect to the influence of matrix constituents on the collection (*30*). With the aid of matrix modifiers, the trapping efficiency could be increased considerably, as shown for the case of Se with an Ir-modified transversally heated graphite tube atomizer (*31*). For the case of Sb, trapping in a flame heated quartz tube enabled a differentiation between Sb(III) and Sb(V) through the use of reduction with L-cysteine down to the 0.2 ng mL^{-1} level, and the approach could be used for the total Sb contents of soils, sediments, coal fly ash, sewage, and river water (*32*). For Pb, the hydride could be formed through the reaction with $NaBH_4$ in the presence of a hydrochloric acid-potassium ferricyanide medium and trapping could be achieved on the interior walls of a slotted T-tube under highly oxidizing flame conditions. The procedure could be applied to the determination of Pb in soil and plant standard reference materials (*33*). Apart from hot-trapping, cryotrapping has been further used, e.g., after the reduction of pentavalent arsenicals by thioglycolic acid for speciation (*34*). For Hg, trapping on a gold gauze has been used in the determination of organic, inorganic, and total Hg, when extracting the organic Hg from KBr containing solutions with chloroform and back extraction with L-cysteine (*35*). Also, the use of electrochemical hydride generation was found useful for the generation of volatile species from heavy metals such as Tl (*36*).

Direct Solids Atomic Absorption Spectrometry. Direct solids sampling can be realized in flame AAS but innovation especially occurs in the case of electrothermal atomization. A special problem in direct solids analysis is the calibration. In direct solids GFAAS, it has been proposed to use spiked filter papers for the determination of Cu and Zn in vegetable samples (*37*). For a sampling of powders, the use of slurries is very convenient, as described, e.g., in the direct determination of Cu and Pb in gel forming konjac samples by enzymatic hydrolysis assisted slurry sampling GFAAS (*38*). The direct sampling of powder samples and the injection of slurries under the use of a modifier mixture of Pd and Mg salts and H_2O_2 as digestion reagent for the determination of Cd in wheat flower were compared, where the solid sampling technique was found to be the most sensitive and easy technique (*39*). Also, in the case of the filter furnace, direct sampling and emulsion analysis for the determination of Pb in crude oil by GFAAS were compared. Under the use of Pd and Mg salts as modifier, both techniques were found to deliver accurate results (*40*). With direct solids sampling GFAAS and under the use of background correction and graphite platform atomization, Cr, Cu, Fe, K, Mn, Sb, and Zn could be reliably determined in silicon nitride powders as well (*41*).

Continuum Source Atomic Absorption Spectrometry. Since continuum source AAS is commercially available, the interest in this approach has continuously risen and both the methodological refinement and the use in the case of real samples started to become systematically investigated. The line selection certainly has to be revised, as compared to hollow cathode excited AAS, as now the whole spectral range is available and the topic of interfering lines in the lamps now has been excluded. For the sequential determination of Cu, Fe, Mn, and Zn in soil, alternate lines for Fe, e.g., were examined and the figures of merit in the case of GFAAS analysis of real samples were evaluated (*42*). Especially, the background correction in continuum source AAS becomes more reliable, as the whole spectral information due to the use of CCD technology is available. Accordingly, the use of exact background correction and of an internal standard in the case of the determination of Pb in phosphoric acid under the use of continuum source flame AAS could be shown (*43*).

As the molecular bands also can be used for absorption measurements, elements like P, S, and the halogens easily can be determined using the molecular bands of bromides and iodides, also, as reviewed in ref 44. For the case of Br, both AlBr and CaBr molecular bands at 278.914 and 625.315 nm, respectively, could be used. However, the presence of inorganic acids was found to influence the signals with both bands in a different way (*45*). As the spectral resolution of Echelle spectrometers is sufficient to resolve spectral lines of different isotopes of an element boron isotope, ratios could be estimated by continuum source FAAS (*46*).

As in direct solids sampling, real spectral background correction is very important; this approach can well be realized in continuum source GFAAS. This has been shown at the hand of the determination of Ag in geological samples (*47*). For the determination of Hg in polymers by solid sampling GFAAS, the use of line source and continuum source AAS has been compared and the continuum source technique has been concluded to be superior because of the better possibilities for real spectral background correction, both for polyethylene, polystyrene, polyvinylchloride, and acrylonitrile butadiene styrene (ABS) based polymers (*48*). Also, in biodiesel, the determination of P under the use of a Pd modifier and Triton X-100 as a wetting agent was possible under the use of a direct solids sampling unit (*49*).

ATOMIC FLUORESCENCE SPECTROMETRY

Atomic fluorescence remains of practical interest especially for the determination of Hg, which is important especially for environmental samples as well as for the determination of the volatile hydride forming elements and for the determination of elements with high excitation energies like Pb and Cd. Especially, under the use of spectral lamps as primary sources, instruments were developed and new applications were investigated.

For the determination of the chemical vapor generating elements by atomic fluorescence spectrometry, a flame-in-gas-shield miniature flame hydride atomizer was proposed and detection limits for the elements As, Sb, Bi, Se, Te, and Sn by dispersive atomic fluorescence spectrometry were determined (*50*). For the determination of Hg, gold-coated silica under the form of nanoparticles, prepared by chemical reduction of a Au(III) solution with hydroxylamine in the presence of suspended silica particles, was proposed as a preconcentration phase, and in natural water, total Hg could be determined with detection limits down to 180 pg mL^{-1} (*51*).

Also, for the speciation of these elements, atomic fluorescence could be used as a detection technique. For the determination of monomethylmercury in low- and high-polluted sediments, micro-

wave assisted extraction under acidic conditions was used and the ethylated derivates of the analytes were injected into a gas chromatograph coupled to atomic fluorescence (*52*). Even organics and biological substances, such as *S*-nitrosoglutathione and other nitrosothiols, subsequently to derivatization with *p*-hydroxymercurybenzoate, can be determined by reverse phase chromatography coupled with chemical vapor generation atomic fluorescence detection. Under the use of a 50 μL loop for injection, detection limits on the order of 30 nM could be obtained (*53*).

A further refinement for the case of the volatile hydride forming elements was the development of an integrated electrochemical hydride generation cell for the determination of As. The cell uses a graphite tube cathode and a reticulate Pt wire anode without an ion-exchange membrane and an individual anolyte; a limit of detection for As of 0 ng mL^{-1} could be obtained, and real samples were analyzed (*54*). Also multielement determinations could be realized, as shown at the hand of the simultaneous detection of Se by atomic fluorescence and S by molecular emission by flow injection hydride generation with online reduction for the determination of selenate, sulfate, and sulfite (*55*). Apart from volatile species generation, also, electrothermal vaporization could be used for forming the atom vapor, as shown by the determination of Cd in rice and water by tungsten coil electrothermal vaporization-atomic fluorescence spectrometry after cloud point extraction (*56*). Also, plasmas such as the medium power argon radio frequency capacitively coupled plasma could be used as an atomization cell in the atomic fluorescence spectrometry of Cd (*57*). Even the sample preparation can be integrated in the system, as shown by the fully automated online digestion system for the ultra trace determination of Hg in natural waters by means of flow injection cold vapor atomic fluorescence spectrometry (*58*).

ATOMIC EMISSION SPECTROMETRY

In atomic emission spectrometry, the innovation takes part through the optimization and further development of the radiation sources, among which new ones such as miniaturized discharges are introduced, the improvement of spectrometers, and the possibilities of the new detectors.

DC Arc and Low-Power RF Radiation Sources. With classical arc and spark sources, innovation is minimum. However, research on the use of two jet sources for the determination of trace elements in bone by atomic emission spectrometry (AES) has been published. Here, one used powdered samples to which graphite powder and NaCl were added as spectroscopic puffer, and a large number of elements (Ag, Al, Ba, Be, Bi, Cd, Co, Cu, Cr, In, Fe, Ga, Mn, Mo, Ni, Pb, Sn, Tl, Sr, and Zn) could be determined down to the submicrogram per gram level by direct solids analysis (*59*). DC arcs such as the U-shaped argon plasma with a tangential aerosol introduction also were further optimized for determinations in solutions after their pneumatic nebulization (*60*).

Graphite and tungsten furnaces themselves since long are used as emission sources. In the double furnace tungsten coil, through the use of the second coil, more energy is delivered for atomization and excitation of the sample. Elements like V, Ti, Ba, and Sr can be determined in water samples down to low concentrations (*61*). A He plasma in a graphite furnace at a power of 70 W could be well used in connection with vapor generation for the determination of Hg. $SnCl_2$ can be well used as reducing agent, resulting in a detection limit at the 200 pg mL^{-1} level, but in the case of $NaBH_4$, too much H_2 is generated and the He plasma is extinguished (*62*).

Apart from direct current (dc) discharges, a radio frequency (rf) plasma similar to the ICP but at low power and with an Ar consumption of 0.6 L min^{-1} could be realized. Excitation temperatures of 5000−8000 K, rotational temperatures of 3100−4000 K, electron temperatures of 9000 K, electron number densities of $5-8 \times 10^{15}$ cm^{-3}, and ionization temperatures of 6250−7750 K were measured for a power of 1.1 kW (*63*). The source could be used for atomic emission spectrochemical analysis of water-soluble LaF_3 nanocrystals doped with different lanthanide ions by introducing colloidal solutions to a pneumatic nebulizer. No differences in the signals between solutions and the colloids were found, and detection limits at the microgram per liter level were obtained (*64*).

Inductively Coupled Plasmas. The inductively coupled plasma (ICP) is the most widely used source for atomic emission spectrometry, and accordingly, instrumentation is found in almost any analytical laboratory. Despite that it is used as a mature analytical method for multielement trace determinations, investigations on its basic characteristics, its improvement, its modification, and its optimization still are a main topic in the spectrochemical literature.

As a result of the better knowledge of temperatures and other plasma parameters, the processes in the ICP can be better understood, which also allows one to better optimize its analytical performance. Work on computerized simulation of the solute−particle vaporization helps us to obtain a dynamic picture of the plasma vaporization kinetics (*65*). Also, the study of the evaporation of individual droplets released in an analytical ICP and the related local temperature changes on a time-resolved basis are very informative for the understanding of analyte emission intensity changes (*66*).

Much work has been done on the optimization of the analytical performance of ICP-AES. It has been shown that by studying vertically resolved plasma emission, matrix effects and also drifts can be traced and also minimized in the case of practical analysis by working at the so-called crossover point (*67*). After a careful optimization of internal standardization and calibration by standard addition, it has been shown that concentration uncertainties less than 0.2% could be realized with variable matrix concentrations (*68*). Accordingly, ICP-AES under the use of so-called exact matching is very valuable for the characterization of standard reference materials, as shown, e.g., for the case of a beryllium oxide powder (*69*). Further studies related directly to the analytical performance deal with matrix effects caused by spectral interferences, where especially the knowledge of the spectra of the rare earth elements present in pure rare earth matrixes are very valuable (*70*). With respect to the analytical performance, also, the chemical form under which the elements are present can play a role, which is especially important in the case of organic matrixes, as it has been show for Si present in a xylene matrix (*71*). The presence of carbon-containing compounds in the sample solutions anyhow can have a considerable influence on the analyte emission, as shown by systematic studies using various organic

substances in the solutions (*72*). By the knowledge of the processes in the ICP and the use of double ratio plasma diagnostics combined with an internal standard, one has a chance to arrive at a calibrationless ICP-AES method for the determination of trace elements in aqueous solutions (*73*).

Several groups worked on the understanding of the consequences of axial or radial viewing for the analytical performance of the ICP. Especially, the matrix effects are studied, as, e.g., in a contribution on the study of the matrix effects of Al, Ca, and Mg in axially viewed ICP-AES (*74*). An interesting study made use of bottom-viewed ICP-AES, which is made possible through the use of a straight quartz tube used as a hollow light pipe to collect plasma emission. In this way, it was shown to be possible to reject part of the background emission from the core of the plasma that encircles the plasma central channel and yet to be efficient in collecting light from the plasma central channel (*75*).

Many studies in ICP-AES deal with sample introduction. Here, pneumatic nebulizers, which can be operated at the submilliliter liquid consumption rate with high efficiency, such as the commercially available NAR-1 using microcapillary arrays, certainly are important for several applications (*76*). Also, multimode nebulizers which allow both solution nebulization and, e.g., hydride generation are very useful (*77*). Their optimization for the specific analytical problem to be solved remains a challenge for the analytical chemist. Dual-channel nebulizers, with which two flows of liquid can be nebulized with one gas flow, are a further interesting approach making standard addition much easier and allowing a number of matrix effects to be nearly removed by the selection of the correct internal standard element and line (*78*). Also, the direct injection nebulizer approach was further pursued, as shown by the description of a direct injection nebulizer with a replaceable capillary (*79*), of which the performance is similar to the one of the conventional high efficiency direct injection nebulizer DIHEN, described earlier. Further, efforts are made for aerosol desolvation so as to improve the analytical performance of ICP-AES. By the use of microwave-assisted desolvation, the effect of ethanol on the analyte signals in wine analysis can be decreased, which facilitates calibration (*80*). The use of heated spray chambers in the case of a so-called torch integrated sample introduction system was investigated, and it was shown that by increasing the spray-chamber temperature by 100 K and using a sheath gas the limits of detection in the case of a DIHEN nebulizer could be considerably increased (*81*). A further new nebulizer is the so-called flow focusing multiple nebulizer, where four nebulization nozzles with independent liquid feeding and a common gas inlet are used. Here, it is possible to decrease the liquid uptake considerably and to make the use of internal standardization more flexible (*82*). The internal standardization as a means for depressing matrix effects also could be studied by stirred tank experiments, allowing the use of many internal standards and analytes in a flexible way (*83*). Slurry nebulization also continues to be used for the analysis of real samples. Here, the analysis of coal slurries has been studied along with a careful investigation on the particle size of the coal powders, the use of wetting agents, and the Zeta potentials of the slurries (*84*). For boron carbide powders, ICP-AES using slurry nebulization with a Babington-type nebulizer without addition of any dispersant was found to be more sensitive than conventional nebulization ICP-AES or solid dc-arc atomic emission spectrometry (*85*). ICP-AES using pneumatic nebulization also remains an interesting technique for element-specific detection in various separation techniques, as it was shown by the differentiation between free Ca and Ca-containing species in human plasma samples by capillary electrophoresis coupled to ICP-AES (*86*). Also, in combination with field flow fractionation, ICP-AES is a powerful tool for particle size analysis (*87*).

Apart from pneumatic nebulization, vapor generation techniques similar as those used in AAS also continue to find use in ICP-AES. In the case of hydride generation, the use of various borane reducing agents ($NaBH_4$, $C(CH_3)_3NH_2-BH_3$, and $(CH_3)_2NH-BH_3$) and acids (HCl and CH_3COOH) with respect to their influence on the plasma parameters and the analyte intensities were studied; $NaBH_4$ was found to have the largest influence, and one even could come to a plasma which is not in robust conditions (*88*). Also, for the determination of sulfide, besides sulfate, the vapor generation principle can be used, as one only has to measure the signal enhancement subsequent to acidification (*89*). A further way to convert the analytes into volatile species is the use of microwave-induced combustion, as it can be applied in the determination of S in extra-heavy crude oil. Here, a combustion under oxygen atmosphere allows it to volatilize both S and Cl which then can be trapped in absorption solutions to be analyzed by ICP-AES (*90*). Hydride generation also was shown to be useful as a postcolumn technique in liquid chromatography used for the determination of 4 As species in soil extracts when ICP-AES for element-specific detection is used (*91*). Also, electrospray remains a useful technique for interfacing liquid chromatography to element-specific detection by ICP-AES. Here, heat-assisted systems could be shown to be very effective, especially when organics are involved, which could lead to carbon deposits in the ICP (*92*).

Electrothermal vaporization remains an attractive approach for sample introduction in ICP-AES, for which the according equipment is commercially available. A magnetic drop-in tungsten furnace vaporization unit was shown to be a suitable technique for the direct solid sampling of iron and steel samples, with which S, Se, and Sb could be determined by ICP-AES (*93*). It could be shown that under the use of modifiers trace and minor elements could be determined by ICP-AES coupled to graphite furnace evaporation in plant materials, on the basis of calibration by the addition of aqueous analyte solutions and under the use of graphite standards as laboratory reference materials (*94*). By the use of modern CCD based ICP-AES spectrometers, a dynamic background correction and, at the same time, a simultaneous measurement of different analyte and internal standard lines are possible. The electrothermal vaporization (ETV) approach not only allows one to omit a time-consuming sample decomposition which often introduces risks of contamination but also one can circumvent spectral interferences when a trace matrix separation can be achieved. This could be shown at the hand of the determination of Cd in soil samples, which can be separately vaporized from Pb and Fe (*95*). From a tungsten sample, cuvette, and tetramethylammoniumhydroxide, as a chemical modifier, it even was possible to evaporate boric acid, boron carbide, and boron nitride separately and to detect them by ICP-AES (*96*). Also, the spark ablation

technique as a technique for direct solids analysis in ICP-AES still offers suitable solutions for a number of analytical problems. It could be shown that refractory powders such as silicon carbide, after mixing them with Cu powder and briquetting pellets, could be reliably analyzed by spark ablation ICP-AES and that a calibration with the aid of spiked powders was possible. Here, detection limits down to the lower microgram per gram level were obtained (*97*).

Microwave Induced Plasmas. Microwave induced plasmas (MIP) continue to be interesting sources for atomic emission spectrometry. Due to the hundred fold higher frequency than ICPs, the skin depth is of an order of magnitude smaller than with the ICP and toroidal plasmas of a 10-fold smaller dimension can be realized. Studies on the asymmetry of the H_β-line profiles were made and used for the diagnostics of atmospheric pressure MIPs (*98*). It is interesting that MIPs easily can be realized with Ar and He but also with Ne as the working gas. In the latter case, spectroscopic characterizations of a surface-wave MIP at 2.54 GHz and at atmospheric pressure were made (*99*). The robustness of the MIP could be considerably increased in the case of a magnetically excited microwave plasma source, with which under the use of pneumatic nebulization and either nitrogen or air as the support gas the detection limits are in the same range as those of an ICP (*100*). Through the use of a TEM cavity and 3 L min^{-1} of He, a plasma into which wet aerosols generated by ultrasonic nebulization could be introduced could also be obtained (*101*). The microwave plasma torch was shown to be suitable for being combined with electrochemical hydride generation without the need for a removal of the excess of hydrogen produced. With the system, determinations in wastewater and in digested biological standard reference materials under the use of a calibration by standard addition were possible (*102*). MIPs remain interesting sources for the determination of gases in metals after applying carrier gas hot extraction (*103*). MIP-AES and MS remain appropriate sources for element-specific detection subsequent to gas-chromatographic separations of volatile element compounds, as shown for the speciation of butyl- and phenyltin compounds in human urine by headspace solid-phase microextraction after derivatization with tetraethylborate and separation by capillary gas chromatography (*104*). Here, quadrupole mass spectrometry was used in parallel for the confirmation of the identity and the molecular structure of the eluted compounds.

Microplasmas. Research on microplasmas was further performed in several groups and continues to be a very innovative direction of work in spectrochemical analysis. A number of publications were included in special issues of journals (see, e.g., ref 105). A review on dark, corona, and glow discharges for analytical applications realized by barrier layers was published (*106*). Such discharges were found to be good atomizers for the determination of As by atomic fluorescence using hydride generation which even has perspectives for field use (*107*). Also, the determination of Hg by the cold vapor generating technique and atomic emission spectrometry was reported to be possible without the need for removing residual water vapor (*108*). The miniaturized microwave induced plasma with a plasma that exits from the channel in the wafer into the atmosphere was found to be stable when coupled to electrochemical hydride generation for the determination of As and Sb with detection limits of 6 and 7 ng mL^{-1}, respectively. With the system, determinations in real samples such as coal fly ash after digestion or galvanic baths gave accurate results (*109*). In general elements volatilized by any volatile compound, the formation reaction can be determined as shown for the case of Br, Cl, S, and C (*110*). Another $He-H_2$ dc microplasma was realized between two needle electrodes positioned in plastic substrates and could be well used for exciting analyte vapors released from a miniaturized electrothermal evaporation unit. In the case of microliter samples containing Cd, Cu, K, Li, Mg, Mn, Na, Pb, and Zn, the detection limits were between 1.5 and 350 ng (*111*). Also, ultrasonic nebulization with cooling down for moisture removal could be used for sample introduction in a He-microchip plasma operated in a quartz tube placed inside the central channel of a poly(dimethylsiloxane) polymer chip, with which detection limits for Na, K, and Cu in the 0.2 mg L^{-1} range were obtained (*112*). Microplasmas also could be formed as nonthermal corona discharges inside liquids around electrodes with ultrasharp tips, allowing determinations of dissolved elements within nanoseconds and with femtoliter volumes of liquid (*113*). Fascinating innovation brings the exploration of microdischarges for portable sensing applications for the case of gases, e.g., ref 114. Further, many useful applications of microdischarges in further fields of science also were published, such as, e.g., the use of stenciling with an air microplasma for patterning cell lines on hydrophobic and cell repellent poly(dimethylsiloxane), methylated glass, and bacterial grade polystyrene surfaces (*115*).

LASER INDUCED BREAKDOWN SPECTROSCOPY

In the last years, laser produced plasmas have found a wide entrance as sources for atomic emission spectrometry. This is shown by the success of conferences such as EMSLIBS 2007 and the fifth International Conference on Laser-Induced Breakdown Spectroscopy (LIBS 2008), of which the proceedings have been published (see refs 116 and 117, respectively).

Many studies deal with the material volatilization and removal from the sample surface by laser action. For Al samples, the influence of the background gas was studied and a complex picture was drawn, where vaporization, melt displacement, melt expulsion, and phase explosion take place at different laser fluences (*118*). Also, the expansion phenomena of aerosols generated by laser ablation under a He and Ar atmosphere were studied in the case of near IR femtosecond laser and brass samples (*119*). Further, studies deal with the elemental fractionation and stoichiometric sampling in femtosecond laser ablation, as it can be studied by sampling the aerosol and subjecting it to electron probe X-ray analysis (*120*).

In other groups, especially diagnostic time and spatially resolved measurements at the laser, induced plasmas were performed by optical emission spectrometry, as described, e.g., in a review in ref 121. In another paper, the Stark broadening of the H_β line was studied for a plasma generated in air at an Al surface so as to evaluate time- and space-resolved changes of electron number densities and temperatures (*122*). Instrumental innovation dealt with the use of spatially confining the laser-induced plasma so as to obtain an enhancement of the LIBS

signal (*123*). Also, the use of a duplicating mirror to evaluate self-absorption effects in laser induced breakdown spectroscopy was described (*124*).

A numerical model describing laser−solid interaction (i.e., heating, melting vaporization), vapor plume expansion, plasma formation, and laser−plasma interaction, to the conditions of double pulse laser ablation or LIBS, was applied by Bogaerts et al. (*125*). A comparison was made with the results of a single pulse with the same total energy. Because the model is limited to plume expansion times on the order of a few 100 ns, the interpulse delay times were varied between 10 and 100 ns. The maximum target temperature was found to be slightly lower in the double pulse configuration, which resulted in a somewhat lower amount of target evaporation. On the other hand, target temperature was found to rise again upon the second laser pulse, and it remained somewhat higher for longer observation times. Hence, the target remains in a molten state for a longer time, which might result in more laser ablation due to the splashing of the molten target. Furthermore, the plasma shielding was found to be clearly lower in the double pulse configuration, so that relatively more laser energy can be available for the laser ablation process itself. Finally, the plasma expansion dynamics clearly demonstrated two different waves of the expansion velocity, due to the two laser pulses. The second velocity pulse is clearly higher, due to the reduced background gas pressure in front of the target, as the background gas is already pushed away from the target as a result of the first laser pulse. Also, the maximum plume temperature and electron density remain somewhat higher at later observation times in the double pulse configuration.

Analytical studies with LIBS are manifold. A generally interesting approach is the work done on the absolute characterization of laser-induced breakdown spectroscopy detection systems (*126*), including CCD and intensified CCD detection and both Czerny-Turner and Echelle spectrometers.

Many studies deal with metal samples. A challenging aspect is the solution of problems related to the inhomogeneous optical thickness of the plasmas, which was studied in the case of the Co−Cr−Mo alloy (*127*). Here, a two-region plasma picture of a hot dense core surrounded by a colder periphery, where both self-absorption and inhomogeneity effects were taken into account, was used to come to a standardless calibration. Interesting studies were made with double pulse laser induced breakdown spectrometry. Here, studies on the variations of the lead emission intensities with the wavelengths and the sample matrix were made (*128*). It was found that for ZnAl and CuSn samples different sensitivities were found in the case of different emission lines. Also, in the case of electrically nonconductive powders such as silicate raw materials for the brick-and-tile industry, the use of double-pulse and single-pulse LIBS was compared (*129*). It was found that in the first case the detection limits for Si and Mg after optimization of all parameters were 10 times lower. The use of femtosecond lasers also found entrance in LIBS. A comparison of nanosecond and femtosecond laser induced breakdown spectrometric analysis of bronze samples was performed and a series of binary (Sn−Cu), ternary (Sn−Zn−Cu or Sn−Pb−Cu), and quaternary (Sn−Zn−Pb−Cu) reference alloys were analyzed (*130*). It was found that in every case a detailed optimization of the working parameters was necessary so as to realize the full analytical performance. A promising way to come to standard-free calibration has been shown for the case of aluminum alloy samples by working under vacuum conditions (*131*). This included the use of a Monte Carlo simulated annealing optimization method and the recording of the plasma emission in the imaging mode and binning the resulting image into 11 different spatial portions along the axial direction. The use of a complementary metal oxide semiconductor sensor array based detection system for LIBS also was described, and an evaluation of the calibration strategies in the case of the determination of manganese in steel was performed (*132*). The 1024 pixel array covered the wavelength range of 250−390 nm, and both univariate and multivariate calibration strategies determinations in the concentration range of 0.2−0.6% could be performed.

Further, work was done on the direct analysis of powders with LIBS. For iron oxide powders, the use of a simple powder delivery system for loose powder was tested as well as the use of powder pellets for the case of nanoparticle powders and determinations of Al, Si, Ni, and Mn performed (*133*). LIBS was found to be a prominent method for determining the percentage of uranium in thorium−uranium mixed oxide fuel samples as a part of the chemical quality assurance of fuel materials (*134*). Except for U I 263.533 nm, all the other emission lines exhibited a saturation effect due to self-absorption when the U concentration exceeded 20% wt in the Th−U mixture. Both the combination of a single-pulse laser ablation with spark excitation of plasma plume triggering the gap between electrodes close to the target surface and a conventional double-pulse LIBS were used for total carbon determinations in soils (*135*). In both cases, a nonlinear calibration curve was obtained. In the combined laser-spark approach, the use of low-cost and portable laser instrumentation is possible and only microdamage of the target surface is accomplished. Further, LIBS was shown to be of great use as a tool for discrimination of glass for forensic applications (*136*). The sample preparation was found to be minimal, and glass materials could be characterized by their unique spectral fingerprint. Glass spectra from car windows could be linked through linear correlation combined with the use of a spectral mask, which eliminates some high-intensity emission from the major lines present in glass. LIBS was also shown to be of use for the detection of residues of explosives (*137*). Here, a reduction of the air entrainment in the plasma was important, as they hampered quantification for O and N being instrumental for the identification of explosives, and also, remote analyses have been shown to be possible. Instrumental innovation deals with the use of acousto-optical tunable filters coupled to photomultiplier detection for the determination of Mn in steel by LIBS (*138*). Here, it was shown that the same analytical performance could be obtained as with a commercial Echelle-intensified charged-coupled device detection system. Also, a spatial and temporal probing of a laser-induced plasma plume by cavity ringdown spectroscopy has been described (*139*). Here, a model was developed to perform a forward convolution of atomic absorption line profile measurements.

Laser induced spectroscopy was also applied for the analysis of liquids (*140*). In the case of wet aerosols, even from a distance of 10 m, the doublet of Na could be measured and a detection limit at the 50 μg mL^{-1} was obtained. With LIBS performed directly at the surface of solutions, the H_α and H_β lines could

be used to determine electron number densities with spatial resolution (*141*). Ultrasensitive trace metal determinations in aqueous solutions could be performed by LIBS after electrical deposition of the analytes on an aluminum surface (*142*). In this way, detection limits for Cr, Mn, Cu, Zn, Cd, and Pb of 0.6, 0.4, 0.08, 6, 0.5, and 0.6 $\mu g\ L^{-1}$ could be obtained. Instead of solutions, also, slurries can be directly analyzed by LIBS (*143*). This was shown in applications for slurries, as obtained in the vitrification process of liquid radioactive wastes.

When at the laser-produced plasma plume detection by laser-excited fluorescence is used instead of atomic emission spectrometry, the power of detection, generally can be much improved (*144*). Here, the laser beams for sample ablation from the frequency-quadrupled Nd:YAG laser and for fluorescence excitation, respectively, were entered under different angles, and for Fe and Pb, detection limits of 65 and 39 ng mL^{-1} were obtained. In an independent study with a micro-LIBS system, a similar detection limit for Pb in drinking water (35 $\mu g\ mL^{-1}$) could be obtained (*145*). The combination of LIBS and laser-induced fluorescence, also in the case of steel samples, enables it to determine P in steel down to the level of several tens micrograms per gram (*146*).

For the generation of spatially resolved information on the molecular and elemental composition, Raman and laser-induced breakdown spectroscopy can easily be integrated into a single system, in which even the same laser is used as well as a dual arm Echelle spectrograph (*147*). The LIBS system enables detection limits at the microgram per gram level, and the capabilities of the system are demonstrated by the mapping of heterogeneous mineral samples and layer-by-layer ablation of pigments. Such a system of course is also very powerful for spectroscopic studies at works of art, when a single LIBS and pulsed Raman spectroscopy are used (*148*). Examples in the studies of frescoes, Terra-cotta, and a bronze head were given.

GLOW DISCHARGE OPTICAL EMISSION AND MASS SPECTROMETRY

Glow discharge optical emission spectrometry (GD-OES) and mass spectrometry (GDMS) have been routinely used for many years for bulk and depth profiling analysis of solid materials, and also, in the last two years, a great number of papers were published in this field. However, also, several new developments and fundamental studies were reported, mainly on the effect of gas impurities and on pulsed glow discharges (GDs). For the latter, also, a great number of application studies have been reported, especially in combination with time-of-flight mass spectrometry (TOF-MS). Besides, the trend of previous years toward novel applications, such as gas and liquids analysis, has been continued. In this respect, several new source designs have been proposed, most often working at atmospheric pressure.

Fundamental Studies. To further improve the analytical performance of GD-OES and GDMS, fundamental studies continue to be important. In the last two years, fundamental research was mainly carried out in two distinct fields, namely, the effect of molecular emission and gas impurities, as well as the characterization of pulsed discharges.

Bengtson (*149*) presented a review paper on the effects of molecular emission in compositional depth profiling by GD-OES. It is demonstrated that molecular emission gives rise to elevated backgrounds due to a continuum spectrum, leading to false depth profile signals of several atomic lines. Molecular emission spectra from mixed gases were presented, illustrating that dissociation and subsequent recombination processes occur, leading to the formation of molecular species not being present in the original plasma gas. The possibilities to make adequate corrections for such molecular emission in the depth profile analysis of polymer coatings and very thin films were also discussed.

Steers et al. (*150*) presented an overview of the effects of H_2, N_2 (both ~2% v/v), and O_2 (~0.25% v/v) on the electrical characteristics, the sputtering rate, and the emission spectrum of GDs in noble gases. Most emphasis was given to the effects of H_2 addition. Some of the effects can be explained in terms of the excitation processes, but it is stated that further work will be required for other sample materials and noble gases before a comprehensive picture can be obtained. The effect of H_2 and N_2 (up to 2% v/v) on the atomic emission line intensities of Fe and Ti was investigated by Smíd et al. (*151*). Some interesting features were observed, some of which yet unexplained. In the case of H_2, when plotting the intensity ratios (i.e., measured in Ar/H_2 compared to pure Ar) vs the excitation energies, a rise in the intensity ratios was observed between 3 and 5 eV for both elements. In addition, an enhancement between 5.3 and 5.6 eV was observed for Fe. Hence, these lines should be avoided in analytical use. On the other hand, for N_2, no enhancements in emission line intensities were observed. Finally, Martin et al. (*152*) studied the effect of H_2, with concentrations of 0.5%, 1%, and 10% v/v, on the emission spectra of some atomic lines for Cu, Zn, and Ni, by rf-GD-OES. Different trends were observed, depending on the line characteristics. In general, the emission intensities of the nonresonance lines did not change significantly, whereas the resonance lines exhibited a very pronounced increase in emission yields, which could be related to the possible drop in self-absorption upon H_2 addition (*152*).

Bogaerts performed computer simulations to study the effect of H_2 addition (in the range of 0.1−10% v/v) to an Ar Grimm-type GD (*153*). The species described in the model include electrons, Ar^+, ArH^+, H^+, H_2^+, and H_3^+ ions, H atoms,H_2 molecules, Ar atoms in the ground state and the metastable level, and sputtered Cu atoms. Sixty-five different reactions between these species were taken into account. Similarly, in refs 154 and 155, a hybrid model was developed for $Ar-N_2$ and for $Ar-O_2$ Grimm-type GDs, respectively. In the $Ar-N_2$ model (*154*), the relevant species are the electrons, Ar^+, N^+, N_2^+, N_3^+ and N_4^+ ions, N atoms, and N_2 molecules in the ground state and in 6 different electronically excited levels, as well as the Ar atoms in the ground state and in the metastable level. These species interact with each other in 74 different chemical reactions. Finally, the $Ar-O_2$ model (*155*) considers 87 different reactions, which take place between the following species: electrons, Ar^+, O^+, O_2^+, and O^- ions, O atoms in the ground state and one metastable level, O_2 molecules in the ground state and two metastable levels, O_3 molecules, and the Ar gas atoms in the ground state and the metastable level. Hence, although the three gases are all diatomic in nature, different species appear to be formed in the glow discharge. The $Ar-O_2$ discharge is especially interesting, because also negative ions

(O^-) are present in the discharge, although still at a lower concentration than the positive ions. Typical results of these models include the density profiles of the various plasma species, the relative importance of their production and loss mechanisms, and the ionization and dissociation degree, as well as the effect of the gas addition on the sputtering process (*153–155*).

The effects of N_2 impurities were also investigated by this group for an atmospheric pressure glow discharge (APGD) in He, by means of fluid and Monte Carlo simulations (*156*). More specifically, an APGD design developed by Hieftje and co-workers in 2006 was studied. It operates in He between a rod-shaped cathode and an anode characterized by a conical end, which are separated by a 1 cm distance. Because some nitrogen peaks were detected in the emission spectrum, 10 ppm N_2 was assumed to be present in the discharge. In another paper by this group (*157*), it was demonstrated that at small concentrations (in the lower parts per million range) the nitrogen ions can already play a dominant role in the plasma composition. Therefore, the species included in the model comprise the background gases He and N_2, the He^+, He_2^+, N_2^+, and N_4^+ ions, the metastable He atoms, and He_2* excimers, as well as the electrons (*156*, *157*). Typical calculation results include the potential and electric field distributions inside the plasma, the density profiles of the various plasma species, and the mean electron energy, as well as the rates of the various collision processes in the plasma and the relative importance of the different production and loss mechanisms for the various species. Also, the similarities and differences with low pressure GDs were discussed (*156*).

As mentioned above, several groups also performed fundamental research on pulsed discharges. Fliegel and Günther (*158*) investigated the electrical characteristics and breakdown conditions of a microsecond (μs) and millisecond (ms) pulsed GD. Current−voltage profiles were obtained for different discharge frequencies, pulse durations, cathode materials, gas pressures, and discharge gaps. The breakdown voltage was found to be dependent on the cathode material. A higher discharge frequency leads to a rise in the electrical current, attributed to a more dense plasma during the pulse. It was concluded that the ms pulsed discharge follows the principle equations of a dc steady-state GD and, therefore, that the operating parameters of the pulsed GD can be optimized on the basis of already established knowledge of dc GDs.

Hoffmann et al. (*159*) presented measurements of electrical current and voltage for GDs in continuous and pulsed, dc and rf modes. In continuous dc and rf mode, the transformation of current−voltage into power-voltage curves simplifies the determination of threshold voltages and saturation currents. From the comparison of those curves, it could be concluded that the effective voltage in rf mode corresponds best to the voltage in dc mode. In pulsed mode, the variation of pulse length and frequency influences the current−voltage curves. It was demonstrated that the current−voltage curves in continuous dc mode were nonlinear, and this was attributed to gas heating. For the same reason, a dependence of the current−voltage curves on the duty cycle of pulsed discharges was observed. By comparing these curves with those at low duty cycle (i.e., cold plasma), a rough estimation of the gas temperature could be made.

Voronov and Ganeev (*160*) presented a model for a μs-pulsed GD in hollow cathode geometry. The pulse-on period was described by Monte Carlo simulations and a new method for electric field calculation. The afterglow was treated by continuity equations and Poisson's equation. Processes such as sputtering, ionization, and transfer of sample were investigated. Similarly, Martin et al. (*161*) applied a Monte Carlo model to study the thermalization of electrons in the afterglow of a μs-pulsed glow discharge. Special attention was paid to the electron−electron Coulomb collisions. The electron energy distributions, the average electron energy, electron density, and the rates of the various electron induced processes were calculated for different times during and after the pulse and for different positions in the plasma. The electron thermalization time in the afterglow was found on the order of 50 μs.

Finally, Nelis and co-workers (*162*) published a review paper on pulsed GDs. In the first part, the most important physical processes (such as excitation and ionization) occurring during the plasma ignition phase and the afterglow were outlined, as well as the time evolution of electron and sputtered atom densities. In the second part, the analytical applications, for both MS and OES, were presented, with emphasis on the importance of time-resolved signal acquisition.

Methodological Studies and Applications of GD-OES and GDMS. As most of the routine applications of GD-OES and GDMS are related to depth profiling, a number of methodological studies focus on this application field. Molchan et al. (*163*) proposed a plasma cleaning procedure to improve the elemental depth profiling of shallow layered materials by either GDMS or GD-OES. The procedure is based on two approaches applied before the real depth profiling, either individually or sequentially. The first approach was based on a low energy ("soft") plasma that removes contaminants from the cathode surface. The second approach used a so-called sacrificial material, which was first sputtered, under normal depth profiling conditions, to clean the inner surface of the GD cell (at anode potential). The plasma cleaning procedure was found to improve the analytical results, especially at the beginning of the sputtering, due to stabilization of the plasma as a result of contaminants removal.

Klemm et al. (*164*) demonstrated the potential of both dc and rf GD-OES for the quantitative surface and depth profile analysis of adsorbed organic monolayers, by the use of advanced vacuum instrumentation and presputtering with silicon.

Escobar Galindo and Albella (*165*) presented a method to model the broadening effects found in depth profiles of periodic multilayers obtained by GD-OES. The method assumes that the surface roughening due to ion bombardment leads to a partial mixing of the layers, thereby smoothening the depth profiles. Therefore, the concentration profiles of each layer are described by Gaussian functions, with parameters that are determined by fitting the theoretical spectra to experimental profiles. The method appears to properly describe the depth profiles of multilayer structures of two elements in the 10−100 nm range.

In a later paper (*166*), the same group compared the capabilities of GD-OES with those of Rutherford backscattering spectrometry and secondary ion mass spectrometry for the depth profiling analysis of nanometer-metal multilayers. It was concluded that GD-OES allows for quick and accurate depth profiling,

although the depth resolution degrades linearly with depth due to sputtering effects. Similarly, Wienold et al. (*167*) compared GD-OES with spark OES and IR laser ablation for the elemental analysis of Cu and Mg alloy samples. In general, the three methods appeared to yield similar results in terms of precision.

Hodoroaba et al. (*168*) performed a feasibility study on different coatings, i.e., electroplated zinc, carbon-rich coatings, and amorphous silicon layers, to be used as potential new certified reference materials for the determination of hydrogen concentration by GD-OES. The latter can be useful also for other analytical methods.

Weiss et al. reported that a new catalogue of GD spectra will be collected, on the basis of a high resolution Fourier transform spectrometer and two commercial CCD spectrometers (*169*). Preliminary data were presented for Fe as well as for Cu, and it was illustrated that the future catalogue could be used to identify and evaluate line interferences and select the most suitable analytical lines for a given application.

The analytical performance of krypton and argon as discharge gases for GD-OES was compared by Wagatsuma (*170*). He observed particular intense ionic lines, which were different depending on the discharge gas. This was attributed to the selective population of certain excited ionic levels due to collisions with the gas ions. These observations, therefore, confirm earlier studies by several research groups about asymmetric charge transfer being responsible for the selective excitation of certain ion levels.

Gusarova et al. investigated the hollow cathode effect for sensitivity enhancements of Grimm-type dc GD-OES (*171*). Signal enhancements up to a factor of 150 were demonstrated, in comparison to flat samples, allowing also a better separation of the analytical lines from spectral interferences. Similarly, Qayyum and Mahmood also compared a dc GD-OES system with plane and hollow cathode configuration (*172*). It was demonstrated that the source with hollow cathode configuration was operated at a lower input power and generates higher Cu I and Cu II line intensities.

Zenatini et al. (*173*, *174*) measured two-dimensional emission images (in the radial direction) from a GD source and demonstrated that the emission intensities were higher in the center and became weaker at a larger distance from the central zone. They attributed the nonuniformity in emission intensities to a spatial variation in the excitation efficiency of the plasma (*173*). They also reported on depth profiling of the metallic coatings based on the emission images (*174*).

Finally, the solid-state speciation capabilities of rf-GD-OES were demonstrated by Malherbe et al. (*175*, *176*) , by determining the oxidation states of Fe, Cr, and Al in iron or chromium oxide and in alumina films. The quantitative depth-profile analysis of these films was also carried out, by an alternative quantification methodology with correction for the dc bias voltage (*175*). Furthermore, in ref 176, the effect of sputtering on the modifications in the surface morphology was discussed. It was found that preferential sputtering of the oxygen atoms resulted in a metal-enriched surface, thereby promoting the reduction of the metal elements.

With respect to GDMS, nearly all papers published in the last two years report the use of TOF-MS, mostly in combination with a pulsed or rf GD, for various applications, ranging from bulk and depth profiling of different samples (such as glass, polymer films, etc.) to solid-state speciation.

Ganeev et al. (*177*) measured relative sensitivity factors (RSFs) for a pulsed GD in a combined hollow cathode, coupled with TOF-MS. The RSFs were found to be close to unity for the majority of elements, and the range was significantly narrower than for dc GDs. This might open new perspectives for semiquantitative analysis without the use of certified reference samples.

The Oviedo group was very active in the field of GD-TOF-MS, both for methodological studies and applications, with different types of GD sources. Vega et al. (*178*) presented the construction and analytical capabilities of a compact magnetically boosted rf GD in combination with TOF-MS. The effect of the magnetic field on the basic GD processes, such as sputtering, ionization, and ion transport into the TOF-MS, was investigated. The authors claim that a magnetic field of 60−75 G resulted in higher analyte signals while decreasing the Ar ion signal. Meanwhile, this field did not affect the sputtering rates and the crater shapes, so that fast and sensitive analysis of thick coated samples with high depth resolution appears possible (*178*). González Gago et al. (*179*) reported on the analysis of small bubbles in glass by rf-GD-TOF-MS. The operating conditions of the rf-GD (i.e., pressure and applied power) were optimized, and detection limits on the order of nanoliters were obtained for molecular nitrogen, oxygen, and carbon dioxide. Lobo et al. (*180*) compared a nonpulsed and pulsed rf-GD-TOF-MS system. The sensitivity in the pulsed mode was improved compared to the nonpulsed mode, as well as the ion separation capability, the accuracy, and precision for determining isotope ratios. Muniz et al. (*181*) used a pulsed rf-GD-TOF-MS for the direct analysis of bulk and thin coated glasses. Complete mass spectral information was obtained from the different GD pulse domains (prepeak, plateau, and afterglow). The analyte ions exhibited their peak maxima in the afterglow, some hundred μs after the Ar ion signal, but the delay times were different for the different elements or isotopes. The operating conditions were optimized for the best analytical performance. Moreover, the system was evaluated for qualitative depth-profile analysis of thin coatings and a depth resolution in the nanometer range was obtained. A μs-pulsed dc-GD-TOF-MS system was used by Solà-Vázquez et al. (*182*) for obtaining elemental and molecular chemical information. The analytical capabilities of this setup were explored using bromochloromethane as model analyte.

King and co-workers (*183*) used a ms-pulsed rf-GD-TOF-MS system for the direct speciation of chromium in solid-state samples. Elemental, structural, and molecular information could be obtained. By careful tuning of the operating parameters, the plasma chemistry could be reached that favors cluster ion formation. In this way, differentiation between Cr(III) and Cr(VI) in chromium oxide samples could be made. In a subsequent paper (*184*), Zhang and King presented the quantification of Mn(II)/Mn(IV) oxidation states in solid-state samples, by pulsed GD-TOF-MS. This method allows direct speciation for solid-state materials, without extraction procedures. By optimization of the operating parameters of the pulsed GD source, the production of the cluster ion, $Mn_2O_3^+$, which is characteristic for Mn(IV) dioxide, could be favored, enabling the differentiation between the two oxidation states.

Canulescu et al. (*185*) reported on the detection of negative ions for halogens and halogenated molecules in the afterglow of a pulsed GD in Ar coupled with TOF-MS. Indeed, the plasma sampling interface was capable of switching between positive and negative ion mode. A considerable enhancement of the negative ion signal for halogens and halogenated molecules and a reduction in the background signal were observed in the afterglow region. The usefulness of this method was illustrated for the analysis of a polytetrafluoroethene (PTFE) polymer film. The same groups demonstrated the potential of pulsed rf-GD-TOF for the molecular depth profile analysis of polymer materials (*186*). Indeed, in the afterglow, fragment ions were found to be present that could be related to the structure of the polymers. Multilayered structures of different polymers were analyzed, and different layers with similar elemental composition but different polymer structure could be distinguished.

The only GDMS study, which did not make use of a TOF-MS system, was reported by Voronov et al. (*187*). The authors combined a μs-pulsed GD with an existing commercial sector-field mass spectrometer (Element). Although improvements in the detection limits had been expected, they turned out to be similar to the dc case, which was explained by the geometry of the existing GD cell. However, with time-gated ion detection, the signal-to-noise ratio can probably be improved, so that better detection limits can be obtained. This is planned for future work.

Finally, Pisonero et al. (*188*) published a critical review about the analytical performance, capabilities, pros, and cons of GDMS, LA-ICPMS, and SIMS for the characterization of solid samples. It was stated that further developments and improvements of these techniques requires the fundamental understanding of key-phenomena, such as sputtering/ablation and ionization/vaporization processes, the characterization of sputtered/ablated surfaces, ion/particles transport, and detection methods. The characteristics, advantages, and limitations of the three techniques were summarized in a table, and it could be concluded that they are complementary analytical tools, which cover together many fields of application for solid sample analysis. LA-ICPMS provides a high lateral resolution (tens of micrometers) and an adequate depth resolution (hundreds of nanometers) and can be used for a wide range of applications. GDMS is mainly used for materials science applications (both bulk and depth profiling), showing a poor lateral resolution (~millimiter) but an excellent depth resolution (~nanometers). Finally, SIMS gives excellent lateral (nanometers to micrometers) and depth resolution (~nanometers) and is particularly interesting for imaging and depth profiling applications in biology and materials science.

New GD Sources for Novel Applications and Combined GD-LA Systems. As mentioned in the beginning of this section, a number of new GD source designs were presented in the last two years for liquid and gaseous analysis, typically operating at atmospheric pressure, and were often applied as a detector for liquid or gas chromatography. Also, the combination of GD sources with laser ablation (LA) has been reported a couple of times.

Shekhar et al. (*189*) developed an electrolyte-as-cathode GD (ELCAD) with a new design. Plasma fluctuations arising from the variations in the gap between anode and liquid cathode were eliminated by providing a V-groove to the liquid glass capillary. The analytical performance, in combination with AES, was evaluated.

The Hieftje group was particularly active in the field of new GD source development. In ref 190, Webb and Hieftje presented a feature article about the short history and different types of solution cathode discharges. It is concluded that their most fruitful applications are in miniaturized and/or portable devices. Their small size and lower power consumption make them well suited for field analysis. In ref 191, this group reported on a solution-cathode GD, used for cold vapor generation of mercury. Dissolved mercury species were converted to volatile Hg vapor, which was transported to an ICP for determination by AES. The technique appears to offer several advantages compared to other vapor generation methods. Indeed, it is very efficient, extremely rapid and, therefore, easy to couple with flow injection. It is also sensitive, simple in operation, and requires no auxiliary reagents. Finally, it is applicable to both inorganic and organic Hg determination.

Hieftje and co-workers also developed an atmospheric pressure glow discharge (APGD) used in the flowing afterglow mode (so-called flowing atmospheric pressure afterglow, FAPA), to be used as a chemical ionization source for organic mass spectrometry (*192*). The species generated by this APGD were mixed with ambient air to generate reagent ions (such as ionized water clusters and NO^+), which are used for the ionization of gaseous organic compounds. A wide variety of compounds can be ionized. The analytical capabilities of this source were evaluated with a TOF-MS. In ref 193, the source was also applied to the direct analysis of solid compounds. Examples of the analysis of pharmaceutical compounds or foods were provided. Furthermore, the ability of this source to perform spatially resolved analysis was also demonstrated. In ref 194, this FAPA was combined with a laser ablation system, to perform 2D molecular mass spectral imaging. A spatial resolution of ~20 μm was reported. Moreover, depth information could also be obtained over 2 mm, with a resolution of ~40 μm. A comparison of this FAPA source with another ambient ionization source, called DART (direct analysis in real time), was performed in ref 195. Although both sources appear similar at first sight, they show clear differences. Indeed, DART was found to operate with a corona-to-glow transition, whereas the FAPA operated with a glow-to-arc transition, which is characterized by a higher gas temperature (i.e., 235 °C vs 55 °C for DART). In addition, the FAPA source produced a greater abundance and a wider variety of reagent ions. Spatially resolved emission maps of both discharges also showed clear differences. Because both discharges were found to be fundamentally different, it was concluded that they should have different optimal applications for ambient desorption/ionization mass spectrometry. Finally, in ref 196, the capabilities of this source for the detection of gas phase elemental species, produced by hydride generation, were demonstrated, including the possibility of performing speciation by coupling with a separation technique.

Jecklin et al. (*197*) built a flowing afterglow (FA)-APGD after the design of Hieftje and co-workers (*192*, *193*) and coupled it with tandem MS (APGD-MS/MS) for the analysis of trace amounts of pesticides in fruit juices and oil fruit peel. The analytical capabilities of the method were investigated, and it was demon-

strated that no sample pretreatment was necessary to analyze the pesticides by direct desorption/ionization with APGD-MS. In another paper (*198*), the same group used this method for fast polymer fingerprinting and for different types of polymers including biopolymers and synthetic homo- and copolymers. They stated that the main advantages of this technique are the speed (<30 s per sample), the analysis at atmospheric pressure, the wide variety of polymer samples that can be analyzed (i.e., liquid and solid (soluble and insoluble) bulk polymers and granulates, irrespective of their conductivity), and no sample preparation requirements.

Dong et al. (*199*) developed an APGD used for ion mobility spectrometry (IMS), to overcome the problems associated with the conventional ^{63}Ni source. The authors showed that this new source has great potential for applications in IMS, such as online monitoring of environment pollutants and halogenated compounds.

GD sources are also being used as detectors for chromatographic separations. Quarles and Marcus (*200*) presented their particle beam hollow cathode optical emission spectroscopy source (PB/HC-OES), interfaced with a high resolution polychromator, allowing simultaneous multielement analysis, for the use as a species-specific detector for chromatographic separations. The operating parameters, such as nebulization conditions, desolvation temperature, GD current and pressure, and the source block temperature, were optimized. The ability of this method to monitor both metals and nonmetals was demonstrated, which opens new possibilities of this system to be used for metallomic studies. Similarly, Balarama Krishna and Marcus (*201*) investigated the role of the cathode material (Cu, Ni, or Ta, which have high, moderate, and low sputtering rate, respectively) in liquid chromatography particle beam GDMS (LC-PB/GDMS), more specifically the ionization, fragmentation, and analytical characteristics of organic, organometallic, and metal species. Relative detection limits for the test species were found in the order of Cu > Ni > Ta, hence following the order of the sputtering characteristics.

A particle beam (PB) pulsed GD-TOF-MS was combined with a laser ablation (LA) system, by Fliegel and Günther (*202*). They used this setup for fundamental studies and showed that particles ablated from metal and glass, with high melting and vaporization points, were not ionized in the GD, due to the typically low gas temperature. On the other hand, particles ablated from soft materials, such as PTFE and PVC polymers, were successfully vaporized and ionized in the GD. Lowering the GD electrical power favored the appearance of fragments, such as CF_x^+, whereas higher plasma powers favored the ion signals of the elements (C^+, F^+). Furthermore, the capability of LA-PB-GD-TOFMS for the quantitative analysis of halogens in organic particulate matter was demonstrated. In ref 203, Günther and co-workers also combined GD-TOF-MS with LA, to study the analytical capabilities resulting from the interaction of a laser-generated sample plume with a pulsed GD. Two ablation configurations were studied, either with the laser-generated plume introduced in the GD or with the plume generated inside the GD. It was found that ablation into the afterglow of the pulsed GD leads to an ion signal enhancement up to a factor of 7, compared to the LA process alone. The duration of the enhanced signal was found to be around 2 ms. Finally, Tereszchuk et al. also combined a glow discharge, operating in either steady-state or pulsed mode, with a pulsed LA system, to additionally excite the material ablated by the incident laser pulse (*204*, *205*). In this way, the laser pulse energy could be reduced below the excitation and ionization thresholds, to values needed solely for the material ablation, thereby limiting the sample damage and improving the lateral resolution. The new dual GD-LIBS synchronization scheme provided clear signal enhancements compared to both GD or LIBS under identical conditions. Moreover, in ref 205, the advantages of this GD-LIBS setup for depth profile analysis were demonstrated.

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Recent developments in the field of elemental mass spectrometry are still driven by the increasing demand for high sample throughput in routine analysis and the need for the highest possible sensitivity and precision combined with fast and preferably simultaneous multielemental detection capabilities. Also, remaining ionization source- and spectrometer-related shortcomings are the major subjects of modern research. Therefore, 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 further increased substantially during the last two years. Also, high-resolution multiple collector sector field ICPMS has been further expanded in the field of isotope analysis. In contrast, a decreasing number of novel or fundamental studies using collision and/or reaction cells for the specific removal or reduction of polyatomic ions was recognized, although many applications are still being published, especially in the field of the analysis of biological material and environmental samples. This indicates that ICPMS has finally become a routine method for elemental analysis, which is also the case for hyphenated techniques for speciation and bioanalysis, e.g., structure determination of organometallic species.

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 (*4*) of this review series. It should be mentioned, that the selection of representative or significant papers was again 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: *Applied Spectroscopy*, *International Journal of Mass Spectrometry*, *TRAC-Trends in Analytical Chemistry*, *Rapid Communication in Mass Spectrometry*, *Journal of the American Society for Mass Spectrometry*, *Mass Spectrometry Reviews*, *Proteomics*, and *Metallomics*.

In an interesting paper by Hieftje (*206*), the reader is guided on a somewhat subjective historical walk through instrumental developments. It is based on the author's viewpoint and on both his personal and his research group's experiences. Hieftje shows that exciting opportunities still exist for even greater capabilities from future instrumentation for plasma source mass spectrometry. Alternative ion sources and mass analyzers were also examined in this trend article. Commercial perspectives from scientists working in the instrument companies on the growth and development of quadrupole, high resolution, and multiple collector ICPMS markets were given by Potter (*207*) and Douthitt (*208*). Technological and methodological achievements in ICPMS to acquire and handle short transient signals were reviewed by Tanner and Günther (*209*) to outline capabilities and limitations of such technology or hyphenated techniques. In the authors' opinion, the dynamic processes in the plasma have to be controlled to ensure quality of quantitative results. Although most precise instrumentation is used, which is to date multicollector sector-field MS, drifting isotope ratios are still observed in transient signals, thus limiting precision of such measurements. In principle, while TOFMS is found as an alternative to provide fast simultaneous multielement detection, scanning instruments are fundamentally restricted. It was mentioned that new commercial ICPMS instruments can be expected in the near future, making short transients more and more attractive to shorten acquisition times and to increase the signal-to-noise ratio of element analyses. Vanhaecke and coworkers (*210*) presented an extensive review on the subject of electrothermal vaporization (ETV) ICPMS. The possibilities of this technique for dealing with very challenging analytical applications were evaluated, and the establishment of a reference guide for method development in ETV-ICPMS was given. Topics such as milestones in the development of the technique, basic processes occurring in the furnace and during analyte transport, comparison of newer types of ICPMS instrumentation, and the latest contributions in the main application areas of the field were treated. Special emphasis was given to speciation analysis and to "thermal" resolution, enabling complex matrixes to be analyzed and spectral overlap to be avoided, as well as to the direct analysis of slurries and solid samples. In a review paper on the application of ICPMS in clinical pharmacological oncology research, Brouwers et al. concluded that ICPMS is a powerful tool for the quantitative analysis of metal based anticancer agents from multiple sample sources (*211*). A systematic survey of publications was given, describing the analysis of Pt- and Ru-containing anticancer agents through the determination of total metal concentrations and speciation of metal compounds in biological fluids, DNA- and protein-adducts, and environmental samples.

Fundamental Studies. The semiquantitative analysis mode in ICPMS is routinely used for fast screening purposes. Despite its benefits, its performance of application in real-world routine analyses has so far rarely been reported. In a study by Chen et al. (*212*), the reliability of semiquantitative analysis mode was evaluated through interlaboratory comparison using two different ICPMS systems with one multielement calibration standard. The suitability of this analysis mode in a routine analysis laboratory was demonstrated by evaluating its application in different laboratories and in real production laboratory practices. Various elements were determined in different fresh water reference samples, and good results concerning accuracy (better than 10%) and reproducibility (lower than 5%) were obtained in more than 90% of analyzed samples at concentrations equal to or greater than 10 times the detection limit. According to the authors, the results demonstrate the potential of semiquantitative analysis mode as a reliable approach in routine laboratory determination of simple matrixes, where high throughput and cost-effectiveness are desired, as well as in emergency situations where speed of analysis is critical and limited sample information is available.

In the case of liquid sample nebulization and HPLC- or CE-couplings, various groups focused on the comparison, optimization, and development of alternative nebulizer systems. Chung et al. (*213*) described a comparison of microconcentric (MCN) and membrane-desolvation (Aridus) sample introduction systems for the determination of low rare earth element concentrations in surface and subsurface waters using sector field ICPMS. Figures of merit were outlined, such as sensitivities, limits of detection, REE-oxide formation rates, matrix induced interferences, long-term signal variations, and recovery rates from spiked seawater samples and a pristine water CRM. A comparison of two CE-ICPMS interfaces with respect to precision, limits of detection, and ease-of-use was performed by Gammelgaard and co-workers (*214*) for the quantification of carboplatin in plasma samples. The CETAC CEI-100 and the Mira Mist CE from Burgener Research, the only other commercially available interface, where the CE capillary itself acts as the nebulizer, were considered for this study. It was described that the CEI-100 interface was more suited for the detection of carboplatin in the respective experimental setup. A relative detection limit for Pt of 21 μg L^{-1} corresponding to an absolute detection limit of 0.1 fg of Pt was found for the CEI-100 interface. Adsorption of the plasma proteins to the incubation vial or to the capillary and the formation of carboplatin adducts in concentrations below the limit of detection were found to limit the achievable accuracy. The authors conclude that data from quantitative CE-ICPMS measurements for kinetic profiling have to be critically evaluated. In a study by Lokits et al. (*215*), three nebulizer and four spray chamber configurations were evaluated to develop a selective and sensitive capillary interface to analyze phosphorothioate oligonucleotides by ICPMS. Nebulizers consisted of two of the most common low flow nebulizer designs, concentric and microconcentric. Spray chambers utilized were a Scott chamber, a Cinnabar chamber, and two single pass configurations, all with different internal volumes. The influence of nebulizer designs and spray chamber volumes were determined by peak width measurements through flow injections made with and without the capillary column. Comparisons of nebulizer/spray chamber responses were based upon absolute sensitivity for the 24 mer oligonucleotide. Microflow injection analysis generated absolute detection limits of ^{31}P and ^{32}S of 0.17 pg and 0.16 pg, respectively, corresponding to 16 fmol of 24 mer oligonucleotide injected.

Accuracy and precision of the $^{238}U/^{232}Th$ ratio in ICPMS analysis using pneumatic nebulization and repetitive pulsed nanosecond (ns) and femtosecond (fs) laser ablation (LA) at 266 nm were evaluated by Russo and co-workers (*216*). All three methods were thoroughly optimized, and it was shown that ns pulsed LA provided the greatest inaccuracy (>30%) from

the nominal isotope bulk ratio. This deviation was attributed to incomplete vaporization of large particle agglomerates produced by ns LA. Femtosecond pulsed ablation provided a 1−3% inaccuracy, approaching that of liquid nebulization (similar to 1%). In terms of temporal relative standard deviation (TRSD) and relative standard deviation (RSD), liquid nebulization provided the best precision for the $^{238}U/^{232}Th$ ratio (TRSD: 3−5%, RSD: 0.2−0.6%), followed by fs LA (TRSD: 5−12%, RSD: 1%) and ns LA (TRSD: 25−48%, RSD: 9−12%). However, LA requires less sample material to achieve this performance, in some cases less than a factor of 100-times depending on the entrainment and transport efficiency.

Hu et al. studied the effects of adding N_2 to the Ar and He central gas flow of an Ar plasma in LA-ICPMS (*217*). The optimum central gas flow rate was found to be negatively correlated with the N_2 gas flow rate. It was reported that the addition of 5−10 mL min^{-1} N_2 to the central channel gas in LA-ICPMS increased the sensitivity for most of the 65 investigated elements by a factor of 2 to 3. The degree of enhancement depended, to some extent, on the first ionization energy of the investigated element. One order of magnitude reduced oxide ratios (ThO^+/Th^+) were found to be an additional advantage of N_2 mixed gas plasma for LA-ICPMS. Through this measure, the hydride ratio (ArH^+/Ar^+) was also significantly reduced, whereas the doubly charged ion ratio (Ca^{2+}/Ca^+) and the nitrogen based polyatomic interferences were increased. Diagnostic measurements revealed that, compared to the spatial profiles of the ion distributions in the mode without N_2, the addition of 5 mL min^{-1} N_2 led to significant wider axial profiles and more uniform distribution of ions with different physical and chemical properties.

To minimize nonstoichiometric sampling in LA-ICPMS, an aerosol transport efficiency of less than 100% requires a representative aerosol composition for precise and accurate quantitative analysis (*218*). Therefore, Günther and co-workers used an in-cell aerosol extraction strategy to study aerosol expansion related changes in the composition of aerosols generated by a 193 nm excimer laser. The gas flow pattern within the ablation cell in the proposed local aerosol extraction was modeled using computational fluid dynamics techniques. Compared to commonly applied ablation cell geometry, the peak height of a single laser shot was increased by a factor of 13.5, the signal width was reduced by a factor of 12, and the washout time of the sample cell was consequently shortened to approximately 2 s, thereby almost eliminating processes of aerosol recirculation within the cell. The selective extraction of aerosol from different positions of the expanding laser plume was realized by subsequently changing the sampling distance between the ablation site and the gas outlet nozzle tip. The results showed a similar distribution of siderophile, chalcophile, and some of the lithophile elements within the expanding plume, and the plume composition was found to strongly depend on the ambient gas used within the ablation cell. The proposed local aerosol extraction strategy was found to be suitable for the identification of position dependent and, therefore, was an indirect indicator for particle size-dependent elemental composition of 193 nm laser generated aerosols under He atmosphere. In contrast to the ablation in He, the changes of the aerosol composition in Ar were less variable among different elements when sampling at different distances from the ablation crater. Results indicated that aerosol expansion within the ablation in UV ns LA can be a significant source of nonstoichiometric sampling, especially induced by aerosol deposition on the sample surface.

Fundamental studies and theoretical assumptions on matrix-dependent mass-discrimination in multicollector ICPMS along with experimental verifications were performed by Meija et al. (*219*). The authors found parts-per-thousand deviations from the conventional mass bias correction models which occurred with the use of multicollector ICPMS. On a similar topic Ohata et al. investigated the difference between a shielded and an unshielded ICP on the above-mentioned discrimination in quadrupole ICPMS isotope-ratio measurements of $^{52}Cr/^{53}Cr$ (*220*). Standard solutions prepared in different matrixes were examined, and thus, different Cr isotope ratios were observed under shielded ICP-QMS conditions. In contrast, such an effect was not observed with an unshielded ICP. It was found that the ion lens voltages strongly influence the matrix-dependent mass-discrimination effect under shielded ICP conditions, resulting in similar Cr isotope ratios after lens voltage optimization. The authors concluded that the space charge effect plays an important role in terms of mass-discrimination, particularly for lighter elements such as Cr.

An experimental investigation and computational modeling of polyatomic ions in ICPMS were performed by Ferguson et al. (*221*). Novel calculations based on spin-restricted open shell second order perturbation theory and coupled cluster theory were performed to determine the energies, structures, and partition functions of the ions. These values were combined with experimental data to evaluate a dissociation constant and gas kinetic temperature value. In the authors' opinion, these values can be interpreted to deduce the location where the polyatomic ion of interest is generated. All of these measured values were found to correspond to the formation of extra polyatomic ion in the interface or extraction region. The computations revealed the existence of isomers, which have virtually the same m/z values and have to be considered in the interpretation of results.

An internal correction of spectral interferences and mass bias in ICPMS through isotope pattern deconvolution (IPD) and its application to the determination of Se in biological samples by isotope dilution analysis were reported by Rodrgiuez-Castrillon et al. (*222*). The procedure is based on the measurement of the intensities at masses of 76−82 in the spiked samples, followed by the calculation of the isotopic composition of Se. This composition would be a linear function of the isotopic composition of natural abundance Se and that of enriched ^{77}Se if no mass bias or spectral interferences were present or if they were adequately corrected. Therefore, the molar fractions of natural abundance Se and isotopically enriched Se were calculated using IPD along with the variance of the multiple linear regression model. The variance of the regression was first calculated when no correction was applied, and then, this value was minimized by applying different factors for mass bias and the ratios of SeH/Se and BrH/Br. It was demonstrated that this procedure can eliminate the need for any external correction of mass bias or isobaric interferences in isotope dilution

analysis provided that enough isotopes of the element were measured.

Finley-Jones and Holcombe (*223*) presented a fundamental study on the selection of internal standards for ICPMS. It was investigated, whether previously selected "good" internal standards for several elements (51 different elements were previously ratioed to each other under a variety of altered matrix and instrumental conditions to find pairs that made good internal standards for each other) would remain good choices for the used instrument over an extended time period and whether changing instrumental platforms would alter the internal standard selections. The performance of these previously selected standards was evaluated on an ICP-TOFMS after several optimizations, a torch change, and nebulizer replacement and also on an ICP-QMS with a different nebulizer system, torch, etc. It was found that the internal standards predicted in the initial study continued to perform well on both platforms considered in the present study. In fact, overall errors were smaller in the second set of TOF data and on the quadrupole than those in the first set of TOF data. Mass and ionization potential trends were also similar to those from the previous study. Although there remains to be an equation allowing a priori selection of the ideal internal standard, the authors conclude that the prediction program developed in the previous study is effective over time and instrumental platforms.

In order to optimize the design of the ICPMS sampling interface, the knowledge of the gas flow upstream and in the sampling nozzle is of great importance. Therefore, Spencer et al. (*224*) applied a Direct Simulation Monte Carlo algorithm to the flow of neutral argon gas through the first vacuum stage of the ICPMS. Good agreement was found between the simulation results and the equations of fluid dynamics. The simulation revealed details of boundary layer formation in the nozzle, including a reduction in the total flow through the nozzle of about 15% from the ideal value calculated through fluid dynamics equations. In a second study, a comparison of ion and atom behavior in the first stage of an ICPMS vacuum interface was performed and evidence of the effect of an ambipolar electric field was found (*225*). Velocities of Ar atoms and Ca ions were measured in the first vacuum stage using high-resolution laser-excited fluorescence spectroscopy. The Ca ions reached terminal velocities in the supersonic expansion that were consistently 5 to 6% higher than those of Ar atoms, despite minimal differences in the masses of the two species. A computational model of the expansion was developed that shows the development of an ambipolar electric field along the expansion axis. With reasonable assumptions about electron temperatures in the expansion, the suggested model accounts for the differences between the terminal velocities of the neutral Ar atoms and the singly charged Ca ions.

The use of enriched stable isotopes and isotope pattern deconvolution (IPD) is well-known in the field of elemental species analysis. Iglesias et al. developed a mathematical tool to calculate supplemented and endogenous total Se contents in urine and feces by ICPMS (*226*). Also, quantification of endogenous and exogenous Se-species by HPLC-ICPMS has been worked out. The proposed IPD methodology, for total determinations and for quantitative speciation, was applied to reference materials to validate total Se quantification in feces and quantitative Se speciation in urine samples. Selenium apparent absorption and retention and natural and exogenous Se distribution in urine samples were calculated.

Instrumental Developments and Applications. An automated system for online preconcentration, separation, and detection of plutonium in a urine sample was developed by Lariviere et al. (*227*), on the basis of the coupling of a multisolvent delivery system, remotely controlled switching modules, and an ICPMS. Effective separation between spectral and nonspectral interferences and Pu was performed. The automated flow injection system (AFIS) allowed the quantification of Pu isotopes for urine analysis at the submillibecquerel per liter range in less than 15 min, with a chemical recovery exceeding 70%. The simplicity, speed, and automation of this approach were found to be advantageous by the authors for radiological emergency response, considering high possible sample throughput as a result of fast flow rates and the reusability of the extraction resin.

On a similar topic, Prohaska and co-workers (*228*) developed a fully automated Sr/matrix separation method, on the basis of flow injection (FI) hyphenated to a multiple collector (MC) ICPMS. In comparison with the common, manual, batch Sr/matrix separation procedure, the developed method is advantageous with respect to labor and reagent investment. It was validated through the analysis of Sr isotope reference material and digests of *Asparagus officinalis* at Sr concentrations of approximately 30−40 ng g^{-1}. Consecutive runs of the analysis resulted in an RSD of 0.03%, yielding an average $^{87}Sr/^{86}Sr$ isotope ratio of 0.71030 which was well within the certified range. Results were in agreement with those previously obtained via off-line Sr/matrix separation, and subsequent measurement of the respective isotope ratios was done by MC-ICPMS.

Brenner et al. (*229*) compared the analytical figures of merit (sensitivity, background, oxide rates, and time dependent and matrix induced interference effects) for solutions containing up to 500 mg L^{-1} Na for a conventional sampler cone designated as the high performance interface (HPI) with that obtained with a so-called Xi cone (both Thermo Scientific). HPI counts were higher than those observed using the Xi cone by factors of about 10 at low mass, the difference decreasing with increasing mass, and at high mass, they were approximately equal to those observed with the Xi cone. As a consequence of low sensitivity when the Xi interface is used, there is potential for determining high concentrations of low mass elements. The 4-times lower $^{40}Ar^{16}O^+$ signals and up to two times lower percentage of $^{140}Ce^{16}O^+$ of the Xi cone were found to be important analytical figures of merit for minimizing polyatomic ion interferences. The authors concluded that the HPI cone when coupled to a robust ICP is more suited for routine analysis of environmental samples. However, in cases where oxide ion interferences must be reduced and high concentrations of low mass analytes have to be determined, the Xi cone offers advantages.

In a report by Newman et al. (*230*), a number of prototype high sensitivity skimmers, which have been developed at Nu Instruments Ltd., were characterized. Signal enhancements of up to a factor of 5 were observed, depending on the element and the sampler-skimmer spacing. However, when these high sensitivity skimmers are used, the instrumental mass fractionation for Nd displayed a large nonlinear component that could not be corrected

for the use of the accepted mass fractionation laws. It was proposed that the origin of this nonlinear mass fractionation is the formation of NdO^+ close to the skimmer surface. In the authors' opinion, the degree of oxide formation and, hence, fractionation is isotope dependent but it is not a linear function of mass. A decrease in the measured $^{x}Nd/^{144}Nd$ ratio, relative to standard values, was found to be associated with a concomitant increase in the same ratio in NdO^+ (and vice versa). The observed inverse relationship between the metal and oxide species is consistent with mass balance calculations. The magnitude of this effect was dependent on conditions at the skimmer surface (geometry, surface coating, etc.) and could be suppressed by the addition of small amounts of N_2 to the carrier gas flow. A simplified energy-resonant ion-atom reaction was postulated to explain these observations and was extended to a general model of REE oxide formation in the supersonic expansion. The nonlinear fractionation observed also correlates with deviations from a linear function of mass in the nuclear charge radii. This is the first report on nuclear volume effects contributing to the instrumental mass fractionation in ICPMS.

An interesting approach for the ultratrace determination of iodine by ICPMS based on UV-photochemical generation of volatile iodine species was introduced by Grinberg and Sturgeon (*231*, *232*). Several UV based systems were studied, the most advantageous design was found to be a modified cyclonic spray chamber fitted with a 6 W mercury pen lamp supplying 1 mL min^{-1} sample to a glass concentric nebulizer. Optimal conditions utilized a 5% v/v solution of acetic acid as the generation medium. The presence of the UV field enhanced signal intensity approximately 40-fold, providing a limit of detection (LOD) of 0.7 pg mL^{-1} $^{127}I^+$ and a precision of replicate measurement of 4% RSD at 10 ng mL^{-1} iodine. Using DRC technology and O_2 as the reaction gas, suppression of $^{129}Xe^+$ provided an estimated LOD of 6 fg mL^{-1} $^{129}I^+$ in aqueous samples. Gil et al. developed a headspace single-drop microextraction (HS-SDME) method in combination with electrothermal vaporization (ETV) ICPMS for the simultaneous determination of As, Sb, Bi, Pb, Sn, and Hg in aqueous solutions (*233*). Vapor generation was carried out in a 40 mL volume closed vial containing a solution with the target analytes in hydrochloric acid and potassium ferricyanide medium. Hydrides and Hg vapor were trapped onto an aqueous single drop (3 μL) containing Pd(II), followed by the subsequent injection in the ETV. Experimental variables were fully optimized, and the achieved LODs for As, Sb, Bi, Pb, Sn, and Hg were 0.2, 0.04, 0.01, 0.07, 0.09, and 0.8 $\mu g\ L^{-1}$, respectively. Enrichment factors of 9, 85, 138, 130, 37, and 72 within 210 s were reported.

Elemental Speciation, Analysis of Biological Samples and Nanomaterials. The application of methods based on hyphenating separation techniques with element-specific detectors such as ICPMS is steadily becoming a routine approach for elemental speciation analysis. In recent years, a vast number of papers on this topic in general and on the role of various elemental species in health issues have been published. Feldmann and co-workers (*234*) described a technique for the separation and molecular identification of Hg and methylmercury complexes derived from their reactions with cysteine and glutathione (GS). Corresponding complexes were characterized by electrospray ionization (ESI) MS equipped with an ion trap and the fragmentation pattern of MeHgCys indicated Hg-amine interactions in the gas phase. Chromatographic baseline separation was performed within 10 min with formic acid as the mobile phase on a reversed-phase column. Detection was done by online simultaneous coupling of ESI-MS and ICPMS. When the mercury complexes were spiked in plant extracts, no perturbation of the separation and detection conditions was observed; thus, the authors suggested that the presented method is capable of detecting Hg−biothiol complexes in plants.

Lafleur and Salin introduced an interesting strategy for the speciation analysis of Cr based on the combination of high-performance thin-layer chromatography (HPTLC) with direct determination by LA-ICPMS (*235*). Cr(III) and Cr(VI) were separated in seconds on silica gel plates using aqueous mobile phases. LA was used to volatilize the chromium species directly from the chromatographic material. A linear calibration was obtained, and detection limits of 6 ng for Cr(VI) and 0.4 ng for Cr(III) were achieved with precision ranging from 3 to 40% at the 95% confidence level. The silicon present in the stationary phase was used as an internal standard. This procedure allows for a rapid separation and quantification and requires only 0.5 μL of sample, and lower detection limits can be achieved through preconcentration.

An alternative thermodiffusion interface was designed and constructed by Yan et al. for the effective online coupling of capillary gas chromatography (cGC) and ICPMS for simultaneous speciation of various organic and inorganic lead and mercury species (*236*). The species of interest could be quantitatively separated within 7 min using a 15 m long capillary column, allowing the determination and speciation of organic and inorganic Pb and Hg species in a single run. Methodological detection limits for Me_4Pb, Et_4Pb, Me_3Pb^{3+}, Pb^{2+}, $MeHg^+$, $EtHg^+$, and Hg^{2+} were found to be 0.07, 0.06, 0.04, 7.0, 0.09, 0.1, and 0.2 pg g^{-1}, respectively. Moreover, tri-*n*-propyl-lead chloride was synthesized and used as an alternative internal standard for the accurate and simultaneous speciation analysis of Pb and Hg in complicated environmental and biological samples for the first time.

Heilmann and Heumann presented a species-specific isotope dilution (ID) technique for accurate determination of sulfur species in low- and high-boiling petroleum products by GC-ID-ICPMS (*237*). For the isotope dilution step, ^{34}S-labeled thiophene, dibenzothiophene, and mixed dibenzothiophene/4-methyldibenzothiophene spike compounds were synthesized on the milligram scale from elemental ^{34}S-enriched sulfur. Thiophene was determined in gasoline, "sulfur-free" gasoline, and naphtha. The accuracy of species-specific ID-GC-ICPMS was demonstrated by the analysis of appropriate reference material. The detection limit was determined for thiophene to be 7 pg absolute. By parallel GC-ICPMS and GC-EI-MS (electron impact ionization) experiments, the substantial influence of coeluting hydrocarbons on the ICPMS sulfur signal was demonstrated, underlining the advantage of ID analysis. Species-specific isotope dilution was also used by Infante et al. (*238*) for the accurate determination of ultratrace Se species of relevance to cancer research, such as γ-glutamyl-Se-methylselenocysteine (γ-glutamyl-SeMC), using HPLC-ICPMS. The ^{77}Se-enriched spike

was produced in-house, and its Se content was characterized using reverse isotope dilution mass spectrometry (IDMS). The isotopic composition of this spike was checked prior to quantification of the natural abundance dipeptide species in garlic using speciated IDA. The effect of ultrasonic nebulization, in comparison with the loading of the ICP with carbon (through the online addition of CH_4), on the detection of Se associated with γ-glutamyl-SeMC using collision/reaction cell ICPMS with H_2 as collision gas, was investigated. Sensitivity enhancements of approximately 4-fold and 2-fold were achieved using USN and methane mixed plasma, respectively, in comparison with conventional nebulization and conventional Ar ICPMS.

In the context of high-level nuclear waste (HLW) disposal in deep and stable geological formations and to understand the radionuclide migration in the near- and far-field of a repository caused by an incident, Kautenburger investigated the complexation behavior of Eu and Gd (as homologues of the actinides Am and Cm) with humic acid (HA) by capillary electrophoresis (CE) hyphenated with ICPMS (*239*). The influence of lanthanide concentration as well as the presence of competing cations like Ca, Mg, and Al on the HA-complexation have been studied. The lanthanide speciation by CE-ICPMS revealed weak and strong HA binding sites for the used trivalent lanthanides subject to the given lanthanide concentration. The influence of the competing alkaline earth ions can be assumed to be relevant at very high concentrations only while Al at an already low concentration represents a strong competitor to Eu and Gd in HA-complexation and may affect toxic metal speciation and, thus, metal mobility in the geological barrier of a future disposal.

Metal−biomolecule interactions comprise an important research area in metallomics and are significant for biology, medicine, pharmacy, nutrition, metabolism, and environmental science. Separation of such macromolecules is often performed through CE since it exhibits high resolution, minimal sample, and reagent consumption, and rapid and efficient separations with minor disturbance of the existing equilibrium between the metal species and their biomolecular complexes. In a trend article by Yin et al. (*240*), an overview of CE-ICPMS for the study of metal−biomolecule interactions was presented. The applications of this technique to the study of interactions between metals or metalloids and natural ligands, such as humic substances or fulvic acids, and the interchange of metal complexes with metal species in metalloproteins was extensively discussed. Wrobel and Caruso highlighted epigenetics as an important challenge in metallomics studies, introducing the basic epigenetic concepts, followed by the early applications of ICPMS classified as (a) detection of ^{31}P as a natural element tag for DNA, (b) analysis of DNA adducts with metal based drugs, and (c) element species as epigenetic factors (*241*). For the absolute quantification of peptides using genetic standards, Navaza et al. (*242*) employed capillary HPLC-ICPMS and tyrosine iodination. Characterization studies by capHPLC with parallel ICPMS and ESI tandem mass spectrometry (ESIMS/MS) detection revealed that such labeling of an iodination reaction allows one to obtain the most accurate peptide determinations. The excellent detection limits for iodine using ICPMS allowed robust and highly sensitive tyrosine-containing peptide quantification (480 pM, 480 amol absolute). The approach was optimized for tyrosine labeling and then validated by application to the absolute quantification of the three standard peptides present in the only reference material for peptide quantity (NIST 8327) commercially available.

In any analytical procedure appropriate for elemental speciation, the accurate and representative extraction of sample material and species conservation are still the weakest steps. An interesting study by Bluemlein et al. (*243*) confirmed, for the first time, that As peptides can be extracted by formic acid and chromatographically separated on a reversed-phase column without significant decomposition or denovo synthesis during the extraction step.

The biotransformation of heteroelements in the environment was studied by Diaz-Bone et al. (*244*) using parallel molecular and elemental mass spectrometry hyphenated with gas chromatographic separation (GC/EI-MS/ICPMS) for nontarget screening and subsequent identification of volatile As compounds formed by fecal microorganisms. The authors succeeded in identifying five mixed As/S species (Me_2AsSH, Me_2AsSMe, $Me_2AsSSMe$, $(Me_2As)_2S$, and MeAs(SMe)(SEt)) as well as one mixed As/Se compound ($Me_2AsSeMe$) in the headspace of fecal incubations. Identification of all compounds was verified by synthesis experiments. Three of these species, namely $Me_2AsSeMe$, $(Me_2As)_2S$, and MeAs(SMe)(SEt), have not been described in environmental or human matrixes before. Ellis et al. (*245*) presented a study on the complementary molecular and elemental detection of speciated thioarsenicals after HPLC separation using ESI-MS in combination with Xe based collision-cell ICPMS for the analysis of freeze-dried urine samples. A 34-fold improvement in the ^{32}S detection limit was achieved after thorough optimization and using Xe instead of He as a collision gas. The optimized Xe based CC-ICPMS was then used with electrospray ionization MS to provide elemental and molecular based information for the analysis of a fortified sample of NIST freeze-dried urine. The achieved detection limits for dimethylthioarsinic acid and trimethylarsine sulfide were 15 and 12 ng g^{-1}, respectively.

A comparison of different nebulizers in combination with aerosol desolvation for the determination of trace elements in small amounts of liquid samples of animal tissues by ICPMS was performed by Pozebon et al. (*246*). A micronebulizer/desolvator system (APEX) and a MicroMist nebulizer fitted to a minicyclonic spray chamber were used for liquid sample introduction. The nebulizers were compared with respect to LODs and sensitivity, revealing that both parameters were improved for the most investigated elements by the use of the APEX system. Slug specimens were analyzed, and it was observed that most investigated elements were enriched in the salivatory or digestive glands of the slugs.

Postcolumn ID analysis in combination with size exclusion chromatography (SEC) was proposed by Wang et al. as a method for the analysis of mercury-containing protein fractions in the brain cytosol of maternal and infant rats after exposure to low doses of methylmercury chloride (*247*). The enriched spike was continuously added into the eluate from the HPLC column, and the isotope diluted fractions were online measured by ICPMS. The absolute amounts of S, Hg, Zn, and Cu in the eluted protein fractions could be attained after calculation of the corresponding peak areas in the mass flow chromatogram. The detection limits

for S, Cu, Zn, and Hg were found to be 11, 0.1, 1.5, and 0.2 ng, respectively. The results demonstrated that different Hg-containing protein fractions may exist in brain cytosol between maternal and infant rats and the quantitative calculation may be helpful for the toxicological study.

Jakubowski and co-workers (*248*) developed a LA-ICPMS based method for concomitant detection and semiquantitative determination of electrophoretically separated and blotted structurally and enzymatically similar cytochromes P450 (CYPs). First, results were given for the two enzymes CYP1A1 and CYP2E1. Specific monoclonal antibodies directed against the enzymes were differentially labeled with Eu via a covalently linked chelator and with iodine, respectively. Analysis of the modified antibodies showed that both europium and iodine were coupled to the heavy and the light chains of the antibodies. Also, the antibodies maintained their antigen-binding properties after being labeled, as demonstrated by LA-ICPMS-analyzed immunoblots. Although the results presented here were only for labeling with the elements iodine and europium, the same strategy could also be applied for other lanthanide elements in combination with chelating compounds, as stated by the authors. Thus, LA-ICPMS of Western blots might offer new capabilities for the application of highly multiplexed CYP determinations via labeled antibodies. Becker et al. used matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) and LA-ICPMS for studying metal-binding proteins (metalloproteins) in life sciences (*249*). Specifically, protein complexes present in liver and kidney tissues of rats were separated in their native state in the first dimension by blue native gel electrophoresis (BN-PAGE). Essential and toxic metals, such as Zn, Cu, Fe, Ni, Cr, Cd, and Pb, were detected by scanning the gel bands using LA-ICPMS with and without the collision cell as a microanalytical technique. Several proteins were identified by the use of MALDI-TOF-MS combined with a database search. By combining biomolecular and elemental mass spectrometry, it was possible to characterize and identify selected metal-binding rat liver and kidney tissue proteins.

Seuma et al. (*250*) presented LA-ICPMS as a tool for the imaging of cancer biomarkers in tissue sections. The distribution of two breast cancer-associated proteins, MUC-1 and HER2, was studied on the basis of multiple line rastering of tissue sections and measurement of relevant Au/Ag tagged antibodies bound to the tissue. Comparisons with optical microscopy indicated an extremely high sensitivity for the LA technique and sufficiently good resolution to permit fine scale feature mapping at the cellular level. Application to the quantitative assessment of HER2 expression in tissue microarrays was demonstrated. Similarly, LA-ICPMS was employed by Becker and Lobinski (*251*) for the detection of metalloproteins through metal imaging in nondenaturating 2D electrophoresis gels. Protein complexes, extracted with water, were separated in their native state in the first and second dimension by blue native gel electrophoresis (BN-PAGE). Metals were monitored after gel ablation by a focused laser beam in a way that the total surface of a selected fragment of the gel was totally ablated. The metal distribution of this part of the gel was then constructed by plotting the metal (isotope) signal intensity as a function of the *x*, and *y* (isoelectric point and molecular mass) coordinates of the gel. The proteins at locations rich in metals were cut out, digested with trypsin, and analyzed by MALDI-TOF-MS.

Jakubowski and co-workers described the labeling of three different polyclonal antibodies with iodine and lanthanides and demonstrated the application in a Western blot assay (*252*). For this purpose, target protein standards were separated by sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) and were electroblotted onto membranes. After the immunoreaction of the labeled antibodies with the antigen, the element label was detected by LA-ICPMS directly on the Western blot membrane. For validation, chemiluminescence detection was applied and similar limits of detection at nanogram levels of antigen were achieved by both methods. In comparison to chemiluminescence detection, the Western blotting procedure in combination with LA-ICPMS detection was found to be less time-consuming and the elemental signatures on the blots showed long-term stability. It was concluded that LA-ICPMS offers multiplexing capabilities, and therefore, simultaneous detection of differentially labeled antibodies in one single Western blot assay was possible. In a similar study, Jakubowski et al. (*253*) also reported on the labeling of three different proteins with iodine using a commercially available reaction kit for total protein amounts of 500 μg. The assay described was applied with the stable isotope ^{127}I combined with ICPMS detection. The reaction conditions were optimized for proteins separated by SDS-PAGE and electroblotted onto suitable membranes while detection was performed by LA-ICPMS on the membranes. A calibration was performed for bovine serum albumin from 0.015 to 15 pmol, but the limit of detection was already reached at about 150 fmol due to high iodine blank values, only. The authors concluded that the labeling procedure does not affect protein mobility in SDS-PAGE, because the change of the molecular weight is very moderate for the proteins investigated in this study, which is opposite to those procedures where chelating compounds are applied. Labeling with stable isotopes was also used by Sarmiento-Gonzalez et al. (*254*) to assess quantitatively the Ti(IV) uptake by transferrin in human blood serum (Tf) through HPLC-ICPMS in order to help to determine the biochemical pathways of this metal when used as an anticancer drug or to describe the amount of wear of Ti prostheses. Isotope dilution (ID) analysis was applied to the quantitative speciation of Ti-Tf in standards and human blood serum samples, and species-unspecific and species-specific isotope dilution modes were explored. Species-specific ID was shown to be much more accurate. An isotopically enriched standard of ^{49}Ti-Tf was synthesized and applied to the quantitative speciation of Ti-Tf. Through this strategy, errors resulting from Ti-Tf dissociation inside the chromatographic columns were corrected, and thus, quantitative Ti-Tf binding in serum (92−102%) was observed.

A liquid-phase immunoassay was developed by Terenghi et al. (*255*) for the simultaneous determination of five cancer biomarker proteins: alpha-fetoprotein, human chorionic gonadotropin, carcinoembryonic antigen, ovarian tumor antigen, and gastrointestinal tumor antigen. The method was based on the incubation of a serum (or tissue cytosol) with five antibodies, each labeled with a different lanthanide followed by the specific determination of the immunocomplex formed by SEC-ICPMS. The

sensitivity of the method was comparable with that attainable by enzyme-linked immunosorbent assay (ELISA) or radioimmunoassay. However, multiplexed analysis capacity, virtually no sample preparation, and sample amount consumption, ca. 3 times lower than an ELISA test, were found to be advantageous. The method was proven to be able to discriminate human ovary and uterus tumor tissue samples from those of healthy subjects. Two complementary methods were compared by Careri et al. (*256*) for the identification and determination of peanut allergens in a complex food matrix like a chocolate rice crispy based snack based on Eu-tagged ICPMS immunoassay and on LC/ESI-MS/MS. Both approaches, used for screening or confirmative purposes, showed the power of mass spectrometry when used as a very selective detector in difficult matrixes even if some limitations still exist, i.e., matrix suppression in the LC/ESI-MS/MS procedure and the change of the antigen/antibody binding with matrix in the ICPMS method.

Carazzone et al. directly coupled nanoelectrospray (nES) in conjunction with macro-ion mobility spectrometry (macroIMS) with ICPMS for sizing large proteins, DNA, and nanoparticles (*257*). Technical challenges involving the coupling of the air based nES-macroIMS with the argon based ICPMS were addressed and overcome. The resulting novel hyphenated technique was used to determine the elemental composition of nanoparticles resulting from the electrospraying of solutions containing inorganic salts and acids. Although the sensitivity of the used ICPMS did not allow for the simultaneous sizing of proteins and the determination of their metal, metalloid, or halogen content, it was shown that this method is feasible to detect and accurately size proteins at femtomole levels by adding CsI to their solutions and detecting the resulting Cs adducts, which is also possible with DNA molecules. A linear relationship was found between protein amount and ICPMS response for $^{133}Cs^{+}$, indicating that this method might also be helpful for quantitative analysis of large biomolecules. ICPMS was also used for the quantitative characterization of natural colloids and synthetic nanoparticles in combination with asymmetric flow field-flow fractionation (AsFlFFF) by Bouby et al. (*258*). Reproducibility of the size calibration and recovery of elements were examined. Channel flow fluctuations were observed by the authors notably after initiation of the fractionation procedure. Their impact on quantification was considered using ^{103}Rh as internal reference; intensity ratios measured for various elements and Rh were calculated for each data point. These ratios were found to be independent of the metal concentration, and total sample solution flow was introduced into the nebulizer within a range of 0.4−1.2 mL min^{-1}. The method was applied to study the interaction of Eu, U(VI), and Th with a mixture of humic acid and clay colloids and to the characterization of synthetic nanoparticles (CdSe/ZnS-MAA (mercaptoacetic acid) core/shell-coated quantum dots).

Laser Ablation for Direct Solid Sampling. The substantially increasing need to characterize complex materials, both in industry and in various fields of research, is the driving force for ongoing developments in the area of laser ablation (LA). Thus, the number of applications of LA-ICPMS to the determination of major, minor, and trace elements as well as isotope-ratio measurements in different sample types has substantially increased during the last two years. A review by Niemax and co-workers (*259*) discussed current shortcomings of LA-ICPMS and offers practical suggestions for improving performance. An extensive and critical review on the most widespread and powerful inorganic mass spectrometric methods, currently, further improved and applied for the direct characterization of solids was given by Pisonero et al. (*188*). Analytical performance, capabilities, advantages, limitations, and trends of LA-ICPMS, secondary ion (neutral) mass spectrometry (SIMS/SNMS), and glow discharge mass spectrometry (GD-MS) were discussed.

Laser ablation in combination with plasma source mass spectrometry has evolved to a mature tool in the field of spatially resolved elemental analysis of solid samples, although accurate calibration is still difficult, since it is hampered by elemental fractionation and the lack of available standard reference materials. Therefore, Fittschen and Bings et al. (*260*) investigated, for the first time, the characteristics of dried residues of picoliter droplets of aqueous standard solutions, which qualify these as reference materials in the direct analysis of single particles, single cells, and other microscopic objects using, e.g., LA-ICP-TOFMS and micro-X-ray fluorescence (MXRF). Different single-, two-, and three-element solutions were transferred in picoliter volume (around 130 pL) by the use of a modified thermal inkjet printing technique. An achievable dosing precision of 4−15% was calculated by total reflection X-ray fluorescence (TXRF) determination of the transferred elemental mass of an array of 100 droplets. The size of the dried residues was determined by optical microscopy to be 5−20 μm in diameter, depending on the concentration and the surface material. The elemental distribution of the dried residues was determined with synchrotron MXRF analyses showing high uniformity for element deposition of every single droplet with an RSD of 4−6%, depending on the concentration of spotted solution. The shape and height profile of dried residues from picoliter droplets were studied using atomic force microscopy, and the potential of this novel dosing technique for calibration in direct LA-ICP-TOFMS analysis was shown. Reports on the production and characterization of a set of ten calibration standards based on acrylonitrile-butadiene-styrene terpolymer (ABS) containing the elements Br, Pb, Cd, Cr, and Hg for X-ray fluorescence analysis (XRF) and LA-ICPMS were given by Simons et al. (*261*) and Mans et al. (*262*). The mass fractions of all elements were 0−1500 mg kg^{-1}, and the materials were produced as granulates and solid discs with a diameter of 40 mm and thicknesses of 1, 2, and 6 mm. Sufficient macroscopic and microscopic homogeneities for all elements was achieved, and it was observed that organic additives show a better homogeneity than oxides. XRF and LA-ICPMS were successfully calibrated with the new materials, which were considered as candidate reference materials (RM) by the Federal Institute of Materials Research and Testing (BAM, Germany). In a different approach, Fitzpatrick et al. (*263*) applied a sol−gel process for the fabrication of solid multielement calibration standards for LA-ICPMS. The addition of an analyte (Se) and an internal standard (S) to a normal sol−gel method was found to not impair the production of the glass-like discs (xerogels). Heterogeneity of Se and S concentrations in the xerogels was less than that of NIST SRM 610 and 612 glass standards. Small differences in slopes of calibrations based on sulfide standards and those based on xerogel

standards reflected differential matrix effects. The calculated S contents in the NIST SRM 610 and 612 reference materials, using the xerogels as standards, were comparable to available S concentration data. In the authors' opinion, the xerogels represent potential standards for a variety of elements in glasses, minerals, and other materials. Kovacs et al. (*264*) characterized two solid Au calibration materials in terms of element composition and distribution to investigate their applicability for fingerprint studies on Peruvian Au objects using LA-ICPMS. The two calibration materials provided access to elements, which are important for archeological investigations and fingerprint studies of Au objects. Also, the investigated calibration materials contained Ag as a major element, which provided matrix-matched calibration for the analysis of Au artifacts. The quantification of the potential calibration materials was carried out by LA using solution calibration. The applicability of this calibration approach was validated, and the accuracy and precision were found to be better than 8%, for most of the determined elements. The applicability of the produced gold calibration materials was also proven by the authors. Traub et al. (*265*) evaluated different calibration strategies in fs-LA-ICPMS for the analysis of pure Cu and Zn certified reference materials (CRMs). Solution-doped metal powder pellets as well as aspirated liquids were used as calibration samples, and it was demonstrated that calibration by Cu pellets resulted in relative deviations up to 20%, whereas Cu based CRMs led to inaccuracies in the same range unless nominal mass fractions were chosen to be <3 mg kg^{-1}. Calibration by Zn pellets generally provided better accuracy. Depending on the analyte considered, deviations below 10% were obtained even for mass fractions close to the limit of quantification. It was concluded that solution-doped metal powder pellets are suitable as calibration samples for fs-LA-ICPMS of metals. Furthermore, the utilization of liquid standards for calibration was found to result in stronger deviations of up to 50% for both Cu and Zn samples, which was dependent on the plasma conditions. In an additional study, liquid standard calibration was, therefore, used for the analysis of brass and silicate glass by fs-LA-ICPMS (*266*) and online addition of desolvated as well as nondesolvated liquid standards. Depending on the material considered, accuracies varied from a few up to 50% for critical elements such as Zn and Cd. The average deviation calculated from concentration values of all elements monitored during the analysis of silicate glass amounted to 11.1% and 8.4% for desolvated and nondesolvated aerosols, implying similar but slightly improved performance under "wet" plasma conditions. The analysis of silicate glass applying "matrix-matched" calibration was found to result in accuracies comparable to those obtained by liquid standard calibration except for Zn and Cd, which improved by 9% and 25%, respectively, when a solid calibration material was used. In contrast, the precision of analysis decreased due to a higher uncertainty of concentration values specified for the external standard used.

In the past years, UV-ns-LA-ICPMS has been studied in detail, and it is nowadays very well accepted that aerosol generation, aerosol transport, and aerosol excitation-ionization within the ICP contribute to fractionation effects, which prevent this method from a more universal application to all matrixes and all elements. Recent progresses in IR-fs and UV-fs laser ablation coupled to ICPMS have been reported by many groups, which increase the intermatrix and multielement quantification capabilities of this method. These fundamental improvements in LA-ICPMS are of significant importance for entering new applications in material science and related research fields and were reviewed by Pisonero and Günther (*267*). The influence of particle size on elemental fractionation in ns- and fs-LA-ICPMS was studied by Saetveit et al. (*268*) using a differential mobility analyzer (DMA). This device passed LA particles and agglomerates within a narrow range of electrical mobilities to the ICPMS, and no particle collection or off-line particle analysis was required. Elemental fractionation was assessed with the Cu^+/Zn^+ signal ratio. Results presented support previous findings that ns-LA provides many small Zn-rich particles and some much larger Cu-rich particles and that fs-LA produces large agglomerates of small particles. The composition of the aerosol produced by fs-LA was found to fall between the relatively Zn-rich and Cu-rich extremes of ns-LA. It was concluded that fs-LA provides elemental ratio measurements that remain more stable with respect to time, which allows a greater degree of confidence in LA results. The suppression of particle size related fractionation with fs-LA was clearly attributed to laser pulse length. Garcia et al. (*120*) also studied elemental fractionation in fs-LA-ICPMS. They applied successive single laser shots to binary metallic and semiconductor samples as well as to multicomponent glasses. Fractionation was observed in the first laser shots in particular if the laser fluence was near the ablation threshold of the sample. However, the element ratio in the laser-sampled masses changed from shot to shot until it reached an asymptotic fluence-independent value representing stoichiometric sampling. The asymptotic stoichiometric ratios were obtained with fewer shots if higher laser fluences were applied. By the use of electron probe X-ray analysis, it was also shown that different elemental ablation probabilities modified the element compositions in the surface layers of the laser craters until equilibrium conditions were obtained. These conditions could be reached by applying either many shots of low laser fluence or one high-fluence laser shot only. It was concluded that in most cases the elemental ablation probability can be correlated with the respective ionization energies of the elements, i.e., the elements with lower first ionization energy have higher ablation probability. No or only very weak fractionation was observed when elements with nearly the same ionization energies were sampled. In a systematic study by Claverie et al. (*269*), the influence of the repetition rate of fs-LA on elemental fractionation effects in ICPMS analysis of silicate glass SRM NIST 610 was investigated. The ablation strategy developed in this work consisted of a series of concentric circle trajectories ablated at high repetition rates by moving the laser beam rapidly with a scanning beam device. Two scanner speeds (0.25 and 1.5 mm s^{-1}), five laser repetition rates (0.1−10 kHz), and three fluence values (5, 14, and 25 J cm^{-2}) were investigated in detail. Elemental ratios ($^{238}U/^{232}Th$, $^{208}Pb/^{238}U$, and $^{66}Zn/^{65}Cu$) of aerosols produced by fs-LA of silicate glass were studied to evaluate the impact of the different laser parameters on elemental fractionation. No heating zones or preferential evaporation of elements were found depending on the repetition

rate employed. However, particle-size-fractionation was measured during the ablation of the sample surface, and this effect was reduced by the use of a high repetition rate as well as a high scanner speed which allowed the dilution of the large particles coming from the surface layer with finer particles coming to deeper levels. Additionally, the ablation rate induced by the selected ablation strategy was found to have a low influence on fractionation effects due to the high robustness of the used ICP and, on the other hand, fractionation indices were not particularly affected by the laser repetition rate although they could be improved by the use of high fluence values. No differences on the structure of the aerosol particles collected on membrane filters were found, depending on the ablation parameters.

Gonzalez et al. (*270*) described the feasibility of performing bulk chemical analysis based on laser ablation for good lateral resolution with only nominal mass ablated per laser pulse. The influences of the laser repetition rate (1−1000 Hz) and its scan speed (1−200 μm s^{-1}) using a low energy (30 μJ) and a small spot size (similar to 10 μm) UV-fs-laser beam were evaluated for ICPMS analysis of silica glass samples. Accuracy to approximately 14% and precision of 6% relative standard deviation (RSD) were achieved.

Günther and co-workers (*271*) provided insight into the mechanisms underlying performance differences between Ar and He used as aerosol carrier gases for LA-ICPMS through investigating transport efficiencies of aerosols released by NIR- and UV-fs-LA of brass applying laminar or turbulent in-cell flow conditions and Ar as carrier gas. Aerosol particles were collected by low-pressure impaction or filtered by fine porous membranes. On the basis of aerosol masses collected and mass differences derived from the target weight prior to and after LA, transport efficiencies varied in between 75% and 95%. The total aerosol mass released during LA was found to be strongly dependent on the relative focus position, i.e., surface area irradiated, even if the laser pulse energy delivered to the target was kept constant. Furthermore, a physical model only making use of input parameters such as laser spot size and pulse energy was implemented to qualitatively describe the correlation between aerosol mass and laser focus position.

Autrique et al. (*272*) performed detailed fluid dynamics calculations to investigate the gas flow patterns and mass transport efficiency in a laser ablation cell and transport tubing toward the ICP. The calculation results revealed that the mass transport efficiency was around 90%, independent of the carrier gas (He or Ar). On the basis of the calculated washout times of the aerosol particles, generated by a fs laser ablation pulse, the transient signal was constructed and experimentally validated. Bimodal peak structures were observed, which were attributed to turbulent effects in the transport tubing. In a subsequent paper (*273*), an optimized laser ablation setup was proposed, again on the basis of computational fluid dynamics simulations. The design was modified in such a way that it operated completely in the laminar flow regime. The modified setup was also built in practice, and the experimental results indeed confirmed the computer simulations. With the new setup, a washout time of 140 ms has been achieved for a 3% signal area criterion, allowing repetition rates of 7 Hz, which is of interest, e.g., for 2D imaging or depth profiling. Furthermore, an upper limit for the washout times for similar setups can be predicted, on the basis of elementary formulas.

A new simple design of a high-efficiency low-transport-time cell for LA was presented by Hergenröder et al. (*274*). The main feature of the design is that the particles are transported by a laminar spiral gas flow into the outlet without any contact with the cell walls. The efficiency of the particle transport and the dependence of the ICPMS peak shape on experimental conditions were measured. The peak duration on the 10% level was found to be as short as 30 ms, and the transport efficiency reached 100% when analyzing a standard brass sample. As an example of application to real samples with fine inhomogeneities, the profiles of ^{13}C, ^{44}Ca, and ^{208}Pb were measured by LA-ICPMS across a tree core. As a result, the very quick particle transport time of the cell enabled the fine, seasonal variation in wood composition to be resolved. Asogan et al. (*275*) designed a novel, open, non-contact cell for LA, capable of sampling large planar samples, embedded planar samples, or samples of less than 2 mm mounted on a planar platform, without an outer containment enclosure. This interesting cell, when tested on NIST-613 CRM, exhibited rapid washout (<3.6 s for 99% signal reduction), low limits of detection, and good signal precision in LA-ICPMS. The cell uses a dual, annular, microjet gas flow array to exclude atmospheric gases and to entrain the ablated sample aerosol. The microjet array employed enabled a sampling height, between the sample surface and the lowest plane of the cell, of up to 200 mm. The microjet array has the facility to be electrically biased if the application demands it, e.g., extracting a charged plume in MALDI or desorption electrospray ionization experiments. A micro jet-pump was coupled to the cell to extract the ablated aerosol from the low-volume inner ablation chamber for mixing the aerosol with the injector flow of the ICP and to isolate the cell from downstream conditions in the injector flow.

Wälle et al. (*276*) calculated detection efficiencies of LA-ICPMS, defined as the ratio of ions reaching the detector and atoms released by LA. For this purpose, LA of silicate glasses, zircon, and pure silicon was performed using ns- and fs-LA. The use of He as in-cell carrier gas during ns-LA of silicate glass resulted in detection efficiencies between approximately 1×10^{-7} for low and 3×10^{-5} for high mass range elements which were almost independent of the laser wavelength and pulse duration chosen. The application of Ar as carrier gas was found to suppress the detection efficiencies systematically by a factor of up to 5 mainly due to a less efficient aerosol-to-ion conversion and ion transmission inside the ICPMS. The same group investigated and compared specific expansion phenomena of aerosols generated by NIR-fs-LA of brass under a He and Ar atmosphere (*119*). Particles were visualized by light scattering using a pulsed laser source. Aerosols were found to be captured in symmetric vortices when striking a solid boundary during their kinetic stage of expansion. Furthermore, high-repetitive LA resulted in the formation of a complex, macroscopic flow pattern driven by a pressure gradient locally built up. It was concluded that aerosols released under those conditions experience only minor losses of around 1% if they get in contact with the inner walls of ablation cells operated at atmospheric pressures. Also, a general study on transport phenomena and

elemental fractionation in LA-ICPMS was given (*277*), and the influence of transport tube materials on signal response and drift was described (*278*). Perdian et al. performed time-resolved studies of particle effects in LA-ICPMS (*279*). Transient signal responses for ablated samples as a function of particle size and laser parameters were characterized, and data were acquired with time resolution of 5 or 6 ms per data point. Large positive spikes in signal were observed and increased in amplitude and frequency with increasing particle size. A comparison of lasers with pulse widths of 370 fs and 5 ns showed that shortening the pulse width significantly reduces the frequency and amplitude of positive spikes in the measured signal, which were attributed to the vaporization, atomization, and ionization of individual large intact particles, a major cause of fractionation in laser ablation ICPMS. The influence of experimental parameters on ICP-induced fractionation effects was also investigated (*280*). Differences in sample composition and morphology were found to have a profound effect on the time-resolved signal while He carrier gas decreased large positive signal spikes.

An interesting analytical method for rapid categorization of nuclear forensic evidence based on the isotopic composition of U was presented by Stefanka et al. (*281*). The investigation of nuclear materials seized in Hungary was carried out by ICP-SFMS applying LA for sample introduction. The results were compared with independent analytical techniques, and the advantage and limitations of the presented method were critically discussed. Similarly, single (*282*) and multiple collector LA-ICPMS were used on uranium-oxide grains retrieved from contaminated soil and dust samples (*283*) and on other microsamples (*284*) to reveal details of the history of U processing and emissions of the respective particles.

A simple LA-ICPMS procedure for the determination of Pb in whole blood was introduced by Hsieh et al. (*285*). It requires little sample pretreatment and offers direct analysis of a dried blood spot on a filter membrane. Aqueous standards and matrix-matched calibration were used. Precision of better than 10% was achieved, and a sample throughput of approximately 5 min per sample allowed for screening a large number of samples.

In a comparative study, Janssens and co-workers (*286*) used LA-ICPMS as a supporting method for elemental analysis of historical glass investigated by means of scanning electron microscopy with energy dispersive X-ray spectroscopy. LA-ICPMS allowed the determination of a number of elements which were present below the detection limit of SEM/EDS and to evaluate the homogeneity of investigated material. Results obtained by SEM/EDS were also used for the evaluation of the selection of standard reference materials for LA-ICPMS measurements. A satisfactory correlation between the results for major and minor elements obtained by both applied methods was achieved with a complementary determination of trace elements by means of LA-ICPMS.

Laser ablation ICPMS was also used in combination with isotope dilution analysis. Fernandez et al. (*287*, *288*) developed a method for the direct and simultaneous multielement determination of Cu, Zn, Sn, and Pb in soil and sediment samples using fs-LA-ICPMS in combination with in-cell isotope dilution (ID). The method was based on the quasi-simultaneous ablation of the natural abundance sample and the isotopically enriched solid spike, which was performed using a high repetition rate laser and a fast scanning beam device in a combined manner. Both the sample preparation procedure and the total analysis time were drastically reduced, in comparison with previous approaches, since a unique multielement isotopically enriched solid spike was employed to analyze different powdered samples. Numerous experimental parameters were carefully selected to ensure the complete mixing between the sample and the solid spike aerosols. Accurate and precise determinations of trace elements in powdered samples were demonstrated, reducing the total sample preparation time to less than 5 min. A similar technique was used by Heilmann et al. (*289*) for simultaneous determination of trace metals in different oil samples. Metallo-organic solutions of isotope spikes (^{50}V, ^{53}Cr, ^{65}Cu, ^{57}Fe, ^{62}Ni, ^{68}Zn, ^{113}Cd, ^{117}Sn, and ^{206}Pb) were prepared from corresponding aqueous stock solutions by the use of liquid−liquid extraction of complexed metal ions. The isotope-diluted sample was absorbed by a cellulose material, which was fixed in a special PTFE holder for ablation, using a laser system with high ablation rates. Under these conditions, no time-dependent spike/analyte fractionation was observed for the metalloorganic spike/oil mixtures and the measured isotope ratios of the isotope-diluted samples remained constant over the whole ablation time. The accuracy of ID-LA-ICPMS determinations was demonstrated, and detection limits in the range of 0.02 μg g^{-1} (V) to 0.2 μg g^{-1} (Fe) were obtained.

In an interesting study by Guillong et al. (*290*), the quantification capabilities for sulfur microanalysis in quartz-hosted fluid inclusions were investigated with LA in combination with ICP-QMS and ICP-SFMS, allowing resolution of sulfur from polyatomic interferences. The achieved precision and accuracy were not limited by interferences but by a so far unknown sulfur contamination source when ablating the host mineral quartz. Due to this contamination, a careful baseline correction was necessary which was described and discussed in detail.

Lafleur and Salin used LA-ICPMS on a novel centrifugal microfluidic solid phase extraction (SPE) device for field sampling and on-site preconcentration of water samples (*291*). Laser ablation was employed to directly vaporize the analytes from the SPE column, instead of eluting the preconcentrated analytes for introduction in an ICPMS by conventional solution nebulization. Absolute detection limits ranging between 0.1 and 12 ng were obtained for Ni, Cu, V, Pb, and Co in drinking water Certified Reference Materials. These centrifugal devices required only 1−600 μL of samples and a simple motor to actuate fluid flow. Such discs were found to be useful to perform multiple extractions simultaneously as well as to allow easy storage of samples before transport to the laboratory for LA-ICPMS analysis.

A number of papers were published by Becker and co-workers on imaging LA-ICPMS, i.e., the determination and visualization of the spatial distribution of various elements in different sample matrixes, such as nutrient elements in leaves and other metals and nonmetals in tissue samples (*292–296*). Also, the technique was applied to the investigation of surfaces of micro- and nanoelectronic devices to demonstrate the capabilities of measuring at nanometer scale (*297*). Becker et al. also introduced near-field (NF) LA-ICPMS as a novel elemental analytical technique

at the nanometer scale (*298*, *299*). The method utilizes the already known near-field effect to enhance the incident light energy on the thin tip of an Ag needle during the LA process. A robust needle etching procedure was developed to produce the thin needles with a tip diameter in the range of hundreds of nanometers. An experimental arrangement was constructed to control the "sample-to-tip" distance. The method was applied to the analysis of thin Au films deposited onto a Si substrate and to the characterization of standard reference materials. The authors stated that the near-field enhancement at an optimum sample-to-tip distance resulted in a 6-fold increase in the ion intensity of the analyte.

Collision and Reaction Cells. ICPMS instruments that employ collision or reaction cells to overcome specific polyatomic based spectral overlaps due to induced ion−molecule reactions became widely accepted in the last two years, although, as stated in the introductory chapter of this section, a decreasing number of novel or fundamental studies rather than applications was recognized.

To better constrain possible reduction mechanisms, Arnold et al. (*300*) practically and theoretically studied the reactions of ArO^+ and $ArOH^+$ with H_2 in the hexapole of a MC-ICPMS. Addition of H_2 into the hexapole caused the signal of $ArOH^+$ to increase (+30%), suggesting its formation there. It was observed that reactions in the hexapole cell become dominant over transmission at a lower rf-power of the ICP for $ArOH^+$ than for ArO^+, indicating that $ArOH^+$ reacts more efficiently within the hexapole. Increasing H_2 flow rate caused a decrease in background equivalent concentrations of both ArO^+ and $ArOH^+$ with a lower $ArOH^+$ decrease rate. De Muynck and Vanhaecke (*301*) reported on the development of a method, based on the use of an ICPMS equipped with a quadrupole based dynamic reaction cell (DRC) for the simultaneous determination of P, Ca, and Sr in bone and dental tissue. The use of NH_3 allowed interference-free determination of Ca via its low-abundant isotopes ^{42}Ca, ^{43}Ca, and ^{44}Ca and of Sr via its isotopes ^{86}Sr and ^{88}Sr that were freed from overlap due to the occurrence of $ArCa^+$ and/or Ca^{2+} ions. Also, the determination of ^{31}P was shown to be achievable using the same DRC operating conditions. Detection limits of P, Ca, and Sr in dental tissue digests were established as 3 $\mu g\ L^{-1}$ for P, 2 $\mu g\ L^{-1}$ for Ca, and 0.2 $\mu g\ L^{-1}$ for Sr. It was suggested that this method can be used to simultaneously (a) evaluate the impact of diagenesis on the elemental and isotopic composition of buried skeletal tissue via its Ca/P ratio and (b) determine its Sr concentration. Sharp and co-workers proposed a reliable method for the determination of iodine and Mo in milk samples, using alkaline digestion followed by ICPMS analysis (*302*). The use of He + O_2 as collision gas to remove $^{129}Xe^+$, initially to enable the determination of low levels of ^{129}I, also resulted in the quantitative conversion of Mo^+ to MoO_2^+ which enabled the Mo in the milk to be determined at similar mass to the iodine with the use of Sb as a common internal standard. To be able to separate and preconcentrate iodine at submicrogram per liter concentrations, a novel method was developed using a cation-exchange column loaded with Pd^{2+} and Ca^{2+} ions to selectively retain iodide. An investigation of the iodine species formed during oxidation and extraction of milk sample digests was also carried out. Similarly, P was measured by Popp et al. (*303*) as PO^+ using O_2 as reaction gas for the simultaneous determination of the herbicide glyphosate (*N*-phosphonomethylglycine) and its main metabolite aminomethyl phosphonic acid with DRC-ICPMS in combination with high-performance cation chromatography.

In two studies by Castro et al. (*304*) and Elwaer and Hintelmann (*305*), the performance of a quadrupole based collisions/reaction cell ICPMS and a double-focusing sector field ICPMS were compared for the detection of Fe in glass for forensic purposes, in terms of accuracy, precision, and method detection limits and regarding resolving spectral overlaps on Se isotopes. It was found in the latter study that except a lower mass bias for Se in ICP-SFMS the use of CC-ICPMS and a mixture of H_2 and He as collision gas was somewhat advantageous over ICP-SFMS.

Time-of-Flight Instruments. Since the commercial availability of ICP-TOFMS in the late 1990s, extensive research on its developments and applications has been performed, although the number of published manuscripts continued to decrease during the last two years. Bandura et al. introduced a novel ICP-TOFMS instrument, designed for real time analysis of individual biological cells or other microparticles (*306*). The instrument comprises a three-aperture vacuum interface, a dc quadrupole turning optics for decoupling ions from neutral components, an rf quadrupole ion guide discriminating against low-mass dominant plasma ions, a point-to-parallel focusing Dc quadrupole doublet, an orthogonal acceleration reflectron analyzer, a discrete dynode fast ion detector, and an 8-bit 1 GHz digitizer. A high spectrum generation frequency of 76.8 kHz provides capability for collecting multiple spectra from each particle-induced transient ion cloud, typically of a 200−300 μs duration. It was shown that the transients can be resolved and characterized individually at a peak frequency of 1100 particles per second. Design considerations and optimization data were presented. Rogers et al. (*307*) presented the design of a novel dual source TOFMS, which employs ICP and electrospray ionization sources simultaneously for comprehensive elemental speciation analysis. The mass analyzer shares a third-stage vacuum system, extraction region, acceleration region, field-free region, and two-stage reflectron between both sources. Most of the other components, such as first and second-stage vacuum systems, pre-extraction ion optics, microchannel plate detectors, and data acquisition are independent, to provide the greatest degree of flexibility in source operation and signal optimization. A detailed description was given of the design and optimization of the orthogonal acceleration and spontaneous drift geometry, energy discrimination, and the reflectron, and preliminary performance data were presented.

A new ICP-TOFMS, offering measurement and readout of mass spectra with a 30 μs time resolution, was introduced by Tanner and Günther and was applied to in-torch LA-ICPMS (*308*). The measurements confirmed previously observed fine structures of in-torch generated signals and provided new insights in the dynamic processes in the plasma on a μs time scale. The new setup was described in detail, and first figures of merit were given.

An intercomparison study between ICP-TOFMS, -QMS, and -SFMS on the determination of rare earth elements determined in Antarctic ice was given by Dick et al. (*309*). It was shown that the ICP-TOF-MS technique meets the demands of restricted sample mass, and the data obtained were in good agreement with

ICP-QMS and ICP-SFMS results. The ICP-TOFMS system determined accurately and precisely REE concentrations exceeding 5 ng L^{-1} while between 0.5 and 5 ng L^{-1} accuracy and precision were found to be element dependent.

Rowland and Holcombe evaluated isotope ratio inaccuracy on ICP-TOFMS and proposed a corresponding correction procedure (*310*). Systematic bias of the ratios was found when the analog detection mode was used. This bias was dependent upon the value of the ratio, the intensity of the signal, and the gain of the electron multiplier tube. The cause of this isotope ratio inaccuracy was rooted in a disproportionate recording of the analog signal because of the need to filter out noise by blocking analog signals below a threshold voltage. This attenuated smaller signals to a greater degree than larger signals. This variable "detection efficiency" caused a larger systematic error in the isotopic ratio. A method of analyzing solutions using natural, known isotopic ratios to produce an efficiency correction curve was presented. The average error of several isotope ratios for a 500 ng mL^{-1} solution of various elements with ratios between 3.4 and 10 was found to be 6.5% without correction, 3.0% with increased detector gain, 1.1% with efficiency correction, and 0.6% with both increased gain and efficiency correction.

High Resolution and Multicollector Instruments. The number of applications of high resolution ICPMS (HR-ICPMS) to environmental studies and high precision isotope ratio analysis has increased significantly during the last two years. This is due to the technique's extremely low achievable detection limits, high sensitivity and precision, and high mass resolution to overcome spectral interferences for the reliable determination of many trace elements. A study by Fontaine et al. (*311*) focused on the variation of mass bias in multicollector ICPMS. Different instrumental parameters such as the carrier gas flow rate and the sampling depth in the plasma as well as the ion optic settings were considered. Differences and similarities were shown between the isotope ratio variation profiles for liquid sample introduction by solution nebulization only and for membrane desolvation. They were assigned to the different behavior of their resulting aerosols in the plasma. A promising approach toward stabilization of mass bias by measuring at elevated carrier gas flow rates was also shown. Yang et al. (*312*) used Zr for mass bias correction with implementation of a combination of standard-sample-standard bracketing and internal normalization in determinations of isotope abundance ratios and isotopic composition of Sr in a biological sample through MC-ICPMS. In agreement with previous studies, evidence was presented for variation of $^{88}Sr/^{86}Sr$ in samples. Estimation of the measurement uncertainty confirmed that the major source of imprecision arises from the uncertainty in the certified value of $^{88}Sr/^{86}Sr$ in NIST SRM 987 used for mass bias correction. The development and application of a calibration strategy for routine isotope ratio analysis by MC-ICPMS was described and assessed by Doherty et al. (*313*). Internal standardization was used to account for mass bias, and a general solution for polynomial isotope ratio mass bias functions was derived. The resulting linear isotope ratio mass bias function was demonstrated to be mathematically consistent and experimentally realistic for the analysis of acidified aqueous solutions of analyte and internal standard elements.

A comparison of thermal ionization mass spectrometry (TIMS) and MC-ICPMS for Cs isotope ratio measurements in spent nuclear fuels was presented by Isnard et al. (*314*). Since no standard reference material is available to evaluate the accuracy of Cs isotopic measurements (natural Cs is monoisotopic whereas Cs in spent fuels contains the isotopes ^{133}Cs, ^{134}Cs, ^{135}Cs, and ^{137}Cs), an interinstrumental comparison of Cs isotopic composition in spent nuclear fuels has been performed. For TIMS measurements, isotopic fractionation was evaluated by studying the behavior of Cs isotope ratios ($^{133}Cs/^{137}Cs$ and $^{135}Cs/^{137}Cs$) during the analyses. For MC-ICPMS measurements, the mass bias effects were corrected with an external mass bias correction using Eu and Sb. The results obtained by the two techniques showed good agreement. Also, the quantification of the $^{135}Cs/^{238}U$ ratio by isotope dilution was presented in the case of a mixed oxide spent fuel sample. The combination of MC-ICPMS with a collision reaction cell was used by Moureau et al. (*315*) to measure Mo isotope ratios in natural Mo and ^{95}Mo enriched sample solutions with high accuracy and in situ Mo/Zr separation, instead of using chemical separation techniques. N_2O was selected as reaction gas, resulting in the formation of ZrO_2^+ from the sample matrix, whereas Mo was found to be not reactive.

Vanhaecke and co-workers reported on the capabilities of the combination of an electrothermal vaporization (ETV) unit and an ICP-SFMS (*316*). The basic analytical characteristics of this setup were evaluated and compared to those of the more traditional combination of ETV-ICP-QMS. ETV-ICP-SFMS was found to provide a superior performance in terms of sensitivity and, also, in terms of selectivity, as in medium resolution mode significantly lower LODs were achieved, especially for some low-mass elements, for which the most abundant nuclide suffers from spectral overlap as a result of the occurrence of carbon-containing polyatomic ions at low mass resolution. No deterioration was established in terms of stability, linear dynamic range, or tolerance to matrix effects in comparison with ETV-ICP-QMS. Also, the possibilities for multielement monitoring were studied and shown to be similar, owing to the enhanced scanning speed and reduced magnet settling time that current SF-ICPMS displays when compared to older SF instrumentation.

Dzurko et al. (*317*) developed a method for the determination of compound-specific Hg isotope ratios from transient signals using GC-MC-ICPMS with purge-and-trap preconcentration. Several methods of calculating isotope ratios were evaluated for their precision and accuracy. A newly developed average peak ratio method yielded the most accurate isotope ratio in relation to values obtained by a continuous flow technique and the best reproducibility. Compound-specific isotope ratios obtained after GC separation were statistically not different from ratios measured by continuous flow cold vapor measurements.

A method for the determination of fission products and their isotopic composition in nuclear samples by CE in combination with ICP-QMS and ICP-SFMS, respectively, was developed by Pitois et al. (*318*). Typical detection limits of 6 ng mL^{-1} and 4 pg mL^{-1} for Ce as well as 8 ng mL^{-1} and 7 pg mL^{-1} for lanthanides were obtained. Additionally, the high speed of the analysis, the low microliter range sample volume, and nanoliter range injection volume were found to be advantageous, consequently

reducing the radiation dose for the personnel as well as the volume of nuclear liquid wastes generated during the measurements.

A new approach for pharmaceutical counterfeit detection using LA-MC-ICPMS and HPLC-MC-ICPMS has been proposed by Santamaria-Fernandez et al. (*319*). A homogeneity study of 288 pharmaceutical tablets from different batches of the genuine drug has been performed, and a characteristic S isotopic signature has been obtained for the genuine product. δ^{34}S measurements by MC-ICPMS using Si internal standardization for the correction of instrumental mass bias effects led to a δ^{34}S of 3.6‰ and an associated combined expanded uncertainty of 1‰ ($k = 2$). The active pharmaceutical ingredient (API) of the tablets, a S-containing compound, has been separated by HPLC, and S isotope amount ratios have been measured by MC-ICPMS. δ^{34}S values obtained by HPLC-MC-ICPMS for the genuine tablets agreed with those obtained by LA-MC-ICPMS, thus confirming that the S isotopic signature is inherent to the S-containing API. Following the initial development work, a blind exercise was performed for 400 tablets. The discriminating power of the technique was assessed, and uncertainties associated to δ^{34}S values for counterfeit and genuine tablets varied depending on the sample introduction technique utilized. The three approaches were able to differentiate genuine from counterfeit tablets.

Several studies were performed using MC-ICPMS for the high precision determination of isotope ratios of different elements in various sample matrixes, e.g., of Ag in commercial products (*320*), of Cr (*321*) and Hg (*322*) in geological samples, and of Pb in infant bone tissue dating from the Roman era (*323*). All studies underline the power of MC-ICPMS as an outstanding tool for elemental and isotopic analysis especially for fingerprinting sources of the investigated elements in the environment and for the determination of variations in their isotopic composition in nature.

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