

Atomic Spectroscopy

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Innovation in atomic spectrometry for chemical analysis deals with the investigation and use of new atom reservoirs, radiation and ion sources, novel spectrometer concepts, and new types of detectors or innovation in their use. Important subfields in atomic spectrochemical analysis are new developments in atomic absorption spectrometry, innovation in plasma atomic emission work with arc, and spark and microwave plasmas as well as with inductively coupled plasmas (ICP), innovation in glow discharge atomic spectrometry, and ICP-mass spectrometry. A textbook in the field has been published under the title *Analytical Atomic Spectrometry with Flames and Plasmas* (1).

In the present review, we will focus on the new developments in atomic absorption, atomic fluorescence, atomic emission, glow discharge, and ICP-mass spectrometry, covering the period between October 1999 and October 2001, in the field of fundamental studies, instrumental developments, and applications. Only new applications, using new methodology, will be dealt with, because purely application papers are thoroughly treated in the reviews appearing in alternate years in this journal and in the Updates section of the *Journal of Analytical Atomic Spectrometry*.

ATOMIC ABSORPTION SPECTROMETRY

Atomic absorption spectrometry (AAS), both from the side of instrumentation and from the side of its features for solving challenging tasks in chemical analysis, also through combination

with chemical separation principles, still knows a lot of innovation and this applies both for flame electrothermal evaporation AAS and hydride or other volatile species generation techniques.

Flame Atomic Absorption Spectrometry. Flame atomic absorption spectrometry (FAAS) is a mature analysis method. Detailed innovation, however, still takes place with respect to studies on the noise, e.g., caused by pumps for on-line dilution (2) or studies on the low-frequency noise in general (3). Especially with respect to the nebulizers used, much still is to be done. Mora et al. (4) treated the possibilities of a single-bore high-pressure nebulizer for the analysis of oils. Also direct powder sampling for the case of pulverized biological samples by fluidized bed systems could be used successfully, as shown by de Moraes Flores et al. (5). Further, indirect methods allow the determination of important but for AAS difficult elements such as iodine, for which Yebra and Cespon (6) showed that a redox reaction with chromate is very useful. Especially for speciation, combinations of all types of chromatography with FAAS as detection remain important. Innovative is the use of micelle-mediated methods (7) or the application of biosorption as a species separation principle (8) for the case of chromium.

Diode Laser-Based Atomic Absorption Spectrometry. Diode laser AAS continued to be investigated because the use of spectral apparatus is becoming superfluous. The feasibilities of isotope dilution work in the case of graphite furnace atomization were shown (9). Through the use of low-pressure discharges and here especially of miniaturized dielectric barrier-layer discharges, where metastable levels of chlorine and fluorine are well-populated, these elements through diode laser AAS can be determined down to the ppb level in the case of organic halogenated compounds, as described by Miclea et al. (10). Also, in combination with laser ablation, it was possible to do uranium isotope ratio measurements directly in solids, as described by Quentmeier et al. (11).

Electrothermal Atomization Atomic Absorption Spectrometry. In electrothermal atomization spectrometry, basic studies deal with the mechanisms and kinetics of analyte release in the furnace, as described by L'vov (12), as well as with gas-phase chemistry (13) and surface chemistry (14). Special attention has been paid to fluorides (15) and fluorination as a means for thermal matrix removal (see, for example, ref 16). Special features remain the use of radiotracer methods for the study of volatile species generation, as shown by Docekal et al. for the case of nickel volatilized as Ni(CO)₄ (17).

Much attention has been paid to the use of chemical modifiers, as described by Tsalev et al. (18). Their mechanism could be traced back to the formation of intercalation compounds, as

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described by Bulska and Ortner (19). Especially the use of palladium (20), but also of platinum group elements (21), has been studied. For the determination of boron by ETAAS, the use of calcium chloride, zirconium chloride, and mixtures of both as modifier has been proposed by Nowka et al. (22).

For the minimization of volatilization interferences, the use of isothermal furnaces has been shown to have special features, especially in the case of metal furnaces, as discussed by L'vov et al. (23). Carbide-forming metals such as chromium and barium were shown to be efficiently evaporated from a tungsten coil platform, as described by Camero and Alvarado (24). In the case of a transversally heated filter atomizer, mercury could be determined without the use of matrix modifiers after its isolation as dithionite from water samples, as described by Marais et al. (25).

Despite AAS being known as a monoelement method, efforts for simultaneous determination are worthwhile, as in this way, internal standardization for the improvement of analytical precision becomes possible and measurement time as well as sample can be saved. The direct and simultaneous determination of chromium and manganese in urine has been described (26). Under the use of palladium as modifier and platform atomization, chromium, aluminum, and manganese could be determined simultaneously in urine, as described by Lin and Huang (27). Special efforts for multielement determinations by AAS continue to be made by the use of continuum sources as primary sources. With a CCD spectrometer, arsenic and selenium could be determined with detection limits being as low as in-line source AAS, as described by Schuetz et al. (28). The coherent forward scattering method remains especially suited for simultaneous determinations. This was shown by Bernhardt et al. (29), who used an electrostatic solid sample deposition technique for the multielement analysis of plant and cereal materials. For ETAAS, background correction remains of high importance and can be effectively performed by Zeeman AAS. This is of use both for continuum source ETAAS, as shown by Becker-Ross et al. (30), and for line source AAS (see, for example, ref 31).

Metal atomizers remain an important topic in ETAAS work and especially for the determination of very volatile elements as well as for the determination of carbide-forming elements. For the determination of selenium, e.g., tungsten coil AAS, using iridium as a permanent modifier enabled one to obtain detection limits down to 0.2 ng, as reported by Hou et al. (32).

For direct solids analysis by ETAAS, slurry atomization in the case of powders is a viable approach for a wide variety of materials and often with the possibility of calibrating by standard addition of aqueous solutions containing only the element to be determined. This could be shown by Dong and Krivan (33) for the determination of silicon in oxides of niobium, titanium, and zirconium. Also here the use of matrix modifiers is very useful, as shown by Dobrowolski for the determination of selenium in soils by slurry ETAAS and the use of poly(tetrafluoroethylene) as silica modifier (34). Conto and de Loos-Vollebregt used slurry ETAAS for the determination of cobalt in sewage sludge (35). As a special technique, sedimentation field-flow fractionation with ETAAS could be used for delivering particle size-resolved information in the case of soil and sediment samples, as described by Chen and Beckett (36).

Enrichment techniques further enhance the power of detection of ETAAS and are especially attractive, when performed on-line. This has been reviewed by Alonso et al. (37). As an example of the approach, complexation in a precoated knotted reactor for water analysis was found to be a powerful approach for water analysis, as described by Benkhedda et al. (38) Another interesting way of on-line preenrichment is continuous precipitation–dissolution in a flow system, as described by Gonzalez et al. (39). Also, preconcentration by sequential injection in microcolumns with ion-exchange beads has been used and both elution of the beads and transportation of the beads directly into the graphite furnace have been applied (40). On-line sorbent extraction of APDC complexes has been applied in the case of the determination of cadmium in seawater, as described by Xu et al. (41). By combining chemical methodology to ETAAS, not only preenrichment but also speciation can be achieved. This effectively could be accomplished by using *in situ* graphite furnace electrodeposition in the presence of EDTA, where a differentiation between Ni^{2+} and Ni became possible (42). As shown for the case of the chromium species, selective adsorption of the species on Lemna minor and slurry atomization ETAAS also could be successfully applied, as described by Zhu and Li (43). Also, indirect methods can be applied in the case of ETAAS, where for a determination of iodide, the latter is oxidized to free iodine, distilled by means of microwave energy, and reduced back to iodide. A 100% recovery at the trace level and detection limits down to 0.2 $\mu\text{g}/\text{mL}$ in the case of whole milk could be obtained, as described by Barmejo-Barrera et al. (44). An interesting way of further increasing the power of detection of FAAS lies in the use of the thermospray flame furnace, as described by Gaspar and Berndt (45). Here a liquid sample is transported through a very hot, simple metal capillary tip acting as a flame-heated thermospray into a glowing atomization tube (flame furnace) positioned into the air/acetylene flame of a standard FAAS burner head. With 10- μL samples, detection limits of 0.19 ng/mL cadmium, 1.3 ng/mL copper, 5.2 ng/mL thallium, 13 ng/mL lead, and 21 ng/mL mercury were reached. Similar improvements in power of detection were also realized by Gaspar and Berndt (46), when transporting the sample as a high-speed liquid jet into the heated tube.

Volatile Species Generation Atomic Absorption Spectrometry. The generation of volatile species as a means to enable a very efficient analyte introduction as well as an efficient matrix removal further attracts the interest of methodological research in AAS. For arsenic, for which hydride generation is best known and widely used, the formation of arsenic chloride in the case of the use of high hydrochloric acid concentrations could be proved by using electron impact ionization mass spectrometry, as described by Mester and Sturgeon (47). For selenium, gas flow patterns and the longitudinal distribution of free selenium atoms in quartz tube atomizers were studied by Matousek et al. (48). He used light scattering on ammonium chloride particles and by observation of iodine vapors found a laminar flow pattern, with a turbulent region at the T-junction and irregularities at the tube ends. By the use of derivative signal processing in the determination of tellurium in urine by hydride generation AAS, a 26-fold improvement in power of detection could be realized, as shown by Ha et al. (49). For the speciation of tin and arsenic, high-performance liquid chromatography coupled to hydride generation

AAS can be used when the organotins and organoarsenicals are decomposed by on-line UV photooxidation with peroxodisulfate subsequent to their leaving the column, as described by Tsalev et al. (50). The automated on-line prereduction of arsenate, monomethylarsonate (MMA), and dimethylarsinate (DMA) using flow injection hydride generation AAS was found feasible, and the kinetics of prereduction and complexation were found to strongly depend on the concentration of L-cysteine and on the temperature in the sequence As(V) < DMA < MMA. The L-cysteine complexes can be separated on an acidic cation-exchange column, as described by Tsalev et al. (51). For the determination of arsenic in soils, slurry sampling-on-line microwave extraction-hydride generation AAS was shown to be a viable approach, as described by Gürleyük et al. (52). For the thermal decomposition of the hydrides formed, the use of a multiple microflame by Dedina and Matousek (53) was shown to be a useful alternative to the commonly employed externally heated quartz tube atomizer.

The power of detection of hydride generation AAS from its beginning was enhanced considerably by using trapping techniques. The hot trapping techniques especially remained attractive, as this can be efficiently done in the furnace and it is much more convenient than working with liquid nitrogen in cold trapping. Both for arsenic and selenium, the mechanisms of hot trapping in a tungsten atomizer were studied, including the use of platinum, iridium, and rhenium as modifiers, as described by Docekal and Marek (54). By radiography experiments, it could be shown that the major part of selenium at low temperature was trapped on a relatively small spot opposite the injection hole, whereas it spreads out more at higher temperatures. Graphite tubes permanently treated with uranium, tantalum, lanthanum oxide, niobium, beryllium oxide, chromium oxide, tantalum carbide, chromium carbide, and vanadium carbide were investigated with respect to their trapping properties for arsenic, antimony, and selenium in water analysis; their properties were found to be inferior to those of iridium, tungstate, and zirconium-treated graphite tubes, as described by Moredo-Pineiro et al. (55). For the determination of arsenic, antimony, selenium, tin, and mercury in beer, a batch system using in situ preconcentration of the analytes on palladium (for As, Sb, Se, and Sn) or gold-treated (for Hg) interior wall surfaces of a graphite furnace was studied by Matusiewicz and Mikolajczak (56).

For the determination of mercury, the cold vapor AAS technique is still one of the most sensitive. When it is combined with pre-enrichment by gold amalgamation, determinations in environmental and biological samples by pyrolysis AAS in a range of 0.035–7 mg/kg can be performed, as shown by Costley et al. (57). By a species-specific preconcentration by *Escherichia coli*, phenylmercury could be determined in a biomass with detection limits of 0.05 ng/mL (58). Also, the use of chemically modified chloromethylated polystyrene-PAN (ion exchanger) for preconcentration purposes has been investigated, as described by Hafez et al. (59). For the determination of mercury by cold vapor AAS, organomercurials must be decomposed efficiently. Capelo et al. (60) showed how this effectively could be done by the use of room-temperature sonolysis-based advanced oxidation processes in the case of flow injection cold vapor AAS.

Apart from the classical volatile hydride-forming elements, the approach also has been further elaborated for other elements.

Accordingly, cloud point preconcentration of germanium prior to its determination by hydride generation AAS has been developed (61). To further improve the power of detection of the volatile compound-forming elements, trapping has long been used. For the determination of lead by flow injection hydride generation AAS, trapping in a heated graphite furnace has been found to be very efficient, as described by Tyson et al. (62). For the case of nickel, volatilization from solutions can be efficiently accomplished by nickel tetracarbonyl generation. Trapping in a transversally heated graphite furnace could be accomplished with an efficiency of 80% (63). Also, for silver volatile species, generation through the use of reduction with tetrahydroborate(III) has been reported, and with a diffusion flame or a multiple microflame quartz tube atomizer, characteristic masses of 7 and 0.6 ng, respectively, were obtained (64). For the determination of methylcyclopentadienyl-manganese tricarbonyl in gasoline and water, solid-phase microextraction and detection by quartz furnace AAS after thermal desorption have been found to be very effective, as reported by Fragueiro et al. (65). Feng et al. (66) described that reduction with tetrahydroborate(III) could be used for volatile species of a large series of noble and transition metals, including Pt, Co, Ag, Cu, Rh, Pd, Au, Ni, Ir, Ti, and Mn. Several physicochemical factors were identified that impact on their yield, which, at present, is estimated to range from 0.02 to 2% absolute.

ATOMIC FLUORESCENCE SPECTROMETRY

Atomic fluorescence spectrometry (AFS) has especially low detection limits when lasers are used as primary sources, as then saturation of the excited level becomes possible. As reviewed by Stchur et al. (67), new instrumental techniques here occur through the availability of solid-state deep UV tunable lasers and CCD spectrometers. Combined with hydride generation, also in the case of conventional primary sources, AFS was thoroughly studied. D'Ullico et al. (68) used continuous flow hydride generation for the determination of arsenic, bismuth, and tin and after optimization realized detection limits for As, Sb, Bi, Sn, Se, and Te of 6, 5, 3, 2, 2, and 9 ng/L using nondispersive AFS through the use of filters. Craig et al. (69) reported on the determination of inorganic Sb(V) and of methylantimony species by HPLC coupled to hydride generation AFS and described optimization studies and matrix interferences caused by MgSO₄ and NaCl. Pacquette et al. (70) reported on the use of continuous-flow hydride generation laser-induced fluorescence and laser-enhanced ionization spectrometry for the determination of parts per trillion level concentrations of arsenic, selenium, and antimony in the case of an electrothermal atomizer as an atom reservoir. Moreno et al. (71) reported on the speciation of inorganic selenium in environmental samples by flow injection analysis-hydride generation AFS and compared the features of off-line, pseudo-on-line, and on-line extraction and reduction methods.

ATOMIC EMISSION SPECTROMETRY

Developments in atomic emission spectrometry deal with innovation in spectrometric instrumentation as well as with novelties in the case of the different types of sources or the development of new sources. Important new developments in the concepts of spectrometers include the use of quartz acoustooptic tunable filters for wavelength selection in atomic emission spectrometry, as described by Gillespie and Carnahan (72). Here

in a spectral range extending from 206 to 405 nm, measurements are possible with extremely accurate wavelength calibration and band-passes of 0.06 and 0.36 nm at 226 and 405 nm, respectively. Another interesting development with respect to spectrometers is the adaption of high-resolving Echelle spectrometers to commercial bidimensional electronic detectors, such as CCDs, with the aim of realizing small but high-resolving instruments for a well-defined wavelength range, as done by Florek et al. (73). Electronic detector technology indeed makes the dream of emission spectrography possible, as one has the whole spectral information available, however, in a digitized way with respect to intensities and wavelengths. The different detectors have been discussed in terms of signal-to-noise ratios and achievable precision, as, for example, done for CID detection in ICP-OES by Pennemaker and Denton (74). An important concept with respect to sources for atomic emission spectrometry is the "tandem source" concept introduced by Hieftje et al. Here one source should enable good atomization and the other one high signal-to-noise levels or minimum matrix influences. The concept has been demonstrated for an inductively coupled plasma/microwave-induced plasma tandem source (75).

The largest innovation in atomic emission spectrometry deals with the investigation of sources. Classical sources remain an important topic, as, for example, shown for the case of flame sources for the determination of the alkali elements by Kékedy-Nagy and Cordos (76). Also, studies of dc arc emission spectrometry, with respect to the effects of easily ionized elements (see, for example, ref 77), or with long-term stability, as discussed by Florian et al. (78), were performed. For direct solids analysis, in addition, glow discharges remain a strong topic and are treated in a further chapter, whereas also lasers are an important field of innovation. Here the availability of femtosecond lasers for laser ablation is an actual point of research, as discussed by Margetic et al. (79). Microwave plasmas and inductively coupled plasmas form two strong groups of sources and are treated in extenso, as well.

Microwave-Induced Plasmas. Microwave plasmas have long been propagated as alternative sources to the inductively coupled plasmas, as they enable it to operate with less gas and power consumption and, as apart from argon, also helium and even air can be used as the working gas. A wide variety of devices both as single-electrode plasmas and as electrodeless discharges, and this at widely differing power levels and in very differing resonant cavity and waveguide structures, have been described.

Capacitively coupled plasma, which was known since the 1950s, has been shown to be a powerful and low-cost source for air and stack gas quality monitoring with respect to heavy metals. It could be shown that for Cd, Co, Cr, Fe, Mg, Ni, and Pb the legally fixed maximum values are far above the detection limits in the case of an air discharge and that high amounts of water vapor and CO₂, which as the rule are present in stack gases in large concentrations, do not gravely disturb the monitoring capacities (80). Therefore, Yamada and Okamoto (81) showed the possibilities of a 1-kW helium microwave-induced plasma for the determination of the halogens and, for chlorine and bromine, obtained detection limits at the 100–200 ng/mL level in the case of ultrasonic nebulization with desolvation. Ohata et al. (82) showed that a high-power nitrogen microwave-induced plasma also is a powerful

source for atomic emission spectrometry and investigated the effect of the addition of oxygen on the temperatures and on analyte atom and ion line intensities. Garcia et al. (83) performed diagnostic studies of a surface-wave-sustained argon plasma column at atmospheric pressure by means of a plasma interruption technique and could show that the plasmas, as a result of departures from local thermal equilibrium in the case of an argon MIP, are two-temperature plasmas.

The microwave plasma torch (MPT), which has been known for 10 years as a rather robust microwave discharge, was further developed and studied. Zhao et al. (84) studied the possibilities of an end-on-viewed torch for atomic emission spectrometry, whereas Huan et al. (85) studied the features of a Nafion dryer as desolvation device and especially performed optimization studies.

According to Beenakker, the microwave-induced plasma has been commercially available for a large period together with a diode array spectrometer for element-specific detection in chromatography. This approach especially was successful for the determination of organometal compounds after derivatization, as required in speciation work. Tin and lead organic compounds could be determined by solid-phase microextraction-gas chromatography-atomic emission detection (SPME-GC-AED) after in situ propylation with sodium tetrapropylborate. Detection limits of 0.2 ng/L as metal were obtained when applying headspace sampling in the case of a 20-mL volume, as described by Crnoja et al. (86). Dietz et al. (87) used a capillary cold trap coupled with microwave-induced plasma atomic emission spectroscopy for mercury speciation and achieved detection limits of 6, 0.95, and 1.25 ng/L for dimethylmercury, methylmercury, and inorganic mercury, respectively. Determinations in real samples such as oyster, tuna fish, and sediment samples could be performed after microwave-assisted extraction. For the determination of alkylphenols, derivatization to ferrocenecarboxylic acid esters can be applied to enable gas chromatography-atomic emission detection, as described by Rolfes and Andersson (88). Also, in combination with laser ablation, MIP-AES in argon or helium at atmospheric or reduced pressure, in the case of an echelle spectrometer with CCD detection, is very useful, as shown by the direct determination of additives such as Al, Ca, Cu, Sb, and Ti compounds or recycling relevant nonmetals such as F, Cl, Br, I, and P in polymers by Leis et al. (89). The estimated detection limits for metals are at the 0.001–0.08% level and for the nonmetals at the 0.05–0.7% level. MIP-AES also remains a favorable detection principle for the volatile hydride-forming elements, as shown for the case of selenium released by electrochemical hydride generation in a miniaturized electrolytic flow cell by Schermer et al. (90). The use of an advanced system for speciation of mercury has been described by Slaets and Adams (91). It is based on the combination of a purge and trap concentrator, an isothermal oven housing a multicapillary column for the separation of the analytes, and a miniaturized plasma emission detector incorporating a filter monochromator.

An analytical performance similar to that with the MIP according to Beenakker can be achieved with capacitively coupled high-frequency discharges operated at up to 100 W. Rahman and Blades (92) investigated the ionization of Mg and Cd in an atmospheric pressure parallel plate capacitively coupled plasma

operated at 200 W in the case of sample introduction by electrothermal evaporation. Herwig and Broekaert (93) described the use of direct sample insertion of a quartz stub carrying dry solution residues into a 100-W capacitively coupled high-frequency plasma operated in argon or helium and for Pb, Cu, Cd, and Mg and reported detection limits in the 20–600 pg range.

An important trend is the development of microplasmas in systems produced by microstructural technologies. Eijkel et al. (94) used an atmospheric pressure dc glow discharge on a microchip as molecular emission detector whereas Bass et al. (95) described a helium plasma, formed using a parallel plate, capacitively coupled geometry, operating at atmospheric pressure, at a 13.56-MHz frequency and a power level of 5–25 W. The stability area and some band features emitted were described. Engel et al. (96) described a microwave-induced plasma based on microstrip technology and its use for the atomic emission spectrometric determination of mercury with the aid of the cold-vapor technique. At a power of 10–40 W and gas flows of 50–1000 mL/min argon, rotational temperatures of 650 K and excitation temperatures determined with Fe line intensities of 8000 K were measured. Mercury could be determined down to the 50 pg/mL level; the system had excellent long-term stability (fluctuations of <1.4% within 80 min at a concentration level of 10 ng/mL Hg) and it enabled determinations in real samples. In a subsequent paper, a helium MIP operated at 2.54 GHz at atmospheric pressure and based on microstrip technology was described by Bilgic et al. (97). The plasma was self-igniting and was operated at 5–30 W with gas flows between 50 and 1000 mL/min, and in gas flows, chlorine in the form of HCCl_3 could be determined at the picogram level. This demonstrates that the plasma has great potential for element-specific detection in gas chromatography.

Inductively Coupled Plasmas. Inductively coupled plasmas remain the most widely used radiation sources for atomic emission spectrometry especially when working with solutions. Though intensively investigated and used in many fields of application, much innovation is still going on. It especially comprises diagnostic studies as well as developments in spectrometric instrumentation and progress in sample introduction.

Thermodynamic and diagnostic studies of the plasma itself continue to be performed. Vacher et al. (98) calculated the composition, monoatomic spectral line intensities (Cu, O, N), and enthalpy for thermal and nonthermal equilibrium conditions in a plasma composed of three plasma gas mixtures of N_2 , O_2 , and an aerosol of copper sulfate in water and for this ICP measured rotational and excitation temperatures. Yang et al. (99) compared simulated and measured fundamental parameter mappings in the case of electron number densities, electron temperatures, and heavy-particle temperatures for an argon inductively coupled plasma. They found agreements partly better than within 10% with especially large deviations toward the edge of the plasma. Further incoherent Thomson scattering spectra were shown to enable it to derive electron energy distributions for the ICP, as described by Huang et al. (100). The approach allowed it to show up the existence of deviations from a Maxwellian energy distribution in the electron energy range of 0.1–6.6 eV. Not only for conventional ICPs but also for novel ICP sources such as the enclosed ICP, spatially resolved profiles of rotational temperatures and analyte atom distributions were measured with a CCD spectrometer by

Breer et al. (101). Rotational temperatures in the range of 3750–4350 K were found, and an M shape of the plasma was reported for gas flows of 80–740 mL/min. The dependence of the temperatures on the absolute gas flows and the moisture load was found to be minimum. For aerosol formation, diagnostic studies were performed as well. Xu and Agnes (102) reported on the use of laser light scattering signals to study the effect of a direct-current-biased mesh screen placed in a spray chamber on the formation of the tertiary aerosol and especially investigated the influence of NaCl. McLean et al. (103) described the features of optical patterning as a technique for three-dimensional aerosol diagnostics. Here the aerosol is illuminated with a thin laser light sheet to capture images of the fluorescence and Lorenz–Mie scattering signals from the aerosol field with a charge-coupled detector. Three-dimensional maps of spray structure, mass distribution, and droplet size distribution are obtained for the entire aerosol field by image stacking. A simulation of droplet heating and desolvation in an ICP was performed by Benson et al. (104). The combination of desolvation and transport models allowed it to obtain first predictions of droplet concentrations and evaporation rates in an ICP flow for the case of the spray of a DIHEN nebulizer.

With respect to instrumentation, an important topic remains the use of axial and lateral viewing of the ICP. Chausseau et al. (105) studied the influence of the operating conditions on the self-absorption effects in radially and axially viewed ICP-OES. A further instrumental innovation lies in the use of ICP systems with which the VUV region can be fully used. Wieberneit and Heitland (106) reported on the features of a new argon-filled CCD spectrometer using spectral lines in the VUV spectral range. The application of prominent spectral lines in the 125–180 nm range for ICP-AES was investigated (107). A most important innovation in the instrumentation for ICP-AES is the availability of array detector technology, which allows real-time dynamic background and line interference correction as well as truly simultaneous measurements at different wavelengths, by which the full precision of ICP-AES can be achieved. This is well documented by high-precision determinations of noble metals in catalytic converter samples by carius tube dissolution and ICP-AES using charge injection device detection (108). In the case of echelle monochromators, background acquisition over a limited spectral range also is possible, as discussed by Becker-Ross et al. (109). Wavelength identification in the case of scans is improved through the use of a neon reference spectrum, and especially low stray-light intensities were found to result from the use of a double monochromator, as shown by measurements in ICP-AES under the presence of high concentrations of calcium in the sample solutions. Also, the use of the VUV lines in the case of an echelle spectrometer with charge injection device detection in ICP-AES has been described (110). Here a thin coating of lumogen, used as a wavelength conversion phosphor, is applied to the surface of the CID detector, and for chlorine, a detection limit of 100 ng/mL in the case of the Cl 134.724-nm line has been obtained. In the case of array detector technology, the time correlation between different channels has an important influence on the possibilities for background correction as shown by Chausseau et al. (111) for ICP-AES using multichannel detection.

Apart from the innovation in the spectrometer, studies on alternative ICP sources are important as well. The helium ICP is

important as here also the excitation of nonmetals is most effective. As up to now the ignition and stable operation of helium ICPs remained problematic, improvements through the use of a free-running system enabling the operation of a 600–800-W plasma with a total helium consumption of below 10 L/min are important (112). In this source, plasma rotations at a frequency of 75–275 Hz were found and rotational temperatures, excitation temperatures, and electron number densities were found to be 1600–1800 K, 3800–4300 K, and $3 \times 10^{13} \text{ cm}^{-3}$, respectively.

The prime field of innovation in ICP-AES is still sample introduction. Pneumatic nebulizers here are the standard devices, and their operation as well as the use of new types of nebulizers was the topic for many studies. Danzaki and Wagatsuma (113) studied the influence of acid concentrations in the case of pneumatic nebulization on the excitation temperature for vanadium ionic lines. As the nebulizer and the spray chamber form a unit with respect to the properties of the aerosol formed, spray chamber studies are of high importance. Todoli et al. (114) compared the properties of different spray chambers such as the conventional spray chamber according to Scott, a conventional cyclonic chamber, and two low-volume spray chambers in the case of a glass concentric pneumatic micronebulizer with respect to washout times and memory effects. In a further study, Todoli and Mermet (115) studied the effect of the spray chamber design on steady and transient acid interferences in ICP-AES. In view of the use of ICP atomic spectrometry for elemental detection in liquid chromatography, low-consumption high-efficiency pneumatic nebulizers are very important. Accordingly, Todoli and Mermet (116) studied the performance of the direct injection high-efficiency nebulizer (DIHEN) and compared its features with those of the high-efficiency nebulizer (HEN) coupled to a cyclonic spray chamber as a liquid sample introduction system for ICP-AES. As an effect in spray chambers, Xu et al. (117) studied aerosol static electrification and its consequences for ICP-AES. With properly optimized pneumatic nebulization and simultaneous measurements of line and spectral background intensities, ICP-AES now is suitable for high-precision analyses. This was shown by Salit et al. (118) using an example of the determination of the Li and Al mass fractions and the Li/Al amount-of-substance ratio, which could be determined in LiAlO_2 with an uncertainty of 0.2%. A similar precision was shown to be possible by Geilenberg et al. (119) in the analysis of Y–Ba–Cu–O and (Pb)Bi–Sr–Ca–Cu–O high-temperature superconductors, where for minor compounds relative standard deviations of below 1% can be achieved, especially when using CCD-based simultaneous spectrometers. Slurry nebulization with pneumatic nebulizers for a number of tasks involving fine powders such as cement can be well used in routine application, as shown by Marjanovic et al. (120).

Since the early beginnings of ICP-AES, ultrasonic nebulization has been proposed and continuously improved. In dissolved plant samples, elements such as arsenic can then be determined. However, a careful investigation of possible matrix effects is required, as shown by Vassileva and Hoenig (121). As a further high-efficiency sample introduction technique, thermospray nebulization as possible with a low-powered microwave system was studied by Ding et al. (122).

Graphite furnace evaporation remains very attractive for the analysis of microsamples but also because of the high sampling

efficiencies as compared to pneumatic nebulization. Kantor (123) discussed the effects of streaming conditions and gaseous-phase additives on the sampling efficiency in the case of novel electrothermal vaporizer devices for volatile (Cd, Zn) and medium volatile (Cu, Mg, Mn) elements and investigated the addition of CCl_4 vapors. Gras and de Loos-Vollebregt (124) studied the limiting effects of the matrix load on the transport efficiencies achieved. Venable and Holcombe (125) studied peak broadening from an electrothermal vaporization sample introduction source into an ICP and investigated the influences of diffusion coefficients, tube diameters, transport tube length, and gas flow rates. Tianyou et al. showed that electrothermal vaporization ICP-AES is especially useful in routine for the case of slurry sampling of powders, as shown for the determination of trace impurities of B, Mo, Ti, and Zr in SiC when PTFE was used as a fluorination aid (126). Fluorination-assisted electrothermal vaporization ICP-AES also could be used for the determination of traces of rare earth elements in high-purity Y_2O_3 with detection limits in the subnanogram range, as shown by Cai et al. (127). For the determination of fluorine itself, electrothermal vaporization from a tungsten boat furnace in ICP-AES under the use of the F I 685.602-nm line was shown by Okamoto et al. (128) to be possible with a detection limit of 9 μg .

Direct sample insertion makes an efficient sampling possible without risking transport losses. Badieli and Karanassios (129) showed that elements such as Pb, Zn, Cd, Mn, Mg, V, Sr, and Be could be evaporated from dry solution or slurry residues or from solids carried on a rhenium foil, which is brought near to the ICP discharge, and this in the case of ICP-AES with detection limits in the femtogram range. A similar approach was followed by Rybak and Salin (130), however, for larger samples. Here metals can be determined in soils and sediments by applying induction heating-electrothermal vaporization ICP-OES using slurry sampling in graphite cups, which are then placed in a radio frequency field and vaporized in a carrier flow of 15% (v/v) SF_6 –Ar.

Hydride generation ICP-AES and other volatile compound-generating techniques in the case of ICP-AES have the advantage of enabling multielement determinations. Batistoni et al. (131) investigated the influence of the introduction of the hydride generation gases into the ICP on the electron number densities and found increases by up to 25%. Apart from the volatile hydride-forming elements, other volatile compound using techniques were also used. They include the determination of nickel through the formation of volatile compounds by a reaction with potassium borohydride instead of using the nickel tetracarbonyl formation, as described by Guo et al. (132). Even for Au, Pd, and Pt volatile species in media of HCl, HNO_3 , or H_2SO_4 , a mixture of HCl and HNO_3 (3:1) and CH_3COOH could be generated in a gas–liquid-phase separation system by reaction with sodium tetrahydroborate. Signal enhancements by factors of 2.3, 2.0, and 1.1 as compared to pneumatic nebulization were obtained, as shown by Pohl and Zyrnicki (133). Volatile species generation first enables the power of detection in ICP-AES required for organometal work, as shown by the determination of organotin compounds (134).

A further important aim in sample introduction is the direct analysis of compact solid samples. In the case of metals, on-line electrolytic dissolution coupled to flow injection ICP-AES was found to enable the determination of Fe, W, Mo, V, and Cr in

tool steels, as described by Gervasio et al. (135). Also, spark ablation of metals under a liquid could be shown to enable rapid dissolution of metal samples (136).

Laser ablation is a most favorable technique for the production of aerosols at solids, and the aerosol analytes can be determined by ICP-AES. The approach is very useful both for electrically conductive and for electrically nonconductive samples and, in addition, both for bulk and for in-depth profiling analysis. Kanicky et al. (137) showed the features of UV laser ablation ICP-AES for the analysis of tungsten carbide coatings. Kehden et al. (138) used the so-called LINA (laser-induced argon) spark ablation combined with ICP-AES, where the Nd:YAG laser plasma ablates the sample and the latter can even be rotated to cope with sample homogeneities. They obtained ablation rates in the microgram per second range and detection limits in the low tens of micrograms per gram range for the relevant elements in steel, aluminum, and brass sample and showed the importance of internal standards.

GLOW DISCHARGE ATOMIC SPECTROMETRY

The use of glow discharges in analytical chemistry is classically based on the sputtering of solid samples, which are used as the cathode of the glow discharge. The sputtered atoms arrive in the plasma where they are subject to ionization and excitation. The corresponding ions are then measured in a mass spectrometer, giving rise to glow discharge mass spectrometry (GDMS). The excited atoms emit characteristic photons, which can be detected with an optical emission spectrometer, yielding glow discharge optical emission spectrometry (GD-OES). Finally, the sputtered atoms can also directly be probed with an external light source, for atomic absorption or fluorescence spectrometry (GD-AAS and GD-AFS). It should, however, be mentioned that the latter two techniques are clearly of minor importance compared to GDMS and GD-OES. For example, in the last two to three years (i.e., the time period covered by this review), there have been no papers published in the scientific literature about new developments in GD-AAS and GD-AFS.

Fundamental Studies. To improve the analytical capabilities of glow discharges, a good insight into the fundamental plasma processes is desirable. This can be obtained by modeling the behavior of the various plasma species or by plasma diagnostics (i.e., measuring the plasma characteristics).

In the last couple of years, Bogaerts et al. have developed a comprehensive modeling network, based on Monte Carlo, fluid, and collisional-radiative models, for the various species present in an argon glow discharge with a copper cathode, i.e., Ar gas atoms, Ar⁺, Ar₂⁺, and Ar²⁺ ions, fast Ar atoms, Ar atoms in various excited levels (including the metastable levels), sputtered Cu atoms and Cu⁺ ions, both in the ground state and in various excited levels, and Cu²⁺ ions. Typical calculation results are the densities, fluxes, and energies of the various species, the potential and electric field distributions, information about collisions in the plasma and about cathode sputtering (e.g., erosion rates, crater profiles), prediction of relative sensitivity factors for GDMS, and optical emission intensities for GD-OES. The modeling network has been applied to dc (e.g., ref 139), rf (e.g., ref 140 and references therein), and microsecond pulsed (e.g., 141) glow discharges. The model results have been compared with a variety of experimental data, and reasonable agreement has been reached,

showing that the models present a realistic picture of the analytical glow discharge. Three papers about such a comparison with experiment have been published in the last two years, i.e., for optical emission intensities as a function of distance from the cathode, for Ar I, Ar II, and Cu I lines (142), and for the electrical characteristics, erosion rates, and optical emission intensities in a dc and rf Grimm-type glow discharge (143).

Pitchford and collaborators have also recently published a few papers about the modeling of analytical glow discharges, i.e., for Ar gas heating and for electrical characteristics in rf discharges (e.g., ref 144). They used a modeling approach similar to that of Bogaerts et al., i.e., a hybrid Monte Carlo-fluid model, but limited only to the Ar⁺ ions and electrons. For Ar gas heating, good agreement with Bogaerts' results has been reached. For the rf electrical characteristics, some discrepancies were observed, i.e., in the importance of the displacement current and the capacitive or resistive behavior of the rf discharge. The difference in results has in the meantime been clarified; i.e., one model focused only on the plasma currents, whereas the other model included part of the electrical circuit (140).

There is little research going on with respect to plasma diagnostics experiments in analytical glow discharges (e.g., measuring the electric field distribution, the plasma species densities, or energies), mainly because (i) a typical analytical glow discharge cell is rather small (order of a few cm³), making measurements not straightforward, and (ii) dedicated instrumentation (such as lasers) is required, which is not available for plasma diagnostics in most of the analytical laboratories.

Plasma characteristics, which are easier to measure, are the macroscopic quantities, such as the electrical characteristics, erosion rates, and optical emission intensities (see above). In the last two years, a few papers have been published by Hodoroaba et al. (e.g., ref 145), dealing with the addition of small amounts of hydrogen to an argon glow discharge and the effects on the optical emission intensities of several Ar I, Ar II, Cu I, and Cu II lines. It was found that the intensities of some lines increase, while others decrease, upon hydrogen addition. Different modes of hydrogen introduction (i.e., either externally in gaseous form or sputtered as a sample constituent) appeared to cause similar effects, suggesting that similar changes occur in the discharge processes (145). Some interesting features on the emission spectrum of hydrogen were also observed, i.e., the presence of lines, bands, and a continuous spectrum in the range of 220–440 nm. The latter appears to be due to quenching of Ar metastable atoms by H₂ molecules, leading to excitation and subsequent decay to a repulsive state of H₂, with emission of the continuum radiation. This explanation was confirmed when the effects of hydrogen addition to an argon and to a neon discharge were compared. Indeed, in the latter case, this continuum emission was absent, because quenching of neon metastables by H₂ molecules could not occur. Because routine GD-OES and GDMS are often concerned with unavoidable source and sample contamination, these investigations are essential, e.g., for improvements in GD-OES quantification.

To obtain a better understanding of the effects of hydrogen addition to an argon glow discharge, a review was presented by Bogaerts et al. (146), concerning all relevant processes that can occur between argon and hydrogen species, including the corre-

sponding cross sections or rate coefficients (to give an idea about the importance of the various processes). Finally, a review was published by Wagatsuma, on glow discharges with mixed plasma gases (147). The gas mixtures investigated include Ar–He, Ar–O₂, Ar–N₂, Ne–He, and N₂–He. The effect of type and content of the gases was investigated on excitation processes and emission characteristics in GD-OES and on ion intensities in GDMS. It was concluded that mixed gases can either improve or deteriorate the analytical performance of glow discharges (147).

Instrumental Developments. (1) Glow Discharge Source: dc, rf, and Pulsed Operation Modes. As mentioned above, glow discharges can operate in three different modes, i.e., the dc, rf, and pulsed mode. The dc mode is already well established, and it is still mostly used, especially because most commercial instruments are available for this operation mode. It has, however, a disadvantage in that it is not able to analyze nonconductors directly (see also below), because of charging-up of the nonconducting material as a result of bombardment by Ar ions. This problem is overcome by applying an rf voltage to the electrodes, so that the surface charging due to Ar ion bombardment is neutralized by electron bombardment during a part of the rf cycle. In the section on Applications of GDMS and GD-OES, some new methodology and new applications of rf discharges will be discussed. Here we will focus only on the rf operation mode itself.

Wagatsuma and co-workers (e.g., ref 148) investigated the effect of an additional dc bias voltage, and corresponding dc bias current, on an rf Grimm-type glow discharge. It was found that sputtering rates, electron densities, excitation, and corresponding emission intensities were enhanced, leading to an improvement of the detection sensitivity (148). Furthermore, the frequency of the rf plasma appeared to be an important factor for determining the self-bias voltage; i.e., lower rf frequencies induce larger self-bias voltages. Hence, in comparing rf discharges operated at 13.56 and 6.78 MHz, the latter offered a better analytical performance, attributed to the higher self-bias voltage.

The third operation mode, which is gaining increasing interest in recent years, is the pulsed mode. Because voltage and current are applied during short pulses (order of milliseconds or microseconds), a higher peak power can be obtained for the same average power as its dc counterpart, yielding higher sputtering, ionization, and excitation efficiencies, and hence greater signal intensities and better analytical sensitivities. On the other hand, the short pulses followed by a relatively long afterglow allow the sample to cool, which minimizes sample overheating. Finally, background argon signals and analyte signals appear to reach their maximum at different moments in time (during or after the pulse). Hence, when combining the pulsed discharge with time-resolved detection, efficient discrimination against interferences from the discharge gas is possible. The capabilities of pulsed glow discharges and some example applications are illustrated by Harrison and co-workers in an excellent A-page review article, recently published in this journal (149).

In the last couple of years, the Harrison group developed a microsecond-pulsed Grimm-type glow discharge for GD-OES (e.g., refs 150–152). The effect of pulse voltage, pulse frequency, pulse width, and Ar pressure on Cu atomic and ionic emission intensities was studied, and comparison was made with a dc glow discharge.

For atomic line emission, the optimized pulse width is around 10 μ s. Voltage and pressure also appear to be dominant factors affecting emission profiles (150). The source was also investigated for GD-OES depth profiling, and the effect of the above discharge conditions on the depth resolution was examined (e.g., ref 151). The two additional parameters, specific for pulsed operation, i.e., pulse width and frequency, permit better control over the sample removal rate, allowing thin samples to be analyzed, which is very difficult with the dc counterpart. It appeared that a flat crater bottom and good depth resolution could only be obtained within a limited range of voltages, whereas pulse width and frequency had only little effect on the depth resolution. This implies that a wide dynamic range of layers, from several nanometers to tens of micrometers, can be analyzed, by increasing or decreasing the pulse width and frequency (151). Further, the temporal response of the elemental emission lines was studied. The signal-to-background ratio was found to increase by a factor of 5–10, compared to its dc counterpart, because of the higher instantaneous pulse power and the possibility of time-resolved detection (152). It was observed that certain nearly nonconductive materials, which cannot be run in dc mode, could be run in the microsecond-pulsed mode, because of the limited overall surface charging (152). The microsecond-pulsed Grimm-type glow discharge is also applied as an ion source for time-of-flight mass spectrometry (TOFMS), to gain complementary information about the pulsed plasma behavior (153). Furthermore, the microsecond-pulsed Grimm-type source is also designed in the hollow cathode (HC) configuration for GD-OES (154). This HC configuration appears to offer several advantages, including even more efficient excitation and ionization, and hence higher sensitivity, as well as rapid sample exchange. It is suitable not only for bulk solids but also for solution residue analysis (154). Finally, the so-called “double pulse method”, in which a second pulse is applied at a variable delay after the first pulse, is demonstrated for the HC configuration (155). The net discharge then consists of a series of double pulses, in which each second pulse enhances the emission intensity of the analyte atoms produced in the first pulse (155).

The groups of King and Majidi have also been quite active in the research field of pulsed glow discharges (e.g., refs 156–158). An interesting application, demonstrated both for millisecond- and microsecond-pulsed GD-TOFMS, is that elemental, structural, and molecular information of samples can be obtained, depending on the extent of interaction of the samples with the plasma, which is controllable by the user (e.g., ref 156). Indeed, spectra acquired during the prepeak region provide structural information through molecular fragmentation, as well as elemental information, whereas spectra acquired during the afterpeak region provide intact, molecular ions, as a result of soft chemical ionization. This is illustrated, among others, for toluene, *p*-xylene, and ethylbenzene (e.g., ref 156). The coupling of laser ablation to a pulsed glow discharge is realized in ref 157. Laser-ablated material was introduced into the pulsed glow discharge during the afterpeak, yielding ionization and excitation (157). Finally, based on two-dimensional maps of the spatial distributions of excited and ionized sputtered Cu atoms in a millisecond-pulsed glow discharge, the temporal and spatial dependences of different excitation and ionization processes were investigated (158). It appears that transitions from low-energy electronic states dominate in the

plateau time of the pulse, due to electron excitation of the ground-state Cu atoms. Transitions from high-energy atomic states, on the other hand, occur during the afterpeak time regime, which is explained by relaxation of highly excited Cu atoms produced by electron recombination with Cu⁺ ions. The Cu⁺ ion emission itself was found to be only important during the plateau regime (158).

(2) Instrumental Developments for Mass Spectrometry and Optical Emission Spectrometry. Beside developments in the GD operation mode, some papers were also published that reported instrumental developments for mass spectrometry and optical emission spectrometry. Sanz-Medel and co-workers coupled a dc-GD to a TOFMS commercially used for inductively coupled plasma mass spectrometry (ICPMS). Hence, the GD source was designed to be easily and quickly (less than 10 min) exchanged with the ICP source (159). With respect to software for GDMS, Robben et al. developed a new and powerful program for automatic data analysis and interpretation of mass spectra for the VG9000 GD mass spectrometer (160). Finally, Marcus and collaborators have reported the development of a Microsoft Excel Visual Basic program, called Peakfitter, which can process multiple Gaussian-shaped spectral peaks quickly and easily and gives background-corrected peak areas. The software, described in *Spectrochimica Acta Part B Electronica*, is applied to rf GD ion trap mass spectrometry (161).

With respect to GD-OES, Weiss developed a formalism to calculate uncertainties of the calibration parameters, sputter factors, and predicted concentrations of analyte elements. This formalism is intended for evaluation of the analytical performance of different experimental GD-OES setups and as a basis for further developments of a calibration model for GD-OES (162).

(3) Boosted GD Sources. To improve detection limits, both in GDMS and in GD-OES, GDs have been combined with other sources, into so-called "tandem sources". Duan et al. coupled a GD to a microwave-induced plasma (MIP) (e.g., ref 163). The GD provided sputtering and partial ionization, and the MIP served to enhance the ionization (so-called "microwave boosting"). The tandem source was coupled to a TOFMS, and significant signal enhancement was observed compared to a single GD source. Microwave boosting of a GD was also carried out for OES by Ülgen et al. (164), to eliminate spectral interferences caused by molecular bands and lines of the plasma gas. By suitable modulation of one of the two excitation sources, and phase-sensitive amplification, the analyte signals could be selectively amplified, whereas the molecular bands and lines of the plasma gas were hardly influenced by the modulation and did not appear in the amplified spectrum. In particular, the OH interference on the most important analytical lines of Mg, Bi, and Sn and the interference of Ar II on A I were eliminated to a high degree (164). Finally, the effect of the magnetic field on rf gas-jet boosted GD-OES was studied by Kim and co-workers (165). The magnetic field was found to enhance only the excitation of sputtered atoms and not the sputtering itself. Detection limits for the magnetic boosted GD were tens of ppb for many trace elements in low-alloy steels, which is 1 order of magnitude improvement compared to conventional rf GD-OES (165).

Applications of GDMS and GD-OES. The major application of GDMS and GD-OES, i.e., the bulk analysis of solid conducting materials, is in a stage of maturity and is mainly used for routine

analysis, e.g., in an industrial environment. Consequently, there are not many scientific papers in the literature reporting about this application, and the few papers that have been published are purely application papers, which are outside the scope of this review. We focus here only on those applications for which new methodology is developed.

(1) Depth Profiling Analysis. A widely used application of glow discharge spectrometry (mainly GD-OES), for which there are, however, still a lot of scientific challenges (as follows from the large number of papers; see below), is depth profiling. Indeed, the measurements yield signal intensities versus sputter time, but for quantitative depth profiling, this should be converted into analyte concentrations versus sputter depth, which appears not always straightforward.

Bengtson et al. developed a method for quantitative depth profile analysis of Zn-based metallic coatings by dc-GD-OES, based on the calibration of the emitted light per unit weight of each element (166). An interlaboratory comparison was carried out involving 12 laboratories from 8 countries. The method worked well for the accurate and rapid determination of coating thickness and concentration of the major element (Zn), but certain improvements are still necessary for the concentrations of the alloying elements (166). Sanz-Medel applied rf-GD-OES depth profiling for the same Zn-based metallic coatings, and the results were in agreement with the data obtained by this dc-GD-OES interlaboratory test. It was found that the sputter rates for different matrixes were of the same order for both operation modes (167).

Payling et al. performed quantitative depth profiling by rf-GD-OES for various hard coatings (e.g., TiN, TiC, and TiCN) on steel, based on dc bias voltage correction and hydrogen correction (168). These corrections involve a term called the "inverse relative emission yield" and are simple functions of the dc bias voltage and hydrogen signal. According to the authors, correct quantitative depth profiling can now be obtained, even in the presence of significant amounts of hydrogen in the coating (168). Marcus and co-workers developed a technique for on-line determination of sputter depth (i.e., during GD operation) for rf-GD-OES, based on a laser confocal displacement sensor that optically measures the distance between the sensor head and the sample (i.e., displacement of the surface) (169). The method enables the determination of the real-time sputter depth, which is necessary for quantitative depth profiling.

Shimizu et al. have published a large number of papers in recent years demonstrating the suitability of rf-GD-OES for the depth profiling analysis of surfaces coated with multilayers of widely differing thicknesses, ranging from a few tens of nanometers to several tens of micrometers (e.g., refs 170 and 171). Indeed, the highly uniform sputtering rate yields an excellent depth resolution, enabling the analysis of very thin films. On the other hand, the high sputtering rates typical for GD-OES allow thick films to be analyzed, within a reasonable time (170). The depth resolution and sensitivity were found to be comparable to, or better than, secondary ion mass spectrometry (SIMS). Two additional advantages compared to SIMS are the short analysis time for thick films (see above) and the fact that nonconducting alumina films could be analyzed, because surface charging is insignificant (because of rf powering). For successful application, however, the surfaces should be microscopically flat, because a

surface roughness with dimensions similar to the thickness of the films can lead to almost total degradation of the depth profiles. Moreover, the Ar pressure strongly affects the depth resolution, through the shape of the crater. The best depth resolution was obtained at 0.41 mbar Ar pressure. In ref 171, it was reported that the depth resolution degraded more or less linearly with depth. A depth resolution of 1.3 nm was realized to depths of ~25 nm (171).

Chen et al. investigated the effect of crystal orientation on the sputter rate of pure Fe in GD-OES and found a correlation between the crystal orientation normal to the surface, the surface texture, and the sputter rate (172). It is clear that this has implications for the depth resolution in GD-OES; i.e., samples with small grain size will have better depth resolution in GD-OES (172).

An interesting application of rf-GD-OES depth profiling was described by Hoffmann and co-workers, i.e., the determination of either thickness or refractive index of transparent coatings on reflecting substrates, based on interference phenomena, causing intensity oscillations of certain spectral lines (e.g., ref 173 and references therein).

Finally, although depth profiling analysis is far more popular with GD-OES than with GDMS, a few papers have recently been published using high-mass-resolution GDMS for depth profiling. Spitsberg and Putyera measured trace element compositions of PtAl coatings and their depth profiles on Ni-based alloys, from the near-surface region to more than 100- μ m depth. The conventional conversion procedure of ion intensities versus sputtering time into concentration versus depth was evaluated and corrected with the necessary correction factors (174). Betti and co-workers used dc GDMS depth profiling to study the incorporation of impurities (Li, B, Zn) in ZrO₂ layers grown on Zircaloy samples, for corrosion mechanism studies (e.g., ref 175). The depth profile of insulating ZrO₂ layers was determined using the secondary cathode technique (see below).

(2) Analysis of Nonconducting Materials. As mentioned above, dc GDs are very suitable for the analysis of solid conducting materials, but nonconducting samples would be charged up, due to the continuous sputter bombardment of positive ions. Several methods have been reported in the literature to overcome this problem. The first and most used technique is the application of an rf discharge. Because the sample acts now alternatively as cathode and anode, the charge accumulated by positive ion bombardment is neutralized due to electron bombardment during part of the rf cycle (see also above).

Sanz-Medel and co-workers used rf-GD-OES for the direct elemental analysis of bone (176). Three sample preparation strategies were investigated (i) using a metallic holder for samples of 1 mm thick, (ii) embedding the samples (0.5–1 mm thick) in a conducting resin, and (iii) encapsulating a thin layer (8–20 μ m thick) bone sample in poly(methyl methacrylate) and pasting it over a flat support. From a medical point of view, the latter approach is of course the most practical one, because it requires the smallest amount of the patient's bone. Moreover, this approach also yielded the best analytical sensitivity (176).

Anfone and Marcus reported the analysis of solid glass samples by rf-GD-OES (177). The major operating parameters, such as discharge power and pressure, and sample thickness, were evaluated. Because the sample can be directly used in the rf-GD,

sample preparation is fast, simple, and economical, and it avoids the propagation of errors and potential contaminations, which can occur during the dilution processes used in conventional solution-based methods, such as those based on the ICP (177). Also, the direct polymer analysis by rf GDMS and GD-OES was described by Marcus (178). Interesting results were obtained, both for bulk polymers and for thick coatings on polymers. The inert conditions of the plasma yield mass spectra, which are relatively easy to interpret. Both elemental and molecular composition analyses were possible (178).

However, besides using an rf GD, nonconducting samples can also be measured with a dc GD, when applying certain tricks to make the sample conductive. The first and most classical method is based on grinding the solid sample into a powder (or starting from a nonconducting powder) and it mixing with a conductive host matrix (e.g., Cu powder). This technique has been used in the past both for GDMS and for GD-OES and has reached the stage of routine applications.

The second method, which is not yet so well known in the GD community, and which has only been used up to now for GDMS, is based on applying a conductive diaphragm (so-called "secondary cathode") on top of the nonconducting sample. Hence, the nonconducting solid sample can directly be used, without sample preparation (such as grinding into powder form). Wayne explored the secondary cathode technique with dc-GDMS for several nonconductors (179). Scanning electron microscopy (SEM) and micro X-ray fluorescence (μ -XRF) measurements revealed that the sputter-deposited Ta film (which originated from the secondary cathode) is nonuniform, being thicker at the perimeter and thinner in the central region. Further, this secondary cathode technique is also frequently used by Betti and co-workers for the analysis of nonconducting nuclear samples with dc-GDMS (VG 9000 instrument in a glovebox) (e.g., ref 175).

Finally, Barshick et al. recently reported an interesting new concept to sputter Si-containing nonconducting samples in a dc HCD, by the addition of about 1% CF₄ to the argon gas (180). The radical fluoride species react with the nonconducting substrate (i.e., silica) to produce volatile SiF₄, which spontaneously evolves in the gas phase, carrying with it the trace elements. This approach is analogous to plasma etching, a well-established technique for semiconductor processing.

(3) Gas and Liquid Analysis. Beside the classical application to analyze solid samples based on cathode sputtering, the application field of GDs has in recent years significantly widened to the analysis of liquids and gases, mainly as a detector for gas and liquid chromatography (GC, LC). Recently, a special issue of *Journal of Analytical Atomic Spectrometry* (2000, 15 (1)) focused on the use of so-called "tunable plasma sources" in analytical spectroscopy, i.e., sources that can be operated in two different modes, to detect either atoms or molecules of mainly organic compounds, depending on the conditions of source operation. Several GD papers, reporting about the capabilities of GDs for both atomic and molecular analysis, were published in this special issue (see below).

Hietje and co-workers developed a gas-sampling GD, coupled to TOFMS, to obtain both atomic and molecular fragmentation mass spectra (e.g., ref 181). This gas-sampling GD is used as detector for GC (182). The GD can be rapidly switched between

atomic and molecular ionization modes, by altering the gas composition, pressure, and current (e.g., helium for atomic spectra and argon for molecular spectra) or by applying either a positive or negative potential to the sample introduction electrode (for molecular and atomic spectra, respectively) (182). The molecular spectra resemble those from a simple electron impact source. This tunable source is applied to a variety of chlorinated hydrocarbons, and speciation of different compounds is accomplished based on the $^{35}\text{Cl}^{+}/^{12}\text{C}^{+}$ elemental ratios (181, 182). Further, the same group coupled an atmospheric sampling GD with a microwave plasma torch (183); the atomic mass spectra are now generated from the MPT, whereas the molecular spectra originate from the GD. Changing between atomic and molecular modes of operation is accomplished by igniting or extinguishing the MPT.

Sanz-Medel and co-workers used hollow cathode rf-GD-OES in helium as an on-line detector for GC and HPLC, for the elemental speciation of mercury, tin, or lead (e.g., ref 184). A comparison was also made between hollow cathode and flat cathode GD-OES, in both dc and rf modes, as detectors for the determination of arsenic and antimony by on-line flow hydride generation (185). The results indicate that, for low volumes of sample, the HC discharge allows better analytical signals than the flat cathode. Detection limits up to 5–10 times better were obtained for HC-GD-OES, in comparison to those encountered with flat cathode GD-OES (184). Moreover, aside from the advantage of the multielement capability inherent to OES, as compared to AAS, it was reported that GD-OES, in comparison to, for example, ICP-OES or MIP-OES, offers favorable detection limits, a low cost of instrumentation and maintenance, and low consumption of the He plasma gas (184, 185).

HC-dc-GD-OES in helium was also used by Broekaert and co-workers as an element-specific detector for GC, for chlorinated and brominated hydrocarbons (186). The influence of the dimensions and the materials of the cathode on the signals for the Cl and Br lines was evaluated. Detection limits in the low-picogram per second level could be obtained (186).

Marcus and co-workers developed a particle-beam (PB) GDMS system as a detector for LC (e.g., ref 187). The PB interface was used to introduce the analyte species from the LC into the GD, for subsequent vaporization and ionization. The system was applied to the analysis of polycyclic hydrocarbons, steroids, seleno amino acids, and alkyllead compounds. The mass spectra display classical electron impact ionization fragment patterns for the organic compounds, as well as elemental and molecular information for the organometallic compounds (187). The PB interface was also employed in combination with HC-GD-OES, as element-specific detector for LC, for the aromatic amino acids and organomercury and organolead compounds (188). The analyte particles are introduced into the heated HC-GD by a high-efficiency thermoconcentric nebulizer (188). Moreover, the effect of the HC diameter and temperature on the analyte emission intensities was also investigated for the PB-HC-GD-OES system (189, 190). Optimum signal intensities were obtained with a 3-mm-inner diameter HC (189). The optimum HC temperature, i.e., for maximum analyte desolvation and vaporization, was defined at 200–300 °C, for a range of Cu salts. Moreover, the analyte particle size also appears to play an important role in the vaporization, atomization, and excitation processes; indeed, smaller particles

produce higher emission intensities (190). It is worth mentioning that the PB GD was also employed earlier by Marcus' group for the analysis of particulate matter by both GD-OES and GDMS.

Finally, atmospheric pressure glow discharges (APGDs) have also been employed in recent years as a detector for GC. Eijkel et al. reported the use of a small (0.1-mm equivalent radius) dc APGD in helium, as an optical emission detector for GC, for the detection of a number of carbon-containing compounds (191). Kim et al. also used a dc APGD in helium, with a 0.2-mm gap between anode and cathode, for the sensitive signal detection for GC (192). The detection was, however, not based on OES or MS but on changes in the oscillation frequency of the discharge current. It appeared that the discharge gap and current have a strong influence on the detector response. The latter was found in the femtomole and picomole range for carbon-containing compounds (192).

Further, the use (or potential use) of some related atmospheric pressure capacitively coupled (cc) rf discharges in helium as a detector for GC was also reported by Guevremont and Sturgeon (193) and by Blades and co-workers (95). In ref 193, volatile analytes separated by GC were admitted to the source through a coaxial rf-powered center electrode. Variation of the forward power (in the range 5–100 W), and the position of the plasma relative to the extraction orifice of the MS, permit control over the relative intensities of parent and daughter ion products of the decomposition of organometallic compounds. Both atomic ions, the parent molecular compounds, and combinations of the two were observed, depending on the operating conditions (193). The so-called capacitively coupled microplasma (CC μ P) of Blades et al., with dimensions of 0.25 × 0.25 × 5 mm, also has great potential as a detector for a miniaturized GC system, as is demonstrated in ref 95. The reported advantages are a very simple electrode structure (two parallel plates) and the fact that it does not require tuned or resonant structures (95).

Another type of APGD, completely different from the ones reported above, was developed a few years ago by Mezei and co-workers for liquid analysis. A stable GD is obtained between an electrolyte solution cathode and an anode, by applying a voltage of 1–2 kV, a current of ~100 mA, and a 2–6-mm discharge gap. Some kind of "cathode evaporation" of the solution surface and subsequent excitation in the plasma occur when the pH of the solution is 1–2.5. This so-called "electrolyte-as-cathode" APGD-OES system was recently applied to the on-line measurement of trace heavy metals in tap and drinking waters and in other liquid samples, such as fresh milk, by Mezei and Kim and co-workers (e.g., ref 194).

Marcus and co-workers developed a liquid sampling atmospheric pressure GD (LS-APGD) for OES (e.g., ref 195) based on the above idea. One of the electrodes (either the cathode or anode) is the electrolyte solution containing the analyte specimen. The passage of an electrical current (due to either electrons or positive ions) across the solution/gas-phase interface causes local heating and the volatilization of the analyte species. The latter are subject to excitation in the GD plasma and are measured with OES. The operating conditions depend on the electrolyte concentration and the gap between solution surface and counter electrode. Typical discharge conditions, for an electrolyte solution with pH (or pNa) of 0.5–2, and interelectrode gaps of 0.5–3 mm,

are 30–60 mA and 0.5–1 kV, with current–voltage characteristics in the abnormal GD regime (195). The difference with the electrolyte-as-cathode GD of Mezei et al. (see above) is that, in the LS-APGD, the solution can act either as anode or cathode. Moreover, the LS-APGD can operate with a variety of electrolyte species, and at considerably lower flow rates (typically 0.5–1.5 vs 5–10 mL/min for the electrolyte-as-cathode APGD) (195). Hence, the LS-APGD is promising as a low-cost, low-power OES detector for volume-limited samples, because direct introduction into the plasma of the solution is possible, by a “total-consumption vaporization step” (i.e., no waste). A challenge for the near future is the application as a detector in LC and capillary electrophoresis (195).

Finally, we conclude this section by mentioning a recent review by several authors about the use of GD atomic spectrometry (OES, MS, AAS, AFS) for the analysis of environmental samples (196). Beside powdered and particulate samples (e.g., sediments, soil, and airborne dust), the review focuses on liquids, gases, and volatilized samples and reports as the main advantage compared to, for example, the ICP, the generally lower cost of the GD, concerning source construction, power supply, and gas consumption (196).

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

The increasing demand for high sample throughput with high sensitivity combined with the capabilities of fast and simultaneous multielemental detection has led to further developments in the field of elemental mass spectrometry. Interests were focused on alternative ionization sources and modifications of the inductively coupled plasma, as well as time-of-flight, multicollector, and high-resolution instruments. Nevertheless, most of the material published within the period covered by the review mainly deals with applications of ICPMS and different sample introduction techniques. An increasing activity on the development and application of collision and reaction cells for the specific removal or reduction of polyatomic ions was recognized.

Fundamental Studies. The detector dead time and its proper adjustment play an important role in accurate analysis. Therefore, a calculation method for the determination of the detector dead time and its uncertainties was described by Held and Taylor (197). The method was based on the use of isotope ratios since they were more precise than the measurement of ion currents. Typical relative uncertainties of the dead time for the investigated continuous dynode detector was in the range of 10–20%. Similarly, Appelblad and Baxter (198) focused on the development of a model for the simultaneous determination of detector dead time and mass bias correction factor uncertainties in ICPMS. Representative isotope systems of Mg, In, and Tl were used for extensive testing of the novel model, which was additionally applied to the estimation of the effects of flicker noise and counting statistics on isotope ratio measurement precision (199). Barwick et al. (200) described a method for uncertainty measurements in ICPMS analysis based on the use of a cause and effect diagram for the identification of sources of uncertainty associated with the determination of ^{60}Ni in aqueous solutions. They concluded that uncertainty was significantly caused by method precision and instrument drift, whereas uncertainties associated with sample dilution or calibration standard concentrations were insignificant.

The automatic selection of internal standards by using a cluster analysis algorithm was documented by Sartoros and Salin (201). This algorithm was based on the use of kinetic energy, ionization potentials, oxide bond strength, and electronegativity to group the analytes. The weight of each parameter within this set depended on the sample matrix. The used samples contained a single sample matrix element but up to 25 analytes covering the atomic mass and ionization potential ranges. The authors concluded a good performance of the developed method in terms of automatic selection of internal standards for most of the investigated analytes and matrices.

A supplemental electron source in a negative extraction lens can serve the reduction of mass bias in ICPMS, as described by Praphairaksit and Houk (202). The electrons were created inside the extraction lens from a tungsten filament and were driven toward the skimmer interface where they might move through the ion path and reduce space charge effects between positive ions in the beam. The ion transmission was improved by a factor between 2 and 27 for high- and low-mass ions, respectively, and the greater sensitivity improvement for the latter resulted in a substantial reduction in mass bias. Pupyshev et al. (203) proposed ion transport models of the ion beam for ICPMS and concluded a good agreement between experimental data and theoretical calculations. This model could be used for the determination of the total ion current and average ion mass at the interface orifice and could be of importance for a quantitative analysis of the ion loss process during their transport in the ion beam. An ion trajectory simulation study was conducted by Sakata et al. (204), based on a newly proposed plasma interface model, which considers the formation of a plasma boundary by interaction between the plasma behind the skimmer cone and the electric field of the extraction lens system. An estimated plasma boundary position, or charge separation position, was used to determine the initial conditions of the simulation study. Two regions of conditions, in terms of rf power for the ICP and first extraction lens voltage showing characteristic sensitivity, were found to be reasonably explained by this simulation. The authors suggested that the location and shape of the plasma boundary are key factors that affect the focusing properties and transmission of the ion lens.

The effect of gas flow entrainment on the gas-sampling, ion-sampling, and ion detection processes in ICPMS was investigated by Stewart et al. (205). Isolated, single droplets of sample from a monodisperse dried microparticulate injector (MDMI) were used in conjunction with time-resolved ICPMS, photographs of ion cloud movement, and time-gated imaging using a gateable, intensified charge-coupled device (ICCD) detector mounted on an imaging spectrometer. The results indicate that gas flow entrainment into the sampling orifice can have a significant effect on the plasma gas velocities as far as 7 mm from the sampling orifice. The effects are most pronounced within 3 mm of the sampling orifice.

Memory effects caused by B in ICPMS were characterized theoretically and verified experimentally by Al-Ammer et al. (206). It was stated that these effects originate from the tendency of B to volatilize as boric acid from the sample solution layer that covers the inside surface of the spray chamber. The interface, the ion lenses, the quadrupole, and other components of the mass spectrometer were not responsible for the memory effect at trace

boron concentration levels. Addition of ammonia solution was reported to be effective in completely eliminating the memory effect and reducing the B signals to background levels within 20 s for a conventional concentric nebulizer-double pass spray chamber arrangement due to the conversion of the volatile boric acid to the nonvolatile ammonium borate. Diegor and Longerich (207) performed systematic signal optimization studies of an ICPMS instrument using concentric- and Babington-type nebulizers. Various parameters were considered for optimization, such as applied rf power, sampling depth, and nebulizer gas flow rate. Emphasis was given on the multidimensional characteristic of optimization, because the three important parameters interact to a very significant degree and thus it is very important when characterizing an instrument setup to be aware of the interactions of all ICP parameters.

Du et al. (208) described the operation of quadrupole mass filters in the second and third stability regions and briefly reviewed the theory of quadrupole operation. The higher zones allowed a resolution of up to 9000 (half-height) on atomic ions and made the authors believe that the development of high-resolution quadrupole ICPMS instruments might be possible.

Instrumental Developments and Applications. (1) Inductively Coupled Plasma. The performance characteristics of magnetic sector field ICPMS were studied by Appelblad et al. (209) with a Pt shield torch. The importance of the optimization procedure and the matrix effects caused by a seawater matrix were assessed for 20 elements, and oxide and doubly charged ion formation were also investigated. Use of the grounded shield allowed a significant increase in ion transmission, by a factor up to 20, resulting in improved instrumental detection limits. The improvement in sensitivity was mass dependent, with the highest gain observed for lower mass elements. At the same time, significantly greater oxide formation was observed when the shield was operated grounded rather than in the floating mode and severe spectral interferences from oxide species were often unresolved, even in high-resolution mode. It was concluded that all possible advantages and limitations of the use of the guard electrode should be carefully considered prior to the analysis of real samples. Similarly, Becker and Dietze (210) investigated the capabilities of a shield torch in combination with a double-focusing sector field ICPMS for the determination of long-lived radionuclides at nanogram per gram concentration levels. Four different nebulizer/spray chamber systems were compared, and the microconcentric nebulizer combined with a microcyclonic spray chamber showed the best performance. Highest sensitivities were provided in combination with lowest sample consumption. The detection limits were in the subpicomole per liter range and the precision ranged from 1 to 2% RSD ($n = 5$) at the 1 ng/L concentration level. In contrast, the use of direct injection high-efficiency nebulizer resulted in a decrease in sensitivity when a shielded torch was employed, which was believed to be related to the high solvent load delivered by this kind of nebulizer.

Waggoner et al. (211) described the use of a low-power, reduced-pressure He ICP for the detection of GC eluents from organobromine and derivatized organotin compounds. Total elemental information obtained with plasma source ionization was augmented with a capability to take fragment spectra that provided structural information. Limits of detection for bromobenzene,

1-bromoheptane, and benzyl bromide were 11, 6, and 4 pg, respectively. Molecular ions for all organobromine compounds were obtained, as well as some characteristic alkyl chain fragments for 1-bromoheptane, resembling electron impact mass spectra. High-speed video images of He ICPs were obtained by Iacone et al. (212) at a rate of 1000 frames/s under conditions suitable for MS. In the authors' opinion, these experiments established, for the first time, that the He ICP is a rotating discharge at the forward powers (500–1000 W) used for He ICPMS. The rotational frequency of the He ICP ranged from 80 to 250 Hz, depending on the forward power and whether analyte was introduced. When not coupled to the mass spectrometer, the rotational frequency of the He ICP decreased slightly as the forward power was increased. Coupling of the plasma to the mass spectrometer resulted in enhanced plasma oscillations. The implications of these variations on the sensitivity and precision of analytical measurements were discussed. Results were contrasted with data obtained for an Ar ICP. Milstein et al. (213) described quantitative and qualitative MS results, obtained for organotin compounds, which were introduced into a mixed gas He/Ar low-power/reduced-pressure (LP/RP) ICP. Molecular fragmentation of 10 mg/kg tetraethyltin, introduced by GC, with respect to pressure and mixed gas composition of the LP/RP ICP was observed. Detection limits for the organotin compounds introduced at the pressure producing the optimum analyte signal were in the low-picogram range. The source demonstrated "tunable" fragmentation with variation in the helium/argon mixed gas ratio. In addition, tunable fragmentation with pressure variations similar to that previously observed with He-rf-GD was found with the LP/RP He ICP. O'Connor et al. (214) have optimized a low-pressure ICPMS (6 W, with 7 mL/min He and 1.8 mL/min isobutane) for the determination of tetraethyllead in fuel, achieving detection limits of 7 pg. A chromatogram of a standard reference fuel yielded a single peak, which was identified as tetraethyllead by comparison with an electron impact ionization spectra library. Quantitative analysis of the fuel yielded a tetraethyllead concentration of $13.1 \pm 0.9 \mu\text{g/mL}$ as Pb, which was within the certified range of $12.9 \pm 0.07 \mu\text{g/mL}$. A low-flow torch specifically designed for ICPMS was developed and evaluated by Praphairaskit et al. (215). The outside of the torch was cooled by pressurized air flowing at approximately 70 L/min through a fourth tube sealed onto the usual "outer" tube of a standard minitorch. Although plasmas could be sustained at operating powers as low as 400 W with a 2 L/min outer Ar flow, stable and analytically useful plasmas needed higher values (850 W with an outer Ar flow rate of 4 L/min). The optimized externally air-cooled plasma produced sensitivities, M^{2+}/M^+ signal ratios, matrix effects, and other analytical figures of merit comparable to those produced by a conventional torch while using much less argon, although MO^+/M^+ signal ratios were slightly higher.

Minnich and Montaser (216) investigated a cool plasma ICPMS fitted with a direct injection high-efficiency nebulizer. A group of elements was investigated that was suitable for analysis in the cool plasma only by measurement of the metal oxide ion because the sensitivity and precision of the atomic ion were inferior to those obtained for the metal oxide ion. The sensitivity and precision obtained for these molecular species were comparable to those obtained for the atomic ions of elements that were suitable for analysis using the cool plasma. Calibration curves for

the metal oxide signal as a function of the metal concentration in the cool plasma were linear over 6 orders of magnitude, covering the concentration range from 1 ppt to 1 ppm.

(2) Collision and Reaction Cells. Studies on an ion-guiding buffer gas-filled hexapole collision and reaction cell in ICPMS have been performed by Feldmann et al. (217, 218). He and H₂ were used as buffer and reaction gases, respectively. Addition of the latter resulted in a reduction of typical argon-induced polyatomic ions (Ar⁺, ArO⁺, Ar₂⁺) by orders of magnitude owing to gas-phase reactions. Molecular interferences generated in the cell could be suppressed by a retarding electric field established by a dc hexapole bias potential of -2 V. For the investigated elements, application of a buffer and a reaction gas resulted in improved sensitivities which were lowest for Be with about 7 × 10⁷ counts s⁻¹ μg⁻¹ mL⁻¹ and highest for Ba with about 6 × 10⁸ counts s⁻¹ μg⁻¹ mL⁻¹. RSDs better than 0.1% were obtained. Ca, K, Cr, Fe, As, and Se were determined in nitric and hydrochloric acid and in methanol with LODs of 6 pg/mL for Cr in 2% methanol, 23 pg/mL for As, and 9 pg/mL for Se in 0.28 M HCl. For other elements, LODs of <1 pg/mL were realized in the medium- and high-mass range. Additionally, the performance of a hexapole collision and reaction cell in ICPMS for the speciation of selenium in human urine by reversed-phase and ion-pair high-performance liquid chromatography was described (219). The relative limits of detection for ⁸⁰Se were in the range 30–80 (using a hydraulic high-pressure nebulizer) and 100–200 ppt (using a Meinhard nebulizer) for the seleno compounds not interfered by the urinary matrix.

The dynamic reaction cell (DRC) is a rf/dc quadrupole that may be pressurized with a reactive gas in order to promote ion–molecule reactions intended to suppress plasma-based isobaric interferences for trace elemental analysis. Tanner et al. (220) investigated the performance of a cell with adjustable band-pass in order to suppress the appearance of new interferences produced through sequential reactions within the reaction cell. The DRC could alternatively be operated at low pressure (vented, under collision-free conditions) to emulate conventional ICPMS. A practical optimization procedure for both the vented and pressurized modes was described and examples showed the suppression of both plasma-based and cell-based isobaric interferences. The analytical performance characteristics of the instrument, including efficiency of isobar rejection, detection limits in clean water and in neat hydrogen peroxide, short- and long-term stability, determination of arsenic in chloride solution, and Se isotope determination, were provided. Latino et al. (221) discussed the advantages of dynamic band-pass tuning which, in conjunction with chemical resolution, could eliminate interfering species in the analysis of complex matrixes by ICPMS. The use of an active quadrupole inside the DRC allowed a mass band-pass window with both low-mass and high-mass cutoff regions to be established. This mass band-pass window was tunable and changed appropriately with the analyte mass being passed through the analyzer quadrupole. Because undesirable product ions could be expelled from the reaction cell, highly reactive gases that provide superior interference reduction such as ammonia, oxygen, and methane could be used.

The application of ICP-DRC-MS to the determination of selenoamino acids and the measurement of Se isotope ratios was

described by Sloth and Larsen (222). The potentially interfering argon dimers at Se *m/z* 74, 76, 78, and 80 were reduced in intensity by approximately 5 orders of magnitude by using methane as reactive cell gas in the DRC. By using 3% (v/v) methanol in water for carbon-enhanced ionization of Se, the sensitivity of ⁸⁰Se was 10⁴ counts s⁻¹ ng⁻¹ mL⁻¹ Se, and the estimated LOD was 6 pg/mL. The almost interference-free detection of selenium by ICP-DRC-MS made the detection of the ⁸⁰Se isotope possible for detection of selenoamino acids separated by cation-exchange HPLC. The LOD of the HPLC-ICP-DRC-MS method was in the range of 3–5 pg. Hattendorf and Günther (223) investigated the characteristics of a DRC for dry sample introduction into an ICPMS. The dependence of the signals from molecular ions formed in the ICP or in the interface region was monitored with the variation of the concentration of reaction or buffer gas used. The differences between wet aerosols, generated with a standard cyclonic spray chamber and concentric nebulizer, and dry aerosols, generated by a desolvating nebulizer or laser ablation, were determined. The comparison of prominent background signals to ion signals from selected analyte ions was used to determine parameters that lead to optimum signal/background ratios and analytical performance for laser ablation analysis. Ammonia and hydrogen were used as reactive gases in these experiments. Additionally, He, Ne, and Xe were used as a buffer gas to enhance thermalization in the DRC. The reaction rate with ammonia was found to be distinctly higher than with hydrogen but side reactions with analyte ions, leading to additional interferences and analyte loss through the formation of clusters, were severe. Hydrogen, having a smaller reactivity, reduced cluster formation and retained analyte sensitivity even at a high gas concentration. It was concluded that H₂ is therefore better suited for methods that allow only short measurement times, like LA or ETV. The capabilities of the DRC for LA are demonstrated through the determination of Ca in a quartz sample and Nb in a chromium matrix, which suffered from either Ar ions or Ar-based interferences. Reduction of the background intensities and use of the most abundant isotope led to a reduction of the LOD for Ca in quartz by 2 orders of magnitude and an improvement of accuracy for the determination of Nb in a chromium matrix. Additionally, the capability of a dynamic reaction cell for multielement analysis with short transient signals generated by LA was studied for the simultaneous determination of major, minor, and trace element concentrations in single fluid and melt inclusions (224). Analyses performed with the dynamic reaction cell were compared with results obtained with the standard mode operation of the ICPMS. The results show that the reaction cell is well suited for fast transient multielement analysis, providing very comparable results to the standard mode. Hydrogen has been found efficient for removing polyatomic ions, and the LODs for Ca were improved by 2.5 orders of magnitude and a factor of 20 for Fe.

Simpson et al. (225) quantified the oxides that interfere with noble metals in ICPMS analysis relative to CeO⁺/Ce⁺ ratios. A DRC-based solution to the problem was introduced, which worked in complete contrast to conventional ICPMS analysis where the formation of oxides was undesirable and operating conditions were optimized to limit their production. O₂ reaction gas was utilized actively to promote oxidation of interfering species to higher oxides, with a resulting separation of analyte from interfering

oxide. Results were presented for Hf, Ta, Nb, and Zr where the single oxide interfered with a noble metal analyte mass. Various higher oxides were formed, which resulted in complete absence of interferences on the respective mass. The authors observed improved detection limits and isotope ratio precision, and the method was found to be suitable for general environmental use, which was demonstrated by the analysis of a certified soil reference material and isotope ratio analyses.

Recent progress in the development of rf quadrupole ion trap ICPMS instrumentation was presented by Eiden et al. (226) in terms of performance figures of merit for trace elemental and isotopic analysis. Conventional polyatomic ion interferences were avoided using collisional dissociation techniques inherent to ion trap operation. The current detection limits were in the low-picogram per milliliter range, as obtained over extended mass scans. The dynamic range linearity was nearly 6 orders of magnitude using variable injection times to control ion density in the trap. The abundance sensitivity was 10^5 – 10^6 using selective ion monitoring. Other performance figures approached or exceeded those of conventional linear quadrupole-based ICPMS instrumentation.

(3) Time-of-Flight Instruments. TOF mass spectrometry has become an important method of mass analysis and commercial ICP-TOFMS instruments have recently become available. The use of an ICP-TOFMS was examined in detail by Ray and Hieftje (227), with emphasis placed on the attributes of the different instrument geometries. The common and contrasting design concepts, operating principles, and experimental performance of both orthogonal-acceleration and axial ICP-TOFMS instruments were examined and contrasted. The analytical performance of an axial ICP-TOFMS, in terms of accuracy, precision, resolution, signal stability, repeatability, reproducibility, precision of isotope ratios, and LODs has been reported by Tian et al. (228). Cool plasma conditions allowed the determination of K, Ca, and Fe at trace levels. LODs for 64 elements were reported with typical values from 0.5 to 20 pg/mL. The long-term stability over 4 h for the raw signal ranged between 1.0% for ^7Li and 2.1% RSD for ^{40}Ca operating under cool plasma conditions. Under normal plasma conditions, the corresponding values were 6.9% for ^{208}Pb to 12.8% RSD for ^{59}Co . Results from the analysis of 16 elements in SRM (NIST 1643d) were considered accurate, and isotope ratio precision was in the range of 0.07–0.7% RSD for a short data acquisition period. Analytical data illustrating the typical response characteristics of a commercial orthogonal acceleration ICP-TOFMS were presented by Sturgeon et al. (229). With optimum instrument response tuned at mid-mass ^{103}Rh , the LOD for a suite of elements representative of m/z 9–238 were estimated to be typically 1 ppt. Background counts across the mass range averaged 0.5 Hz; sensitivity for Rh was 7 MHz per microgram per milliliter; resolution (fwhm) ranged from 500 ^7Li to 2200 ^{238}U ; long-term drift over 700 min was $0.7\% \text{ h}^{-1}$; abundance sensitivity was 2.8×10^{-6} (low-mass side) and 7.4×10^{-5} (high-mass side). Mass bias ranged from 10% per mass unit at ^{24}Mg to <1% at $m/z > 80$, and isotope ratio precision was demonstrated to be limited by counting statistics when the detector was operated in the pulse counting mode.

Guilhaus (230) provided an overview of key issues in the combination of TOFMS with the ICP source. The advantages of

ICP-TOFMS and the technological challenges in this combination were discussed in terms of basic principles of TOFMS. The concepts described include the following: sources of peak broadening; ion gating, duty cycle, and mass analyzer efficiency; signal digitizing in the nanosecond regime; comparisons with scanning mass analyzers; and selective quenching of ion signals in TOFMS.

A significant problem in plasma source TOFMS is the saturation of detectors due to plasma gas and matrix ions. Hang et al. (231) outlined two experimental procedures to minimize the detector response to large ion currents exemplified by a GD-TOFMS. One novel solution was a deflection device that included two parallel plates for ion ejection and two sleeve plates (after the deflection plates) to reduce ion and neutral scattering. Another approach was to gate the detector, by lowering the voltage on the microchannel plates, when an intense ion pack was expected. Both approaches were efficient in eliminating the plasma gas peaks and matrix ions in plasma source TOFMS. The matrix ion intensity could be reduced by several orders of magnitude, with minimal influence on the analyte ions. The detector gating technique required a high peak current pulse with a flexible rise time. This approach caused an electrical ringing to be superimposed on the analytical signal, and ion deflection was found to be the method of choice for plasma TOFMS.

Guzowski and Hieftje (232) reported the design of a hexapole collision cell, which has been incorporated into an orthogonal ICP-TOFMS. The ion guide assembly was constructed from 20-cm-long, 3.175-mm-diameter stainless steel rods, and the cell was positioned between the second and third vacuum stages of the mass spectrometer. The signal levels were found to be strongly influenced by pressure in the cell, rf voltage applied to the rods, and operating frequency of the ion guide. Lighter ions (m/z 7) were transmitted more efficiently at higher frequencies and reduced rf voltages, while signals for heavier ions (m/z 238) were greater at lower frequencies and elevated voltages. Detection limits with the conventional static ion optics and hexapole collision cell were comparable, in the range of 0.4–2 ng/mL and similar when either He or H_2 collision gas was used. Precision for the peak height measurement was 5.4% RSD with the hexapole ion guide, slightly better than when static optics were employed (7.3% RSD). The strong signals from $^{40}\text{Ar}^+$ could be reduced by 4 orders of magnitude through use of hydrogen as a collision gas because of efficient and selective charge-exchange reactions. Isotope ratio precision was found to be counting-statistics limited, and the mass resolving power (fwhm) of the spectrometer was improved through the use of the hexapole ion guide assembly (2915) relative to that obtained with static ion optics (1510). An axial-acceleration inductively coupled plasma time-of-flight mass spectrometer has been equipped with an octopole ion guide/collision cell by Leach and Hieftje (233). Ion-energy experiments proved that the instrument duty cycle improved by up to 100% over values determined for conventional ion optics. Both sensitivity and noise were found to decrease with the ion guide in place. Consequently, limits of detection for most elements were found to be comparable to those calculated for conventional ion optics. The exceptions were low-mass ions that enjoyed only a relatively small gain in duty cycle and thus exhibited significantly degraded detection capability. Collisional cooling caused the spectral resolving power to improve

by up to 80% compared to the conventional optics. The determination of K, Ca, and Fe, elements that usually suffer from isobaric overlaps, was possible under robust plasma conditions.

Longerich and Diegor (234) described the evaluation of a water-jacketed spray chamber at several temperatures between 4 and 30 °C for its use with an ICP-TOFMS instrument. When the spray chamber was operated at lower temperatures, less water vapor was transported to the ICP. However, sensitivity was unchanged when the nebulizer gas flow was optimized at each of the different temperatures, and the expected lowering of the degree of formation of oxide polyatomic ions was not achieved. The effect of lowering the cooling temperature apparently did lower the rate of introduction of water vapor into the ICP, which resulted in an apparent increase in plasma temperature followed by a decrease in sensitivity, which was regained by increasing nebulizer gas flow. The maximum sensitivity was comparable at all spray chamber temperatures studied, with higher nebulizer gas flows being required with lower spray chamber temperatures. Other parameters of interest, the background, oxide formation, doubly charged ion formation, and detection limits, were comparable at all spray chamber temperatures. In the authors' opinion, this study emphasizes the importance of making multidimensional studies of the ICPMS.

The application of ICP-TOFMS combined with capillary electrophoresis (CE) for rapid simultaneous multielemental speciation was described by Bings et al. (235, 236). Fast electrophoretic separation of a mixture of several anionic species and negative-charged metal–cyanide complexes was achieved by using a linear polyacrylamide-coated capillary. The separation of three arsenic species and two cobalt–cyanide complexes required less than 70 s in the presence of other anions and metal cyanides of Cu(II), Cr(VI), Ni(II), and V(V). Simultaneous element-selective detection was provided by ICP-TOFMS, enabling mass spectral separation of several metal species that were not electrophoretically resolved. Absolute detection limits for the different metal species were 1–20 pg for 20-nL injected sample volumes. Peak area and elution time reproducibility were typically better than 4 and 1% RSD, respectively, for 10 successive injections.

Speciation analysis of organolead compounds in environmental waters was described by Heisterkamp and Adams (237), employing separation and detection by capillary gas chromatography (GC) hyphenated to ICP-TOFMS. The construction of the transfer line was achieved by means of a relatively simple and rapid coupling procedure. Derivatization of the ionic lead species was achieved by in situ propylation with sodium tetrapropylborate; simultaneous extraction of the derivatized compounds in hexane was followed by separation and detection. LODs for the different organolead species ranged from 10 to 15 fg (as Pb), corresponding to procedural detection limits between 50 and 75 ng/L, on the basis of a 50-mL snow sample, extraction with 200 μ L of hexane, and subsequent injection of 1 μ L of the organic extract on to the column. The accuracy of the system was confirmed by additional analysis of a standard reference material.

The analytical potential of complementary chromatographic separations such as size exclusion (SEC) plus anion-exchange chromatography coupled with ICP-TOFMS was evaluated by Ferrarello et al. (238) for the multielemental speciation of trace elements associated with methallothionein-like proteins in mussel

hepatopancreas. The initial separation of the proteins was performed by “off-line” SEC, collecting fractions, which were then analyzed for the trace elements by ICP-TOFMS in small sample volumes. The separated proteins were detected by UV absorption, and the specific detection of 16 metals was performed on-line with ICP-TOFMS. This hybrid approach was applied to investigate the metal-binding patterns of the proteins expressed by mussels, which had been previously exposed to 16 trace metals in an aquarium tank for 1 and 2 weeks. The authors believe that the exceptional characteristics of ICP-TOFMS for quasi-simultaneous monitoring of many trace elements in transient signals are illustrated by this “on-line” coupling to fast protein liquid chromatography (FPLC) separation.

Benkhedda et al. (239) described a flow injection (FI) on-line sorption system, for the preconcentration and separation in a knotted reactor (KR), which was coupled with ICP-TOFMS for fast, selective, and sensitive determination or ultratrace concentrations of rare earth elements (REEs) in environmental waters. The on-line preconcentration and separation of the REEs was achieved by sorption of the REE complexes formed in the pH range 3.7–4.6 on the inner walls of a (300 cm \times 0.5 mm) PTFE KR precoated with the chelating reagent 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (PMBP) at a pH of 9.6. The analytes were eluted and transported to the ICP-TOFMS system with 2% (v/v) HNO₃ containing 0.5 μ g/L Rh and In as internal standards, using ultrasonic nebulization. The REEs were effectively preconcentrated and separated from the major matrix constituents—alkali and alkaline earth elements. Of particular significance was their separation from barium, which produced considerable isobaric interferences on some of the analytes. Using a preconcentration time of 30 s and a sample flow rate of 4.4 mL/min, enhancement factors of 15–22 for the different REEs were achieved. LODs ranged from 3 to 40 pg/L and the precision for nine replicate determinations of 0.1 μ g/L of each analyte was better than 5% RSD. The accuracy of the method was demonstrated by the analysis of environmental waters and by recovery measurements on spiked samples.

Emteborg et al. (240) assessed the performance of an axial ICP-TOFMS in terms of precision and mass bias for isotope ratio measurements and accuracy of isotope dilution (ID) by measurements of isotopic reference materials for Li, Mg, Rb, Pt, and Pb. Because of simultaneous ion extraction from the plasma, remaining flicker noise was minimized, resulting in improved precision for isotope ratios compared to sequential mass spectrometers. Experimental relative standard deviations of <0.05% for isotope ratios were obtained at high signal levels measured in the analog detection mode. Effects on isotope ratios derived from changes of instrumental parameters, such as detector voltage and transverse rejection ion pulse settings, were evaluated. Isotope ratios for different concentrations changed when operating at too low detector voltages. An appropriate detector voltage setting was important, but optimum voltages differed depending on the age and previous history of the detector. Results obtained for ID measurements of magnesium and rubidium content were believed to compare well with results from quadrupole ICPMS and thermal ionization mass spectrometry. Mass bias per mass unit was high in the low-mass range (13% for ⁶Li/⁷Li) but around 0.2% in the high-mass range. The long-term stability of ratios, measured

discontinuously over several hours, was moderate; therefore, measurements of an isotopic reference material at regular intervals was necessary to correct for small variations in mass bias over time.

The coupling of an electrothermal vaporization (ETV) apparatus to an ICP-TOFMS was described by Mahoney et al. (241). A signal-averaging data acquisition board was employed to rapidly record complete elemental spectra throughout the vaporization stage of the ETV temperature cycle; a solution containing 34 elements was analyzed. The reduction of both molecular and atomic isobaric interferences through the temperature program of the furnace was demonstrated. Isobaric overlaps among the isotopes of Cd, Sn, and In were resolved by exploiting differences in the vaporization characteristics of the elements. Figures of merit for the system were defined with several different data acquisition schemes capable of operating at the high repetition rate of the TOF instrument. With the use of both ion counting and a boxcar averager, the dynamic range was shown to be linear over a range of at least 6 orders of magnitude. LODs of 10–80 fg were calculated for seven elements, based upon a 10- μ L injection.

To investigate the capabilities of ICP-TOFMS in combination with an excimer laser ablation system, ablation studies on reference materials and geological samples were carried out by Bleiner et al. (242). Various ICP-TOFMS parameters were optimized for laser-induced aerosols. Transverse rejection ion pulse was used to extend the dynamic range in concentration. A reduced-volume ablation cell was designed and used in order to increase the sample density in the ICP. Results for 63 simultaneously measured isotopes lead to LODs in the 1–100 μ g/g range for a 80- μ m crater diameter. The reproducibility of signal ratios was determined to be better than 2% RSD for transient signals using 102-ms integration time. Preliminary results of multielement analysis and isotopic ratio determinations on individual fluid inclusions demonstrated the capabilities of ICP-TOFMS for the analysis of short transient concentration-variable signals as produced in laser ablation.

In a study performed by Leach and Hieftje (243), a data analysis technique was evaluated to improve measurement precision obtained by single-shot laser ablation combined with ICP-TOFMS for the direct elemental analysis of solid samples with high spatial resolution. The technique exploited the simultaneous full-spectrum acquisition capability of an ICP-TOFMS. A normalization factor was computed from the summed signal generated by all sample constituents, the reasoning being that the summed spectrum should be proportional to the total mass of sample ablated. This scheme resulted in a greater than factor of 2 improvement in precision, moderately better than is possible with a single internal standard. The enhancement in measurement precision was found to be concentration dependent, with the greatest improvement (10–50-fold) experienced by high-concentration elements. Additionally, a method was developed that allowed the accurate, standardless measurement of the elemental composition of metal samples from LA pulses (244). This technique provided a fast, low-sample-consumption means for the characterization of samples having a range of matrixes. The method directly compared adjusted elemental signals with the total mass spectrometric signal to produce relative percent composition information. Three mathematical techniques were used to deter-

mine the accuracy and precision of single-shot LA measurement. Comparison of the techniques showed that a linear regression calculation, which plots individual elemental signals as a function of the summed signal for all elements in the sample on a point-by-point basis during a laser ablation transient, proved superior. A typical concentration dynamic range of 3 orders of magnitude, from 0.1 to 100%, was achieved. However, by measuring low-abundance isotopes for matrix elements, the dynamic range of the technique was extended to 4 orders of magnitude. The new technique was found to be largely immune to sample matrix effects commonly experienced in LA.

(4) Multiple-Collector Instruments. Isotope ratio measurements have mainly been performed by the use of single-collector ICPMS instruments, with reported precisions in the range of 0.05–0.5%. This limited precision is a result of the unstable nature of the ICP. For many purposes, e.g., geochronological applications, a much higher precision is required. Multiple-collector ICPMS, (MC-ICPMS) in which each isotope ion is measured simultaneously in an appropriate space array of detectors, are instruments of choice for this kind of work, to minimize the effect of ion beam fluctuations.

Halicz et al. (245) have reported the use of a MC-ICPMS for the precise measurement of natural variations in the isotopic composition of Ca. The interference of Ar in the Ca mass region was assessed, and the repeatability of the $^{44}\text{Ca}/^{42}\text{Ca}$ ratio of a sample Ca solution relative to the NIST SRM 915a CaCO_3 standard is better than 0.1 parts per 10^3 at 95% confidence. Variations in sample $^{44}\text{Ca}/^{42}\text{Ca}$ ratio were expressed as $\Delta^{44}\text{Ca}$ units, which were deviations in parts per 10^3 from the same ratio in the SRM Ca standard. Measurements of $\Delta^{44}\text{Ca}$ were presented for terrestrial and marine carbonates, which showed a variation of up to 0.7 parts per 10^3 . These data were believed to be in good agreement with previous studies by thermal ionization mass spectrometry (TIMS). A method developed by Ehrlich et al. (246) was found to be precise and accurate for the determination of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios by using a MC-ICPMS. Mass discrimination and instrumental drift were corrected by the use of the natural constant $^{86}\text{Sr}/^{88}\text{Sr}$ ratio as an internal standard. This also corrected for matrix effects, which allowed the direct analysis of natural water, carbonates, and related materials without chemical separation. The precision of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was 0.002%, even in samples with total dissolved solid levels of up to 500 mg/L. Nakai et al. (247) developed chemical and mass spectrometric procedures for Th isotopic analysis of volcanic rock samples using a highly sensitive MC-ICPMS equipped with a retardation lens. The sensitivity for Th was about 80 V/ppm, which allowed obtaining a strong enough ion current to measure $^{230}\text{Th}/^{232}\text{Th}$ ratios with a 10 ppb solution. With these procedures, the amount of Th required for precise isotopic analysis was reduced to <10 ng. Mass fractionation correction and Daly/Faraday multiplier gain calibration were applied using a natural U standard solution. The method was found to be accurate due to the analysis of three standard rocks, with eruption ages of older than 350 000 years, which $^{230}\text{Th}/^{232}\text{Th}$ radioactivity ratios were in equilibrium with those of $^{238}\text{U}/^{232}\text{Th}$.

Evidence for the presence of ^{92}Nb , which constrains the time scale of nucleosynthesis and formation sequence of the early solar system, can be detected by precise determination of the isotopic

composition of Zr. Therefore, enhanced sensitivity MC-ICPMS coupled with LA was used by Hirata and Yamaguchi (248) to determine Zr isotopic ratios for five terrestrial zircon samples. Typical achieved analytical precisions of the $^{92}\text{Zr}/^{90}\text{Zr}$, $^{94}\text{Zr}/^{90}\text{Zr}$, and $^{96}\text{Zr}/^{90}\text{Zr}$ isotopic ratio measurements were 0.01–0.02, 0.02–0.03, and 0.03–0.04%, respectively, and these values were found to be a factor of 2–3 worse than those achieved by solution analysis. In the authors' opinion, the resultant Zr isotopic ratios for zircons showed excellent agreement with those for chemical reagents obtained by conventional solution nebulization; normalized to $^{91}\text{Zr}/^{90}\text{Zr}$ equivalent to 0.218 14, the isotopic ratios were $^{92}\text{Zr}/^{90}\text{Zr} = 0.333\,939 \pm 0.000\,020$, $^{94}\text{Zr}/^{90}\text{Zr} = 0.339\,172 \pm 0.000\,041$ and $^{96}\text{Zr}/^{90}\text{Zr} = 0.054\,627 \pm 0.000\,009$. Although neither isotopic variation in the $^{92}\text{Zr}/^{90}\text{Zr}$ ratio due to radiogenic contribution from ^{92}Nb nor isotopic heterogeneity could be found for any of the Zr isotopic data obtained from terrestrial zircons and chemical reagents, the data presented were believed to clearly demonstrate that LA-MC-ICPMS has the potential to become a strong tool for the detection of possible ^{92}Zr excess in older Zr samples.

(5) High-Resolution Instruments. Coupling ICP with high-resolution sector field MS has led to a remarkable improvement of the analytical capabilities in the field of trace element determinations during the past decade. Evans et al. (249) presented a novel method for measuring S concentration in fossil fuels with high accuracy, based on isotope dilution high-resolution magnetic sector field ICPMS. The natural and spiked $^{32}\text{S}/^{34}\text{S}$ isotopic ratios of digested fuel samples were determined by using the medium resolution ($R = 3000$) operational mode to avoid the spectral interference of O_2 on the S isotopes. The natural isotopic composition of S varies in nature, which therefore had to be measured in each sample. The combined uncertainty of natural ratio measurements in S solutions and sample digests was about 0.4%. The developed ID-ICPMS method was found to show excellent agreement with both, the certified values for NIST SRM 2724b and the industry standard methods of analyses for low-sulfur diesel.

High-resolution ICPMS was used by Yu et al. (250) to certify a new SRM (Trace Elements in Indoor Dust) regarding Pb, As, Cd, Cr, and Hg concentrations at 17, 10, 140, and 5 $\mu\text{g}/\text{g}$. Isobaric interferences at masses of As and Cr were resolved by using the high-resolution mode ($R = 8000$) and the medium resolution mode ($R = 3000$), respectively, of the instrument. The effects of a significant drift in analyte sensitivity in the course of measurement were rectified by use of internal standardization, single-spike standard addition, and an optimized analysis sequence. The results were compared with those obtained by instrumental neutron activation analysis and ID-ICPMS and were believed to show good agreement.

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