Innovation in atomic spectrometric methods for chemical analysis

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Abstract

The importance of chemical-physical methods of analysis for a wide variety of applications in different fields of relevance to technological innovation, risk assessment in public and environmental health and sustainability is shown up at the hand of necessary developments in the methods of analysis. At the example of plasma atomic spectrometry and new developments in x-ray spectrometry for the determination of elemental and species concentrations it is shown up how herewith challenging analytical tasks in the fields mentioned before can be solved. Examples for material analysis, among others at the hand of novel ceramic powders such as precursors for high-temperature superconductors, water analysis and determinations in food as well as the determinations of hazardous species of heavy metals in waste water will be presented. Important lines of development toward the improvement of the power of detection, the minimization of efforts for sample pretreatment and the increase of the cost performance ratio also from the point of the instrumentation, as a result of the use of cheaper sources than the inductively coupled plasmas such as microwave plasmas, miniaturized devices and glow discharges, will be treated. Also progress in the calibration for the case of total reflection X-ray spectrometry by the use of picodroplets will be discussed.

Keywords: Atomic spectrometry, chemical analysis, plasma spectrometry, X-ray spectrometry

Introduction

Progress in science and technology as well as in risk assessment for public and environmental healthy and the search and development of new sources of energy all in a sustainable way ask for chemical characterization and analysis. Indeed, in all these areas the dose-effect relation both for the elements and for their chemical species is relevant. In this respect a wide variety of methods for chemical analysis is required so as to cope with the many species to be determined in a wide variety of types of samples and compartments of the biosphere and the environment. Here not only classical methods for the determination of the elements and the species such as titrimetry, gravimetry or spectrophotometry play a role, but also more sensitive and multicomponent methods are required to determine the elements and their species with a high power of detection, a high reliability in terms of precision and accuracy as well as with an affordable cost-performance ratio, with respect to the instrumentation required, the manpower and the demands to the education of the workforce as well as to the consumables required. Among these methods, chromatography systems with various types of detection, mass spectrometry and atomic spectrometry including optical methods and x-ray methods and even neutron activation analysis are indispensable. In this contribution it will be shown up, how for fields of interest from materials development and production to risks assessment in the food sector and in the environment, a continuous development of chemical-physical methods of analysis, such as plasma atomic spectrometry [1] and x-ray spectrometry (for a development of the field, see Ref. [2]) with special reference to X-ray fluorescence spectrometry in total reflection with laboratory and synchrotron sources is required so as to cope with the requirements from the ever further challenging fields of application.

Plasma atomic spectrometry

Plasma atomic spectrometry in its origin goes back to the work of Bunsen and Kirchhoff in the 19th century with flames as radiation sources and atom reservoirs. Here we have the possibility of multielement determination at the trace level for the case of liquid samples. However, the limited power of detection and the direct application to solid samples can be realized by the use of other sources of radiation. Indeed, arc and spark sources since the 1950s were used for direct trace determinations in metal samples as well as in electrically non-conductive powders. These classical methods now have a revival due to the availability of new types of spectrometers with CCD detectors, which enable it to measure all spectral lines and their spectral background signals in the complete analytically relevant wavelength range simultaneously and to have the data electronically available. DC arcs together with the use of thermochemical reagents, which even allow it to isolate the analytes from the sample matrix prior to excitation can be worked out. This now is an...
important method for the production and product analysis of refractory powders as used as the base for high-tech ceramics, such as SiC a.o. (see e.g. Ref. [3]).

The best known radiation source for atomic emission spectrometry now is the inductively coupled plasma, which now is widely used for elemental determinations in liquids or solids subsequent to sample dissolution (Fig. 1).

![Figure 1 Inductively coupled plasma (ICP) source](image)

**Table 1** Determination of Ba, Cu and Y in precursor for YBaCuO<sub>x</sub> superconductor powder subsequent to sample dissolution by CCD-ICP-OES using internal standardization. 5 sample preparations, 8 replicate measurements, number behind ± is the standard deviation. Reference signal: intensity of Sc 255.235 nm line. (M. Bauer, University of Hamburg, unpublished work).

<table>
<thead>
<tr>
<th>Elements</th>
<th>Measured values (% w:w)</th>
<th>indicative values (not certified) (% w:w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>2.059 ± 0.004</td>
<td>2</td>
</tr>
<tr>
<td>Cu</td>
<td>2.918 ± 0.005</td>
<td>3</td>
</tr>
<tr>
<td>Y</td>
<td>1.022 ± 0.003</td>
<td>1</td>
</tr>
</tbody>
</table>

However, new developments are reported especially in the field of sample introduction. Here not only direct solids sampling, e.g. with spark ablation (see e.g. Ref. [5]), but also innovative approaches for pneumatic nebulizers are described. Here, with a dual-solution uptake cross-flow nebulizer it could be shown that on-line standard addition and internal standardization become more easy [4] but also that oil analysis under the calibration with aqueous solutions of the elements to be determined is possible in an on-line sample uptake and calibration mode [6].

The ICP now is widely used as ionization source for elemental mass spectrometry (ICP-MS), which is used in many laboratories related with clinical and environmental sample analyses. ICP-MS, e.g. is a most powerful method for elemental determinations in drinking water (for a treatise see Ref. [7]). To cope with the problems of spectral interferences of a number of isotope signals with so-called cluster ion signals both high-resolution ICP-MS and collision cell technology have found wide interest. Especially the coupling of chromatography and ICP-MS is a powerful tool for elemental speciation, as required in many fields of life and environmental sciences. Indeed, not the element concentrations but the concentrations of well-defined compounds often are of toxicological relevance. This since longer is impressively known for the case of the chromium compounds, where the Cr(III) compounds are even thought to be essential for the glucose cycle whereas Cr(VI) components due to their oxidizing power and the small volume of the chromate ion can penetrate in the cell and be mutagenic. An early method allowing isolation of the Cr compounds after complexation with APDC so as to avoid species transformations and HPLC coupled to ICP-MS using suitable nebulization such as high-pressure nebulization was described (Fig. 2)[8]. For advanced chromatographic techniques such as capillary electrophoresis the use of high-
efficiency and direct injection nebulization coupled to ICP-MS is very useful. Speciation now for many organometallic compounds such as alkylated Pb, Hg, Sn, Ge and V-species, sulfur, bromine and iodine compounds to metalloproteins is a very important task for analytical chemistry (for a treatise see Ref. [9]).

Figure 2 Experimental arrangement for RP-HPLC coupled “on-line” to ICP-MS using hydraulic high pressure nebulization (HHPN) for sample introduction (taken from Ref. [8]).

All techniques known from ICP-OES for sample introduction are also important for ICP-MS. Especially, laser ablation under the use of various types of mass spectrometers including time-of-flight mass spectrometry (see e.g. Ref. [10]), developed to a standard method for direct solids analysis. Also the coupling of electrothermal vaporization and ICP-MS is very useful. It could be shown that for the analysis of refractory powders such as Al$_2$O$_3$ powders used for the production of advanced ceramics, trace determinations can be well done by slurry introduction into the graphite furnace [11]. Apart from Fe the technique is much more sensitive than when coupling ETV to ICP-OES. It could be shown from neutron activation of the analytes in the samples and measurements of the radioactivity of the sample residue in the furnace and of the trapped aerosols in the transport line that so-called thermochemical reagents such as NH$_4$Cl or mixtures of Pd and Mg nitrates earlier improve the transport efficiencies than the analyte volatilization [12].

As alternatives to the ICP sources which are cheaper with respect to instrumentation and consumables have been investigated. Here especially microwave plasma sources have to be mentioned. This started already with the capacitively coupled microwave discharges known from the 1950s and the microwave induced plasma described by Beenakker at the end of the 1970s [13]. An interesting plasma with a toroidal form and high robustness is the microwave plasma torch described by Jin et al. [14]. This source e.g. can easily be used for element-specific detection in gas chromatography. When using time-of-flight MS detection, the signals of several isotopes can be monitored without loss of chromatographic resolution. This is very important for brutto formula determinations allowing identification of the peaks [15]. Especially for organometallic compound determinations such as of alkylated Hg in food, derivatization and gas chromatography subsequent to purge-and-trap procedures under the use of detection of the Hg signals by on-line MIP-OES is very useful (for an application see e.g. Ref. [16]).

Microwave discharges also can be realized in microstructured systems, which are provided on a wafer by etching and metal strips deposition, as described for a system that could be used for the determination of Hg in environmental samples [17]. It could be shown that both with argon and helium, discharges can be sustained inside the wafer channel but that by adoption of the artificial load also systems where the plasma exits from the wafer can be operated (Fig. 3)[18]. The latter allow a more efficient acquisition of the signals both in optical as well as in mass spectrometry. Miniaturized microwave plasmas could be well used together with the cold-vapour generation technique for the determination of Hg [19], but also with chemical and electrochemical hydride generation for the determination of As and similar elements [20, 21] as well as in combination with oxidation reactions for the determination of the halogens or acidification for the case of S and C [22] species. Apart from microwave induced plasmas also high-frequency [23] and barrier-layer discharges [24] now are very promising as miniaturized sources.

Figure 3 Argon microstrip microwave induced plasma in a cylindrical channel in a quartz wafer. Diameter of channel: 600 µm; power: 40 W; argon flow: 15 mL.min$^{-1}$ (as used for the experiments described in Ref. [19]).

Since long glow discharges under reduced pressure have been used as sources for atomic spectrometry. In the form of the Grimm type glow discharge [25] they found use both for bulk and in-depth profile analysis of solid samples. Where they originally were operated as dc discharges they later...
also were obtained as r.f. discharges [26] then enabled measurements both as electrically-conductive samples such as metals as well as at electrically non-conductive samples such as ceramics. In the case of metal samples the matrix influences in calibration could be shown to be less than in spark optical emission spectrometry in a number of cases. However, through the use of ballast resistors in series with the discharge stable glow discharges also can be operated at atmospheric pressure.

With such systems the use of discharges with an electrolyte sample liquid as the cathode is well possible, as first described by Cserfalvy [27] and recently refined by Marcus et al. [28] and Hieftje et al. [29]. Glow discharges at atmospheric pressure also have been found powerful emission and ion sources for gaseous compounds such as volatile hydrides. As shown in Fig. 4 a dc glow discharge can be operated between a ring cathode and the Fig. 5. sampling plate of a mass spectrometer and used for the ionization of the volatile hydrides of several elements simultaneously [30].

X-ray spectrometry methods for elemental determinations

X-ray spectrometric methods have known a continuous development with respect to the determination of the elements (for a treatise see Ref. [2]). For trace determinations especially X-ray fluorescence is especially important and it is nowadays a routine method.

Through the development of total reflection X-ray fluorescence spectrometry the absolute power of detection of the method can be considerably improved and matrix effects as a result of the absorption of the excited and the fluorescence radiation widely avoided (for a thorough treatment of the method, see Ref. [31]). Through recent experiments, it could be shown that for fine ceramic Al$_2$O$_3$ powders direct analyses of dry suspension residues on quartz or silicon carriers are possible under the use of an internal standard added as solution [32]. The approach enables it to

**Table 2** Determination of trace impurities in Al$_2$O$_3$ powders by total reflection X-ray spectrometry using slurries under the addition of Co as reference element. (according to Ref. [32]). TXRF: 8030C (F.E.I.). 10 µl of 0.1 % slurry + 1 µl of 10µg/ml solution of Co on quartz carrier (spot diameter: ca. 5 mm)(concentrations in µg/g and numbers behind + are the standard deviations)

<table>
<thead>
<tr>
<th>Element</th>
<th>ME/03</th>
<th>AKP20</th>
<th>AKP30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu found</td>
<td>1.6 ± 0.4</td>
<td>1.2 ± 0.7</td>
<td>1.4 ± 0.4</td>
</tr>
<tr>
<td>accepted</td>
<td>1.4 ± 0.2</td>
<td>1.3 ± 0.1</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>Fe found</td>
<td>240 ± 80</td>
<td>9 ± 3</td>
<td>8 ± 2</td>
</tr>
<tr>
<td>accepted</td>
<td>260 ± 50</td>
<td>10.1 ± 0.9</td>
<td>6.9 ± 0.9</td>
</tr>
<tr>
<td>Ga found</td>
<td>100 ± 30</td>
<td>&lt;cL</td>
<td>&lt;cL</td>
</tr>
<tr>
<td>accepted</td>
<td>93 ± 8</td>
<td>0.16 ± 0.03</td>
<td>0.07 ± 0.02</td>
</tr>
<tr>
<td>Ni found</td>
<td>12 ± 3</td>
<td>1.5 ± 0.7</td>
<td>1.7 ± 0.7</td>
</tr>
<tr>
<td>accepted</td>
<td>10.4 ± 1.5</td>
<td>0.42 ± 0.01</td>
<td>0.7 ± 0.4</td>
</tr>
<tr>
<td>Zn found</td>
<td>5 ± 1</td>
<td>&lt;cL</td>
<td>&lt;cL</td>
</tr>
<tr>
<td>accepted</td>
<td>4.1 ± 1.4</td>
<td>1.3 ± 0.2</td>
<td>0.7 ± 0.3</td>
</tr>
<tr>
<td>V found</td>
<td>14 ± 3</td>
<td>&lt;cL</td>
<td>&lt;cL</td>
</tr>
<tr>
<td>accepted</td>
<td>14 ± 3</td>
<td>1.3 ± 0.2</td>
<td>0.2 ± 0.1</td>
</tr>
</tbody>
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obtain very low detection limits, when applying synchrotron radiation for excitation. However, so as to allow a highly reproducible deposition of the samples drying larger volumes of suspensions is troublesome and here the use of picodroplets which can be deposited very reproducibly with programmable ink-jet printers can be a powerful alternative and recently shown by Fittschen et al. [33]. The approach not only is valid for powder samples as such but also for atmospheric aerosol particles samples by impaction. X-ray methods further are of high interest for a direct differentiation between the species on the base of the absorption profiles.

Conclusions

From the examples shown it can be concluded that atomic spectrometric methods including plasma atomic spectrometry and x-ray spectrometric methods are very useful instrumental approaches for analytical tasks in many fields of technological innovation including materials development and production as well as in risk assessment related with public and environmental health and for problem-solving in many field of science and culture.

References