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The development of microplasmas for spectrochemical analysis

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Abstract Miniaturized microwave, high-frequency, and dc-powered microplasmas are discussed, with emphasis on the state-of-the-art and development trends. Specific atomic emission sources discussed include the microstrip microwave plasma operated in argon and helium at ca 10–30 W and below 1 L min^{-1} gas at atmospheric pressure, the capacitively coupled microplasma, operated at 13.56 MHz, 5–25 W, and 17–150 mL min^{-1} helium, the miniaturized inductively coupled plasma operated at several watts and reduced pressure, and dc glow-discharge plasmas on a chip, including a barrier-layer discharge as atom reservoir for atomic absorption spectrometry. Diagnostics for these sources are discussed and some of their figures of merit are compared with those of conventional sources. Current possibilities for introduction of gaseous samples are reported and scope for further development and outlook are both discussed.

Keywords Microplasmas · Spectrochemical analysis · Atomic spectrometry

Introduction

The development of plasma atomic spectrometric methods is closely related to innovation in sources, spectrometric systems, and detector technology. With regard to sources, early work by Bunsen and Kirchhoff started with flames in the mid 19th century; for solid-state analysis arc and spark work in the first half of the 20th century were instrumental in enabling geochemical work and developments in the metal industry, respectively. For rationalization of elemental analysis in both product control and environmental analysis atomic absorption spectrometry with flames and furnaces and, especially since the 1980s, inductively coupled plasma atomic emission and mass spectrometry, became of vital interest. Further, laser ablation, as an approach for direct analysis of solids, enables the direct bulk and microdistributional analysis of electrically non-conducting samples, and glow discharge atomic spectrometry has become an important method both for bulk analysis and depth-profiling (for treatment of this field, see Ref. [1]). As driving forces in analytical innovation the power of detection achievable, the reliability of the results obtained, and the cost-to-performance ratio of the analytical procedures, both in terms of the labour invested and the cost of instruments and consumables, must be mentioned. In this respect work with microsystems has several advantages:

- they can require small amounts of sample and reagents only;
- they can be used in the field, or on the spot, and eventually are portable as, e.g., required for process control; and
- instruments and operation might become inexpensive.

The plasma sources mentioned above have been found to be very powerful excitation and ionization sources in many fields of application. They are also very robust, but are too expensive to buy and to operate for some fields of application, where smaller, better optimized sources have become desirable. This has led to substantial effort being devoted to miniaturization of radiation and ionization sources for use in atomic spectrometry. It is the aim of this paper to discuss the development of small and possibly miniaturized plasma sources for analytical atomic spectrometry. Several miniaturized plasmas already described in the literature will be discussed, and the way they were developed and their analytical capabilities will be described. Analytical applications of these sources, where they already exist, will also be treated. An important aspect of this is the sample-introduction techniques that can be used with these sources. It will be shown that for sample introduction alone there is much potential for analytical research and development. Progress in the development of miniaturized sources will be mentioned, as also will prob-

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lems preventing their optimum coupling with the other components of the analytical system, especially the spectrometer and detection system used. In optical spectrometry recent successful developments toward the production of small spectrometers will be discussed, even though optimum coupling with the sources might still require much refinement. Possible scope for improving detection power in mass spectrometry, by use of the miniaturized sources as ion sources, will also be treated. Finally, directions in development towards miniaturized sources from existing sources will be identified. The usefulness of miniaturized sources for the direct determination of chemical compounds, by use of hyphenated systems and advanced sources, will also be discussed.

Microwave plasmas

Microwave discharges started to play an important role in analytical atomic spectrometry with the work of Mavrodineanu and Hughes in the 1950s [2]. They described a powerful single-electrode plasma which could be operated at 200–600 W both with argon and helium (and, as shown later, with air also). This source was named the capacitively coupled microwave plasma. The plasma was formed at the tip of a metal electrode and the surrounding metal tube conducting the working gases acted as counter-electrode. The metal used for the electrode tip was very important. A copper electrode was used initially but later gold electrodes were also used. Because burn-off occurred the metal should have a line-poor atomic-emission spectrum, to keep risks of spectral interference low. A crucial factor limiting both the power of detection and analytical accuracy was the difficulty of introducing a sample in the form of an aerosol or a cold gas flow centrally into the plasma, because the central zones are the hottest. This is clearly shown both by gas temperatures and excitation temperatures as reported by Kirch et al. [3], and by the radially resolved measurements acquired by Bings et al. [4]. Efforts have been made to improve the introduction of aerosols into the CMP by use of mantle gases, enabling wall stabilization of the plasma, and by introducing the sample aerosols through parallel cylindrical channels in the axial direction near to the electrode tip. The CMP can be operated with air only, making it highly suitable for monitoring metals in gas flows, including stack gases. In the latter application Seelig and Broekaert [5] showed that the system could tolerate the rather high water loadings (up to several 100 g m^{-3}) and CO_2 concentrations always present in stack gases, especially after washing with the aim of reducing concentrations of sulfur dioxide and nitrous oxides. Detection limits were as low as 0.03–80 μg m^{-3} for elements such as Cr, Cd, and Pb in optical emission spectrometry, making the plasma useful for environmental monitoring, or at the sub-μg mL^{-1} level for solution analysis. It was also shown by Okamoto that high-power microwave plasmas, when used as ion sources for mass spectrometry, are powerful sources for trace analysis [6]. This plasma, however, was an electrodeless plasma, very similar to that described by Leis and Broekaert [7]. A rectangular resonator is used and a plasma which can be operated with several noble and molecular gases is obtained. Detection limits in optical emission spectrometry with an argon discharge were found to be considerably higher than for inductively-coupled plasma coupled with optical emission spectrometry (ICP–OES), especially for elements forming refractory oxides. Concomitant effects were also found to be considerably higher than in ICP–OES.

Electrodeless microwave plasmas at a much lower power first became available with the work of Beenakker at the end of the 1970s [8]. Plasmas with diameters of approximately 1 mm and a length of 10–20 mm could be operated at 20–100 W and with gas flows down to 0.1 L min^{-1} argon or helium in a so-called TM_{010} cavity. These plasmas have a filament-like form and are stable if used with dry samples and analyte vapour. They proved ideal for use as element-specific detectors in chromatography and were widely used in commercial GC–MIP–AED instrumentation (Agilent) for determination of organometallic compounds in environmental samples and food; examples include organolead compounds [9], alkylated tin [10], organomercury [11] and sulfur [12] compounds. Different types of plasma with interference filters for spectral isolation of the analytical lines have been proposed as element-specific detection channels [13]. According to Beenakker MIPs have also been successfully used for the analysis of real samples evaporated from a graphite furnace [14]. In combination with hydride generation they could also be used for ultratrace determination of As and Se, among others, if the excess hydrogen produced was removed by freezing the hydrides and sweeping them into the plasma after evaporation of the condensates [15]. In a cavity, according to Beenakker, toroidally-shaped MIPs could be obtained when the argon used was wettened and the tube centred very accurately in the resonator [16]. This device could be used for element-specific detection even in liquid chromatography [17] but, because of stability problems, has not been used routinely. High stability and robustness toward excess hydrogen during hydride generation was experienced with a TE_{101} cavity described by Matusiewicz [18]. Excess hydrogen produced during electrochemical hydride generation [19] could be tolerated by the plasma, making the set-up much less complicated than when the hydride species had to be released into the plasma after separation from the hydrogen. This also applies to the surfatron described by Moisan and Hubert [20] and refined by Selby and Hieftje [21]. In flow-cell hydride generation all reaction gases could be fed into the MIP argon discharge operated at ca 100 W [22].

Another electrodeless microwave plasma is the microwave plasma torch described by Jin et al. [23] in the early 1990s. In this the microwave power is coupled through a side-arm into the plasma and the latter is operated at the tip of two concentric copper tubes. The plasma is toroidal in form, so sample aerosols or vapours can be fed into the plasma with high efficiency. When the depth of the cavity is properly selected there is no need to retune the plasma after ignition [24] and in atomic emission spec-

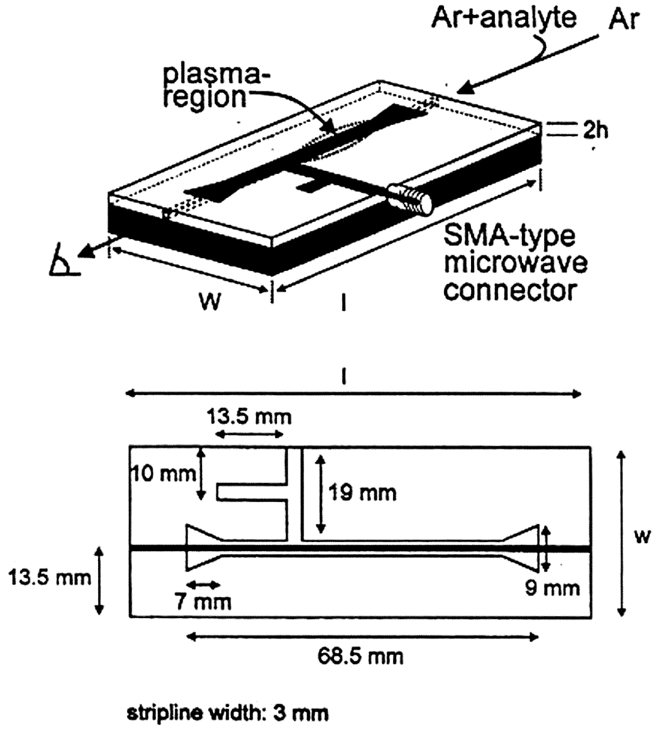

Fig. 1 Microstrip plasma (MSP) device for optical emission spectrometry [27]

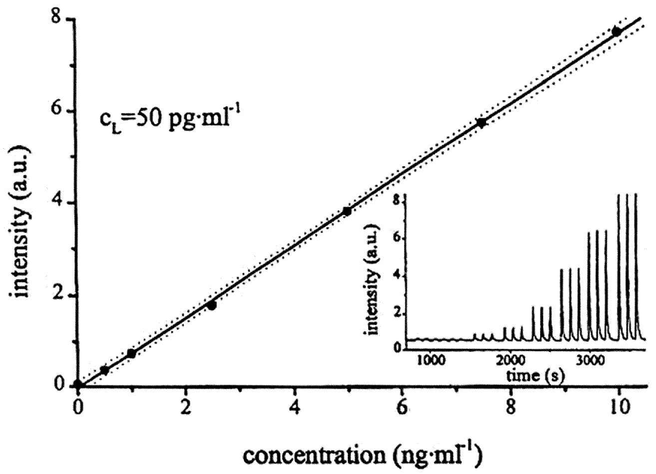

Fig. 2 Calibration curve for Hg obtained by analysis of standard solutions containing Hg at concentrations between 0.5 and 10 ng mL^{-1} (plasma conditions: 30 W forward power and an Ar gas flow of 300 mL min^{-1} plasma gas plus 400 mL min^{-1} carrier gas flow) [27]

trometry detection limits for volatile-hydride-forming elements were at the 5–10 ng mL^{-1} level, only half an order of magnitude higher than in ICP–OES. The best limits of detection were obtained with a helium discharge, although at the expense of operating stability [25].

Experience gained with different microwave structures enabled the development of a microwave-powered microplasma in a quartz wafer, with microstrip technology for power transmission. In a first version of the microstrip device a groove was made in two quartz plates, by means of a diamond saw, and the two plates were glued together with water glass. The microwave power was brought to the plasma channel by providing energy via microstrip-powered electrodes fabricated on one side of the wafer by photolithographic procedures; the copper cooling block on the opposite side of the wafer was grounded and acted as the counter electrode (Fig. 1) [26]. The copper microstrip had a side-arm acting as an artificial load; by use of this the reflected power and its variation during plasma operation, and fluctuations during sample introduction, were kept to a minimum. In an argon plasma operated at approximately 20 W in a 600-µm wide channel, rotation temperatures, measured by monitoring the intensity distribution for the rotational lines in the 310 nm OH band, were 600 K and the excitation temperatures, determined from Fe I atomic emission lines, were found to be approximately 5000 K. In the flow-cell mercury cold-vapour technique signals for mercury were very stable (Fig. 2) [27] and a detection limit of 50 pg mL^{-1} was obtained. Improvements should still be possible, because the opening angle of the CCD spectrometer used and the plasma channel were not optimized. When, instead of $SnCl_2$ as reducing agent, $NaBH_4$ solutions and acids are used it was found that the blank signals and background intensity changes were larger when excess hydrogen was conducted into the discharge. The discharge was still stable, however, implying that the source could also be used for simultaneous determination of volatile-hydride-forming elements. The dimensions of the quartz wafer in a subsequent model were reduced to 40 mm×40 mm. With quartz wafers with a cylindrical channel from one end of the plate to the other, smaller devices in which helium discharges at a similar level of power and gas flows could also be operated. Signals for the Cl I atomic emission lines at 470 nm could be measured when chlorinated hydrocarbon vapour was introduced into the discharge. Estimated detection limits were in the pg s^{-1} range for atomic emission spectrometry [28]. This implies that this type of microplasma is certainly a potential detector for element-specific detection in gas chromatography.

The microstrip plasma described is certainly only one of many possible designs. Much optimization work must still be performed, especially on plasma form and location, and on optimum illumination of the spectrometer used. Further, cold-vapour techniques for Hg and hydride techniques are merely the easiest ways of introducing the analyte into the plasma. The other techniques known from ICP atomic spectrometry, e.g. pneumatic and ultrasonic nebulization, and the various direct solid-sampling techniques, should be investigated, and innovative work resulting in new sampling techniques is also required.

High-frequency plasmas

The inductively coupled plasma is certainly the best known and most widely used source in routine atomic spectrometric analysis of dissolved solids or liquid samples. In its standard form it is operated at a power of 1–2 kW and

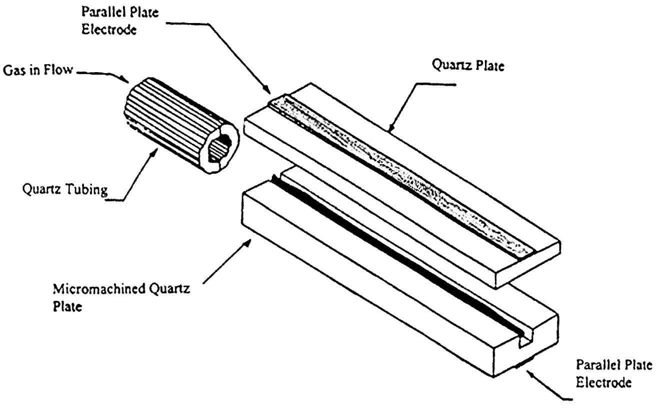

Fig. 3 Capacitively coupled microplasma for optical emission spectrometry. The length of CCμP can be changed by changing the length of the metal strips used to transfer power from the 13.56 MHz plasma generator. The channel widths are 200 and 500 μm [32]. (Reproduced with permission from the Royal Society of Chemistry)

with argon consumption between 10 and 20 L min^{-1} both in atomic emission and in elemental mass spectrometry. Low-power versions of ICPs operating well at 200 W have been described as research tools [29] but never stimulated widespread practical interest. For element-specific detection in gas chromatography, however, Gross et al. [30] developed a stabilized capacitive plasma operated at 100 W in argon or helium. This plasma is formed inside a quartz tube between two ring-shaped electrodes positioned around the tube at a distance of ca 20 mm. By this means the plasma is so well fixed between the electrodes that a stub of quartz or graphite can be inserted into the plasma and a dry solution residue can be evaporated from its surface. With this approach detection limits at the 0.1 ng level for elements such as Cd, Mg, Pb, and Cu can be achieved by atomic emission spectrometry [31].

Bas et al. [32] recently described a capacitively-coupled radiofrequency-powered microplasma operated in a quartz structure with the power transmitted through copper-plate electrodes. A plasma is produced in a quartz wafer made from two plates, each of which contains a groove, which are glued together. A copper plate electrode is placed on one side of the wafer and a copper block serving both for cooling and as a ground electrode is placed at the other side of the wafer (Fig. 3). At an r.f. power of 9–25 W and a frequency of 13.56 MHz a stable plasma could be obtained at helium gas flows between 17 and 150 mL min^{-1}. With the aid of an Ocean Optics fibre-optical emission spectrometer spectral lines from OH, N_2, N_2^+, and He I species could be measured. The plasma is certainly of potential interest for detection in gas chromatography but no literature data are yet available indicating which analyte elements give atomic emission lines, or about signal-to-background ratios.

Again this miniaturized type of high-frequency plasma is only one of many types possible. Another interesting approach dealing with a capacitively coupled high-frequency plasma on a chip has recently been described by Yoshiki and Horiike [33]. They also use a two-plate arrangement; one plate is grounded and the other powered at 13.56 MHz. Both plates are planar and the spectrum is observed through the powered electrode, i.e. perpendicular to the plasma channel. The latter is obtained by providing two grooves 65–500 μm wide in the two quartz plates, which are glued together. Etching with hydrofluoric acid was proposed for making grooves of depth <500 μm. At a power of 5 W and helium pressures ranging from 60 torr to atmospheric pressure excitation temperatures of 2000 and 1900 K were measured. Helium, oxygen, and hydrogen atomic lines and OH-bands were reported to occur in the spectra.

Miniaturization of inductively coupled plasma sources was very successfully realized by Hopwood and co-workers as early as 1999. Yin et al. [34] used a planar r.f. coupling with a spiral coil to generate a 15-mm-wide plasma extending into a vacuum chamber at argon or air pressures up to approximately 1 torr. By means of a Langmuir probe electron number densities of 10^{16}–10^{17} m^{-3} could be measured. Electron temperatures of 2000 to 8000 K were measured, and depended on the gas pressure. The effect of different coil diameters on the power at which a plasma could be sustained was studied for frequencies of 100–500 MHz.

In another paper Hopwood described a hybrid package of an impedance-matching network for the ICP, an inductive coupler in a microstructure on a quartz plate, and a glass tube forming the vacuum chamber [35]. At 350 mW and 454 MHz a stable plasma could be obtained in argon at 8 torr. The effects of different working conditions on the stability of plasma operation were studied in detail for air and argon as working gases.

It can generally be stated that further innovative experimental work must be performed to test plasmas in structures with different geometries and made of different materials. The question of which techniques can be successfully used for sample introduction for analytical purposes and which analytical figures of merit can be expected must also be answered. Means of introducing wet aerosols must also be developed.

Glow-discharge plasma sources

Micro DC plasmas, mainly operated at reduced pressure, have also been described in the literature. The device described by Eijkel et al. [36] (Fig. 4) has a 50-nL plasma chamber; it is operated at a pressure of 75 torr and the electrical conditions when helium is used are i=60 μA and U=850 V. The discharge requires voltages up to 6 kV to ignite. It was found to suffer from electrode sputtering, which severely limits the lifetime of the device. For methane in air-contaminated helium detection limits were 3×10^{-12} g s^{-1} (600 ppm) when measuring the signals for the molecular bands at 432 nm. The device thus seemed promising for detection in gas chromatography, although no atomic emission signals could be detected. In a subsequent paper the authors also reported obtaining similar results with a discharge operated at atmospheric pressure [37].

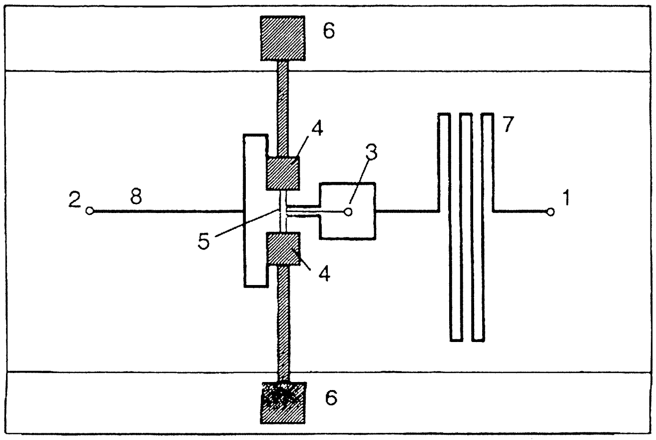

Fig. 4 Low-pressure dc discharge molecular-emission detector. Chip with (*1*) gas inlet, (*2*) gas outlet, (*3*) pressure sensor connection, (*4*) electrodes, (*5*) plasma chamber, (*6*) electrode connection paths, (*7*) inlet channel, and (*8*) outlet channel etched in 20 mm×30 mm bottom plate [36]. (Reproduced with permission from the American Chemical Society)

Elemental information could be readily obtained by using diode laser atomic absorption spectrometry with miniaturized discharges, e.g. the barrier-layer discharge, as atom reservoir – as developed and recently described by Miclea et al. [38]. Their discharge chamber comprises two glass plates, each with a 50-mm long aluminium electrode deposited by Al vapour deposition (thickness 0.1 µm, width 800 µm) on which a 20 µm glass layer was provided as dielectric layer. The plates were separated by 1 mm by two glass spacers, forming a 60-mm long discharge channel which was provided with quartz windows for entry and exit of the diode laser radiation. An ac discharge in helium with a rectangular voltage pulse up to 750 V was used at a frequency of 5–20 kHz; the power level was 0.5–1 W at a pressure of 10–180 mbar. The discharge, despite a gas temperature of only 600 K, enabled reasonably efficient dissociation of halogenated hydrocarbons. Atomic absorption from metastable chlorine energy levels by irradiation with long-wavelength diode laser radiation, for which laser diodes are available, resulted in very sensitive determinations of chlorine species. Detection limits of 400 ppt and 2 ppb for CCl_2F_2 in helium using the Cl 837 nm and the F 685 nm lines, respectively, could be achieved by diode laser absorption spectrometry. No monochromators were required to isolate superfluous atomic absorption radiation, which enables the miniaturization of a chlorine-specific detection channel; this might be extremely useful for gas chromatography.

Another glow discharge, operated at atmospheric pressure, was described by Clay and Marcus [39]. The device aims at direct analysis of solutions and uses an electrolytic solution containing the analyte specimen as one of the discharge electrodes. Passage of an electrical current across the solution–gas-phase interface causes local heating and a volatilization of the analyte species. Collisions in the negative glow region of the plasma result in optical emission characteristic of the analyte elements. This results from the reasonable atomization conditions – from OH band measurements rotational temperatures were estimated to be of the order of 4000–5000 K. The device can be operated with the analyte solution acting as either the cathode or the anode. Typical discharge conditions include discharge currents of 80 mA, potentials up to 1000 V, and i–V characteristics indicative of "abnormal" glow discharge behaviour. The analyte-containing solution is not limited to hydronium ions – the conductivity of other salts (e.g. Li^+ and Na^+) is also sufficient to sustain the discharge. The use of a coaxial gas flow of nitrogen around the stainless-steel capillary outlet enables stable plasma operation at low liquid flow rates (0.1–0.3 mL min^{-1}). Analytical response curves for Hg, Mg, Na, and Pb were found to be quite linear, and preliminary detection limits were determined to be in the 1–2 µg mL^{-1} range (10 ng) for 5-µL sample volumes. This makes the system worth consideration for element-specific detection in liquid chromatography. Although the system certainly cannot be regarded as a microplasma, it can be expected that miniaturization preserving much of the analytical performance is highly likely. Similar glow discharge devices operated with a liquid as one of the electrodes have been described by Kim et al. [40], who used an open-air discharge. Detection limits for Cu, Fe, Mn, Ni, and Pb were in the 0.01–0.03 mg L^{-1} range, which makes the system of potential interest for drinking water quality surveillance. Again the system is not yet a microplasma, but developments show that miniaturization of this system is one possible development.

Outlook

From the results described it can be concluded that dc, radiofrequency, and microwave power enable production of microplasmas which, at the current state-of-the-art, can already be used for real sample analysis, if suitable sample-introduction techniques are used. The sample to be analysed must usually be introduced in the vapour state and without water loading. This is understandable, because the evaporation capacities of the microplasmas are limited by low temperatures and the low residence times of the analytes in the hot plasma zones. For this reason liquid-sampling devices other than those producing droplets might be the only solution practicable. The microplasmas so far described in the literature are, however, only a few of many possibilities, and more work on the development and characterization of other types of microplasma, tailored for well-defined problems, will be necessary in the future.

Further development of microplasmas can be expected, especially coupling with suitable spectrometers. Optical emission spectrometers the size of a computer card, including optics, grating, and CCD detection, are now available. As shown by Florek et al. [41], the use of small Echelle systems already enables high spectral resolution with simultaneous detection of radiation of different wavelengths by use of minispectrometers. Optimum coupling of such spectrometers with microplasmas, including well-designed fibre couplings or waveguide systems, will then enable the production of small systems of great potential interest for process analysis, e.g. when requiring control of the composition of gas flows for trace, minor, or main components. Much lower detection limits and ultratrace analysis will certainly become possible when using mass spectrometric detection, which might also be included in the miniaturization approach. Such coupling of TOFMS and MIP have already been shown to be very powerful for element-specific detection in gas chromatography, and much less expensive than ICP–MS [42]. Then not only will elemental determination be possible. When soft ionization sources such as gas sampling glow discharges are used molecular information will be also available [43], and with very high detection power suitable for use in the environmental or life sciences.

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