

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

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A new low-power, small-scale 2.45 GHz microwave plasma source at atmospheric pressure for atomic emission spectrometry based on microstrip technology is described. The MicroStrip Plasma (MSP) source was produced in microstrip technology on a fused-silica wafer and designed as an element-selective detector for miniaturized analytical applications. The electrodeless microwave-induced plasma (MIP) operates at microwave input power of 10–40 W and gas flows of 50–1000 mL·min⁻¹ of Ar. Rotational (OH) and excitation (Fe) temperatures were found to be 650 and 8000 K, respectively. Spatially resolved measurements of the Hg I 253.7-nm atomic emission line with an electronic slitless spectrograph (ESS) showed that a cylindrically symmetric plasma with a diameter of about 1 mm is obtained. With the MSP, Hg could be determined by applying the flow injection cold vapor (FI-CV) technique with a detection limit of 50 pg·mL⁻¹. In terms of the relative standard deviation, a time stability of <1.4% for 45 replicates within 80 min can be realized at a concentration level of 10 ng·mL⁻¹ of Hg. Hg could be determined in the leachate of a certified standard reference soil (STSD-4) obtained by treatment with aqua regia at the 930 ± 76 ng·g⁻¹ level. Results obtained by calibration with aqueous solutions of Hg and with standard addition were found to be in good agreement with those of cold-vapor atomic absorption spectrometry.

INTRODUCTION

In analytical chemistry the trends to miniaturize parts or whole chemical analysis systems nowadays are very important.¹ Indeed, size reduction of analytical systems has several advantages. It leads to a reduced consumption of reagents and production of waste and, at the same time, it may enable a faster analysis as a result

of reduced transport lengths and the possibility to better optimize mass transport for chemical reactions and separations. Further, less sample volume is required and the whole system can be constructed portable. The latter may be important for the monitoring of environmentally relevant elements and compounds directly at their sources of origin in industrial processes. Microwave plasma sources may be made small and nevertheless may have interesting analytical figures of merit. For their structures, chip-fabrication processes based mostly on photolithography and wet etching of substrates such as silicon, glass or quartz, or polymers² may be used just as they recently became of interest for the manufacturing of separation techniques such as capillary electrophoresis (CE),³ in which even pumps and valves are provided “on-chip”.² When using laser-induced fluorescence-detection coupling through a quartz fiber to small spectrometers provided on a computer card,⁴ e.g., the whole system could be made very small and portable.

A new low-power microwave plasma device based on a metallic wave-guiding structure on a fused-silica wafer with a small gas channel inside was recently described⁵ (Figure 1). In this device, a stable argon plasma at atmospheric pressure with a longitudinal extension of 2–3 cm can be generated at a forward power of 10–40 W. Accordingly, it can be powered with the aid of a cheap and small semiconductor microwave power generator. The microstrip structure was obtained by a photolithographic process. The copper electrode at 30 μm thickness was brought precisely and reproducibly onto a fused-silica wafer by subsequent sputtering and electroplating. The electrode consists of a small strip over a gas channel, a small matching device, and an electrical contact to a SMA-type microwave connector. The quartz wafer is a sandwich of two quartz plates with dimensions of 1 × 33 × 90 mm (h/w/l). Both plates have a 0.45 × 1 × 90 mm (h/w/l) groove and are glued together with water–glass so as to obtain a gas channel with a cross section of 0.9 mm². These grooves were obtained

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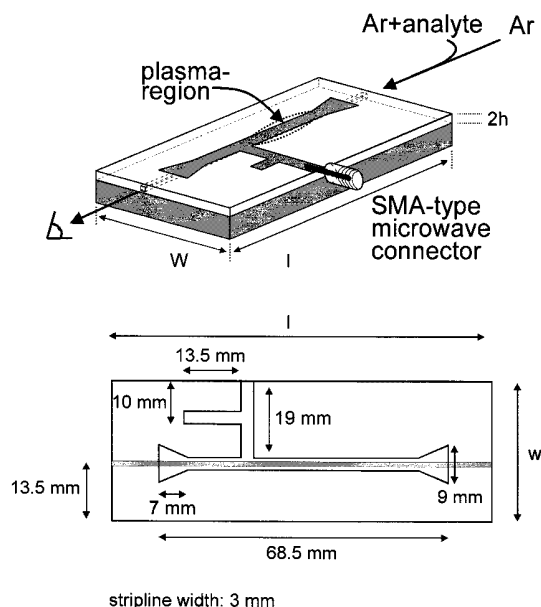


Figure 1. MSP device.

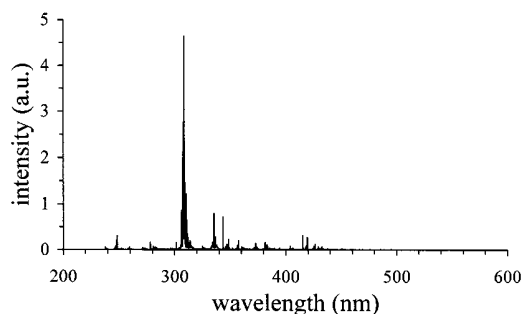


Figure 2. Emission spectrum of a 15 W Ar MIP in the MSP.

with the aid of a commercial dicing-saw. The wafers lie on a copper plate, which works as the ground electrode and is cooled by a computer processor cooler. The plasma could be ignited with the piezo discharge from an electric lighter. The plasma was generated within the quartz glass body and is not affected by contaminations from the plasma-sustaining device or by air components. Only a high signal from the OH bandhead at 306.4 nm, caused by traces of moisture in the plasma gas, and a small signal of the NH bandhead at 336.0 nm could be detected (Figure 2).

The MicroStrip Plasma (MSP) source described is very small, and a further downscaling easily could be reached. It is manufactured by conventional chip technology and fulfils all criterions to be integrated in a miniaturized total analysis system (μ TAS),⁶⁻⁸ as recently shown also for dc discharges.⁹ The power consumption is very low so that it could be operated with a semiconductor microwave source powered by a car battery. To efficiently collect the emitted radiation, a fiber-optic coupling to a miniaturized spectrometer provided on a PC card is feasible. In this way a complete multielement element-specific detection system could be installed on a single computer board as a part of a μ TAS. In

this work the analytical features of this new plasma source are demonstrated by a determination of traces of Hg in aqueous solutions with the aid of a flow injection cold-vapor technique (FI-CV). This application is of high environmental interest^{10,11} because of the high toxicity of Hg and its compounds.¹¹⁻¹³ The latter are released in the environment through the use of batteries or in industrial processes such as the chlorine-alkaline electrolysis, which is still the largest anthropogenic emission source of Hg.

EXPERIMENTAL SECTION

The experimental parameters of the setup used are given in Table 1. In a SpectroMerc (Spectro Analytical Instruments, Kleve, Germany) flow injection cold-vapor atomic absorption (FI-CV-AAS) spectrometer, the atomic absorption detection was replaced by the MSP. The radiation of the MSP was imaged onto the entrance slit of a 0.5 m Czerny-Turner monochromator with the aid of a quartz lens. The widths of the entrance and the exit slit of the monochromator were 40 and 70 μ m, respectively. The intensities of the Hg I 253.7-nm line were measured with a photomultiplier, which was read out by a current to voltage converter and a personal computer equipped with a data acquisition card. The transient emission signals could be recorded and evaluated with the aid of the computer programs LabView 3.0¹⁴ (National Instruments, Munich, Germany) and Grams 3.0 (Galactic Industries Corp., Salem, NH). In Figure 3 the flow injection system used for the FI-CV-MSP-OES system is given. The exit of the gas/liquid separator is connected to the MSP via the drying tube containing $\text{Mg}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$, provided in the FI-CV-AAS system. Additionally, the gas flow was bubbled through a vessel containing H_2SO_4 to remove any traces of moisture from the gas flow leaving the FI-CV system. Afterward, this dried gas was mixed in a T-connector with the plasma gas flow before entering the MSP. The plasma was powered by a semiconductor microwave generator, of which the forward and the reflected power were measured by two power meters. The FI-CV system is operated in a segmented-flow mode, and the sample, acid, and SnCl_2 solution flows are injected separately through tubings with the aid of a peristaltic pump. All flows are regulated by magnetic valves, which are switched under computer control. The optimized parameters of the Hg vapor generator and more details about the system used were given by Haase et al.¹⁵ When the AAS cell in the FI-CV system is replaced by the MSP, the delay time between each measuring circle must be increased and Ar must be used instead of N_2 . Also, both gas restrictors are to be kept in the position "open" during the whole measurement cycle.

For the determination of the plasma temperatures in the MSP plasma, the monochromator was equipped with a turnable mirror. Herewith the spectrally resolved radiation was imaged either onto an exit slit in front of a photomultiplier or onto a charge coupled device (CCD) camera placed in the focal plane. With the latter

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Table 1. Instrumentation

semiconductor microwave source	2.45 GHz, 0–40 W, (Dirk Fischer Elektronik, Dortmund, Germany)
microstrip plasma	laboratory-built (ref 5)
monochromator	0.5 m Czerny-Turner SPEX 500 M; grating, 1200 groves mm ⁻¹ (SPEX Industries, Edison, NJ)
CCD	ST-8 (Santa Barbara Instruments Group, Santa Barbara, CA)
PC	IBM PC-AT, 486 CPU 100 MHz
data acquisition card	AT-MIO 16L-9 (National Instruments, Munich, Germany)
current–voltage converter	model 564 current preamplifier (Ithaco, Leverkusen, Germany)
IDL (interactive data language)	version 4.0 for Linux (Creaso, Gilching, Germany)
LabView	LabView 3.0 for Windows 3.11 (National Instruments, Munich, Germany)
Grams	Grams/386 3.0 for Windows 3.11 (Galactic Industries Corp., Salem, NH, USA)
power meter	432A Power Meter (Hewlett-Packard, Böblingen, Germany)
lens	Quartz; focal length, 7 cm; diameter, 4.5 cm (Beckmann Instruments, Munich, Germany)
FI-CV-AAS system	SpectroMerc (Spectro Analytical Instruments, Kleve, Germany)

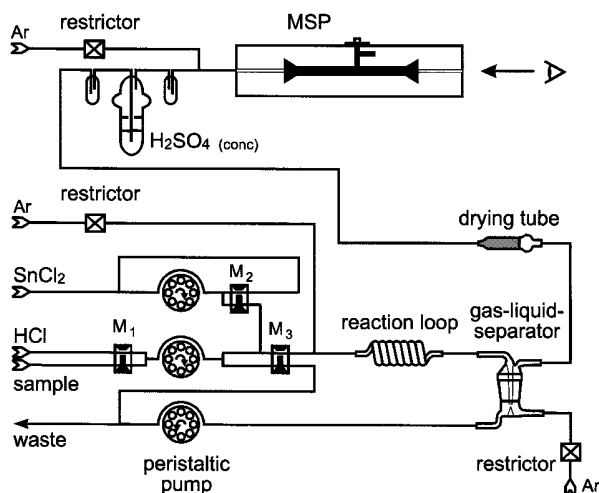
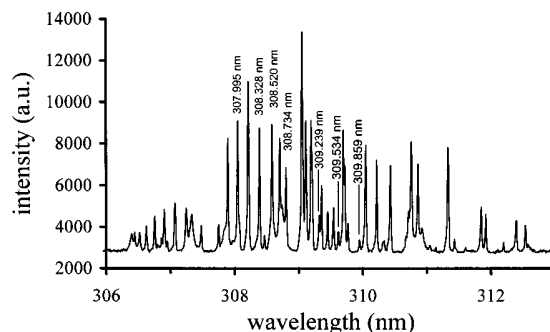
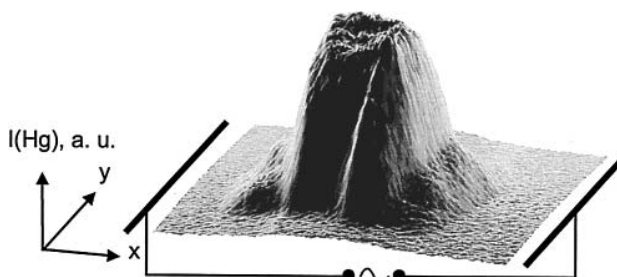


Figure 3. FI-CV-MSP–OES system for the determination of Hg in aqueous solutions.

Table 2. Iron Atomic Emission Lines Used for the Determination of T_{exc}^{17}

wavelength ν (nm)	statistical weight (g) and oscillator strength (f): (g·f)	excitation energy E (cm ⁻¹)
371.99	0.3719	26 875
373.49	2.0746	33 695
373.71	0.2675	27 167
374.56	0.1693	27 395
374.82	0.0964	27 560
374.95	1.4491	34 040
375.82	0.9396	34 329
376.38	0.5776	34 547

setup, intensities of lines within a wavelength range of about 20 nm could be observed simultaneously. The rotational temperature measured from the intensity distribution of the rotational lines in the OH bands may be accepted to be a good estimate for the gas temperature. It is obtained from the band head of the OH radical at 306.4 nm, as described by Ishii and Montaser.¹⁶ Furthermore, the excitation temperature was determined from the emission intensities of Fe lines (Table 2), as described by Rahman and Blades.¹⁷ An emission of Fe atomic lines was obtained when entering a small amount of ferrocene into the Ar gas flow. To reach a sufficient spectral resolution, the entrance slit was made

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as small as to 20 μm and the OH band head was observed in the second order (Figure 4). The CCD allowed it to correct well the slightly interfered lines so that the Boltzmann plot showed that they still could be used in the rotational temperature determination. Both temperatures were determined at an Ar gas flow of 500 mL·min⁻¹ and a forward power of 15 W.

To investigate the geometry of the discharge and the spatial distribution of the Hg emission, the entrance slit of the monochromator was opened up to 1500 μm . When using the CCD camera this arrangement works as an electronic slitless spectrograph (ESS) as a result of the stigmatic properties of the monochromator, as described by Olesik and Hieftje.¹⁸ With the ESS, two-dimensional images of the Hg I emission line at 253.7 nm can be obtained when the plasma is imaged onto the wide-opened entrance slit of the monochromator. To get a stable Hg emission signal the Ar flow sustaining the plasma was led over a

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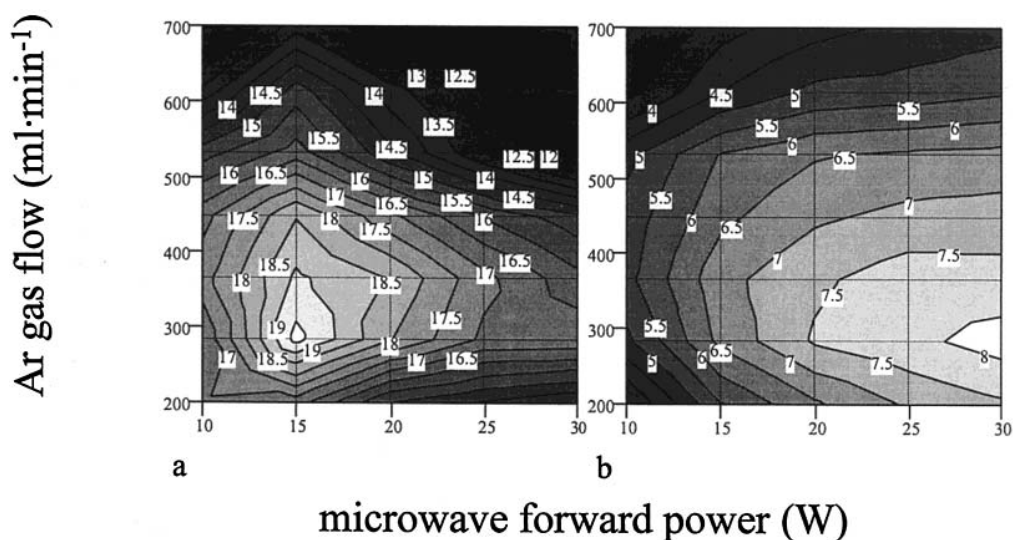


Figure 6. Influence of the plasma gas flow and the forward microwave power on the (a) S/B ratio and (b) relative emission intensity of the Hg I 253.7-nm emission line.

small Hg droplet, which was placed inside the Ar feeding. The plasma was imaged 1:1 on the entrance slit, and the CCD images were evaluated with the aid of the computer program IDL 4.0 (Creaso, Gilching, Germany).

All reagents (HCl, Hg, HNO₃, H₂SO₄ (conc), ferrocene, SnCl₂·H₂O, K₂Cr₂O₇, Mg(ClO₄)₂·xH₂O) used were of analytical-reagent-grade and purchased from Merck (Darmstadt, Germany). The used Ar was 99.998% pure (Messer Griesheim, Krefeld, Germany). Standard solutions were prepared from a stock standard solution containing 1 g·L⁻¹ of Hg (as chloride) (Riedel-de Häen, Seelze/Hannover, Germany). Deionized water obtained from a Milli-Q reagent-grade water system (Millipore, Bedford, MA) was used throughout. The rinsing solution of HCl (5% v/v), the reducing agent (SnCl₂), the standard, and the sample solutions were prepared according to DIN EN 1483,¹⁹ which describes the determination of Hg by CV-AAS. To stabilize the Hg standard and sample solutions used, a solution was prepared by dissolving 0.5 g of K₂Cr₂O₇ in 50 mL of HNO₃ and diluting to 100 mL with deionized water. Standard and sample solutions were prepared with 5% v/v HCl and 1% v/v of the stabilization solution. As standard reference material (STSD-4), a soil sample was used and leached with *aqua regia* according to DIN 38414 S-7,²⁰ as is done in the analytical service laboratory "Agrar- und Umweltanalytik" (Jena, Germany).

RESULTS AND DISCUSSIONS

Visually, the origin of the plasma could be recognized to lie under the upper electrode. When the plasma gas flow is very low no homogeneous plasma is formed in the MSP device but some small stable discharges between the two edges of the gas channel close to the electrodes could be observed. When increasing the Ar gas flow these discharges start to overlap in the direction of the gas flow and to build one plasma, which homogeneously fills

out the whole discharge channel cross section, but is less dense along the axis of the plasma. In Figure 5 the spatially resolved intensity distribution of the observed Hg I 253.7-nm emission line in *x* and *y* directions as obtained by the ESS is presented. According to the visually observed plasma form, it can be recognized that in the center of the gas channel the obtained intensities of the Hg I 253.7-nm emission are somewhat lower. The plasma thus almost fills out the gas channel homogeneously.

The rotational and excitation temperatures measured were 650 ± 30 K and 8000 ± 1600 K, respectively. The errors in the determination of the temperatures were determined by the errors in the slopes of the Boltzmann plots. As expected, the plasma is far away from local thermal equilibrium (LTE), as is the case in many other microwave-induced plasmas. The relatively low rotational temperatures explain why the plasma has a low tolerance against traces of water, e.g., in the Hg-vapor-containing gas flows. Therefore, it was required to dry the analyte containing gas flow additionally by leading it through a sulfuric acid containing vessel. The high excitation temperature and the high analyte number densities in the MSP device explain the good excitation capacity of the MSP. In Figure 6 the influence of the forward power and the plasma gas flow at an analyte-containing gas flow of at 400 mL·min⁻¹ on the signal-to-background ratio (S/B) (Figure 6a) and the relative signal intensity of the Hg I 253.7-nm line (Figure 6b), respectively, are shown. Whereas the S/B was found to be a maximum at 15 W and at an Ar gas flow of ~300 mL·min⁻¹, the maximum of the emission intensity is reached at a forward power of 30 W. All further measurements were performed with a plasma gas flow of 300 mL·min⁻¹ and a forward power of 30 W, because the plasma stability at 30 W was better than that at 15 W.

The long-term stability and the precision achievable over a time period of about 80 min were tested by performing 45 replicate measurements with solutions of 10 ng·mL⁻¹ Hg (Figure 7). The relative standard deviation for the heights of the transient emission signals obtained was only 1.4%.

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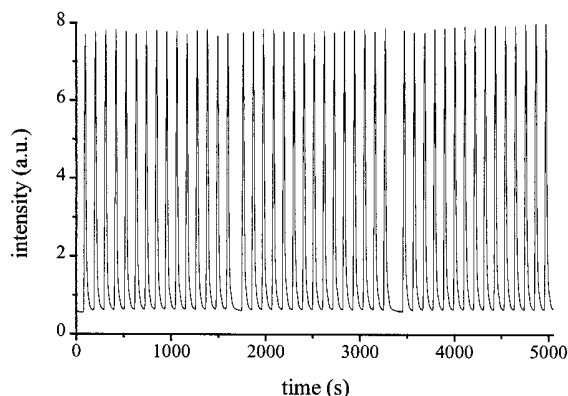


Figure 7. Investigation of the long-term stability of FI-CV-MSP-OES for a solution of $10 \text{ ng}\cdot\text{ml}^{-1}$ Hg (plasma conditions used were 30 W forward power and an Ar gas flow of $300 \text{ mL}\cdot\text{min}^{-1}$ plasma gas plus $400 \text{ mL}\cdot\text{min}^{-1}$ carrier gas flow).

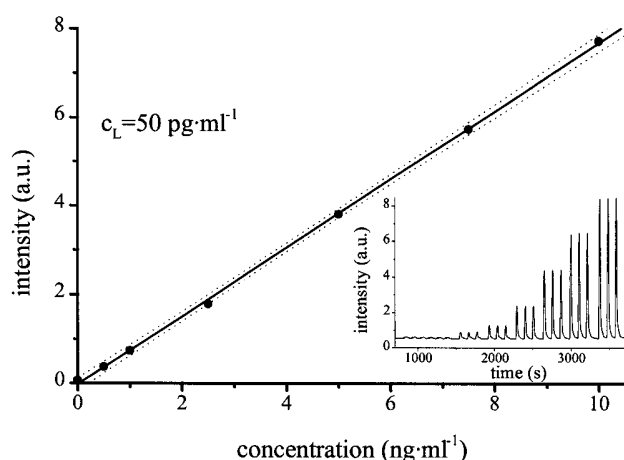


Figure 8. Calibration curve for Hg obtained with standard solutions containing Hg between 0.5 and $10 \text{ ng}\cdot\text{ml}^{-1}$ (plasma conditions used were 30 W forward power and an Ar gas flow of $300 \text{ mL}\cdot\text{min}^{-1}$ plasma gas plus $400 \text{ mL}\cdot\text{min}^{-1}$ carrier gas flow).

In Figure 8 a calibration curve obtained with standard solutions having concentrations of Hg between $0.5 \text{ ng}\cdot\text{mL}^{-1}$ and $10 \text{ ng}\cdot\text{mL}^{-1}$ is given. The relative standard deviations for the replicate measurements were between 0.5 and 1% in the case of peak-height measurements, the correlation coefficient was 0.9998, and the limit of detection calculated according to $3\sqrt{2}(dI/dc)^{-1}\sigma_b$ (ref 21²¹) was $50 \text{ pg}\cdot\text{mL}^{-1}$. In Table 3 the concentrations of Hg in the leached standard reference sample STSD-4 obtained by FI-CV-MSP-OES and by FI-CV-AAS when calibrating with synthetic standards and by standard addition are presented. All concentra-

Table 3. Determination of Hg in STSD-4 ($\text{ng}\cdot\text{g}^{-1}$)

	calibration with synthetic standards	calibration by standard addition
certified value	930 ± 76	
FI-CV-MSP-OES	1002 ± 40	890 ± 36
FI-CV-AAS ⁽¹⁵⁾	1000 ± 11	913 ± 15

tions found for the standard reference sample did not differ significantly from the certified value of STSD-4.

CONCLUSIONS

The analytical features of the new miniaturized microwave plasma source based on microstrip technology for OES showed that it has great potential for use in μTAS . The rotational and excitation temperatures of 650 and 8000 K, respectively, explain both its low tolerance for water-loaded aerosols and its good excitation capacity. The spatial intensity distribution for the Hg I 253.7-nm line, as investigated by an ESS, showed that the MSP device is able to excite the analyte in a suitable way and that the plasma channel in the MSP device is almost completely filled by the plasma. With the experimental setup for the determination of Hg in aqueous solutions by FI-CV-MSP-OES, a limit of detection, which is only slightly higher than that in FI-CV-AAS, could be obtained. Therefore, the use of the MSP device instead of the AAS detection offers the possibility of multielement determinations. The latter, in principle, should be easily possible with all types of vapor generation or volatile compound formation by chemical methods (e.g., Ni as $\text{Ni}(\text{CO})_4$, I, S,...), electrothermal vaporization of dry solution residues, laser and spark ablation for direct solids sampling, and so on. However, in every particular case the limiting factors, such as the accompanying gases formed, eventual gas pressure jumps, or influences of the sample vapor clouds on the plasma, still have to be investigated in detail for the types of samples to be analyzed.

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