The Use of Optical Emission Spectrometry with Microwave Induced Plasma (MIP) Discharges in a Surfatron Combined to Different Types of Hydride Generation for the Determination of Arsenic

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Abstract. The stability and analytical figures of merit of argon microwave induced plasma (MIP) discharges in a surfatron as sources for optical emission spectrometry (OES) are described. These MIPs have been used for the determination of arsenic after hydride generation. They could cope with the excess of hydrogen developed during the hydride generation step and thus not necessitated an isolation of the hydrides before releasing them into the MIP. Two methods for the generation of the volatile AsH₃ were applied. First a micro method was used with solid NaBH₄ on which 10 μl of the acidified sample solution is transferred. Its capabilities were compared to those of continuous hydride generation using a 5% (w/w) NaBH₄-solution and continuous liquid removal in a flow cell. Both methods were optimized for an argon MIP operated at a power of 120–160 W and gas flows of 20 l/h Ar. In the case of solid NaBH₄ the detection limit for As has been found to be 1.0 μg/ml (10 ng) and with the flow cell hydride generation 50 ng/ml. The calibration curves are linear over three orders of magnitude. Interferences caused by Sb, Fe, Sn and NaCl were investigated. No interferences occurred for Sb up to an interferent concentration of 250 μg/ml. The presence of Fe causes a significant depression of the As signal whereas an increase of the As signal was observed in the case of Sn. High NaCl concentrations did not influence the As signals when using continuous hydride generation, but had a great influence when using solid NaBH₄.

Key words: arsenic, microwave induced plasma, surfatron, hydride generation, plasma emission spectrometry.

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Plasma atomic emission spectrometry with various types of electrical plasma discharges has become of routine use. The reasons for this are the low detection limits, the linear dynamic range extending over three to five orders of magnitude and its high multielement capacity. The most important plasma source in this respect is the inductively coupled plasma (ICP). However, as the ICP requires a power of 1000–1500 W and its gas consumption is mostly beyond 10 l/min argon, there is a demand for plasma sources which have similarly good analytical properties as the ICP but lower instrumentation and operation costs. In a number of special cases these conditions are fulfilled with microwave induced plasmas (MIP). A first MIP at atmospheric pressure with argon and helium could be realized in 1976 by Beenakker [1] in a TM_{010}-resonator and was improved by van Dalen et al. [2]. Further the surfatron MIP which was first described by Hubert et al. [3] found great interest. Typically these plasmas are operated at a forward power of 50–300 Watt and a gas consumption of about 2 l/min. Richts et al. [4] used both plasmas in combination with electrothermal evaporation, and found that the surfatron has the better analytical performance; the detection limits for Cu and Cd are a factor of up to 5 lower and there are less ionization interferences in the case of a MIP operated in a surfatron. Because of their low power, MIPs can only be used with a limited number of sample introduction techniques [5]. Pneumatic nebulization can only be applied in combination with desolvation [6] or the case of toroidal MIPs [7]. With sample introduction methods where dry aerosols or a gaseous compound of the analyte is produced, MIPs have the best performance [8–10]. This applies to hydride generation as a technique for the determination of As, Se, Sb and others. Bulska et al. [11] described various methods for the determination of volatile hydride forming elements such as As, Sb and Se with a MIP operated in a TM_{010}-resonator. The direct introduction of these hydrides into the MIP was found difficult because the plasma stability decreased as a result of the presence of an excess of generated hydrogen. They separated the hydrogen from the analyte by in-situ trapping of the hydrides in a liquid nitrogen cooled trap and also investigated hot trapping with a graphite furnace. The detection limits in the case of these preconcentration techniques are 0.4–0.8 ng/ml for the cold trapping and 0.25–0.40 ng/ml with hot trapping. In the case of hydride generation and hot trapping with a graphite furnace the detection limits of the surfatron for As, Sb and Se are by a factor 1.6 to 2.2 lower than with the TM_{010}-resonator [12]. Tao et al. [13] described continuous hydride generation in combination with a helium MIP for the detection of Ge, As, Sb, Sn and Hg. In this case the hydrides were separated from the hydrogen and the water vapor using a hollow-fiber membrane. The detection limits for these elements are 0.04–6.1 ng/ml. As a further type of microwave discharge the single electrode plasma, or the capacitively coupled microwave plasma (CMP) can be used. It is based on the work of Mavrodineanu and Hughes [14] and is operated at several 100 W and about 120 l/h of gas. Ali and Winefordner [15] used the CMP in combination with electrothermal evaporation from a tungsten filament and achieved absolute detection limits in the 1–100 pg range. Patel et al. [16] used a modified CMP with hydride generation for the detection of Sn and reached a detection limit of 7 ng/ml.

In this work a MIP operated in a surfatron with < 60 l/h argon was combined with the two methods of hydride generation mentioned. After a careful determination of the stability areas, it was possible to find conditions where the developed