A simple radiofrequency helium discharge plasma (RFP) for spectroscopic purposes

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In this work a radiofrequency powered helium discharge plasma (RFP) for optical or mass spectrometry purposes was developed and investigated. Research focussed on the spectroscopic properties of the RFP, and its suitability as an alternative excitation source for plasma spectroscopy was proved. Halogenated organic compounds were injected into the gas flow to detect fluorine, chlorine, bromine and iodine at their most intense spectral lines resolved from interferences. With this plasma, the detection of Cl down to 125 ng without background correction is possible. Injection of air samples causes few interferences and shows the robustness of the radiofrequency plasma against large sample volumes of up to 500 mL. A Cl selectivity against N 2, O 2 (both more than 5000 5 1) and C (250 5 1) is achieved without background correction. A fluorine quantification is possible for 0.25 mg only. I and Br detection also can be achieved down to 0.25 mg without any background correction.

Introduction

In many analytical laboratories commercially available inductively coupled plasmas (ICP) are in use as an excitation source for atomic emission spectrometry (ICP-AES) or mass spectrometry (ICP-MS). A great amount of argon is needed to operate this plasma and maintenance costs are accordingly high, not to mention the high initial price of this system.

Another widespread excitation source is the microwave induced plasma (MIP). An unsolved problem is the sample introduction, as pressure changes can easily disturb the plasma. Also, with large amounts of analytes the excitation source cannot be maintained. With a MIP it is possible to use helium as the plasma gas.

A new excitation source is the radiofrequency plasma (RFP), which had been developed as a detector for gas chromatography (GC) by Pedersen-Bjørgaard and Grebbrok. The end of a GC-capillary without the polyimide coating between two electrodes was used to maintain the excitation. Pedersen-Bjørgaard and Grebbrok described detection limits at a 50 pg s −1 level for oxygen and nitrogen.

A distinctive advantage of the RFP compared with ICPs is its low running cost (200 mL min −1 of He) and compared with MIPs its stability against gas flow changes or humidity. Nevertheless, the detection limits are comparable to a MIP or ICP. Therefore the RFP cannot only be used in a detector for GC, but is especially suitable in a multi-element detector for HPLC or in nebulizer applications.

Experimental

Instrumentation

The helium discharge is maintained between a simple brass connector as one electrode and a stainless steel ring electrode at the end of a ceramic tube (P. Sindhauser Pulver & Keramik Vertrieb, Kaufbeuren, Germany) with an inner diameter of 4 mm and a length of 60 mm. As an alternative, a quartz tube with the same dimensions was used. A radiofrequency power supply (Puls-Plasmatechnik, Dortmund, Germany) generates a radio wave with an excitation frequency of 108 kHz. The plasma gas flow is 220 mL min −1 and the additional analyte gas flow 20 mL min −1, controlled by two gas flow controllers (Model MRF.01, Rota, Yokogawa, Japan). The analyte is prepared in a 500 mL gas-tight container, filled with helium and a definite amount of the volatile organic compound. This mixture is injected through the injection block (Fig. 1) into the plasma.
the analyte gas flow by means of a 250 μL or 500 μL gas-tight syringe (Precision Sampling Corp., Baton Rouge, Louisiana, USA). The plasma is viewed end-on with a 0.46 m monochromator (Model HR 460, Jobin Yvon, Longjumeau, France). The asymmetrical Czerny–Turner optical configuration has a focal distance of 46 cm and provides a 0.3 nm resolution with 100 μm slits. The 1200 mm−1 grating allows measurement of the emission spectrum of the RFP and is set in the wavelength region from 600 to 1200 nm. As a detector, a photodiode with integrated amplifier (105330DA2, IPL, Dorchester, Dorset, UK) is used and its signal is expanded by an amplifier. The monochromator is controlled by a DataScan Mono Drive (Model 2, Jobin Yvon). The evaluation is performed by SpectraMax software (Version 1.0, Instruments S. A. Jobin Yvon, Edison, New Jersey, USA). Fig. 2 shows the instrumental set-up.

### Preliminary results and discussion

Volatile halogenated organic compounds were injected into the helium plasma with a gas-tight syringe, and the elements fluorine (1,1,1,2,2,2-hexafluoropropan-2-ol), chlorine (2-chloropropane), bromine (1,1,1-tribromomethane) and iodine (1-iodobenzene) could be quantified at the wavelengths of 685.6 nm (F), 837.6 nm (Cl), 889.9 nm (Br) and 973.2 nm (I), respectively, with limits of detectability in the nanogram region. For fluorine quantification, a range of 0.25–2.00 μg was measured, but peak tailing was observed (Fig. 4). This effect is supposed to be caused by reactions on the inner tube surface. For bromine, quantifications in the range 0.25–2.00 μg were shown. From Fig. 5 it can be seen that for different bromine compound injections a respectable reproducibility can be achieved. A real-time diagram of iodine compound injections is shown in Fig. 6. Detection was possible in a range of 0.25–2.00 μg and limits of detectability down to 100 ng are possible. The injection of 100 μL of air caused only few interferences. Thus, the robustness of the radiofrequency plasma makes it possible to introduce large sample volumes containing interfering gases. For Cl measurements selectivities against N₂ and O₂ of more than 5000:1 were achieved without background correction. CI selectivity against C was at 250:1.

These preliminary results prove that it is possible to determine analytes in gaseous samples by using this small and
In the near future, investigations regarding the detection of various metals (e.g., Na, K and Fe), sulfur, phosphorus and nitrogen will be studied. Furthermore, sample introduction using a direct injection nebulizer (DIN), an ultrasonic nebulizer (USN) and electrothermal vaporization will be optimized.

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References

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