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GC–MIP–PED as an Element-Specific System for the Determination of Organomercury Compounds

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The application of the combination of gas chromatography and a self-developed plasma emission detector for organomercury speciation is presented. The system, basing on interference filter technology, is described briefly. The plasma and the optical system have to be optimized to reach highest sensitivity for mercury detection. Dimethyl-, methyl- and inorganic mercury as selected compounds have been separated on a GC column and calibrated to obtain the analytical performance data of the system used. Finally, the analysis of some real samples has been performed.

Keywords: organomercury compounds; gas chromatography; microwave induced plasma; atomic emission spectrometry

INTRODUCTION

Hyphenated techniques using capillary gas chromatography (CGC) and element-specific detectors are important tools for the speciation of organometallics.[1] Particularly, since the appearance of the GC–AED system (atomic emission detector),[2,3] atomic emission spectrometry (AES) has often been applied in this important field of analytical chemistry.[4–8]

The most important advantages of GC–AES for the detection of metal compounds are the wide dynamic calibration range, the possibility of simultaneous multielement detection and the high elemental selectivity. However, when a microwave-induced plasma (MIP) is used, the low tolerance to introduction of the solvent is disadvantageous for the plasma stability and its atomization properties, even for small amounts.

In this paper, first studies of the application of coupling CGC with an atmospheric helium microwave-induced plasma (He–MIP) and the plasma emission detector (PED) are performed for the determination of mercury compounds (methylmercury, dimethylmercury and inorganic mercury). The PED uses interference filters for wavelength selection, which perform an oscillation for background correction. Recent publications have demonstrated the efficiency of this simple system for the determination of nonmetals like hydrogen, carbon and halogen compounds.[9,10]

EXPERIMENTAL

Instrumentation

The principal experimental set-up is based on the work of Cammann *et al.* and is described elsewhere.[11] The measurements were carried out with the following instruments: gas chromatograph (Hewlett–Packard HP 5890A with split/splitless injector), GC–MIP interface (AHF, Tübingen, Germany), resonator (TM 010 Resonator Model HMW 25-471 N-W, AHF)[12,13] microwave generator (GMW 24-301 DR, AHF) and integrator (C/R6A Chromatopac, Shimadzu, Duisburg, Germany).

The PED shows several differences in comparison with the detectors normally used in atomic emission spectrometry. Instead of expensive poly- or monochromator systems, interference filter technology is applied for optical selection of the wavelength desired. These filters with narrow bandwidth (full width at half maximum FWHM < 1 nm) perform a controlled oscillation (modulated frequency: 20 Hz) against the optical path to obtain spectral background correction. For detection of the radiation emitted from the plasma, photomultiplier tubes and a lock-in amplifier are used, so that the measurements are selective in phase and frequency. The schematic set-up is shown more precisely in Fig. 1. It should

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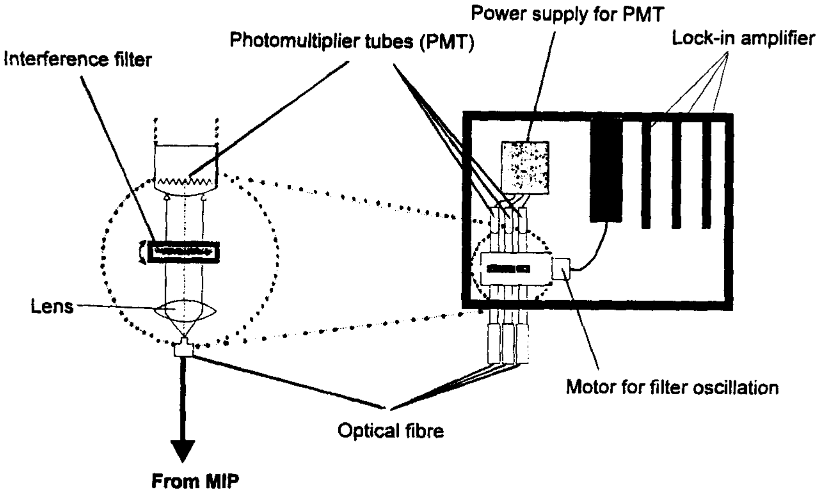

Figure 1 Schematic description of the plasma emission detector (PED).

be mentioned that normally three elements could be detected simultaneously, but in this case only one interference filter for mercury detection has been applied. The interference filter used for this study has a transmission maximum at 254.6 nm with an FWHM of 0.9 nm resulting in a transmission of 12%. With the variation of the angle position it is possible to monitor the Hg(I) emission line at 253.652 nm. The gas-chromatographic conditions are given in Table 1.

Reagents, standard solutions and extraction procedure

Mercury chloride p.a., dimethylmercury and n-pentane (99%) were obtained from Merck (Darmstadt, Germany). Acetic acid 100% p.a., methanol p.a., sodium acetate trihydrate p.a. and sodium hydroxide p.a. (all obtained from Merck) have been used for real sample analysis. Methylmercury chloride was obtained from Alfa

Table 1 Gas chromatographic conditions for the separation of the mercury compounds

Gas parameters	
Column	Ultra-1
Dimensions	25 m × 0.32 mm id × 0.52 µm film thickness
Column head pressure	70 kPa helium
Injection port temperature	250 °C
Injection volume	0.2 µl
Injection	Split/splitless
Split ratio	1:20
Purge valve	
On	0–2 min
Off	2–7 min
Oven program	
Initial temperature	45 °C
Initial time	2.5 min
Ramp rate	25 °C min^{-1}
Final temperature	145 °C
Final time	0.5 min
Interface parameters	
Transfer line	Ultra-1
Transfer temperature	250 °C

Ventron (Karlsruhe, Germany). Stock solutions of the analytes (about 100 mg l^{-1} as Hg) were prepared in methanol, as expected for inorganic mercury in double-distilled water, and stored at 4 °C. To convert methylmercury and inorganic mercury into a volatile species, ethylation with sodium tetraethylborate (Strem Chemicals, Newburyport, USA) was used.[14,15]

For real sample analysis, e.g. of soils and sediments, methanolic NaOH (10%, w/w) has been applied for the extraction procedure according to the method of Bloom.[15] After sample treatment at 50 °C, the methanolic solution was diluted with double-distilled water and an aliquot was adjusted to pH 5 with acetate buffer. After ethylating the analytes with 1% sodium tetraethylborate the aqueous phase was extracted with n-pentane. The organic phase was injected into the GC system.

RESULTS AND DISCUSSION

Optimization procedure

For optimizing the detection sensitivity, several parameters concerning the detector and the plasma have to be adjusted and co-ordinated. For this, 1 ng absolute (as Hg) of dimethylmercury (Me_2Hg) was injected into the GC column isothermally at 45 °C.

First the entry angle of the light was investigated with the result that the optimum signal/noise ratio was found to be at +7° (Fig. 2). The second parameter of the PED having a great influence on detection is the oscillation angle, which was varied between 1.1 and 11° (Fig. 2). Maximum sensitivity to the S/N ratio was at 9.9°. The two parameters mentioned above were to be adjusted on the detector side only.

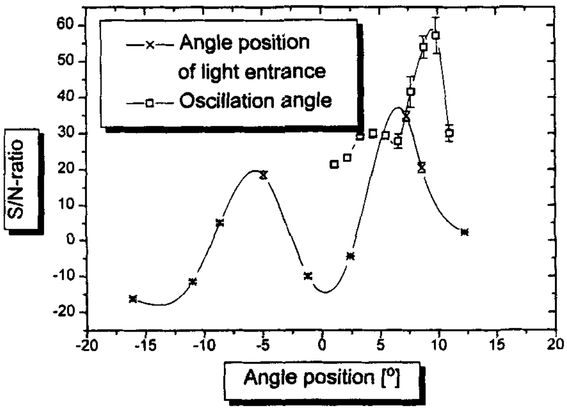

Figure 2 Influence of the entry angle of the light and the oscillation angle on the detection of mercury

The MIP, consisting of a Beenaker TM_{010} cavity with the modifications of van Dalen *et al.*,[13] has shown good stability in the following ranges: microwave power 80–90 W; He gas flow 100–165 ml min^{-1}. Outside this region the plasma was extinguished or showed a high noise level and an anomalous flicker.

The optimization procedure for the two parameters is demonstrated in Fig. 3. The most sensitive detection was reached at a power of 85 W and a gas flow of 105 ml min^{-1}. Under these conditions the plasma was stable and existed without any disturbance.

A chromatogram recorded under the optimized conditions is shown in Fig. 4. The retention times for the compounds were as follows: Me_2Hg,

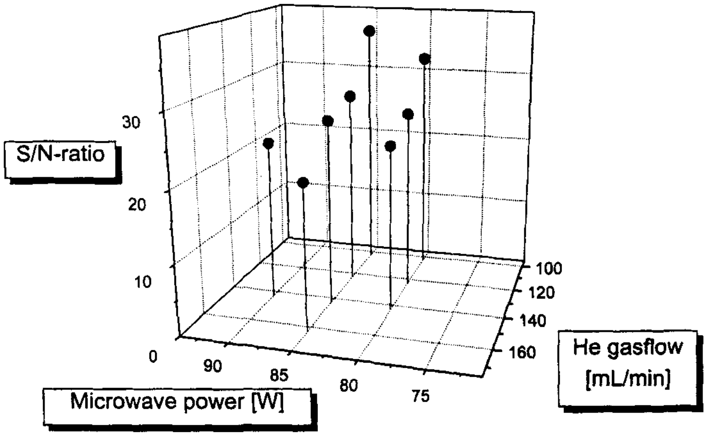

Figure 3 Influence of the microwave power and the gas flow on the detection of mercury.

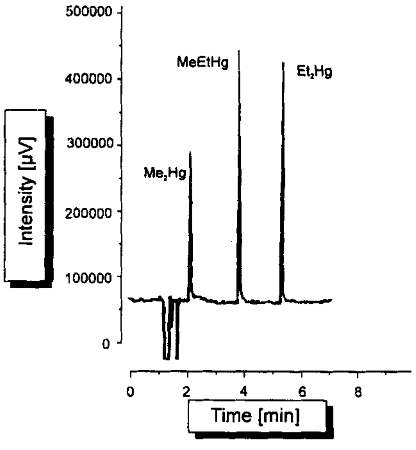

Figure 4 Chromatogram of the organomercury compounds.

2.17 ± 0.01 min; MeEtHg 3.87 ± 0.02 min; Et_2Hg, 5.41 ± 0.04 min.

Calibrations and detection limits

With the three compounds mentioned above calibrations have been carried out using the optimized parameters (Table 2). Over almost three decades the functions were linear for peak height as well as peak area evaluation, which allows determinations over a wide concentration range. The relative operational standard deviation for the determination of the organomercury compounds is between 4 and 5%.

Real sample analysis

To demonstrate the ability of the system, the analysis of three sandy soils using a standard addition method was investigated. Organomercury compounds could not be detected, but nevertheless the quantification of inorganic mercury was performed. For comparison of the results, the same samples were analysed by another method, the combination of the Wickbold combustion method and CV-AAS[16] (Table 3). The results show a good agreement between these different working methods.

Table 2 Analytical parameters of the calibrations

	Me_2Hg	$MeHg^+$	Et_2Hg
Intercept *a* (a.u.)[a]	1060	−2392	−708
Slope *b* (a.u. ng^{-1})	128613	111370	117763
Linear range [ng abs. as Hg]	0.07–18	0.075–15	0.04–12
Coefficient of regression, *R*	0.9998	0.9994	0.9997
Detection limit (pg abs. as Hg)	12	15	10

[a] a.u., area units.

Table 3 Results for mercury compared with the method described in Reference 16

Sample	GC-MIP-PED: Hg^{2+} (µg kg^{-1})	Ref. 16 method: total Hg (µg kg^{-1})
1	358 ± 25	403 ± 15
2	103 ± 9	122 ± 8
3	188 ± 9	180 ± 9

A sample of human hair in which methylmercury could be detected was taken from a coworker who had been working with organomercury compounds for several years. The chromatogram (Fig. 5) shows the extract of the hair sam-

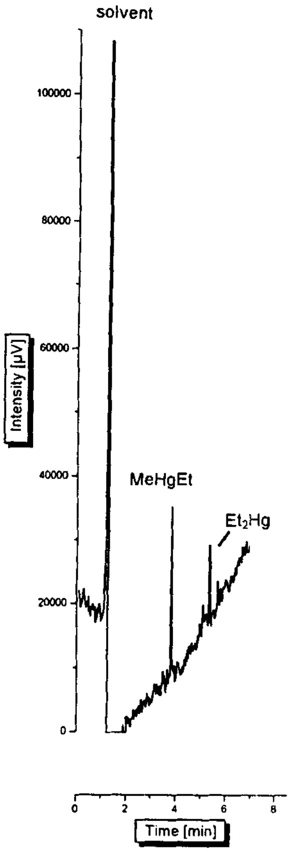

Figure 5 Chromatogram of a real sample (human hair).

ple. The result for methylmercury using the combination of the extraction procedure mentioned above and the GC–MIP–PED-system was 20.5 ± 1.9 μg kg^{-1}.

CONCLUSIONS

The application of a plasma emission detector (PED) for the determination of organomercury compounds has been presented. Optimization procedures and calibrations have been carried out to obtain the highest sensitivity. As an example of real sample analysis, three soils and one human hair sample have been analysed; however, only in the hair sample methylmercury could be detected. It should be noticed that the detection limits are not satisfactory at the moment due to the limited injection volume (0.2 μl), but the system seems to be promising for the future by coupling it with solvent-venting. Further research work should result in a more sophisticated method for the determination of organometallics.

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