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Determination and speciation of organotin compounds by gas chromatography–microwave induced plasma atomic emission spectrometry

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Abstract

An optimized analytical method for the determination of organotin compounds in environmental samples is described. After derivatization the resulting compounds were measured with a hyphenated technique, gas chromatography coupled with element-selective detection by helium atmospheric pressure microwave induced plasma atomic emission spectrometry (GC–MIP–AES). The sensitivity of the most intensive emission lines in the range of 180–350 nm was investigated. The best results were obtained by using the 326.23 nm line. The influence of the reagent gases (H_2, O_2) on the signal intensity was determined. After the optimization of the source conditions a calibration was realized on the base of a multicomponent standard solution, prepared by pentylation of organotin salts. A detection limit of 0.8 pg Sn could be achieved. Measurements of the sensitivity on mixtures of organotin compounds with different alkylation showed a dependence of the grade of pentylation. This could be caused by plasma effects (formation of CO and OH molecular bands).

The proposed method was applied to the analysis of organotin compounds in a sediment of the Elbe river. Furthermore, a new arrangement of GC–MIP–AES was studied. It consists of a gas chromatograph, directly coupled to a newly designed MIP (without interface) and a quartz fibre optics to transmit the emitted light to the spectrometer.

Parameters, such as gas flow, power of the microwave generator, distance of the capillary column to the plasma, were optimized.

1. Introduction

During the last decade a fast development of species-selective analytical methods for organometallic compounds in environmental samples has been observed. Organotin compounds have been used in increasing large amounts in industry as stabilizing agents in poly(vinyl chloride) [1,2], as biocides in antifouling paints [3], etc. The increase in the industrial use of all

these materials cause environmental pollution. Because of the great differences in toxicity of the various organotin compounds, depending on the structure, it is important to develop an analytical technique capable of speciation of various organotin compounds in environmental samples. The organotin compounds cannot be analyzed directly; a derivatization step is necessary. The resulting compounds can be measured by GC with a modified flame photometric detector [4–7], GC–MS [8] or GC–AAS [9,10]. A hyphenated technique for the separation and charac-

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terization of such compounds is the use of GC coupled with helium atmospheric pressure microwave induced plasma atomic emission spectrometry (MIP-AES) [11–16].

This article describes an optimized analytical method for the determination of organotin compounds with GC–MIP-AES and first results of measurements to explain processes in the plasma interfering the determination of tin, such as the formation of two-atomic molecules.

2. Experimental

2.1. Instrumentation

GC–AES

An HP Model 5890 Series II gas chromatograph (Hewlett-Packard, Avondale, PA, USA) equipped with a split/splitless injection port interfaced to an HP Model 5921A atomic emission detector was used. Injections were made by means of an HP Model 7673A automatic sampler.

A new arrangement of GC–MIP-AES was investigated. It consists of a gas chromatograph HP 5890 II (Hewlett-Packard), microwave generator GMW 24-302 DR and a resonant cavity HMW 25-471 N-W (both AHF Analysentechnik, Tübingen, Germany), a monochromator SPM-2 (Carl-Zeiss-Jena, Jena, Germany) and a registration unit.

2.2. Reagents

The plasma gas and the carrier gas used for the GC–AES were helium, 99.9999%. Hydrogen, 99.999% and oxygen, 99.999%, were used for the determination of tin as reagent gases. All the gases were supplied by Linde (Leipzig, Germany).

The following organotin compounds were used. Tetrabutyltin, Bu_4Sn (98%), (Fluka, Neu-Ulm, Germany); tributyltin chloride, Bu_3SnCl (96%); dibutyltin dichloride, Bu_2SnCl_2 (95%); butyltin trichloride, BuSnCl_3 (95%); and *n*-pentylmagnesium bromide, PeMgBr (2.0 mol/l) in diethylether (all obtained from Aldrich, Steinheim, Germany).

Tetraethyltin, Et_4Sn and the used solvents *n*-hexane and *n*-octane, respectively, were purchased from E. Merck (Darmstadt, Germany).

Stock solutions were prepared by dissolving the appropriate amount of the organotin salt in hexane in order to yield a theoretical concentration of 500 $\mu\text{g/ml}$ (as Sn) and the solutions were stored at 4°C in the dark.

Working standard solutions were prepared daily by a series of dilutions with *n*-octane–*n*-hexane from the stock solution.

Pentylated alkyltin standards were prepared by pentylation of organotin salts as described in Ref. [9].

2.3. Extraction procedure for the analysis of a sediment

Sediment (5 g) were acidified with 6 ml HCl (5%, v/v), then 20 ml of a 0.05% w/v solution of tropolone in hexane were added. This mixture was shaken for 30 min. The organic phase was separated and dried over NaSO_4 . The Grignard reagent (pentylmagnesium bromide solution) was added to the hexane extract and stirred for 30 min. Carefully, 15 ml 0.5 M H_2SO_4 and 60 ml H_2O was added and the organic phase was separated and dried over Na_2SO_4 .

2.4. GC–AES conditions

Working conditions for the gas chromatograph, injector, interface and atomic emission detector are summarized in Table 1.

3. Results and discussion

3.1. Optimization of GC–AES conditions for the determination of organotin compounds

On the base of conditions given in Ref. [11] the parameters emission lines and reagent gases concentration were optimized. A standard solution of 200 ng/ml tetrabutyltin in hexane was used.

Table 1
GC-AED Parameters

<i>GC parameters</i>	
Injection port	split/splitless
Injection port temperature	170°C
Injection volume	1 μ l
Split ratio	splitless
Column	HP-1: 25 m \times 320 μ m \times 0.17 μ m I.D.
<i>Oven program</i>	
Initial temperature	110°C
Ramp rate	28°C
Final temperature	230°C (0.75 min)
<i>Interface parameters</i>	
Transfer line temperature	250°C
<i>AES parameters</i>	
Helium make up flow	240 ml/min
<i>Scavenger gases</i>	
H ₂ pressure	2.0 bar
O ₂ pressure	2.0 bar
N ₂ spectrometer purge flow	2 l/min
Solvent vent off time	1.5 min

Determination of the most intensive emission signals of Sn

In order to reach a higher sensitivity and an improvement of the detection level, measurements have been carried out using the following wavelengths: 189.98, 235.48, 242.17, 242.95, 257.16, 270.65, 284.00, 286.33, 300.91, 303.41, 317.50 and 326.23 nm. Fig. 1 shows the comparison of signal intensities. For the measurements to follow the 326-nm wavelength was used.

Influence of the reagent gases on the signal intensity

As reagent gases either oxygen or hydrogen (or both) may be added to the gas flow in order to increase the sensitivity. For the analyses of organotin compounds the presence of oxygen is necessary to prevent the deposition of carbon at the discharge tube. The presence of oxygen leads, on the other side, to the formation of refractory oxides of tin inside the MIP interface. The tin oxides tend to accumulate on the inner wall of the quartz discharge tube changing the parameters of the MIP and resulting in a de-

crease of sensitivity, peak tailing, and subsequent memory effects. The negative effect of oxygen on the determination of tin can be compensated for by adding of some hydrogen to the plasma gas. Hydrogen seems to support tin excitation probably by forming very volatile hydrides which are easily atomized and excited [11].

The influence of the reagent gases on the signal intensity (for tetraethyltin in hexane) is shown in Fig. 2. It can be seen, that a maximum intensity is found using 2.4 bar hydrogen and that the intensity is minimal using oxygen.

3.2. Calibration

Using the optimized parameters a calibration for tin was made on the basis of tetrabutyltin in hexane. In all cases an excellent linearity for a concentration range over 3 orders of magnitude is realizable. An evaluation of the peak heights shows that the detection limits for the different Sn emission lines are in the range from 0.8 to 8.4 pg Sn, listed in Table 2. Looking at the signal intensities in Fig. 1 one should expect the 284.00 nm line is characterized by the best detection limit. The data given in Table 2 show, however, that the best detection limits are obtained at the 326.2 nm Sn emission line. This is caused by the high background using the 284.00 nm line and the fact that the detection limit is given by the 3σ criteria. The effect of background emission will be discussed in Section 3.3.

Investigations of mixtures of organotin compounds

First studies were done with butyltin species which play an important role in polluted aqueous systems. Because these organotin compounds, besides tetrabutyltin, can not be analyzed directly (the volatility of this cationic species is insufficient), a derivatization was realized (Grignard reagent). A multicomponent standard solution was prepared by pentylation of organotin salts. It consist of tetrabutyltin, tributylpentytin, dibutylpentytin, and monobutyltripentytin. Measurements of mixtures of organotin compounds were carried out in hexane (Fig. 3) and

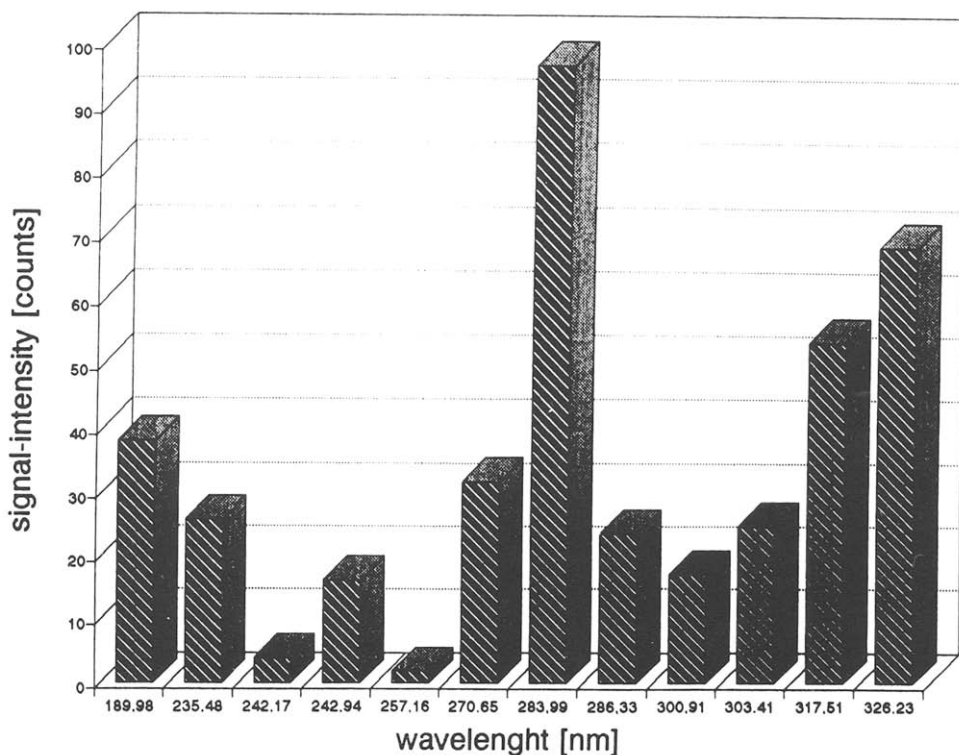


Fig. 1. Comparison of signal intensities of tin at the most sensitive emission lines, conditions are given in the Experimental section. A solution of tetrabutyltin in hexane with 500 ng/ml Sn was used.

octane, respectively. It was found, that there is no influence on the sensitivity of the used organotin compounds for both solvents. But it was found that with an increase of the degree of

pentylation there is a remarkable decrease in sensitivity.

In order to exclude influences due to derivatization and extraction, tetraethyltin which

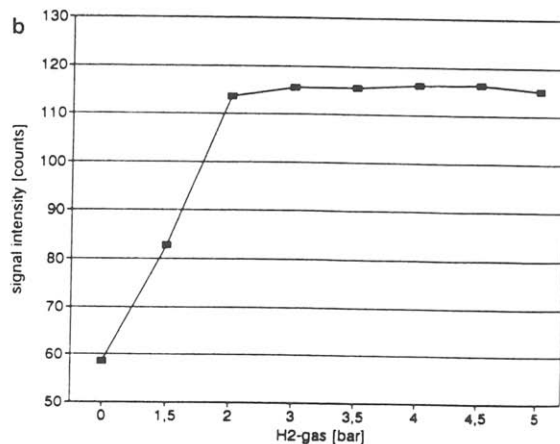
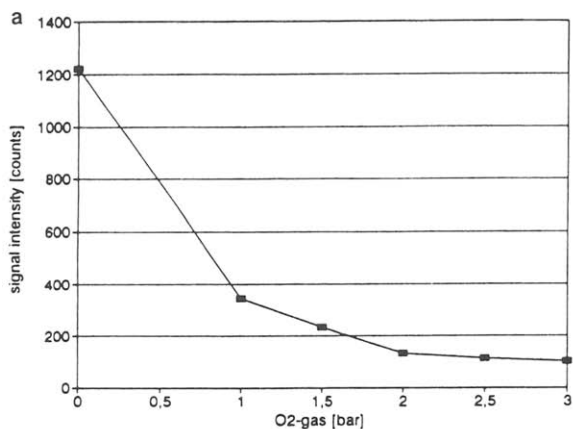


Fig. 2. Influence of the reagent gases on the signal intensity, using tetrabutyltin in hexane with 500 ng/ml Sn. (a) Influence of O₂ on the signal intensity; (b) influence of H₂ on the signal intensity.

Table 2
Detection limits for tin at the most intensive wavelengths

Wavelength (nm)	Detection limit (pg Sn)
189.98	1.4
270.65	2.3
284.00	2.1
303.41	2.5
317.50	8.4
326.23	0.8

does not have to be derivatized was calibrated and compared with calibration of tetrabutyltin. Even here, a distinctly lower sensitivity of tetraethyltin in comparison with tetrabutyltin can be noticed. That means that the detection limit is depending on the binding of the element, in contrast of the claim of the manufacturer that the response factors for each element should be nearly the same for all compounds. In the literature [13,14,17] differences were also reported. Sensitivities and detection limits for the different compounds are listed in Table 3.

3.3. Plasma investigations

The device used in this study has the possibility to confirm the identity of a peak with a

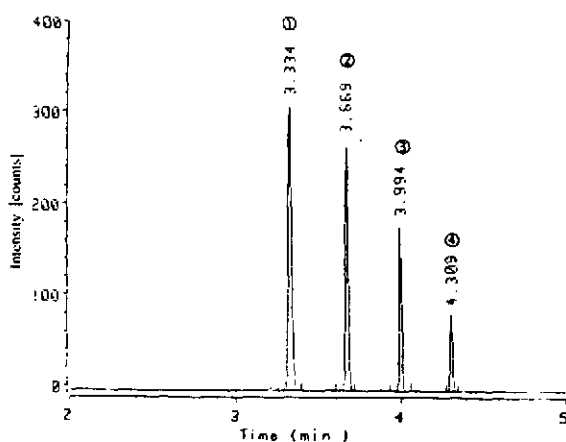


Fig. 3. Chromatogram of a mixture of Bu_4Sn , Bu_3PeSn , $\text{Bu}_2\text{Pe}_2\text{Sn}$ and BuPe_3Sn (containing 400 pg Sn each, in hexane, measured at the 326 nm Sn line, conditions listed in Table 1). 1 = Bu_4Sn ; 2 = Bu_3PeSn ; 3 = $\text{Bu}_2\text{Pe}_2\text{Sn}$; 4 = BuPe_3Sn .

Table 3
Sensitivities and detection limits for the different compounds

Compound	Sensitivity (counts/pg Sn)	Detection limit (pg Sn)
Bu_4Sn	0.77	0.8
Bu_3SnPe	0.67	0.9
Bu_2SnPe_2	0.45	1.4
BuSnPe_3	0.21	3.1
Et_4Sn	0.07	8.3

so-called snap shot. It takes an instantaneous spectrum of the wavelength range where the photodiode array (PDA) is positioned. The typical emission spectra with wavelengths ranging from 260 to 340 nm are shown in Fig. 4.

An investigation of the background (Fig. 5) showed that the 284.00 nm line and the 317.50 nm line are superimposed by molecular bands. That is the reason for the worse detection limits at this wavelengths. The band at 317.50 nm is probably an OH molecular emission, the band at 284.00 nm turned out to be a CO-band. For verification a (CO) molecular emission during a run of a organotin compound was measured at a wavelength of 342.57 nm at the retention time of the organotin compound. The obtained signal is shown in Fig. 6.

The formation of molecules (CO, OH, SnO , SnH , SnOH) can be explained by the relatively low gas temperature within the MIP. The plasma temperatures are lower than for other plasmas such as ICP. (The intense spectral emission for many elements, including non-metals is giving by the high electron temperatures in the plasma.) Besides the presence of OH and CO confirmed by the bands of both species, the formation of SnO_2 in the MIP was tested. The inner surface of the discharge tube was analysed using the combination of ICP-MS and laser ablation. The semiquantitative analysis of an used discharge tube showed a high concentration of tin.

3.4. Analysis of an environmental sample

The potentials of the method described, were studied by the analysis of an environmental sample, a sediment from the river Elbe near

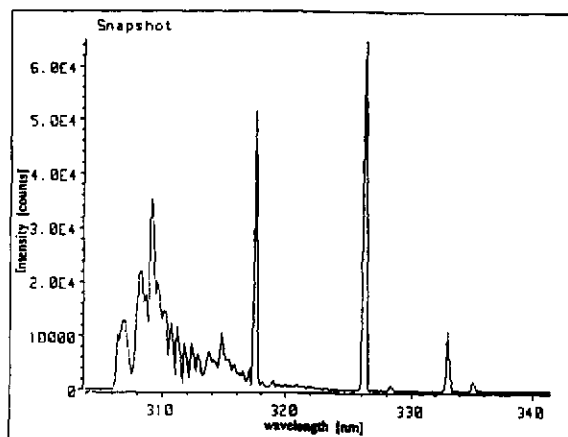
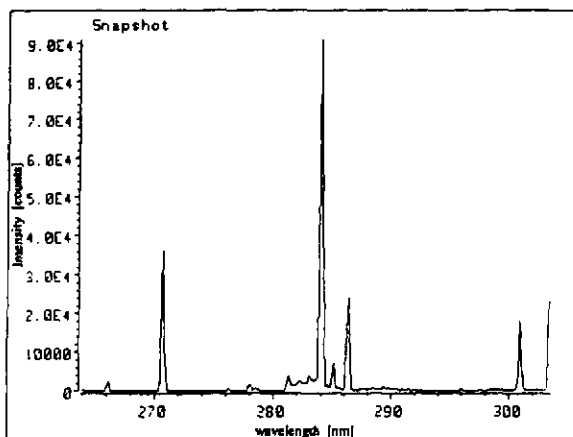


Fig. 4. Snap shot: atomic emission spectrum of tin in the range from 260 to 370 nm taken from the peak maximum of a tetrabutyltin peak (500 pg Sn).

Hamburg, harbour Teufelsbrück. For the preparation of this sample 5 g of sediment were extracted with a hexane–tropolone solution and the extract was derivatized using pentyl magnesium bromide [8]. The procedure is given in Section 2.3. A volume of 1 μ l of the extract was injected into the GC–AED system. The chromatogram is shown in Fig. 7. The presence of tin was confirmed by snap shots in a preliminary qualitative analysis.

All peaks of the chromatogram on the Sn 326 nm line were identified as tin in organotin compounds by adding of a mixture of known tin organic compounds to the extract. It was impossible to quantify the results because of the

insufficient degree of extraction of the organotin species from the sediment by the used technique.

3.5. Preliminary results with a laboratory-made arrangement of a GC–MIP–AES coupling

A new microwave induced He plasma sustained under atmospheric pressure was used in conjunction with a monochromator as an element-specific detector in capillary GC for the determination of tin. This arrangement (Fig. 8) is simple, cheap and was used for first measurements, to test the capability for the determination of tin compounds. It is planned to couple this MIP arrangement with an Echelle spec-

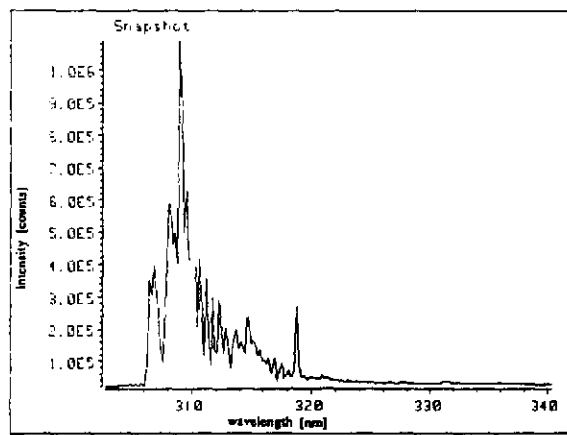
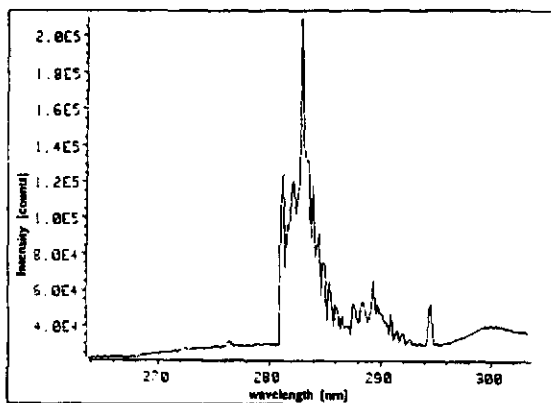


Fig. 5. Background in the range from 260 to 370 nm.

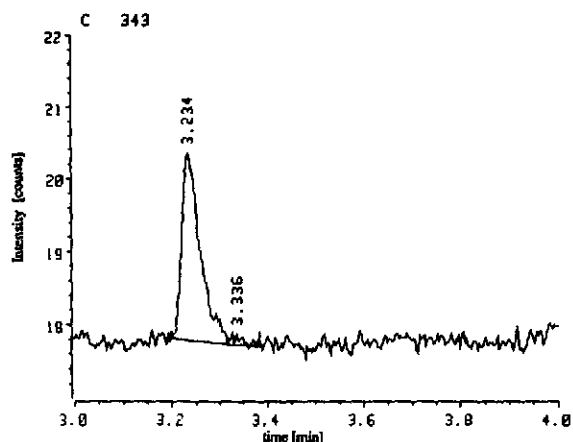


Fig. 6. Emission intensity of the CO band (342.57 nm), obtained during a run of tetrabutyltin in hexane (conditions listed in Table 1).

trometer to detect up to 12 elements simultaneously.

The specificity of this MIP is an concentric dual flow torch. This design (Fig. 9) utilizes two concentric alumina tubes and two plasma gas flows. The first gas flow passed between the two tubes while the second flow passed through the inner tube. This arrangement prevents the plasma interacting with the walls and makes it more spatially stable. Plasma centering in the discharge tube reduces interactions with the walls. The second make-up flow, passing through the

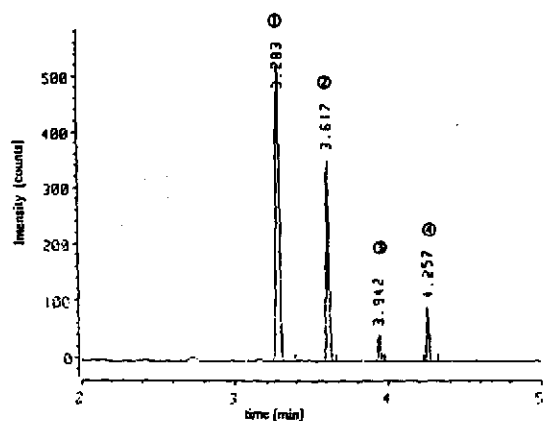


Fig. 7. Chromatogram of a sediment sample from the River Elbe after extraction and derivatization with Grignard reagent. 1 = Bu_4Sn ; 2 = Bu_2PeSn ; 3 = $\text{Bu}_2\text{Pe}_2\text{Sn}$; 4 = BuPe_3Sn (conditions listed in Table 1).

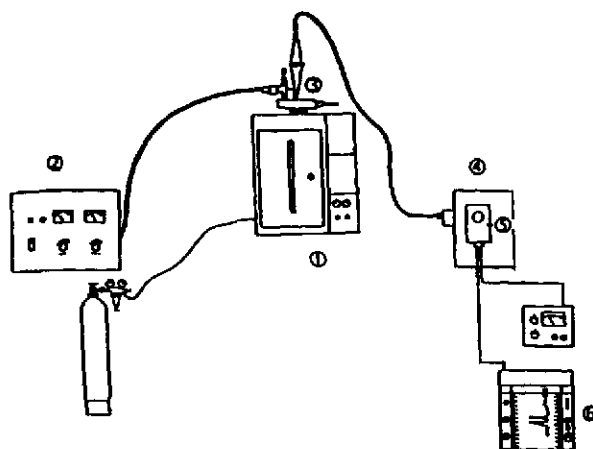


Fig. 8. The schematic diagram of the laboratory-made arrangement of the GC-MIP system. 1 = Chromatograph, 2 = microwave generator; 3 = cavity with plasma; 4 = spectrometer; 5 = photomultiplier tube; 6 = registration unit.

inner tube, is usually at a relatively low flow to sweep analyte into the plasma at a relatively low flow-rate, hence providing long residence times of analytes in the plasma. This has been described earlier in Ref. [18].

Working conditions

It was first necessary, to study the amount of solvent (hexane) which is acceptable for the

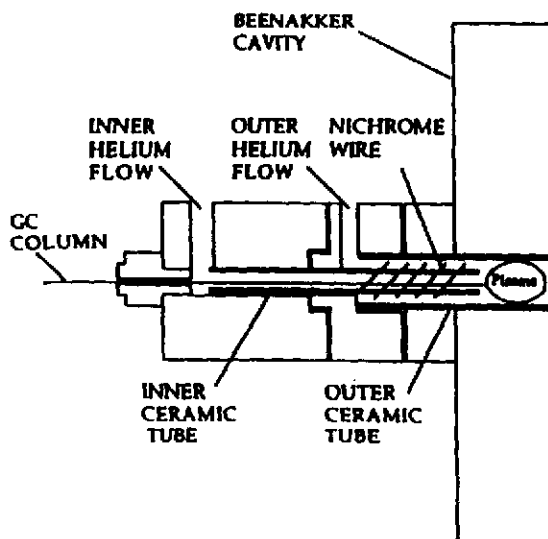


Fig. 9. Dual flow torch. From Ref. [18].

plasma. Using splitless injection and a column head pressure of 18 bar it was possible to inject 0.5–5 μ l of hexane. The parameters inner flow, outer flow, power of the microwave generator, distance of the capillary column to the plasma were investigated for the analysis of tin organics. Optimum plasma conditions are: inner flow 20 ml/min, outer flow 120 ml/min and a power of 95 W. We found, there is no influence of the distance between the end of the capillary column and the plasma on the signal intensity.

The detection limit obtained in this preliminary studies was 4 ng Sn absolute. This detection limit is worse compared with that obtained with the commercially device. The reason for this is the optics and the data requisition of the very simple spectrometer used. Further investigations will be done with a polychromator.

4. Conclusions

The two methods using GC–MIP–AES were successfully applied for the determination of organotin compounds. The GC–AES (Hewlett-Packard) allows to achieve absolute detection limits in the range of a few pg (as Sn). A quantitative analysis of these compounds in polluted aqueous systems is realizable.

The signal intensity is influenced by several parameters of the MIP and GC system, such as added reagent gases and the Sn emission lines used. An investigation of the parameters showed that the analytical response depends on the kind of tin compounds itself. This behaviour could not be fully explained. First, studies reveal an incomplete destruction of all bondings in the organotin compounds and thus an incomplete atomization of Sn, which is also shown by the presence of molecules inside the plasma (CO, OH) and in the discharge tube (SnO₂). These processes can

be explained by the relatively low gas temperature within the MIP.

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