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Capillary gas chromatography coupled with microplasma mass spectrometry for organotin speciation

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Abstract

Gas chromatography was coupled with microplasma mass spectrometry for selective detection of organotin compounds. The microplasma ion source was a capacitively coupled radiofrequency helium plasma, which was located inside the high vacuum area of the mass spectrometer. Only 1–3 ml min^{-1} of helium carrier gas from the gas chromatograph was necessary for sustaining the plasma while 0.15–1.5 ml min^{-1} of hydrogen was added as reagent gas. Hydrogen was applied for prevention of carbon deposition and served to minimize the interactions between tin and the fused-silica inner surface of the microplasma ion source. Both carbon and tin were detected as positively charged atomic ions, which were expelled from the microplasma ion source and directly focused by electrostatic lenses towards the quadrupole mass analyzer. Tin exhibited high selectivity to carbon ($>10^4$) and a detection limit of 3.5 pg s^{-1}.

Keywords: Mass spectrometry; Microplasma mass spectrometry; Organotin compounds

1. Introduction

Organotin compounds are generally known to be toxic. This explains their commercial value as active ingredients in products that act as biocides against a broad range of organisms. For instance, tributyltin (TBT) compounds have long been added to ship and boat paint in order to prevent the growth of marine microorganisms. Additionally, their use has included fungicidal preservation of wood, textiles and industrial waters [1]. Generally, the toxicity of organotin compounds increases with decreasing length of the alkyl chains [2,3]. Therefore, determination of the specific organotin compounds are necessary to reveal their impact on the environment.

Organotin species, which usually exists as water soluble mono-, di- and trialkylated species, can be converted to volatile compounds by complete alkylation, e.g., with sodium tetra(*n*-propyl)borate [4], sodium tetraethylborate [5], or an alkyl Grignard reagent. These derivatization techniques enable the use of gas chromatography (GC) for determination of the tetraalkylated organotin compounds.

Both atomic emission detection (AED) [6–13] and bench-top mass spectrometry (MS) [14–18] have been utilized for detection. Both techniques provide high sensitivity and selectivity. However, of these two relatively expensive detector techniques, only AED offers a well established multielement-selective detection. In the tin-selective mode, AED is capable of detecting organotin compounds at trace levels (1 pg Sn s^{-1} as specified by manufacturer [19]), even

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when highly contaminated samples are encountered. Similar element-selective detection with GC–MS instrumentation would naturally be advantageous in terms of detector flexibility and saved instrumentation costs, but would require the use of a plasma ion source, which today is not commercially available for common bench-top GC–MS instruments. When GC has been coupled with plasma MS detection [20,21], organotin speciation has included work with inductively coupled plasmas (ICPs) [4,18,22–26], microwave induced plasmas (MIPs) [27], and radiofrequency glow discharge plasmas (rf-GDs) [28,29]. These plasmas have been located outside the MS system, due to relatively large dimensions in terms of volume, electrode configuration, or plasma gas flow-rate. Therefore, plasma MS has been performed with a differentially pumped pressure reducing interface, which clearly differs from the direct introduction interface of conventional capillary GC–MS.

Recently, the microplasma (MP) ion source was developed for GC–MS [30,31]. In contrast to conventional plasma MS, MP-MS was performed without a pressure reducing interface. The MP ion source, which was located inside the MS high vacuum region, was a capacitively coupled radiofrequency plasma sustained inside the end of the GC capillary column by use of small external ring electrodes. Only the GC carrier gas (1–3 ml min^{-1} of helium) was used as plasma gas, with addition of trace amounts of oxygen or oxygen combined with hydrogen as reagent gases [32,33]. Therefore, the MP ion source was compatible with GC–MS instrumentation of low pumping capacity, which might enable future incorporation into bench-top instruments. This was considered an advantage both in terms of detection flexibility and cost efficiency. So far, element-selective detection by GC–MP-MS has included C, F, Cl, Br and I. In this work, tin-selective detection was explored in order to provide a new tool for the speciation of organotin compounds, and to evaluate GC–MP-MS for metal-selective detection.

2. Experimental

2.1. Gas chromatography

GC was performed with a GC17A (Shimadzu, Kyoto, Japan), which was equipped with electronic pressure control. The separating fused-silica capillary column was a 30 m×0.32 mm I.D. CP-Sil 8 CB-MS (Chrompack, Middelburg, The Netherlands), which was coated with a 0.25 μm film of 5% phenyl- and 95% dimethylpolysiloxane. Samples of 1.0 or 2.0 μl were injected either splitless or in the split mode (split ratio 1:20) at an injector temperature of 250°C. The carrier gas was 99.9999% helium (Aga, Oslo, Norway) at a flow-rate of 2.2 ml min^{-1}. A 1.0 m×0.32 mm I.D. HP-1 fused-silica capillary column (Hewlett-Packard, Wilmington, DE, USA) coated with a 0.17 μm dimethylpolysiloxane film was used as transfer tubing from the column outlet to the MS instrument (Fig. 1A). This capillary was contained in a laboratory built heated and isolated transfer line, which was made of 0.7 mm I.D.×1/16 in. O.D. steel tubing and heated to 300°C by a Model E-03122-61 flexible heating cord (Cole Parmer, Niles, IL, USA) in combination with the auxiliary temperature controller of the gas chromatograph (1 in.=2.54 cm). Near the MS entrance, the capillary was connected to a 1/16 in. tee (Fig. 1G) (VICI, Houston, TX, USA) where the GC effluent was mixed with an additional reagent gas flow. The reagent gases were introduced through a 10 cm×50 μm I.D. fused-silica restrictor (Fig. 1H) (Polymicro Technologies, Phoenix, AZ, USA) from another 1/16 in. tee, which allowed two gases to be mixed from one 2.8 m×20 μm I.D. (99.95% oxygen, Aga) and one 2.5 m×50 μm I.D. (99.995% hydrogen, Aga) fused-silica restrictor. Additionally, a 2.6 m×100 μm I.D. fused-silica restrictor was used for higher hydrogen flows. Each of the reagent gas flows (0.5–15 μl min^{-1} of oxygen and 0.01–3 ml min^{-1} of hydrogen) was controlled by the inlet pressure (0–3 bar) prior to the restrictors and calibrated against off-line measurements at different pressures. The second inlet of the mixing tee was blocked in cases where only hydrogen was introduced.

2.2. Mass spectrometry

The mass spectrometer was a modified Model 201 Dedicated Thermospray LC–MS (Vestec, Houston, TX, USA), where the thermospray probe, tip heater, sampling cone and discharge electrodes were removed. The MS system consisted of a quadrupole

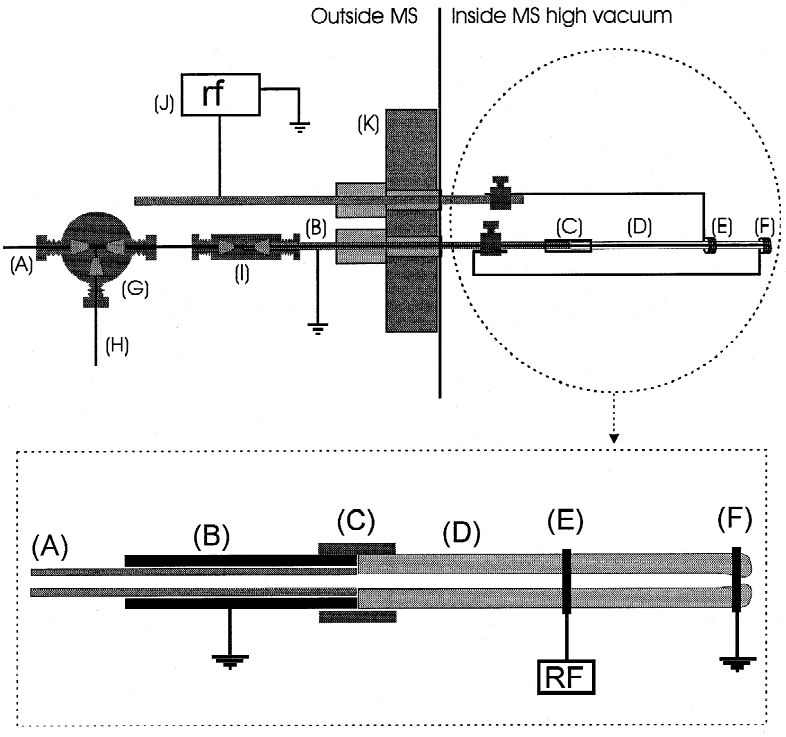

Fig. 1. Microplasma ion source. A = 0.32 mm I.D. fused-silica capillary column, B = 1/16 in. O.D. × 0.5 mm I.D. grounded steel tubing containing the fused-silica capillary column, C = PTFE tubing connecting the steel tubing and the fused-silica tube, D = 1.6 mm O.D. × 0.3 mm I.D. fused-silica tube, E = rf-electrode made by twisted steel wire, F = grounded electrode made by twisted steel wire, G = 1/16 in. tee, H = 10 cm × 50 μm I.D. fused-silica capillary for reagent gas introduction, I = 1/16 in. union for vacuum sealing, J = rf-generator, and K = transparent acrylic disc. Not to scale.

mass analyzer (Hewlett-Packard), a Model 342 channeltron electron multiplier (Detector Technology, Sturbridge, MA, USA), control electronics from the Hewlett-Packard Model 5970 MSD, and a Hewlett-Packard 59970C Pascal Series ChemStation with Rev. 3.1.1 MS-MSD software. The mass range was 3–800 u with both positive and negative ion detection included. In this work, positive ion detection was used in the selected ion monitoring (SIM) mode. The data files were copied to floppy disks and transferred to a personal computer by version A.00.03 of the MS-DOS program Lifutil.exe (Hewlett-Packard), and subsequently viewed by a program library [34] for LabView 4.0 (National Instruments, Austin, TX, USA).

In order to obtain optimum detection performance of tin, it was necessary to tune and calibrate the MS system at m/z values up to 120. Therefore, xenon was introduced in trace amounts through the septum of the injector, by a fused-silica linear restrictor (10 μm I.D.). The familiar isotope pattern of xenon was then observed on the mass spectrum at m/z 124–136, and applied for tuning of the MS electrostatic lenses and for adjustment of the mass scale.

2.3. Microplasma ion source

The microplasma ion source (Fig. 1) was mounted on a transparent acrylic disc of 50 mm diameter and 10 mm thickness (Fig. 1K), and was introduced to the MS high vacuum region as a probe. Similar to the set-up which was used earlier [33], two 4 mm holes were drilled in the middle of the disc 8 mm apart, center to center, in which two PTFE plugs were fitted. A 10 cm × 0.5 mm I.D. × 1/16 in. O.D. steel tubing (Fig. 1B) was placed in one of them. This tubing was electrically grounded and contained the fused-silica capillary column from the GC sys-

tem. A 1/16 in. ZU1T union (Fig. 1I) (VICI) was attached to the GC capillary by a graphite ferrule and to the steel tubing by a Vespel ferrule. The other PTFE plug contained a 10 cm×1.6 mm O.D. steel rod. This was connected to the rf-electrode and carried the rf voltage from the generator (Fig. 1J), which was either an HPG-2 (ENI, Rochester, NY, USA) that provided four impedance levels, 0–150 W of power, and a frequency range of 125–375 kHz, or an AG0201HV-U00 (T&C Power Conversion, Rochester, NY, USA) that provided four impedance levels, 0–20 W of power, and a frequency range of 100–500 kHz. The plasma was generated between the rf-electrode (350 kHz) and two grounded electrodes. One grounded electrode was the steel tubing (Fig. 1B), which contained the capillary column. The other grounded electrode (Fig. 1F) and the rf-electrode (Fig. 1E) were made of steel wire, which both were twisted around a 41 mm×1.6 mm O.D.×0.3 mm I.D. fused-silica tube (Fig. 1D). This tube was the microplasma ion source in which the plasma was sustained, and was connected to the steel tubing by a 15 mm×1/8 in. O.D.×1/16 in. I.D. PTFE tubing (Fig. 1C). The tube was drawn at the local glass workshop, and was heated in a hydrogen–oxygen flame in order to produce a short converging section at the tip with an internal diameter of about 200 μm, which was believed to decrease the divergence of the plasma spray [35]. The focusing of the ions was performed by the repeller and electrostatic lenses towards the quadrupole ion trajectory at a 90° angle to the MP ion source probe.

2.4. Chemicals and sample preparation

Tributylvinyltin, tetrabutyltin (both Fluka, Buchs, Switzerland), and tetraethyltin (Sigma–Aldrich, St. Louis, MO, USA) were dissolved in cyclohexane (Rathburn, Walkerburn, UK) and used as model compounds. Tetraethyltin and tributylvinyltin were used to find the detection limit for tin and to measure the selectivity of tin to carbon. The applicability of the technique was briefly investigated by analysis of a sodium tetraethylborate derivatized cod liver sample, which was prepared according to Følsvik et al. [36]. Finally, the selectivity was demonstrated by application of a complex sample, which was 13.8 mg of a North Sea crude oil spiked with 50 μg of each of tetraethyltin, tributylvinyltin and tetrabutyltin, and dissolved in 5 ml cyclohexane.

2.5. Detection limits and selectivity

Selectivity of tin to carbon was defined as the ratio of response per mole of tin to the response per mole of carbon on the tin-selective chromatograms [37]. The detection limit was defined as the amount of tin required to produce a signal two-times the noise level divided by the peakwidth at half height [37].

3. Results and discussion

3.1. Operational parameters for microplasma mass spectrometry

Previous work with capillary GC coupled with microplasma mass spectrometry has revealed the prospect of utilizing common bench-top GC–MS instrumentation for simultaneous carbon-, fluorine-, chlorine-, bromine- and iodine-selective detection [33]. SIM of the positively charged atomic ions resulted in low picogram detection limits for these elements, in addition to high halogen to carbon selectivities. The microplasma ion source, which was located inside the high vacuum area of the MS system, was essentially a 0.3 mm I.D. fused-silica capillary with a short converging section at the outlet. The capillary contained a capacitively coupled radiofrequency plasma, which was generated by external ring electrodes. The narrowing at the tip of the capillary improved detectability, possibly by decreasing the divergence of the plasma spray [35], or by producing a slightly higher pressure inside the capillary. The plasma could be stabilized with only the carrier gas from the GC system (2.2 ml min^{-1} of helium). Oxygen (1–10 μl min^{-1}) or oxygen combined with hydrogen (1–70 μl min^{-1}) was added as reagent gases to the plasma gas, for the purpose of carbon deposit removal and to avoid interaction of the analyte species with the inner fused-silica surface of the capillary. Peak tailing was then avoided, and a high signal-to-noise ratio could be obtained by optimization of the reagent gas level.

In order to achieve tin-selective detection, similar operational parameters to the above were initially

applied. This resulted in a lack of signal or broad peaks with severe peak tailing in the tin-selective chromatogram. However, since peaks for organotin compounds in the carbon-selective chromatogram showed neither tailing nor lack of sensitivity, it was concluded that tin was strongly retained in the MP ion source. This was probably due to production of tin oxides, which tended to accumulate on the fused-silica wall, as reported by Estes et al. [38] and by Besner and Hubert [39]. This problem has been discussed in several later reports on GC–AED [7,8,10,13]. Therefore, in order to make GC–MP-MS useful for tin-selective detection, tin oxide deposition had to be minimized. This was accomplished by an increase of the hydrogen gas level. Hydrogen is expected to react with tin to form volatile tin species [7], and possibly to react with oxygen to compete with the oxygen–tin reaction. The helium flow, however, was kept below 2.5 ml min^{-1}, in order to maintain compatibility with bench-top MS instrumentation, and was therefore not adjusted for the optimization of the tin signal.

3.2. Oxygen–hydrogen mixture as reagent gas

When applying a mixture of hydrogen (30 μl min^{-1}) and oxygen (1 μl min^{-1}) as reagent gas, no signal was found on the tin selective chromatogram. The hydrogen flow was increased to 200 μl min^{-1}, while applying different amounts of oxygen and finally without oxygen. With decreased oxygen flow, less peak tailing and higher signal-to-noise ratios were found in the tin-selective chromatograms, and the most satisfying result was obtained without even the smallest amount of oxygen introduced (Fig. 2). This tendency corresponded well with the theory of tin-oxide formation. In fact, at 0.55 μl min^{-1} of oxygen, the hydrogen flow had to be increased to as much as 760 μl min^{-1} in order to avoid peak tailing in the tin channel and to get an acceptable signal-to-noise ratio. At such high hydrogen levels, hydrogen was probably acting as a carbon scavenger, i.e., to dynamically remove carbon. Additionally, tin oxide formation was prevented. It was thus realized that a plasma gas mixture of helium and hydrogen could be sufficient for tin-selective detection.

3.3. Hydrogen–helium plasma

Initially, it was believed that a hydrogen-rich plasma would facilitate the tin-selective detection in two ways. One was to dynamically remove oxygen

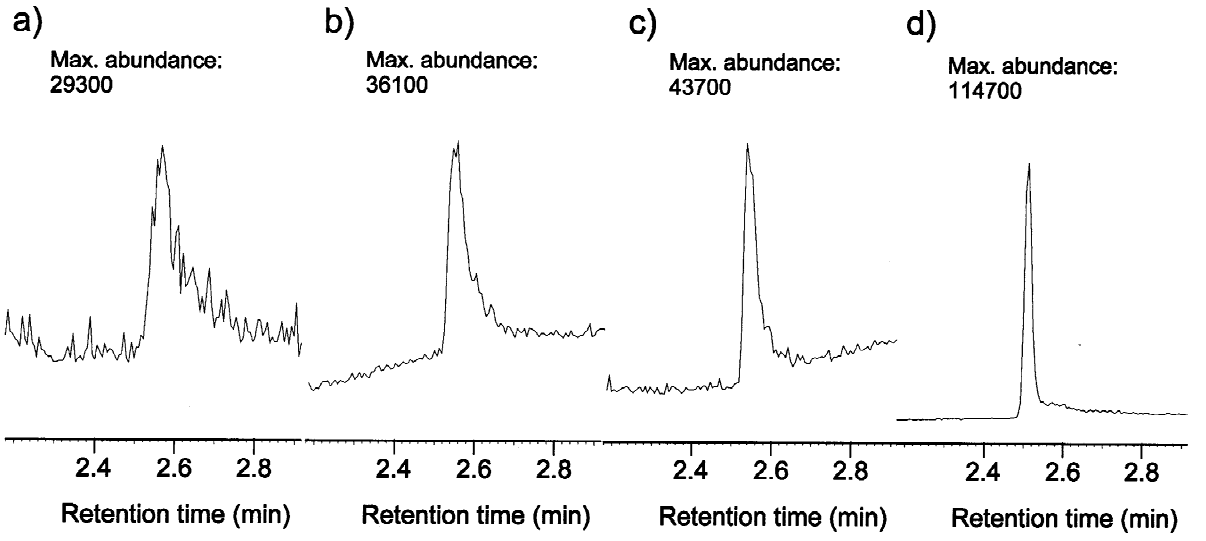

Fig. 2. Tetraethyltin injected in the split mode (2.5 ng Sn on column) at an oven temperature of 100°C and a helium carrier gas/plasma gas flow-rate of 2.2 ml min^{-1}. The reagent gases were 200 μl min^{-1} of hydrogen mixed with (a) 2.8 μl min^{-1}, (b) 1.2 μl min^{-1}, (c) 0.55 μl min^{-1}, and (d) 0 μl min^{-1} of oxygen.

or oxygen containing species (e.g., by formation of H_2O^+ or H_3O^+) from the plasma and thus compete with the unwanted tin–oxygen reaction. Secondly, hydrogen could react with tin itself to make it more volatile [7], and keeping the tin in the hot center of the plasma. To further investigate this theory, a preliminary experiment with a mixed hydrogen–helium plasma was conducted. Capacitively coupled plasmas are known to be easily ignited with other gases than helium, which was also the case in the present work. During these initial experiments, it was found that only 0.5 W of power was required to produce a stable plasma with 1 ml min^{-1} of helium (carrier gas) and 1.75 ml min^{-1} of hydrogen. Previously, with much lower levels of reagent gas [32,33], a higher power level was used (approximately 5 W). By increasing the mass offset of the MS system, it was possible to monitor ions as low as m/z 1, which revealed ion species at m/z 1, 2, 3 and 4 with the present plasma conditions. These m/z values corresponded to H^+, H_2^+, H_3^+ and He^+, respectively (Fig. 3a). The coexistence of H_3^+ (m/z 3), H_3O^+ (m/z 19) and N_2H^+ (m/z 29) confirmed a hydrogen-rich plasma with the possibility of hydrogen attachment to the background ion species. However, the power level strongly influenced the intensity of the H_3O^+ signal (m/z 19). A similar effect was observed for H_3^+ (m/z 3) and N_2H^+ (m/z 29). By increasing the power from 0.5 W to 0.75 W, the relative intensities of these ion species shifted towards the ions of less hydrogen attachment, which were H^+, H_2^+, H_2O^+, and N_2^+ (Fig. 3b). Followed by a tuning of the power, tin-selective detection with symmetric peaks was achieved with this plasma. However, the plasma appeared to be quite dim at the power level that produced the optimum tin signal, and some plasma quenching was observed at higher carbon loads. Therefore, lower hydrogen concentrations were applied (2.2 ml min^{-1} of helium carrier gas with 0.15–1.5 ml min^{-1} of hydrogen added). These 6–40% (v/v) of hydrogen in the helium resulted in a brighter plasma, which was more robust towards plasma quenching, and as much as 300 ng of a hydrocarbon compound (per single GC peak) could now be introduced. After several weeks of operation with this plasma, no evidence of carbon deposition was found by microscope inspection of the fused-silica microplasma ion source capillary. It was therefore concluded that hydrogen acted as a reagent gas for both carbon and tin, when applied at such high levels.

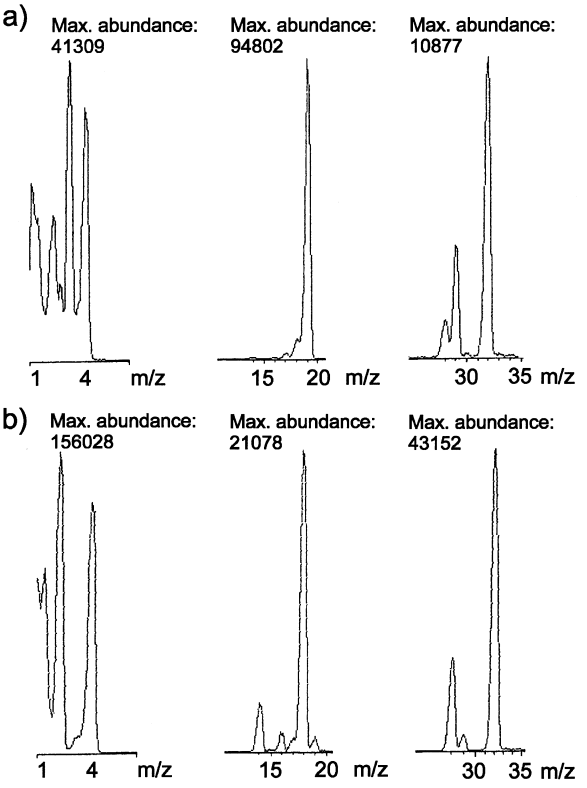

Fig. 3. Mass spectrum (selected m/z values) of a mixed hydrogen–helium plasma. Plasma gases: 1 ml min^{-1} of helium and 1.75 ml min^{-1} of hydrogen. Plasma power: (a) 0.50 W and (b) 0.75 W.

3.4. Optimization of signal-to-noise ratio and selectivity

For optimization of the tin signal at m/z 116–120, tetraethyltin was injected in the split mode at different concentration levels of hydrogen, and for each of these at several small intervals of power. With 2.2 ml min^{-1} of helium (carrier gas), the highest signal-to-noise (S/N) ratio for tin-selective detection was found at 760 μl min^{-1} of hydrogen and a power of 1.1 W (Fig. 4). The detection limit for tin was then estimated to 8.9 pg s^{-1} (m/z 120), although a lower detection limit of 3.5 pg s^{-1} could be obtained by a

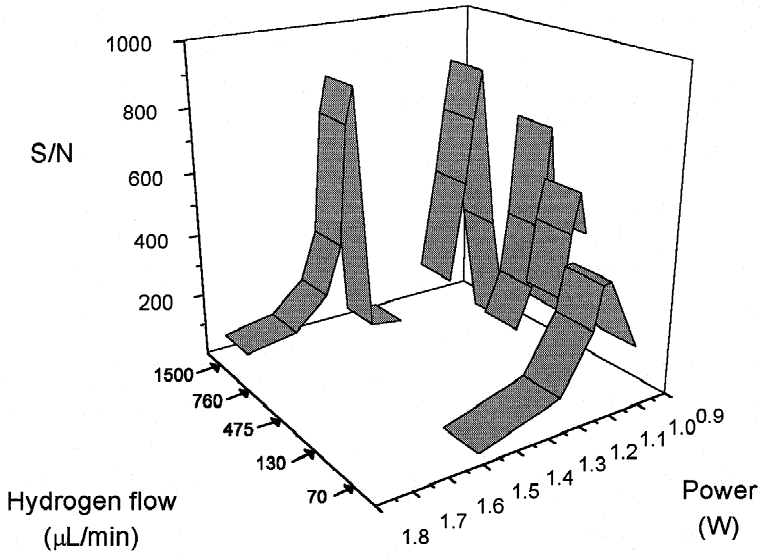

Fig. 4. Effect of hydrogen and power level on the S/N ratio of tin (4.9 ng tetraethyltin on column, corresponding to 2.5 ng Sn).

reconstructed ion chromatogram (RIC) of the major tin isotopes (m/z 116–120). The tin peak asymmetry values at 10% of the peak heights varied from 1.3 at high concentrations to 4.0 at low concentrations. As the hydrogen flow was increased above 300 μl min^{-1}, no strong influence on the signal was observed with variation of the hydrogen flow. This was probably due to a substantially lower plasma quenching effect of hydrogen than observed previously with oxygen [32]. Consequently, a larger span of hydrogen concentrations could be utilized. In order to further characterize the detectability of tin with the hydrogen–helium plasma, the selectivity of tin to carbon was investigated for different hydrogen flows (Fig. 5) and found to be approximately $1 \cdot 10^4$ at hydrogen flows above 300 μl min^{-1}. At these settings, tetraethyltin produced a tin response that was repeatable with a relative standard deviation of 6.3% (four consecutive manual injections) and linear ($R = 0.996$) in the investigated 0.05–50 ng range.

3.5. Applications

A cod liver sample was analyzed by the present GC–MP-MS setup and revealed two organotin compounds – tetraethyltin and butyltriethyltin, respectively (Fig. 6). The carbon-selective chromatogram contained a significant amount of matrix peaks, which clearly emphasize the need for selective detection. In order to fully evaluate the high selectivity of tin to carbon, another complex sample was applied, which was a diluted North Sea crude oil sample spiked with tetraethyltin, tributylvinyltin and

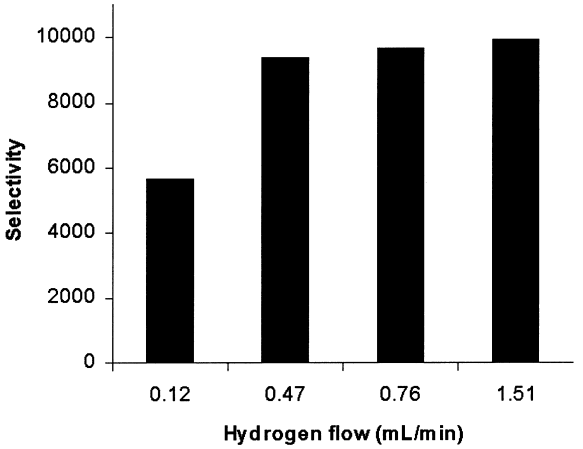

Fig. 5. Selectivity of tin to carbon at different flow-rates of hydrogen and 2.2 ml min^{-1} of carrier gas flow-rate.

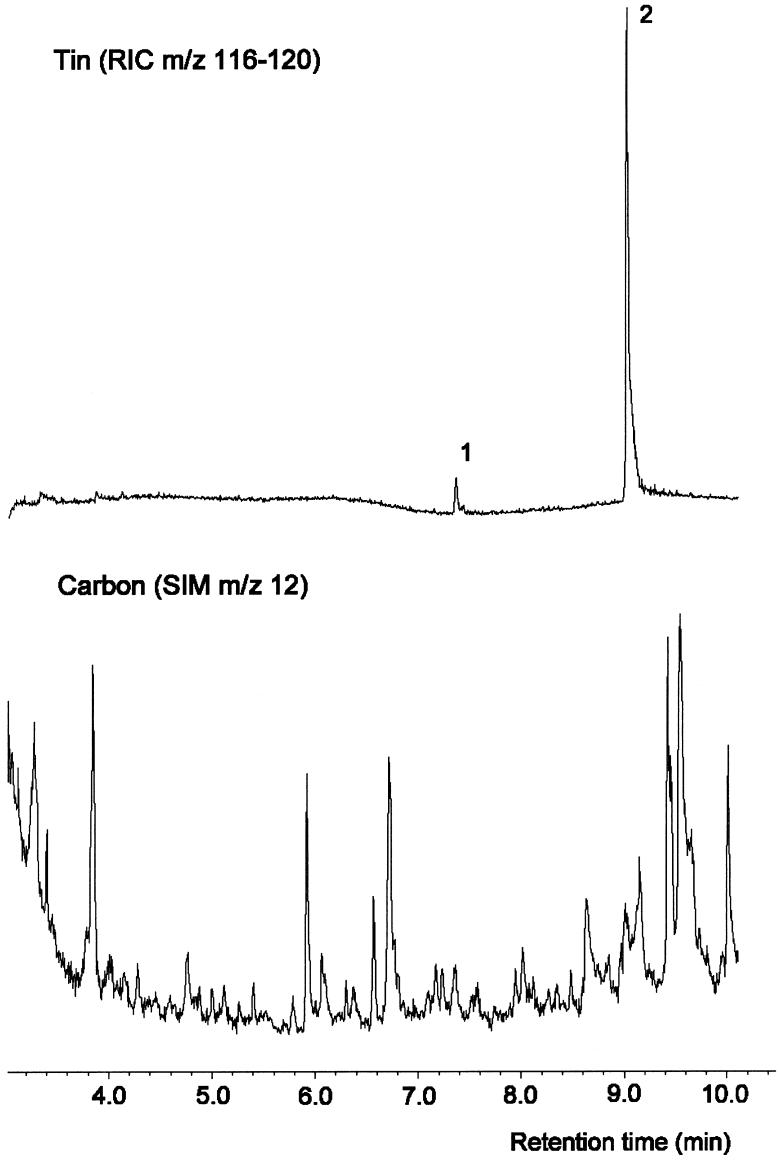

Fig. 6. Tin-selective and carbon-selective chromatograms of a cod liver sample. The two organotin compounds found were (1) tetraethyltin and (2) butyltriethyltin. GC conditions: 2 μl splitless injection at 50°C, hold for 3 min, then temperature programmed to 130°C at 10°C min^{-1}, while pressure programmed at 3.8 kPa min^{-1} to keep a constant mass flow of carrier gas. Reagent gas flow: 300 μl min^{-1} of hydrogen. RIC = Reconstructed ion chromatogram.

tetrabutyltin (Fig. 7). Only three peaks appeared on the tin-selective chromatogram, which corresponded to the three organotin compounds, while the high hydrocarbon content of the sample was exposed on the carbon-selective chromatogram.

4. Conclusions

The present paper is the first study on GC–MP-MS with tin-selective detection. It has opened up the possibility of utilizing a combined hydrogen–helium

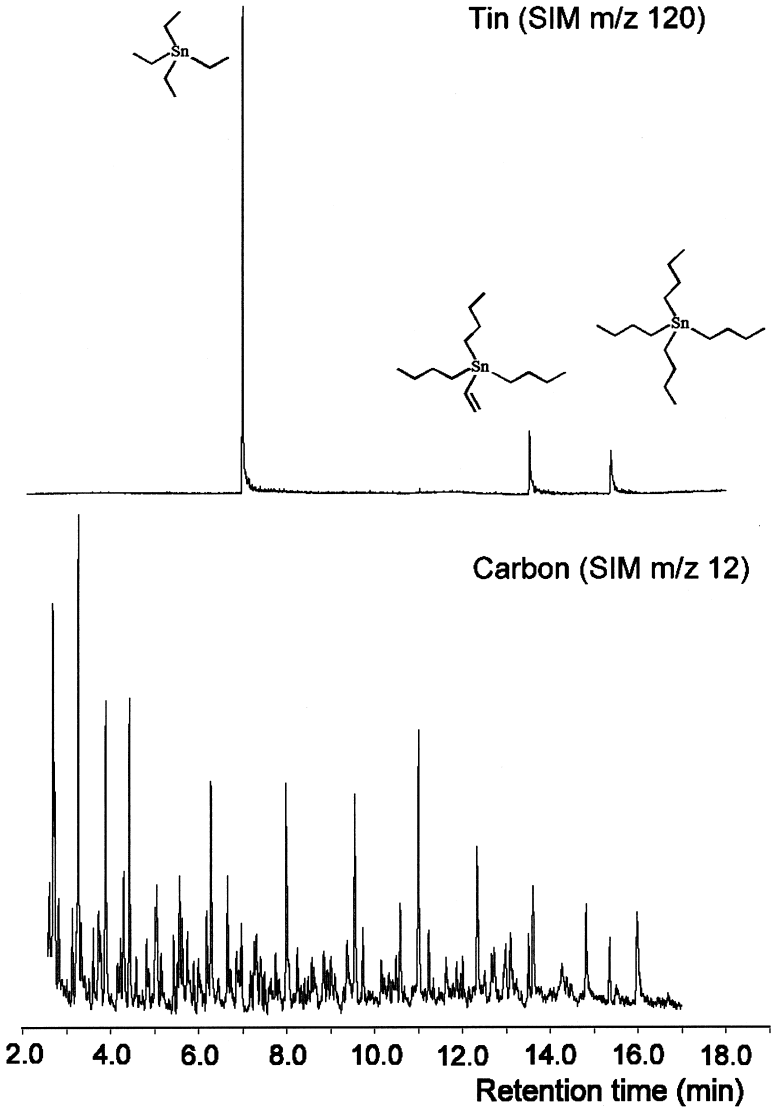

Fig. 7. Tin-selective and carbon-selective chromatograms of 13.8 mg of a North Sea crude oil spiked with 50 μg of each of tetraethyltin, tributylvinyltin and tetrabutyltin, and dissolved in 5 ml of cyclohexane. GC conditions: 1 μl splitless injection at 50°C, hold for 3 min, then temperature programmed to 200°C at 10°C min^{-1}, while pressure programmed at 3.8 kPa min^{-1} to keep a constant mass flow of carrier gas. Reagent gas flow: 300 μl min^{-1} of hydrogen.

plasma for the purpose of obtaining a high signal-to-noise ratio for tin, and to avoid problems with tin oxides. Additionally, hydrogen helped to avoid carbon deposition. This plasma differed from the plasmas used in previous work with GC–MP-MS, because of the relatively high amount of reagent gas (hydrogen) that could be added without an excessive decrease in sensitivity. At such high flows of hydrogen, it was possible to detect tin down to the low picogram level with a selectivity to carbon of 10^4.

The study also indicates a potential of using a hydrogen–helium plasma for other metals. This requires metal reactivity with hydrogen, which might be the case for lead and mercury. Hopefully, future

work will explore the applicability of GC–MP-MS for the speciation of these environmentally interesting metals.

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