A Comparative Study of Gas Chromatography with Atomic Absorption and Atomic Emission Detection for the Speciation Analysis of Organotin

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Two techniques, megabore column gas chromatography quartz furnace atomic absorption spetrometry (MCGC-QFAAS) and MCGC graphite furnace AAS (MCGC-GFAAS), were developed for the determination of pentylated organotin species and compared with the existing techniques, packed column (PC) GC AAS and capillary column (CC) GC-atomic emission spectrometry (AES). Particular attention was given to the design of the interface between a GC column and the detector cell (GF or QF) as well as optimization of the operational variables of the interface and detector. The accuracy of the developed techniques is discussed on the basis of an intermethod comparison analysis of 15 water samples.

Keywords Gas chromatography, atomic absorption spectrometry, atomic emission spectrometry, speciation analysis, organotin, water analysis

Hyphenated techniques based on liquid or gas chromatography (GC) along with an atomic spectrometric detector are widely accepted approaches to the speciation analysis of organotin compounds in environmental samples.[1,2] GC is usually preferred as a separation technique due to a large resolving power accompanied by relatively easy interfacing to selective and sensitive detectors. Analysis by a coupled technique is preceded by a sample preparation step involving purge-and-trap or solvent extraction preconcentration, often aided by the derivatization of ionic organotin species with sodium tetrahydroborate[3-5], sodium tetraethylborate[6-8] or Grignard reagents.[9-12]

Atomic absorption spectrometry (AAS) is a well-established detection technique in speciation analysis. Several approaches were made to exploit a quartz furnace (QF), heated electrothermally[13] or flame[14], and a graphite furnace (GF) used as an atomization device.[15-17] Analytical applications of this techniques to tin, however, are relatively rare unless hydride-generation sample processing is used.[3]

Irrespective of the atomizer used, AAS shows a low sensitivity for tin due to the high atomization temperature and possible formation of refractory oxides. Plasmas providing higher atomization temperatures are more advantageous. Microwave-induced plasma atomic emission spectrometry (MIP AES) has recently been shown to offer good selectivity and high sensitivity for the detection of tin in the GC effluent.[10,11]

This paper presents the development of megabore column (MC) GC-QFAAS and MCGC-GFAAS for the determination of pentylated organotin compounds, and compares them critically with other techniques used so far for this purpose: packed-column (PC) GC-QFAAS and capillary-column (CC) GC-AES.

Experimental

Gas Chromatography

A Varian Model 3700 gas chromatograph (Varian, Sunnyvale, CA) and an HP Model 5980 Series II gas chromatograph (Hewlett-Packard, Avondale, PA) were used to separate the analytes before detection by AAS or AES, respectively. For PCGC, a 1.8 m×2 mm i.d.×6 mm o.d. glass column packed with 3% OV-101 on Chromosorb WHP (100 - 120 mesh) was used. A RSL-150 column (15 m×0.53 mm i.d.×1.2 μm) (RSL, Eke, Belgium) and an HP-1 (25 m×0.32 mm i.d.×0.17 μm) column were used for the MCGC and CCGC, respectively.

Samples were injected directly onto the PC. For injections onto an MC a wide-bore on-column liner provided with a 1-m retention gap of 0.53 mm deactivated fused silica tubing (RSL) was used. Injections onto the CC were made using a temperature-programmed cool injection system (Gerstel, Mülheim, Germany). Injections were performed with an HP Model 7673A autosampler (1 μl) or manually (larger volumes).

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Interface design

GC-AES. A commercial GC-AED interface (HP) was used.

GC-QF AAS. The interface used for the PC GC-QFAAS coupling was described earlier.[18] To connect the MC with the QF, a 2-m long section of deactivated fused silica tubing (0.53 mm i.d.) was used. The column and transfer line (TL) were connected by means of a push-and-fit connector. The TL was inserted into an insulated nickel tubing and heated by applying a transformator-controlled voltage between the tube ends. The temperature of the TL was monitored with a thermocouple. The design of the interface at the AAS side is shown in Fig. 1a. The connection of the nickel tubing to the side-arm of the QF was made by means of a modified reducing union (Fig. 1b). It was made of a conventional stainless-steel reducing union (1/8″×1/4″) by making in the middle part of it two 1/8″ holes (perpendicular to the symmetry axis), which served as inlet ports for the support gases, hydrogen and air. Such a design enabled the gases to flow between the outer wall of the megabore tubing and the inner walls of the

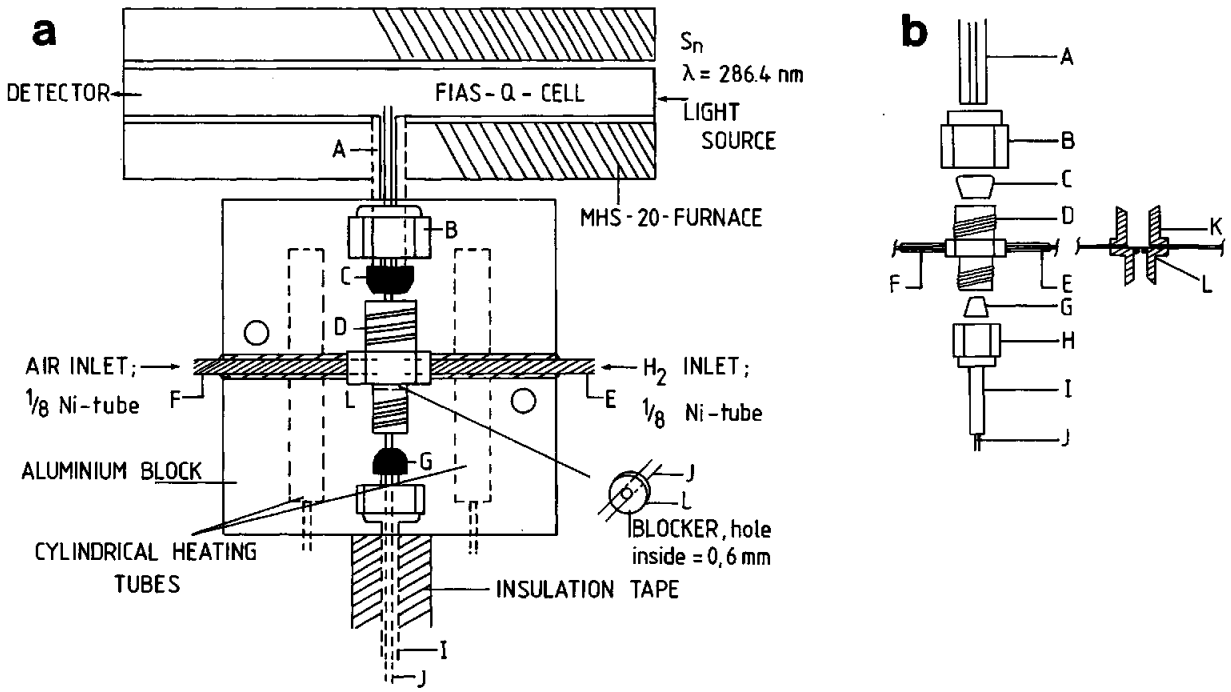

Fig. 1 a) The design of the interface at the atomic absorption spectrometer: A, lower tube of quartz T-furnace; B, 1/4″ (0.64 cm) Swagelok nut; C, 1/4″ (0.64 cm) graphite ferrule; D, 1/4″ (0.64 cm) to 1/8″ (0.32 cm) Swagelok reducing union; E, hydrogen inlet; F, air inlet; G, 1/8″ (0.32 cm) graphite ferrule; H, 1/8″ (0.32 cm) Swagelok nut; I, 1/8″ (0.32 cm i.d.) Ni transfer tube; J, 0.53 mm deactivated fused silica transfer line; K, longitudinal section of D; L, metal disc with 0.60 mm hole. b) Details of the reducing union connecting the transfer line to the side arm of the QF.

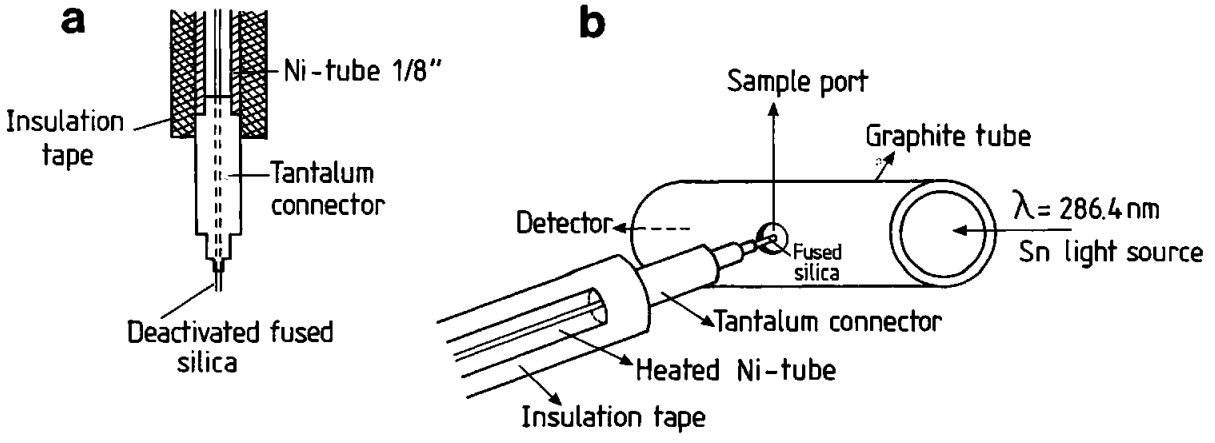

Fig. 2 Details of the tantalum connector (a) and tantalum connector positioned in the graphite furnace (b).

reducing union and, further, of the QF side arm. The body of the reducing union was placed inside a 10-cm cubic aluminum block made of two identical parts, each housing two cylindrical heating elements. The shape of the reducing union was cut in both parts of the block so as to make the union fit tightly inside the block during assembly (lock-and-key connection). The heated block ended just in front of the MHS-20 heating unit. The fused silica TL was pulled through the reducing union and positioned one millimeter inside the side arm of the furnace. The temperature of the block was controlled with a thermocouple placed in its middle.

GC-GF AAS. The TL was connected to the GF atomizer in a way similar to that described by Radziuk *et al.*[17] and is shown in detail in Fig. 2. The end of the nickel tube was equipped with a 15 mm long tantalum connector which was machined from a 5 mm thick tantalum rod (Fig. 2a). The smaller tip of the connector was placed in the sample introduction port of the graphite tube, as shown in Fig. 2b. The fused silica tubing came out of the tantalum tip at approximately 3 mm in such a way that it finally ended 2 mm inside the graphite tube.

Detectors

AES. An HP Model 5912A detector (Hewlett-Packard) was used.

QF AAS. APE Model 2380 AA spectrophotometer (Perkin Elmer, Norwalk, USA) equipped with a quartz cell, heated either on a one-slot burner or inside a PE MHS-20 furnace system, was used. The radiation source was an 8-W tin electrodeless discharge lamp. Background correction was not used.

The detector design used for the PCGC has been described earlier.[9,18] For MCGC detection, the quartz cell was heated electrothermally using an MHS-20 unit. Three types of QF cells (an MHS-20 cell, a laboratory modified MHS-20 cell and a FIAS-200 cell) were used. The modified MHS-20 cell differed from the original with respect to the side-arm dimensions, which were 6 mm (o.d.), 1.8 mm (i.d.) and 50 mm (length).

GF AAS. The same AAS instrument, but equipped with a PE HGA-500 GF atomizer, was used. The latter was modified by turning the graphite contact pieces of the furnace by 45° so that the injection hole of the graphite tube was placed horizontally. Pyrolytically coated graphite tubes (Perkin Elmer) were used.

GC-AAS chromatograms were recorded on a Hitachi PE56 chart recorder or on a Spectra-Physics Model SP 4290 integrator in the peak-height mode.

Reagents, standards and procedure

Reagents and gases as reported elsewhere were used.[9,10] A mixture containing 10% (v/v) of H_2 (99.99%) and 90% (v/v) of Ar (99.996%) was used as a support gas in GC-GFAAS measurements. Preparation of the organotin standards and checking their purity have been described earlier.[9,10]

The sample preparation procedure and the GC-AES parameters have also been reported elsewhere.[9,10] The operating conditions for GC-QFAAS and GC-GFAAS are summarized in Tables 1 and 2.

Results and Discussion

GC conditions

Figure 3 shows chromatograms obtained for a mixture of organotin species using packed, megabore and capillary columns. Generally, good resolution is obtained on any column. Some problems may arise regarding the separation of TEBT (tetrabutyltin), MMT (monomethyltin) and TBT (tributyltin) on a packed column, especially in case of different concentrations of particular compounds. The peak shape and resolution are significantly better for the CC, thus enabling much more

Table 1 Operating conditions for GC-QF AAS

Parameter	Packed column GC-QFAAS	Megabore column GC-QFAAS
Injection port temperature, °C	170	230
Injection volume, µl	4–20	4
Carrier gas (Ar) flow rate, ml/min	32	6
Oven program	130°C (10°C/min) 250°C	100°C (10°C/min) 260°C
Transfer line temperature, °C	250	285
Heating block temperature °C	—	305
Atomization temperature, °C	900	900
Hydrogen make-up gas, ml/min	470	350
Air make-up gas, ml/min	9	45
Wavelength, nm	286.4	
Slit, nm	0.7	

Table 2 Graphite furnace program in MCGC-GFAAS measurements

Step	Temperature/°C	Ramp time/s	Hold time/s	Internal gas flow/ml min^{-1}	Comment
1	200	1	10	Ar, 50	injection
2	200	1	90	Ar/H_2, 300	solvent vent
3	1500	1	730	Ar/H_2, 10	atomization

The gas chromatographic conditions were identical, as shown in Table 1.

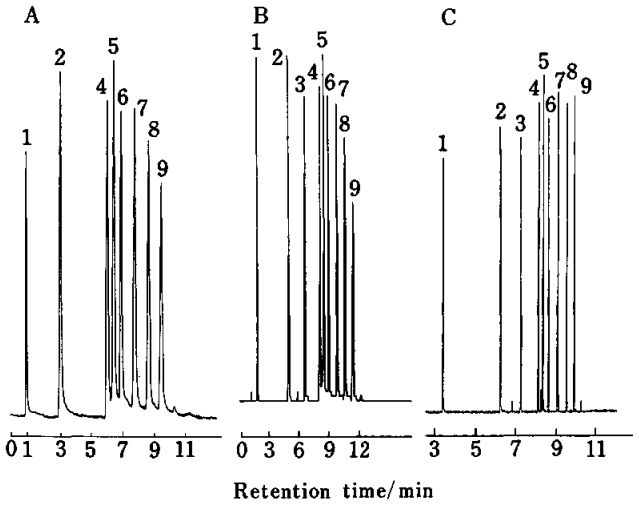

Fig. 3 Chromatograms obtained for a mixture of organotin species: 1, Me_3SnPe; 2, Me_2SnPe_2; 3, Pr_3SnPe; 4, $SnBu_4$; 5, $MeSnPe_3$; 6, Bu_3SnPe; 7, Bu_2SnPe_2; 8, $BuSnPe_3$ (internal standard, not added for PCGC-AAS); 9, $SnPe_4$. (A) packed column GC-AAS; (B) megabore column GC-AAS; (C) capillary column GC-AES.

sensitive detection of closely eluting compounds, almost irrespective of their concentration ratio. The use of a CC makes it possible to separate even a very small peak of dipropyldipentyltin eluting between the TEBT and MMT peaks. In the chromatogram obtained with an MC, although the dipropyltin peak can also be seen, it is difficult to quantify.

Interface design

Due to the relatively small differences in the retention times of the pentylated organotin species, quantification of all the compounds present is critically dependent upon their separation. The most important factors in order to achieve the maximum sensitivity as well as minimum peak tailing and broadening are proper design of the coupling, careful inspection of any dead volumes in the connections used as well as the best choice of carrier and support gases and optimization of their flow rates. The length of the TL does not seem to be critical.

MC-QF interface. The use of 1/8″ nickel tubing in the way described earlier[9] to couple an MC to the QF would lead to dead volumes associated with the significantly lower diameter of an MC than that of a PC. Therefore, a section of deactivated fused silica tubing (0.53 mm i.d.) was examined as a TL. Dead volumes were avoided by using a push-and-fit connector.

In the beginning of this study the TL was led directly into the QF. This configuration yielded good resolution and a better sensitivity (compared to that of PCGC-QFAAS) for the most volatile species (Me_nSnPe_{4-n}, $n=1-3$), while problems with tailing, distorted peak shape and loss of sensitivity still remained for higher boiling compounds (Bu_nSnPe_{4-n} and $SnPe_4$). They were identified as probably being caused by a partial condensation of these species on cold surfaces induced by the addition of support gases or on cold spots created just in front of the QF. Therefore, an essential modification of the interface design was necessary. A heated block (shown in detail in Fig. 1) was designed. In this setup hydrogen and air were heated before coming into contact with the analytes, and did not seem to create any cold spots. In addition, an extension of the heated elements too close to the MHS-20 furnace caused atomization to occur as soon as the analytes entered the furnace enclosure. This interface design enabled an effective speciation analysis of the methyl- and butyltin compounds. Although even higher boiling pentylated phenyl- and cyclohexyltin species could be determined, no effort was undertaken to optimize the interface for these species.

MC-GF interface. In GC-GFAAS coupling, it is of great importance to heat the transfer line as close as possible to the atomization zone and to avoid any temperature gradient in the final part of the interface. This can be done by enlarging the sample port of a conventional graphite tube in order to let the column effluent impinge directly onto the heated GF.[15,17,19] However, some specific problems associated with the use of fused silica as a TL material, appear. The end of the TL must be fitted into the graphite tube and, therefore, the maximum operating temperature allowed is limited by the melting point of the fused silica. At an atomization temperature higher than 1500°C the TL partly melted inside the graphite tube, thus leading to irreproducible chromatograms. Furthermore, if the end of the fused silica tubing is not properly positioned in the middle of the sample port of the graphite tube, the fused silica can start to transform at even a lower temperature due to an arising tension against the graphite tube wall. This effect leads to a negative base-line drift as well as a drop in the sensitivity for the last species eluted. This decline in the sensitivity can be explained by the induction of adsorption sites on the transformed fused silica at the sample port or, more probably, due to the fact that the last species do not reach the graphite tube because of a destruction of the liner.

The use of a connector made of refractory metal and fitted into the entry port of the graphite tube seems to be a viable approach to circumventing these difficulties. When a tantalum connector is used, the furnace may be heated to 2500°C without any damage to the TL. However, direct contact of the analytes with a very hot metal surface may be the reason for premature sample decomposition or, if mixtures of compounds are present, disproportionation reactions. The atomization process may even occur in the tantalum piece. These phenomena make the appropriate position of the fused silica inside the tantalum connector important. The highest and most reproducible results were obtained when the fused silica tubing ended approximately 2 mm inside the graphite tube.

Detector design (QF atomic absorption spectrophotometer)

An appropriate design of the atomization cell is a

crucial factor which affects the sensitivity.[19] When an MHS-20 quartz cell was used a large dead volume developed at the connection between the nickel TL and the side arm of the furnace. Reducing the diameter of the side arm resulted in a considerable increase in the sensitivity. A similar effect was also observed upon reducing the diameter of the upper tube, though to a lesser degree. Though some laboratory-made quartz cells were examined, the best results were obtained with a commercial FIAS-200 furnace, which was finally chosen.

Detector design (GF atomic absorption spectrophotometer)
The GF program. Continuously maintaining a high-temperature (1500 - 2000°C) results in a premature deterioration of the graphite tube, thus making the operation of a GC-GFAAS system expensive. To reduce the running costs, careful optimization of the GF program to match the peak elution times was found to be necessary. Three steps are required while operating a GC-GF AAS system. In the first step, the graphite tube is cleaned by purging it with argon while a solution of analytes is injected onto the GC column. The second step begins when the solvent vapor appears at the entrance of the GF. The hold time in the first step should be adjusted so as to match this moment. The eluting solvent peak must be entirely blown out of the graphite tube before atomization of the analytes begins. This is realized by increasing the internal gas flow rate to 300 ml/min during the second step. The hold time in this step is adjusted in order to obtain the best possible resolution between the solvent peak and the first eluting compound (Me_3SnPe) peak. The second step is completed just before the Me_3SnPe peak starts to appear. By this time the graphite tube must reach the optimized atomization temperature. Atomization (step 3) is the longest step, since it is completed only after the last eluting peak is determined. It also makes the GF program cycle much longer than in a conventional GF-AAS analysis. In the third step the internal gas flow rate must be severely reduced; otherwise, the analytes are removed too rapidly from the optical beam of the spectrophotometer, to the detriment of the detector response. The optimum GF program is given in Table 2.

The lifetime of a pyrolytically coated graphite tube, operated at 1500°C, ranged between 40 and 50 measurements. Since one measurement takes less than 15 min, it is possible to work for an entire day using the same graphite tube.

Atomization temperature. The dependence of the peak height on the atomization temperature is very similar for all of the alkyltin compounds, and shows one maximum at 1550°C. However, after three successive measurements at this temperature the part of the transfer line inside the graphite tube became irreversibly damaged. Therefore, analyses were performed at an atomization temperature of 1500°C, which could be maintained for a reasonablly long time without any damage to the GF and fused silica TL.

Effect of auxiliary gases. Argon and a mixture of Ar with 10% H_2 were examined as internal flow gases in step 2 of the furnace program. The flow rate of H_2 or that of H_2-doped (10%) argon was changed from 0 to 40 ml/min at 10 ml/min intervals during the atomization step. The shape of the response curve varied depending on whether an inert (Ar) or a reactive (10% H_2 in Ar) internal flow gas was used in step 2. Figure 4A shows that when argon alone was used, the first eluting species (Me_3SnPe, Me_2SnPe_2 and $SnBu_4$) behaved differently from the rest of the analytes, while when Ar doped with 10% of H_2 was used the response curve had a similar shape for all organotin species showing one maximum (Fig. 4B).

Therefore, for applications, Ar gas doped with 10% of H_2 must be used in step 2, since only then all the species

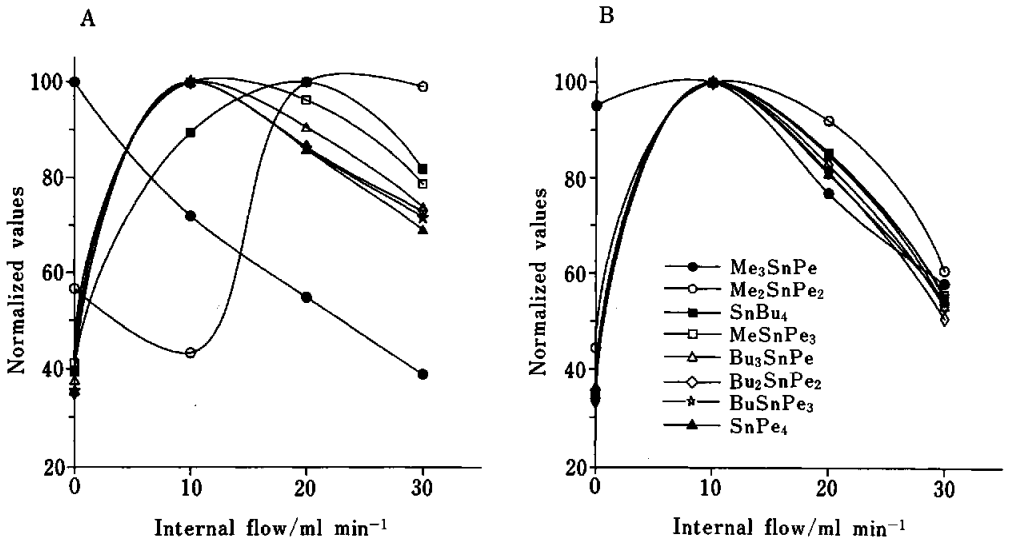

Fig. 4 Effect of the internal H_2/Ar flow rate in step 3 of the graphite furnace program on the absorption intensity of different pentylated organotin compounds: (A) 300 ml/min of argon added in the step 2; (B) 300 ml/min of 10% H_2+Ar added in the step 2.

Table 3 Detection limits obtained in this work using different hyphenated techniques

Hyphenated technique	Injected volume/μl	Instrumental detection limit[a] (pg as Sn)	Relative detection limit[b] (ng l^{-1} as Sn)	Precision[c], %
PCGC-QFAAS	20	160 - 400	0.7 - 1.7	2.5 (100 - 200 ng)
MCGC-QFAAS	4	17 - 37	0.35 - 0.8	2 - 4 (4 ng)
MCGC-GFAAS	4	33 - 71	0.7 - 1.5	3 - 7 (8 ng)
CCGC-AES	1	0.10 - 0.15	0.008 - 0.013	1 - 2 (50 pg)

a. Amount of Sn per species required to give a signal 3 times the standard deviation of the base-line noise. b. Based on a sample volume of 3 l. c. For 5 injections (the injected amount given in the bracket).

produce a maximum response under the same experimental conditions.

Analytical characteristics

The values of the detection limits and the precision of the techniques used are summarized in Table 3. The use of an MC and optimization of the interface increased the detection power of the system by about an order of magnitude compared to the PCGC-QFAAS system. The GC-GFAAS setup is two times less sensitive than the GC-QFAAS. Despite some loss in the performance of the GC-AED instrument with respect to the former work[10], a gain in sensitivity of about two orders of magnitude over GC-AAS can routinely be obtained. The gain in instrumental detection power for systems using CC and MC is partly levelled by the smaller sample volume which can be injected. In all of the techniques, except for GC-AED, the response decreases for higher boiling compounds.

Interferences. During the GC-GFAAS analysis of water spiked with organotins it was observed that for some species serious losses in response were noticed when compared to GC-QFAAS analysis. The signals measured for MMT, DBT and TBT constituted only 25, 80 and 75% of the total, respectively. Diethyldithiocarbamate (DDTC) and/or products of its decomposition were found to be responsible. Decreasing its concentration in the aqueous phase by a factor of four resulted in an increase in the corresponding signals to 65, 95 and 86% for MMT, DBT and TBT, respectively. These problems are caused by the elution of an unidentified compound which modifies the surface of the graphite tube, resulting in signal depression. The use of D_2-background correction did not result in a signal increase. Washing the organic phase with alkaline agents (ammonia or NaOH) only partly solved the problem.

Accuracy of the analysis. A series of 15 water samples (Antwerp harbour) were analyzed by GC-QFAAS and GC-AES. The results obtained by GC-QFAAS *vs.* those obtained by GC-AES could be approximated by straight lines with slopes of 0.997±0.049, 0.967±0.050 and 1.26±0.12 for TBT, DBT and MBT, respectively. The respective correlation coefficients were 0.987± 0.043, 0.967±0.065 and 0.965±0.028. This good agreement could only be obtained in the split mode at the expense of the sensitivity. When the samples were run in the splitless mode, higher results (by about 20%) were obtained with AED for all of the compounds.

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