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Advanced GC/ICP-MS design for high-boiling analyte speciation and large volume solvent injection

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A home made multifunctionary interface has been developed to connect a capillary gas chromatograph (GC) and an inductively coupled plasma mass spectrometer (ICP-MS). It can analyze high boiling analytes with a boiling point as high as that of C_{26} n-paraffin (412 °C) at only 140 °C temperature in the transfer line. The design performs splitless large volume solvent injection to analyze sensitively very low and high boiling analytes in one run. The thin and flexible transfer line is heated by a combination of hot argon mixed with the GC effluent *before* passing the transfer line using a T-joint in the GC oven, and by electrical resistance heating. The flow through the transferline can be reversed to eliminate the solvent peak and to prevent graphite deposition onto the ICP-MS cones after large volume splittless injection. The detection limits for organotin (the propyl derivatives of all methyl and n-butyl, mono- and di-n-octyl, and all phenyltin), range from 68–250 fg absolute and are in the pg l^{-1} range for 80 ml water samples extracted with 1 ml of solvent. The instrumental repeatablility is about 2% uncorrected and the linearity ranges to 5 ng absolute. This interface design is potentially useful for coupling more than one GC with one ICP-MS, for other plasma spectrometers (ICP-AES), for other types of large volume injection, and for high temperature (HT)-GC-ICP-MS.

Introduction

Trace element speciation is based on the identification and quantification of organic compounds having at least one carbon–metal(loid) bond. The analysis of organometal(loid) species of toxic or biological relevance is becoming increasingly important for the biosciences and for the exploration of the anthropogenic, biogenic and chemogenic environmental routes of these compounds in complex samples.[1]

These compounds can be analyzed by gas chromatography if they are volatile or can be transformed into volatile derivates. Coupling of capillary gas chromatographic (GC) separation and inductively coupled plasma mass spectrometer (ICP-MS) detection[2–15] offers unique features such as simultaneous multi-element detection, multi-isotopic information, and low detection limit.

Heating problems

The first heated transfer line for capillary GC-ICP-MS was published by Ebdon[2] and co-workers. Numerous other applications followed, many of them for low boiling volatile analytes or gases[3,11] where transfer line heating is easier.

An advanced home-made[5] and new commercial[12] interface (Agilent) for high boiling (semi-volatile) analytes is able to transfer triphenyltin (ethylated). The fused silica capillary which transfers the analytes into the ICP torch is heated by hot argon flowing in a surrounding 1/16″ stainless steel tube and by electrical resistance of the tube. The transfer lines work at about 250 °C, at which many of the thermoinsulating tubing materials used, such as PTFE, are at the edge of stability.

An unheated transfer line was claimed[10] to solve this problem. The GC effluent was diluted with a large gas flow (1 l min^{-1} of argon) before entrance into the transfer line. The authors explain their success by arguing (page 1320, paragraph 2) "…a high velocity intermediate *sheathing* Ar flow to transport the analytes from the GC to the ICP-MS, avoiding condensation effects on the wall of the interface…".

However, if the "velocity" and "sheathing"of the transfer line flow prevents condensation, this should also work for high boiling compounds such as phenyltin. Instead, these semi-volatiles cannot be analyzed with this interface.[10] The "velocity" interpretation of make up gas (which is acceptable for spray chamber aerosol injection into an ICP-MS) is not useful here for a long transfer line into a stand-alone detector such as an ICP-MS.

Graphite deposition on the ICP-MS sampling cone after injection of 2 μl of methanol solvent, and signal perturbation continuing up to 2 min longer than the elution of methanol, was reported.[8] This effect was eliminated by adding 14 ml min^{-1} of oxygen into the central gas flow (see also ref. 11). Feldmann[15] found no graphite deposition and claims that oxygen from his added aqueous standard can oxidize carbon but can also destabilize the plasma.

We found, however, that oxygen addition was not sufficient to oxidize 20 μl of solvent from a large volume injection, as used in this presentation, because graphite deposition increases dramatically. Using more oxygen made the plasma unstable. We do not know of relevant publications which address the problem of ICP-MS cone graphite deposition due to a large solvent peak.

Goals

GC-ICP-MS interfaces need more efficient heating for high boiling analytes or even for future high temperature (HT)-GC-ICP-MS.

An interface has to be created which can keep the solvent away from the ICP-MS torch to prevent graphite deposition.

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The result would be an unlimited solvent sample size and subsequent signal increase by large volume injection.

At least the signal repeatability of present[6,12] GC-ICP-MS designs, which is of the order of 20% (uncorrected), must be improved.

Material and methods

Our interface is multifunctional. We define an *interface* as the entity composed of all the necessary parts (tubing, adapters, isolations, vents, *etc.*). A *transfer line* is the essential tube which transfers the sample between the coupled GC and ICP-MS torch.

Preparation of the samples

The standard samples were usually prepared by adding 10 μl of 0.1 μg ml^{-1} tin as organotin chlorides into 80 ml of distilled water. This results in 12.5 ng l^{-1} tin in water. The aquatic sample was magnetically stirred and propylated with sodium tetrapropylborate at pH 4. The derivatized species were extracted with 1 ml cyclopentane, after which 20 μl of extract were injected into the GC. This results in 20 pg tin (before derivatization and extraction).

GC materials and operating conditions

Gas chromatograph (GC): HP 6890.

Oven temperature: 3 min 50 °C, 30° min^{-1}, final temperature 320 °C.

GC carrier gas: He + 10 vpm Xe, 2 ml min^{-1}.

Injector: HP 7683 series injector.

Column: HP5MS 30 m, 0.25 mm id, 0.25 μm film thickness.

GC column operation: carrier gas flow 2 ml min^{-1}.

Large volume (20 μl) hot split–splitless injection

A 20 μl injection was improvised with a standard injector by using a pressure pulse, an extra-large liner, extra-long pulse time and purge time, extra-long retention gap and solvent trapping.[16] The problems of using cold on-column injection[17] (contamination of the retention gap or GC column by non-volatile sample matrix) and of the early vapor exit[18] technique (loss of low boiling analytes) were avoided.

Principle, material and operation of the home made interface (see Fig. 1)

Principle. The derived solution for the heating problem is to dilute the GC effluent in the GC oven greatly before it passes the transfer line with preheated argon as a make up gas and thermostated medium (Fig. 1).

The *dilution* of the GC effluent results in a major reduction of the minimum transfer line temperature, which can come down from 250 °C (without dilution) to only 140 °C. A rule of thumb can be derived from a simple analyte vapour-pressure–temperature model, that a dilution of the GC effluent with make-up argon by a factor of 1000 is reducing the dew (condensation) temperature of the analytes contained by about 100 °C.

The *preheating* of the added argon prevents a cold spot (analyte condensation) in the T-joint. It also reduces complementary transfer line resistance heating to minimize a hot spot (analyte thermo-degradation) of the hot oven section of the transfer line (the additional "short circle" prevents this hot spot almost completely).

Material and operation. Stainless steel tubing 1/16″ and Swagelok T- and X-joints were used to connect the assembly in the GC oven as shown in Fig. 1. The GC column exit is connected with a pressfit connector and 15 cm fused silica capillary. The capillary is connected to the T-joint using a

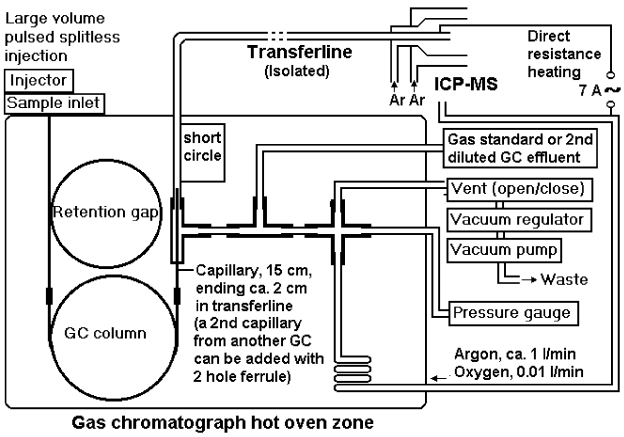

Fig. 1 GC-ICP-MS interface design with multiple functions. Functions are efficient heating, solvent peak elimination, post-column addition of gas standard to tune the ICP-MS, and more efficient mixing of the GC effluent with argon for improved signal repeatability. The GC effluent is mixed with 1 l min^{-1} argon in the T-joint in the GC oven before the transfer line (contrary to common[6,12] transfer lines where the GC capillary ends in the ICP torch).

polyimide reducing ferrule. Occasionally, we used a double-hole ferrule to couple simultaneously a second fused silica capillary transfer line from another GC. The transfer line (1.5 m length, 1/16″ od, 0.04″ id, "Silcosteel" deactivated stainless steel tubing, Restek, cat. no. 20595) is adapted at the upper port of the T-joint. The outlet of the capillary is carried through the T-joint and another 20 mm into the "Silcosteel" transfer line. Another T-joint is added to the argon flow for the addition of gas standard to tune the ICP-MS for dry plasma operation.

We also found that the length of the transfer line is only limited by safety measures due to the rising necessary power voltage and does not influence the performance. We found that any sufficiently inactivated tubing, such as PTFE coated stainless steel, can be used for the transfer line. A higher argon flow can be produced without excessive pressure rise by using tubing with an id of more than 0.04″.

Electrical resistance heating and insulation (Fig. 1). The transfer line was carried through a 5 mm hole on top of the GC oven and outside the oven insulated with PTFE tubing. The stainless steel tubing carrying the argon make up gas into the GC oven and the interface tubing were heated by their electrical resistance with a single power source of 10 V dc and 7 A, resulting in 140 °C temperature. One pole was fixed at the start of the 1/16″ stainless steel tubing carrying the argon make up gas into the GC oven. The other pole was fixed by soldering 2 mm away from the end of the transfer line. The transfer line and the electrical wire connected to the torch side were sealed by using a PTFE stopper. The end of the transfer line was centered by a ceramic tube.

Solvent peak elimination by periodic flow reversal in the transferline. A vacuum pump (Fig. 1) reversed the flow in the transfer line during the first 240 s of the GC run. A needle valve limited the vacuum measured at the pressure gauge at about −0.03 bar below atmospheric pressure during pumping to prevent disturbances of the plasma. This pressure after pumping was +0.2 bar. The "dark channel" in the plasma is immediately recovered after the pump is switched on.

As a general benefit of diluting the GC effluent with argon, we found the diluted effluent easy to manipulate for many purposes (Fig. 1). Before we utilized dilution of the GC effluent, we had to perform these operations with fused silica tubing and fragile "press-fit" capillary connectors and had problems with sealing, dead volume and peak broadening.

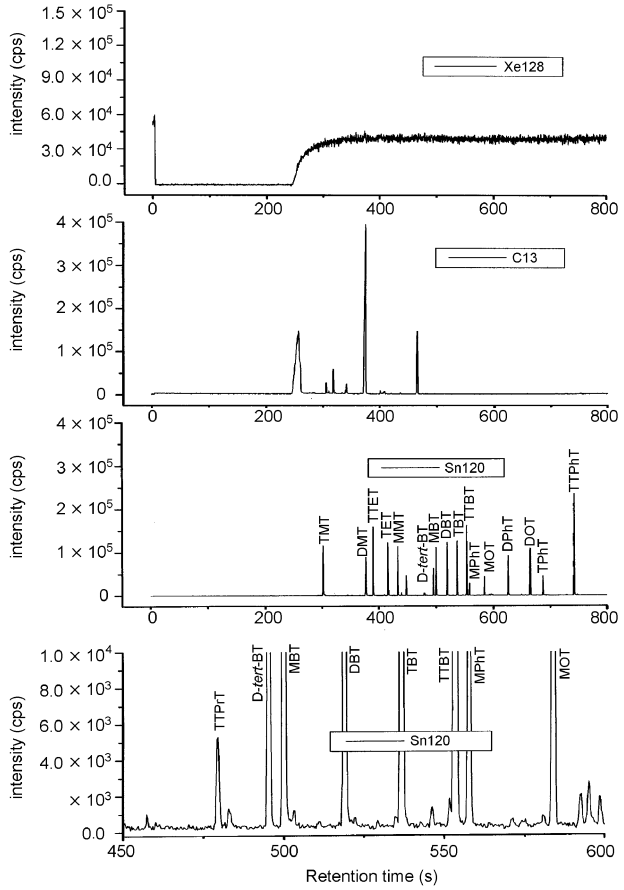

Fig. 2 GC-ICP-MS gas chromatogram of the GC-ICP-MS design for organotin species of a wide boiling point range. Large volume hot split–splitless injection of 20 µl of cyclopentane extract of propylated water sample. 140 °C transferline temperature. Top and upper middle: reduction of the carrier gas internal standard ^{128}Xe signal and ^{13}C signal during solvent (cyclopentane) peak elimination (0–240 s). Lower middle: ^{120}Sn signal (and bottom: magnification by factor of 40) of n-propyl derivates of organotin compounds (each peak 50 pg, TTPhT 100 pg tin before derivatization and extraction from 80 ml water). TMT trimethyl, DMT dimethyl, TTET tetraethyl, TET triethyl, MMT monomethyl, D-tert-BT di-*tert*-butyl, MBT monobutyl, DBT dibutyl, TBT tributyl, TTBT tetrabutyl, MPhT monophenyl, MOT monooctyl, DPhT diphenyl, DOT dioctyl, TPhT triphenyl, TTPhT tetraphenyl tin.

Essential ICP-MS parameters

Type of ICP-MS: PerkinElmer Elan 5000. Coolant gas 14 l min^{-1}. Auxiliary gas 1 l min^{-1}. Nebulizer gas 0.6 l min^{-1} Ar + 0.015 l min^{-1} O_2. Used masses/abundances: Sn (120/32.97), Hg (202/29.8), Pb (208/52.38), Xe (internal gas standard (128/10.44), C (13/1.108)). The ICP-MS was manually tuned for dry plasma operation by using a continuous flow of gas standard (tetramethyltin, dimethylmercury, tetramethyllead) from a pressure cylinder.

Results and discussion

The experiments selected for this chapter were selected to show primarily the technical performance of the proposed interface design to eliminate the solvent peak and to transfer low boiling and semi-volatile analytes in one run.

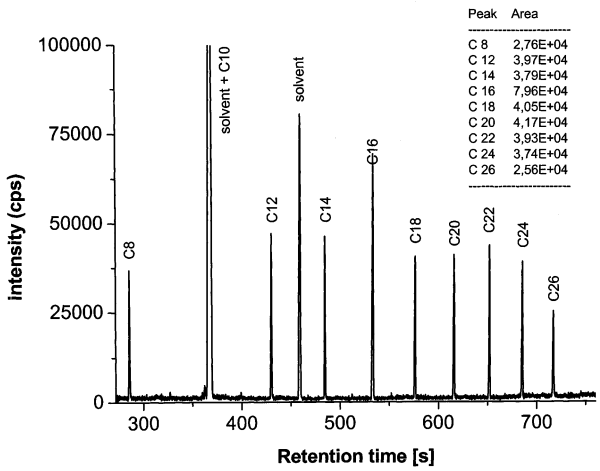

Fig. 3 GC-ICP-MS ^{13}C gas chromatogram of even-numbered n-alkanes (C_8, C_{12}, C_{14}, C_{18}–C_{26}, each 100 ng C, C16, 200 ng C added directly into the solvent). "Solvent" means impurities of the solvent. Large volume (20 µl) hot split–splitless injection. 140 °C transfer line temperature.

Interface performance to eliminate the solvent peak

The gas chromatograms in Fig. 2 (^{128}Xe and ^{13}C) show successfully eliminated signals during the initial elimination of the solvent peak where the GC effluent flow in the transfer line is reversed to prevent graphite deposition in the ICP-MS.

Chromatographic and transfer line performance

Fig. 2, lower middle and bottom, show a successful chromatographic separation of propyl derivatives of organotin-compounds after 500 injections of environmental samples.

Fig. 3 shows the successful separation of a n-paraffin standard.

Figs. 2 (lower middle) and 3 show, in particular, the good shape of the first peaks (trimethylpropyltin TMT, n-octane) which are nearest to the solvent peak.

Repeatability of the GC retention time

The analyte peak standard deviation of the retention time of organotin analytes measured with the modified GC, as in Fig. 1, measured over 10 d and 50 chromatograms, was about 2 s for 300–750 s of total retention time.

This result shows that the large volume injection and the periodic pressure-reduction (solvent elimination) do not have a significant influence on the retention time.

Analytical performance (Table 1)

Repeatability. 10 repeated injections of 20 µl of the same standard sample were made. The sample was prepared by adding 10 µl of 0.1 µg ml^{-1} tin into 80 ml water, derivatizing and extracting with 1 ml of solvent and injecting 20 µl of extract.

The repeatability for organotin compounds ranges from

Table 1 Comparison of analytical performance

	TMT	TTET	DBT	TTBT	DOT	TPhT	TTPhT
Repeatability: uncorrected (%)	1.62	1.25	1.13	1.38	1.34	2.10	2.91
Repeatability: Xe-corrected (%)	2.81	2.94	2.10	3.46	1.93	2.23	2.79
LOD (Xe-corrected)/fg	95	68	82	72	97	250	110
Linearity from LOD to…/ng	5	5	5	5	5	5	5

1.93 to 3.46% (Xe-corrected) or 1.13 to 2.91% (uncorrected). The repeatability corrected by Xe has a higher variation than when uncorrected.

The repeatability is significantly better than reported in the literature. De Smaele *et al.*[6] found about 24% repeatability for 10 repeated injections of 1 μl of the same solvent sample containing butyltin species. Similar values can be calculated from SPME-GC-ICP-MS repeatabilities in the literature[12] (whole procedure, 17–62%) using the square error sum method, utilizing the good repeatability of SPME-GC-FPD (3–16%) as the error of the sampling method and subtracting it from the error of the whole procedure.

The reason for the improved repeatability could be that GC effluent and make-up argon enter the torch after they have mixed completely in our transfer line (Fig. 1) and form a massive jet which is almost identical with the plasma "dark channel" and properly fixed onto the ICP-MS cones. Also, the longitudinal fixation of our 1/16″ steel transfer line onto the ICP-MS cones is probably much more stable in the torch than a flexible fused silica capillary in common transfer lines.[6,12]

The fact that the central argon jet forms a form-stable "dark channel" could indicate that turbulent mixing is limited in the channel. Therefore, in common transfer lines, where the GC effluent enters the torch undiluted with argon, the effluent could form a narrower "flag" channel inside the dark channel and, therefore, the signal could be fluctuating depending on the actual direction of the fluttering "flag" or of the flexible fused silica capillary against the ICP-MS cones. If the ICP cones are tuned for the actual direction of the analyte channel, the resulting sensitivity might be high. But, in turn, sensitivity could become low if the GC effluent channel changed its direction. The period times of these sensitivity fluctuations could be in a time order which causes inefficient analytical repeatability.

Another reason for the improved repeatability could be the permanent prevention of solvent peak graphite deposition on the ICP-MS cones, which could otherwise influence the signal.

The *absolute detection limits* for the organotin compounds (whole procedure LOD including extraction and derivatization) based on three times the standard deviation of the noise given in Table 1 are in the range of 68 fg Sn (TTET, purchased) to 250 fg (TPhT, propylation efficiency contained). Literature[6] results with the same type of ICP-MS instrument for butyltin compounds (instrumental LOD) range between 15 and 34 fg Sn.

The *relative detection limit* for an 80 ml water sample (propylation and extraction) ranges between 42.5 and 156.25 pg l^{-1} Sn for these analytes.

The *linearity* ranges from the detection limit to 5 ng tin absolute.

Applicability

Up to 54 ng l^{-1} trimethyltin (groundwater) and 400 ng kg^{-1} triphenyltin (organic forest soil, water extraction) were found in environmental samples. These compounds represent very low and high boiling analytes which are difficult to analyse in one GC run.

Any peralkylated or volatile organometal compound with a chromatographic retention time similar to n-paraffins and organotin compounds tested in Figs. 2 and 3 can be analyzed with this design at only 140 °C transfer line temperature.

The presented method was used in our laboratory to analyse routinely volatile propylated organometal compounds of tin, mercury and lead. It is not the aim of this paper to discuss sampling and sample preparation for real samples or the efficiency of derivatization procedures. Interested readers are referred to future papers of the authors.

Outlook

The suggested GC-ICP-MS design combines easy production and operation with a wide analyte boiling point range, low relative detection limits and probably the best reported (uncorrected) repeatability.

The suggested interface design can utilize high temperature (HT)-GC-ICP-MS for the analysis of organometallic compounds in crude oil, *etc.*, for an estimated boiling point range of up to 550 °C. We were able to rise the interface temperature from 140 to 270 °C by applying higher heating voltage, but we had no HT-GC system available to produce such a chromatogram.

Additionally to ICP-MS, other spectrometric detectors, such as ICP-AES (OES), should be coupled for high temperature GC. To use the invented GC effluent plus argon dilution they must either provide or must be able to take a 1 l min^{-1} inert gas flow.

We believe that splitless (or on-column) *large volume solvent injection* GC-ICP-MS will become an established practice which can compete with solvent-free SPME[13] and stir bar sorptive extraction[14] in detection limit and analytical quality.

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References

1 J. S. Thayer, *Environmental Chemistry of the Heavy Elements*, VCH, New York, 1995.
2 A. W. Kim, M. E. Foulkes, L. Ebdon, S. J. Hill, R. L. Patience, A. G. Barwise and S. J. Rowland, *J. Anal. At. Spectrom.*, 1992, **7**, 1147–1149.
3 A. Prange and E. Jantzen, *J. Anal. At. Spectrom.*, 1995, **10**, 105–109.
4 J. Feldmann and A. V. Hirner, *Int. J. Environ. Anal. Chem.*, 1995, **60**, 339–359.
5 H. Hintelmann, R. D. Evans and J. Y. Villeneuve, *J. Anal. At. Spectrom.*, 1995, **10**, 619–624.
6 T. De Smaele, L. Moens, R. Dams and P. Sandra, *Fresenius' J. Anal. Chem.*, 1996, **355**, 778–782.
7 S. M. Gallus and K. G. Heumann, *J. Anal. At. Spectrom.*, 1996, **11**, 887–892.
8 C. Pecheyran, C. R. Quetel, F. M. M. Lecuyer and O. F. X. Donard, *Anal. Chem.*, 1998, **70**, 2639–2645.
9 J. Poehlman, B. W. Pack and G. M. Hieftje, *Am. Lab.*, 1998, **30**, C50.
10 M. M. Bayon, M. G. Camblor, J. I. Garcia Alonso and A. Sanz-Medel, *J. Anal. At. Spectrom.*, 1999, **14**, 1317–1322.
11 J. P. Snell, I. I. Stewart, R. E. Sturgeon and W. Frech, *J. Anal. At. Spectrom.*, 2000, **15**, 1540–1545.
12 S. Aguerre, G. Lespes, V. Desauziers and M. Potin-Gautier, *J. Anal. At. Spectrom.*, 2001, **16**, 263–269.
13 J. Vercauteren, A. De Meester, T. De Smaele, F. Vanhaecke, L. Moens, R. Dams and P. Sandra, *J. Anal. At. Spectrom.*, 2000, **15**, 651–656.
14 J. Vercauteren, C. Peres, C. Devos, P. Sandra, F. Vanhaecke and L. Moens, *Anal. Chem.*, 2001, **73**, 1509–1514.
15 J. Feldmann, L. Naels and K. Haas, *J. Anal. At. Spectrom.*, 2001, **16**, 1040–1043.
16 K. Grob and B. Schilling, *J. Chromatogr.*, 1987, **391**, 3–18.
17 K. Grob, T. Laubli and B. Brechbuhler, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1988, **11**, 462–470.
18 E. Boselli, K. Grob and G. Lercker, *HRC-J. High Resolut. Chromatogr.*, 1999, **22**, 327–334.