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Analysis of Volatile Metalloid Species in Gas Samples using a Commercial Cryotrapping System (TDS-G-CIS GC) Coupled to ICP-MS with PH_3 and SF_6 as Example Compounds

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ABSTRACT

A variety of volatile organometalloid species finds application in industrial processes. Among these are e.g. the fumigation of tobacco leaves or flour with phosphine (PH_3) for elimination of insects, or the use of sulfurhexafluoride (SF_6) as arc extinguishing media in electrical circuits. The occurrence of volatile metal(loid) species was also proved in emissions of landfills and sewage treatment plants. Most of these volatile compounds are extremely toxic even at very low concentration levels ($< mg/m^3$), therefore a demand for trace analysis of these species exists in industrial hygiene and environmental monitoring.

For this, analytical techniques using cryotrapping preconcentration prior to GC separation and multielement detection by ICP-OES or ICP-MS have shown to be extremely sensitive and efficient. The most critical step in the analytical procedure after cryosampling is the transfer of the collected species into the GC for separation prior to detection. The usually applied home-made techniques using cryofocusing on glass-wool or support-packed glass tubes cooled by liquid nitrogen at –196°C are tedious to apply, and specially the transfer of the cryocollected sample into the analytical system is subject of complicated handling. In order to facilitate the analytical procedure, we used a commercial system of cryosampling directly connected to a cooled injection system of a GC (TDS G – CIS, Gerstel, Germany) as sample introduction. As example species, we chose synthetic mixtures of PH_3 (bp. -88°C) and SF_6 (bp. -68°C). We investigated the influence of cryosampling temperature in the CIS and the effect of the sample flow during cryotrapping. The optimum cryosampling temperature was found to be –170°C. The sampling flow was varied between 40 and 200 mL/min, and in this flow range no impact on the results was observed. Species separation was performed by capillary GC coupled to ICP-MS (HP7500, Agilent) as specific multielement detector. A home made transfer line was used for the connection of the GC with the ICP-MS. Using this setup, the absolute detection limit for PH_3 was determined to be 3 pg and 1 ng for SF_6 measured on the isotope ^{34}S with an analytical reproducibility of 3 to 10 % RSD.

INTRODUCTION

Several volatile organometal(loid) species are today being used for a variety of applications in industrial processes. Among these are e.g. the fumigation of tobacco leaves or flour with phosphine (PH_3) for elimination of insects, or the use of sulfurhexafluoride (SF_6) as arc extinguishing media in electrical circuits. In the semiconductor industry, other volatile metal(loid) species, e.g. $AsMe_3$, are used during the process of cold vapour deposition for doping of semiconductor elements. $PbEt_4$, used as antiknocking agent in fuel, was determined in town air and has been the major source for lead in road dust. The occurrence of volatile metal(loid) species (AsH_3, $AsMe_3$, SnH_4, $SnMe_4$, $BiMe_3$, $HgMe_2$) was also proved in emissions of landfills and sewage treatment plants [1]. In coal combustion flue gas, volatile mercury, tin copper and selenium species were evidenced [2] and volatile metal and metalloid species (Pb, Hg, Se) in a urban atmosphere were also detected [3]. In natural environments, volatile species of As, Se, Sb and I were detected in the gas produced by bacteria in geothermal hot springs [4]. Most of these volatile compounds are extremely toxic even at very low concentration levels (< mg/m^3), therefore a demand for trace analysis of these species exists in industrial hygiene and environmental monitoring.

The analytical techniques applied for these volatile species determination using cryotrapping preconcentration prior to GC separation and multielement detection by ICP-OES or ICP-MS and have shown to be extremely sensitive and efficient [5]. The usually applied home-made techniques using cryofocusing on glass-wool or support-packed glass tubes cooled by liquid nitrogen at –196°C are tedious to apply, and specially the transfer of the cryocollected sample into the analytical system is subject of complicated handling and usually the major source of analytical error.

So, in fact, metal and metalloid speciation analysis of volatile compounds lacks easy to handle instrumentation. Thus, in order to facilitate the analytical procedure, we used a commercial system of cryosampling directly connected to a cooled injection system of a GC (TDS G – CIS, Gerstel, Germany) as sample introduction unit. The analytical performance of this cryogenic trapping unit / thermodesorption system followed by capillary gas chromatography (HP 6850) coupled online to an inductively coupled plasma mass spectrometer (HP 7500/Agilent) allowing on-line preconcentration, separation and simultaneous multielement detection of metal species in air has been investigated. As the most volatile species with boiling points far below 0°C are most critical to analyze, we chose PH_3 (bp. - 88°C) and SF_6 (bp. –68°C) as example species. Figure 1 gives an overview of the overall analytical system.

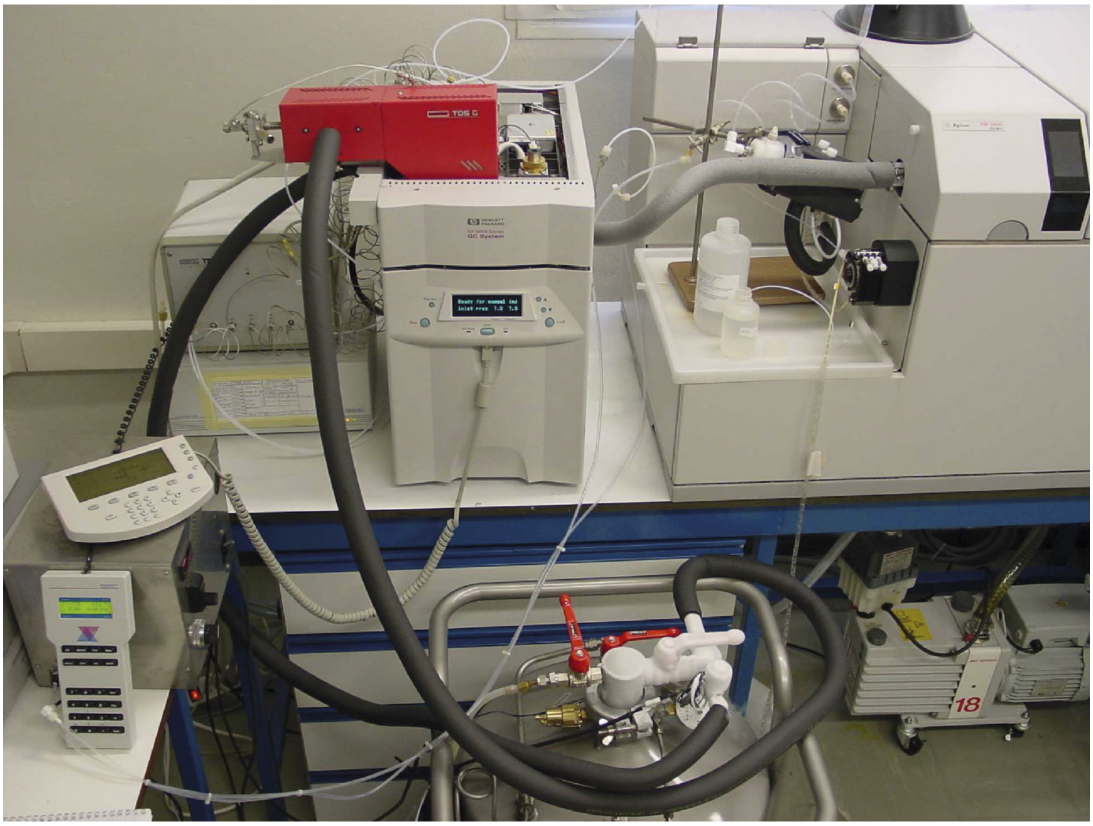

Figure 1. Overall system setup with TDS G, Agilent 6850 GC coupled to 7500 ICP-MS.

EXPERIMENTAL SETUP

Figure 2 gives a detailed description of the sample introduction system. It consists of an online thermodesorption unit (TDS G) and a temperature programmable GC inlet (CIS, Cooled Injection System). The TDS G is equipped with 6-port valve and an external pump to enrich gaseous samples online on adsorbent tubes (online-mode; flow scheme A). After sample enrichment the 6-port valve switches to allow the carrier gas flow through the adsorbent tubes via the transfer line and though the CIS to the gas chromatography column (thermal desorption (TDS) mode, flow scheme B). By heating the TDS chamber the analytes are transfered to and cryofocussed in the CIS. After this thermodesorption step the CIS is heated up with a temperature ramp up to 12°/sec to transfer all analytes as a narrow peak onto the analytical column.

For all studies presented in this paper the online-mode of the TDS G was not used. Here samples were collected with an external sampling device (see application part) or using a septumless injectorhead and the TDS G was just used as a thermodesorption sample introduction system.

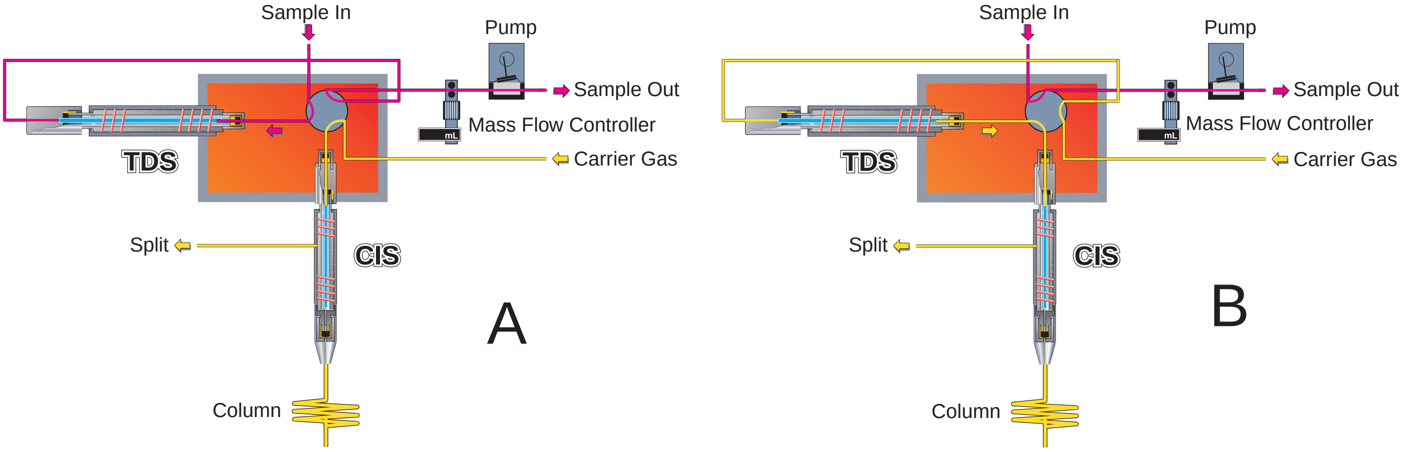

Figure 2. Flow schemes of TDS G, in online sampling mode (A) and thermal desorption mode (B).

Analysis conditions.

TDS G system (thermal desorption (TDS) mode)	
Cryosampling trap:	silanized glass wool
Tube filling:	silanized glass wool
TDS temperature:	200°C
Valve and transferline temperature:	150°C

CIS	
Temperature:	varied from -120 to -180°C
CIS final:	150°C
Heating rate:	12°C/s

Chromatographic parameters	
Column:	MXT silcosteel, 100% PDMS, 5 µm, 0.53 mm i.d., 30 m
He flow:	10 mL/min
Temperature program:	isothermal 80°C
Inlet mode:	splitless
Transferline:	MXT silcosteel, 0.53 mm i.d., 1m, not heated

ICP-MS parameters	
Nebulizer gas flow:	0.95 L/min
Cooling gas flow:	15 L/min
Aux. gas flow:	0.8 L/min
Power:	1250 W
Dwell time:	20 ms/mass
Isotopes:	^{31}P, ^{34}S, ^{126}Xe (internal standard)

Calibration sample preparation. Gas samples were collected from two different gas standard cylinders (PH_3 10.7 ppm in helium and SF_6 97.4 ppm in argon, Air Liquide, France) in two different gas bags (Tedlar bags) stored at ambient temperature in the dark to avoid possible photodegradation (at least for PH_3). In these storage conditions, PH_3 stability was estimated to be around one week and during the same time no degradation of SF_6 was observed. For calibration gas-tight syringes were used to inject the samples into the analytical device, either into the TDS G or directly into the CIS. Therefore the TDS lock cone or the CIS were equipped with a septumless injectorhead

VALIDATION

Validation of the system. The most critical part of the TDS G system for quantitative analysis of very volatile compounds will be the refocusing step in the inlet liner. Species residence time in the liner has to be long enough and the liner temperature cold enough to allow quantitative trapping.

So, in order to validate this commercial analytical system for very volatile compounds, the influence of helium flow and sampling temperature on cryofocussing efficiency were investigated. For these experiments, gas samples were injected either into the hot TDS and the cold CIS or directly into the hot CIS via the Gerstel septum less head injector using a gastight syringe. The analytical performances in terms of reproducibility (RSD) and detection limits for PH_3 and SF_6 are also reported.

Figure 3 represents a typical chromatogram obtained for SF_6, PH_3 injections and internal standard (xenon).

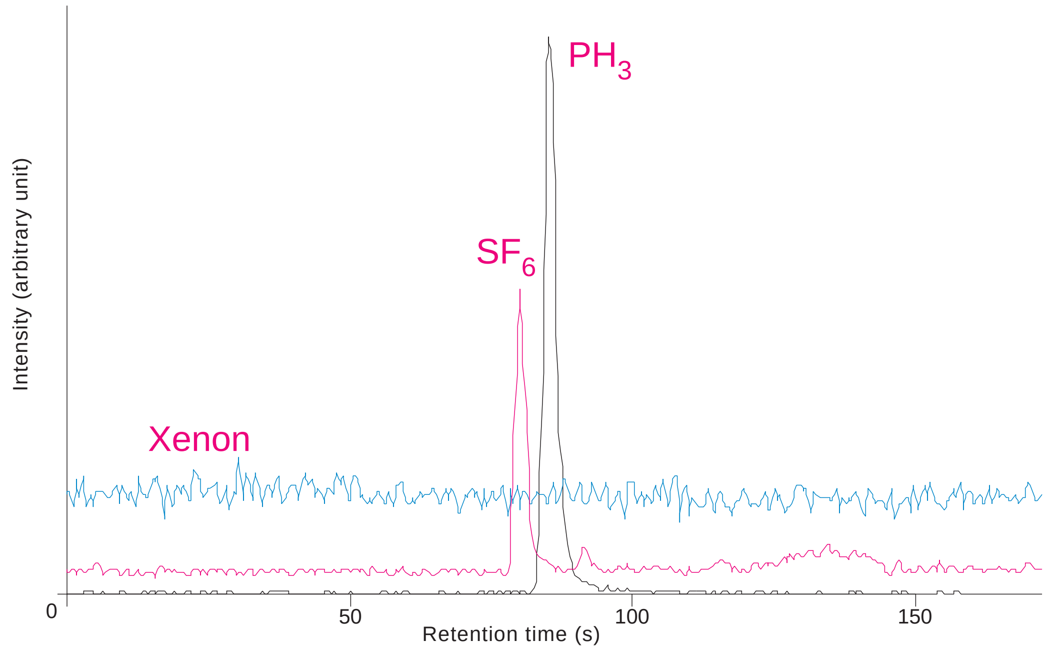

Figure 3. Typical chromatogram obtained for SF_6, PH_3 and internal standard (xenon).

1- Influence of helium flow on PH_3 and SF_6 trapping efficiency in the liner at –170°C

Experimental conditions. TDS Mode (see flow scheme B, figure 2); TDS temperature 200°C (isothermal); CIS initial temperature -170°C; CIS final temperature 150°C.

Sample injection. Samples were injected into the TDS tube via the septumless injectorhead connected to the TDS (200°C) using a gastight syringe under different helium flows. The analytes were directly transferred to the CIS and there croyfocussed at –170°C.

Sample Analysis. For transferring the collected species from the CIS to the analytical column the CIS was heated from –170°C (initial temperature) to +150°C (final temperature) at 12°C/s and analysed under the chromatographic conditions as described before.

Using an CIS inlet liner temperature of –170°C, no significant helium flow influence on trapping efficiency and reproducibility have been demonstrated (Table 1).

2- Influence of sampling temperature on PH_3 and SF_6 trapping efficiency

Experimental conditions. Manual mode; CIS initial temperature varied from –120 to –180°C; CIS final temperature 150 °C.

Sample injection. PH_3 and SF_6 were injected in the inlet liner of the CIS via the septumless injectorhead at different temperatures.

The results obtained were compared to injections into a hot CIS at +150°C. Recoveries in % are reported in table 2. Results demonstrated that sampling temperature for PH_3 and SF_6 quantitative trapping has to be below –150°C.

Table 1. Influence of carrier gas flow on cryofocussing efficiency for CIS.

	PH_3		SF_6	
Helium flow [mL/min]	Peak area mean (n=5)	RSD [%]	Peak area mean (n=5)	RSD [%]
40	164 000	3	112 700	6
100	156 600	5	114 350	6
200	153 600	4	118 250	4

Table 2. Influence of CIS initial temperature on cryofocussing efficiency.

CIS temp. (°C)	-180	-170	-150	-120
% recovery (SF_6)	100	100	100	17
% recovery (PH_3)	100	100	98	16

3- Calibration curve

Experimental conditions. Manual mode; CIS initial temperature –170°C; CIS final temperature 150°C *Sample injection.* Different volumes of PH3 and SF6 were injected in the inlet liner of the CIS via the septum less head injector. The quantities of PH_3 (10.7 ppm) and SF_6 (99.4 ppm) introduced in the analytical system correspond approximately to 0.1 to 3 ng for PH_3 and 6 to 120 ng for SF_6 according to the injected volumes.

The calibration curves obtained are displayed in figure 4.

Volume [L]	PH_3 [ng]	SF_6 [ng]
10	0.14	5.82
20	0.29	11.64
100	1.44	58.20
200	2.88	116.40

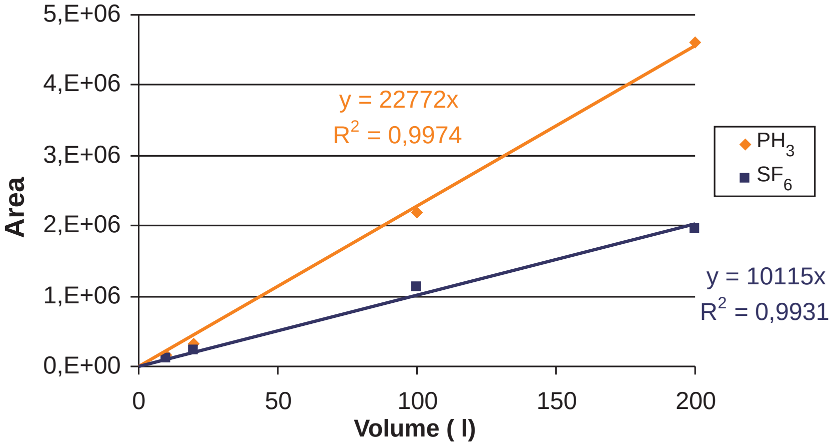

Figure 4. Calibration function for SF_6 and PH_3.

4- Recovery

Recoveries of the analytical system were evaluated using two different configurations: gas samples were injected either into the hot TDS and trapped in the cold CIS (TDS mode) or directly into the cold CIS (manual mode). The results obtained were compared to direct injections into the hot CIS at 150°C (manual mode). Recoveries in % are reported in table 3.

Table 3. Recoveries for different operation modes of TDS G or CIS with injections into the hot CIS as reference.

	manual mode CIS -170 to 150°C	TDS 2 mode TDS 200°C, CIS -170 to 150°C
% recovery (SF_6)	111	119
% recovery (PH_3)	91	73

5- Detection limit

An absolute detection limit of 3 pg for PH_3 (measured on ^{31}P) and 1 ng for SF_6 (measured on the ^{34}S isotope; relative isotopic abundance: 4.2%) were calculated by the 3σ-criterion.

6- Humidity in the gas samples

Some difficulties were observed with a blocked transferline because of ice clogging during ambient air sampling either using online TDS G sampling mode or TDS mode for the analysis of externally collected samples with a laboratory made cryosampling device at –175°C (see application part for cryosampling device description). In order to remove ambient air humidity, a drying system has to be used before cryosampling and the maximum air volume that could be collected will depend on drying efficiency. Application part gives an example of the possible collected volume under the corresponding sampling conditions.

APPLICATION

A sampling campaign was conducted in a factory (confidential) in order to measure workers exposure to hydrides. Ambient air sampling was performed by cryogenic trapping at -175°C on silanized glass wool (Supelco, pesticide grade) packed in a glass tube using a laboratory made air sampler (LCABIE) at 0.2 NL/min. Before cryogenic trapping, the gas was dried using an empty

U-shaped glass traps held at –20°C. In these conditions, the collected volume for each sample was 3 liters. The collected samples were stored at at least -190°C in a dry atmosphere cryocontainer (Voyageur 12, L'air liquide, Paris, France) for further analysis in the laboratory. Samples analysis was performed using the analytical system described above. The frozen samples were transferred from the cryocontainer into the TDS for analysis. According to previous experiments concerning PH_3 analysis, the sample connection time has to be lower than 15 seconds in order to avoid volatile compound loss. TDS analytical conditions are:

Analysis conditions.

TDS:	50 mL/min desorption flow
	-170°C; 60°C/min; 120°C (5 min)
	150°C valve/transferline temperature
CIS:	-170°C; 12°C/sec; 200°C (4 min)

PH_3, SbH_3 and AsH_3 could be detected and quantified (range µg/m³) in different places of the factory.

CONCLUSION

The analytical technique introduced here proved to be well suited for reproducible determination of extremely volatile metalloid species in gas samples. Easy sample handling and easy transfer of the investigated species was achieved with the TDS G / CIS system, and application of the technique to real samples was shown. For successful application to real samples, the gas humidity will yet be a problem limiting the sample volume, so efficient gas drying will have to be applied before cryogenic sampling.

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