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# Direct determination of trimethylgermanium in water by on-column capillary gas chromatography with flame photometric detection using quartz surface-induced germanium emission

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## Abstract

This paper describes a method for the direct determination of trimethylgermanium chloride in water by on-column capillary gas chromatography with a laboratory-modified flame photometric detector using quartz surface-induced germanium emission. Pretreatment of the HP-1 capillary column by injection of 2% HCl in methanol prior to the experiment is important for obtaining reproducible results. The linear dynamic range is over three orders of magnitude for TMGeCl (as Ge) and ranges from 0.01 ng to 10 ng. The instrumental detection limit measured as the signal that equals three times the baseline noise is 3 pg. Using a 100-ml water sample, a relative detection limit of 15 ng l<sup>-1</sup> can be routinely achieved. The recovery in 100 ml water spiked with 0.2 µg TMGeCl is in the range 86–111%. The reproducibility and precision of the overall procedure are of the order of 5% and 7%. No trimethylgermanium chloride was found in water samples.

*Keywords:* Water analysis; Trimethylgermanium chloride; Germanium; Organogermanium compounds

## 1. Introduction

Until the mid-1980s, methylgermanium species, (CH<sub>3</sub>)<sub>n</sub>GeCl<sub>4-n</sub> (0 ≤ n ≤ 3), have been reported as absent in natural waters. Hambrick et al. [1] reported the existence of monomethylgermanium (MMGe) and dimethylgermanium (DMGe), which accounts for about 70% of total germanium levels so far detected in seawater. Lewis et al. [2,3] determined the presence of trimethylgermanium (TMGe) in a rainwater sample and a liquid fraction of sludge

samples taken from both aerobic and anaerobic digesters of a sewage treatment plant. The conclusion was that the methylgermanium species are apparently very stable and inert, and display conservative behaviour in estuaries and in the ocean [2,3].

In analytical chemistry, hydride generation (HG) is among the best techniques currently available for separation of inorganic and methylgermanium species from environmental waters; it has been coupled to atomic absorption spectrometry [1–6] and other spectroscopic techniques [7–9]. However, during HG, methylgermanium species are derivatized to their corresponding methylgermanes, which exhibit quite different behaviours in terms of their yield,

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stripping-off solution and atomization [1,8,10]. Furthermore, interferences due to metal ions pose serious problems [11].

Recently, the determination of organogermanium in environmental samples has become of increasing interest owing to its industrial and biological significance, its potential function in the retardation of human ageing and as antitumour agents in medicine. A sensitive and reliable measurement is, hence, required.

A gas chromatographic method was used by Flinn and Aue to investigate the flame photometric detection (FPD) of organogermanium compounds in both surface and gas phase emission modes; their studies demonstrated that surface luminescence is the most sensitive emission mode for  $\text{Bu}_4\text{Ge}$  but there is no indication of any analytical application [12]. In our previous studies, an hyphenated instrument was developed based on gas chromatography with a laboratory-modified flame photometric detector using quartz-surface induced tin and germanium emission [13]. During an earlier study of the chromatographic conditions for pentylated methylgermanium compounds, we observed that trimethylgermanium chloride (TMGeCl) can be directly eluted without pentylation. By using a HCl-pretreated HP-1 capillary column, a symmetric TMGeCl peak a detection limit at the pg level can be obtained. The objective

of this paper is to present an analytical method for the direct determination of TMGeCl in various environmental water samples.

## 2. Experimental

### 2.1. Apparatus

#### 2.1.1. GC-FPD

A CP-9001 gas chromatograph (Chrompack, Middelburg, Netherlands) equipped with an air-cooled on-column injection system is used. A 1.8-m deactivated fused-silica column serving as retention gap is installed between the on-column joint and the capillary column via a press-fitted back connector (Chrompack). A 25 m×0.32 mm, 0.17  $\mu\text{m}$  HP-1 capillary column (Hewlett-Packard, Avondale, PA, USA) is used as the analytical column. The optimized chromatographic conditions are given in Table 1.

The laboratory-modified FPD system is similar to that previously described [13], but the straight aluminium delivery tube, placed between the detector body and the photomultiplier tube (PMT), is replaced by a straight stainless steel tube fitted with a 150×10 mm I.D. quartz bar, which allows the detector to be operated over a wide temperature

Table 1  
GC-FPD operating conditions

System	Conditions
<i>On column injection parameters:</i>	
Cooling air flow-rate	300 ml min <sup>-1</sup>
Injection volume	2 $\mu\text{l}$
Injection port temperature	Air cooled
<i>GC parameters:</i>	
Column	HP-1 (25 m×0.32 mm, 0.17 $\mu\text{m}$ crosslinked methyl silicone)
Column head pressure	100 kPa N <sub>2</sub>
Oven temperature	40°C
<i>FPD parameters:</i>	
PMT	PF-1042
Hydrogen	200 ml min <sup>-1</sup>
Air	140 ml min <sup>-1</sup>
Detector temperature	200°C
<i>Data processing:</i>	Chrompack PCI revision 5.0 software with RS-232 C interface

range. A 75 mm high  $\times$  6 mm I.D. clean and transparent quartz tube is slipped over the burner to provide the necessary quartz surface. The emitted light is measured by a conventional photomultiplier tube (PF-1042, Burle, USA) through a 394-nm interference filter. The high-voltage supply and electrometer requirements to amplify the output from the PMT were obtained using the Chrompack 906A system. Output signals are treated by a Chrompack PCI revision 5.0 data acquisition and processing system with a RS-232C interface.

### 2.1.2. GC-MS

GC-MS identification was performed in a HP-5890 gas chromatograph with a 30 m  $\times$  0.53 mm I.D., 0.83  $\mu$ m thickness DB-1 megabore column linked to a Fisons Trio-2000 quadrupole mass spectrometer with electron impact (EI) ionization. The data processing was carried out with a laboratory-base data system. Scans were obtained from 50 to 400 u every second. A 1- $\mu$ l volume of sample was automatically injected using splitless mode at 225°C in the injector port and the oven was maintained at a constant temperature of 40°C. The transfer line and ion source were held at 250°C and 225°C, respectively.

### 2.2. Reagents and standards

Trimethylgermanium chloride (TMGe, 90%) was purchased from Alfa Products (Karlsruhe, Germany). When stored in a refrigerator at 4°C, this solution was stable for at least six months without detectable concentration changes. A working standard, obtained by diluting the concentrated standard stock solution with pentane was used for the experiments.

All other reagents used were of analytical reagent grade; the water was deionized and further purified through a Milli-Q system (Millipore, El Paso, TX, USA).

### 2.3. Analytical procedure

A 100-ml volume of the aqueous sample to be analyzed is transferred to a 200-ml separatory funnel and 25 ml of concentrated hydrochloric acid is added. One ml of pentane is added as an extractant, the funnel is manually shaken for 5 min and the funnel is allowed to stand quietly for about 2 min

until phase separation occurred. The lower aqueous phase is discarded in a beaker and the upper part of pentane phase is pipetted into a small cap vial. The solution is direct used for GC-FPD analysis, which typically requires an injection of 2  $\mu$ l of sample. In the recovery experiment, 1 ml of the working standard containing TMGeCl is spiked giving a concentration of about 2  $\mu$ g l<sup>-1</sup> as Ge.

## 3. Results and discussion

### 3.1. Optimization of detector conditions

The detector conditions were generally adapted from the already optimized parameters for GC-FPD [13]. A low oven temperature was necessary to obtain better separation between solvent and TMGeCl. While the detector temperature considerably affects the response for organotin, it is not crucial above 200°C for TMGeCl. However, as mentioned previously [13], the detector response depends on the hydrogen and air flow-rates. In Fig. 1, when hydrogen flow-rate is kept constant at 120 ml min<sup>-1</sup>, the detector response reaches a maximum between 130–190 ml min<sup>-1</sup>, whereas in Fig. 2, when air flow-rate is kept constant at 140 ml min<sup>-1</sup>, the detector response reaches a maximum between 100 and 220 ml min<sup>-1</sup>. Increasing the hydrogen flow-rate results in the solvent response dropping quickly (dashed trace in Fig. 2). Hence, it is possible to

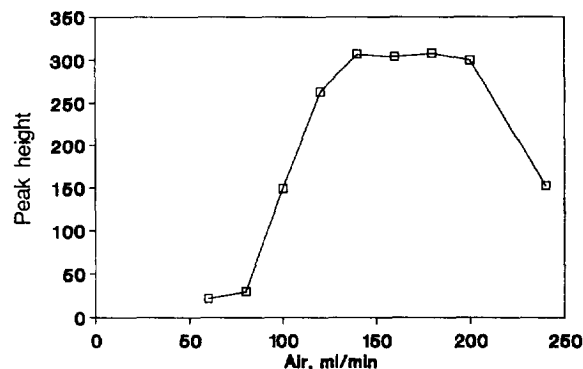


Fig. 1. Influence of air flow-rate on detector response. A 2-ng amount of TMGeCl (as Ge) was injected into the chromatographic system. Column temperature, 40°C; detector temperature, 200°C; hydrogen flow-rate, 120 ml min<sup>-1</sup>.

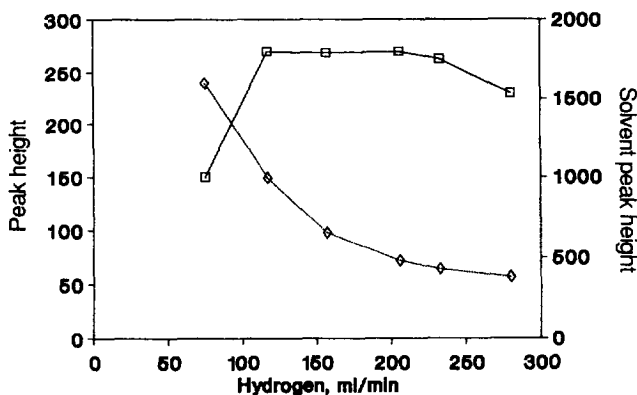


Fig. 2. Influence of hydrogen flow-rate on detector response. A 2-ng amount of TMGeCl (as Ge) was injected into the chromatographic system. Column temperature, 40°C; detector temperature, 200°C; air flow-rate, 140 ml min<sup>-1</sup>. (□) TMGeCl, (◇) pentane.

choose a hydrogen rich flame for the determination of TMGeCl with minimum solvent interference. The optimal detector gas flow-rates used were 200 ml min<sup>-1</sup> for hydrogen and 140 ml min<sup>-1</sup> for air.

### 3.2. Column pretreatment

The direct chromatographic determination of organometallic halides, which are mainly used for the analysis of organotin compounds, was reported by a number of authors [14–17]. The key factor in these methods is the column pretreatment with hydrohalogenic acid. For instance, in the study of Siu et al. [16] on the determination of butyltin species as chlorides in sediment, HCl was introduced into a DB-608 open tubular column by either injection of 0.5 M HCl in methanol or continuous doping of a few ml min<sup>-1</sup> of 1% HCl gas in nitrogen. In the case of TMGeCl measurement, pretreatment of a HP-1 capillary column with hydrochloric acid is important to obtain reproducible results. It is rather simple to do this by two consecutive injections of 2 μl of a 2% HCl in methanol solution daily prior to analysis. Experimental results indicated the effective performance of the HP-1 column treated with 2% HCl during the course of TMGeCl measurement. Neither peak tailing nor distortion in peak shape were observed even after several months of use.

### 3.3. Extraction

The extraction behaviour for inorganic germanium and organogermanium compounds from hydrochloric

acid has extensively been studied [18–20]. However, no procedure has been described up to now for the extraction of TMGeCl at trace levels. Fig. 3 shows the effect of HCl concentration on the extraction of 5 μg TMGeCl in 100 ml water. When the concentration of HCl is more than 2 M, about 90% of TMGeCl can be quantitative extracted by a single extraction, and the recovery does not depend on the initial amounts of TMGeCl present, which typically varied from 0.1 to 100 μg l<sup>-1</sup>. As for the extraction time, the equilibrium between organic solvent and water phase is reached within a few min, hence a shaking time of 5 min was used.

### 3.4. Separation and identification

Owing to the high volatility of TMGeCl (97°C), pentane was used as solvent and extractant. Under

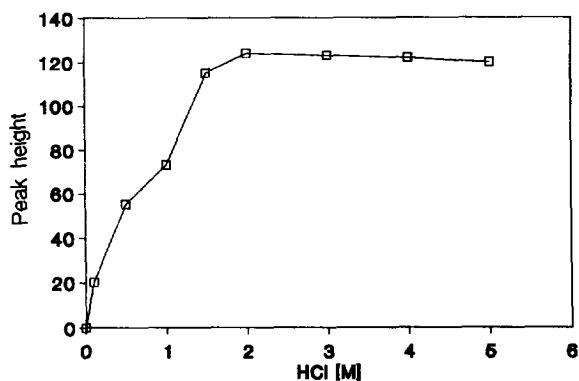


Fig. 3. Effect of HCl concentration on TMGeCl extraction.

isothermal conditions at 40°C and optimized detector parameters, baseline resolution of TMGeCl with a retention time at 1.4 min was obtained. Mono-methylgermanium chloride (MMGeCl<sub>3</sub>) and dimethylgermanium chloride (DMGeCl<sub>2</sub>) do not elute from the column under the same or similar experimental conditions. The TMGeCl extract was identified by GC–MS as shown in Fig. 4. Identities of *m/z* ions of each fragmentation shown in Fig. 4 are listed in Table 2. Unlike the spectra of pentylated methylgermanium compounds, in which no molecular ion was obtained [21], the molecular ion of TMGeCl was identified, though its intensity was weak. The most abundant peak was confirmed as the loss of methyl group at *m/z* 139 [M–CH<sub>3</sub>]<sup>+</sup>, whereas other typical peaks as well as germanium isotopic patterns correspond to the cleavage of chlorine at *m/z* 119 [M–Cl]<sup>+</sup> and the cleavage of methyl group at *m/z* 109 [M–(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, were also confirmed. Calculations were based on the <sup>74</sup>Ge isotope.

### 3.5. Method evaluation

The linear dynamic range was over three orders of magnitude for TMGeCl (as Ge) and ranges from 0.01 ng to 10 ng. The calibration curve was established by

Table 2

EI spectrum identification for TMGeCl<sup>a</sup>

<i>m/z</i>	Origin
GeCl <sup>+</sup>	109
GeMe <sub>3</sub> <sup>+</sup>	119
GeMe <sub>2</sub> Cl <sup>+</sup>	139
GeMe <sub>3</sub> Cl <sup>+</sup>	154

<sup>a</sup> Calculated based on Ge<sup>74</sup>.

injecting 0.1–0.5 ng of TMGeCl standards. All standards were obtained through the entire extraction procedure in order to compensate for losses during a single extraction. By using peak-height measurements, good linearity was obtained with *y*-intercept, slope (*m*) and correlation coefficient (*γ*) calculated from the regression equation as 0.7, 267 and 0.9997, respectively. The instrumental detection limit measured as the signal equal to three times the baseline noise is 3 pg. For a 100-ml water sample, a detection limit of 15 ng l<sup>-1</sup> can routinely be achieved. The reproducibility of this GC–FPD system was determined by consecutive injecting (*n*=12) 0.4 ng TMGeCl as Ge; the relative standard deviation (R.S.D.) was 5%. The recovery in 100 ml water spiked with 0.2 μg TMGeCl was in the range 86–111%. A R.S.D. of 7% (*n*=7) was obtained from

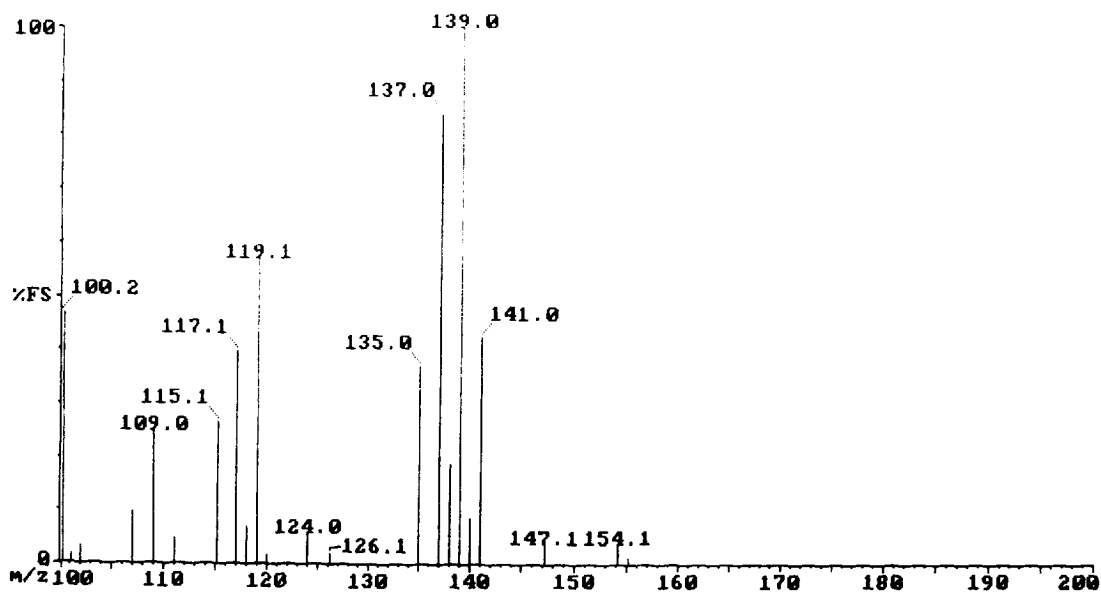


Fig. 4. EI Mass spectrum of TMGeCl.

independent measurements. All this indicates a good precision for this procedure.

### 3.6. Interference of various ions

The possible interference effects of various ions that can be co-extracted with TMGeCl in 2 M HCl was investigated. Special attention was paid to arsenic(III) and organotin species. Indeed, in a previous study it was found that arsenic(III) is co-extracted as chloride with germanium in concentrated HCl solution [18,19], while organotin species appear to be highly sensitive in the GC–FPD system

Table 3  
Effect of several ions on the extraction of 0.2 µg TMGeCl in 100 ml water

Group	Ion			
	Ion	Added as	Added amount	Recovery (%) <sup>a</sup>
1	As <sup>3+</sup>	As <sub>2</sub> O <sub>3</sub>	1 mg	99.7±4.4
2	Na <sup>+</sup>	NaCl	1.02 g	98.7±3.2
3	Na <sup>+</sup>	NaCl	1 mg	103±7.3
	Li <sup>+</sup>	LiNO <sub>3</sub>	1 mg	
	K <sup>+</sup>	KCl	1 mg	
	Mg <sup>2+</sup>	Mg(NO <sub>3</sub> ) <sub>2</sub>	1 mg	
	Cs <sup>+</sup>	CsNO <sub>3</sub>	1 mg	
	Ca <sup>2+</sup>	Ca(NO <sub>3</sub> ) <sub>2</sub>	1 mg	
4	Ba <sup>2+</sup>	Ba(NO <sub>3</sub> ) <sub>2</sub>	1 mg	97.3±9.4
	Cd <sup>2+</sup>	Cd(NO <sub>3</sub> ) <sub>2</sub>	1 mg	
	Al <sup>3+</sup>	Al(NO <sub>3</sub> ) <sub>3</sub>	1 mg	
	Hg <sup>2+</sup>		1 mg	
	Zn <sup>2+</sup>	Zn(NO <sub>3</sub> ) <sub>2</sub>	1 mg	
5	Cu <sup>2+</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub>	1 mg	99.1±6.6
	Pb <sup>2+</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	1 mg	
	Sb <sup>3+</sup>		1 mg	
	As <sup>5+</sup>	As <sub>2</sub> O <sub>5</sub>	1 mg	
	Se <sup>4+</sup>	SeO <sub>2</sub>	1 mg	
6	Bi <sup>3+</sup>	Bi(NO <sub>3</sub> ) <sub>3</sub>	1 mg	102.5±4.8
	Fe <sup>3+</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub>	1 mg	
	Co <sup>2+</sup>	Co(NO <sub>3</sub> ) <sub>2</sub>	1 mg	
	Ni <sup>2+</sup>	Ni(NO <sub>3</sub> ) <sub>2</sub>	1 mg	
7	Sn <sup>4+</sup>	SnCl <sub>4</sub>	1 mg	99±9.2
	TMT	(CH <sub>3</sub> ) <sub>3</sub> SnCl	8 µg	
	DMT	(CH <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub>	8 µg	
	MMT	CH <sub>3</sub> SnCl <sub>3</sub>	8 µg	
	TBT	(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> SnCl	8 µg	
	DBT	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> SnCl <sub>2</sub>	8 µg	
	MBT	C <sub>4</sub> H <sub>9</sub> SnCl <sub>3</sub>	8 µg	

<sup>a</sup> Mean values±standard deviations.

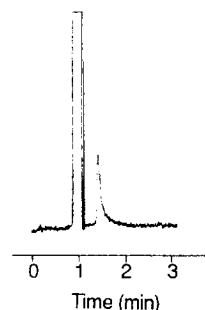


Fig. 5. Typical on-column capillary GC–FPD chromatogram of TMGeCl extracted from a seawater sample. Injection, 2 µl; attenuation: 7; spiked with 0.5 µg l<sup>-1</sup> TMGeCl (as Ge), see Table 1 for chromatographic conditions.

[13]. As shown in Table 3, no interference effects were found in the recovery of 0.2 µg of TMGeCl in 100 ml water when 8 µg of each organotin species, 1 mg of As(III) and other metal cations or 0.02 M of NaCl were present. The only co-extracted species observed in group 7 was identified as (C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnCl (TBT), but its elution (at 9 min) was far beyond TMGeCl in the chromatograms, and showed no interference effect.

### 3.7. Application

A typical chromatogram of a seawater sample is shown in Fig. 5, to which 0.5 µg l<sup>-1</sup> of TMGeCl as Ge was added. Measurements are performed by means of a standard calibration curve with at least triplicate analysis. For all samples determined baseline resolution of TMGeCl was obtained under isothermal conditions and no peak distortion or interference were noted (see Fig. 4). Various water samples, such as tapwater, rainwater, riverwater and seawater were determined by the proposed method, from which no detectable TMGeCl were obtained. The results are given in Table 4.

## 4. Conclusions

A method was developed for the rapid and direct determination of ultra-trace amounts of TMGeCl in water by on-column GC–FPD using quartz surface-induced germanium emission. The treatment of a HP-1 capillary column by injection of 2% HCl in

Table 4  
Determination of TMGeCl in 100-ml water samples<sup>a</sup>

Samples	Spiked level, ng as Ge	Found, ng as Ge
Tap water	50	52.6±4.9 <sup>b</sup>
Rain water	50	49.8±2.4
Sea water 1	50	47.3±3.1
Sea water 2	25	26.2±0.7
Sea water 3	10	9.9±1.2
River water	25	23.9±4.3

<sup>a</sup> Results given are averages of at least triplicate analyses.

<sup>b</sup> Mean values±standard deviations.

methanol prior to analysis is important to obtain reproducible results. Sample preparation is quite simple, the whole extraction procedure can be completed within 10 min followed by 3-min measurement. There is no interference of various ions, especially As(III) and organotin compounds.

No GC-FPD system is reported up to date for the separation and determination of methylgermanium in environmental samples. The proposed method is sensitive, selective, simple and cheap.

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