

Quantitative extraction of methylgermanium species at trace levels and determination by on-column capillary gas chromatography with flame photometric detector *

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Abstract—A solvent extraction procedure for the quantitative extraction of trace levels of methylgermanium species as their chloride complex has been developed and the extract was determined by an on-column capillary gas chromatography with a lab-modified flame photometric detector (FPD) using quartz surface-induced germanium emission after pentylation with Grignard reaction. The extracted percentages for TMGe, DMGe and MMGe in a 100ml 9mol/L HCl aqueous solution by a single extraction with 1 ml hexane are 86.6%, 87.4% and 96.2%, respectively. The precision for overall procedure is ranged from 3.9% to 7.5%. The extraction was found to be independent of the initial concentration of methylgermanium species in the aqueous phase, which typically varied from 0.1 to 10 μg . This method is suitable for most types of environmental samples and, are superior to all hydride generation coupled spectrometric and spectrophotometric methods in terms of selectivity and tolerance ability to interference.

Keywords: solvent extraction; methylgermanium; GC-FPD.

1 Introduction

Germanium can be presented in environment in the form of inorganic Ge and methylgermanium species $(\text{CH}_3)_n\text{GeCl}_{4-n}$ ($1 \leq n \leq 3$) (Lewis, 1988). Inorganic Ge has been determined mainly by spectrophotometric methods, the reaction of germanium with phenylflurone in acid solution was widely used for analysis in the microgram range (Burns, 1980). Due to its tendency to form very stable oxide species, germanium shows relatively poor sensitivity in flame atomic absorption method (Johnson, 1973). Hydride generation technique, based on germane formation, has been coupled with various spectrometric technique for quantification, with the detection limits so far reported at ng to sub-ng levels (Guo, 1990; Hahn, 1982; Brindle, 1987). Until recently, however, methylgermanium species has not been among the popular organometallic compounds to be detected in environmental samples. During the last fifteen years, only a few publications included the speciation of methylgermanium species; hence no more than 10

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publications could be traced in the literatures. Apparently successful methods up to date are all based on a coupled hydride generation technique. Braman and Tompkins (Braman, 1978) determined monomethylgermanium (MMGe) and dimethylgermanium (DMGe) as hydrides by passing the gas into a dc discharge atomic emission detector and obtained detection limits at the sub-ng range. Hambrick *et al.* (Hambrick, 1984) separated germanium on a cryogenic trap packed with 15% OV-3 silicone oil on 60–80 mesh chromosorb W-AW-DMCS and confirmed the existence of MMGe and DMGe in seawater by using sodium tetrahydroborate to create the corresponding volatile hydrides, followed by cryogenic trapping and atomic absorption spectrometric determination. The presence of trimethylgermanium (TMGe) has been detected in a rainwater and a liquid fraction of sludge samples with the same system (Hambrick, 1984; Lewis, 1989). Jin *et al.* (Jin, 1991) compared several packing materials and developed a procedure using salinized quartz beads to separate Ge from methylgermanium species. The detection limits at the sub-pg level could be obtained by inductively coupled argon plasma mass spectrometry (ICP-MS). However, hydride generation itself is not free from interference which to be considered very severe for germanium (Brindle, 1990; Donaldson, 1984).

In view of analytical methodologies, the application of solvent extraction procedure to inorganic Ge was one of the most widely used methods over the past several decades (Brink, 1957; Marzenko, 1986). Recently, Sohrin (Sohrin, 1991) reported the study of the solvent extraction behavior of organometallic and inorganic germanium, a 5×10^{-5} mol/L– 1×10^{-3} mol/L (3.7–74 mg as Ge) range of organogermanium compounds as their chloride complex can be extracted from different concentrations of hydrochloric acid by carbon tetrachloride. Although no analytical and quantitative extraction of germanium species was up to now performed at trace levels, which is essential to the studies of environmental samples, it seems possible to develop chromatographic or spectrometric method based on solvent extraction.

During our previous studies, a system by on-column capillary gas chromatography with flame photometric detector using quartz surface-induced luminescence was established and optimized to the determination of organotin and methylgermanium species. The detection limits of 0.7–2.3 pg of organotin as Sn and 50–150 pg of methylgermanium as Ge can be routinely obtained (Jiang, 1996; 1997). In this paper, the quantitative extraction of trace levels of methylgermanium species as their chloride complexes is investigated and the GC-FPD using quartz surface-induced emission system is further improved and optimized.

2 Experimental

2.1 Apparatus

A CP-9001 gas chromatograph (Chrompack, Middleburg, The Netherlands) equipped with an air-cooled (300 ml/min) on-column injection system was used throughout the experiments. A 1.8 m piece of deactivated fused silica column serving as retention gap was installed between the on-

column injection port and the capillary column via a press-fitted back connector(Chrompack). A 25 m × 0.32 mm × 0.17 μm HP-1 capillary column (Hewlett-Packard, Avondale, PA, USA) was used as the analytical column. The column temperature was programmed at 50°C for 1 min and then heated to 200°C at 20°C/min. The carrier gas was nitrogen (99.999%, Alphagaz, Belgium) without further purification. The column head pressure was maintained a 150 kPa. A combination of hydrogen and air was used for the detector gases, typical flow rates are 280 ml/min for hydrogen, and 140 ml/min for air(both from Alphagaz, high purity grade).

A lab-modified flame photometric detector(FPD) was housed in the same place by removing the commercial FPD. The basic configuration of the detector was described earlier ((Jiang, 1997a). The detector body was machined from stainless steel with a movable burner made by coaxially soldered three stainless steel tubes. A 6 mm i. d. × 75 mm high clean and transparent quartz tube was slipped over the burner to shield the flame. The previously used straight aluminium delivery tube insulated by water-cooled copper coils placed between flame region and the photomultiplier tube was replaced by a 150mm × 10mm i. d quartz bar, which allows the detector to be operated over a wide temperaure range and hence, the introduction of purge gas to protect the PMT surface from water condensation was unnecessary. The measurement was carried out by using a conventional photomultiplier tube (PF-1042, Burle, USA) with a 394 nm interference filter. Output signals were recorded by a Chrompack PCI revision 5.0 data acquisition and processing system.

2.2 Reagents

Monomethylgermanium trichloride (98%), dimethylgermanium dichloride (99%) and trimethylgermanium chloride(90%) were purcheshed from Alfa products. *n*-pentylmagnesium bromide (2.0 mol/L) in diethyl ether was obtained from Aldrich Chemical Co. (Milwaukee, WI, USA). The individual standard stock solutions were prepared by dissolving methylgermanium chlorides in water-methanol (70/30) solutions, each containing a concentration of about 1 mg/ml as Ge. When stored in a refrigerator, these solutions were stable for at least six months without detectable concentration changes. A mixed working standard, obtained by diluting 1 ml of each of the concentrated standard stock solutions in 100 ml with deionized water(10 μg/ml, as Ge), was used in extraction recovery experiments.

All other reagents used were of analytical reagent grade; the water was deionized and further purified through a Millipore Milli-Q system.

2.3 Extraction and pentylation

Most of our work has been done with 100 ml sample size. When aqueous volume of up to 400 ml was analyzed, 500 ml separatory funnels were used. For a routine operation, 100 ml of an aqueous phase containing the desired concentration of acid was placed in a 100 ml Teflon capped glass separatory funnel, a 1 ml of standard solution containing 0.1 μg—10 μg of TMGe, DMGe and MMGe was added and allowed to stand 1 min for equilibration. A 1 ml portion of hexane as extractant was then added, the separatory funnel was manually shaken for 5 min. After

equilibration, the funnel was allowed to stand for 2 min until phase separation occurred. The lower aqueous phase was run off into a breaker and the upper part of the hexane phase was removed to a 10 ml reaction vessel for the following pentylation.

Three methylgermanium extracts, $(\text{CH}_3)_n\text{GeCl}_{4-n}$ ($1 \leq n \leq 3$), were directly pentylated by adding 0.5 ml of pentyl magnesium bromide (PeMgBr) in diethyl ether (2 mol/L solution). The reaction mixture was gently swirled around for 5 min at room temperature and subsequently treated with 10 ml of a 0.5 mol/L H_2SO_4 solution to destroy the excess of Grignard reagent. After washing with Milli-Q water, the organic phase containing $(\text{CH}_3)_n\text{GePe}_{4-n}$ ($n = 1, 2$ and 3) was pipetted into a small cap vial. This solution was then ready for GC-FPD analysis, which typically required 1–2 μl of sample.

The pentylated methylgermanium standards were confirmed by a GC-MS system using electron impact ionization (Jiang, 1997b).

3 Results and discussion

3.1 Effect of extractant

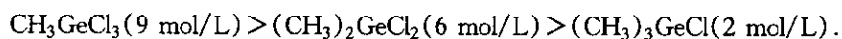
Although carbon tetrachloride, chloroform, and other heavy solvent were most commonly used for the extraction for inorganic germanium (Strickland, 1955; Luke, 1956), some authors found that the extraction was not complete even when the volume ratio of aqueous to organic phase is 1:1 (Strickland, 1955). An extraction with non-polar solvent of specific gravity < 1 from 9.4 mol/L HCl has been recommended (Donaldson, 1984). To evaluate the difference, the extraction of TMGe from hydrochloric acid solutions by solvents has been examined. It is found that carbon tetrachloride is not suitable for the direct pentylation by Grignard reaction, since the product is divided into two parts, the carbon tetrachloride remaining on the bottom of the reaction vessel, while the light solvent from the Grignard reagent, such as diethyl ether, distributed in the upper part of the aqueous phase and caused loss of the analyte. Similarly, pentane reacts vigorously with diluted H_2SO_4 and water during the washing step, which also results in irreproducibility and low recovery. Hexane was chosen because it is readily available and has a favorable extraction capacity with respect to all the three methylgermanium species, and more importantly, the Grignard reaction can proceed smoothly and completely during derivatization. Moreover, unlike extraction with carbon tetrachloride and other heavy solvents, which requires the use of three funnels for the extraction and subsequent washing steps, the use of hexane as extractant resulted in a quicker and simpler procedure because all these operations could be carried out in the same funnel.

3.2 Effect of HCl and HBr

It is believed that the methylgermanium species, similar to Ge (IV) with tetrahedral structures, are present as uncharged forms rather than free ions in aqueous. The hydroxide ions occupy the residual coordination sites of the central Ge atom, producing a nonionic hydroxide complexes $(\text{CH}_3)_n\text{Ge}(\text{OH})_{4-n}$, $n = 1, 2$ and 3). In solutions of hydrohalogenic acid, however,

halide ions occupy the residual coordination sites, forming the methylgermanium halide complexes $((\text{CH}_3)_n\text{GeX}_4)_n$, $X = \text{Cl, Br and I}$, which can be extracted into carbon tetrachloride and other organic solvent (Donaldson, 1984; Brink, 1957).

The concentration of hydrohalogenic acid has a significant effect on the extraction. Fig.1a shows the extraction curves with various HCl concentrations. For all methylgermanium species, the percentage increases with increasing acidity, and reaches a constant above a specific concentration for the acid for each germanium compounds. This trend is similar to that observed in the extraction of other elements such as arsenic, antimony and tin with sulfuric acid system (Byrne, 1972; Suzuki, 1986). Furthermore, as the number of methyl-group attached to germanium increases, this specific concentration becomes lower. The extraction curves show that a considerable difference exists among the concentrations of hydrochloric acid needed to quantitative extraction of each methylgermanium species:



It is not yet clear which effect is responsible for these apparent difference in the concentrations of HCl. Some author attributed this to the inductive effect of the methyl-group, which weakens the Lewis acidity of the germanium atom and reduces the stability of the hydroxide complexes ((Sohrin, 1991).

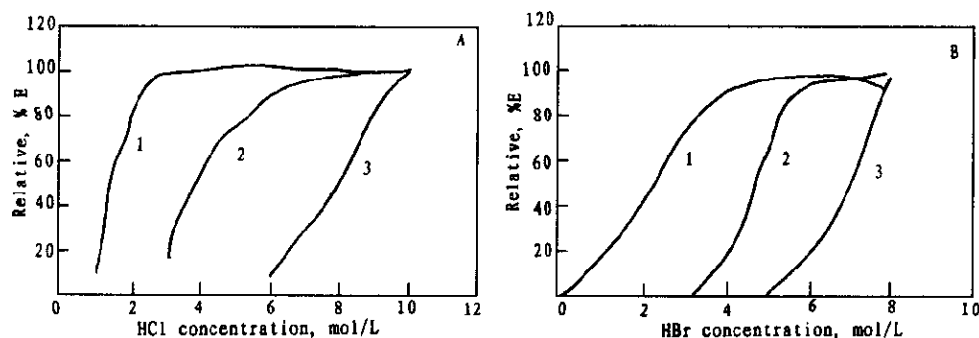


Fig.1 Effect of HCl(Fig.1a) and HBr(Fig.1b) concentrations on extraction

1. TMGe; 2. DMGe; 3. MMGe

The extraction behavior of HBr was also studied as the function of hydrobromide complexes. Although hydrobromide acid can be used to extract methylgermanium compounds, Fig.1b shows that it appears to offer no advantages over HCl medium since the HBr concentration necessary for quantitative extraction of TMGe is higher, and the extraction recovery for all three methylgermanium species are slightly low.

3.3 Extraction time

The distribution equilibrium between two phases can be reached quickly in 9 mol/L HCl for all three methylgermanium species. We found that the extraction time did not depend on the initial concentration of these compounds in the aqueous phase, which typically varied between

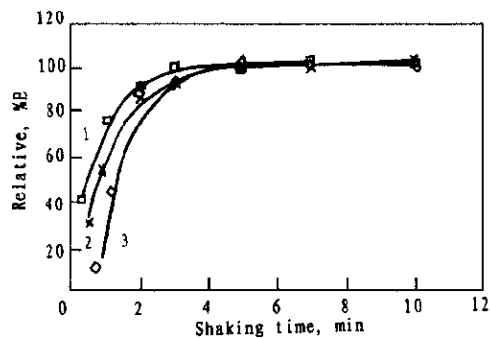


Fig. 2 Influence of extraction time

1. TMGe; 2. DMGe; 3. MMGe

evaporation, a large volume of organic phase as extractant is considered not suitable because of the difficulty of condensation. Fig. 3 shows the extracted percentages obtained by using 50:1—400:1 aqueous to hexane phase ratio. For the aqueous-hexane ratios typically at 50:1 and 100:1, more than 86.6% of TMGe, 87.4% of DMGe and 96.2% of MMGe can be obtained by a single extraction, and no TMGe and DMGe were detected in the water phase after three consecutive extractions, whereas no significant amount of MMGe was found in the second extraction. Upon increasing of aqueous volume, however, the extracted percentages by a single extraction for all methylgermanium drops quickly down to less than 60%. For instance, at the aqueous-hexane ratio of 400:1, the extracted percentage of TMGe for a single extraction was 53.9%, the second extraction was 27.6%, hence a third extraction was necessary, which extract the rest part of 17.3%. Therefore, an aqueous volume of 100 ml or less and 1 ml of hexane are recommended for quantitative extraction of methylgermanium species.

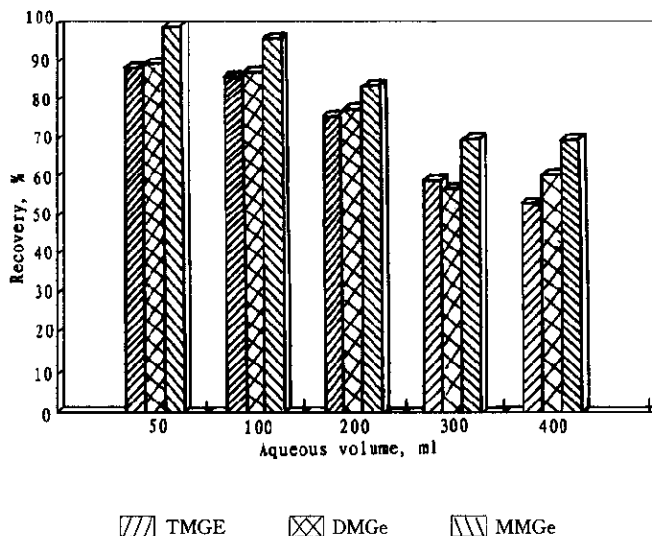


Fig. 3 Recoveries in different aqueous volume

0.1—10 μg . Fig. 2 shows the effect of extraction time on the relative recoveries. A shaking time of about 4 min was necessary to attain quantitative recovery, and for routine operation 5 min was used.

3.4 Influence of aqueous-organic phase ratio

The recovery not only depends on the distribution ratio(D) but also on the volume ratio of aqueous to organic phases. The volatilization of methylgermanium proved to be important in an attempt to reduce the volume of extracts by rotary

3.5 Calibration curve

To avoid errors in experiment results, it is necessary to compensate for the loss of methylgermanium during a single extraction procedure by including the extraction in the preparation of the calibration curve, which was done by taking all the solutions used for calibration purposes through the extraction step. The calibration curve obtained were linear over the range of 1–5 μg Ge in 100 ml aqueous phase. The parameters calculated from calibration functions is shown in Table 1. The correlation coefficients were 0.9998, 0.9986 and 0.9987 for TMGe, DMGe and MMGe, respectively.

Table 1 Calibration data and method evaluation for organogermanium using GC-FPD

Compounds	Concentration range, ng as Ge	Slope, m	Y-intercept	Correlation coefficient	Detection limit, pg^a	Reproducibility ^b , %	Precision ^c , %	Instrument stability ^d
TMGe	1–5	61.6	-23.8	0.9998	50	3.4	3.9	3.4
DMGe	1–5	33.1	-41.4	0.9986	70	5.1	6.2	5.4
MMGe	1–5	27.3	-25.8	0.9987	100	4.8	7.5	6.0

a. Based on signals equal to 3 times the baseline noise; b. 10 times consecutive injections of the same standard solutions; c. measurements through the entire procedure; d. checking everyday for a week.

3.6 GC-FPD determination

The optimal GC-FPD parameter were worked out using standard pentylated methylgermanium compounds. The peak shape and height were observed to be strongly dependent on the quartz tube. By using a 6 mm i. d. \times 75 mm high clean and transparent quartz tube, which slipped over the burner to shield the flame, a sharp and symmetric GC-FPD chromatogram as represented in a typical example in Fig.4 was obtained. It was also proved that the peak height was considerably influenced by hydrogen and air flow rates. The optimized values were 280 ml/min for hydrogen and 140 ml for air. The retention times for TMGe, DMGe and MMGe are 1.7 min, 4.4 min and 6.6 min, respectively, which are in a fair agreement with a GC-MIP-AES system using PDA detector and the similar column conditions. The pentylated methylgermanium compounds were further identified by a GC-MS system using electron impact ionization(Jiang, 1997b).

To evaluate the performance of this GC-FPD system and the proposed method, several parameters were measured. The results are listed in Table 1. Reproducibility was determined by carrying 10 times

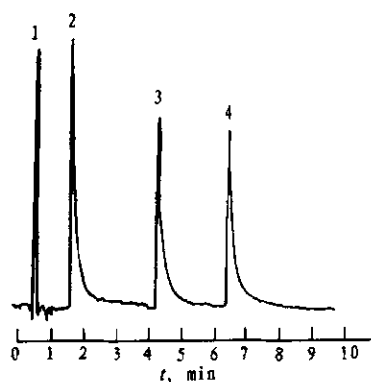


Fig.4 Typical on-column capillary chromatogram of 3 methylgermanium species under optimized GC-FPD conditions. Peak identified as: 1. solvent; 2. TMGe, 0.5ng; 3. DMGe, 1.0ng; 4. MMGe, 1.2ng

consecutive injections of 5 ng methylgermanium standard. It was noted that the error during the measurement was mainly due to the on-column syringe and the injection port rather than the detector itself. Hence, to increase the accuracy of injection, a 2 μ l injection volume was used. The precision of the method was evaluated by analyzing seven 100ml aqueous solutions spiked with 5 μ g of methylgermanium species through the entire analytical procedure. Instrument stability was checked daily by injecting 5 ng of methylgermanium standard prior to analysis. The detection limits (3σ) for tri-, di-, and monomethylgermanium were 50, 70 and 100 pg, respectively.

3.7 Recovery

Owing to the lack of certified standards for methylgermanium species, the accuracy of the extraction procedure cannot be estimated directly. Therefore, standard additions of known amounts of methylgermanium compounds to 50 ml and 100 ml aqueous solutions were performed. The overall mean recoveries calculated by calibration curve were 97%—101% for TMGe, 97%—103% for DMGe and 98%—104% for MMGe. The experimental results shown in Table 2 suggested that there is no significant systematic error in the described procedure, and moreover, the recoveries did not depend on the initial concentration of methylgermanium species between 0.1 and 10 μ g range in 100 ml aqueous phase.

Table 2 Recovery experiment

Spiked, μ g	Aqueous volume, ml	Recoveries, %		
		TMGe	DMGe	MMGe
5	100	99 \pm 6	98 \pm 9	102 \pm 8
5	50	100 \pm 4	103 \pm 7	98 \pm 8
1	100	97 \pm 4	99 \pm 4	104 \pm 13
0.5	100	101 \pm 5	97 \pm 4	102 \pm 6

3.8 Interferences

Unlike the usage of hydride generation coupled with varied spectrometric detectors which is considered virtually not free from interference, the solvent extraction procedure has high selectivity, and was further improved by a specific pentylation and measurement procedure, therefore, such interferences in the GC-FPD system could be considered not present. However, previous investigations found that some metal cations, such as arsenic(III) as chloride and osmium and ruthenium as the tetraoxides, are co-extracted into the organic phase at high hydrochloric acid concentrations (Brink, 1957). Os and Rh are rarely present in environmental samples. It was considered necessary to investigate the possible interference effect of various elements that would be completely or partly co-extracted. Table 3 lists the results of the effects of one or more commonly encountered metal ions on the determination of 5 μ g methylgermanium species. Those results showed that, when 5 μ g Ge is presented in 100 ml aqueous sample, up to at least 1 mg of As (III) can be presented during the extraction step without interfering in the extraction of

methylgermanium species. All other metal cations tested do not interfere when present in 40 to 400 fold w/w ratio to the methylgermanium. The organotin compounds, which can be detected at sub- μg levels by this GC-FPD system, do not interfere the determination at the 50—100 μg range.

Table 3 Effect of interferences on the determination of 5 μg methylgermanium species

Group	Ion, added form, amount	Found, μg , as Ge		
		TMGe	DMGe	MMGe
1	As ³⁺ , As ₂ O ₃ , 1mg; Li ⁺ , LiNO ₃ , 1mg; Na ⁺ , NaCl, 12mg; K ⁺ , KCl, 1mg; Mg ²⁺ , Mg(NO ₃) ₂ , 1mg	5.22 ± 0.14	5.58 ± 0.28	5.13 ± 0.25
2	Cs ⁺ , CsNO ₃ , 1mg; Ca ²⁺ , Ca(NO ₃) ₂ , 1mg; Sr ⁺ , SrNO ₃ , 1mg; Ba ²⁺ , Ba(NO ₃) ₂ , 1mg	4.92 ± 0.22	4.89 ± 0.26	5.11 ± 0.30
3	Co ²⁺ , Co(NO ₃) ₂ , 1mg; Ni ²⁺ , Ni(NO ₃) ₂ , 1mg; Mn ²⁺ , Mn(NO ₃) ₂ , 0.8mg; Al(NO ₃) ₃ , 1mg; Cr ⁶⁺ , CrO ₄ ²⁻ , 0.8mg	4.79 ± 0.08	4.72 ± 0.16	4.79 ± 0.19
4	Zn ²⁺ , Zn(NO ₃) ₂ , 0.5mg; Cu ²⁺ , Cu(NO ₃) ₂ , 0.7mg; Hg ²⁺ , 0.2mg; Cd ²⁺ , Cd(NO ₃) ₂ , 0.2mg; Bi ³⁺ , Bi(NO ₃) ₃ , 0.4mg; Sb ³⁺ , 0.2mg; As ⁵⁺ , H ₃ AsO ₄ , 0.5mg	5.03 ± 0.19	5.21 ± 0.28	5.29 ± 10.39
5	Pb ²⁺ , Pb(NO ₃) ₂ , 0.5mg; Fe ³⁺ , Fe(NO ₃) ₃ , 0.2mg; Se ⁴⁺ , SeO ₂ , 0.5mg; P ⁵⁺ , KH ₂ PO ₄ , 0.5mg	4.79 ± 0.11	4.77 ± 0.18	4.94 ± 0.19
6	Sn ⁴⁺ , SnCl ₄ , 0.5mg; TMT, (CH ₃) ₃ SnCl, 50 μg ; DMT, (CH ₃) ₂ SnCl ₂ , 50 μg ; MMT, CH ₃ SnCl ₃ , 50 μg ; TBT, (C ₄ H ₉) ₃ SnCl, 100 μg ; DBT, (C ₄ H ₉) ₂ SnCl ₂ , 100 μg ; MBT, C ₄ H ₉ SnCl ₃ , 100 μg	5.20 ± 0.12	4.57 ± 0.22	4.46 ± 0.19

4 Conclusions

The proposed method is highly sensitive, selective and less troublesome than others. Interferences from arsenic and other metals are not present. The method is suitable for sediment, soil, sludge, and other environmental samples. For water, the sample can be concentrated by evaporation after being made slightly alkaline with NaOH (Marczenko, 1986).

Considerable difficulty was experienced toward establishing an alternate conditions other than concentrated HCl for extraction of methylgermanium species from water samples in order to develop a suitable extraction procedure for large volume of sample.

The proposed GC-FPD using quartz surface-induced emission is indeed cheap enough and especially worthy of attention for the determination of organotin and organogermanium compounds in environmental samples.

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