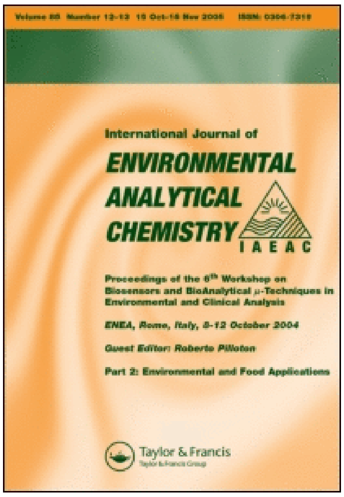

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Analysis of Malodorous Sulfur Gases and Volatile Organometalloid Compounds in Landfill Gas Emissions Using Capillary Gas Chromatography with Programmed Temperature Vaporization Injection and Atomic Emission Detection

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ANALYSIS OF MALODOROUS SULFUR GASES AND VOLATILE ORGANOMETALLOID COMPOUNDS IN LANDFILL GAS EMISSIONS USING CAPILLARY GAS CHROMATOGRAPHY WITH PROGRAMMED TEMPERATURE VAPORIZATION INJECTION AND ATOMIC EMISSION DETECTION

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Volatile compounds containing Group V and Group VI elements in landfill gases are of concern as a source of toxic pollutants and unpleasant odors. Conventional analytical techniques for these compounds e.g. ICP-MS, ICP-AES are complicated, expensive and time consuming. The use of a simple programmed temperature vaporization injection (PTV) technique coupled to gas chromatography with atomic emission detection (GC-AED) has been successfully demonstrated to identify compounds containing arsenic, antimony, and sulfur in landfill gas. With an adapted PTV injection system (using a combination of a ten-port and a six-port Valco valves), problems associated with AED discharge tube damage due to high carrier gas flow rate during sample loading can be overcome. The gas samples generated from both a laboratory biowaste digester and a domestic landfill site were characterized using these techniques. Large sample gas volumes were adsorbed onto a cooled sorbent trap containing Porapak Q, followed by rapid liberation onto a porous layer open tubular column (PLOT) using programmed thermal desorption. Arsenic and antimony were also detected in the landfill leachate collected from the same landfill site using hydride generation-atomic absorption spectrometry (Hy-AAS). The efficiency of different traps has also been compared.

Keywords: Programmed temperature vaporization (PTV); GC-AED; Landfill gas; Arsenic; Antimony; Sulfur

INTRODUCTION

Compounds containing Group V and Group VI elements arise in the environment from both natural[1] and anthropogenic[2] sources. Increasing household and commercial

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applications of these compounds have led to an increase in environmental discharge. Many organometallic compounds are toxic and can be transformed via biomethylation[3] into volatile compounds. The conditions necessary for biomethylation are present in landfill sites, sediments, and sewage works. Additionally, compounds containing sulfur can be transformed into volatile forms by micro-organisms, which are the main source of unpleasant odors associated with landfill sites. There have been several studies of sulfur compounds in landfill gases as mentioned in previous work[4]. Few studies, however, have been focused on organometallic compounds in landfill gases. Certain volatile organic compounds have been identified in landfill gases by Hirner *et al.*[5] and Feldmann *et al.*[6] using ICP-MS. Volatile silicon, vanadium, arsenic, bromine, tin, antimony, tellurium, iodine, mercury, lead and bismuth species have all been identified in landfill gas. Semi-quantification of arsenic, tin, antimony, bismuth, selenium, tellurium, mercury, and lead compounds has been achieved in landfill gas using GC-ICP-MS[7]. ICP-MS however, has several disadvantages such as high running costs, time consuming sample preparation, and the need to interface the separation technique to an ICP-MS instrument. For the same reasons, the routine on-site application of the technique is impractical.

A large volume injection technique coupled to GC-AED has been developed in order to provide a routine method of analysis capable of on-site measurements. The atomic emission detector (AED) is a multi-element detector theoretically capable of identifying any element (except for helium, the plasma gas) with high sensitivity and selectivity. It is capable of monitoring up to four elements simultaneously from a single injection and can define empirical formulae[8–9]. The PTV system allows a large volume of gas to be injected which can be varied according to the species monitored. The samples can be easily adsorbed onto a sorbent trap and then desorbed into a GC column using programmed thermal desorption. This technique eliminates the use of solvents and is more sensitive than the solvent desorption technique. Additionally, the sorbent tube is reusable. However, the choice of the appropriate material is not easy. Each adsorbent material has different adsorption and desorption characteristics. The retention volume of each adsorbed compound depends on the adsorbent surface specific parameters such as the number of active surface area and total surface areas. This study has been carried out to evaluate the effectiveness of thirteen commercially available adsorbent materials using nine volatile compounds in order to choose the most suitable adsorbent trap for trapping volatile organic compounds especially organometalloid compounds in landfill gas.

The valve configuration in this work, linking the PTV to the chromatographic column, has been adapted further from previous work[10] ensuring all sample gas passes through the sorbent trap and eliminates any effect of increasing pressure and also contamination of the GC column during loading of the gas sample. An additional advantage of the developed injection system is that the carrier gas passes through the GC column at all times. This technique allows the helium passing through adsorbed sample on the sorbent trap to reduce the moisture content in the gaseous sample before thermal desorption into the GC. In order to elute the whole sample through the PLOT column and provide well-resolved peaks, a high carrier gas flow rate is required. The balance of flow rate during sample loading and injection is maintained using the developed valve configuration using an additional needle valve placed between the ten-port valve and the GC column. This ensures a steady flow of carrier gas through the column, minimizing the possibility of AED discharge tube damage.

The main aim of this work was to develop simple techniques for the analysis of highly volatile compounds containing Group V and Group VI elements, in particular organometalloid and sulfur species, in landfill gas. Using the developed techniques, characterisation of trace volatile organometalloid and sulfur compounds in domestic landfill gas can be easily identified by monitoring their characteristic emission line spectra. Identification of compounds containing sulfur, arsenic and antimony has been demonstrated by monitoring the emission lines at 181 nm, 189 nm and 218 nm, respectively. Determination of arsenic and antimony in landfill leachate collected from the same site using Hy-AAS has confirmed that the landfill site contains these elements. A comparison of the emission of volatile sulfur compounds from a laboratory biowaste digester and domestic landfill gas has been made.

EXPERIMENTAL

Materials and methods

PTV-GC-AED method

A Hewlett-Packard HP 5921A atomic emission detector and a HP 5890 series II gas chromatograph were coupled to a programmed temperature vaporization injection (PTV) (AI-Cambridge, ATAS, UK) containing a sorbent trapping material. The GC column employed was a GS-Q, 30 m × 0.53 mm i.d. PLOT column (J&W Scientific Incorporated, UK). The PTV injection system used a combination of a VICI ten-port valve and a six-port valve, assembled with stainless steel and VESPEL rotor seals (Valco Instrument Co., Inc., USA) and stainless steel tubes, 1.63 mm o.d., as the connection, as shown in Fig. 1. These valves were held at room temperature during operation. About 1 g of 80–100 mesh Porapak Q (Waters Assoc. Inc., USA) was used as the trapping sorbent. The PTV injector was programmed from 1°C (initial

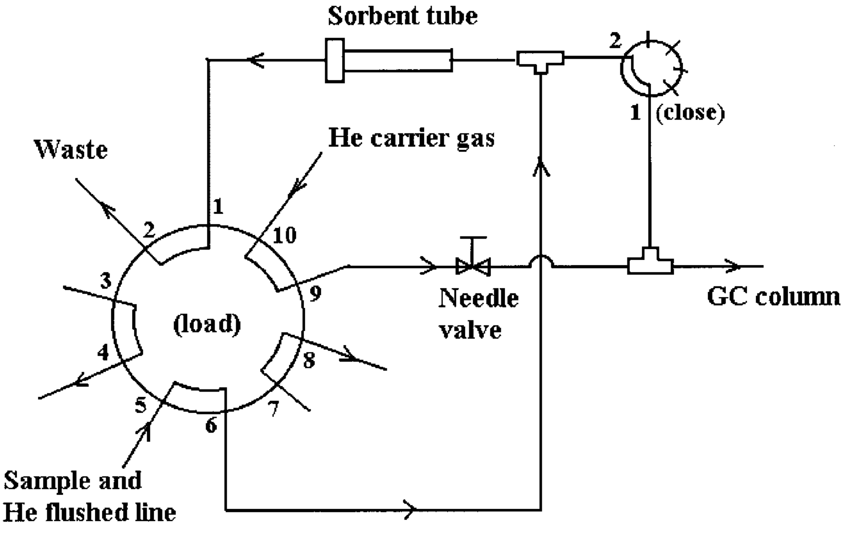

FIGURE 1 Schematic of ten-port valve injection system.

temperature) to 210°C at 16°C min^{-1}, holding at 210°C for 10 min. Cooling of the PTV injector was performed using liquid carbon dioxide (BOC, UK). However an ethylene glycol jacket has previously been demonstrated to be sufficiently cooled [10]. The GC oven was programmed from 60°C (initial temperature), holding at 60°C for 1 min, to 170°C at 8°C min^{-1}, then increased from 170°C to 240°C at 4°C min^{-1}, holding at 240°C for 20 min. Helium (99.999% purity, Air Products, UK) was used as the carrier gas at a flow rate of 10 ml min^{-1}. The transfer lines to the AED and the AED cavity were operated at 320°C. The spectrometer was purged with nitrogen at 2 l min^{-1}. A high flow rate of helium gas was used as a make-up gas and hydrogen gas was used as the reagent gas. The cooling water temperature was 63°C. Emission lines used to detect carbon, sulfur, arsenic, and antimony were 193.03 nm, 181.38 nm, 189.04 nm, and 217.58 nm, respectively. Data was processed using a HP 382 Chemstation and HP 35920A GC-AED software. The solvent vent was opened for 5 min. The sample was loaded onto the cooled sorbent trap through the ten-port valve in loading position and flushed with helium at a flow rate of 100 ml min^{-1} for 1 min to reduce/eliminate the moisture content of the gaseous sample. With the valve in the injection position, the trap was heated rapidly and flushed with helium resulting in sample desorption onto the GC column. After each analytical run, the sorbent trap was cleaned with the transfer valve in the loading position to remove contamination. The cleaning cycle consisted of purging the PTV injector with helium whilst maintaining the trap 210°C for 10 min. For each analysis, a blank run was performed after cleaning. The cleaning cycle ensures that high molecular weight residues contained in the trap do not pass through to the GC column and minimizes ghost signals. Instrument, laboratory and field blanks were all obtained using the same instrument conditions as the sample.

Hydride-AAS method

A Hydride vapor generator (Varian Model 65) connected to an atomic absorption spectrometer (Spectra AA-10 Varian) was used for analysis of landfill leachates for As, Se, Sb. Absorbance, standard addition, and peak height were used as instrument, calibration, and measurement modes, respectively. An air–acetylene flame was used. There was no delay time and the measurement time was 10 s without replication. Background correction was employed. Nitrogen purge flow rate was 1 l min^{-1}. Wavelengths for As, Se, and Sb were set at 193.7 nm, 196.0 nm, and 217.6 nm and slit widths for As, Se, and Sb were set at 0.5 nm, 1 nm, and 0.2 nm, respectively.

Description of landfill site

The landfill site contained primarily domestic wastes but also contained some chemical wastes in limited volumes. The landfill site was situated on an old quarrying site with a lining system and had been capped for approximately two years. Leachate, which is produced from biodegradable materials by micro-organisms in landfill, was collected from a leachate pond at the site. Leachate was circulated into the landfill in order to increase the number of micro-organisms, and add food supply, and moisture for the growth of micro-organisms in the landfill. The remainder of the leachate is treated via wastewater treatment processes before release into a river.

Sample preparation

Standard preparation

In view of the wide range of compounds in the sample matrix, only semi-quantitative determinations were possible, and these were based on detection responses determined as follows.

1 µl of each liquid sulfur standard (dimethyl sulfide, ethyl methyl sulfide and dimethyl disulfide) (Aldrich) and 1 µl of liquid hydrocarbon (benzene (Vickers, UK), *n*-pentane (Riedel-deHaen)), chlorinated hydrocarbon (dichloromethane and trichloromethane) (Riedel-deHaen), and oxygen containing standards (methanol and ethanol) (Riedel-deHaen) were mixed in a 500 ml flask sealed with a SUBA seal, previously flushed with nitrogen gas. Hydrogen sulfide, sulfur dioxide, carbonyl sulfide (COS) and methyl mercaptan were injected without precise knowledge of concentration and were only used to determine retention times of standards and to estimate semi-quantitative data. To select the suitable sorbent traps for highly volatile compounds, 0.5 ml of the flask contents was injected into the sorbent trap, using a gas tight syringe, and then desorbed into the GC-AED by programmed thermal desorption. For production of a standard curve, the standard was diluted 50 times and 5, 10, 20, 30 and 50 ml of this standard were adsorbed onto a Porapak Q sorbent tube and then desorbed into the GC-AED using the same analytical sequences mentioned above. All standards were prepared at room temperature.

Sorbent trap preparation

About 1 g of Chromosorb G 80–100 mesh, Molecular Sieve 5A 60–80 mesh, (Phase Separation Ltd, UK), Porapak type S 50–80 mesh, PS 50–80 mesh, Q 80–100 mesh, QS 50–80 mesh (Waters Assoc. Inc., USA), Carboxen 1000 60–80 mesh, Carbopack™ B 60–80 mesh, Tenax TA 60–80 mesh, Carbosieve SIII 60–80 mesh, 10% SP-2100 (Supelco, UK), Aluminium oxide (neutral) 100–240 mesh (Hopkin and Williams Ltd., UK), and Graphite powder synthetic (BDH, UK) were packed into the sorbent tubes. The packed sorbent tubes were cleaned by simultaneous heating at 210°C for 1 h and flushing with helium gas at 100 ml min^{-1}. A blank was run before analysis with each sorbent tube to ensure that no contamination was present. However, increasing cleaning time may be required for a trace analysis (ng m^{-3} level) to remove artefact materials.

Biowaste samples

To test the analytical methodology, a series of biowaste gases were studied. 500 g of mixed meat, vegetable and fruit were liquidized with 500 ml of water and transferred into a 1.5 l gas seal digester. 50 ml of sewage sludge were inoculated into the digester. Nitrogen gas was purged through the digester for a few minutes to remove oxygen, providing an anaerobic environment. The digester consisted of a heated vessel fitted with an exhaust gas vent and a feed vent. The exhaust vent was connected via a Teflon tube to a two-liter polypropylene cylinder (BDH, Merck Ltd, UK) enabling collection of gas by displacement of water. The feed vent was capped to prevent gas escape. The schematic diagram of the digester is shown in Fig. 2.

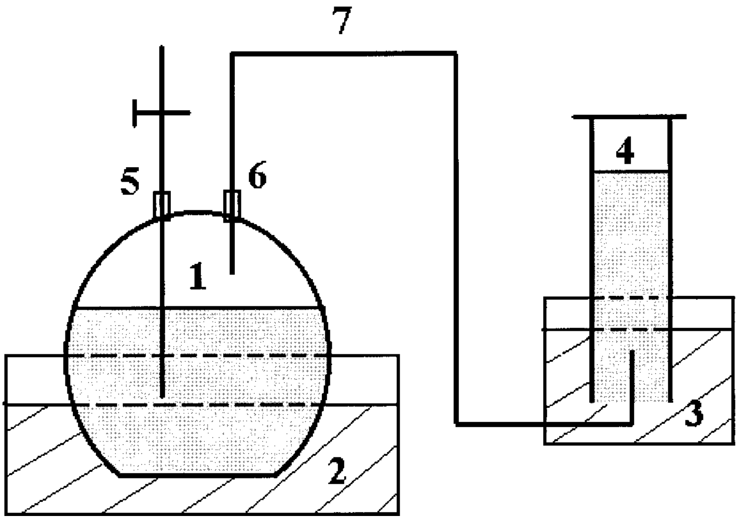

FIGURE 2 Schematic diagram of a biowaste digester: 1, Digester; 2, Water bath; 3, Water container; 4, Two-litre polypropylene cylinder; 5, Feed vent; 6, Exhaust gas vent; 7, Teflon tube.

Two digestion experiments were studied. One was incubated at a temperature of 36°C (mesophilic condition) and the other was incubated at 55°C (thermophilic condition). An aliquot of 80 ml of fresh biowaste was added to the mesophilic digester every day whilst the same amount of the digester contents were removed with a syringe to maintain the volume of the digester contents. Similarly 150 ml of fresh biowaste was added into the thermophilic digester daily and the same volume of the digester contents were removed to maintain the volume. The digesters were operated over a hydraulic retention time of 10 days. Calcium oxide was added to the digesters to adjust the pH to about 7 in order to prevent any inhibition of microbial activities. Biowaste gas, collected by displacement of water in the two-liter polypropylene cylinders, was taken from the cylinder with a gas tight syringe. A 20 ml aliquot of the gas (at atmospheric pressure) was loaded onto the sorbent trap containing Porapak Q using a gas tight syringe and liberated into the GC-AED by programmed thermal desorption.

Landfill gas samples

Landfill gases were taken directly from ducts through a 1 m long Teflon tube (1.58 mm i.d.) (Thames Restek, UK) into three liter UV protected Tedlar bags (SKC Inc., USA) to prevent photodegradation. All samples were collected at room temperature. The filled bags were brought back to the laboratory. As a result of the study of sorbent trap efficiency, Porapak Q was used as a sorbent material. 100 ml samples of landfill gas (measured at atmospheric pressure) were passed through the sorbent trap and desorbed into the GC-AED.

Leachate sample

Samples of landfill leachate were collected from a leachate pond in the same domestic landfill site as the domestic landfill gas. A number of inorganic compounds, principally heavy metals, disposed of in the landfill are dissolved in leachate when the leachate is under acidic condition. In this work the leachate was analyzed for arsenic, selenium and antimony using hydride generation-AAS.

Determination of metals using hydride generation-AAS

An arsenic standard (H_3AsO_4) 1000 mg l^{-1} in 0.5 mol l^{-1} nitric acid (BDH, Merck Ltd, UK), selenium standard (SeO_2) 1000 mg l^{-1} in 0.5 mol l^{-1} nitric acid (BDH, Merck Ltd, UK) and antimony standard ($SbCl_3$) 1000 mg l^{-1} in 5 mol l^{-1} hydrochloric acid (BDH, Merck Ltd, UK) were used as standard stock solutions. Analysis of the leachate samples was performed using a standard addition calibration technique. Sample solutions were prepared by mixing 1 ml of leachate with 100 ml distilled water. 2.5% sodium borohydride solution was prepared by dissolving sodium borohydride powder 98% ($NaBH_4$) (Aldrich) in 0.1% sodium hydroxide solution (NaOH), which was prepared from NaOH pellets (AR, Prolab, UK). 1 : 1 HCl was prepared by diluting conc. HCl (AR, Fisher Scientific, UK) in distilled water.

10 ml of standard addition or sample was mixed with 10 ml of 1 : 1 HCl in the hydride generator. Five milliliters of 2.5% sodium tetrahydroborate ($NaBH_4$) in 0.1% NaOH were then injected into the generator. Hydride gas generated was swept to a heated T-shaped absorption cell using nitrogen gas (BOC, UK) at 1 l min^{-1}. Each sample was measured with 3 replicates.

RESULTS AND DISCUSSION

Table I shows minimum detectable levels and linear dynamic ranges of the AED detector[8] for monitored Group V and Group VI, and carbon elements. As the concentration of compounds containing Group V and Group VI in landfill gas is low, a pre-concentration step before gas chromatographic analysis is required. A cryogenic trap is widely used for the pre-concentration method for reduced sulfur gases[11–12]; however the use of a solid adsorbent trap for pre-concentration of these compounds has increased[13–17]. A cooled sorbent trap without the use of secondary cryogenic trapping[18] was used in this work. Selectivity of the adsorbent is a useful property for the analysis of trace compounds in complex samples such as landfill gas because it can reduce the problem of matrix component interference and also increase the

TABLE I Principal spectral emission lines, minimum detectable limits (MDL), and linear dynamic range of some commonly monitored elements [8]

Element	*Wavelength* (nm)	*MDL* (pg s^{-1})	*Selectivity over carbon*	*Dynamic range*
Carbon	193	1	–	2×10^4
Sulfur	181	2	8000	1×10^4
Phosphorus	178	1	5000	1×10^3
Nitrogen	174	50	2000	2×10^4
Arsenic	189	25	10000	1×10^3
Selenium	196	25	10000	1×10^3
Antimony	218	25	5000	5×10^2

TABLE II Order of the efficiency of different traps

Sorbent trap	*MeOH*	*EtOH*	*DCM*	*Pentane*	*TCM*	*Benzene*
Aluminium oxide	10	11	9	9	9	9
Carbopack® B	7	5	6	5	6	6
Carbosieve SIII	3	9	8	11	11	11
Carboxen 1000	4	8	5	6	5	5
Chromosorb G	9	6	13	13	13	13
Graphite powder	8	10	11	10	10	10
Molecularsieve 5A	12	13	10	8	8	8
Porapak Q	2	3	4	3	4	4
Porapak QS	6	7	7	7	7	7
Porapak S	1	4	3	4	2	2
Porapak PS	5	2	2	2	3	3
10% SP-2100	11	12	12	12	12	12
Tenax TA	13	1	1	1	1	1

Remarks: 1 means higher efficiency and 13 means lower efficiency; MeOH = methanol; EtOH = ethanol; DCM = dichloromethane; TCM = trichloromethane.

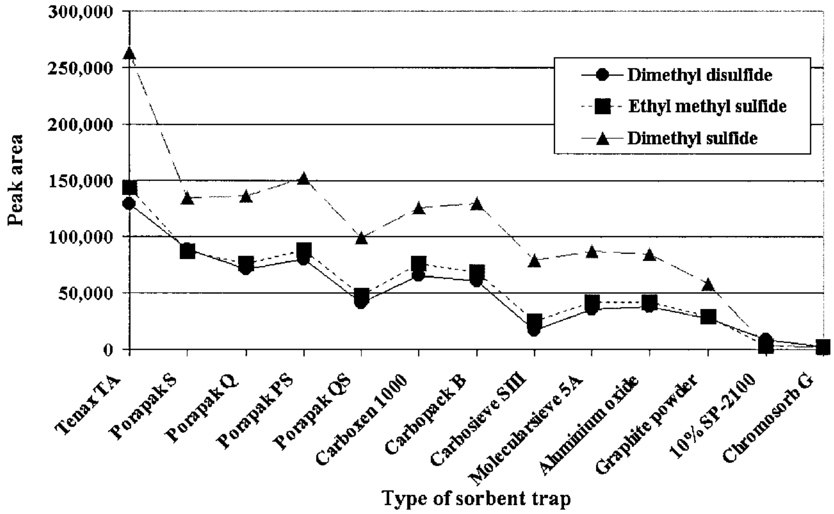

FIGURE 3 Efficiency of different adsorbent traps for trapping volatile sulfur compounds.

analytical detection limit. The six hydrocarbon and three sulfur standards were analyzed in triplicate using each of the different trapping materials on the carbon channel (193 nm) as shown in Table II and sulfur channel (181 nm) as shown in Fig. 3, respectively. A comparison of different sorbents for trapping the standards has been made for the same weight of sorbent trap (0.1 g). In Table II the highest efficiency was indicated as 1 whereas the lowest efficiency was indicated as 13. From the results (Table II and Fig. 3), which represent adsorption based on the same weight, Tenax TA is the most effective sorbent trap but it has a lower affinity for highly volatile compounds and highly polar compounds. However, the mass of Tenax TA packed in the sorbent tube is less due to its low density. Porapak sorbent traps are suitable for both highly volatile and polar compounds because of its high surface area and polarity. The adsorption efficiency of Porapak Q and Tenax TA has been compared for landfill gas by a calculation on the same weight of sorbent trap (0.1 g) as shown in Fig. 4.

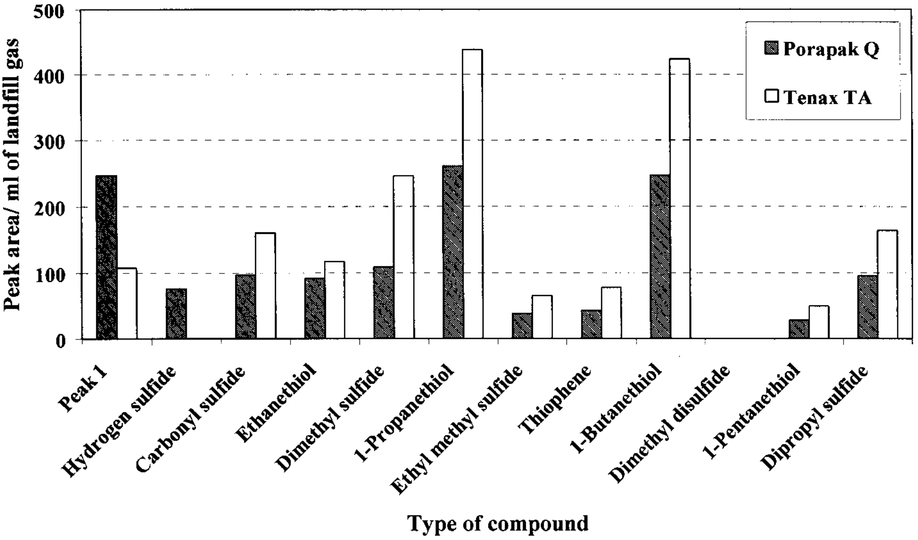

FIGURE 4 Comparison of the efficiency of Porapak Q and Tenax TA sorbent trap for trapping domestic landfill gas using PTV-GC-AED.

Porapak Q is more efficient than Tenax TA for trapping highly volatile compounds. Moreover, hydrogen sulfide is not adsorbed on Tenax TA. As this study is preliminary to identify organometalloid compounds in landfill gas using simple developed methods, only qualitative analysis has been examined; however, % recovery and efficiency, and breakthrough volume (BTV) of the adsorbent trap will be required for quantitative analysis.

The use of a PLOT column produces better resolution for sulfur compounds and enables the more volatile compounds to be more easily identified than in the previous work[10]. The method was found to be repeatable ($< 5\%$ RSD, $n = 3$ for Porapak Q) based on four hydrocarbon standards but not for methanol and ethanol. The highly volatile compounds containing sulfur from both the biowaste digesters and the domestic landfill were clearly resolved using PTV-GC-AED and a PLOT GC column. Figure 5 shows chromatograms of sulfur compounds emitted from the mesophilic digester (36°C) (Fig. 5A), thermophilic digester (55°C) (Fig. 5B), and domestic landfill (Fig. 5C). Compounds containing sulfur were confirmed using elemental emission spectra ‘snapshots’ and were identified using retention times of standards. Operation of the mesophilic digester produces higher sulfur emissions and more odors than the thermophilic digester. The sulfur compounds emitted from the mesophilic digester are similar to those of a domestic landfill site although the proportions are different. As can be seen from Fig. 5, the amounts of higher molecular weight sulfur compounds present in landfill gas are greater than those produced from the mesophilic digester. The results indicate that the reactor temperature affects the generation of highly volatile sulfur compounds significantly; this is seen especially by the reduction of peak 1 and hydrogen sulfide under thermophilic conditions. This is probably due to the influence of temperature on both type and growth rate of the micro-organisms present and other conditions in the digester. The results are consistent with the results of Sipma *et al.*[11] who reported that sulfur compounds were removed from biogas under thermophilic (55°C) and

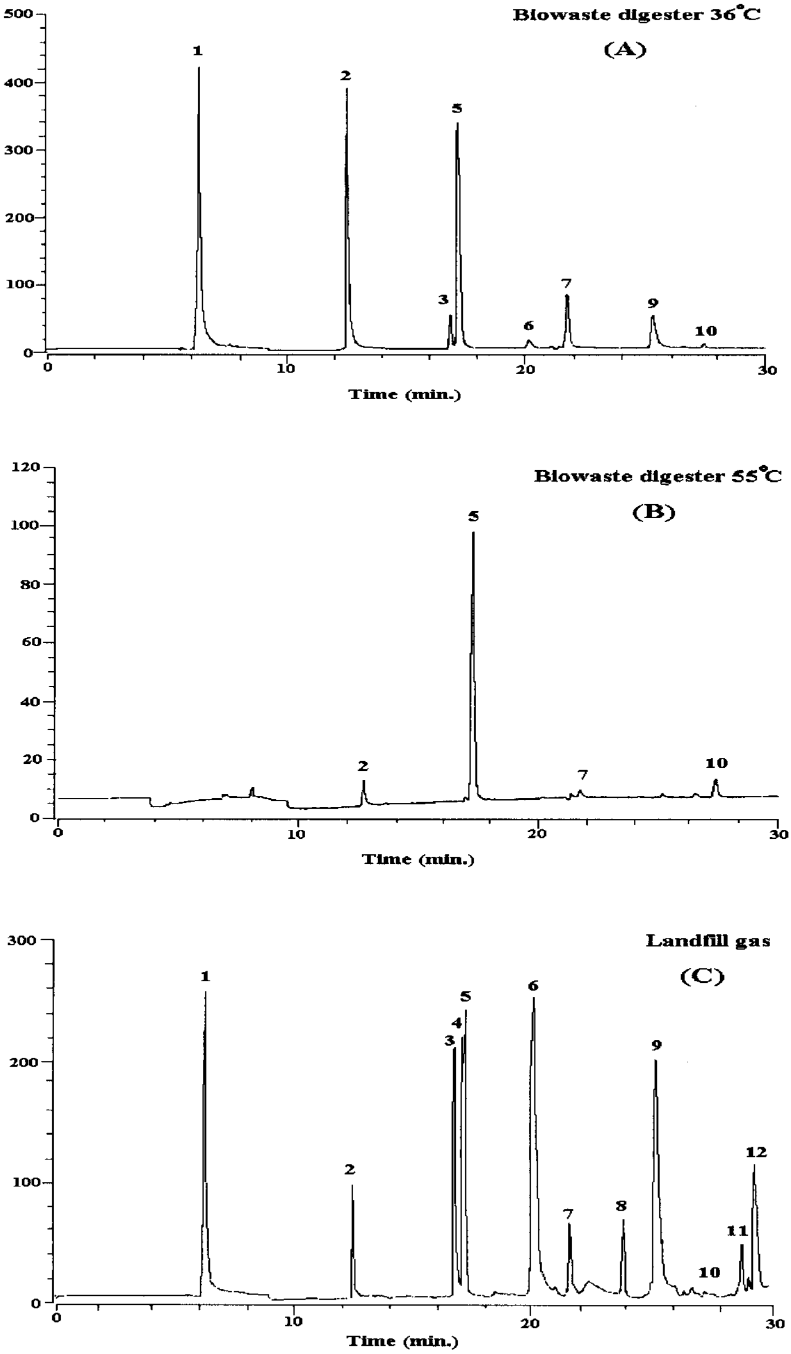

FIGURE 5 PTV-GC-AED sulfur selective chromatograms of gas from bio-waste digester at 36°C (A), from bio-waste digester at 55°C (B), and from domestic landfill (C). Peak identifications: 1, unidentified sulfur; 2, hydrogen sulfide; 3, carbonyl sulfide; 4, ethanethiol; 5, dimethyl sulfide; 6, 1-propanethiol; 7, ethyl methyl sulfide; 8, thiophene; 9, 1-butanethiol; 10, dimethyl disulfide; 11, 1-pentanethiol; 12, dipropyl sulfide.

anaerobic conditions because more thermophilic sulfate-reducing bacteria develop under these conditions. We suggest that the different emission profiles of compounds containing sulfur from biowaste digesters could be used to simulate the conditions in landfill sites. Where standards were not available, tentative identifications were made from the relative retention of sulfur compounds separated by others on this column (a fused silica megabore GS-Q column, 30 m × 0.53 mm i.d.)[12]. Using relative retention of sulfur compounds in the literatures[12,13] and referring to a list of sulfur compounds previously[14–16] found in landfill gas, sulfur peaks could be identified, and are listed in Fig. 5.

Arsenic and antimony peaks were identified in chromatograms from landfill gas as shown in Fig. 6. Inset into this figure, the elemental emission spectral snapshots confirm the presence of these compounds. Due to the high selectivity of the AED, carbon breakthrough from the channel (Fig. 6A) is not problematic because of the selectivity of the AED for As and Sb (Table I). The contaminants such as permanent gases, methane, carbon dioxide, and moisture can be reduced or eliminated by flushing with helium after loading the sample in combination with the AED solvent vent[19]. This enables increased selectivity AED detection for compounds of interest. Spectral interference attributable to interfering chromatographic peaks or molecular species when detecting by AED is corrected for primarily using 'recipes' (such as background correction, matched filter) or algorithms used in the construction of 'snapshots' (real time spectra), which are employed to unambiguously confirm the presence of selected elements[17]. No elemental spectra capable of causing interference with the antimony channel were observed. The stability of the identified sulfur, arsenic and antimony compounds was investigated by the analysis of samples collected over a number of weeks. Compounds containing sulfur and arsenic still remained in the Tedlar bag sample after storage for 20 days although antimony signals were not observed after this time. The instability of antimony containing compounds in a Tedlar bag is consistent with the result of Haas and Feldmann[20]. The loss of this compound is likely to be due to oxidation/hydrolysis yielding methylstibonic and stibinic acids in the aqueous phase.

The advantage of AED over MS is the elemental selectivity. Due to the high flow rate required, use of a PLOT column is not possible with GC-MS without the use of a jet separator and has not been employed here. The compounds containing arsenic and antimony found in this experiment are probably trimethyl arsine and trimethyl stibine, respectively. Pickett and co-workers[21] found that trimethyl arsine oxide was easily reduced to trimethyl arsine by micro-organisms in sewage sludge. Trimethyl arsine and trimethyl stibine were also identified in landfill gas by matching the retention time and isotopic fingerprint of the peak in samples to a standard using GC-ICP-MS[22]. In this work, $0.3\,\mu g\,m^{-3}$ of arsenic and $0.5\,\mu g\,m^{-3}$ of antimony were detected in the leachate. This confirms the presence of these elements in the landfill site providing more evidence for the likely emission of volatile arsenic and antimony species in the landfill gas.

CONCLUSIONS

The direct coupling of PTV to GC-AED permits the application of high sensitivity multi-elemental detection to trace gas analysis. The re-concentration of large volumes

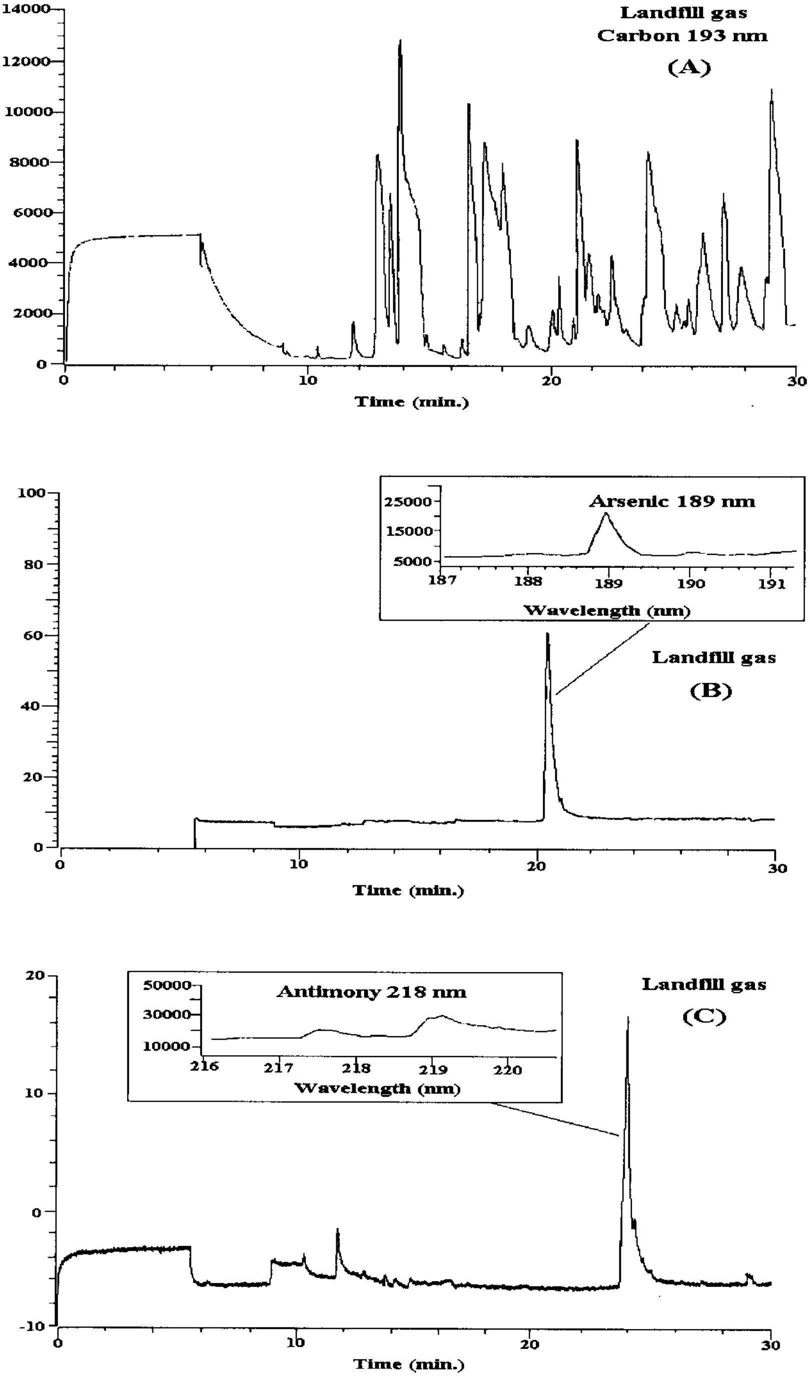

FIGURE 6 (A) Carbon (193 nm), (B) arsenic (189 nm), and (C) antimony (218 nm) AED chromatograms of 100 ml domestic landfill injected via PTV.

of gas enables high detection sensitivities; the direct non-cryogenic injection approach aids in simplification of instrumentation and methodology and does not trap large quantities of water. The use of packed sorbent trap within a PTV injector offers significant flexibility of sample size and allows trapping of the target compounds of interest. In addition, the high selectivity of AED and the combination with a PLOT GC column enable trace volatile compounds in complex gas samples to be clearly identified.

Whilst a more detailed calibration is necessary, the technique has demonstrated the ability to identify volatile compounds containing sulfur, antimony and arsenic with relative ease. The technique is capable with minimal modification to perform on-site measurements of trace volatile compounds containing Group V and Group VI elements.

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References

[1] I. Devai, L. Felfoldy, I. Wittner and S. Plosz, *Nature*, **333**, 343–345 (1988).
[2] S. Hetland, I. Martinsen, B. Radziuk and Y. Thomassen, *Anal. Sci.*, **7**, 1029–1032 (1991).
[3] M.O. Andreae, In: P.J. Craig (Ed.), *Organometallic Compounds in the Environment: Principle and Reactions*, pp. 205–210. Longman Group Limited, Essex, UK (1986).
[4] S. Junyapoon, K.D. Bartle, A.B. Ross, M. Cooke and B.F. Smethurst, *Intern. J. Environ. Anal. Chem.*, **77**, 337–348 (2000).
[5] A.V. Hirner, J. Feldmann, R. Goguel, S. Rapsomanikis, R. Fischer and M. Andreae, *Appl. Organomet. Chem.*, **8**, 65–69 (1994).
[6] J. Feldmann, R. Grumping and A.V. Hirner, *Fresenius J. Anal. Chem.*, **350**, 228–234 (1994).
[7] J. Feldmann and A.V. Hirner, *Intern. J. Environ. Anal. Chem.*, **60**, 339–359 (1995).
[8] J.J. Sullivan, Application note 228–108, Hewlett Packard, 1–7 (1989).
[9] R.L. Firor, *Amer. Lab.*, **21**(5), 40–48 (1989).
[10] S. Junyapoon, A.B. Ross, K.D. Bartle, B. Frere, A.C. Lewis and M. Cooke, *J. High Resol. Chromatogr.*, **22**(1), 47–51 (1999).
[11] J. Sipma, P. Lens, A. Vieira, Y. Miron, J.B. van Lier, L.W.H. Pol and G. Lettinga, *Process Biochem.*, **35**(5), 509–522 (1999).
[12] W.F. Sye and W.S. Jou, *J. Chin. Chem. Soc.*, **40**, 455–461 (1993).
[13] S.O. Farwell, S.J. Gluck, W.L. Bamesberger, T.M. Schutte and D.F. Adams, *Anal. Chem.*, **51**, 609–615 (1979).
[14] B.I. Brookes and P.J. Young, *Talanta*, **30**, 665–676 (1983).
[15] M. Schweigkofler and R. Niessner, *Environ. Sci. Technol.*, **33**, 3680–3685 (1999).
[16] C.K. Wilkins and K. Larsen, *J. High Resol. Chromatogr.*, **18**(6), 373–377 (1995).
[17] J.J. Sullivan and B.D. Quimby, In: P.C. Uden (Ed.), *Element-Specific Chromatographic Detection by Atomic Emission Spectroscopy*, pp. 62–89. American Chemical Society, Washington, DC (1992).
[18] A.C. Lewis, K.D. Bartle, J.B. McQuaid, M.J. Pilling, P.W. Seakins and P. Ridgeon, *J. High Resol. Chromatogr.*, **19**, 686–690 (1996).
[19] B.D. Quimby and J.J. Sullivan, *Anal. Chem.*, **62**, 1027–1034 (1990).
[20] K. Haas and J. Feldmann, *Anal. Chem.*, **72**, 4205–4211 (2000).
[21] A.W. Pickett, B.C. McBride and W.R. Cullen, *Appl. Organomet. Chem.*, **2**, 479–482 (1988).
[22] J. Feldmann, I. Koch and W.R. Cullen, *Analyst*, **123**, 815–820 (1998).