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Determination of phosphine in biogas and sludge at ppt-levels with gas chromatography-thermionic specific detection

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Abstract

A gas chromatographic (GC) system to measure free phosphine in biogas and matrix bound phosphine in manure and sludge is presented. The system consists of a sample preconcentration trap filled with glass beads, connected with a capillary GC equipped with a thermionic specific detector. With a trap temperature as low as −155 °C, a sampling flow of 20 ml/min and a typical total sample volume of 100 ml, free phosphine concentrations in the low ng/m^3 range and matrix bound phosphine in the low ng/kg dry matter range, can be accurately and reproducibly determined. © 2002 Published by Elsevier Science B.V.

Keywords: Biogas; Phosphine

1. Introduction

Phosphine (PH_3) is commercially used as an insecticide for the fumigation of grains, animal feed and leaf stored tobacco and as a rodenticide. It is also used as a doping agent in microelectronics. Phosphine is highly toxic to mammals, the time-weighted average exposure standard (TLV-TWA) is 0.4 mg/m^3 [1].

Generally, it is thought that in living organisms, phosphorus is present only in the 5+ oxidation state. A few biochemical pathways exist that form organophosphonates (3+) and phosphinates (1+) [2,3]. For over a 100 years the possibility of biological phosphate reduction has been claimed and criticised. The subject has recently been reviewed and it was concluded that there are strong indications that phosphine can be produced biogenically. However, based on thermodynamic grounds, it is very likely that organisms will have to invest energy to carry out the reduction of phosphate [4].

Reported phosphine concentrations in biogas and in the headspace of anaerobic cultures are in the order of ng–μg/m^3 [5–10]. The half-life time of phosphine in the atmosphere, in the presence of sunlight is only a couple of hours [11]. A major part of reduced phosphorus (3−) present in the biosphere is bound to soil, sediments, sludge and manure. The latter is called matrix bound phosphine. The reported

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concentrations for matrix bound phosphine are in the order of ng/kg [4].

Wet chemical and instrumental methods have already been developed to measure phosphine. Berck [12] used $HgCl_2$ to trap phosphine. The resulting release of HCl was determined by potentiometric titration. The latter author also reviewed the earlier methods based on the oxidation of phosphine by bromine, $AgNO_3$ or $KMnO_4$ to phosphate followed by colorimetric determination. The NIOSH method 6002 uses silica gel filters coated with $Hg(CN)_2$ to trap phosphine [13]. Carbon filters impregnated with KOH have been used for the same purpose [14]. The KOH impregnated filters are oxidised with H_2O_2 and the phosphite formed is quantified by ion chromatography. Demange et al. used silver nitrate impregnated filters [15]. The phosphorus content of the filters was measured with inductively coupled plasma (ICP) emission spectrometry. The detection limits of the above mentioned methods are too high (at best $\mu g/m^3$) to be useful to study phosphine formation in the biosphere.

In one of the first reports on the gas chromatographic (GC) determination of phosphine, a thermal conductivity detector was used [16]. Later, microcoulometric, thermionic, fluorine-induced chemiluminescence and flame photometric detectors were applied [17–19]. Burford and Bremner [20] failed to detect phosphine evolving from waterlogged soils using a GC equipped with a non-radioactive helium ionisation detector. Dumas and Bond [21] developed a preconcentration technique enabling the quantification of phosphine down to 14 $\mu g/m^3$. Two recent papers describing GC methods without preconcentration reported the same limit of detection (LOD): 10 $\mu g/m^3$ [22,23]. This LOD turned out to be too high to detect phosphine in the headspace of enrichment cultures [22]. Analysis of colon gases resulted only for one subject in a positive signal (40 $\mu g/m^3$) [23].

Gassmann studied the presence of matrix bound phosphine in the fluvial and marine hydrosphere [24]. A two-stage cryotrapping–cryofocussing technique with a detection limit of about 100 fg was used. With a sampling volume of 50 ml this leads to an LOD of 2 ng/m^3. The previous technique was refined to study atmospheric phosphine concentrations and a detection limit of 0.14 ng/m^3 was obtained with 50-ml samples [25,26]. The GC technique used in the latter three cited reports was poorly documented. Trapping, desorbing, refocusing and again desorbing was performed manually.

As a prerequisite of investigating the pathways leading to phosphine formation, a sensitive analytical method was developed to measure free and matrix bound phosphine. A commercially available, automatic, one-stage preconcentration trap combined with gas chromatography–thermionic specific detection (GC–TSD) was tested and is described in detail.

2. Experimental

2.1. Equipment, analysis of samples and experimental conditions

A Varian 3800 GC (Varian, Walnut Creek, CA, USA) equipped with a Varian sample preconcentration trap (SPT) was used. Silcosteel (Restek, Bellefonte, PA, USA) was used for the transfer line tubing to minimize the adsorption of phosphine. A schematic diagram is depicted in Fig. 1. A phosphine containing glass bottle with a general purpose blue septum (Alltech, Lokeren, Belgium) or a Tedlar gas sampling bag (Supelco, Bellefonte, PA, USA) was connected to the inlet. During the first 0.25 min of the analysis, the six-port switching valve (Valco, Houston, TX, USA) was left in the desorption position (solid lines in Fig. 1) to allow the mass flow controller (Sierra, Monterey, CA, USA) to equilibrate.

After equilibration, the valve was switched (dashed lines in Fig. 1) and by means of a vacuum pump (Thomas, Sheboygan, WI, USA) gas was pulled through the SPT. The SPT consisted of a coiled type 316 stainless steel tubing (total length= 39.47 cm, active bed length=29.2 cm, O.D.=3.18 mm, I.D.=2.16 mm) manually packed with glass beads (75–150 μm) secured in place with plugs of glass wool (Varian). The coiled tube was held at −155 °C using liquid nitrogen. For the analysis of free phosphine, a typical trapping time of 5 min and a flow-rate of approximately 20 ml/min was used. Due to the large concentration variations in the main compounds (CH_4, CO_2, air, etc.) of gas samples taken from different locations, the mass flow control-

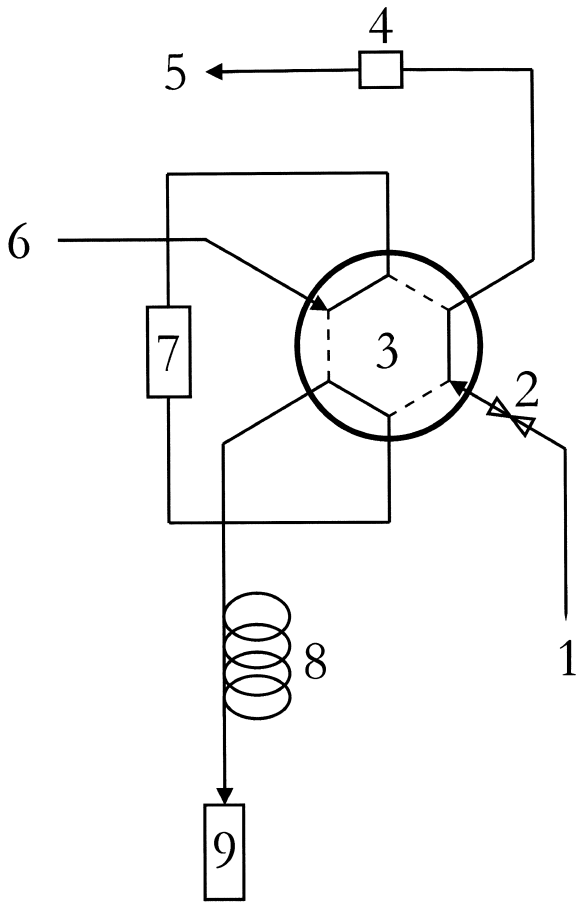

Fig. 1. Schematic diagram of the system for phosphine analysis. (1) Sample introduction, (2) on/off valve, (3) six-port switching valve, (4) mass flow controller, (5) vacuum pump, (6) helium carrier gas inlet, (7) SPT cryotrapping device, (8) capillary column and (9) TSD-detector.

ler needed to be supplemented with a gas burette with which the exact sample volume was measured. After 5.25 min, the six-port valve was switched to the desorption position (solid lines in Fig. 1) and the SPT was heated at a heating rate of up to 40 °C/s. Extremely fast heating of the trap was made possible by utilizing the wall of the trap tubing as an electrical heating element. A helium gas flow of 10 ml/min, corresponding with a column head pressure of 72 kPa, was used to sweep the desorbed phosphine from the SPT to the column. The separation was performed onto a PoraPLOT Q column (25 m, I.D.; 0.53 mm, d_f 20 μm) purchased from Chrompack (Middelburg, The Netherlands). The oven temperature program was 30 °C (10 min) to 100 °C at 40 °C/min. The temperature of the six-port switching valve was maintained at 175 °C with a valve oven. A thermionic specific detector (TSD) was used. The flow-rates of the detector gases were 4.3 ml/min for hydrogen (99.9% purity), 175 ml/min for air (99.9% purity) and 25 ml/min for helium (99.9999% purity), as the make-up gas. The detector temperature was set at 250 °C and the bead current was 3.0 A.

Data acquisition and processing was done with STAR 4.51 software (Varian).

2.2. Sampling, sample pre-treatment

2.2.1. Free phosphine

Pressure resistant Duran glass bottles (Schott Glas, Mainz, Germany) with a volume of 1 l, equipped with open top screw cap (GL 45) and GL 45 silicone rubber sealing with PTFE washer and a specially designed glass adapter with SVL 15 screw thread (Schott), were used for the sampling of the free phosphine. The bottles were sealed with two layers of general purpose blue septum. Sorption of phosphine onto the septa was neglegible since the time between sampling and analysis was kept to a minimum (at max.: 2 h). Prior to sampling, the bottles were flushed with helium (99.9999% purity) and pressurized to approximately 15 kPa relative to atmospheric pressure. At the sampling point, the bottles were evacuated to a pressure of approximately −75 kPa. After sampling, 10 ml of an oxygen-free 10 *M* KOH (technical grade) solution was injected into the bottle to remove H_2S and CO_2. Afterwards the bottle was pressurized with helium to a pressure of 15 kPa and analysed as reported above. A portable tensimeter (SMS, Tucson, USA) was used to measure, at each step, the pressure inside the bottles, to allow for accurate calculation of the dilutions made.

2.2.2. Matrix-bound phosphine

Sludge and manure samples were analysed within 1 week after sampling. The samples were stored at 4 °C. Prior to the analysis, the manure or sludge was mixed to obtain a homogeneous sample. The analysis of the matrix bound phosphine was based on procedures described by Nowicki [27] and refined by

Gassmann and Schorn [28]. A weighed amount of sample (approximately 25 g) was added to a 120-ml penicillin bottle (Merck, Darmstadt, Germany) closed with a general purpose blue septum held in place with an aluminium cap. After three cycles of evacuation (−100 kPa), 10 ml of a 50% KOH solution (technical grade) was added to liberate the phosphine from the matrix. Then the sample was mixed in vacuo over 1 h on a rotary mixer (Cenco, Breda, The Netherlands) with a frequency of 35 cycles min^{-1}. Afterwards, the bottle was pressurized with nitrogen (99.99% purity) to a pressure of 110 kPa and the gases were transferred with a silicone tube to an evacuated 60-ml penicillin bottle. Subsequently, 1-ml of a 1 *N* H_2SO_4 (Merck) solution was added to remove any interfering NH_3. Again, a tensimeter was used to accurately measure the pressure and the dilutions made. Finally, with minor changes, the sample was analysed as discussed above: a typical sampling time of 1 min and a sampling flow-rate of 15 ml/min were applied.

2.3. Preparation of phosphine standards

A certified gas standard cylinder containing 68.4 mg/m^3 (±3%) phosphine in nitrogen was purchased from Messer–Griesheim (Frankfurt, Germany). All other gases were also purchased from Messer. The gas cylinder was equipped with a syringe adapter. Gas standard mixtures with different concentrations were made in the following manner. Of the 68.4 mg/m^3 phosphine standard, 10 ml was withdrawn from the gas cylinder with a plastic, gas-tight syringe and transferred to a 500-ml gas-sampling bulb filled with helium under standard conditions. After 10 min, an appropriate amount was transferred in a 6.35-l glass flask filled with helium under ambient temperature and pressure conditions.

3. Results and discussion

3.1. Calibration curves and limits of detection

The configuration of the system was changed to construct the calibration graph and to check the linearity of response. The column was connected with a second six-port switching valve equipped with a sample loop. The column flow was 7 ml/min and the column temperature was 40 °C. Two sample loops were used (120 and 500 μl) and for each sample loop the calibration curve was measured two times. Slopes were within a 10% relative error boundary. Phosphine concentrations ranging from 0.28 $\mu g/m^3$ to 4.9 mg/m^3 were injected. All the data points obtained were used to construct the calibration graph ($y = 674.34x$, $r^2 = 0.9946$).

The limit of detection (LOD), calculated as the amount of phosphine corresponding to a signal-to-noise ratio of 3, was 0.17 pg of phosphine for the 0.12-ml sample loop. When the 0.5-ml sample loop was used, LOD rose to 0.2 pg of phosphine because of the larger dead volume resulting in increased injection band width. Injection of amounts of phosphine higher than 150 pg resulted in excessive tailing and loss of linearity.

When the SPT configuration was used, a relatively high column flow of 10 ml/min was set, to produce narrow peaks. The LOD with the SPT system was 0.3 pg of phosphine. This resulted, for a typical sampling volume of 100 ml, in a LOD of 3 ng/m^3. Taking into account the fact that the sample was diluted during sample pretreatment, the LOD was 4 ng/m^3 in practice.

3.2. Selection of SPT packing material

There are fundamentally two methods of preconcentrating permanent gases or volatiles: cryogenic trapping and sorbent trapping. Desorption from a cryogenic trap is faster than from a sorbent trap. The temperature at which the trapped components leave the trap will be higher with a sorbent trap than with an inert trap. This can be of importance with very reactive compounds such as phosphine. Therefore, it was investigated whether phosphine could be trapped adequately with an empty SPT.

It has been shown that when empty trapping tubes are used, the type of matrix gas affects the trapping efficiency [29]. Biogas mainly consists of methane and carbon dioxide. Carbon dioxide has a higher boiling point (–78.4) than phosphine (–87.7) [30]. To prevent clogging of the trap caused by trapping carbon dioxide and to prevent the risk of saturating the detector by bringing too much carbon dioxide onto the column, carbon dioxide was removed with

KOH. Removing carbon dioxide was also needed to obtain a correct reading of the amount of gas sucked through the trap with the gas burette. After removal of carbon dioxide, the matrix gases of the gas samples were methane, nitrogen and, to a lesser extent, oxygen.

The empty trap gave good results when the phosphine standard was diluted in helium and in air. The minimal required trapping temperature was −120 °C. When the diluent gas was methane, which was the case when analysing biogas samples, a noisy baseline was observed. The time needed for detector stabilisation, exceeded the phosphine retention time. Therefore, no accurate phosphine measurements could be made in a methane matrix. Several tests in which different amounts of methane were injected using a six-port valve with different loop sizes (see Section 3.1) and using different trapping temperatures with the empty SPT showed that the problem disappeared when less than 1.4 mg of methane was injected.

Subsequently, the empty SPT was manually packed with glass beads deactivated with dimethyldichlorosilane (glass treat, Varian) thus reducing the internal volume of the trap. Using the filled trap, detector stabilisation reduced to less than 1 min which resulted in acceptable chromatograms (Fig. 2).

3.3. Trapping efficiency

Trapping efficiency is influenced by the trap temperature, the composition of the gas sample (diluent gas), the concentration of the compounds of interest and the sampling flow.

First, the trapping temperature and the effect of the diluent gas was examined. Arbitrarily, the flow was set at 10 ml/min. Phosphine standards (695 ng/m^3) were prepared in Tedlar bags (Supelco) for the determination of the trapping efficiency over the temperature range +30 to −160 °C in different matrix gases (air, methane, helium). The trapping efficiency was calculated as the observed detector signal (counts) divided by the expected number of counts (gas burette measurement × concentration × slope of the calibration curve). The results obtained are shown in Fig. 3. It can be seen from Fig. 3 that the trapping curves for the 695 ng/m^3 phosphine standards in different matrix gases at a flow of 10 ml/min are essentially the same. The trapping was nearly absolute at −20 °C. The trapping efficiency curves showed a dip at −80 °C and efficiency rose to 100% at −140 °C.

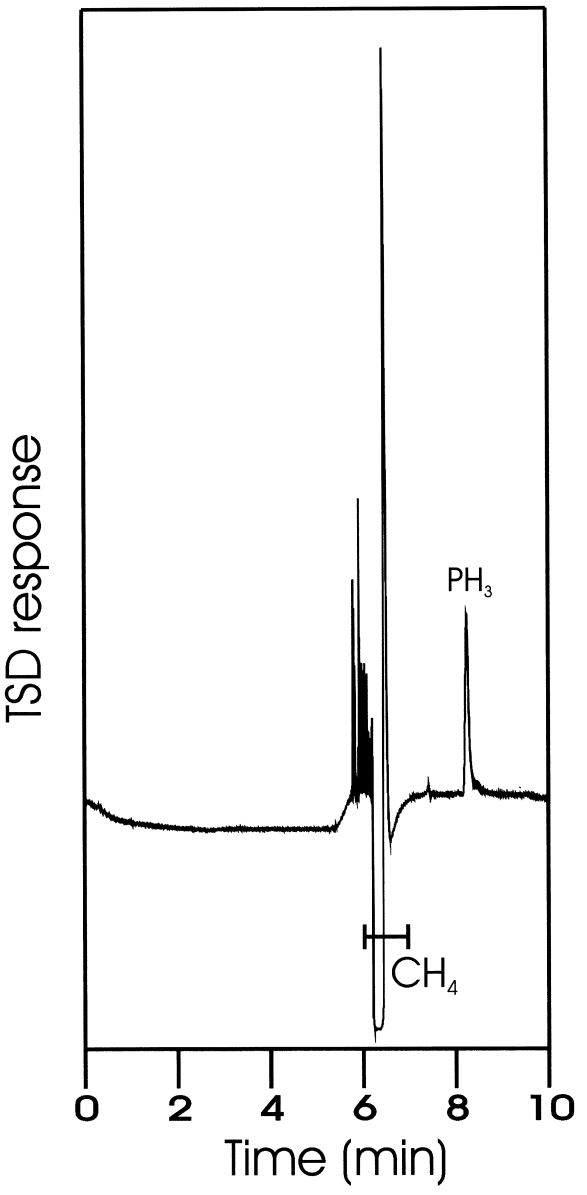

Fig. 2. Typical chromatogram obtained after injection of a biogas sample (PH_3 concentration = 121 ng/m^3).

Condensation of a component in the gas phase occurs when its pressure (p) in the mixture is higher than or equal to the saturated vapour or sublimation

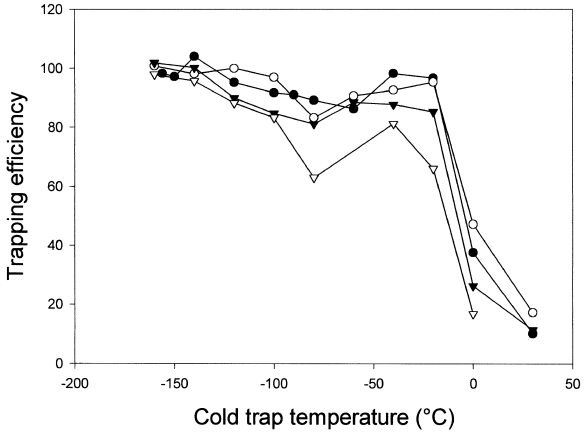

Fig. 3. Trapping curve of the trap filled with glass beads for different matrix gases and different phosphine concentrations: ○, 695 ng/m^3 phosphine in methane; ●, 695 ng/m^3 phosphine in helium; ▼, 695 ng/m^3 phosphine in air; ▽, 139 ng/m^3 phosphine in air.

pressure of the same compound at the given temperature [29]:

$$P_{vap} \leq p = cRT$$

where $c = 2.0 \cdot 10^{-11}$ mol dm^{-3} (695 ng/m^3) at 298 K, so $p = 5.1 \cdot 10^{-5}$ Pa in the bag and in the tube if the temperature is above the dew point and if we consider the gases in the bag to be ideal. Equations exist to calculate the saturated vapour and sublimation pressure of phosphine down to −145 °C [31]. At −145 °C the vapour pressure is still 999 Pa. The enormous difference between the partial pressure of phosphine in the sample and the vapour pressure demonstrates the nature of the trapping. Although the trap was constructed of inert material (SS 316, silylized glass beads and silylized glass wool), the type of trapping was sorbent trapping, rather than condensation.

Next, the effect of the concentration was investigated. The trapping efficiency curve was recorded with a 139 ng phosphine/m^3 standard in air using the same experimental conditions. At a lower concentration, in air, the shape of the curve was essentially the same (Fig. 3). Trapping efficiency decreased with lower phosphine concentration but the difference was less pronounced at lower trapping temperatures.

Higher sampling flows reduce sampling times. The influence of the sampling flow on the efficiency was assessed at different flows for a 695 ng phosphine/m^3 standard in methane (Fig. 4). Sampling flows higher than 30 ml/min negatively affect trapping efficiency.

Based on the experiments discussed above it was decided to use a trapping temperature of −155 °C and a sampling flow of 20 ml/min. The final parameter that was examined was the pressure inside the glass sampling bottles. A 347.5 ng/m^3 phosphine standard in methane was prepared in a 1-l glass bottle. The effect of pressure on trapping efficiency was tested in the range +14 kPa to −50 kPa. Trapping efficiency was affected and decreased from 106% at 14 kPa to 86% at −50 kPa (results not shown). Peak shape and height, however, were influenced more drastically with changing pressure inside the bottles. Peaks were a factor 1.6 higher at 14 kPa than at atmospheric pressure (0 kPa) (results not shown).

Finally, it was examined whether the combination of parameters chosen on the basis of the experiments discussed above was satisfactory. A series of standards of phosphine in methane with concentration ranging from 6 to 1200 ng/m^3 were prepared in glass bottles. The standards were analysed using the conditions noted in the experimental section. At 6 ng/m^3, trapping efficiency was 91%. Efficiency gradually increased with higher concentrations. For

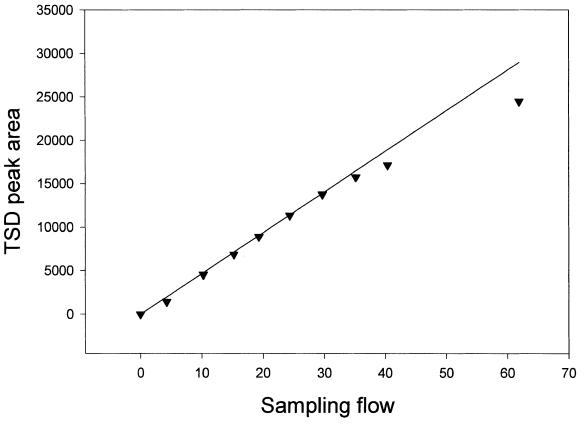

Fig. 4. Comparison between the observed peak area (▼) and the expected peak area (solid line) at different sampling flows for a 695 ng PH_3/m^3 standard in methane.

the assessment of precision and accuracy (observed number of counts/expected number of counts), standards of phosphine (69.5 ng/m^3) in helium and air were analysed several times during a period of 3 weeks. The accuracy for phosphine standards in helium was 89% ($N=8$). In air, accuracy was significantly lower: 65% ($N=5$). Precision, measured as the relative standard deviation was 7.7% in helium and 5.2% in air.

Therefore, it was decided that when the matrix gas was air, lower sampling flows were to be used (10 ml/min).

3.4. Interferences

The sensitivity of the TSD to different compounds was tested using the 120-μl sample loop. The column temperature was 35 °C and the flow was 7 ml/min. A TCD, also mounted on the GC, was used to produce Fig. 5A. Carbon monoxide is not separated from N_2 on the poraPLOT Q column. From Fig. 5B it can be seen that the TSD is almost insensitive for N_2. CO_2 is not detected by the TSD. N_2O, NO_x, H_2S and NH_3 do not interfere with the phosphine determination under the conditions mentioned above. Using the TCD, H_2S showed a symmetrical peak (not shown). Therefore, the tailing observed in Fig. 5F is probably due to the detector. The PoraPLOT Q column is not compatible with ammonia. It is not clear whether the fluctuating signal starting at min 4 in Fig. 5G is caused by the column or/and by the detector. The KOH used to liberate matrix bound phosphine also liberates NH_3. Therefore, NH_3 had to be eliminated from the biogas with H_2SO_4 (Section 2.2.2).

Considering Fig. 5 and the fact that when the cryoconcentration is used approximately 100 times more compound is led through the column, it was assumed that ethane was the most critical compound towards interference. It was indeed observed during the trapping efficiency tests that when the matrix gas was impure methane (Messer, 99.5% purity), ethane interfered with the phosphine determination. The concentration of ethane in the 99.5% pure methane gas was 389 mg/m^3. Trapping of ethane at −140 °C was very poor. This resulted in broad peaks. Lowering the trapping temperature to −155 °C gave rise to better trapping. Trapping efficiency was about 78%

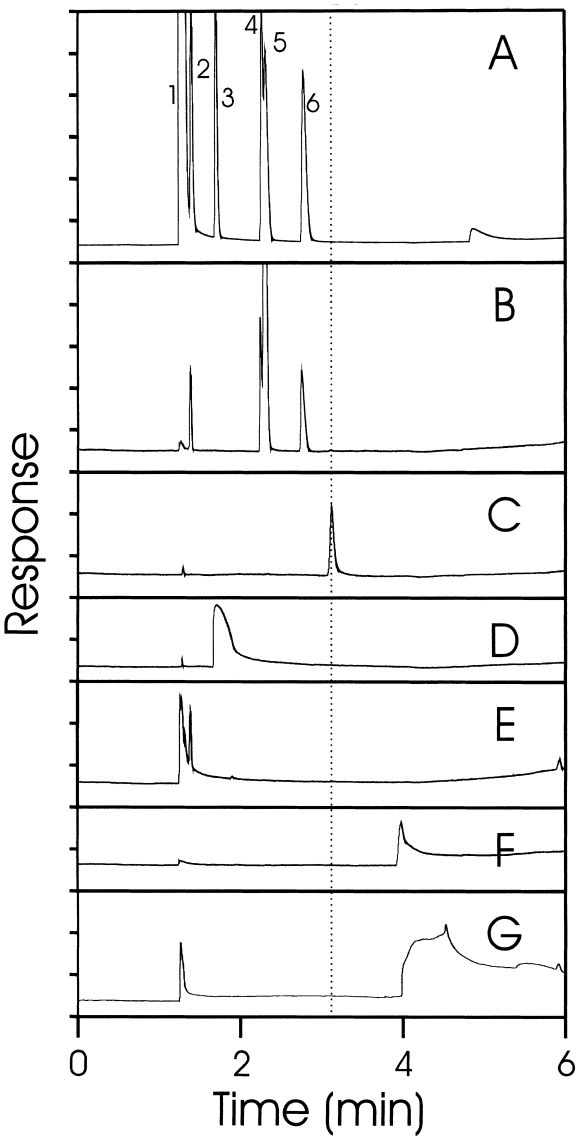

Fig. 5. Possible interference of relevant compounds with the phosphine determination using 120-μl valve injections. (A) Response (TCD, sensitivity = 0.5) for the injection of carbon monoxide, carbon dioxide (3), methane (2), ethane (6), ethylene (4) and acetylene (5) each at 1% in nitrogen (1) (Scotty); (B)response (TSD) for the same mixture as in (A); (C) 69.5 μg/m^3 phosphine in helium (TSD); (D) 100% N_2O (TSD); (E) 20% NO in air (TSD); (F) 1390 mg/m^3 H_2S in nitrogen (TSD); (G) headspace injection of concentrated ammonia 25% pro analysis (TSD).

and narrow peaks were produced. This efficiency is fairly high since the temperature at which trapping should occur as calculated with the equation used by

Table 1
Free phosphine content in biogas collected at five digestors and one landfill

Type of digestion	Concentration (ng/m^3)
Manure	42.3±3.5
Paper	4.5±1.1
Potato	<4
Slaughtery waste	179.2±19.5
Sewage sludge	10.2±0.2
Landfill	6398±685

Görgenyi et al. (2000) is −168 °C. Ethane impurities in methane did not interfere with phosphine when a trapping time of 1 min, a sampling flow of 10 ml/min and a trapping temperature below −150 °C was used. Higher flows and longer trapping times lead to interference. To our knowledge and based on the field measurements, ethane is not present in biogas in the mg/m^3 range.

3.5. Screening for free and matrix bound phosphine

To validate the method for field samples, five anaerobic digestors and one landfill were screened for the presence of free phosphine. Results are shown in Table 1. The measured concentrations are several log units lower than the ones reported by Dévai et al. [32] but correspond well with more recent reports [4,5].

Sludge from the five anaerobic digestors was transported to the lab and the content of matrix bound phosphine was determined (Table 2). One manure sample was taken from a pig farm and was also subjected to the matrix bound phosphine analysis. The standard deviation was calculated based on three independent measurements (sampling, pretreatment and analysis). The measured concentration levels are in agreement with the literature results [33,34]. Only in one case, the free phosphine concentration in the biogas was below the LOD. No reproducible results could be obtained with the potato digestor sludge. We assume that this was due to the high viscosity of the mixed sludge, inhibiting mass transfer. Diluting the sludge, however, did not resolve the problem.

The phosphine concentration in the atmosphere (=free phosphine) in industrialized regions is in the low ng/m^3 concentration range [26]. Therefore, it did not seem appropriate to try to lower the LOD of the system.

Different strategies could be followed if a lower LOD was to be obtained. Reducing column size and length would lead to sharper peaks but the possibility of interferences would increase. Increasing the bead current of the detector leads to a much lower LOD (by a factor of five) but bead lifetime is shortened considerably. The use of a trap filled with a sorbent would allow efficient trapping of very low phosphine concentrations but an additional cryofocussing stage would have to be added, increasing the complexity of the analysis.

In the future, using the analytical method presented in this study, we will start up experiments to get a better insight into the mechanisms leading to phosphine formation.

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Table 2
Matrix bound phosphine content in sludge collected from five digestors and in pig manure

Sludge type	Concentration (ng/kg)	Dry matter (DM) content (%)	ng/kg DM
Manure	22.9±0.8	3.58	639
Paper	2.4±0.3	4.32	56
Potato	nr	2.72	<10
Slaughtery waste	12.2±1.4	7.43	164
Sewage sludge	101.4±5.8	4.27	2373
Pig manure	71.4±20.3	5.73	1245

nr=No reproducible results could be obtained.

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