Sampling and Gas Chromatographic Analysis of Volatile Sulphur Compounds and Gases at Sub-v.p.m. Levels in the Presence of Ozone

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A method is presented for the sampling and analysis of sulphur gases (hydrogen sulphide and methanethiol) and volatile sulphur compounds (higher thiols and organic sulphides) in both ambient air samples and air containing ozone. The method has been developed for the quantitative analysis of hydrogen sulphide and for the semi-quantitative and qualitative analysis of other sulphur compounds. Field sampling and sample storage make use of simple cryogenic techniques and the analysis is carried out using a combination of thermal desorption and cryogenic re-trapping with sulphur-specific gas chromatography. Sample volumes of 100 ml and collection times of 1 min per sample are typically used for hydrogen sulphide in the range 0.1–1.0 volume parts per million (v.p.m.) with a limit of detection estimated to be better than 70 volume parts per billion (v.p.b.). The technique has been used in connection with odour control and measurement at a sewage treatment works, and in the assessment of odour control plant effectiveness.

Keywords: *Sulphur gas analysis; gas chromatography; thermal desorption trapping and pre-concentration; cryogenic techniques*

Sulphur gases such as hydrogen sulphide (H_2S) and methanethiol (MeSH), together with volatile sulphur compounds, for example simple thiols, and organic sulphides and polysulphides, are often implicated in nuisance odours at sewage treatment and disposal works. Levels of hydrogen sulphide in associated buildings, pump houses, wet wells, etc., can be high enough to necessitate ventilation to reduce the level of gas to a safe concentration, which may further aggravate the local odour problem. Various methods have been employed to reduce the ambient levels of sulphur compounds with varying degrees of success, for example wet or dry ozonolysis and chemical scrubbing of airborne compounds, or the dosing of sewage mains with oxidants or disinfectants such as hydrogen peroxide or sodium hypochlorite.

Frequently, the assessment of the effectiveness of control measures tends to be subjective as a result of the insensitivity of measurement techniques, and often no attempt is made to relate plant performance to known odour threshold levels.[1,2]

At a local sewage pumping station, odour complaints and high levels of hydrogen sulphide led to the present investigation being deployed to assess the optimum operating conditions for control plant using wet ozonolysis to remove the sulphur and other odorous compounds. Hydrogen sulphide was considered to be the most important odorous compound, whereas other sulphur compounds were suspected of being present intermittently.

The availability of gas chromatographic equipment and suitable specific detectors provided the basis of a method, although it was uncertain as to whether the conventional gas sampling methods were either sensitive enough or suitable for the reactive compounds involved. The distance of the site from the laboratory meant that samples would have to be transported and stored easily; the presence of ozone in the samples taken from the plant meant that losses of sulphur compounds during sampling and storage could be considerable if steps were not taken to minimise oxidation reactions. Finally, the complexity and special requirements of the gas chromatography equipment precluded the use of the instrumentation on site, which might have been the ideal solution.

A number of papers[3-9] have described methods for similar analytical requirements. Although several of the methods meet the requirements for the sensitivity and range required for sulphur compounds, most were considered unsuitable for reasons of difficulty in sampling, large sample volume requirements or excessively long sampling times, and it was felt that none were likely to succeed in the presence of ozone.

The extreme volatility of hydrogen sulphide and methanethiol (boiling-points −60.7 and 6.2 °C, respectively,[10] indicated that a cryogenic technique offered the best chance of success and would have the added advantage of slowing post-sampling reactions. Methanethiol in particular was likely to decompose if heated to temperatures much in excess of 100 °C,[3] which precluded the use of techniques involving high-temperature desorption or manipulation.

Our investigation indicated that methanethiol and its decomposition product, dimethyl disulphide, were both present at the treatment works. System inertness was an important factor in the study and the determinands did not come into contact with materials other than glass, fluorinated polymers, ceramics or silicone rubbers. A solid adsorbent, Tenax GC (2,6-diphenylphenylene oxide) was chosen as a trapping material, as it has been shown to be suitable as a column packing in the gas chromatography of sulphur compounds,[5] and liquid argon (boiling-point −186 °C) was chosen as the cryogenic medium in order to allow the use of nitrogen as a carrier gas in the chromatograph. Finally, a small portable gas sampling pump, primarily used for personal exposure monitoring, was used for field sampling to give the option of a wide range of sample volumes with the minimum of equipment.

Experimental

Equipment

Gas chromatograph

A Pye Unicam GCV with a flame photometric detector (FPD), sulphur filter and temperature programming facility was used in the investigation. The carrier gas was oxygen-free nitrogen gas and zero grade hydrogen and compressed air were used for flame gases. All the gases were purified by passing through a Type 13X molecular sieve.

Analytical column

A pre-packed glass column (2 m × 2 mm i.d.) filled with 60–80-mesh Carbopack B with a 1.5% XE-60 and 1.0% phosphoric acid stationary phase was used (Supelco).

Sample injection and flow switching valves

Inert low-pressure valves (Rheodyne Model 5020) with a 100-μl loop were used for the syringe injections.

Thermal desorber

A GN Concentrator (GN Instrumentation), fitted with PTFE transfer lines, a glass-lined stainless-steel cold-trap loop and additional flow and metering valves was used.

Computing integrator

A Hewlett-Packard 3380A or Trilab 2000 (Trivector Systems) was employed.

Gas calibration equipment

Calibration gas and pure air were mixed at a ratio of 1 : 100 using suitable flow meters (Platon Flowbits) and further diluted serially with flow meters to give an over-all dilution ratio of between 1 : 1000 and 1 : 10 000 at a final flow-rate of 5 l min^{-1}. The mixing of gases at each dilution stage took place in 300 × 30 mm Perspex tubes containing glass Raschig rings, and the final mix was sampled from a 250-ml round-bottomed flask into which the gas flowed.

Static gas standards were prepared in a 300 × 300 × 300 mm Perspex cabinet equipped with a circulating fan, a septum port for syringe or adsorbent tube sampling and a compressed air inlet for flushing.

The approximate concentration of hydrogen sulphide used for dynamic gas calibration was monitored using a hydrogen sulphide monitor (Neotronics Model HS 102) and potentiometric recorder (Servoscribe Model 1S).

Digital thermometer

A Comark Model 5000 thermometer equipped with Type K thermocouples was used.

Dewar flasks

Various sizes of vacuum flasks for handling liquid argon and sample storage (Thermos and Day-Impex) were used.

Adsorbent tubes

Pyrex glass tubes, 6 mm o.d., 4 mm i.d. and 89 mm long with their ends cut square, packed with approximately 100 mg of 60–80-mesh Tenax GC and plugged at each end with glass-wool, were used. The packing should be as central in the tube as possible, leaving the ends empty, although precise amounts and positioning of the packing is not critical.

Tubes should be conditioned for at least 1 h, six at a time, on a manifold of stainless-steel Swagelok union Tees at a temperature of 250 °C while purging with nitrogen at approximately 40 ml min^{-1} per tube.

Once conditioned, the tubes were capped with plastic caps and stored in the dark at room temperature before use. Tubes prepared in this way showed no response for any of the compounds studied after storage for periods of several weeks, although for critical applications it would be advisable to recondition prior to use.

Sampling blocks

Blocks, 60 × 60 × 60 mm, were cut from suitable polystyrene foam. A high-density foam is the most suitable. A hole was cut using a cork borer, in one face of the block, of 30 mm diameter and 45 mm deep, thus providing a container for the liquid argon. A second hole was cut completely through the block, approximately 15 mm below the top of the first hole, and at right-angles to the hole. This hole should be small enough to provide a tight fit when a sampling tube is pushed through.

The final configuration allows a sampling tube to have its central portion immersed in liquid argon with its ends protruding from the block for attachment of tubing.

Sampling pump

A sampling pump, Model CS1 (Casella), with a flow-rate adjustable between 20 and 200 ml min^{-1} was used.

Gas-tight syringes

Syringes of 1 and 20 ml capacity (J. Young, S.G.E.) were used.

Reagents and Standards

Hydrogen sulphide, 99.6%. BDH Chemicals.
Methanethiol, 99.5%. BDH Chemicals.
Ethanethiol, 99.5%. BDH Chemicals.
Dimethyl sulphide, 98%. Aldrich Chemicals.
Dimethyl sulphide, 99%. Aldrich Chemicals.
Calibration gas. 1000 v.p.m. hydrogen sulphide in nitrogen (BOC Special Gases).
Ozone. Model Trailigaz Labo ozone generator.
Ozone measuring tubes. Draeger Safety.

Caution—Hydrogen sulphide and ozone are highly toxic. Thiols and organic sulphides are toxic and flammable. Suitable precautions should be taken at all stages when handling these materials.

Chromatography and Thermal Desorption

The gas chromatograph was set up according to the manufacturer's instructions and the instrument optimised for sulphur analysis. The conventional septum injector was removed and the carrier gas supply taken to the inlet of the thermal desorber. The desorber has two gas outlets that are selected depending on the mode of use; one simply diverts the carrier gas back to the chromatograph where it flows via a switching valve and sample injection valve in series directly to the inlet of the analytical column. In this mode the gas chromatograph is used conventionally and gas samples are introduced by way of the injection valve and a gas-tight syringe.

The other mode diverts the carrier gas through the desorption oven and cold trap and then back to the chromatograph; flow switching is controlled automatically by the desorber, and by the operator. Flows of gas are controlled at all times by metering valves and flow meters.

The gas chromatographic conditions used were as follows: detector temperature, 150 °C; injector temperature, 60 °C; oven temperature, 50 °C; temperature programme, 2 min at 50 °C isothermal, ramp at 15 °C min^{-1} to a final temperature of 110 °C held for 9 min; carrier gas flow-rate, 40 ml min^{-1}; flame gases, hydrogen at 20 ml min^{-1}, air at 30 ml min^{-1}, air purge approximately 100 ml min^{-1}; amplifier attenuation, 32 × 10^2; output to integrator, 1 V f.s.d.; integrator attenuation, × 1024.

The thermal desorber was modified by replacing the stainless-steel cold trap with a trap of the same dimensions made of glass-lined stainless steel, in order to minimise any adsorption of reactive gases. In some experiments, a length of 1.6 mm o.d. PTFE tubing was passed through the trap if a smaller trapping volume was required. In practice either arrangement worked well. No packing was used in the trap as cryogenic re-trapping proved to be quantitative. All transfer pipework in contact with the samples was either 1.6 or 3.2 mm o.d. PTFE tubing and, where it was necessary to use stainless-steel couplings, they were lined with PTFE or silicone-rubber tubing.

An additional ball valve and fine metering valve were fitted in the sample transfer line and a switch was added to override the automatic flow switching sequence of the desorber. The latter allowed the temperature programmed runs to be completed without disturbing the gas flows. Finally, a septum port was added to allow gas injections during optimisation of desorber conditions.

The desorption and re-trapping conditions used for all the sulphur compound studies were as follows: desorption temperature, 110 °C; desorption time, 3 min; cold trap (trapping), −186 °C; cold trap (volatilisation), 110 °C.

A previous study[11] indicated the need for conditioning the chromatographic system during sulphur gas analyses. The whole system was conditioned prior to a set of analyses by injecting 1 ml of 1000 v.p.m. H_2S in nitrogen through the septum port on to the desorber. This conditioned all parts of the system in contact with the desorbed sample, and was necessary only if the system was not used for more than 2–3 h. The column was conditioned immediately before each analysis by injecting 250 µl of 1000 v.p.m. H_2S through the sample injection valve.

Calibration

Dynamic H_2S gas standards

A concentration of 1000 v.p.m. H_2S in nitrogen was serially diluted with air to give standards in the range 0.1–1.0 v.p.m. H_2S. Each mixture was monitored with the hydrogen sulphide monitor to indicate when the mixture was fully equilibrated; with a final flow-rate of 5 l min⁻¹ going into the sampling flask, a stable mixture is obtained in 4 min, and where the large chamber was used, at least 20 min were required for equilibration.

Static gas standards

Static gas standards of hydrogen sulphide and the other sulphides and thiols were prepared by injecting suitable volumes of gases and vapours into the large chamber through the septum port.

A knowledge of the saturated vapour pressure of the pure volatile liquids at room temperatures allows semi-quantitative standards to be made up in the range 0.1–0.5 v.p.m. by serially diluting the saturated vapour using gas syringes and septum vials. When injected into the chamber, the various compounds were allowed to mix for several minutes using the built-in fan. After mixing, samples were taken immediately as described in the following sections and, in order to minimise losses due to adsorption, etc., no more than 5 min elapsed between mixing and sampling. After sampling, the chamber was thoroughly flushed with air before preparing new standards. Standards made up in this way were used only to provide a qualitative analysis of compounds other than H_2S.

Calibration procedure

After the preparation of standards by one of the above procedures, samples were taken for gas chromatographic analysis; the sampling technique was identical for either type of standard and, with minor variations, identical with the field sampling method.

A freshly conditioned tube was placed in a polystyrene block. A short length of silicone-rubber tubing, approximately 20 cm, was attached to each end of the absorbent tube, one piece of tubing being used to sample the calibration mixture and the other attached to the inlet port of the sampling pump. Liquid argon was poured into the chamber of the block to completely cover the exposed portion of the adsorbent tube. The tube and block were allowed to chill through for about 1 min, topping up the argon as necessary. Care should be taken in handling the block at this stage, particularly with regard to leaks of argon past the tube. Blocks should be tested before use and any that leak significantly rejected. With careful use, blocks can be used many times before leaks occur.

Tests with a micro-probe thermocouple indicated that a considerable temperature gradient existed both along the adsorbent bed and across it. Temperatures at the centre of the packing dropped to approximately −10 °C, whereas temperatures of −166 °C were recorded at the inner wall of the tube directly in contact with the argon. These temperature grad-

ients were considered beneficial, however, as it was likely that a more even spread of adsorbed and condensed materials occurred, and the tube was less prone to blockages due to icing when ambient levels of water vapour were high.

A sample was collected by switching the pump on for the required length of time. For the purpose of this study, the sampling period was set at 1 min with a previously calibrated flow-rate of 100 ml min⁻¹, which gave adequate sensitivity for 0.1 v.p.m. H_2S. The sensitivity of the method may be changed as required by altering the sampling times or flow-rates within certain limitations. It was found that at least 1000 ml of ambient air of 35% relative humidity could be aspirated through the adsorbent tube before the flow-rate was reduced owing to ice formation, but flow-rates should not exceed 100 ml min⁻¹ otherwise trapping will not be quantitative. During aspiration the actual flow-rate was checked by connecting a bubble flow-meter to the outlet of the sampling pump.

When sampling was complete, the pump was switched off, the silicone-rubber tubing removed, argon returned to a Dewar vessel and the tube inserted immediately with forceps into the desorber oven. Approximately 10 s before the tube was inserted into the oven, the automatic cycle of the desorber was started, which allowed the cold trap Dewar to rise into position and thoroughly cool the glass-lined trap. At this stage a ball valve was closed and no flow of carrier gas took place through the adsorbent tube.

When the tube was correctly positioned, the ball valve was opened and a metering valve used to restrict the flow of gas to 4 ml min⁻¹ during the desorption and re-trapping. The completeness of re-trapping at this stage was checked by injecting an aliquot of hydrogen sulphide into the system before the cold trap and observing any breakthrough of H_2S on the chromatograph. Under the conditions described, no breakthrough was recorded. The aliquot of hydrogen sulphide used to condition the system was injected through the sample injection valve immediately after placing the adsorbent tube in the oven, and this peak appeared approximately 1 min before the first analytical peak.

At the end of the pre-set desorption period, the cold trap Dewar lowers automatically, and the trap was heated quickly to 110 °C by resistive heating. At this point, the full carrier gas flow was restored by opening the metering valve fully, the integrator and temperature programming being started simultaneously. For hydrogen sulphide and methanethiol, the whole process was completed in less than 7 min, with retention times of 0.6 and 1.5 min, respectively, whereas dimethyl disulphide eluted in approximately 13 min. On the column described, all five sulphur compounds investigated were completely resolved; using dynamic gas standards, a plot of log (peak area) against log (concentration) yields a linear calibration over the range investigated for H_2S.[11] Typical instrument responses for a series of hydrogen sulphide standards are given in Table 1.

Table 1. Hydrogen sulphide dynamic gas standards. Limit of detection based on the total standard deviation at 0.1 v.p.m. = 0.07 v.p.m. H_2S

Nominal hydrogen sulphide concentration, v.p.m.	Mean peak area, counts × 10⁶,	Total standard deviation, counts × 10⁶
1.00	2.58	0.24 (3)*
0.75	2.22	0.06 (2)
0.50	1.59	0.12 (4)
0.40	1.33	0.08 (2)
0.30	0.94	0.08 (2)
0.20	0.66	0.06 (2)
0.10	0.37	0.04 (6)

* Degrees of freedom in parentheses.

Ozone Removal Investigation

The presence of ozone in some of the field samples was expected to interfere with both sample storage and analysis.

The reaction between ozone and hydrogen sulphide in the absence of water is slow at ambient temperatures, but the technique employed in this investigation included long-term sample storage and thermal desorption, both of which could lead to losses of sulphur compounds through oxidation. It was therefore decided to seek some means of selectively removing ozone prior to trapping the determinands on the Tenax adsorption tube.

The laboratory ozoniser was set up using the ozone production graphs supplied by the manufacturer, and the ozone gas was introduced into the dynamic gas calibration system in such a way that a final mixture containing pure air, hydrogen sulphide and ozone could be manipulated with flow meters to give any combination of gas concentrations in the ranges 0–10 v.p.m. of hydrogen sulphide and 0–50 v.p.m. of ozone. During tests with 10 v.p.m. of ozone and 1 v.p.m. of hydrogen sulphide, it was noted that even with liquid argon cooled adsorption tubes some darkening of the Tenax material took place at the inlet side, which indicated that reaction between ozone and Tenax was taking place, and that the adsorption - desorption characteristics of Tenax so affected would be altered. This was confirmed by placing a Draeger ozone-indicating tube in the sampling line immediately after the Tenax tube and aspirating up to 20 v.p.m. of ozone through the Tenax; under normal sampling conditions, no ozone was detected, it having been adsorbed or reacted with the Tenax. Tests to find an effective and selective ozone adsorbent were conducted by placing the adsorbent under trial in an empty glass adsorbent tube, with glass tubes containing strips of moistened starch - iodide indicator paper before and after the test material, thus giving a semi-quantitative and convenient means of checking the efficiency of ozone removal.

It was observed during tests that where a particular type of silicone-rubber tubing was used to connect the adsorbent and indicating tubes together, ozone appeared to be significantly removed. Further tests showed that the 20 cm length of silicone-rubber tubing used to collect samples, as described under Calibration, was effective in removing ozone up to 10 v.p.m. when used under the sampling conditions of flow-rate, etc. Tests were carried out on a number of other tubing materials of similar dimensions. Synthetic and natural rubber tubing was not effective; nor was poly(vinyl chloride) (Tygon) tubing or certain other types of silicone-rubber such as opaque types. The most effective material that could be easily identified and obtained commercially was a translucent silicone rubber tubing 6 mm o.d., 4 mm i.d., batch number 50318, manufactured by Esco Rubber. The efficiency of the tubing depended on the amount of ozone that it had been exposed to, and its capacity for ozone removal decreased with exposure to ozone, presumably as active adsorption - reaction sites were used up. A fresh length of tubing would reproducibly remove 10 v.p.m. of ozone before the Tenax tube, but attempts to re-activate the tubing by heating or exposure to hydrogen sulphide gas were not successful.

In order to increase the lifetime of the silicone-rubber tubing, tests were carried out with short pre-columns of adsorbants. The columns were made from 80 mm lengths of 6 mm o.d. thin-walled PTFE tubing packed with adsorbent and plugged at each end with glass-wool. Silicone-rubber tubing was dipped into liquid argon and, when brittle, could be filed with a coarse file into a granulated form that was then used to pack the tube; this material proved very effective in removing ozone, and a similar material described as silicone rubber "crumb" was obtained from Esco Rubber. This material was used for all subsequent tests and a fresh PTFE tube containing the crumb was attached to the inlet end of the silicone-rubber sampling tube when sampling for hydrogen

sulphide in the presence of ozone. When these disposable tubes were used, it was never necessary to change the silicone-rubber tubing and it was estimated that the capacity of the pre-column was at least 100 ml of sample containing 10 v.p.m. of ozone. The results of a test in which samples of air containing 1 v.p.m. each of hydrogen sulphide and ozone were subjected to immediate analysis and storage for approximately 24 h followed by analysis are given in Table 2.

The results of this test indicated that the finely divided silicone-rubber material was the best adsorbent for ozone and had little effect on the level of hydrogen sulphide after storage. A further check on this material was made by collecting a nominal 1.0 v.p.m. hydrogen sulphide sample on a number of Tenax tubes after passing the sample through a pre-column. Samples were collected both in the absence of ozone and in the presence of 1.0 v.p.m. ozone, and the results of analyses are shown in Table 3.

Comparison of the means by Student's t-test indicated no significant difference at the 95% confidence level.

Field Sampling

Field sampling was carried out in a manner identical with that described under Calibration. The only additional equipment required for field sampling was a storage Dewar vessel to transport adsorption tubes from the site to the laboratory, and plastic end-caps to seal the ends of tubes after a sample had been taken. A suitable Dewar vessel should have internal dimensions of approximately 30 cm depth and 1 cm diameter. A container with an internal diameter of 100 mm and a depth of 100 mm was provided. This could float on the surface of the liquid argon and allowed capped tubes to lie horizontally on the bottom of the container, the objective being to maintain the tubes in close contact with the liquid argon. Provided that the argon liquid level was maintained as high as practically possible, the storage temperature of the tubes could be maintained below −150 °C. An efficient Dewar vessel should allow the storage of samples for several days without frequent topping up of argon. During later field sampling, liquid nitrogen (boiling-point −196 °C) was used as the trapping and storage liquid, being approximately one third of the cost of argon, but argon was retained as the cryogenic liquid in the desorber to prevent condensation of the carrier gas.

Table 2. Effect of 1 v.p.m. of ozone on the storage of Tenax adsorbent tubes containing hydrogen sulphide, in the presence of various pre-column materials. Nominal hydrogen sulphide concentration, 1.0 v.p.m. All results quoted are a mean of two or more analyses

Pre-column material	Control (immediate analysis), v.p.m.	Storage (analysis after 24 h), v.p.m.
	H_2S	H_2S
10 cm long PTFE tubing	0.73	0.52
20 cm long silicone tubing	1.02	0.76
Finely divided silicone-rubber pre-column	1.06	1.01
Silicone-rubber crumb pre-column	1.12	0.88

Table 3. Results of the analysis of nominal 1.0 v.p.m. hydrogen sulphide in the presence of 1.0 v.p.m. ozone using a finely divided silicone-rubber crumb pre-column

	No ozone (immediate analysis), v.p.m. H_2S	1.0 v.p.m. ozone (24 h storage), v.p.m. H_2S
Mean H_2S concentration, v.p.m.	1.053	1.027
Number of analyses	6	6
Total standard deviation	0.031	0.075
Recovery, %	—	98

A check on the efficiency of storage was carried out by preparing dynamic gas standards of 0.2 and 1.0 v.p.m. H₂S, analysing one batch of tubes immediately and storing others for periods up to approximately 30 h in the storage Dewar vessel. The results of these tests are given in Tables 4 and 5.

Once a sample had been taken on site, the tube was immediately sealed with standard 6 mm plastic or rubber chromatographic column end-caps that had previously been heated to 100 °C to remove trace amounts of volatile sulphur compounds.

To analyse the capped tubes, once removed from the storage Dewar vessel, a tube was placed in a polystyrene block similar to that used for sampling, with slots cut in the top instead of holes bored through. This allowed a tube to be semi-immersed in liquid argon while the caps were removed. In practice, removal was difficult as the caps shrink tightly on to the glass tube when cooled, and are no longer flexible; however, by rotating the tube carefully with the caps between fingers, it is possible quickly and safely to warm the caps to a point at which they can be removed, whilst keeping the Tenax section cooled. A later refinement was to shorten commercially available caps to half their original length (15 mm), which helped the removal process. As soon as the caps were removed, the tubes were analysed immediately, as described previously.

Results and Discussion

Hydrogen sulphide was the only gas that was analysed using dynamic gas standards; the advantage of dynamic standards is that it can normally be assumed that at the low levels a gaseous component will reach equilibrium with its surroundings, and that losses due to physical processes will be minimised; the disadvantage is that a relatively large supply of gas components is required, preferably in undiluted form. Gas standards can be bought in (although stability would be a problem with reactive gases at low concentrations), or produced by serial dilution of a higher concentration, or by some other means such as a permeation oven. In this investigation, a commercial gas standard of H₂S was used, but further dilutions of between 1000- and 10 000-fold were required to achieve levels between 1.0 and 0.1 v.p.m. H₂S. Errors in serial dilution are cumulative and it was considered that the problem of the production of stable calibration standards was the single most important reason for non-reproducible results and for some of the low recoveries in storage tests. The flow meters and dynamic standards technique used were adequate for the purposes of the application, but it is recommended that for more critical measurements, due regard should be given to the provision of high-quality flow controllers, pressure regulators and control of other factors such as temperature. A permeation oven would overcome some of these difficulties and almost certainly would be essential for the production of dynamic standards of the non-gaseous sulphur compounds.

The results of the storage tests (Tables 4 and 5) show variability in the recoveries obtained at the 1.0 and 0.2 v.p.m. levels, more so at the lower level. It was considered significant for the purposes of the investigation that there was no loss of sample over the storage period, and that once the tubes were installed in the storage Dewar vessel at liquid argon or nitrogen temperatures, it would be unlikely that changes in the levels of adsorbed compounds would take place over storage periods longer than those observed.

As previously noted, the variability observed in this investigation was almost certainly due to the difficulties in producing accurate low levels of the compounds under investigation, and at the 0.2 v.p.m. level, the flow meters used were at the bottom of their usable range. At this level, flows

were difficult to reproduce and maintain, and as the calibration standards and storage samples were produced by the same technique, it was concluded that this factor alone would account for variations. It was not possible to investigate this aspect further and the mean recoveries obtained during storage were applied to site samples stored for similar periods.

A second important factor was the manipulation of samples. Calibration adsorption tubes were always placed quickly into the desorption oven, hence minimising losses of determinands, whereas field samples were capped and were subject to varying amounts of manipulation. This was partly confirmed when tubes were sorted without caps at all and gave recoveries as good as tubes that had been capped. The uncapped tubes were removed quickly from the sampling block and placed on the bottom of the storage Dewar vessel inner container, whereas others were placed inside screw-capped test-tubes and immersed directly into liquid argon. It should be noted that liquid argon must not be allowed to enter the sample tubes, as the rapid evaporation of the liquid during manipulation causes severe loss of trapped materials (Table 6). A possible explanation for the good recoveries is that any losses from the tube during storage were balanced by the ease with which tubes could be transferred from the Dewar vessel to the desorption oven without delay.

Storage of tubes, as described under Field Sampling, ensures that the temperature of the adsorbent is kept well below the melting-point of any of the compounds studied, and that losses due to physical processes should be minimal. In practice, it is difficult to maintain a constant low temperature in the tube storage vessel, especially during the removal of tubes for analysis. A possible solution might be to store tubes directly in the liquid argon phase, but it would be necessary to find a means of sealing tubes against the ingress of liquid, and no practical solution to the problem was found that was convenient to use under site conditions.

A brief investigation into the processes involved in the sampling procedure was carried out by using sampling tubes packed only with GC-grade silanised glass-wool, and samples of calibration (H₂S) mixtures collected and analysed by the

Table 4. Mean concentration and recovery of hydrogen sulphide after storage, nominal 1 v.p.m.

Time/h	6	18	24	30
Mean, v.p.m. H₂S	0.83	0.83	0.95	0.99
Total standard deviation	0.06	0.07	0.11	0.05
Number of analyses	4	4	4	4
Recovery, %	83	83	95	99
Mean recovery (all results)	90%			

Table 5. Mean concentration and recovery of hydrogen sulphide after storage, nominal 0.2 v.p.m.

Time/h	6	18	24	30
Mean, v.p.m. H₂S	0.11	0.13	0.14	0.16
Total standard deviation	0.05	0.03	0.06	0.02
Number of analyses	4	4	4	4
Recovery, %	55	65	70	80
Mean recovery (all results)	68%			

Table 6. Comparison of various methods of Tenax tube storage, nominal 0.5 v.p.m. H₂S. Three samples of each tube were analysed

Calibration standard	Mean peaks, counts × 10⁶	Total standard deviation	Degrees of freedom	Concentration, v.p.m.
0.5 v.p.m.	1.34	0.16	2	—
Uncapped tubes, 3 h storage	1.64	0.14	2	0.60
Uncapped tubes, total immersion, 3 h storage	1.38	0.23	4	0.51

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Table 7. Recovery of hydrogen sulphide gas standards from tubes packed with glass-wool compared with the standard procedure

Standard procedure: H_2S concentration, v.p.m.	Glass-wool procedure		
	Peak area, counts $\times 10^6$	Mean calibrated concentration, v.p.m.	Recovery, %
0.98	3.13 3.21	1.10	112
0.79	2.64 2.65	0.88	111
0.60	2.06 2.18	0.70	117
0.41	1.21 1.32	0.40	98
0.21	0.56 0.56	0.16	76

Tenax procedure. The results are shown in Table 7 compared with conventional Tenax tube samples. The recoveries and precision are acceptable, although non-linearity is evident. It is clear that the main process involved in sample collection is condensation, assuming that the glass-wool itself has no adsorptive properties and provides only an inert support for the condensed materials. It was considered, however, that the use of Tenax was preferable as this probably combined condensation and adsorption, and no attempt was made to use glass-wool only in any site investigations.

As previously noted in the section dealing with experimental conditions, there is a possibility of extending the sensitivity of the method considerably; there is no evidence that blank or instrument noise levels would be a problem for an increase in sensitivity of several orders of magnitude. The method is potentially useful in the study of other sulphur compounds of environmental interest, such as sulphur dioxide, carbonyl sulphide and carbon disulphide, and by changing the chromatographic or detection system the method offers a convenient means of qualitative or quantitative analysis of non-sulphur compounds.

References

1. "Compilation of Odour and Taste Threshold Values Data," ASTM Data Series DS 48A, American Society for Testing and Materials, Philadelphia, 1978.
2. Valentin, F. H. H., and North, A. A., "Odour Control, a Concise Guide," Warren Spring Laboratory, Stevenage, 1980.
3. Bailey, J. C., and Viney, N. J., "Analysis of Odours by Gas Chromatography and Allied Techniques," LR 298 (AP), Warren Spring Laboratory, Stevenage, 1979.
4. Stendler, P. A., and Kijowski, N., *Anal. Chem.*, 1984, **56**, 1432.
5. Walker, D. S., *Analyst*, 1978, **103**, 397.
6. de Souza, T. L. C., and Bhatia, S. P., *Anal. Chem.*, 1976, **48**, 2235.
7. Meek, D. M., and Reid, W. J., "Identification of Some Odourous Compounds in Air Samples Taken Near Sewage Treatment Plants," LR 969, Water Research Centre, Stevenage, 1979.
8. Young, P. J., *Effluent Water Treat. J.*, 1984, 189.
9. Pankow, J. F., Isabella, L. M., and Asher, W. E., *Environ. Sci. Technol.*, 1984, **18**, 310.
10. Weast, R. C., *Editor*, "Handbook of Chemistry and Physics," Fifty-sixth Edition, CRC Press, Cleveland, OH, 1975.
11. Hawke, D. J., Lloyd A., Martinson, D. M., Slater, P. G., and Excell, C., *Analyst*, 1985, **110**, 269.