

CHROM. 20 786

THERMAL DESORPTION–CAPILLARY GAS CHROMATOGRAPHY FOR THE QUANTITATIVE ANALYSIS OF DIMETHYL SULPHATE, DIETHYL SULPHATE AND ETHYLENE OXIDE IN THE WORKPLACE

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SUMMARY

Sampling on solid adsorbents followed by thermal desorption and gas chromatography was evaluated as a simple method for the quantitative analysis of dimethyl sulphate, diethyl sulphate and ethylene oxide in the workplace environment. Tenax TA and Carbosieve S-III (for ethylene oxide) were found to be suitable adsorbents. The charged tubes can be stored at 22°C for 4 days. The recovery is better than 98% (> 80% for ethylene oxide) in the mass range 1 ng–1 µg. The recovery is not dependent on air humidity. The limits of detection tested were at the lower parts per billion level.

INTRODUCTION

Industrial users of chemical substances have a duty to protect their workers from any adverse effects of the substances used in their processes. Thus the monitoring of toxic pollutants in the workplace environment is an essential task in industrial hygiene in order to control potential health hazards resulting from exposure to these substances. For many substances, threshold values have been defined. In the F.R.G. these are known as MAK or TRK values¹. In Switzerland the SUVA sets the threshold values². The monitoring of workers exposures requires analytical methods well suited for a reliable quantitative analysis at the required concentrations. For some substances, particularly for established carcinogens such as dimethyl sulphate (DMS), diethyl sulphate (DAS) or ethylene oxide (ETO), the TRK values are too low for a direct analysis. To lower the detection limit, sample preconcentration is necessary. The most common method involves trapping of the target compound on solid adsorbents followed by liquid desorption. Based on this technique, various procedures have been developed for DMS^{3–7}, including its derivatization^{3,4}. A surveillance monitor based on solid adsorbent sampling/thermal desorption has been developed by Widmer *et al.*⁸. Diethyl sulphate can be analyzed analogously to dimethyl sulphate⁴. Sampling of ethylene oxide is usually done on activated charcoal followed by liquid^{9–12} or headspace desorption¹³. Some procedures include a derivatization of the ethylene oxide in order to obtain a more stable analyte for the subsequent quantitation^{9,10}. A comparison of commercially available solid adsorbent samplers has

been published by Kring *et al.*¹⁴. In this paper, solid adsorbent sampling followed by thermal desorption and gas chromatography (GC) is described for the quantitative analysis of DMS, DAS and ETO.

EXPERIMENTAL

Materials and apparatus

DMS, DAS and ETO were obtained from Fluka (Buchs, Switzerland), cyclohexane and hexane from Merck (Darmstadt, F.R.G.). For the desorption, a thermal desorption unit TDAS 5000 (Carlo Erba, Italy) was used. The TDAS 5000 was coupled via an heated transfer capillary (1 m × 0.53 mm × 2.65 μm HP-1) to a Hewlett-Packard 5890 gas chromatograph. A 10-cm length of the transfer capillary was cooled with liquid nitrogen to -150°C in order to focus the broad sample train desorbed from the adsorbent. This cold trap was controlled by a MFA 515 (Carlo Erba) control module. The cold trap was heated rapidly to allow a rapid injection of the substances onto the column. A split/splitless type injector (valve with vent to the atmosphere, controlled by the MFA 515, to permit higher desorption flows in the thermal desorption step) was used. For DMS and DAS a flame ionization detector or a flame photometric detector operated in the S-mode (393 nm) was used, for ETO a flame ionization detector. Helium served as the carrier gas. The chromatographic conditions are given in Table I.

Solid adsorbents

For the enrichment of organic atmospheric trace compounds, various solid adsorbents are known¹⁵. For thermal desorption the best compromise between the following properties has to be evaluated: chemical and physical stability of the ad-

TABLE I
CHROMATOGRAPHIC CONDITIONS

| | <i>DMS, DAS</i> | <i>ETO</i> |
|------------------------|--|-----------------------------------|
| <i>Cold trap</i> | | |
| Splitless time (s) | 30 | Not in action; |
| Start temperature (°C) | -80 | focusing of sample |
| Final temperature (°C) | 150 | at the column head |
| <i>Column</i> | | |
| Type | DB-1 (J+W.Sci.) 15 m x 0.52 mm x 1.5 μm | GS-Q (J+W.Sci.) 30 m x 0.52 mm |
| Flow-rate (ml/min) | 6.5 | 12 |
| Start temperature (°C) | 60 | 35 |
| Start time (min) | 2 | 0 |
| Rate 1 (°C/min) | 10 | 10 |
| Temperature 1 (°C) | 100 | 110 |
| Time 1 (min) | 0 | 0 |
| Rate 2 (°C/min) | 30 | 30 |
| Final temperature (°C) | 250 | 240 |
| Final time (min) | 0 | 5 |

sorbent under the experimental conditions; high retention volume for the substances of interest at ambient temperatures; very low retention volumes at the desorption temperature; high selectivity which means high affinity for the target compounds and a concomitant low affinity for water, CO₂, NO_x, SO₂, O₃) and high capacity to allow for sampling of larger amounts of substance. For DMS and DAS, Tenax TA^{15,16} and for the low boiling ETO, Carbosieve S-III¹⁷ were found to be ideal. Two different glass sample tubes (100 mm × 4 mm I.D.) were either filled with 150 mg Tenax TA, 20–35 mesh (Chrompack, The Netherlands), or with 600 mg of Carbosieve S-III, 60–80 mesh (Supelco, Switzerland), and fixed at both ends with silanized glass wool plugs. Heating in a helium carrier gas stream of 40 ml/min for 20 min at 300–350°C (Tenax TA) or for 20 min at 330–400°C (Carbosieve S-III) was sufficient for clean blanks.

Calibrations

For external standard calibration standard solutions of DMS or DAS in *n*-hexane or ETO in cyclohexane were injected directly (on-column). The standard solutions were prepared gravimetrically. The calibration of the whole analytical procedure was done by two methods.

(1) The tubes were charged directly through evaporation of the standard solution in a GC injector. The standard solution was then completely transferred to the adsorbent tube by a nitrogen flow of 40 ml/min. In the case of ETO most of the cyclohexane was adsorbed in a Tenax TA tube, mounted prior to the Carbosieve S-III tube. To ensure that all ethylene oxide breaks through the first (Tenax) tube, the tubes were flushed with carrier gas for 5 min.

(2) Alternatively, the tubes were charged dynamically from a gas stream containing the substance at the parts per billion level. For example, a standard solution containing 9.5 mg DMS per ml hexane was injected continuously into a GC injector by means of a syringe pump, evaporating the solution at a rate of 0.33 μl/min into a nitrogen flow of 2 l/min. This yields a DMS concentration of 0.3 ml/m³ corresponding to 1.57 mg/m³ (22°C). Other concentrations were generated by variation of the concentration of the standard solution or by variation of the injection or the flow-rates. A fraction of this gas mixture was then sucked through the adsorbent tube for a defined time with a defined flow-rate. A standard personal low flow sampling pump SKC 222 (SKC, Eighty Four, PA, U.S.A.) was used. The flow-rate must be checked with the adsorbent tube investigated prior to use! The tubes were capped immediately after charging with plastic caps.

For calibration of the whole procedure, at least five different samples (each triplicate) with the expected amounts of substances (1 ng to 1 μg) were analyzed. Due to the non-linear response of the flame photometric detector, more calibration points had to be used with this detector for reliable interpolations. The chromatographic conditions are listed in Table I, the parameters for thermal desorption in Table II. The experimental set up for thermal desorption is shown in Fig. 1.

Gas chromatography and thermal desorption

The temperatures of the valve, interface and transfer line (Table II) were adjusted to ensure a quantitative transfer of the respective substance. To remove air from the system, the tubes were purged with the carrier gas and then preheated

TABLE II
PARAMETERS USED FOR THERMAL DESORPTION (TDAS 5000)

| | <i>DMS</i> | <i>DAS</i> | <i>ETO</i> |
|--------------------------------|------------|------------|------------|
| Valve temperature (°C) | 130 | 130 | 120 |
| Interface temperature (°C) | 130 | 130 | 250 |
| Transfer line temperature (°C) | 130 | 130 | 250 |
| Purge flow (ml/min) | 26 | 26 | 28 |
| Purge temperature (°C) | ≈ 25 | ≈ 25 | ≈ 25 |
| Purge time (s) | 10 | 10 | 2 |
| Preheating time (s) | 60 | 60 | 0 |
| Desorption flow (ml/min) | 13.5 | 13.5 | 12 |
| Desorption temperature (°C) | 190 | 190 | 320 |
| Desorption time (s) | 120 | 180 | 180 |
| Cleaning time (min) | 10 | 10 | 0 |

(except for the highly volatile ETO for which there is a risk of losses.). The desorption parameters were adjusted to allow for a quantitative desorption within the temperature limits (400°C) of the apparatus and the adsorbents. The parameters chosen for cold trapping are listed in Table I. During the thermal desorption process DMS and DAS were trapped at -80°C . For the injection of the substance the trap was then heated very rapidly to 150°C and the split valve of the injector was closed for 30 s. For

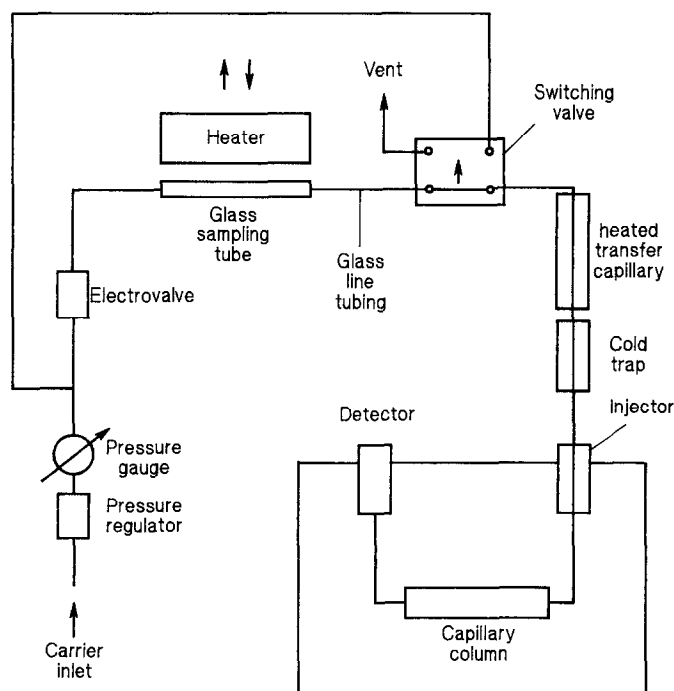


Fig. 1. Experimental set up (TDAS 5000).

TABLE III
RECOVERY OF SUBSTANCE, IN A STREAM OF HUMID NITROGEN

| | <i>DMS</i> | <i>DAS</i> | <i>ETO</i> |
|--------------------------------------|--------------|--------------|--------------|
| Absorbed substance (μg) | 5 | 1 | 1.7 |
| Volume flow (l/h) | 12 | 12 | 6 |
| Purge time (h) | 4 | 4 | 4 |
| Total flow (l) | 48 | 48 | 24 |
| Relative humidity (%) | 0, 40, 80 | 0, 40, 80 | 0, 40, 80 |
| Temperature ($^{\circ}\text{C}$) | ≈ 27 | ≈ 25 | ≈ 25 |
| Loss of substance ($\%/h$) | < 0.5 | < 0.5 | < 5 |
| Recovery (%) | > 98 | > 98 | > 80 |

ETO the cold trap could not be used. Compared with Tenax TA, Carbosieve S-III traps more water which regularly blocked the cold trap by ice formation. This problem could not be overcome by changing the transfer capillary (larger diameter or other coatings). Thus "focusing" of the desorbed ETO was done at the column head of the GS-Q column. The temperature programmes are given in Table I. The chromatographic conditions (Table I) were primarily optimized to separate the solvents and the purge gas impurities (see method tests). The field samples usually did not present chromatographic problems.

RESULTS AND DISCUSSION

Method tests

The comparison of the results from the calibration graphs with the on-column injection (external standard) shows good agreement. This means that the adsorption of the substance from the dry nitrogen calibration mixtures and the subsequent thermal desorption were complete under the conditions specified. In order to check for potential losses during field sampling, charged tubes were exposed to a stream of nitrogen with varying relative humidity. Water is known to be an efficient eluent,

TABLE IV
RESULTS OF METHOD TESTS

| | <i>DMS</i> | <i>DAS</i> | <i>ETO</i> |
|---|----------------------|-----------------------|-----------------------|
| Minimum detectable quantity* | | | |
| by FID (ng) | 1 | 0.1 | 0.5 |
| by FPD (ng) | ≈ 1 | ≈ 1 | — |
| Maximum quantity tested (μg) | 5 | 1 | 15 |
| Range tested (mg/m^3) | 0.05–2.5 | 0.005–0.5 | 0.0005–7.5 |
| Relative standard deviation (%) | 1.0 | 0.8 | 5.3 |
| $n = 6$ (95% confidence limit) | (5 μg) | (1 μg) | (1 μg) |
| | 4.0 | 2.3 | 4.8 |
| | (0.1 μg) | (0.01 μg) | (0.01 μg) |

* FID = flame ionization detection; FPD = flame photometric detection.

which could change the time-dependent recoveries. First the tubes were charged with a defined amount of substance, see Table III. The tubes were then purged (in the same direction as used for the adsorption) with nitrogen at 12 l/h and 0, 20 or 80% relative humidity (DMS, DAS). A total flow of 48 l was applied in each experiment. The tubes were desorbed thermally. The recoveries found for the total purge time are given in Table III. The various relative humidities were generated by volumetric mixing of dry nitrogen with nitrogen which had been saturated with water by passing through a water-filled washing bottle. The effective relative humidity was measured by a hygrometer. For DMS and DAS the recoveries were almost complete within the relative standard deviation of the whole method. For ETO the losses were somewhat higher, only 80% of the amount dosed being recovered after purging with 24 l of nitrogen at 6 l/h, independent of the relative humidity. For practical purposes this is acceptable, as the test conditions are much more rigorous than in field sampling (e.g. sampling at 20 ml/min for 8 h yields a total flow of 9.6 l. The further results of the method tests are listed in Table IV. The range of analyses is limited by the substance's minimum detectable quantity and by the loading capacity of the sampling tube and the cold trap. For our practical needs the range tested was limited to concentrations close to the respective TRK values. There exists the potential to extend the range to extremely low concentrations, even lower than tested for ETO. The relative standard deviation of the whole method is relatively low (0.8–4.8%), dependent on the amount of substance injected.

CONCLUSIONS

Solid adsorbent sampling/thermal desorption has proved successful for industrial hygiene monitoring. The main advantages of the method are the extremely low limits of detection, the high selectivity for the target compounds, particularly when selective (flame photometric) detectors are used, the wide applicability with respect to the compounds to be analyzed, the simplicity of sample preparation and the relative ease of operation. The main disadvantages are the still limited choice of solid adsorbents and the fact that only one analysis per sample is possible.

ACKNOWLEDGEMENTS

We are grateful to D. Hängärtner for development of the DMS method and to U. Gruntz for helpful criticism of the manuscript.

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