

## Note

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### Sampling and determination of carbon disulphide in air by gas chromatography with electron-capture detection

KIMMO PELTONEN

*Institute of Occupational Health, Department of Industrial Hygiene and Toxicology, Topeliuksenkatu 41 aA, SF-00250 Helsinki (Finland)*

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Carbon disulphide is used in the viscose industry as a reactive solvent. It reacts with the hydroxy groups of cellulose to form cellulose xanthate, which dissolves in the alkali to form a viscous colloidal dispersion called viscose. When viscose is forced through a spinnerette into an acid bath, cellulose is regenerated in the filaments, which yield threads of rayon and carbon disulphide is liberated. Carbon disulphide causes severe damage to the nervous system and heart disease<sup>1</sup>. The threshold limit value (TLV) of carbon disulphide is 30 mg/m<sup>3</sup> (10 ppm)<sup>2</sup>.

The first report of the measurement of carbon disulphide was based on the reaction between an amine, carbon disulphide and copper acetate. The reaction product shows UV absorption at 435 nm<sup>3</sup>. McCammon *et al.*<sup>4</sup> subsequently developed a sampling and gas chromatographic (GC) method with flame photometric detection. This method was adopted by NIOSH<sup>5</sup> and the HSE<sup>6</sup>.

In this paper we report the determination of carbon disulphide by GC with electron-capture detection after its collection from air using different absorption tubes.

#### EXPERIMENTAL

Carbon disulphide and toluene were purchased from EGA Chemie. Toluene was doubly distilled and dried with magnesium sulphate. The gas chromatograph was a Hewlett-Packard 5890 A equipped with a nickel-63 electron-capture detector. The column (25 m × 0.32 mm I.D.) contained Nordibond OV-1701 with a film thickness of 1.0 µm (Nordion Instrument). The carrier gas was helium at a flow-rate of 1 ml/min. The analysis was performed isothermally at 85°C with split injection. The splitting ratio was 1:20 and the injector temperature 180°C.

The charcoal tubes tested were MSA 57 (Mine Safety Appliances), Orbo 32 (Supelco), SKC 226-38, SKC 226-65 and SKC 226-01 (SKC). The other sorbent tubes tested were Florisil 226-39, silica gel 226-51, XAD-2 226-30-04, Tenax 226-35-03 and Porapak Q 226-59-30-03, all from SKC. All the tubes contained 100 mg of sorbent in the front section and 50 mg in the back section, except Porapak Q, which contained 150 and 75 mg, respectively. Air was aspirated with the aid of an SKC Universal 224-PC7 air sample pump. At the low flow-rates of air adjustable flow holders were used (SKC

224-26-04). The volume of the desorption solvent was 1 ml and the desorption time was 1 h at room temperature. The sample was used for GC analysis without percolation.

## RESULTS

Standards were prepared by aspirating air at a flow-rate of 50 ml/min from an atmosphere containing  $21 \text{ mg/m}^3$  (7 ppm) of carbon disulphide. The sampling times used were 30 min and 1 h, which theoretically produce 32 and 63  $\mu\text{g}$  of carbon disulphide, respectively. The breakthrough was determined by analysing the two sections of the tubes separately. The results are presented in Table I. The minimum breakthrough was achieved with charcoal tubes. No marked difference in the breakthrough between the different types of charcoals was observed.

The desorption efficiency was measured using a phase equilibrium technique and toluene as solvent<sup>7</sup>. Eight concentrations of carbon disulphide were used. The best desorption efficiency was achieved with porous polymer tubes, and the best efficiency among the charcoal tubes was given by SKC 226-65. However, the coefficient of variation with SKC 226-65 was high. With all the charcoals tested the desorption efficiency increased strongly with increasing carbon disulphide concentration (Fig. 1). The desorption time had no marked effect on the recovery and the time selected for desorption was 1 h.

More detailed experiments were performed with charcoal tube type SKC 226-01. With a 4-h sampling time the effect of flow-rate on the breakthrough was studied. No

TABLE I  
BREAKTHROUGH OF THE TESTED SORBENT TUBES

Carbon disulphide atmosphere, 7 ppm ( $21 \text{ mg/m}^3$ ); flow-rate 50 ml/min.

<i>Sorbent</i>	<i>Sampling time (min)</i>	<i>Breakthrough (%)</i>	<i>R.S.D. (%) (n=8)</i>
MSA 57	30	23	3.4
	60	32	3.9
Orbo 32	30	22	3.2
	60	29	3.6
SKC 226-38	30	23	3.6
	60	31	4.2
SKC 226-65	30	22	4.8
	60	27	5.0
SKC 226-01	30	18	2.8
	60	20	3.0
Tenax 226-35-03	30	49	5.6
	60	100	1.2
Porapak Q 226-59-30-03	30	50	5.7
	60	52	5.8
Silica gel 226-51	30	79	4.2
	60	94	3.2
Florasil 226-38	30	87	3.3
	60	100	2.4
XAD-2 226-30-04	30	46	3.9
	60	48	3.9

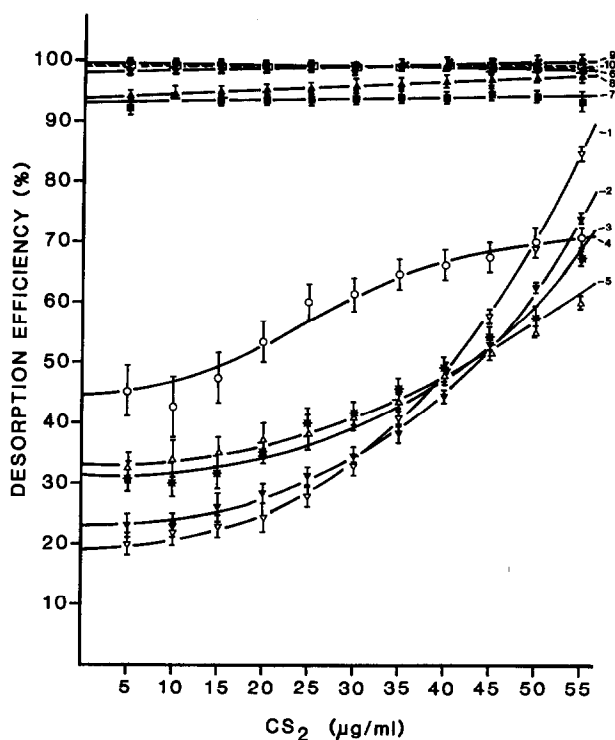


Fig. 1. Desorption efficiencies obtained using a phase equilibrium technique. 1 = SKC 226-01; 2 = SKC 226-38; 3 = SKC 226-65; 4 = MSA 57; 5 = Orbo 32; 6 = Tenax 226-35-03; 7 = Porapak Q 226-59-30-03; 8 = silica gel 226-51; 9 = Florisisil 226-39; 10 = XAD-2 226-30-04.

breakthrough, even at relatively high concentrations, was observed using a flow-rate of 20 ml/min. Breakthrough as a function of flow-rate is shown in Table II.

Owing to the nature of the viscose process, brief "peak" concentrations of carbon disulphide occur. These may cause breakthrough and errors in the determina-

TABLE II

BREAKTHROUGH OF THE SKC 226-01 CHARCOAL TUBE ( $n=8$ ) AS A FUNCTION OF FLOW-RATE AND COLLECTION TIME

Concentration		Collection time (min)	Flow-rate (ml/min)	Breakthrough (%)	R.S.D. (%)
ppm	mg/m <sup>3</sup>				
20	63	240	100	38	6.8
1	3.1	240	100	28	7.2
30	95	240	50	26	5.6
10	32	240	50	24	4.3
1	3.1	240	50	2.1	3.2
1	3.1	120	50	—	—
10	3.1	240	20	—	—
30	95	240	20	—	—

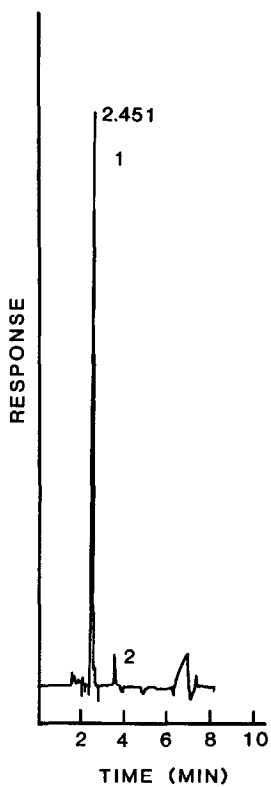


Fig. 2. Gas chromatogram with electron-capture detection of a sample collected from a Finnish viscose plant. 1 = Carbon disulphide; 2 = toluene.

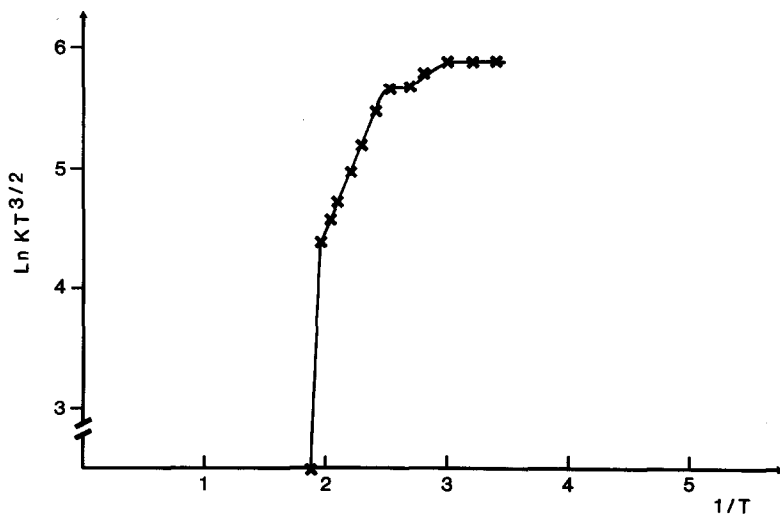


Fig. 3. Correlation of the electron-capture coefficient of the detection used towards carbon disulphide. The detector response was studied at a standard carbon disulphide concentration of 15  $\mu\text{g/ml}$ .

tion of exposure during the whole working day. Therefore, SKC 226-01 charcoal was tested at a "peak" concentration of  $42 \text{ mg/m}^3$  (100 ppm). The sampling time for 100 ppm was 20 min, which followed a 4-h collection of  $15.5 \text{ mg/m}^3$  (5 ppm). The flow-rate was 20 ml/min. However, no breakthrough was observed.

The loss of sample in SKC 226-01 as a function of time was studied by storing the tubes in a refrigerator ( $6^\circ\text{C}$ ) for 3–14 days. The amount of carbon disulphide in each tube was  $20 \mu\text{g}$ , which corresponds to 4.2 ppm for a 1.5-l sample. The observed sample loss was 2.3% [relative standard deviation (R.S.D.) 1.6%,  $n=8$ ] and it was not dependent on the storage time.

Finally, in view of the relatively low desorption efficiency at low concentrations (Fig. 1), the desorption efficiency was studied with different solvents and solvent mixtures. No marked increase in desorption was observed after adding a polar modifier (methanol, ethanol, dimethylformamide) to the toluene or other solvents tested (acetone, methyl ethyl ketone, ethyl acetate or diisopropyl ether). The amount of the desorption solvent did not affect the desorption efficiency. Toluene was selected because of its good chromatographic and low electron-capture response properties.

The detection limit using the SKC 226-01 charcoal tube and toluene as desorption solvent was 1.5 ng per  $1\text{-}\mu\text{l}$  injection. The desorption efficiency was 27% (R.S.D. 6.2%,  $n=8$ ), which corresponds to  $1.25 \text{ mg/m}^3$  (0.5 ppm) using a flow-rate of 20 ml/min and a collection time of 1 h.

A typical chromatogram for carbon disulphide in toluene is shown in Fig. 2. The peak was symmetrical and a good baseline separation was achieved at a column temperature of  $85^\circ\text{C}$ . The isothermal mode permits a fast analysis. The detector response was linear and the detection limit using pure carbon disulphide was 150 pg per  $1\text{-}\mu\text{l}$  injection at a signal-to-noise ratio of 1:10. The ionization potential of carbon disulphide is 10.08 eV and the mechanism of the response of the electron-capture

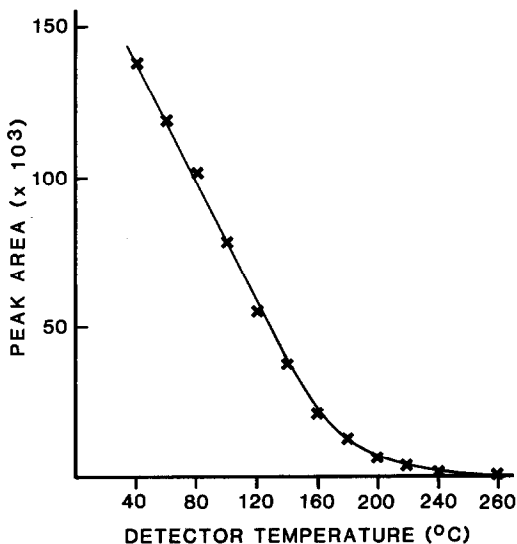


Fig. 4. Effect of detector temperature on detector response for the carbon disulphide.

detector seems to be a non-dissociative attachment to produce a stable negative molecular ion (Fig. 3). However, the electron-capture mechanism of carbon disulphide seems to be strongly dependent on temperature and the best response can be achieved at 40°C (Fig. 4).

#### CONCLUSION

The collection efficiency of the charcoal tubes is good, but the desorption efficiency at low concentrations is only moderate. Recommended sampling conditions are a charcoal tube, a flow-rate of 20 ml/min, a collection time of up to 4 h and desorption in toluene for 1 h, followed by GC with electron-capture detection.

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