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# Identification of Artefacts in the Desorption of Active Charcoal Tubes with Carbon Disulphide and Methanol. Reduction of Artefact Formation by Selecting Other Polar Additives

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Trapping of organic air pollutants on active charcoal tubes and subsequent desorption with carbon disulphide methanol mixtures is a widely used method. Unfortunately, several artefacts are formed during the the desorption process. In this study the various artefacts have been identified. Polar additives other than methanol have been investigated on their ability both to reduce the artefact formation and to enhance the desorption efficiency in comparison with pure carbon disulphide.

**KEY WORDS:** Organic air pollutants, active charcoal tubes, artefact formation, desorption efficiency

## INTRODUCTION

During the last two decades various methods have been developed to determine organic pollutants in air. Most of these methods are based on the trapping of the pollutants on a solid adsorbent in a glass tube where the polluted air is pulled through.<sup>1-3</sup> The adsorbent tube behaves like a chromatographic column: the pollutants elute from the tube with a rate which depends on the interaction between the organic pollutants and the adsorbent surface. For efficient sampling a relative strong interaction is necessary. After sampling the air the trapped pollutants are desorbed from the tube and analyzed, for which gas chromatography (GC) is used in most cases. Considerable research is performed on improving both the adsorbent materials and the desorption techniques.<sup>4-7</sup> Unfortunately, the ideal combination of adsorbent and desorption technique has not yet been found. Nevertheless, there are two combinations of adsorbent material and desorption technique which show good performance in the determination of certain groups of pollutants. These combinations are active charcoal as an adsorbent in combination with a solvent desorption technique<sup>8</sup> and porous polymers as adsorbents in combination with thermodesorption.<sup>9</sup> Although the latter have some advantages in certain applications, active charcoal is used as the adsorbent in most cases; it is even prescribed by the National Institute of Safety and Health in the US (NIOSH).<sup>10</sup>

According to the NIOSH manual,<sup>10</sup> desorption of the pollutants from the charcoal tube can be achieved with carbon disulphide as a solvent in 78% of the cases. For about 14% of the cases carbon disulphide modified with 1-10% of methanol is recommended, while for the other applications various other solvent mixtures are suggested. Mixtures of carbon disulphide and methanol or other polar modifiers are especially applied in the desorption of polar pollutants. By the use of the modifier the desorption efficiency is enhanced from 30-70% in pure carbon disulphide to 70-100% in carbon disulphide with a modifier.<sup>11</sup>

Unfortunately, the use of carbon disulphide with 1-10% of methanol results in artefact formation.<sup>11</sup> In the present study the various artefacts have been identified using gas chromatography/mass spectrometry. Other polar organic modifiers have been investigated on their suitability both to reduce the artefact formation and

to enhance the desorption efficiency relative to unmodified carbon disulphide.

## EXPERIMENTAL

### Apparatus

Identification of the reaction products was performed using a type 2091 gas chromatography mass spectrometry system (LKB, Bromma, Sweden) equipped with a single stage jet separator. Both Electron Impact and Positive Chemical Ionization with methane and ammonia as reagent gases were applied. The gas chromatographic column was 30 m 0.30 mm ID glass capillary column coated with SE-30 (film thickness of 0.27  $\mu\text{m}$ ). A temperature program from 50 to 230 °C with a rate of 10 °C/min was used; injector temperature was 200 °C; temperatures of the jet separator and the ion source were 225 °C.

For the determination of the desorption efficiencies a type 5700 gas chromatograph (Hewlett-Packard, Palo Alto, CA, USA) was used. The column was a 35 m 0.12 mm ID glass capillary column with a OV-101 stationary phase (film thickness of 0.06  $\mu\text{m}$ ). A temperature program from 55 to 250 °C with a rate of 8 °C/min was used. Injector and flame ionization detector temperatures were set at 250 °C.

### Chemicals

Four types of active charcoal material were studied in preliminary investigations, i.e., coconut shell charcoal tubes from Dräger (Drägerwerk, Lubeck, FRG), DuPont (DH International, Bussum, The Netherlands), MSA (MSA Nederland BV, Hoorn, The Netherlands) and SKC (Chrompack, Middelburg, The Netherlands). These materials were used without further treatment. All these materials gave the artefacts identified in this study; the relative abundance of the various artefacts appears to depend on the type of charcoal material. However, this aspect has not been studied further. The Dräger charcoal material was used in all experiments described in this paper.

All solvents were of analytical-reagent grade. They were obtained

from Baker (Deventer, The Netherlands), Merck (Darmstadt, FRG) and Brocacef (Maarsen, The Netherlands). Carbon disulphide and methanol were checked for the presence of the artefacts studied.

For the investigation of the desorption efficiency standard solutions of *n*-butanol, cyclohexanone, 2-methoxyethanol and 2-propanol in carbon disulphide were made with concentrations of about 8 mmol/l.

## Procedures

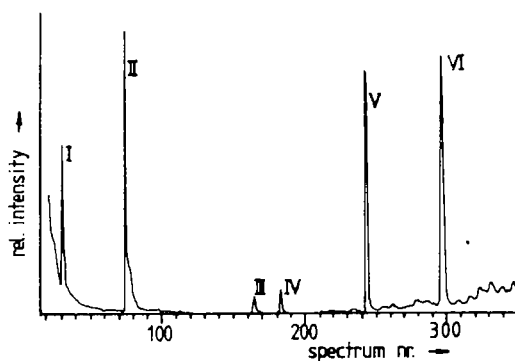
The desorption efficiency of *n*-butanol, cyclohexanone, 2-propanol and 2-methoxyethanol was studied according to the phase equilibrium method.<sup>11-13</sup> The active charcoal was quantitatively transferred from the glass tube into a 5 ml vial. A 1 ml aliquot of a previously analyzed standard mixture of the compounds of interest dissolved in carbon disulphide was added. The mixture was vigorously shaken for 30 s prior to the GC analysis of the liquid. In the next step 50  $\mu$ l of the polar modifier, either methanol or another solvent, was added. After vigorously shaking the mixture the liquid was analyzed with GC again. By comparing the peak areas in the three GC runs the desorption efficiency can be calculated.

O,S-dimethylxanthate and Bis(methoxy(thiocarbonyl))-disulphane were synthesized according to the prescriptions of Barany and Schroll.<sup>14</sup> The yields of these products were 38 and 67%, respectively. Methyl xanthate, which serves as a starting product of the previous mentioned synthetic routes, was synthesized according to the prescription of Singh.<sup>15</sup> The yield was 90%.

## RESULTS AND DISCUSSION

### Structure determination of the artefacts

Contents of unsampled charcoal tubes have been treated as described above, and analyzed by GC-MS upon standing for 30 days. A typical total ion chromatogram is given in Figure 1. The molecular masses of the products are given in Table 1. The shapes of some of the peaks in the chromatogram indicate the presence of isomers of the artefacts. This aspect has not been investigated further.



**Figure 1** Total ion chromatogram of a mixture of 1 ml carbon disulphide and 50  $\mu$ l methanol and active charcoal upon standing for 30 days. The indications of the peaks refer to the products given in Table 1 and Figure 2. Conditions: 30 m 0.30 mm ID glass capillary column coated with SE-30 (film thickness of 0.27  $\mu$ m), temperature program from 50 to 230  $^{\circ}$ C with a rate of 10  $^{\circ}$ C/min. Injector temperature 200  $^{\circ}$ C, temperature of ion source and jet separator 225  $^{\circ}$ C.

**Table 1** Identified artefacts from the chromatogram of Figure 1

Compound No.	Name	$M^+ \cdot CH_3OH$	$M^+ \cdot CD_3OD$
I	O,S-dimethylthiocarbonate	106	112
II	O,S-dimethylxanthate	122	128
III	S(methoxy(thiocarbonyl))- S'(methyl)disulfane	154	160
IV	Bis(methoxycarbonyl)disulfane	182	—
V	S(methoxy(thiocarbonyl))- S'(methylthio(carbonyl)disulfane	198	204
VI	Bis(methylthio(carbonyl)disulfane	214	220

To facilitate identification of the six artefacts observed, methanol has been replaced by  $d_4$ -methanol,  $CD_3OD$ , in a separate experiment. From the shift in the molecular mass observed, it is possible to establish the number of methyl groups present in the artefact, whereas the ratio of the  $M+2/M$  ions in the experiment with undeuterated methanol yields the number of sulfur atoms present in each compound.

The artefacts have been identified as a thiocarbonate, a xanthate and four disulfanes. In all cases, except the artefact with molecular mass 214, it is possible to establish the presence of functional groups like  $\text{CH}_3\text{O}$ -,  $\text{CH}_3\text{S}$ - and  $\text{CH}_3\text{SS}$ - from the fragmentation patterns. Therefore, structure elucidation is possible for all artefacts except for the artefact with molecular mass 214 (VI). Compound II has been synthesized by an independent route.<sup>14</sup> The mass spectrum of the synthesized product is identical with the mass spectrum of artefact II.

The identified artefacts are summarized in Table 1 and their structures are given in Figure 2.

For the artefact with molecular mass 214 three structures are possible: Bis(methoxy(thiocarbonyl))disulfane, Bis(methylthio(carbonyl))disulfane, or S(methoxy(thiocarbonyl))-S'(methylthio(carbonyl))disulfane. One of the possible structures has been ruled out by comparing with Bis(methoxy(thiocarbonyl))disulfane prepared independently.<sup>14</sup> The mass spectrum of the synthesized product is not identical with the mass spectrum of the artefact VI with molecular mass 214. Artefact VI can be identified when methanol is replaced by a higher homologue as a modifier of carbon disulphide. More readily interpretable mass spectra are obtained: with ethanol ( $M=242$ ), *n*-propanol ( $M=270$ ) and *n*-butanol ( $M=298$ ). This leads to the structure VI, as given in Figure 2, for the artefact with molecular mass 214.

Typical mass spectra obtained are given in Figure 3.

Mass spectra obtained with chemical ionization, using ammonia as the reagent gas, are in agreement with the structures given in Figure 2. Protonated molecular ion peaks and little fragmentation has been observed in the spectra of the compounds with structures I, II and VI. Protonated and ammoniated molecular ion peaks and little fragmentation has been observed for the other three structures.

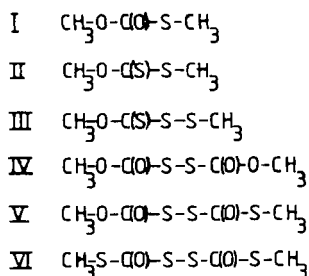


Figure 2 Structural formulae of the identified artefacts

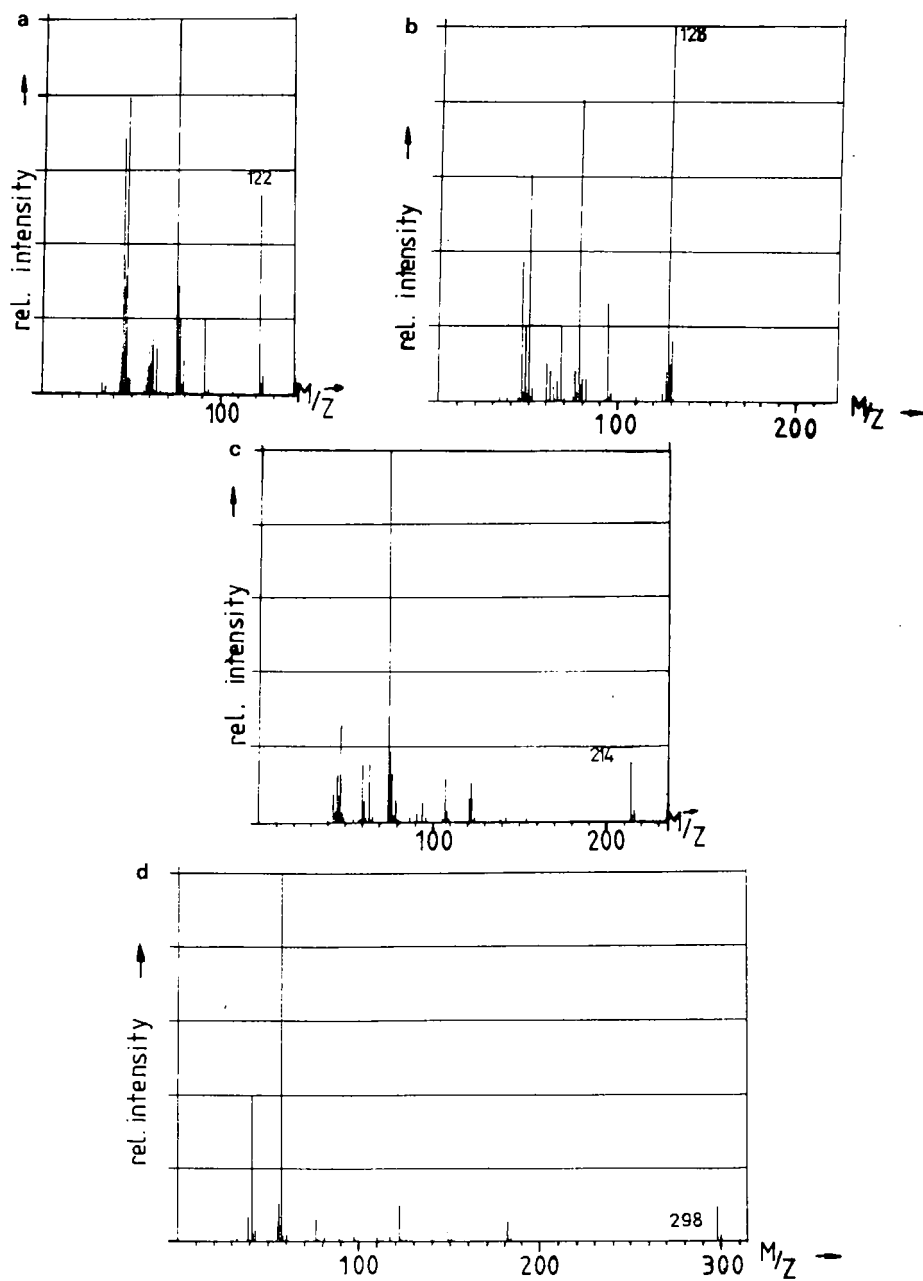


Figure 3 Mass spectra of: (a) II/CH<sub>3</sub>OH; (b) II/CD<sub>3</sub>OD; (c) VI/CH<sub>3</sub>OH; (d) VI/n-C<sub>4</sub>H<sub>9</sub>OH. Conditions see Figure 1.



### Formation of artefacts with other modifiers

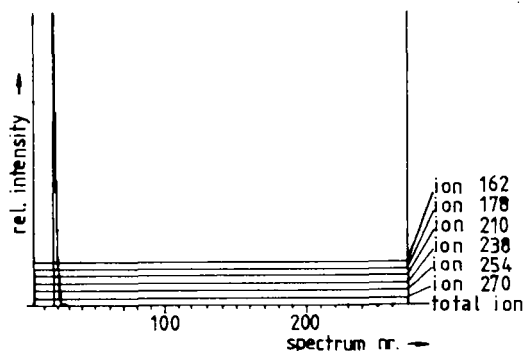
Firstly, in order to establish whether analogous artefacts are formed when methanol is replaced by the same amount of higher alcohols, a number of experiments were carried out, the results of which are summarized in Table 2.

From this table it is seen the artefacts III, IV and V are not formed with the higher alcohols. No artefact formation at all was observed with 2-propanol (Figure 4). With 2-butanol only little artefact formation was found. Therefore, 2-propanol and 2-butanol

**Table 2** Formation of artefact analogues when different aliphatic alcohols are used

Modifier	Artefact number					
	I	II	III	IV	V	VI
Methanol	++(106)	+++(122)	+(154)	+(182)	+++ (198)	+++ (214)
Ethanol	+(134)	++ (150)	-	-	-	++ (242)
1-propanol	+(162)	++ (178)	-	-	-	++ (270)
2-propanol	-	-	-	-	-	-
1-butanol	+(190)	++ (206)	-	-	-	++ (298)
2-butanol	+(190)	++ (206)	-	-	-	++ (298)

Artefact observed (+ to +++) or not observed (-); (M)



**Figure 4** Total ion current chromatogram (lower trace) and mass fragmentograms of expected products from 2-propanol as moderator (six upper traces). Conditions see Figure 1.

are two moderators which may be used instead of methanol in studies to determine the desorption efficiency of some compounds (see below).

Secondly, four other additives have been investigated: acetone, dichloromethane, diethylether and chloroform. The first three yield no artefacts, whereas the latter gives a large amount of products which have not been analyzed further in this study.

Reaction conditions have also been varied. No artefact formation is observed when a mixture of  $\text{CS}_2$  and methanol, without active charcoal, is allowed to stand for a prolonged period of time. Apparently the charcoal acts as a heterogeneous catalyst. In the presence of active charcoal, the use of super dry solvents, or the addition of a neutral drying agent, such as magnesium sulphate, does not influence formation and yield of the artefacts, nor does the presence or absence of light. It is known from literature data<sup>15,16</sup> that the reaction between  $\text{CS}_2$  and methanol is a base-catalyzed process. In agreement with this, the addition of ammonia ( $50\ \mu\text{l}$  concentrated solution) results in a slightly enhanced artefact formation. The addition of nitric acid ( $50\ \mu\text{l}$  concentrated solution) does not have any effect.

### Determination of desorption efficiency

Within the scope of the present study the determination of the desorption efficiency is only useful with modifiers which do not give artefact formation. These modifiers are: 2-propanol, 2-butanol, acetone, dichloromethane and diethylether.

For these experiments four polar organic compounds have been selected, which show desorption efficiencies between 30 and 60% when pure carbon disulphide is used as the desorbing solvent.<sup>7,17-19</sup> These compounds are: *n*-butanol, cyclohexanone, 2-propanol and 2-methoxyethanol.

The desorption efficiency from active charcoal of these compounds have been determined with carbon disulphide to which 5% of the selected modifiers is added, according to the procedure described above. The results are given in Table 3.

The present study, which is rather limited, does not allow general statements about the solvent to be selected in various applications. From this table it is clear that 2-propanol or 2-butanol are well

**Table 3** Desorption efficiency of standards with CS<sub>2</sub> and CS<sub>2</sub>+5% modifier. R.s.d. < 10% (n = 3)

Solvent	Compound			
	<i>n</i> -butanol	Cyclo-hexanone	2-propanol	2-methoxy-ethanol
Carbon disulphide	24	67	45	13
CS <sub>2</sub> + methanol	109	92	54	33
CS <sub>2</sub> + 2-propanol	138	124	—	70
CS <sub>2</sub> + 2-butanol	100	80	110	11
CS <sub>2</sub> + acetone	23	73	20	11
CS <sub>2</sub> + dichloromethane	27	54	26	7
CS <sub>2</sub> + diethylether	36	72	5	13

suitable as a modifier to the carbon disulphide in desorbing these four polar organic pollutants from the active charcoal tubes. The use of other modifiers may be considered for particular cases as well.

## CONCLUSIONS

During the desorption of polar organic air pollutants from active charcoal tubes with carbon disulphide methanol mixtures artefacts are formed. These artefacts have been identified as a thiocarbonate, a xanthate and four disulfanes. Other polar modifiers added to the carbon disulphide have been studied for their ability both to reduce the artefact formation and to enhance the desorption efficiency. Although the limited design of the present investigations does not allow statements to be made for all applications, 2-propanol appears to be a good alternative for methanol.

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