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DIMETHYLFORMAMIDE AND CARBON DISULPHIDE DESORPTION EFFICIENCIES FOR ORGANIC VAPOURS ON GAS-SAMPLING CHARCOAL TUBE ANALYSES WITH A GAS CHROMATOGRAPHIC BACKFLUSH TECHNIQUE

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SUMMARY

The NIOSH-approved charcoal tube–gas chromatographic method to quantify workplace air pollution recommends carbon disulphide (CS_2) as desorption solvent. CS_2 is a toxic substance with high vapour pressure (275 mmHg at 20°C) and low desorption efficiency for polar compounds. Furthermore, the short retention times on most columns result in interferences with the organic analytes.

The aim of this study has been to compare the desorption efficiency of N,N-dimethylformamide (DMF) and CS_2. DMF, too, is a toxic solvent, but with a low vapour pressure (2.65 mmHg at 20°C) and a long retention time on polar columns. Consequently, DMF may be backflushed without affecting any important analytes.

Gas chromatographic analyses were carried out on 25 industrially used organic compounds in five solutions, each containing one compound from the five chemical classes: alcohols, esters, ketones, aromatic hydrocarbons and chlorinated compounds. The experimental design stratified retention times and concentrations through each class and each solution. Desorption efficiencies for polar compounds were close to 100% using DMF, whereas CS_2 was a better desorption solvent for non-polar compounds.

With the use of backflush it may be concluded that DMF is a useable and safer alternative to CS_2 as the solvent of desorption for routine charcoal tube gas sampling from workplace air.

INTRODUCTION

The U.S. National Institute of Occupational Safety and Health (NIOSH) has worked out procedures for the quantification of many organic vapours[1,2]. According to the general procedure, a measured volume of air is sucked through a charcoal sampling tube to trap the organic vapours present. Before analysis the charcoal is transferred to a small vial, and desorbed with carbon disulphide (CS_2). An aliquot of the desorbed sample is injected into a gas chromatograph and the resulting peak area determined and compared with areas obtained from the injection of standards. The

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method has been thoroughly tested[3] and recently reviewed[4], and suggestions for refinements have been reported[5].

The present study has focused on an alternative desorbent to CS_2 in order to overcome some of the following disadvantages associated with this solvent. (i) CS_2 is a toxic substance (maximum allowable concentration (MAC) at the workplace is 5 ppm in Denmark) with a high vapour pressure (*ca.* 275 mmHg at 20°C). Consequently, it is very difficult to avoid human contact with the vapours, and possible evaporation of CS_2 during and after addition of precise amounts to the charcoal constitute a possible source of error. (ii) CS_2 has a short retention time on most gas chromatographic (GC) columns. Merging with compounds of interest in the chromatogram is often unavoidable, although the small response of CS_2 to flame ionization detection tends to diminish the problem. (iii) CS_2 is a useful all-round solvent, but desorption efficiencies for polar compounds are poor. For the analyses of polar compounds it is recommended to add small amounts of, for example, butanols to the CS_2. This, however, results in further merging of peaks in the gas chromatogram.

N,N-Dimethylformamide (DMF) has the potential of overcoming these problems. (i) Although DMF is in the same range of toxicity as CS_2 (MAC = 10 ppm in Denmark), its low vapour pressure (2.65 mmHg at 20°C) makes it much easier to handle both in safety and analytical senses. (ii) On polar columns merging is no problem owing to the very long retention time of DMF. A correspondingly long time of analysis is avoided, when a backflush system is used[6,7]. (iii) Being a polar solvent DMF should have much better desorption efficiencies for polar compounds than CS_2, but possibly with expense on non-polar analytes.

THEORY AND EXPERIMENTAL DESIGN

After desorbent has been added to the charcoal the analytes distribute between the liquid phase and the solid phase with an equilibrium constant K. It is assumed that this constant is not affected by the head space above the liquid phase. This assumption is discussed later.

The desorption efficiency (D) is related[8] to K by eqn. 1:

$$\frac{1}{D} = K \frac{\text{mass of solid phase (mg)}}{\text{volume of liquid phase (ml)}} \tag{1}$$

The value of D is determined by comparison with a standard solution analysed without the addition of charcoal, from eqn. 2:

$$D = \frac{\text{area sample} - \text{area blank}}{\text{area standard}} \tag{2}$$

If the analytes initially were adsorbed on to the charcoal the experimentally estimated value for K will be to low if the analytes are irreversibly bound at the surface or if their kinetic rate values are low.

In order to evaluate DMF as desorbent in comparison with CS_2, 25 compounds were selected from five chemical classes: alcohols, ketones, esters, aromatic hydrocarbons and chlorinated compounds. Values of D were determined for both

desorption solvents from either side of the phase equilibrium, *i.e.* the analytes initially in the liquid phase respectively adsorbed on to the solid phase. In the latter case charcoal tubes were prepared according to the NIOSH procedure. Appropriate amounts of a stock reference solution were injected with a microlitre syringe. Relative concentrations of the Danish MAC values were approached to 130%, 100%, 50%, 30% and 10% in each class of compounds.

The retention times of the compounds could be ranked into five logarithmic approximately equal intervals, *i.e.* 1–2.5 min, 2.5–5 min, 5–9 min, 9–20 min and above 20 min.

Five stock reference solutions were used in the experiment, each containing one compound from each chemical class, *i.e.* five compounds in each stock reference solution (Table I). All retention times and all relative concentrations were embodied in each solution.

EXPERIMENTAL

Sample preparation

Commercially available pure chemicals were used. The charcoal tubes were purchased from SKC (Pittsburgh, PA, U.S.A.) and containing a 100-mg sample charcoal layer and 50-mg back-up charcoal layer. All tubes came from the same lot. The stock reference solutions were prepared by weighing approximate volumes of the pure compounds making up a total volume of a 10-ml volumetric flask.

With a microlitre syringe, 4.5 μl of each stock reference solution was injected on ten charcoal tubes from which the back-up layer had been removed. The same volume was injected from all five stock reference solutions to gain maximum accuracy[9]. Every second tube was desorbed with 1 ml of CS_2 and the others with 1 ml of DMF, reducing the possible effect of human learning during preparation.

Standard solutions in CS_2 and DMF were prepared with concentrations close to that derived from the desorbed charcoal. From each standard two samples were analysed by GC directly and five after addition of charcoal to 1 ml of standard. The purities of the desorbent solvents were checked before and after adding 1-nonene as an internal standard.

Gas chromatographic analyses

All sample analyses were carried out on a Hewlett-Packard (HP) gas chromatograph Model 5840 modified for backflush by use of a slightly changed capillary column pressure regulator system (Fig. 1).

The gas chromatograph was equipped with a flame ionization detector (FID) and an HP 7671A Autosampler. The autosampler shows a standard deviation of less than 2% for injection[10]. The sample tray will hold 35 small sample vials sealed with septum caps using a special crimping tool. The injected amount was 0.58 μl.

GC conditions in connection with the backflush technique were as follows. FID: hydrogen flow-rate 30 ml/min, air flow-rate 240 ml/min; carrier gas: nitrogen, flow-rate 30 ml/min; stationary phase: 12% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on Chromosorb P, 60–80 mesh; columns: packed stainless-steel columns of 1/8 in. O.D., precolumn, 1.5 m, main column, 2.0 m; temperatures: oven, 92°C; injection, 175°C; detector, 200°C.

TABLE I

MAC VALUES, RETENTION TIMES AND RELATIVE CONCENTRATIONS FOR THE ANALYTES

The table gives data on the Danish MAC values, experimentally obtained retention times and target concentrations for the analytes relative to the MAC values. The final column gives the five stock reference solutions for GC. They have been constructed to stratify compound type, retention time intervals and concentrations, *i.e.* reference solution S1 is a mixture of 2-methylpropan-1-ol, methyl methacrylate, 4-methylpentan-2-one, styrene and 1,2,3-trichloropropane.

	Danish MAC (ppm)	*Retention time (min)*	*Relative conc. (%)*	*Stock reference solution*
Alcohols				
2-Methylpropan-2-ol	50	2.65	130	S1
Propan-2-ol	200	2.93	50	S2
2-Methylpropan-1-ol	50	5.64	10	S3
2-Ethoxyethanol	100	18.10	100	S4
2-Butoxyethanol	50	37.74	30	S5
Esters				
Ethyl acetate	300	2.91	10	S5
Methyl methacrylate	100	4.48	100	S1
Butyl acetate	150	6.34	30	S2
Hexyl acetate	50	15.67	130	S3
2-Ethoxyethyl acetate	100	28.36	50	S4
Ketones				
Acetone	500	3.05	30	S4
Butanone	150	4.07	130	S5
4-Methylpentan-2-one	50	6.01	50	S1
4-Methylpent-3-en-2-one	25	11.11	10	S2
Cyclohexanone	50	33.59	100	S3
Hydrocarbons				
Benzene	10	3.10	50	S3
Toluene	100	4.81	10	S4
Ethylbenzene	100	6.70	100	S5
Styrene	50	13.89	30	S1
Indene	10	47.10	130	S2
Chlorinated and nitrated compounds				
Dichloromethane	100	2.31	100	S2
1,2-Dichloropropane	75	4.80	30	S3
1,2-Dichloroethane	20	5.37	130	S4
2-Nitropropane	25	12.53	50	S5
1,2,3-Trichloropropane	50	38.30	10	S1

The integration programs were optimized individually for each reference solution, and fifteen samples were set up with determination in duplicate for each of the two desorbents to be compared. These fifteen samples were arranged in the sample tray as follows: one blank for the solvent, one blank for solvent plus internal standard, one standard solution without charcoal, one blank for the charcoal, five stan-

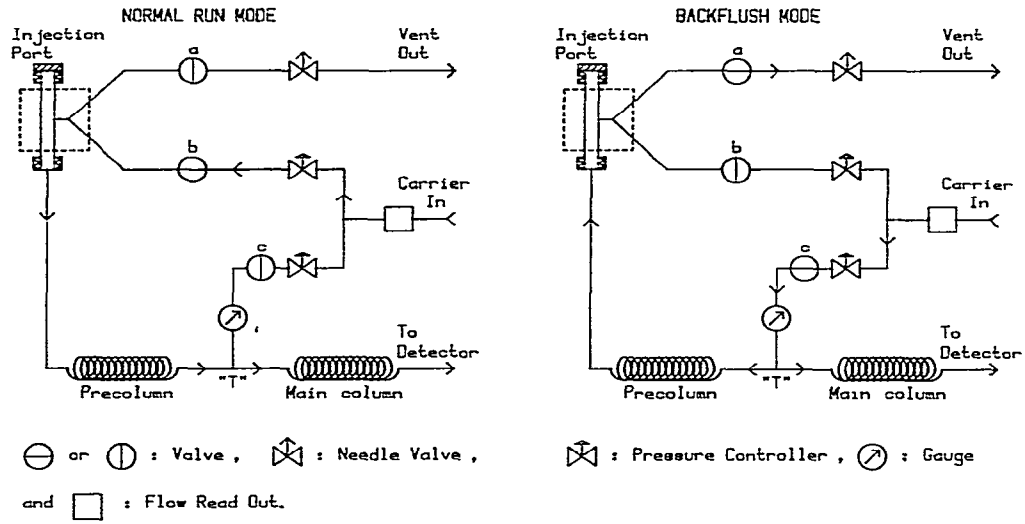

Fig. 1. Diagram showing the two-column backflush system. In the normal run mode, valves a and c are closed and valve b is open, allowing the carrier gas to go through the injection system and both columns. The pressure controller preceding valve b is set to give appropriate flow through the columns. When DMF is about to enter the main column, all the low boiling substances of interest have eluted into the main column. Valves a and c are then opened and valve b is closed. The carrier gas splits at point "T". The gauge measures the pressure at this point. The pressure is the same in normal mode and in backflush mode, securing no baseline abruption and no flow changes through the main column. The pressure is regulated by the pressure controller preceding valve c. The needle valve beyond valve a controls the backflush flow through the precolumn.

dards with charcoal alternating with five samples from charcoal tubes and one standard without charcoal. This set-up reduces the analytical error due to linear drift over time of the gas chromatograph.

GC analyses on the stock reference solutions were initiated on Friday mornings and finished during the weekend. On Monday mornings the analyses were reinitiated to get an impression of sample stabilities.

Calculations

Integrated areas were calculated per weight unit in total sample as an average of the duplicate GC determination. The resulting number constitutes the average FID response for the specific compound. In the following this number will be denoted the response area.

The GC variations turned out to be small and further limited owing to the arrangement of the sample vials. Although 1-nonene was added as internal standard, correction would not have any significant effect in eliminating GC variations. It would, however, reinforce errors in the sample preparation. Addition of desorbent solvent in excess of 1 ml would dilute the analyte desorbed from the charcoal but concentrate the internal standard relatively, because the charcoal–solvent ratio has decreased. The presence of any undetected interaction effect between analytes would not have any effects on the conclusions in comparing CS_2 and DMF as desorbents.

The mean response areas for the 25 analytes from the two sample vials of each

desorbent solvent containing "pure standard" were estimated. These are the "area standard" numbers to be used to calculate the desorption efficiency in eqn. 2.

From both sides of the phase equilibrium the mean response area for each analyte was calculated from the response areas of the appropriate five samples. These are the "area sample" numbers to be used in eqn. 2. A small gap between the two-side phase equilibrium determination of response areas reflects the existence of a true phase equilibrium.

The blank samples had no significant areas.

TABLE II

DESORPTION EFFICIENCY

The table gives desorption efficiencies calculated from both sides in the two-phase equilibrium system, liquid to solid (l → s) and solid to liquid (s → l). The third column gives the difference between the two calculations. See text for details.

	DMF			*CS_2*		
	l → s	*s → l*	*Difference (%)*	*l → s*	*s → l*	*Difference (%)*
Alcohols						
2-Methylpropan-2-ol	102.37	100.30	2.1	86.13	87.20	−1.1
Propan-2-ol	101.55	91.63	9.9	82.04	75.54	6.5
2-Methylpropan-1-ol	101.14	93.82	7.3	82.54	77.74	4.8
2-Ethoxyethanol	100.00	92.67	7.3	60.87	53.32	7.6
2-Butoxyethanol	99.66	97.51	2.2	37.82	41.94	−4.1
Esters						
Ethyl acetate	102.71	107.76	−5.0	99.26	103.92	−4.7
Methyl methacrylate	97.33	93.69	3.6	92.93	91.43	1.5
Butyl acetate	99.61	90.23	9.4	98.34	90.66	7.7
Hexyl acetate	96.25	93.52	2.7	100.31	95.98	4.3
2-Ethoxyethyl acetate	101.12	98.05	3.1	98.37	91.82	6.6
Ketones						
Acetone	100.91	94.42	6.5	94.51	93.75	1.0
Butanone	101.50	87.31	14.2	98.12	80.19	9.0
4-Methylpentan-2-one	100.57	94.84	5.7	93.49	88.02	5.5
4-Methylpent-3-en-2-one	95.00	79.87	15.1	81.34	72.00	9.3
Cyclohexanone	99.04	67.77	31.3	86.58	58.22	28.4
Hydrocarbons						
Benzene	84.13	81.83	2.3	101.01	101.77	−0.8
Toluene	76.15	74.59	1.6	99.60	95.20	4.4
Ethylbenzene	87.98	85.44	2.5	97.84	93.69	4.2
Styrene	52.45	49.28	3.2	84.87	82.13	2.7
Indene	0.04	0.00	–	81.27	32.05	–
Chlorinated and nitrated compounds						
Dichloromethane	99.78	91.26	8.5	100.74	102.25	−1.5
1,2-Dichloropropane	100.49	98.15	2.3	103.95	101.89	2.1
1,2-Dichloroethane	97.05	93.78	3.3	100.78	97.03	3.8
2-Nitropropane	11.66	0.01	–	23.19	0.02	–
1,2,3-Trichloropropane	73.04	63.26	9.8	101.15	96.97	4.2

RESULTS

For each of the 25 analytes the experimental data were used to calculate a mean response area in each desorbent solvent for the "pure" standard and corresponding areas for the two-side estimation of the phase equilibrium. From these data the desorption efficiencies were derived from eqn. 2. The results are given in Table II.

An increase in the relative standard deviation might be expected when compound concentrations are small, or when peaks are broad because of a long retention time. However, our experiment did not reveal any such effects. The estimated relative standard deviations are all in the range 0.5–3% (data not shown).

Sample stability over time was not influenced significantly by the charcoal

TABLE III

SAMPLE VIAL STABILITY

The table gives values for the percentage change in areas after analyses following 3 days storage in the autosampler at room temperature. Samples are standards without charcoal.

	DMF	*CS_2*
Alcohols		
2-Methylpropan-2-ol	−0.53	+2.74
Propan-2-ol	−0.98	+3.10
2-Methylpropan-1-ol	−0.33	+0.55
2-Ethoxyethanol	−2.43	+4.36
2-Butoxyethanol	+0.32	+15.05
Esters		
Ethyl acetate	+1.30	+5.95
Methyl methacrylate	−0.64	+5.60
Butyl acetate	−1.13	+13.43
Hexyl acetate	−0.55	+9.89
2-Ethoxyethyl acetate	−2.21	+10.43
Ketones		
Acetone	−2.82	−1.49
Butanone	+0.91	+5.58
4-Methylpentan-2-one	−0.66	+8.25
4-Methylpent-3-en-2-one	−1.18	+13.23
Cyclohexanone	−0.45	+9.02
Hydrocarbons		
Benzene	−0.31	+3.31
Toluene	−2.46	+7.86
Ethylbenzene	+1.27	+14.57
Styrene	−0.93	+12.27
Indene	−1.00	+16.35
Chlorinated and nitrated compounds		
Dichloromethane	−1.10	+1.21
1,2-Dichloropropane	−0.44	+3.79
1,2-Dichloroethane	−1.88	+2.29
2-Nitropropane	+0.63	+8.37
1,2,3-Trichloropropane	−2.25	+12.21

addition. For a specific compound the same order of sample stability was found in the same desorbent independent of the presence of charcoal in the sample. The stabilities through the 3 days of storage of the 25 compounds in samples of pure standards without charcoal are given in Table III as the percentage change.

DISCUSSION

Desorption efficiency

The data on desorption efficiencies (Table II) confirm that the polar solvent DMF has the better desorption efficiency for polar compounds, *i.e.* alcohols and ketones, whereas CS_2 shows better desorption efficiency for non-polar compounds, *i.e.* hydrocarbons and chlorinated compounds.

In the cases of observed low desorption efficiencies, part of an explanation could be the head-space in the sample vials, which amounts to *ca.* 900 μl. A distribution ratio between solvent and head-space of an analyte much in favour of the head-space will result in too low calculated values for the desorption efficiency. The head-space cannot be diminished without affecting the proper work of the autosampler. But a desorption efficiency close to 100% does not necessarily result in a better quantification than a less efficient desorption, *e.g.* 80%, apart from a gain in sensitivity.

The difference between the desorption efficiencies of benzene and toluene in DMF is the result of an integration error due to a poor separation between toluene and 1,2-dichloroethane. A later experiment has revealed a value for toluene similar to that for benzene. Others have reported a better desorption efficiency for styrene using DMF[11]. The recovery found for ethyl acetate exceeding 100% using either desorbent solvent has been found by others[12].

Even though CS_2 has the better desorption efficiency for the hydrocarbons the phase equilibrium constant is determined equally well in both solvents. The same is true for the alcohols, where DMF has the better desorption efficiency. So whether a true phase equilibrium exists seemingly depends on the interaction between the actual compound and the charcoal rather than on the choice of organic desorbent, when sufficient time to equilibrate between the phases is allowed. We believe that some of the extremely low desorption efficiencies reported previously[13,14] have arisen because the time to reach a phase equilibrium has been underestimated. Our results based on 20 h desorption time before analysis do not justify the addition of small amounts of *e.g.* alcohols to CS_2, for better quantification of other alcohols, as recommended by NIOSH.

A significant difference between the phase equilibrium constant determined from either side may indicate irreversible binding of the analyte to the charcoal. This phenomenon is observed in our experiment for 2-nitropropane, indene, cyclohexanone and to a lesser extent for butanone and mesityl oxide. No reliable quantification can be made on 2-nitropropane and indene using charcoal as adsorbent. If cyclohexanone, butanone or mesityl oxide are to be quantified by the charcoal method, accurately determined standard curves should be produced, as also recommended by NIOSH.

The phase equilibrium for the remaining compounds seems to be well established in both desorption solvents, possibly with a slightly smaller gap for the two-side determination in CS_2.

Sample stability

Sample stability over time is a function of both analyte and desorbent evaporation (Table III). The low vapour pressure of DMF together with the low concentrations of analytes result in very stable samples. The concentrations in DMF are constant within 2% through 3 days. This is in contrast to samples in CS_2. Its high vapour pressure causes the solvent to evaporate significantly through 3 days with the result of concentrating the analytes up to 16%. The analytes themselves have escaped the CS_2 samples in amounts that not only reflect their vapour pressures but in addition reflect some other effects, presumably the distribution ratio between air and CS_2.

Clearly solvents as well as analytes must enter the head-space in order to escape the vial. Therefore a pronounced analyte head-space concentration would lead to a greater loss. A distribution ratio for acetone in favour of the liquid phase would be predicted using DMF. Consequently little loss of acetone with time is seen in DMF. If only a little acetone was lost using CS_2 as desorbent, an increase in acetone concentration of 10–15% would be predicted. An actual observed decrease of 1.5% therefore corresponds to an acetone loss exceeding 15%. The difference between acetone loss in DMF and CS_2 can be explained only by a considerably larger acetone head-space concentration in the CS_2 experiment.

Generally, there is a variation in analyte losses from CS_2 much greater than from DMF. Some compounds are not lost from CS_2 during storage, with a resulting increased concentration of 10–15%, whereas others are lost at rates close to the loss of CS_2. Presumably the high CS_2 concentration in the head-space influences the distribution ratio for the non-polar compound in favour of the head-space. The CS_2 sample instability could prove to be the most serious source of error in quantitative workplace air analysis, and at this point DMF greatly surpasses CS_2 as a desorption agent.

CONCLUSION

Comparison of DMF and CS_2 as desorption solvents in the gas-sampling charcoal tube–GC method for quantification of workplace air pollution may be summarized as follows.

(1) DMF elutes after analytes on the GC column. Thus, there is no interference with the low boiling analytes that constitute the greater part of the compounds of interest. The disadvantage is a broadening of the analyte peaks and, to a certain extent, retention of the analytes reducing the FID response.

(2) CS_2 elutes early on the GC column. Presumably this produces a solvent effect analogous to what is known from capillary columns, with narrow peaks and consequently better separation and more theoretical plates. The disadvantage is that the retention time for CS_2 is in the range where many analytes elute. Thus, merging with these compounds is hard to avoid. A very poor FID response for CS_2 tends to diminish the problem.

(3) When CS_2 is used as desorption solvent the phase equilibrium is better obtained as compared with DMF (Table II).

(4) DMF greatly surpasses CS_2 as desorbent, with respect to sample stability. This is important when samples are left in the sample tray of an autosampler for some days during analysis.

(5) Although DMF is toxic to the liver and is adsorbed through the skin, it is a much safer solvent to handle than CS_2 owing to its low vapour pressure at room temperature.

Our overall conclusion is that DMF is a useable and safer alternative to CS_2 as desorption solvent in the routine analyses of workplace air samples collected on charcoal tubes. The long retention time, being the only practical disadvantage, may be overcome with the use of a backflush system.

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