EFFECT OF WATER VAPOUR ON THE DETERMINATION OF TRACE SUBSTANCES TRAPPED ON ACTIVATED CARBON

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The effect is studied of the activated carbon moisture on the recovery (R) of some organic substances, *viz.* benzene, acetone, tetrahydrofuran, ethanol, 2-methy-1-propanol, and 1-butanol, trapped from air of different humidity and desorbed with carbon disulphide to equilibrium. If the weight fraction of water in the activated carbon is $w = 0.02$, the variations of R lie within the limits of error (for 0·3 g of activated carbon and 5 ml of CS_2), whereas if $w = 0.15$, the variations of R, if disregarded, can result in errors as high as -45% for ethanol and -6 to -12% for butanol and acetone. In the case of benzene and tetrahydrofuran, the increase in the water content in the carbon does not affect the R value. The error increases as the activated carbon-to--carbon disulphide weight ratio is raised. For the standard addition method, the relative error was in average 18% (largely negative) for ethanol and -4.5 to -13% for the remaining substances.

In the analysis of air for vapours of organic substances present in low concentrations, preconcentration methods consisting in their complete (conservation)[1-6] or equilibrium[7,8] trapping on solid sorbents are used. The substances trapped can be desorbed either with a suitable liquid eluent or thermally, and analyzed gas chromatographically. As sorbents can serve, *e.g.*, activated or graphitized carbon, silica gel, organic polymers, molecular sieves, *etc.* Of these, activated carbon (AC) is distinguished by its high dynamic capacity, advantageous particularly in the analysis of substances in trace quantities. For a gas chromatographic analysis employing flame ionization detection, carbon disulphide can serve as a convenient eluent, giving rise to a low response in the detector. The desorption is usually achieved by shaking a mixture of the activated carbon with CS_2 to equilibrium, but washing of an AC column with the solvent is also feasible[4,7].

A permanent component of the atmosphere is water vapour; its concentration usually exceeds that of organic pollutants, and so it is also sorbed in higher quantities than the other substances. The capability of activated carbon to sorb water is due to the occurrence of surface oxides of carbon, playing the role of the primary adsorption centres. Each sorbed water molecule then becomes a secondary adsorption centre[9]. Organic substances that form associates in the liquid state (*e.g.*, *via* hydrogen bonds) as well as water have been observed to associate[10,11] also in the sorbed state on activated carbon, and an interaction can be assumed to occur between water and these substances. As compared with water, organic substances will desorb more easily. For instance, in the alcohol series the recovery of methanol is very low against that of higher alcohols[1], and the recovery of water will be still lower and a greater part of sorbed water will remain bonded on the surface of the activated carbon. The presence of water can be thus expected to affect the equilibrium distribution of the other organic substances present, if these are capable of interaction with water (by hydrogen bonding for instance). The effect of the capability of interaction *via*

hydrogen bonding on the equilibrium distribution of a substance in the activated carbon–carbon disulphide system has been established previously[6]. If water enhances the interaction of organic substances with the activated carbon surface, it will cause a drop in the recovery from equilibrium desorptions or a need for increasing the volume of the eluent in the AC column washing approach.

The effect of the humidity of air on the accuracy of analysis using Tenax as sorbent was the concern of Janák and coworkers[8], who found that in the equilibrium method (using a gas–solid system), an error of about $\pm 10\%$ can arise if this effect is ignored. The presence of water caused the sorption of methanol to increase and that of benzene to decrease. In the case of activated carbon, the error may be higher owing to the more extensive sorption of water.

In the present work, the effect is examined of the AC moisture on the recovery of some organic substances in the equilibrium procedure desorption. Activated carbon of the HS type was used with regard to the fact the gas-chromatographic methods of air pollution analysis in Czechoslovak hygienic service have been standardized with this carbon type[12].

Water isotherms on activated carbon of the HS type have been studied by Vaněček[13]. As follows from his work, the weight fraction of water in activated carbon is $w \leqq 0.02$ if the relative humidity of air is below 50%, but attains as much as $w = 0.09 - 0.33$ if the relative humidity of air is $60 - 90\%$ and the equilibrium is allowed to establish $(1.5$ to 10 h for the air flow rate $150 - 1\,000$ ml min$^{-1})$; for sampling in 30 min, $w = 0.03 - 0.15$.

In the desorption procedure in question, the sorbent is allowed to be in contact with the eluent with stirring until the sorption–desorption equilibrium establishes. If an amount m has been trapped on the activated carbon in the conservation manner, then after the sorption this amount is distributed between the solid (m_s) and the liquid (m_l) phases. We have $m = m_s + m_l$ unless losses occur by the heating arising from the contact of the activated carbon with CS$_2$ (this can be prevented by cooling). Let the recovery be defined by the m_l/m ratio. As the distribution constant of the substance is $K_D = m_s m_{CS_2}/m_l m_{AC}$, where m_{CS_2} and m_{AC} are the weight amounts of CS$_2$ and the activated carbon, respectively, the R and K_D quantities are interelated as[14]

$$R = \left(1 + K_D m_{AC}/m_{CS_2}\right)^{-1}. \tag{1}$$

EXPERIMENTAL

Chemicals and Apparatus

Activated carbon HS (Moravské chemické závody, Ostrava), grain size 0·7 to 1·1 mm, was purified by boiling in distilled water, pre-dried under an infrared lamp, activated in a drier at 150°C for 6 h with access of air, and stored in a closed vessel accomodated in a dessicator over activated molecular sieve 4 A. No interfering impurities were found by chromatographic purity check of a carbon disulphide extract of this activated carbon. No impurities were also detected in the CS$_2$ used (Merck, Darmstadt) or in the remaining organic substances (Lachema, Brno).

The measurements were performed on a Chrom 4 gas chromatograph (Laboratorní přístroje, Prague) using flame ionization detection. Glass separating columns, 3 mm i.d., packed with 20% dinonyl phthalate or 10% Carbowax 400 on Chromaton N-AW (Lachema, Brno) were used. The working temperature was 80—90°C, injection chamber temperature 140°C, nitrogen, hydrogen, and air flow rates 30, 35, and 300 ml min^{-1}, respectively.

Preparation of Sorption Tubes, and Sorption of Substances

The sorption tubes were glass ones, 200 mm long and 7 mm i.d., packed with 0·3 g of activated carbon. The packing was fixed with glass microwool or (at the end of the sorption bed) with polyurethane foam[15]. The columns were interfaced to aspiration vessels, and the substances examined were injected into the air stream by means of a Hamilton microsyringe. The air flow rate was 200—500 ml min^{-1}. According to the conditions required, the air was humidified by passing it through a frit absorber containing water of the temperature 20—50°C, or dried by passing it through a silica gel layer. The columns were kept closed, wrapped in polyethylene, and stored in a refrigerator. The increase in the water content was monitored gravimetrically. In some cases, when higher humidity was applied, a checking AC layer was inserted after the sorption tube and analyzed to make sure that no breakthrough of the sorption layer had taken place.

Analysis of Sorbent

The activated carbon from the tubes was poured into a measured amount of CS$_2$ of a temperature not exceeding 7°C, and the internal standard was added. In view of the fact that no activated carbon was added to the calibration solutions, internal standards were chosen such that correction for their sorption was unnecessary (benzene, toluene) or was very small (butyl acetate, where the sorption on AC is about 2%). The system then was allowed to stand at 21—23°C in a closed 20 ml test tube and shaken in 10 min periods. After 90—120 min, 3—5 μl of the solution was injected into the gas chromatograph for analysis. The recovery R was determined by comparing the response (peak height) of the sample to that of the calibration solutions. The latter were prepared in 3—4 replicas by injecting the same amount of the substance as was sorbed on the activated carbon, into the same volume of CS$_2$ as was used for the desorption.

Calibration by Standard Addition

After the analysis, a standard addition amounting to (0·5—1) m was added to the desorbed sample. The system was shaken in 5—10 min intervals, and after 90 min, the sample was analyzed again. Based on the response increment brought about by the standard addition, the intiial amount of substance was calculated by using the balance relations[16].

RESULTS AND DISCUSSION

The measured desorption recoveries R of benzene, tetrahydrofuran, acetone, 2-methyl-1-propanol, 1-butanol, and ethanol in dependence on the weight fraction of water in the activated carbon (w) for the system of 0·3 g of activated carbon and 5 ml of CS$_2$ are shown in Figs 1—3. For the system of 0·3 g of activated carbon and 3 ml of CS$_2$, the dependence, over a narrower region, is depicted in Fig. 4. The variables were supposed to be related linearly and linear regression analysis was performed.
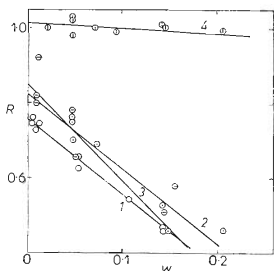
FIG. 1

Dependence of the recovery of benzene and ethanol on the content of water in activated carbon. 0·3 g of activated carbon and 5 ml of CS_2. Sorbed amounts (mg): Ethanol: *1* 0·3, *2* 0·8, *3* 3·2; benzene: *4* 0·3
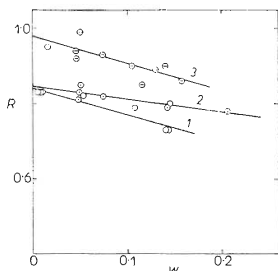

FIG. 2

Dependence of recovery of 2-methyl-1-propanol and acetone on the content of water in activated carbon. 0·3 g of activated carbon and 5 ml of CS_2. Sorbed amounts (mg): 2-Methyl-1-propanol *1* 0·3, *2* 1·1; acetone *3* 0·6
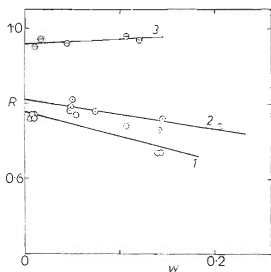

FIG. 3

Dependence of recovery of 1-butanol and tetrahydrofuran on the content of water in activated carbon. 0·3 g of activated carbon and 5 ml of CS_2. Sorbed amounts (mg) 1-Butanol *1* 0·3, *2* 1·1; tetrahydrofuran *3* 0·6—1·8
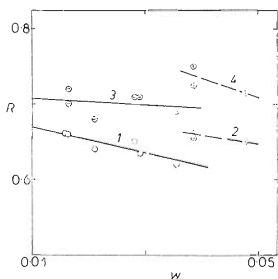

FIG. 4

Dependence of recovery of 1-butanol and 2-methyl-1-propanol on the content of water in activated carbon. 0·3 g of activated carbon and 3 ml of CS_2. Sorbed amounts (mg): 1-Butanol *1* 0·16, *2* 0·26; 2-methyl-1-propanol *3* 0·16, *4* 0·26

The calculated parameters of the regression straight lines $y = a + bx$ along with the correlation coefficients r are given in Table I. As follows from a comparison of the r coefficients with the critical values[17] for the level of significance $\alpha = 0.01$, the dependence of R on w for benzene and tetrahydrofuran is not statistically significant, for the remaining substances the effect of water on the recovery increases in the order butanols-acetone, ethanol.

The dependences enabled us to calculate the effect that the sorption of water can have upon the error of analysis. Assume that the R value has been determined for the lowest possible amount of sorbed water, which in practice is about $w = 0.005$. When w was in the range $0.005 - 0.02$, the error introduced by the effect of water was -3.7 to -4.8% for ethanol, -0.6 to -1.3% for butanol, and -1.2% for acetone. Taking into account the reproducibility of analysis of samples with the same composition (apparent from Figs $1-3$) and the reproducibility of analysis of the same sample, given in Table II, the errors brought about by neglecting the effect of water can be claimed to lie within the limits of experimental errors. On the other

TABLE I

Parameters of the linear regression equations $y = a + bx$ and the correlation coefficients r of the dependences of R on w

Substance	Sorbed amount mg	a	b	r
	0.3 g AC, 5 ml CS$_2$			
Ethanol	0.3	0.7577	−2.0614	−0.9947
Ethanol	0.8	0.8258	−2.0071	−0.9540
Ethanol	3.2	0.8529	−2.5874	−0.8990
2-Methyl-1-propanol	0.3	0.8398	−0.6906	−0.9538
2-Methyl-1-propanol	1.1	0.8449	−0.3288	−0.8566
1-Butanol	0.3	0.7765	−0.6356	−0.8974
1-Butanol	1.1	0.8093	−0.3856	−0.8562
Benzene	0.3	1.0134	−0.1456	−0.4675
Acetone	0.6	0.9755	−0.7074	−0.7974
Tetrahdydrofuran	0.6−1.8	0.9570	0.1532	0.6752
	0.3 g AC, 3 ml CS$_2$			
2-Methyl-1-propanol	0.16	0.7117	−0.4108	−0.2146
1-Butanol	0.16	0.6866	−1.6987	−0.8628

hand, at $w = 0.15$ the error for ethanol attained the values of -36 to -45%, for butanol -6 to -12%, and for acetone -10.8%; these errors exceed those of the experiment.

The error can also increase with the m_{AC}/m_{CS_2} ratio. If the dependence of R on w has been established for an activated carbon-to-carbon disulphide ratio, the dependence for another ratio can be evaluated based on Eq. (1). For instance, for the frequently used system of 0.1 g of activated carbon and 1 ml of CS_2, the error is calculated to be 1.3 to 1.55 times higher. Obviously, except for ethanol, the error will be lower than or comparable to the error of analysis (*e.g.*, in the field of industrial air analysis). However, in conditions that high volumes of humid air are aspirated over the sorbent (analysis of free air), the dependences are to be taken into account; and similarly in the case of water analysis where the organic substances are stripped from water with an inert gas and trapped on activated carbon[18]. As is apparent from Fig. 4, in three cases the decrease in R is higher than with the system of 0.3 g of activated carbon and 5 ml of CS_2. For instance, for 1-butanol ($m = 0.16$ mg) R decreases by 4.4% in the range of $w = 0.005 - 0.02$. For 2-methyl-1-propanol ($m = 0.16$ mg), on the other hand, the data of Table I indicate that the decrease is statistically insignificant. In this narrower range of w, the experimental error clearly can prevail over the dependence of R on w. The R value itself is here lower than for the system of 0.3 g of activated carbon and 5 ml of CS_2. The increase in the error of analysis at low R values has been established before[6,19].

For ethanol and this phase ratio (0.3 g of AC, 3 ml of CS_2), the recovery at $w = 0.123$ was found to be $R = 0.395$. Taking into account the results[20] obtained

TABLE II
Reproducibility of repeated analysis of the same sample for 3—5 repetitions

Substance	Relative standard deviation, %		Number of samples measured
	min. — max.	average	
Ethanol	$0.4 - 6.9$	3.1	14
2-Methyl-1-propanol	$0.4 - 5.5$	1.7	15
1-Butanol	$0.1 - 4.2$	1.6	16
Benzene	$0.1 - 1.3$	0.5	4
Acetone	$1.1 - 3.0$	2.1	5
Tetrahydrofuran	$0.7 - 3.2$	2.2	4

for $w = 0.03$, we have for the range of $w = 0.005 - 0.15$ a decrease in R of 62%, hence more than as anticipated by the theory (50%).

It is beyond the scope of this treatment to offer an explanation of the differences in the dependences of the desorption recovery on the activated carbon moisture. A complex sorption-desorption system is involved in which the equilibrium state can be governed also by the affinity of the substance to both the activated carbon surface and the carbon disulphide. The pore geometry can also be a controlling factor. Water may affect the affinity of the substance to the surface by formation of associates, whose size then may be limited by that of the micropores of the activated carbon[10]. Activated carbon prepared by different methods has been found to have pores of different shape[9]. Therefore, for a different type of activated carbon the dependences of R on w can be different as well. This may be the case the activated carbon GA (Slovenské lučobné závody, Hnúšta), also used in the hygienic service in Czechoslovakia, which is activated with water vapour, in contrast to the HS carbon activated with $ZnCl_2$; the two types differ, among others, in the extent of water sorption[13].

Moreover, the dependences in question are model ones, and the question arises as to the extent to which they will be applicable in practice, where the samples may be trapped from air either during the whole sampling, or at its beginning or towards its end. In the experiments performed, the substances were present predominantly in the first fractions of the aspirated air. We studied this problem for ethanol, where the dependences examined are most pronounced and the motion along the sorption bed is faster as compared with the other substances[21].

By aspiration of 4 l of air, 0.8 mg of ethanol was trapped on 0.15 g of activated carbon in the sampling tube; the increment in the water content was 21 mg. The measurements were carried out on six samples. In the first three samples, ethanol was added to the first fractions (about 200 ml) of air, in the other three samples, to the last 500 ml. The desorption was accomplished by using 1.5 ml of CS_2. In the former cases, R was $0.390 - 0.398$, in the latter cases, $0.398 - 0.405$; these differences lie practically within the limits of errors.

Next experiments were designed to seek whether in addition to water, the desorption recovery is affected also by the amount of the aspirated air. Ethanol, 2-methyl-1-propanol, and 1-butanol (0.3 mg each) were sorbed on four layers of 0.3 g of activated carbon. Two samples were subjected to aspiration of 2 l of air, two samples, to aspiration of 14 l of dried air; the increment in the water content was invariably 2 mg. By desorption with 5 ml of CS_2, the following recoveries were achieved: ethanol $0.745 - 0.76$ and $0.735 - 0.75$ in the two cases, respectively, 2-methyl-1-propanol 0.83 in both cases, and 1-butanol $0.76 - 0.77$ in both cases. Again, the differences observed lie within the limits of errors.

These results indicate that the sorbates were trapped on the front part of the sorption bed. This conclusion, however, is to be confined to trace analyses; if the sorbate is present in higher quantities, it may be expected to penetrate into futher parts of the sorbent, where the inhomogeneity of the water zone can play a part in the resultant effect on the desorption recovery.

TABLE III
Error of analysis in the calibration by standard addition. m Sorbent amount, m_{sa} standard addition, e relative error of analysis

Amount of AC mg	Volume of CS_2 ml	Amount of sorbed water mg	m mg	m_{sa}/m	e %
		Acetone			
300	5	50	0·35	1	— 1·5
300	5	15	0·3	0·75	3·5
		Benzene			
300	5	50	0·3	1	— 6
300	2	27	0·03	1	—11
300	5	15	0·25	0·75	— 2·5
		Ethanol			
300	5	50	0·8	1	—16
300	2	27	0·08	1	—35
300	5	15	0·6	0·75	— 7
300	5	17	0·3	0·5	23
300	5	36	0·3	0·5	29
300	5	3	3·2	0·5	— 5
300	5	16	3·2	0·5	— 6
300	3	12	6·3	0·5	—14
		2-Methyl-1-propanol			
300	5	50	1·1	1	—11·5
300	2	27	0·1	1	—22
100	1	4	0·1	1	—12
100	1	11	0·1	1	—14
300	5	15	0·9	0·75	— 8·5
300	5	17	0·3	0·5	—13
300	5	36	0·3	0·5	— 6·5
		1-Butanol			
300	5	50	1·1	1	—10·5
300	3	5	0·16	1	—10
300	3	5	0·24	1	—12
100	1	4	0·1	1	— 2·5
100	1	11	0·1	1	— 9
300	5	15	0·9	0·75	— 7·5
300	5	17	0·3	0·5	—12·5
300	5	36	0·3	0·5	— 5
		Toluene			
100	1	4	0·1	1	— 5·5
100	1	11	0·1	1	— 3

Presumably, the effect of water on the recovery could be suppressed by using desorbents more polar than CS_2. Addition of methanol to CS_2 has been observed[19] to raise considerably the recovery of substances more difficult to desorb, such as butanol. A two-phase system of water-saturated carbon disulphide + water is even capable of increasing the R value of ethanol and butanol above 0·9 owing to their transfer into the aqueous phase[21]. The combination of CS_2 with an additional component, however, brings about complications emerging from possible interferences with other substances present in the sample or a need for separate analysis of the two--phase system. Another solution to the problem might be desorption with CS_2 alone carried out in two steps.

In order that the knowledge of the moisture or concentration dependences of the recovery should not be prerequisite, we tested the possibility of calibrating by standard addition. We anticipated that the distribution between the two phases would depend on the activated carbon moisture, which was confirmed by the experiment.

The results are summarized in Table III in terms of the relative errors of analysis. Except for ethanol, the errors were negative, which is equivalent to the statement that the equilibrium distribution obtained on introducing the substance into the activated carbon–carbon disulphide system leads to a somewhat higher concentration of the substance in CS_2 than if, in the same conditions, the substance is applied to the activated carbon and subsequently desorbed with CS_2. Relating the response of the substance determined to that of the addition, lower results of analysis are then obtained. If, however, a systematic error of -10% is assumed, the additional error in the method of calibration by standard addition is below 10% for all of the substances except ethanol. In the case of ethanol, the errors were negative for six out of eight results and positive for the remaining two results. On the whole, the error is here higher than in the other cases, which may be related with the rate of establishment of the equilibrium. Better results were attained with higher contents of ethanol $(m \geq 3\ mg)$ – the average error was $-8·3\%$.

REFERENCES

1. Mueller F. X., Miller J. A.: Int. Lab. *4*, 34 (1974).
2. Saalwachter A. T., McCammon Ch. S., jr, Roper C. P., Carlberg K. S.: Amer. Ind. Hyg. Assoc. J. *38*, 476 (1977).
3. Grob K., Grob G.: J. Chromatogr. *62*, 1 (1971).
4. Hovorka J.: Chem. Prům. *29/54*, 147 (1979).
5. Koval M.: This Journal *46*, 1332 (1981).
6. Kaláb P.: Chem. Listy *73*, 416 (1979).
7. Waldman M., Vaněček M.: This Journal *43*, 2905 (1978).
8. Janák J., Růžičková J., Novák J.: J. Chromatogr. *99*, 989 (1974).

 9. Kadlec O., Varhaníková A., Zukal A.: Carbon *8*, 321 (1970).

10. Kadlec O.: Chem. Zvesti *29*, 660 (1975).

11. Zukal A., Kadlec O.: This Journal *38*, 321 (1973).

12. Acta Hyg. Epid. Microbiol., Supplement No 12. IHE, Prague 1975.

13. Vaněček M.: Acta Hyg. Epid. Microbiol., Supplement No 1, 63. IHE, Prague 1977.

14. Dommer R. A., Melcher R. G.: Amer. Ind. Hyg. Assoc. J. *39*, 240 (1978).

15. Koval M.: Chem. Listy *73*, 763 (1979).

16. Drozd J., Novák J.: J. Chromatogr. *136*, 37 (1977).

17. Eckschlager K., Horsák I., Kodejš Z.: *Vyhodnocování analytických výsledků a metod*, p. 103. Published by SNTL, Prague 1980.

18. Mieure J. P., Dietrich M. W.: J. Chromatogr. Sci. *11*, 559 (1973).

19. Fracchia M., Pierce L., Graul R., Stanley R.: Amer. Ind. Hyg. Assoc. J. *38*, 144 (1977).

20. Kaláb P.: Pracov. Lék. *30*, 39 (1978).

21. Langvardt P. W., Melcher R. G.: Amer. Ind. Hyg. Assoc. J. *40*, 1006 (1979).

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