CHROM. 11,224

TEST METHOD FOR ACTIVATED CHARCOAL AIR SAMPLING TUBES BASED ON LIQUID CHROMATOGRAPHIC MEASUREMENTS

M. LÖRINCZ

National Institute of Occupational Health, Department of Chemistry, P.O.B. 22, 1450-Budapest 9 (Hungary)

SUMMARY

An attempt is made to eliminate some disadvantages of the currently used strategy for determination of desorption efficiency and selection of desorption solvent by considering a system of coordinates related to the phenomenon of solvent desorption.

The distribution of an analyte between a solvent and an adsorbent is described by the well known adsorption isotherms. A test method for desorption efficiency based on a wide knowledge of liquid chromatography is proposed with a system of conditions related to qualitative data such as retention volume and skewness factor of a liquid chromatographic peak. Several questions, previously unanswered, can be explained this way, among others, the effect of the matrix on the desorption efficiency of individual components, and a method for eliminating this effect is proposed.

INTRODUCTION

Activated charcoal air sampling is one of the most powerful techniques for application to organic solvent vapours in industrial hygiene[1-5]. Solvent desorption is one of the most popular desorption methods. The desorption efficiency (DE) for a given analyte is calculated by dividing the weight desorbed by the weight sampled or added to the sampling tube[5,6].

Recently, Fracchia *et al.*[7] reported a serious problem, namely that the sample matrix has an effect on the DEs of the individual analytes in the sample matrix itself. Let us consider the test method for DE[3,5,6] used in industrial hygiene from a mathematician's point of view. He would say that only the input and the output values of a function are investigated. Returning to Fracchia *et al.*'s problem of the effect of the matrix on the DE or individual analytes, it seems to be like a complicated mathematical function determined by more parameters than we are able to measure. The present form, strategy and conditions for the determination of DE do not give a satisfactory explanation of the above phenomenon.

We consider that our knowledge of adsorption and desorption processes is

sufficiently wide and detailed. Liquid desorption is simply the distribution of the analyte between a liquid and a solid surface. The distribution coefficient (K) and the DE must be related to each other. DE is expressed by

$$\text{DE}(\%) = \frac{V}{V + GK} \cdot 100 \qquad (1)$$

where V ml is the volume of desorption liquid and G g is the weight of adsorbent placed in the air sampling tube. For example, the increase in DE for ethanol[3] and cyclohexanone[8] with increasing sample size is due to the fact that during liquid desorption the system is not in the linear range of the adsorption isotherm of the convex type.

The liquid adsorption chromatographic behaviour of a system depends considerably on the adsorption isotherm[9,10]. It can be assumed that, under certain circumstances, liquid chromatographic (LC) measurements must serve as a test method for DE studies. In this paper we make an attempt to establish the relationship between some parameters in LC and liquid desorption data.

EXPERIMENTAL

Chemicals

Carbon disulphide, propanol-2, cyclohexanone, chloroform, carbon tetrachloride, toluene and methyl acetate were of reagent grade; n-butanol, isobutanol and ethyl Cellosolve were of technical grade. Activated charcoal with 200–400 grains/cm² (Carlo Erba, Milan, Italy) and of 1.5 mm diameter (E. Merck, Darmstadt, G.F.R.) were used. Carbowax 20M, a regular glass bead (80–120 mesh) and HP Chromosorb W (100–120 mesh) were employed.

Liquid chromatographic apparatus

The LC runs were carried out on a common column chromatograph constructed of Swagelok elements and stainless-steel tubing. The column head pressure was 0.25 atm in every LC run, which was equivalent to a solvent flow-rate of 3–3.3 ml/min. The instrument was tested with a regular glass-filled column. The skewness factor of the carbon tetrachloride and n-butanol peaks varied between 0.7 and 1 ml, which was considered to be ideal with activated charcoal-filled columns.

Both types of activated charcoal were ground in an ETA mill. The 0.125–0.25-mm diameter fraction was separated by sieving and used in the LC studies.

Fraction collection, detection of analytes and construction of liquid chromatograms

The LC fractions were collected in HP-ALS sample vials. The fraction volumes were controlled by means of time measurements. The fraction volume was varied between 0.5 and 3 ml, it was the smallest in the neighbourhood of LC peak maximum. The HP-ALS made two injections from every sample vial into an HP-5840A gas chromatograph equipped with a Carbowax 20M column.

The fraction concentrations were plotted against the fraction volumes and LC curves were drawn through the points. The retention volume was calculated by using eqn. 2, assuming that the two data points on the rising and falling slopes of

a peak in the neighbourhood of the maximum are parts of a three-parameter Gaussian curve:

$$R' \text{ (ml)} = \frac{\ln\left(\frac{C_2}{C_1}\right) - t_1^2 + t_2^2}{2(t_2 - t_1)} \qquad (2)$$

where R' ml is the sample retention volume and C_2 and C_1 are the sample concentrations of the fraction volume mid-points t_2 and t_1 ml of eluate, respectively, with t_1 before and t_2 after the maximum. Finally, the skewness factor (τ) of the LC peak was determined by the method of Roberts et al.[11].

RESULTS AND DISCUSSION

Effect of desorption/elution solvent polarity on DE and LC behaviour
     It was shown in earlier studies that carbon disulphide is a good desorption solvent for chloroform and carbon tetrachloride[1,3,6]. The symmetry of their LC peaks is near to ideal and the DEs obtained from LC data by using eqn. 1 are also in agreement with the experimentally determined values.
     After LC runs with chlorinated hydrocarbons we carried out the same procedure with isobutanol (Fig. 1), the DE of which depends on the amount of sample. The isobutanol peaks showed strong tailing with carbon disulphide as the eluent. The causes of this behaviour are complex, but one of them[9,10] is that the system is not in the linear region of the adsorption isotherm. This may be due to the heterogeneity of the adsorbent surface. The simplest method of overcoming this problem is to use a "stronger" solvent in order to increase the linear capacity of a given system by decreasing the adsorbent heterogeneity. The LC runs were repeated with a more polar solvent. With both eluents the concentration of isobutanol in the 4–5 ml fraction was assigned an arbitrary value of 100.
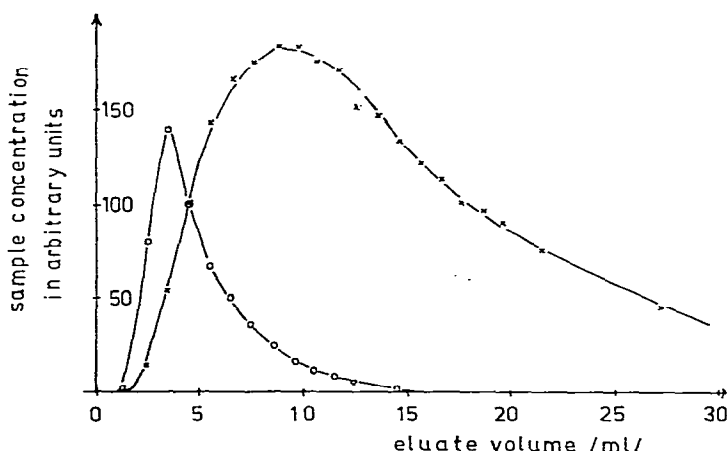

Fig. 1. Liquid chromatograms of isobutanol on Carlo Erba activated charcoal bed. Eluent: ○, 10% (v/v) methyl acetate in carbon disulphide; ×, pure carbon disulphide. Amount of sample: 1 mg.

Mixing carbon disulphide with methyl acetate greatly improved the retention properties of isobutanol, and this also applies to the results of DE measurements. These improvements offer a means of overcoming the problem of the poor DE value of a compound.

We carried out several systematic LC runs with different eluents (see Table I). Each sample contained equal weights of toluene, n-butanol, ethyl Cellosolve and cyclohexanone. In addition, DEs were determined[5,6]. The results obtained with Carlo Erba activated charcoal are given in Table I.

TABLE I

LIQUID CHROMATOGRAPHIC DATA AND LIQUID DESORPTION EFFICIENCIES

Activated charcoal: Carlo Erba. Sample type: multicomponent. DE_{calc}: calculated by eqn. 1. DE_{meas}: measured by the detailed methods. τ: skewness factor (ml). K: distribution coefficient (ml/g). Range of sample amount/component in DE study, 0.1–1.5 mg; in LC experiments, 0.1–5 mg.

Eluent	Parameter	Compound			
		Toluene	Ethyl Cellosolve	n-Butanol	Cyclohexanone
Carbon disulphide	K	0.65	8.0–3.7	5.4–2.8	2.2–1.3
	τ	1.7	35–31	13–9	5.2–3.6
	DE_{calc}	94	65–73	65–78	82–88
	DE_{meas}	91–97	8–19	25–60	45–73
5% (v/v) propanol-2 in	K	0.71	0.95	0.69	0.71
carbon disulphide	τ	2.7–2.3	2.8	2.5	2.6
	DE_{calc}	93	91	94	93
	DE_{meas}	85–89	70–86	86–93	85–92
40% (v/v) methyl acetate in	K	0.78	0.8	0.78	0.66
carbon disulphide	τ	1.0	1.4	3.0	1.5
	DE_{calc}	93	93	93	94
	DE_{meas}	93–98	85–91	85–90	88–92

Where ranges of values are given, the actual value varied with the amount of sample; the left-hand value relates to the smallest and the right-hand value to the largest amount of sample. In our opinion, when the difference between the two concentrations is large, the DE is incorrect and it is necessary to use another solvent for desorption. The distribution coefficient alone is not sufficient for indicating the applicability of a system if the skewness factor of the peak is large. The highest DEs tend to be associated with a low retention volume and skewness factor. Representative chromatograms of n-butanol with two eluents and different amounts of sample on the Merck activated charcoal bed are shown in Fig. 2.

Effect of sample matrix on DE and LC behaviour of individual components of the sample matrix

The problem of this effect arose in earlier work[7] but, because of the absence of an explanation based on adsorption isotherms, the solution remained obscure. We repeated the LC runs with single samples and the retention data for polar compounds differed from those for multicomponent samples with carbon disulphide as the eluent. The results obtained with n-butanol are given in Table II.

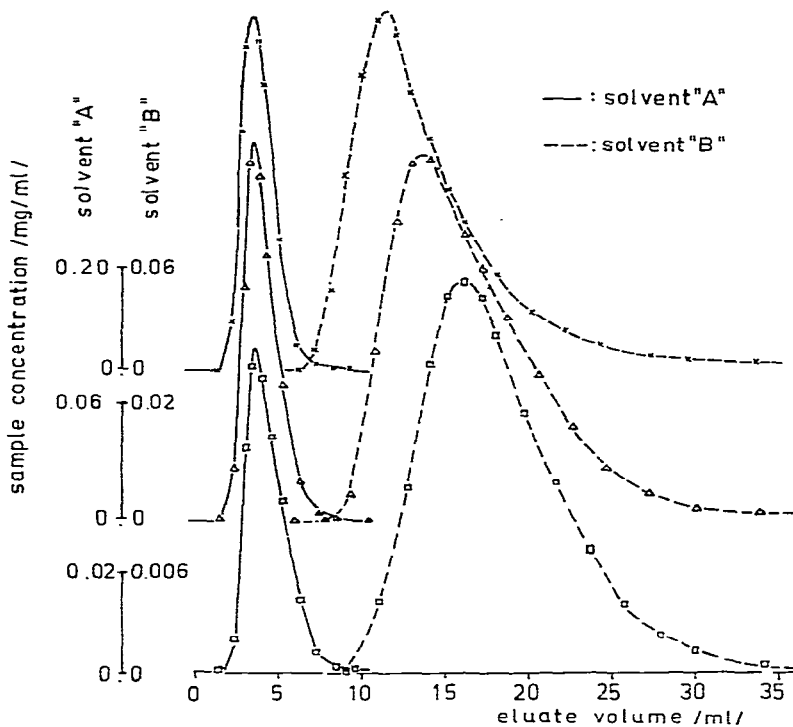In LC, the amount of sample and the matrix commonly have an effect on the

Fig. 2. Liquid chromatograms of n-butanol on Merck activated charcoal bed. Solvent A (solid lines), 40% (v/v) methyl acetate in carbon disulphide; solvent B (broken lines), pure carbon disulphide. Amount of sample: □, 0.15 mg; △, 0.5 mg; ×, 1.5 mg.

TABLE II

LIQUID CHROMATOGRAPHIC DATA AND DESORPTION EFFICIENCIES FOR n-BUTANOL

Activated charcoal: Merck. For other conditions see Table I.

Amount of n-butanol sample (mg)		Parameter	Solvent			
in LC	in DE study		Carbon disulphide		40% (v/v) methyl acetate in carbon disulphide	
			Single sample	Multicomponent sample	Single sample	Multicomponent sample
0.15	0.1	K	11.5	9 9	1.55	1.68
		τ	11.0	8.0	1.1	0.9
		DE_{calc}	47	51	87	86
		DE_{meas}*	26	36	83	86
0.5	0.33	K	10.1	8.1	1.47	1.61
		τ	8.3	6.4	1.2	1.2
		DE_{calc}	50	55	87	86
		DE_{meas}*	40	47	86	86
1.5	1.0	K	8.8	6.8	1.61	1.52
		τ	7.7	4.6	1.0	1.0
		DE_{calc}	53	59	86	87
		DE_{meas}*	46	56	88	88

* A 0.25–0.5-mm diameter fraction of the Merck activated charcoal was used in the DE studies.

chromatographic behaviour of a system, and this applies to *n*-butanol samples, its retention volume being lower for multicomponent samples than for single samples. This is due to the fact that the retention properties of the sample components are similar, and adsorption, desorption and diffusion processes also occur to similar extents. If the chromatographic system is so indefinable, the DE must show similar tendencies in a corresponding range of sample amount. Therefore, it seemed necessary to find a better controlled chromatographic system (see the data for methyl acetate–carbon disulphide in Table II).

Conditions for the LC test method

An eluent can be regarded as an effective desorption solvent only if each component of the sample, including the internal standard in GLC analysis, elutes quickly in a relatively symmetric peak.

The first task is to determine the amount of sample component injected in LC which is appropriate to a given amount of sample in an equilibrium DE determination. The sample concentration in the eluate measured at the end of the column (c_L) is the basis of the calculation. In the middle of the column the concentration of sample in the eluate is equal to the square root of $2c_L$. Taking into consideration the definition of the distribution coefficient, we obtain

$$M_{DE} = 2c_L (KG + V) \tag{3}$$

where M_{DE} is the amount of sample to be used in an equilibrium measurement of DE, suitable for an LC peak relating to a sample concentration of c_L in the eluate. We must select a largest and a smallest amount of sample injected for LC ($M_{inj/min}$ and $M_{inj/max}$) by considering the amount of sample to be collected in the activated charcoal air sampling tubes ($M_{col/min}$ and $M_{col/max}$). In the LC study the amount of sample injected is given by

$$M_{inj/min} = \frac{M_{col/min} w_{1/2}}{1.5} \tag{4}$$

where $w_{1/2}$ is the LC peak width at half-height in millilitres. By this means, M_{DE} calculated from the chromatographic data by eqn. 3 will be similar to M_{col}.

For deciding that a given solvent or solvent composition will be applicable for the desorption of an air sample, the liquid chromatograms with the highest and lowest amounts of sample must fulfil the following conditions:

(1) Each component of the sample (including the internal standard in GLC analysis) must eluate with a peak with a distribution coefficient less than 1.5.

(2) The skewness factor of the LC peak normalized for uncorrected retention volume must be less than 0.4.

(3) The forms of the two normalized liquid chromatograms may not show extreme differences. A normalized chromatogram means that the peak maximum is always taken as 100 in arbitrary units. Two chromatograms are considered to be similar if, when the concentrations of identical fractions are divided by each other and the ratios obtained are plotted against the fraction volume, scattered points around a value of 1 are obtained.

(4) Only 10% of the LC peak may be eluted in fractions with retention volumes, expressed in distribution coefficient units, greater than 3.5.

The last condition makes it possible to use a non-compound-specific detector (*e.g.*, a refractive index detector) for routine work, which greatly accelerates the procedure. If all of the above conditions are fulfilled, the DE will be greater than 85–90%. The speeds of adsorption and desorption processes will be similar. We must prepare a solution of the sample mixture in the chosen desorption solvent with an average concentration c_{ave}, which is defined by

$$c_{ave} = \frac{M_{col/min} + M_{col/max}}{V} \qquad (5)$$

The GLC calibration must be carried out by measuring for G g of activated charcoal V ml of solution described above. If the conditions are fulfilled the kinetic curves of adsorption (in calibration) and desorption (in sample processing) will quickly reach equilibrium[12].

When using solvent desorption, one also has to cope with many LC problems. From investigations of the relationship between LC and liquid desorption, we have found their connection to be satisfactory for more compounds[13] than mentioned here.

ACKNOWLEDGEMENTS

REFERENCES

1 F. H. Reid and W. R. Halpin, *Amer. Ind. Hyg. Ass. J.*, 29 (1968) 390.
2 C. L. Fraust and R. E. Herman, *Amer. Ind. Hyg. Ass. J.*, 27 (1966) 68.
3 L. D. White, D. G. Taylor, P. A. Mauer and R. E. Kupel, *Amer. Ind. Hyg. Ass: J.*, 31 (1970) 225.
4 R. H. Hill, Jr., C. S. McCommon, Jr., A. T. Saalwaechter, A. W. Teass and W. J. Woodfin, *Anal. Chem.*, 48 (1976) 1395.
5 *NIOSH Manual of Analytical Methods*, U.S. Government Printing Office, Washington, D.C., 1974, Method No. 127.
6 M. Lörincz, *Munkavédelem*, 23 (1977) 55.
7 M. L. Fracchia, L. Pierce, R. Graul and R. Stanley, *Amer. Ind. Hyg. Ass. J.*, 38 (1977) 144.
8 A. T. Saalwaechter, C. S. McCammon, Jr., C. P. Roper and K. S. Carlberg, *Amer. Ind. Hyg.Ass. J.*, 38 (1977) 476.
9 L. R. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968.
10 J. C. Giddings, *Dynamics of Chromatography, Part I*, Marcel Dekker, New York, 1965.
11 S. M. Roberts, D. H. Wilkinson and L. R. Walker, *Anal. Chem.*, 42 (1971) 886.
12 M. Lörincz, *Amer. Ind. Hyg. Ass. J.*, submitted for publication.
13 M. Lörincz, *Lectures at the Fifth Congress on Chromatography, Debrecen, October, 1977*, MKE, Budapest, 1977.