STUDY ON THE PRECISION OF THE ACTIVATED CHARCOAL SOLVENT DESORPTION PROCEDURE — CORRELATION OF DESORPTION EFFICIENCIES

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The described method uses activated charcoal sampling tubes for air sampling. Adsorbed compounds are eluted by the static desorption procedure with 1 ml of carbon disulphide, 0·5 ml of the supernatant is filtered off and, after internal standard addition, analysed on a gas chromatograph. Using synthetic calibration mixtures of model organic compounds with air, cumulative sampling and desorption efficiencies for 24 substances were determined for concentration ranges and sample volumes according to current Czechoslovak hygienic standards. Experimental results were treated with the single factor analysis of variance and the precision of the described procedure was estimated for the studied model compounds on the basis of residual sums of squares. Calculated values of cumulative sampling and desorption efficiencies and their precisions were compared with available published data and an acceptable agreement was found. In addition to that, cumulative sampling and desorption efficiencies were also found to be significantly correlated to molar volumes and other related molecular properties for some types of compounds.

For the trace determination of volatile organic compounds in air it is often necessary to employ a concentration step in the analytical procedure. It is now a well established practice to use for this purpose the adsorption of an analyte from air stream on a layer of activated charcoal (AC). This method has been extensively reviewed recently by Crisp[1] and there are some other works on this subject which were not included in this review, namely[2-13].

Adsorbed compounds are, in the case of AC adsorption, usually eluted from the adsorbent by carbon disulphide (CD) because of its small response in the flame ionisation detector (FID). The elution is predominantly carried out statically by suspending the adsorbent in the elutrient[2-11] and, less often, by the flow of the elutrient through the sampling tube[12,13]. The resulting solution of desorbed compounds is, in the case of volatile organic compounds, almost exclusively analysed by gas chromatography (GC).

The main advantage of solvent desorption is in its relative simplicity, in the possibility of performing GC analysis several times under different GC conditions if necessary, in the possibility of using subtractive methods for peak indentifications[14-17], and, in the possibility of using the internal standard (IS) method which results in better precision due to elimination of injection and solvent evaporation errors. So far two AC/CD desorption procedures described by various workers used the IS method but in these cases desorptions were carried out dynamically by the flow of solvent through a sampling tube[12,13]. This approach, although having a serious drawback in the fact, that during the contact of CD with the AC column, the evolving wetting heat causes CD evaporation resulting in bubbles blocking the flow, offers, to a certain extent, the elimination of matrix effects often encountered when mixtures of compounds with widely differing polarities are sampled and desorbed together[4] as described.

The recovery for an analyte is in the case of the AC/CD desorption method usually termed desorption efficiency (DE) and is defined by the formula:

$$DE = (x_F/x_T)\,100\,, \quad (\%) \tag{1}$$

where DE is the percentual value of the desorption efficiency, x_T is the amount of analyte trapped in a sampling tube and x_F is the amount of analyte found in the eluate.

The other important figure is the sampling efficiency (SE) defined by other formula:

$$SE = (x_T/x_E)\,100\,, \quad (\%) \tag{2}$$

where SE is the percentual value of the sampling efficiency and x_E is the amount of analyte entering the sampler in the air stream. The cumulative sampling and desorption efficiency (SDE) is then:

$$SDE = (x_F/x_E)\,100 = DE\,.\,SE/100\,, \quad (\%) \tag{3}$$

and as values of SE are approaching 100%, SDE values are approaching DE values.

The sampling efficiency can be, under real circumstances, influenced by many factors (*e.g.* by the temperature and humidity of sampled air). The common practice for checking the SE value is the use of two sampling tubes connected in series or the use of a backup layer of AC in the sampling tube. Analytical results from the second layer of AC then serve as the indicator of breakthrough of the analyte through the front layer of AC.

However, the bulk of communications published so far do not clearly distinguish between the cumulative SDE value and the DE value with the possible exceptions of the previously mentioned review[1] and of work[11] where rather sophisticated data treatment was used. Thus a difference may arise in values of DE reported by various authors as a result of different methods used for the spiking of sampling tubes with analyte as *e.g.* in paper[7].

Values of DE are also subject to variations due to synergic or matrix effects when several substances of differing polarities are analysed for simultaneously[4]. In some cases a small amount of polar solvent is added purposefully to CD to facilitate the desorption of a polar analyte[4,7].

Aside from the experimental calibration of the AC desorption procedure with the aid of air test mixtures, the insight in the adsorption equilibrium acting during the CD desorption can be gained by the phase equilibrium method as described in paper[18]. However, results presented in the Table I in that work for n-pentane, when treated with the *t*-test, do not support authors' conclusion that no difference in DE values exists between results obtained by spiked tube and by spiked solution methods. Together with differing results for methyl ethyl ketone given in the same work it can be deduced that some bias exists in the proposed procedure. From the theoretical point of view the apparent shortage of the spiked solution method is that it fails to recognize possible "hysteresis" effects during sorption processes. These effects can be very pronounced as, in fact, two different phase equilibria act during the analysis, namely the gas/solid equilibrium during sampling and the liquid/solid equilibrium during desorption. From the practical point of view, the possibility of partial oxidation or other chemical transformation of the analyte during sampling, which is not accounted for in the phase equilibrium method, also cannot be

TABLE I
Experimental Conditions During Measurements

Compound	Perm. tube dimensions $l \times d$, mm	Permeation temperature K	Permeation rate $\mu g\ min^{-1}$	Test atmosphere concentration $mg\ m^{-3}$	Std. sampl. period min	Stationary phase	Column temp. K	Internal standard
Acetone	177 × 4	321·9	115·1	230·2	20	PEG	353·2	methyl isobutyl ketone
n-Amyl acetate	135 × 6	318·4	170·8	341·7	20	PEG	397·2	chlorobenzene
Benzene	30 × 6	296·4	112·5	225·0	10	PEG	362·2	toluene
Butanone	155 × 4	318·2	130·4	260·8	20	PEG	357·6	n-butanol
n-Butyl acetate	70 × 4; 125 × 4[a]	312·2	184·7	369·5	20	PEG	373·2	ethyl acetate
Chlorobenzene	22 × 6	297·7	118·1	236·2	20	PEG	403·2	bromobenzene
Chloroform	8 × 6	297·5	197·2	394·4	3[b]	PEG	367·7	1,2-dichloroethane
Cyclohexane	111 × 6	297·2	261·5	523·0	20	tris	373·2	toluene
Cyclohexanone	305 × 4	318·5	108·4	216·8	20	PEG	405·2	cyclopentanone
p-Cymene	49 × 6	304·6	109·0	218·1	20	PEG	403·2	ethylbenzene
1,2-Dichloroethane	36 × 6	298·8	40·2	80·4	20	PEG	366·2	trichloroethylene
Ethyl acetate[c]	1 660 × 2·5[a]	295·2	235·4	470·8	20	tris	373·2	isoamyl alcohol
Ethylbenzene	34 × 6	298·7	126·0	252·1	20	PEG	403·2	*p*-cymene
Ethyl formate	210 × 4	316·8	151·3	302·6	20	PEG	343·2	isopropyl acetate
n-Heptane	108 × 6	298·7	286·0	572·0	20	tris	373·2	toluene
Isopropyl acetate	188 × 4	321·9	209·7	419·4	20	EGA	358·2	n-butyl acetate
Methyl isobutyl ketone	152 × 4	313·6	88·7	177·5	20	PEG	367·2	n-butanol
Styrene	35 × 6	296·6	112·9	225·8	20	PEG	418·2	cyclohexanone
Toluene[c]	17 × 6	295·2	136·9	273·8	20	tris	373·2	isoamyl alcohol
Tetrachloroethylene[c]	18 × 6	295·2	276·7	553·4	5[b]	DC 550	378·2	n-amyl acetate
Tetrachloromethane	16 × 6	294·2	116·1	232·2	5[b]	squalane	364·2	trichloroethylene
Trichloroethylene[c]	7 × 10	295·2	461·9	923·8	5[b]	DC 550	378·2	n-amyl acetate
1,1,1-Trichloroethane	150 × 4	301·4	256·0	512·0	20	DC 550	354·2	trichloroethylene
p-Xylene	23 × 6	299·0	132·3	264·7	20	PEG	393·2	toluene

[a] Two or more permeation tubes in parallel; [b] high permeation rate, low TLV value, standard sampling period reduced; [c] simultaneous sampling and analysis for two compounds in mixture.

excluded. Recently, this approach has been also criticized by Posner[19] on the basis of the great uncertainty of obtained equilibrium constants K when the DE value exceeds about 80%. Therefore, the spiked solution method as described by Dommer[18] should be used only as a complementary method to the spiked tube method.

Another innovative approach to the prediction of recovery during CD desorption was proposed by Lörincz[20]. However, this method, which uses the chromatographic peak distortion during liquid chromatography of the analyte in the AC/CD system as an indicator of a non-ideal adsorption isotherm suffers essentially from the same problem as the phase equilibrium method, namely that it ignores gas–solid adsorption processes which take place during sampling.

Because of inherent higher precision of the IS method in the GC analysis when compared with the absolute calibration[21] and the lack of communication about the static AC desorption procedure using the IS method, the aim of this work was to asses cumulative sampling and desorption efficiencies for some organic solvents used in industry under conditions typical for industrial hygiene inquiries, to explore the potential for the use of the IS method, and to estimate the precision of the proposed procedure with the aid of common statistical procedures. The other reason for this work was the fact that the bulk of data reported so far the AC/CD procedure was obtained with the coconut AC which differs slightly from grades of AC readily available in Czechoslovakia.

EXPERIMENTAL

Materials and Reagents

Analytical grade carbon disulphide (Merck, Federal Republic Germany) was used without further purification. Model compounds used were mainly analytical grade chemicals and the content of impurities was checked by GC.

Activated charcoal HS 1 (Hrušovské chemické závody, Ostrava, Czechoslovakia), particle size 0·5—1·0 mm. This type of AC is produced by the activation of sawdust and soft wood chips with approximately 60% water solution of zinc chloride at about 970 K. The resulting product has, according to manufacturer's specifications, surface area 1 200—1400 $m^2\ g^{-1}$ and following values were found for the batch used in this work: metal residues: Zn 0·72%; Cu 0·02%; Pb 0·0015% (w/w, by the SW polarography after wet ashing); the apparent mercury density[22] 780 kg m^{-3}; the effective benzene density[22] 2060 kg m^{-3}; wetting heats: benzene 124 kJ kg^{-1}; n-hexane 129 kJ kg^{-1}; water 70 kJ kg^{-1} (the precision of the wetting heat measurement was estimated to be $\pm 10\%$ and reported values were obtained for dry AC after 1 hour activation at 433 K in a laboratory oven). The adsorption capacity determined by the equilibration with a flow of air saturated with benzene vapour at 298 K was about 48% (w/w). The mercury porosimetry gave following values: pore volume for the pore effective radius interval (r_{ef}) 7·5—7500 nm; 0·254 ml g^{-1}; for r_{ef} interval 7500—50 000 nm: 0·112 ml g^{-1}. In the interval between 7·5—7500 nm about 85% of pores had r_{ef} bigger than 25 nm.

GC column packings were commercial products (Lachema, Brno, Czechoslovakia) and used Chromaton N-AW-DMCS 0·20—0·25 mm solid support coated with 10% of one of the following liquid phases: Carbowax 20 M (PEG), ethylene glycol adipate (EGA), DC 550 and 1,2,3-tris-(2-cyanoethoxy)propane (tris). Only in the case of the tetrachloromethane analysis the packing used was prepared by coating Chezasorb N-AW 0·20—0·25 mm (Lachema) with 10% of Squalane (Merck).

Apparatus

Chrom 31b gas chromatograph (Laboratorní přístroje, Prague, Czechoslovakia) equipped with FID and using nitrogen as the carrier gas was used with stainless steel columns of 6 mm i.d. and 1·2 m long. Glass sampling tubes 3·6 mm i.d. and 150 mm long with flame polished ends were used in which AC layer was retained by polyurethane foam separators[23] (approximately 5 × × 5 mm o.d.). For AC dispensing a simple volume dispenser was made by welding a miniature test tube to a glass rod. Sampling tubes' closing caps were prepared from a piece of Tygon tubing by welding its walls together. Pipette filtration tips[24] were prepared by welding a disc of paper Whatman 41 filter (6 mm diameter) to a piece of polyethylene (PE) tubing (4 mm o.d.) on a hot plate covered with an aluminium foil. For preparation of calibration mixtures the air membrane pump, model 1.7.0. (LVDI, Prague, Czechoslovakia) capable of delivering approximately 0·5 l . . min^{-1} of air was used.

Preparation of Sampling Tubes

AC spread in a layer about 1 cm thick was heated in a laboratory oven at 433 K 14—16 hours along with empty sampling tubes and the AC dispenser. Then one polyurethane foam separator was inserted into each still hot tube and about 135 mg of AC was dispensed with the aid of a glass funnel in the sampling tube. After settling the adsorbent by gentle tapping, the second separator was inserted. Sampling tubes prepared in this way were stored in an exsiccator over activated silica gel or capped and wrapped in a piece of aluminium foil in a refrigerator. The length of the AC bed in sampling tubes was about 3 cm. The mean mass of the dispensed adsorbent was 135·5 mg and the coefficient of variation was 3·4% ($n = 15$).

Generation of Test Atmospheres

Test atmospheres consisting of mixtures of studied compounds with air were prepared by permeation of standards from welded PE ampules[25], which is essentially a modification of the earlier procedure described by O'Keeffe and Ortman[26]. The main difference between polytetrafluoroethylene (PTFE) and PE ampules is in the much greater permeation rate of the later which makes them more convenient for the range of concentrations usually encountered in the industrial hygiene practice. This advantage is partly outweighed by the much shorter life of PE permeation tubes as compared with those made from PTFE.

The rate of permeation was checked gravimetrically, thermostating was performed by inserting ampules into a Liebig condenser connected to external circulation ports of the NBE water ultrathermostat. The flow of air purified by passing through an absorber containing about 200 g of AC and measured with a rotameter was supplied by a membrane pump. A dummy resistance consisting of a sampling tube was connected through a three port valve to the outlet of the calibration system to eliminate flow and pressure fluctuations caused by changing of sampling tubes.

The precision of permeant additions to sampling tubes was estimated on the basis of repeated weighings of permeation ampules and was in the range of 0·5—3% depending on the model compound.

Test Conditions

As the knowledge of the precision of analysis in the region of concentrations near Threshold Limit Values (TLV) is of paramount importance, concentrations of model compounds in test atmospheres were set to be approximately equal to current Czechoslovak TLV's for compounds

in question and can be found, with other data concerning experimental conditions during measurements, in Table I. However, for some compounds this was not practical due to low TLV values or high permeation rates of studied compounds or both. In these cases sampling periods were accordingly reduced. The relative humidity of ambient air during measurements was between 40 and 75%.

Preparation of Samples

Eight samples were prepared for each compound including one blanc sample. Of those, five were prepared by employing 20 min sampling period and will be subsequently refered to as standard samples. To assess the risk of breakthrough and the possible dependence of SDE values on the load of analyte on AC, two additional samples were prepared which will be called control samples. The first control sample was prepared by sampling for 1/4 of the standard sample sampling period (usually for 5 min), the second control sample consisted of two sampling tubes connected in series and the back tube was used to monitor the breakthrough. Here, the sampling time was usually twice the standard sample sampling period, *e.g.* 40 min. The flow of the test atmosphere was kept constant at $0{\cdot}5\,1\,\mathrm{min}^{-1} \pm 10\%$. Under these conditions no significant breakthrough occurred for any model compound (back tubes contained generally less than 1% of the amount found in the front tube; in one case about 2·7% was found).

Besides that, the proposed method was applied also to two mixtures of model compounds, namely to the mixture of toluene and ethylacetate and to the mixture of trichloroethylene and tetrachloroethylene.

After sampling, tubes were capped, wrapped in a piece of aluminium foil and stored overnight in a refrigerator. Before the analysis, wrapped sampling tubes were left long enough in the laboratory for temperature equilibration.

Analytical Procedure

1 ml of CD was pipetted into each of eight 3 ml test tubes which were subsequently closed by glass stoppers and cooled in an ice/salt mixture to about 265 K. AC from sampling tubes was then transferred into test tubes which were stoppered again and agitated for 1 h in a shaker at the ambient temperature (295 K).

With the aid of a 1 ml graduated pipette equipped with the filtration tip[24] 0·5 ml of the supernatant was filtered off and transferred into prepared empty test tube. After a stock solution of IS in CD was added by means of a 100 µl syringe, the filtrate was analysed by GC. Each sample was injected four times (0·7—2 µl) with the exception of model compounds analysed in mixtures where only three injections were made for each sample. Simultaneously with every samples series a calibration solution with known concentrations of analysed compound and IS in CD in the same order of magnitude as standard samples was also analysed. IS and calibration solutions were always freshly prepared.

Calculation

The amount of analyte in separate injections of analysed samples was calculated according to the expression:

$$x = Q A_s \, V_2 / V_1 \,, \tag{4}$$

where

$$Q = c_{IS} V \, G_c / A_c \,, \tag{5}$$

and x is the amount of analyte found in a sample (μg); Q is a constant for the same compound, IS stock solution and calibration solution (μg); A_s is the peak height ratio analyte/IS for the analysed sample; V_2 is the added volume of the IS stock solution (ml); V_1 is the volume of filtered portion of the eluate (0·5 ml); c_{IS} is the IS stock solution concentration (μg ml^{-1}); V is the volume of the elutrient used (1 ml); G_c is the calibration solution analyte/IS mass ratio; A_c is the calibration solution analyte/IS peak height ratio.

Using the described procedure, $9 \times 4 = 36$ values were obtained for each model compound (for mixtures $9 \times 3 = 27$). From these, four are blanc values, four are values for the backup tube from the second control sample, eight values belong to control samples and the rest (20 or 15) belongs to five standard samples.

After averages calculated for each standard sample were tested for outliers using the Grubbs' test[27], obtained results were treated by the single factor analysis of variance[28] (ANOVA) in order to investigate to what extent various steps in the described procedure add to the overall variance of results and to calculate, from the residual sum of squares[28], the estimate of the standard deviation and of the coefficient of variation for the studied analytical procedure. ANOVA results are given in Table II.

From the grand average[28] $\bar{Y}$ of amounts found in all 20 or 15 results (or less if there was an outlier) and from the sampled amount, the percentual value of SDE was calculated for each compound (Table III). SDE values for control samples were calculated in the similar manner and are given in Table III.

No attempt was made to study other sources of variations (day to day, between laboratories, instruments and analysts and between various grades of AC).

RESULTS AND DISCUSSION

On the basis of low analytical results for control samples' backup tubes a reasonably safe assumption can be made that in cases of studied compounds SE values were sufficiently close to 100% and resulting recoveries approximate precisely enough DE values.

However, the desorption efficiency estimate DE obtained in this way incorporates errors which can be classified into three main groups: *1*) Random errors originating in inaccuracies in the calibration mixture dosing during sample preparation and in the IS addition, in errors in CD pipetting and, finally, in errors caused by leaks in test tubes' stoppers which result in uncontrollable CD evaporation. *2*) GC analysis errors which are partly random and partly systematic in their nature. *3*) Errors originating in preparation of calibration solutions and of IS stock solutions. These errors are basically random in their character but in calculated values of DE, they will have the effect of systematic errors for one set of values.

In Table II, the zero hypothesis H_0 reflects the fact that no significant difference can be found between variances. The H_1 alternative hypothesis means that the "among samples" variance component of the overall variance is bigger ($s^2_{among} > s^2_{res}$). The H'_1 alternative hypothesis means that the residual variance s^2_{res} is mainly responsible for the overall variance of results ($s^2_{res} > s^2_{among}$).

TABLE II

ANOVA Results for Standard Samples

Compound	Load µg	Average amount found µg	Standard deviation[a] µg	Degrees of freedom among/res	Total sum of squares	MS_{among}	MS_{res}	F	Accepted hypothesis $\alpha = 0.05$
Acetone	2 302	1 890	29·58	4/15	56 955·57	2 739·22	875·21	3·130	H_1
n-Amyl acetate	3 417	3 739	55·23	4/15	215 801·75	10 628·36	3 049·86	3·485	H_1
Benzene	1 125	1 069	4·88	3/12[b]	1 175·68	124·21	23·77	5·226	H_1
Butanone	2 608	2 203	28·25	4/15	42 764·34	1 924·76	797·88	2·412	H_0
n-Butyl acetate	3 695	3 835	133·64	4/15	390 061·80	7 635·96	17 859·10	2·339	H_0
Chlorobenzene	2 362	2 244	23·18	4/15	12 519·55	278·94	537·11	1·926	H_0
Chloroform	591	539	5·85	4/15	7 244·59	420·68	34·22	12·294	H_1
Cyclohexane	5 231	5 288	141·32	4/15	539 588·15	15 002·11	19 970·29	1·331	H_0
Cyclohexanone	2 168	2 030	22·07	4/15	27 340·82	1 252·19	487·05	2·571	H_0
p-Cymene	2 181	2 151	61·80	4/15	102 123·58	2 801·84	3 819·61	1·363	H_0
1,2-Dichloroethane	804	824	8·77	3/12[b]	2 130·84	85·52	92·05	1·076	H_0
Ethyl acetate[c]	4 708	4 282	22·22	4/10[d]	13 573·04	720·49	493·59	1·460	H_0
Ethylbenzene	2 521	2 476	50·91	4/15	47 342·97	528·77	2 592·18	4·902	H_0
Ethyl formate	3 026	1 457	17·73	4/15	18 236·26	844·93	314·49	2·687	H_0
n-Heptane	5 720	6 107	206·04	4/15	1 882 314·06	77 876·18	42 450·56	1·834	H_0
Isopropyl acetate	4 194	4 091	25·73	4/15	38 965·26	1 814·77	661·93	2·742	H_0
Methyl isobutyl ketone	1 775	1 672	38·34	4/15	26 599·70	284·02	1 470·34	5·177	H_0
Styrene	2 258	2 029	37·70	3/12[b]	27 080·92	835·22	1 421·60	1·702	H_0
Toluene[c]	2 738	2 794	11·51	4/10[d]	10 375·74	754·30	132·48	5·694	H_1
Tetrachloroethylene[c]	1 383	1 350	10·62	4/10[d]	13 180·56	1 004·69	112·86	8·902	H_1
Tetrachloromethane	581	560	14·39	4/15	4 488·47	115·06	207·2	1·801	H_0
Trichloroethylene[c]	2 310	2 275	15·85	4/10[d]	101 322·80	8 235,37	251·34	32·766	H_1
1,1,1-Trichloroethane	5 120	5 177	70·30	4/15	86 125·91	749·76	4 942·03	6·591	H_1
p-Xylene	2 647	2 736	40·15	4/15	198 363·76	10 886·62	1 611·85	6·754	H_1

[a] Calculated from residual mean squares MS_{res}; [b] one outlier sample; [c] simultaneous measurements for two compounds in mixture; [d] triplicate injection only.

As can be seen from Table II, for the majority of model compounds both factors contributed an approximately equal share to the resulting variance.

The situation is different with acetone, n-amyl acetate, benzene, chloroform, toluene, tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane and *p*-xylene.

TABLE III

Calculated Parameters and DE Values for Studied Compounds[a]

d_{sph} Diameter of molecules, spherical shape assumed; l_{ell} length of molecule, ellipsoid shape assumed; R_M molar refraction; V_M molar volume; ω area occupied by a single adsorbed molecule; v coefficient of variation.

Compound	d_{sph} nm	l_{ell} nm	Parachor	R_M	V_M ml mol^{-1}
Acetone	0·615	0·806	161·9	16·16	73·40
n-Amyl acetate	0·778	1·020	337·5	36·28	148·73
Benzene	0·656	0·859	206·8	26·20	88·86
Butanone	0·657	0·861	200·0	20·67	89·53
n-Butyl acetate	0·748	0·980	297·6	31·60	132·06
Carbon disulphide	0·576	0·755	144·0	21·41	60·28
Chlorobenzene	0·686	0·899	245·5	31·17	101·79
Chloroform	0·633	0·830	183·7	21·37	80·16
Cyclohexane	0·700	0·917	242·8	27·72	108·09
Cyclohexanone	0·690	0·904	252·5	27·88	103·70
p-Cymene	0·792	1·038	363·0	45·36	156·56
1,2-Dichloroethane	0·630	0·826	189·0	21·02	78·98
Ethyl acetate	0·678	0·887	217·4	22·26	97·83
Ethylbenzene	0·730	0·956	286·3	35·78	122·46
Ethyl formate	0·636	0·830	177·8	17·70	80·20
n-Heptane	0·775	1·015	313·3	34·57	146·55
Isopropyl acetate	0·719	0·942	255·6	29·96	117·15
Methyl isobutyl ketone	0·735	0·963	277·4	30·05	125·11
Styrene	0·714	0·936	275·3	36·49	114·96
Toluene	0·696	0·912	246·8	31·11	106·29
Tetrachloroethylene	0·687	0·900	244·8	30·35	102·19
Tetrachloromethane	0·674	0·883	220·4	26·44	96·50
Trichloroethylene	0·658	0·862	210·0	25·40	89·74
1,1,1-Trichloroethane	0·681	0·893	225·3	26·21	99·74
p-Xylene	0·731	0·958	286·1	36·03	123·30

[a] Calculated from values as given in[39]; [b] calculated according to[31,32]; [c] calculated from sums of squares as given in Table II; [d] calculated from four analyses of a single sample; [e] 5 min control sample not prepared due to the high permeation rate, see also Table I; [f] relative permitti-

As far as 1,1,1-trichloroethane is concerned, the relatively high MS_{res} value results probably from the baseline instability and from the incomplete separation of the analyte and IS.

For the rest of above listed compounds, the main reason for the variance in samp-

TABLE III
(*Continued*)

ω^b nm^2	ε	Standard samples		Control samples			
				5 min		40 min	
		SDE, %	v^c, %	SDE, %	v^d, %	SDE, %	v^d, %
0·268	21·5	82·1	2·9	80·6	0·9	84·4	1·2
0·429	4·8	109·4	2·9	94·6	2·6	110·1	1·8
0·305	2·3	95·0	1·0	92·4	0·2	98·8	0·8
0·306	18·5	84·4	1·8	76·8	2·4	84·9	0·7
0·397	5·0	103·8	3·9	90·2	3·5	104·8	0·7
0·235	2·7	—	—	—	—	—	—
0·333	5·6	95·0	1·1	90·0	1·9	94·1	1·6
0·284	4·8	91·1	3·3	—[e]	—	94·8	2·1
0·347	2·1	101·1	3·2	90·2	1·5	104·2	4·0
0·338	15·2	93·6	1·9	92·2	0·8	97·2	1·0
0·444	2·2	98·6	3·4	96·6	3·2	107·1	0·4
0·282	10·5	103·7	1·4	98·2	1·6	102·7	0·6
0·325	6·4	90·9	1·0	87·0	0·3	89·0	0·6
0·377	2·4	98·2	2·0	99·2	1·9	95·4	1·1
0·285	8·0[f]	48·2	2·1	43·9	1·3	47·4	2·2
0·425	1·9	106·8	5·5	81·3	5·5	97·5	4·7
0·366	5·3	97·5	1·1	100·0	0·7	95·4	0·9
0·383	13·1	94·2	2·1	91·3	3·2	91·6	2·0
0·362	2·4	89·8	1·9	87·4	0·7	89·5	2·3
0·343	2·3	102·1	1·3	95·8	0·3	92·8	0·5
0·334	2·3	97·6	2·3	99·7	1·0	97·3	0·5
0·322	2·2	96·5	2·7	103·9	5·9	97·8	2·4
0·307	3·3	98·5	3·7	95·5	0·5	94·1	4·2
0·329	7·1	101·1	1·3	99·6	0·6	100·5	0·8
0·379	2·3	103·4	3·7	97·4	1·4	90·3	0·5

vity value not available in[39], value approximated from values for neighbouring members of the homologic series.

ling was, as for instance in the case of trichloroethylene, where very high permeation rate was noted, the fluctuation in permeation rate resulting from the short life of permeation tubes. In some of these cases a systematic decrease in amounts found in consecutively sampled tubes was apparent.

Extreme MS values for cyclohexane and n-heptane can be ascribed to fluctuations in FID response. Under conditions used (intended for the determination of the sum of aliphatics in air) these compounds elute and are burnt in the FID flame simultaneously with CD present in a large excess. Although, at the FID sensitivity used for the analysis the CD response was small enough (peak height about 5 mm), it can be expected that the ionization of the analyte was influenced by the simultaneous burning of a considerable amount of this solvent. The other reason for this can be that those compounds elute in very sharp peaks with consequent possibility of the peak distortion due to the slow response of the recorder. However, obtained results show a practical potential of a strongly polar stationary phase (tris in this case) for the determination of the sum of aliphatics in the presence of other compounds, for instance for the determination of white spirit vapours in air.

Calculated DE values are given in Table III and for some compounds values exceeding 100% were found. In those cases the *t*-test was applied for the detection of the statistically significant difference from 100% ($\alpha = 0{\cdot}05$). *t* values calculated for n-butyl acetate, cyclohexane and *p*-xylene did not point to any significant difference. In contrast to that, *t* values calculated for n-amyl acetate, 1,2-dichloroethane, n-heptane, toluene and 1,1,1-trichloroethane exceeded the critical value with the highest values found for n-amyl acetate ($t = 6{\cdot}003$) and for toluene ($t = 3{\cdot}801$), in both cases value exceeding the t_{crit} even for $\alpha = 0{\cdot}01$.

Reasons for these deviations may be errors in weighing and preparation of calibration solutions and of IS stock solutions resulting in a systematic error as well as the uncontrolled evaporation of CD during analyses. However, this is not the only possible explanation.

Under ideal conditions the amount of analyte present in CD after desorption should be equal to the amount adsorbed originally on the AC surface. Thus the concentration of an analyte in the eluate should equal:

$$c_A = x_T/V \,. \qquad (6)$$

Nevertheless, there are two factors which can influence this value. The first one is the fact that the adsorption of a part of CD on the surface, and namely in pores, of AC takes place. Adsorbed solvent molecules thus lose one or even two translational degrees of freedom and are in this way more or less effectively excluded from the solution. This in turn leads to the decrease of V and therefore c_A increases.

The second factor influencing the c_A values is the ease with which adsorbed analyte molecules are removed from the AC surface. Small molecules of size comparable to that of CD can enter easily micropores in the AC structure or, in the case of ink bottle pores[29], can easily pass the narrow neck. During the desorption CD molecules can act as a "plug" in those micropores and trap the adsorbate inside the AC structure. In addition to that, adsorbate molecules are bound more strongly in narrow pores due to overlapping attraction forces from closely spaced walls[30] which makes the effective desorption even more difficult. Which of those factors plays the decisive part is difficult to decide; an insight could be gained by changing the size of molecule of the eluent which cannot be easily done.

To obtain further proofs for these speculations, effective dimensions for studied molecules were calculated and are given in Table III along with values of parachor, molar refraction (R_M), molar volume (V_M), surface area occupied by a single adsorbed molecule (ω)[31,32], relative permittivity (ε), and standard sample DE values found in the course of this work. It can be seen from this table that differences are not large when either spherical or ellipsoid (length to diameter ratio 3 : 2) shapes of molecules were assumed and resulting molecular dimensions fall inside the range between 0·5 and 1·5 nm.

Although the mercury porosimetry did not yield any information about true micropores for the batch of AC used in this work, the limiting volume of the adsorption space W_0, which is closely connected with the micropore volume, was determined for the same type of AC elsewhere[33] and the value of 0·389 ml g^{-1} was given.

At studied analyte loads, the volume of the adsorbed analyte is sufficiently small (0·5 – 5 μl) to allow, in connection with the well established tendency for microporous adsorbents to adsorb first by the micropore filling mechanism[30], for the significant part of adsorbate being adsorbed in true micropores with r_{ef} around 2 nm or less. This is supported also by the tendency for DE values to be lower with smaller loads of analyte as is apparent from 5 min control samples DE values (Table III) or from data in[7]. As the rate of adsorption by micropore filling is limited by the rate of molecular or Knudsen diffusion[34], it can be further speculated that also the concentration of an analyte in the sampled air stream as well as the sampling flowrate will influence the DE value.

As the described analytical procedure measures in fact the concentration of the analyte in the eluate rather than directly the amount of analyte, it can be seen now that besides other influences (the solubility of the analyte in CD, matrix effects, the relative humidity of the sampled air-stream) above discussed factors will have the most pronounced effect on the DE value. Further, it can be easily proved that only when the DE value is 100%, the concentration of the analyte in the supernatant will be the same as in the bulk of AC pores and *vice versa*. For the decreasing size of molecule for similar compounds a decrease in DE can be expected and for larger molecules, the retention of a part of the eluent in the AC structure can explain why

sometimes DE values exceed 100%. This is also in agreement with a known fact[35] that with the decreasing pore size the reversal of the empirical Traube's rule occurs with the result that higher members of homologic series are adsorbed less than lower

TABLE IV

Correlations of DE Values with Adsorbates' Molecular Parameters

r_{xy} Coefficient of correlation; b_0 intercept of the regression line; b_1 slope of the regression line; s_R residual standard deviation of the regression equation; n number of data pairs; $r_{0.01}$, $r_{0.05}$ critical values of the coefficient of correlation for significance levels $\alpha = 0.01$ and $\alpha = 0.05$ respectively.

Parameter	r_{xy}	b_0	b_1	s_R
Esters, $n = 4$, $r_{0.01} = 0.9900$, ethyl formate excluded				
Boiling point	0·9808	74·58	0·235	1·901
d_{sph}	0·9982	—35·95	186·6	0·579
Relative permittivity	—0·9426	156·0	—10·35	3·260
Molecular refraction	0·9972	61·60	1·333	0·731
Molecular volume	0·9992	54·88	0·367	0·402
Molecular weight	0·9994	54·26	0·440	0·340
Parachor	0·9990	57·98	0·153	0·437
ω	0·9990	32·39	179·4	0·426
Ketones, $n = 4$, $r_{0.05} = 0.9500$				
Boiling point	0·9054	75·43	0·129	3·233
d_{sph}	0·9328	—[a]	131·2	2·557
Relative permittivity	—0·9633	116·4	—1·630	2·043
Molecular refraction	0·9853	66·01	0·954	1·300
Molecular volume	0·9171	63·15	0·260	3·035
Molecular weight	0·9884	63·98	0·300	1·155
Parachor	0·9754	62·56	0·117	1·678
ω	0·9223	50·54	117·6	2·944
Esters and ketones pooled, $n = 8$, $r_{0.01} = 0.8343$				
Boiling point	0·7414	74·62	0·188	6·634
d_{sph}	0·9531	—[a]	134·7	3·201
Relative permittivity	—0·8346	107·3	—1·137	5·445
Molecular refraction	0·9476	59·15	1·335	3·157
Molecular volume	0·9605	54·71	0·359	2·752
Molecular weight	0·9837	57·08	0·391	1·776
Parachor	0·9639	55·21	0·157	2·630
ω	0·9572	35·73	167·3	2·862

TABLE IV
(*Continued*)

Parameter	r_{xy} HC, $n = 8$	r_{xy} RX, $n = 7$	r_{xy} HC, RX pooled, $n = 15$
Hydrocarbons (HC) and Halogenated Compounds (RX)[b]			
	$r_{0,05} = 0{\cdot}7067$	$r_{0,05} = 0{\cdot}7545$	$r_{0,05} = 0{\cdot}5139$
Boiling point	—0·2793	0·0986	—0·0132
d_{sph}	0·3369	0·0353	0·3432
Relative permittivity	—0·6869	0·5272	0·0593
Molecular refraction	—0·0826	0·0125	—0·0610
Molecular volume	0·3348	0·0350	0·3510
Molecular weight	—0·0509	—0·0962	—0·2002
Parachor	0·1837	0·0398	0·2610
ω	0·3449	0·0417	0·3502

[a] Hypothesis about $b_0 \neq 0$ rejected on the basis of the *t*-test; [b] only values of coefficient of correlation are given as no significant correlation was found.

ones. These findings can also explain differences found for DE by the phase equilibrium and by the spiked tube method[18] and by other methods, where sometimes only the equilibrium between AC and a spiked solution is monitored for the determination of DE value.

The attempt was also made to correlate measured standard samples DE values for studied compounds grouped according to their chemical structure with molecular parameters listed in Table III. Results for ethyl formate were excluded from these calculations as it was apparent that this compound behaved in an anomalous way during the desorption. The linear regression yielded values listed in Table IV and pointed to highly significant correlations of some of those parameters with DE values, namely of molecular weight and of molar volume for esters and of molecular weight and of molar refraction for ketones. As differences in slopes of those regression lines for corresponding parameters for esters and ketones were found to be statistically insignificant by the *t*-test[36] (which need not be necessarily true due to the small number of studied compounds), these data were pooled and new regression equations were calculated which are also given in Table IV and point to a highly significant correlation, the highest value of the coefficient of correlation being between molecular weights and DE values again.

When tested for statistically significant differences[37], calculated coefficients of correlation were found not to be differing enough to support the hypothesis about the

statistically significant better correlation of DE values with any of studied parameters with the exception of values of coefficients of correlation calculated for relative permittivities where a negative slope was observed in all cases in contrast to other parameters and absolute values of coefficients of correlation were usually lower compared to those obtained for other studied parameters. This can well serve as a clue that indeed, for studied compounds, steric effects are more important that electronic ones which is in agreement with the fact that mainly London dispersion forces[38] are responsible for adsorption processes on the relatively nonpolar AC surface.

Contrasting with those findings are results for halogenated compounds and hydrocarbons. No significant correlation was found in these classes of compounds and one of reasons for that can be that loads for those compounds differed more widely than for esters and ketones. If the assumption is made, in the light of previous findings, that for each compound an essentially constant amount is adsorbed irreversibly during the sampling (which amount will be probably also load dependent), then it is clear that the DE value will decrease with the AC/analyte ratio increasing which trend can be traced, although not very clearly, when DE values for standard and 5 minutes control samples are compared, the difference being more pronounced for oxygenated compounds. Similar observations were also made in works[7,8].

Thus it can be concluded, that for compounds of medium polarity, as for instance for esters and ketones, the most important factor governing the ease of liquid desorption from a nonpolar microporous adsorbent (*e.g.* activated charcoal) appears to be the size of molecule of adsorbate. With the increasing size of molecule the ease with which molecules of adsorbate can enter narrow micropores decreases and, as a portion of the eluent is trapped in these micropores during the desorption, the concentration of adsorbate increases resulting sometimes in DE values exceeding 100%.

Finally, from the comparison of DE values obtained in the course of this work with previously reported values[1,2,3,8,11] it can be seen that an acceptable agreement was found.

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