Journal of Chromatography, 328 (1985) 145–154
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17 691

ADSORPTION CHARACTERISTICS OF ORGANIC EXPLOSIVES COMPOUNDS ON ADSORBENTS TYPICALLY USED IN CLEAN-UP AND RELATED TRACE ANALYSIS TECHNIQUES

J. B. F. LLOYD
Home Office Forensic Science Laboratory, Priory House, Gooch Street North, Birmingham B5 6QQ (U.K.)
(Received January 28th, 1985)

SUMMARY

Distribution coefficients for the adsorption on ten representative adsorbents of sixteen explosives-related compounds in solutions (1 μg ml^{-1} initially) of aqueous methanol, and of other solvents for adsorbents having uncorrelated characteristics, are summarized in terms analogous to Martin's functional group additivity relationship. None of the results is attributable to an adsorption affinity characteristic of any specific feature of explosives compounds. Selectivity is restricted to the adsorbents' varying but non-specific affinity for polar compounds generally. A negative selectivity is exhibited by charcoal under some conditions for nitrate esters.

It is argued that techniques, such as adsorption-based clean-up techniques, can be adequately evaluated for general use only when the distribution coefficients characterizing the processes of interest are known or can be estimated.

INTRODUCTION

The manipulation of trace amounts of organic compounds, for instance in their recovery from complex substrates, their concentration from aqueous and other solvent mixtures, their trapping from the gas phase, and their transfer between different solvents, is commonly based on adsorption techniques that, even for closely related problems, employ widely varying adsorbents and solvents. Thus, in the detection of explosives traces for forensic purposes, vapour phase sampling of explosion debris or other explosives-contaminated materials has been carried out on Chromosorb 102[1], charcoal[2–4], silica gel[5], ODS-Spherisorb and alumina[6], and Tenax GC[7], with desorption in a variety of solvents. For the recovery of explosives traces from solutions of extracts of debris and swabs, Amberlite XAD-7[8], ODS-Spherisorb and alumina[6], and Bond Elut-CH and -CN cartridges[9] have been used. Other examples from the field of explosives detection and analysis in environmental samples are given in a survey by Anspach *et al.*[10], who recommended Amberlite XAD-4 and the Porapaks S and R, depending on the explosives sought, for the examination of water samples. These recommendations are implemented in a recently published procedure[11]. Further environmental examples include the use of Tenax GC[12], and of char-

0021-9673/85/$03.30

coal and the Amberlites XAD-2 and XAD-7[13] for vapour phase sampling. Apart from their explosives use, the alkyl nitrates are of importance in pharmacological work, where the recovery of traces of them from body fluids is sometimes based on adsorption techniques[14,15].

Because all of these applications have been designed empirically for specific circumstances, the methods and results produced are of limited relevance outside their immediate area of application, their translation to other fields cannot be made except by time-consuming trial and error procedures, and the basis of any selectivity they may be claimed to possess is obscure. These problems, which are often compounded by the characterization of proprietary adsorbents only with meaningless names, are not peculiar to explosives work.

The position is alleviated to a considerable extent if the distribution coefficients characterizing the processes of interest are known or can be estimated. A common basis is then provided for the evaluation and comparison of techniques, and their adaptation to particular circumstances is facilitated. To this end, the following presents distribution coefficient data derived from all of the commonly encountered (U.K.) organic explosives compounds and from representatives of the commonly used types of adsorbent, except those such as silica and alumina whose activity is limited to non-aqueous conditions.

EXPERIMENTAL

Standard compounds

These are listed in Table I. The nitrate esters (EGDN, nitroglycerin, and PETN), nitramines (RDX, HMX, and tetryl), the dinitrotoluenes and TNT were obtained through the courtesy of the Royal Armament Research and Development Establishment, U.K. Styphnic acid was prepared by the nitration of resorcinol. The other compounds were from BDH, U.K. No impurities likely to cause interference in the analyses were detected in the standards used.

TABLE I

EXPLOSIVES COMPOUNDS USED

m-Dinitrobenzene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Ethylene glycol dinitrate (EGDN)
Glycerol trinitrate (nitroglycerin)
Nitrobenzene
m-Nitrotoluene
o-Nitrotoluene
p-Nitrotoluene
Pentaerythritol tetranitrate (PETN)
1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane (HMX)
2,4,6-Trinitrophenol (picric acid)
2,4,6-Trinitrophenylmethylnitramine (tetryl)
2,4,6-Trinitrorescorcinol (styphnic acid)
2,4,6-Trinitrotoluene (TNT)
1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX)

TABLE II

ADSORBENTS

	Adsorbent	*Source*	*Particle size (μm)*	*Chemical type**
1	ODS-Hypersil	Shandon	3	Octadecylsilyl silica
2	Porapak R	Waters	75–100	Polyvinylpyrrolidone
3	Porapak S	Waters	75–100	Polyvinylpyridine
4	Porapak T	Waters	75–100	Poly(ethylene glycol dimethylacrylate)
5	Amberlite XAD-4	Rohm & Haas	<100**	Styrene–divinylbenzene copolymer
6	Amberlite XAD-7	Rohm & Haas	<100**	Poly(acrylate ester)
7	Tenax GC	Akzo Research Labs.	170–250	Poly(2,6-diphenyl-*p*-phenylene oxide)
8	Polyamide	Macherey Nagel	50–160	Polycaprolactam
9	Chromosorb 104	Johns-Manville	125–150	Acrylonitrile–divinylbenzene copolymer
10	Charcoal	BDH	70–150**	Carbon

* Taken from suppliers information.
** See Experimental.

Adsorbents

These are listed in Table II. Amberlite XAD-7 was washed by decantation in turn with water, methanol, and diethyl ether, dried at room temperature, and then crushed in a pestle and mortar. The fraction passing a 100-μm sieve was suspended in acetone and the fines were removed by decantation. The product was dried in a stream of air at room temperature, and heated at 80°C for 3 h. Amberlite XAD-4 was treated in the same way.

Charcoal (BDH, "for gas adsorption") was crushed, and the 70–150-μm fraction collected. This was Soxhlet-extracted with 10% (v/v) acetic acid in methanol, freed from acid with methanol, dried at room temperature, and heated at 250°C for 8 h.

The other adsorbents, except ODS-Hypersil, were washed either by Soxhlet extraction or by decantation with acetonitrile, and finally dried at 120°C.

Each of the cleaned adsorbents was made up into a 10 mg ml^{-1} suspension in acetonitrile.

Distribution coefficients

For ODS-Hypersil, the distribution coefficients were calculated from the chromatographic capacity factors and the phase ratio of the column (1.063 g ml^{-1}) used[16].

For the other adsorbents, 0.5 ml was transferred from the rapidly stirred suspension of the adsorbent into a silanized glass centrifuge tube. The supernatant was removed and the residue dried, finally, under vacuum over silica gel. To the adsorbent were added 300 μl of the explosives (1 μg ml^{-1}) in the solvent in question. The mixture was shaken intermittently over 15 min at room temperature (20°C) and centrifuged, and the concentrations of the compounds in the supernatant, after dilution with the chromatographic eluent, were determined by high-performance liquid chromatography with electrochemical detection at a mercury electrode[16]. When the solvent containing the explosives compounds was insoluble in the eluent, a known volume of the solution was added to a known volume of the eluent in the deoxygenation syringe[17], and the injection made after the solvent had evaporated into the eluent-presaturated nitrogen purge. The distribution coefficients (units, ml g^{-1}) were calcu-

TABLE III

MULTIPLE REGRESSION RESULTS FROM LOG [DISTRIBUTION COEFFICIENTS (*K*)]

Solvent methanol–aqueous phosphate (pH 3) (100:86, v/v).

Adsorbent	*Mean exptl. log K*	*Regression coefficients*							*Intercept*	*Multiple correlation coefficient*	*Standard error of estimates*
		Non-ar. carbon	*Phenyl ring*	*Ar.-nitro group*	*Nitrate ester*	*Nitramine*	*Phenol OH*	*o-Nitro methyl*			
ODS-Hypersil	0.325	0.205	0.823	−0.110	ns*	−0.200	−0.304	ns	−0.240	0.969	0.114
Porapak R	2.157	0.256	1.136	0.136	0.180	ns	−0.063	ns	0.717	0.974	0.097
Porapak S	2.385	0.327	0.940	0.129	ns	−0.172	0.875	ns	0.992	0.956	0.238
Porapak T	2.167	0.224	0.536	0.422	0.338	0.271	−0.208	ns	0.595	0.985	0.099
Amberlite XAD-4	2.459	0.414	1.544	ns	ns	−0.264	−0.420	ns	0.988	0.977	0.143
Amberlite XAD-7	2.286	ns	0.991	0.312	0.620	0.600	−0.615	0.163	0.581	0.950	0.221
Tenax GC	1.618	ns	1.106	−0.356	ns	−0.301	−0.638	0.259	1.520	0.966	0.245
Polyamide	1.665	0.343	1.189	ns	ns	−0.190	1.329	ns	0.179	0.953	0.295
Chromosorb 104	2.592	0.167	0.357	0.266	0.200	0.209	0.394	ns	1.440	0.979	0.105
Charcoal	3.824	ns	2.369	−0.098	0.423	0.484	0.655	0.136	1.677	0.969	0.199

* Not significant (inclusion increases the standard error of the estimate).

lated from the concentrations found in the solutions before and after adsorption. An analysis of variance of 55 pairs or replicated results, representing the range of solvents, adsorbents and compounds used, gave a within-replicate variance for the decimal logarithm of the distrtibution coefficients (mean, 2.029) of 0.034.

RESULTS AND DISCUSSION

The large number of results is summarized here in terms of the multiple regression coefficients given by an analysis of the data based on a relationship analogous to the widely used Martin equation[18]:

$$\log K = a + \sum b_i n_i$$

where $\log K$ is the decimal logarithm of the distribution coefficient, a is the intercept found in the regression analysis (instead of the more usual $\log K$ value of a reference compound), and b_i is the regression coefficient corresponding to the ith variable. For $i = 1$–7, the n_i values represent the respective numbers of non-aromatic carbon atoms, phenyl rings, aromatic nitro groups, nitrate ester groups, nitramine groups, phenolic hydroxyls, and *ortho*-nitro/methyl interactions for a particular compound.

The results for the compounds and adsorbents listed in Tables I and II respectively are shown in Table III for the aqueous methanol solvent specified there [methanol–aqueous phosphate (pH 3) (100:86, v/v)]. The regression coefficients given are those that minimize the standard errors of the estimates, which are shown in the last column of the Table. Despite the gross assumptions implicit in group additivity treatments of adsorption data[19], the convenient representation of $\log K$ values in this way gives a satisfactory level of precision for the present purposes. In the instances of the four adsorbents giving the highest standard errors in Table III (Porapak S, Amberlite XAD-7, Tenax GC, and the polyamide) and the most commonly encountered of the compounds (nitroglycerin) the respective estimates of $\log K$ are 1.973, 2.441, 1.520, and 1.208, whereas the actual values are 2.086, 2.638, 1.699, and 1.462.

From Table III it is apparent that under the specified experimental conditions the sets of results from some of the adsorbents are correlated. This is emphasized by the correlation matrix shown in Table IV. The ODS-Hypersil results, which are taken to represent variations in $\log K$ mainly determined by non-polar, unspecific effects (*e.g.* the solvophobic and related effects reviewed by Melander and Horvath[20]), are significantly correlated to the Porapak R, the Amberlite XAD.-4, and the Tenax GC results. If picric and styphnic acids are excluded from consideration, the Porapak S and the polyamide results are similarly correlated (the coefficients are given in the footnotes to Table IV). Under the conditions (pH 3) these compounds are problably dissociated and adsorbed at protonated or other cationic sites, particularly in the case of the basic Porapak S (Table II). The strong adsorption is reflected in the relevant regression coefficients (Table III).

For the remaining adsorbents (Porapak T, Amberlite XAD-7 and charcoal) the high regression coefficients for the polar groups (Table III) are consistent with a predominantly polar adsorption mechanism, together with a substantial contribution from the phenyl ring in the case of charcoal particularly. Evidently, from the

TABLE IV

CORRELATION MATRIX OF LOG [DISTRIBUTION COEFFICIENTS (K)] FROM VARIOUS ADSORBENTS

Solvent methanol–aqueous phosphate (pH 3) (100:86, v/v).

*Adsorbent**	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
1	1	0.637	−0.008**	−0.004	0.920	0.209	0.861	−0.170**	−0.512	−0.101
2		1	0.556	0.469	0.836	0.320	0.424	0.400	0.262	0.466
3			1	0.066	0.160	−0.373	−0.161	0.969	0.591	0.782
4				1	0.168	0.859	−0.291	−0.061	0.662	−0.020
5					1	0.280	0.798	0.026	−0.285	0.201
6						1	−0.003	−0.493	0.240	−0.266
7							1	−0.208	−0.707	−0.017
8								1	0.555	0.754
9									1	0.401
10										1

* The adsorbents are numbered as in Table II.

** With picric and styphnic acids excluded, the results are 0.829 (column 3) and 0.914 (column 8).

negative *ortho*-nitro/methyl coefficient here, and under other entries in Table III, the adsorption of the phenyl ring is influenced as expected by steric hindrance.

Consistent with the similarity in composition between Porapak T and Amberlite XAD-7 (Table II), the respective log K values are correlated (Table IV). The result is of practical importance because in small-scale work Porapak T is the more useful material. It is commercially available in well-defined small particle sizes, and is sufficiently robust not to break down under the conditions of centrifugal microfiltration and of microcolumn clean-up techniques[21]. The Porapak T and Chromosorb 104 results also exhibit a significant level of correlation. The main difference between them is in the coefficients representing the phenolic hydroxyl contribution (Table III).

The implication of a predominantly polar mechanism of adsorption on some adsorbents from such highly polar solvents as aqueous methanol (Table III) is not unprecedented, although the solvophobic effect may become predominant in even more highly aqueous solvents. Thus, as the proportion of water is further increased the extent of adsorption in general increases, and more noticeably in the instances of the less polar compounds. The distribution coefficients are too high for usefully accurate measurements to be made; but as an approximation, an increased water content of 10% (v/v) increases the distribution coefficients by factors of between 2 and 3 (Porapak T).

In further support of the view that solvophobic-type effects are unimportant to adsorption on Porapak T, Chromosorb 104 and charcoal from aqueous methanol, the log K values are significantly correlated with those found in experiments with the same adsorbents in *n*-hexane. The respective correlation coefficients are 0.908, 0.829, and 0.764 (styphnic and picric acids, HMX, and RDX were excluded because of their poor solubility in *n*-hexane and their suspected tendency to become adsorbed on the surfaces of the containers used). However, for Tenax GC, which is amongst the weakest of the adsorbents in polar solvents, the correlation coefficient between the aqueous methanol and the *n*-hexane results is -0.330. Hence, the expected transition away from solvophobic adsorption is occurring here.

The regression results from the log K values characterizing the adsorption onto charcoal, Porapak T and Tenax GC from a variety of non-aqueous solvents are given in Table V. Other solvents that have often been used for desorption purposes, such as acetone and ethyl acetate, gave results similar to acetonitrile, the use of which was preferred here because of its availability in a higher state of purity. Particularly high standard errors occur for the last three solvents listed under charcoal. There is, however, an important effect discernible here. In each case there is a substantial negative contribution made by the nitrate ester group, *i.e.*, the nitrate ester explosives are remarkably weakly adsorbed on charcoal in these solvents (for EGDN, nitroglycerin, and PETN in methanol the respective experimental log K values are 0.800, 0.875, and 1.137; the estimates from Table V are 0.984, 0.865, and 1.072). The effect enables nitroglycerin traces to be selectively retrieved from highly complex mixtures[21], and substantiates Prime and Krebs' use of 2-propanol to desorb nitrate esters trapped from the vapour phase on charcoal[2–4], although other types of explosives compound must be poorly recovered. The log K values in 2-propanol compare closely with those in methanol.

The strong adsorption on charcoal of aromatic compounds generally is emphasized by the present results, which explain the difficulty with which traces of TNT

TABLE V

MULTIPLE REGRESSION RESULTS FROM LOG [DISTRIBUTION COEFFICIENTS (K)] IN VARIOUS NON-AQUEOUS SOLVENTS FOR CHARCOAL, PORAPAK T, AND TENAX GC

Adsorbent	*Solvent*	*Mean exptl. log K*	*Regression coefficients*							*Intercept*	*Multiple correlation coefficient*	*Standard error of estimates*
			Non-ar. carbon	*Phenyl ring*	*Ar.-nitro group*	*Nitrate ester*	*Nitramine*	*Phenol OH*	*o-Nitro methyl*			
Charcoal	Hexane	3.315	ns*	1.062	1.204	0.413	−1.492	exc**	−0.634	1.045	0.984	0.207
	Toluene	1.582	0.098	−1.615	0.669	−0.321	ns	exc	−0.271	2.080	0.979	0.129
	Diethyl ether	2.351	0.231	ns	0.372	−0.457	ns	ns	−0.181	1.817	0.869	0.413
	Methanol	2.620	0.290	1.768	ns	−0.373	ns	0.353	ns	1.114	0.929	0.423
	Acetonitrile	1.944	0.348	1.912	ns	−0.356	ns	0.629	ns	0.189	0.926	0.450
Porapak T	Hexane	1.994	−0.138	−0.583	0.975	0.789	0.220	exc	ns	0.717	0.997	0.090
	Diethyl ether	1.311	ns	−0.699	0.683	0.306	0.615	0.519	−0.109	0.317	0.983	0.211
	Methanol	0.767	0.170	ns	0.213	ns	0.190	−0.374	ns	0.195	0.945	0.155
	Acetonitrile	(Weak adsorption overall)										
Tenax GC	Hexane	1.000	0.088	ns	0.313	ns	0.467	exc	−0.069	0.327	0.977	0.098
	Diethyl ether	0.731	ns	ns	0.217	0.130	0.208	0.385	ns	0.183	0.940	0.146
	Methanol	(Weak adsorption overall)										
	Acetonitrile	(Weak adsorption overall)										

* Not significant.

** Excluded: compounds poorly soluble.

are extracted from the carbon residues remaining from the detonation of TNT[22]. Of the solvents examined, toluene would be the most efficient extractant. Even so, given that the residues are analogous to charcoal, the log K value would still be high (experimental, 2.125; estimate, 2.028) despite the apparent suppression of the phenyl ring contribution by this aromatic solvent (Table V).

Although the choice of a desorption solvent is dependent on the nature of any solvent that may be present on the adsorbent already, *e.g.* the two solvents should preferably be mutually soluble, in many published techniques the solvent selectivity that is available remains unexploited because of the use of excessively strong desorption solvents. For example, the desorption from Tenax GC and from the polyacrylate adsorbents is usually conducted with solvents such as acetone, ethyl acetate, and acetonitrile; whereas, from Table V, most compounds of interest could be desorbed readily (log K less than 1) in, *e.g.*, methanol or diethyl ether, or even in hexane in the case of Tenax GC.

Under none of the conditions examined is the adsorption attributable to any specific feature of explosives compounds. Widely varying types of polar adsorbents exhibit similar selectivity even under conditions where any difference between them should be maximized. Thus, in addition to the results already quoted, in *n*-hexane the correlation coefficient between the Chromosorb 104 and Porapak T results is 0.975 (twelve compounds). From the composition of any of the adsorbents (Table II) there is little reason why specific adsorption should occur; and the same conclusion is implied by the use of many of the adsorbents, or similar ones of different manufacture, for compounds other than explosives.

Where there is, *e.g.*, a substantial nitro group contribution, other polar groups contribute strongly too. Thus, in the case of Porapak T, the contribution made by the aromatic nitro group to log K values in diethyl ether (Table V) is of the same magnitude as that of the phenolic hydroxyl group. Also, the aromatic nitro group contribution is offset by the phenyl group, which explains the loss of nitrobenzene when a pentane extraction of a similar adsorbent, Amberlite XAD-7, is made in a clean-up technique[8]. Presumably, the nitrotoluenes would be lost also.

CONCLUSION

Although the present work refers only to explosives-type compounds, a wide variation in the polarity of the features contributing to adsorption is represented. Hence, despite the statements of several authors to the contrary, apparently the selectivity of the adsorbents that have commonly been employed in explosives detection and analysis to date is largely due to the adsorbents' varying but non-specific affinity for polar compounds generally. The only important specific effect observed is the negative selectivity of charcoal for the nitrate esters. Where polar selectivity is required, most purposes could be met by the poly(acrylate ester) class of adsorbents such as Amberlite XAD-7[8,13] and the more robust adsorbents of this type, *e.g.* Porapak T, or by the correlated nitrile-substituted adsorbents such as Chromosorb 104, and similar materials[9]. The usefulness of these adsorbents is enhanced by the persistence of their polar selectivity in relatively polar solvents.

Apart from the assessment of an adsorption technique with reference to specific compounds, the assessment must refer also to the selectivity of the final analytical

technique, and to the usually unidentified compounds characteristic of the intended application. Clearly, no generalizations are possible, but the problems arising can be dealt with efficiently only on the basis of the known adsorption characteristics of the compounds of interest.

ACKNOWLEDGEMENT

I am indebted to Dr. R. A. Hardcastle for his assistance in the data processing.

REFERENCES

1 J. E. Chrostowski, R. N. Holmes and B. W. Rehn, *J. Forensic Sci.*, 21 (1976) 611.
2 R. J. Prime and J. Krebs, *Can. Soc. Forensic Sci. J.*, 13 (1980) 27.
3 R. J. Prime and J. Krebs, *Proceedings of the International Symposium on the Analysis and Detection of Explosives*, FBI Academy, Quantico, 1983, p. 285 (publ. 1984).
4 R. J. Prime and J. Krebs, *Can. Soc. Forensic Sci. J.*, 17 (1984) 35.
5 I. H. L. Yip, *Can. Soc. Forensic Sci. J.*, 15 (1982) 87.
6 J. B. F. Lloyd, *J. Chromatogr.*, 261 (1983) 391.
7 D. F. Wardleworth and S. A. Ancient, *Proceedings of the International Symposium on the Analysis and Detection of Explosives*, FBI Academy, Quantico, 1983, p. 405 (publ. 1984).
8 J. M. F. Douse, *J. Chromatogr.*, 234 (1982) 415.
9 R. A. Strobel and R. Tontarski, *Proceedings of the International Symposium on the Analysis and Detection of Explosives*, FBI Academy, Quantico, 1983, p. 67 (publ. 1984).
10 G. L. Anspach, W. E. Jones and J. F. Kitchens, *Evaluation of Solid Sorbents for Sampling and Analysis of Explosives from Water*, Report no. DRXTH-TE-CR-82142, Atlantic Research Corp., Alexandria, U.S.A., 1982.
11 M. P. Maskarinec, D. L. Manning, R. W. Harvey, W. H. Griest and B. A. Tomkins, *J. Chromatogr.*, 302 (1984) 51.
12 R. W. Bishop, T. A. Ayers and D. S. Rinehart, *Amer. Ind. Hyg. Ass. J.*, 42 (1981) 586.
13 K. Andersson, J.-O. Levin and C.-A. Nilsson, *Chemosphere*, 12 (1983) 821.
14 G. Idzu, M. Ishibashi, H. Miyazaki and K. Yamamoto, *J. Chromatogr.*, 229 (1982) 327.
15 K. Kral and G. Kainz, *Z. Anal. Chem.*, 316 (1983) 497.
16 J. B. F. Lloyd, *J. Chromatogr.*, 257 (1983) 227.
17 J. B. F. Lloyd, *J. Chromatogr.*, 256 (1983) 323.
18 A. J. P. Martin, *Biochem. Soc. Symp.*, 3 (1949) 4.
19 L. R. Snyder, *Principles of Adsorption Chromatography*, Dekker, New York, 1968, p. 266.
20 W. R. Melander and Cs. Horváth, *High-Performance Liquid Chromatography*, 2 (1980) 113.
21 J. B. F. Lloyd, unpublished results.
22 A. S. Cumming, K. P. Park and M. R. Clench, *Proceedings of the International Symposium on the Analysis and Detection of Explosives*, FBI Academy, Quantico, 1983, p. 235 (publ. 1984).