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A statistical analysis of the effects of loading, desorption volume at constant weight of solute, and the presence of other compounds on desorption efficiency was performed. For non-polar compounds and for a mixture of a polar and a non-polar compound, there was no effect of the presence of any one compound in the mixture on the desorption efficiency of the others. For polar compounds there was a dependency on the presence of other compounds. The implications of these findings and an explanation based on equilibrium considerations are advanced.

Desorption of organic analytes from activated carbon I: Factors affecting the process

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introduction

In industrial hygiene analytical chemistry, desorption efficiency is a correction applied for incomplete transfer of analyte from the sorbent used as the collection medium to the desorption fluid. In the strictest sense, this correction should only be applied to surface phenomena associated with the partition of the analyte between solid and fluid phases; such phenomena may be equilibrium (reversible adsorption-desorption) or non-equilibrium (irreversible adsorption; chemisorption) in nature. Mathematically, the desorption efficiency can be formulated as the fraction of the total weight of analyte which is in the liquid phase after the desorption process is complete. Finally, the desorption efficiency is usually determined in the laboratory by performing batch desorption experiments at various loading levels of the pure analyte. This value of the desorption efficiency is then applied to field samples.(1) In order that the value determined in the laboratory be applicable to the field sample, it must be shown that the desorption efficiency is independent of, or correctable for, those factors over which one has no control in the field, most importantly, loading (the amount of analyte collected per unit weight of sorbent) and the presence of other compounds.

Historically, the work of White *et al.*(2) claimed that for the fourteen organic compounds they studied, the presence of other compounds coadsorbed on the carbon did not have a significant effect on the desorption of any one compound (*i.e.*, there was no effect of the presence or absence of other compounds). The generality of these findings has lately been questioned by others based on experimental evidence(3-5) or by implication.6-8) A loading dependency of the desorption efficiency of several organic compounds has been noted and in one case a correction protocol adopted.(9,10) Another factor which has been shown to influence desorption efficiency is the ratio of the weight of sorbent used to collect the analyte to the weight of liquid used to desorb the sample.(11) These three factors, loading, desorption volume (at constant weight of sorbent), and the presence or absence of other compounds, were selected for a study to determine whether they are important effects in the recovery of adsorbed analytes from carbon using carbon disulfide as desorbent. This combination of sorbent and desorbent is by far the most common for the determination of volatile organic compounds in the industrial environment.

methods and materials

The statistical design was a two-level factorial protocol in which measurements are made at two levels for each factor studied. This allows for a determination of both the "main effect" of each factor and the "interactions" of the factors in combination.(12-14) Independent variables selected were loading, desorption volume, and the presence or absence of other compounds. The dependent variable was desorption efficiency. Ranges were:

Desorption volume:		
	high = 5 mL	low = 0.5 mL
Loading (per 100 mg charcoal):		
2-ethoxyethyl acetate (cellosolve acetate)		
	high = 1.8 mg	low = 0.36 mg
2-butoxyethanol (butyl cellosolve)		
	high = 1.2 mg	low = 0.24 mg
n-butanol		
	high = 2.1 mg	low = 0.42 mg
toluene		
	high = 3.6 mg	low = 0.72 mg
biphenyl		
	high = 0.124 mg	low = 0.050 mg
Presence or absence of other compounds:		
	high = presence	low = absence

The analytes were equilibrated with the sorbent using a method which has come to be called "phase equilibrium".(11) Accordingly, solutions of the analyte or analytes in CS_2 were prepared and chilled. Portions (100 mg) of activated charcoal (SKC, Inc., lots 106 and 107) were added to known volumes of the organic solution and the mixtures were shaken for one hour at room temperature and then analyzed.

TABLE I
Main Effects and Interactions — Polar Compounds

Compound	L	DV	L + DV	P/A	L + P/A	DV + P/A
	Parameter[A]					
Butyl Cellosolve	Lg	Lg	−M	S	S	−S
Butanol	M	Lg	−M	S	I	I
Cellosolve Acetate	M	M	−M	M	S	−S
Toluene[B]						

[A] L = loading, DV = desorption volume, P/A = presence or absence of other compounds.

[B] Not affected. All values of desorption efficiency essentially 1.0.

Desorption efficiencies were calculated as the ratio of the amount of analyte in solution after equilibration with the sorbent to the amount present before carbon was added. This procedure gave better precision than the traditional method of spiking analyte onto the charcoal tube, equilibration, desorption and analysis.(1) Analyses were performed on a Hewlett-Packard 7600A gas chromatograph with a flame ionization detector (FID). A Hewlett-Packard 7670A auto sampler and a Hewlett-Packard 3354B laboratory data system interfaced with the GC provided both automatic sample injection and data collection. Analytical columns were:

1. 1.8 m × 3.2 mm o.d. stainless steel column filled with 3% SP-1000 on 100/120 mesh Supelcoport, used for analyses of samples containing biphenyl.
2. 3 m × 3.2 mm o.d. stainless steel column filled with 20% SP-1000 on 80/100 Supelcoport, used for analyses of samples not containing biphenyl.

The mixtures tested consisted of a polar mixture containing toluene, n-butanol, 2-ethoxyethanol (butyl cellosolve) and 2-ethoxyethyl acetate (cellosolve acetate), a mixture of a polar and a non-polar compound containing cellosolve acetate and biphenyl, and finally a mixture of two non-polar compounds containing biphenyl and toluene.

results

Over the range of parameters in the statistical design, desorption efficiencies were obtained in the following ranges:

Toluene: essentially 100% recovery in all experiments.
Butanol: 0.47 to 0.92.
Cellosolve acetate: 0.53 to 1.03 in the polar mixture experiment and
0.53 to 0.97 in the polar/non-polar mixture.
Butyl cellosolve: 0.12 to 0.77.
Biphenyl: 0.58 to 0.92.

Four runs were made to determine each point in the experiments, and the resulting precision was quite high; the relative standard deviation was always less than 5% and typically in the 1-2% range. Due to this high precision, the analysis of variance showed that all main effects and all two factor interactions were statistically significant at the 95% confidence level. However, on inspection of the absolute values of the results, it became clear that a judgment needed to be made concerning the practical importance of the observed effects. Furthermore, since the values obtained are specific to the compounds and the factor space chosen, we decided that magnitudes of effects would be appropriate to report.

Consequently, values presented for factors and interactions in all the studies have been grouped into four categories according to the magnitude of observed effect on the desorption efficiency:

I = insignificant effect (0.04 or less)
S = small effect (0.05 to 0.08)
M = moderate effect (0.09 to 0.19)
Lg = large effect (greater than 0.20)

The above groupings are completely arbitrary and represent the authors' judgment on the general importance of changes in desorption efficiency to the accuracy of the analysis. All effects on the desorption efficiency of less than 0.04 are therefore considered chemically insignificant, independent of their statistical significance.

The columns in Tables I-III containing a single parameter are main effects, and the columns containing two parameters refer to the interaction between those two effects. For the polar mixture, all main effects were chemically significant as were all two-factor interactions save the loading-presence or absence interaction for butanol. For the mixture of non-polar compounds and for the mixture of a single polar and a non-polar compound, the presence or absence of other compounds was not chemically significant, nor were any interactions involving that parameter.

discussion

The compounds and loading levels chosen for the polar mixture study were dictated by historial considerations. The same mixture was used by Fracchia *et al.*(3) and by Mueller and Miller(5) for their studies. Loading levels used in these experiments were twice and 0.4 times those used in the former study, based on weight of analyte per unit weight of carbon. The loading level used by Mueller and Miller in their study using 100 mg of carbon are similar, but not equal, to the high loading levels in this study; their loading levels using 400 mg of carbon are of the same order as the low levels in this study. This study, therefore, should allow us to draw

TABLE II
Main Effects and Interactions —
Polar and Non-polar Compounds

Compound	L	DV	L + DV	P/A	L + P/A	DV + P/A
	Parameter[A]					
Biphenyl	I	Lg	I	I	I	I
Cellosolve Acetate	M	Lg	−M	I	I	I

[A] L = loading, DV = desorption volume, P/A = presence or absence of other compound.

TABLE III

Main Effects and Interactions — Non-polar Compounds

	Parameter[A]					
Compound	**L**	**DV**	**L + DV**	**P/A**	**L + P/A**	**DV + P/A**
Biphenyl	I	Lg	I	I	I	I
Toluene[B]						

[A] L = loading, DV = desorption volume, P/A = presence or absence of other compound.

[B] Not affected. All values of desorption efficiency essentially 1.0.

conclusions about the genesis of the effects noted in the previous papers.

A negative sign was associated with all important two-way interactions involving the desorption volume. A positive sign means that as one increases the second parameter, the dependent variable associated with the high level of the first parameter will increase more than it will for the low level. For a negative sign, performing the same operation will increase the dependent variable associated with the low level more than it will the one associated with the high level. For example, increasing the desorption volume resulted in a larger increase in desorption efficiency at low loading levels than at high ones.

Based on the results of these few experiments, the following tentative conclusions can be drawn with respect to the batch desorption of organics from activated carbon using CS_2:

1. In mixtures of non-polar compounds or a non-polar and a polar compound, the desorption efficiency of each individual compound is independent of the presence or absence of the other compounds. Further, no important interactions of the presence or absence of other compounds with the other parameters is evident. For these types of compounds, desorption efficiency can be corrected for the important factor or factors which affect it in simple laboratory experiments using only the analyte. It is well to point out, however, that there is a polar compound whose presence on activated charcoal which has been used for vapor sampling is ubiquitous, although hardly over measured. That compound is water. It may be, therefore, that in a practical sense only non-polar compounds belong in this classification.
2. Mixtures of polar compounds do show an important main effect of the presence or absence of other compounds; very often important interactions of this factor with loading and desorption volume are also present. These effects are not correctable by simple laboratory experiments involving single compounds, nor for that matter by any experiments using single compounds.

Obviously, the generality of these postulates needs to be further tested. Equally important, as well, is to define what constitutes a "polar" compound. In the absence of a clear definition, the features which the "polar" compounds studied have in common are the presence of an oxygen functionality, and a substantial dependence of desorption efficiency on loading. Others have suggested that at least one compound not containing oxygen behaves as if it belongs in the "polar" category.(7) A more general operational definition of "polarity" might, therefore, be the existence of a permanent dipole in the molecule together with a substantial dependence of the desorption efficiency on loading.

The statistical design does not, of itself, distinguish between equilibrium or non-equilibrium effects. However, the nature of the effects and interactions often allows one to make an inference. Such is the case in these studies. An adequate explanation of all the main effects and interactions, including the signs of the latter, can be advanced on equilibrium grounds as follows:

1. Desorption volume — Previous workers have shown that the desorption efficiency is a function of the ratio of the weight of desorption solvent to the weight of the sorbent.(11) Therefore, at constant weight of sorbent, one expects, from equilibrium considerations, an increase in desorption efficiency with increasing desorption volume. The exact mathematical treatment for the simple case where desorption volume is the only significant factor has been derived.(15) It predicts that the increase in desorption efficiency, per unit increase in weight of desorption solvent, is greater the lower the initial desorption efficiency. These results, showing the expected increase with desorption volume at constant weight of sorbent, contrast with those of others(5) who found no such dependency, albeit over a smaller range.
2. Loading — Any of the theoretical treatments of the equilibrium relationship between the concentrations in the liquid and solid phases for dilute solutions (*i.e.,* Langmuir, Freundlich, BET, etc.) also predicts that at constant volume and constant weight of sorbent, equilibrium desorption efficiency should increase with loading. Further, the increase in desorption efficiency per unit increase in loading should be greater at lower loadings.
3. Presence or absence of other compounds — The dependence of the desorption efficiency of polar compounds on this effect can be attributed to strong interactive forces between polar compounds in the non-polar solvent, CS_2, (dielectric constant = 2.64) leading to an increase in desorption efficiency. The forces between a polar and a non-polar compound, and those between two non-polar compounds are small and therefore are not seen here. Further, one would expect the interactions between polar molecules to be greater the more concentrated the solution in CS_2, or in terms of the variables used in this experiment, the higher the loading.

This interpretation does not preclude others based on non-equilibrium phenomena, such as were suggested by Mueller and Miller in their study of a more limited scope.(5) However, such an explanation, unless it can explain all the results obtained in this study, is clearly inadequate. The equlibrium explanation advanced above, however, is perfectly compatible with the coexistence of non-equilibrium processes. For example, the irreversible adsorption of a small, but constant, amount of analyte would give the same sort of loading dependence as that observed. However, the existence of the non-equilibrium process would not, of itself, suffice to explain the other dependencies observed.

acknowledgement

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In the August issue of the AIHAJ the table of contents was printed as follows:

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I. An air sampling data base management system
YUNG-SUNG CHENG, HSU-CHI YEH and GEORGE M. KANAPILLY
630 A long-term sampling method for the collection of C_2-C_4 fatty acids in air
BRAD T. GARBER

This is the corrected version:

625 Industrial hygiene applications of microcomputers
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630 A long-term sampling method for the collection of C_2-C_4 fatty acids in air
JAMES C. GILLAND, Jr., GARY T. JOHNSON and WILLIAM A. McGEE

Our apologies to the Authors for any inconvenience this error may have caused.