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SUPERCRITICAL FLUID EXTRACTION OF ADSORBED SEMI-VOLATILE COMPOUNDS FROM SOLID MATRICES WITH MODIFIED CARBON DIOXIDE

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SUPERCRITICAL FLUID EXTRACTION OF ADSORBED SEMI-VOLATILE COMPOUNDS FROM SOLID MATRICES WITH MODIFIED CARBON DIOXIDE

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ABSTRACT

The desorption of an analyte from a sample matrices' surface is the limiting process in a supercritical fluid extraction (SFE). Affinity of adsorbent matrices, and the ability of solvent modifiers to interrupt this affinity under SFE conditions, was investigated for semi-volatile analytes. Eight probe analytes, were extracted from adsorbents which demonstrated different chemical interactions with sample matrices. Three SFE solvent compositions were studied: pure carbon dioxide, carbon dioxide modified with methanol, and carbon dioxide modified with a derivatization reagent, bistrimethylsilyl-trifluoroacetamide (BSTFA). Five manufactured homogenous matrices and two natural matrices were studied:

alumina, silica, amino, phenyl, cyanno, fly ash and marine sediment. Solvent modifiers were necessary to displace analytes which were strongly adsorbed from solid matrices surfaces. The effectiveness of the modifier was related to its ability interact with the adsorbent surface. Methanol was sufficient to achieve quantitative yields from the manufactured adsorbents. However, the stronger desorbing agent, BSTFA, was needed to achieve quantitative recoveries from the highly adsorptive fly ash and marine sediments. Analysis of extraction kinetics allowed evaluation of the adsorbents in terms of probe compounds' desorption rates. Correlation was observed between the total amount of analyte recovered and the analyte's measured rate of desorbtion from that particular phase.

INTRODUCTION

Although analytical-scale supercritical fluid extraction (SFE) has been shown to be a rápid, simple and inexpensive method for sample preparation before chromatographic analysis, the performance of the technique is often inadequate without the addition of solvent modifiers to the supercritical fluid solvent. The physical properties of commonly used supercritical fluids would seem to make them ideal extraction media for several reasons. One, the gas-like mass transfer allows for rapid equilibration, thus faster extraction times than liquid techniques. Two, solvation strength varies with the density of the fluid, approaching that of liquids at higher densities. Three, due to low inter-molecular cohesion, supercritical extraction fluids are gases at room temperature and pressure; hence easily removed from the extract. Allowing the depressurized solvent to escape after the extraction leaves the sample ready for immediate analysis without concentration steps need in liquid phase extraction methods.[1] However, SFE is limited to non-polar solvents; solvents with low intermolecular cohesion, if this concentration advantage is to be realized. The limitation of SFE to weak solvents hinders the extraction of compounds which are strongly adsorbed to sample matrices.

The configuration of a SFE apparatus allows several

additional advantages over traditional liquid extraction techniques. The continuous flow through the extraction cell results in a much higher partitioning efficiency than the finite number of equilibrations of a Soxhlet apparatus, which may cycle only a few times an hour. Solvent modifiers are easily introduced to the extraction vessel before pressurization and extraction. These modifiers can be ether non-reactive such as methanol or reactive such as chemical derivatization regents.[2,3] Liquid phase extractive derivatization procedures are described in the literature but these techniques have low efficiency because they are typically be carried out in a separatory funnel, again limiting the practical number of partition equilibrations to only a few.[4] The closed SFE apparatus allows chemical derivatization reactions to occur without loss of volatile reagents or products while maintaining high extraction efficiency.

Extraction is partitioning of an analyte between the adsorptive matrix active sites and the extraction solvent. Solvation models, such as the Hildebrand solubility parameter theory, have been used to predict the equilibrium solubility, hence the extractability, of compounds in supercritical fluids.[5] The non-polar, low cohesion, solvents used in SFE have low solubility parameters. To increase the solubility parameter it is common practice to add polar compounds such as methanol to the extraction solvent. The addition of polar modifiers

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increases the solubility of polar molecules in the solvent. The solubility parameter theory, originally developed for engineering applications, holds well in systems where the analyte is present in high concentrations and other extractable components are present in low concentrations. However, limitations in this approach are encountered when predicted equilibrium is disturbed by other, often unidentified components, in a sample.[6] The theory also fails for very low analyte concentrations where the compound is thought to be adsorbed to a matrix surface. The model is based on cohesive energy between solute and solvent. It does not consider cohesive forces which adsorb an analyte to a surface. Often the limiting factor in environmental analysis is the cohesion between the analyte and the sample matrix surface, not the analyte and the solvent. Thus, disruption of the analyte—matrix intermolecular interaction is key to extraction, not solvation.

Studying solvent modifiers in supercritical fluid chromatography (SFC), Janssen et. al. concluded that the solvent modifiers they had studied both increased the solvation strength of the supercritical carbon dioxide and interacted with the stationery phase.[7] The increased solvation strength effect is consistent with solubility parameter theory. Both effects increased the capacity factor; the analyte spent less time adsorbed to the packing and more time solvated by the supercritical solvent. They go onto say that the stationary

phase deactivation, due to adsorption of the modifier, was the primary phenomena affecting the faster elution, not the increased solvation strength.

The same solvation and adsorption phenomena noted in SFC are present in an SFE. Hydrogen bonding interactions are thought to be a dominate force of adsorption in both systems. Carbon dioxide, alone does not have hydrogen bonding capability, thus, only interacts weakly with the stationary phase surface. The hydrogen bonds, holding the analyte to the stationary phase surface of the were disrupted by the addition of hydrogen bonding modifiers. The modifiers compete for thoes same adsorptive sites. Examples of improved modified solvent SFE efficiency can readily be found in the literature.[8,9,10,11]

It has been shown that chemical derivatization reagents, when used as reactive solvent modifiers, also enhance extraction efficiencies.[2,3,12] In these studies derivatization reagents enhanced extraction yields by making some polar, derivatizable compounds, such as carboxylic acids and alcohols, more soluble in non-polar supercritical extraction media. As with non-reactive modifiers, chemical derivativization improved extraction efficiencies of molecules which are inert to the modifier/reagent. The reagents are postulated to interact with active sites of the matrix. The result in the presence of derivatization reagents is a permanent chemical modification of the matrix surface, as opposed to temporary modification with a

non-reactive modifier. Once displaced from the matrix surface, analyte molecules are more readily solvated and removed from the sample by the extraction solvent. Further, once the active site is derivatized the analyte is not able to readsorb to the surface at that site.

The kinetics of an extraction can yield information about processes limiting an extraction. Kinetic descriptions of a matrix releasing an analyte have been contributed by both Bartel[13] and Pawliszyn.[14] Bartel considers diffusion of an analyte through a polymer to the surface-fluid interface where it is partitioned into the supercritical fluid solvent. In this treatment the diffusion coefficient of the analyte through the organic material was the limiting parameter. Pawliszyn discusses an analyte desorbing from a solid particulate matrix covered with an organic layer, through which the analyte must defuse before partitioning into the extraction solvent. According to Pawliszyn, if it is assumed the limiting process is the desorption of the analyte from the sorbent surface, the amount of analyte desorbed as a function of time from a homogenous matrix can be expressed

$$m(t)/mo = 1 - Xe^{-kt}$$

where mo is the mass of analyte in the sample, m(t) the mass after time (t), X is the fraction of analyte molecules adsorbed and k is the rate constant of desorption. Extraction rate is

dependent on the desorption time of an analyte from the surface. Plotting the logarithmic version of this equation the slope of the line corresponds to the rate constant of desorption. The rate of desorption is related to the strength of desorption. Disruption of the analyte-surface cohesive interaction will cause the rate constant to increase.

The objective of this work was to demonstrate that both a polar modifier (methanol) and a chemical derivatization reagent (BSTFA) act to displace analytes which are adsorbed to a surface by interacting with the sample matrix. This was accomplished by investigating the effect of the two modifiers on recoveries and recovery kinetics for probe compounds and native analytes from various matrices with known functional groups and unknown surfaces.

EXPERIMENTAL

Apparatus. The extraction system was obtained from ISCO,(ISCO, inc. Lincoln, NE) and consisted of a model 260D pump and a model SFX 2-10 extractor. The extraction solvent was supercritical fluid chromatography and extraction grade carbon dioxide obtained from Scott specialty gases (Plumsteadville, PA) and was used without additional purification. The sample extraction cell consists of a metal tube with an internal volume of 5 mL body and two frit filters that are held by threaded end caps. The low pressure end of the restrictor was placed in the solvent trap, which was a small screw top test tube containing methylene chloride.

Standards, analytes and internal standards were obtained from Resteck (Bellefonte, PA). Materials were obtained as stock solutions 1000 μg/mL for the analyte compounds in methylene chloride or methanol. A five-point calibration curve was prepared from the standard stock solution by serial dilution. Probe analyte compounds were added to the sorbent in two mixtures, base-neutrals (1,2-dichlorobenzene-D4, nitrobenzene-D4, 2-fluorobiphenyl, terphenyl-D14) at 1000 μg/mL and acids (2-fluorophenol, phenol-D5, 2-chlorophenol-D4, 2,4,6-tribromophenol) at 1500 μg/mL. The internal standards (1,4-dichlorobenzene-D4, naphthalene-D4, acenaphthene-D4,

phenanthrene-D10, chrysene-D12, perylene-D12) were added from a 4000 μg/mL stock solution to the extracts in 5 μL injections with a 10 μL syringe.

Sample matrices preparation. The manufactured homogenous adsorbents used were solid phase extraction cartridges (Baker, Philipsburg, PA). The cartridges consisted of 3 mL syringe housings with the solid phase adsorbent packed into the lower portion of the syringe volume. Five SPE packing types were used, alumina, silica, amino, phenyl, and cyanno. The homogenous adsorbent were spiked as received without any pretreatment. A 10 μL syringe was used to deliver 10 μL of each probe analyte solution to the SPE packing. The methylene chloride spiking solution solvent was allowed to evaporate for five minutes. A final drying was ensured by passing air through the SPE syringe with a vacuum system for 5-10 seconds. Municipal solid waste incinerator fly ash was obtained from, K.P. Naikwadi and F. Karasek at University of Waterloo, Waterloo, Ontario. The standard reference material, organics in marine sediment (SRM 1941), was obtained from the National Institute of Standards and Technology (Gaithersburg, MD). Both natural matrices were used as received without any preparation. SRM 1941 contains approximately 4% moisture as delivered. This was taken into account when calculating extraction yield.

Extraction procedure. The solid extraction packing was removed from the syringe housing with a small blade and placed

in a 5 mL extraction cell. The material was extracted at 400 atm 100 °C, with pure carbon dioxide and modified carbon dioxide. The fly ash and marine sediment sample matrices were extracted at 500 atm and 100 °C Two modifiers were evaluated, methanol and bis-trimethylsilyl-trifluoroacetamide (BSTFA),(Supelco, Bellefonte, PA). The modifier was added to the sample in the cell with a 250 μL syringe. After an initial reaction/static extraction period of 5 min., the flow rate of carbon dioxide through the cell was 0.1-0.3 mL/min. at 400 atm measured at the pump. This was continued for one half hour. The flow restrictor was a ca. 20 cm 50μm i.d. fused silica capillary. The extract was collected in ca. 0.5 mL methanol. After the extraction the volume of the extract was brought to 1.0 mL with methylene chloride. Internal standard solution (5 μL) was added to the diluted extract solution. The extract was injected into the GC/MS without further preparation. Time fractions were collected for kinetic analysis of the extraction by changing the trap each 3 minutes for the manufactured homogenous and 5 minutes for the fly ash and marine sediment sample matrices.

Analysis procedure. The extracts from the manufactured homogenous matrices were analyzed by GC/FID (Hewlett-Packard, Avondale, PA), controlled by chemstation software. Quantification was achieved by an internal standard method. The internal standard used for quantification was 2-fluorobiphenyl,

the others were used as retention time standards. Extracts from the fly ash and marine sediment were analyzed by GC/MS (Hewlett-Packard, Avondale, PA) according to EPA CLP semi-volatile method. Splitless injection (2 μL) of all extracts was made onto a 30 m Rtx-5 capillary column (Resteck, Bellofonte, PA) held at 40 °C for 5 min. The carrier gas was helium at 1 mL/min. through the column. All separations were temperature programmed with an initial column temperature of 40 °C with no hold time. The oven was programmed from 40 °C to 270 °C at 10 °C/min. with a final hold of 35 min. The injection port temperature was maintained at 270 °C. Quantification achieved by an internal standard method.

Gas Chromatograph/Mass Spectrometer. The fly ash and marine sediment extracts were analyzed by GC/MS. The GC/MS system used in these experiments was that recommended by the EPA CLP semi-volitile method. It consisted of a Hewlett-Packard 5890 gas chromatograph fitted with a 5970 mass sensitive detector. Operating conditions for the mass spectrometer were as follows: The ion source for the mass sensitive detector was held constant at 250 °C. The voltage for the electron impact ion source was operated at 70 V, but was not turned on until the solvent and excess reagent had eluted from the chromatographic column, 8.5 minutes after injection. The chromatographic conditions were identical to those given above.

RESULTS AND DISCUSSION

Recovery of Probe Compounds. Considering the seven homogenous manufactured matrices, the lowest yields, under all three solvent conditions, were observed from the alumina phase, indicating it had the greatest affinity for the analytes spiked onto its surface. Referring to the data given in tables I, II and III, decreasing affinity of the matrices for the probe compounds follows the order: alumina, silica, amino, phenyl, and finally cyanno. The average recoveries of the eight probes from the five phases were 52% with pure carbon dioxide, 90% with methanol modified carbon dioxide and 92% when BSTFA was present. A significant difference between modified and unmodified carbon dioxide was clear. Little difference in enhancement was seen between the two modifiers. However, when the probe analytes were adsorbed to the fly ash matrix, the association between the analytes and the surface could not be overcome by the addition of methanol. Recoveries for this matrix are given in table IV. The addition of BSTFA was required to achieve quantitative recovery from this surface. Average recoveries of the eight probes were 54%(20% RSD), 43% (10%) and 94% (8%) for pure carbon dioxide and carbon dioxide modified with methanol and BSTFA respectively.

Alumina is generally considered to be a basic adsorbent,

with a strong affinity for acids. However, the surface also has moieties which act as Lewis acids and thus adsorb Lewis bases. This acidity is in large part due to the positively charged metal centers the alumina surface. These adsorptive properties are illustrated by the less than quantitative yields of both the acids (24%) and the base-neutrals (44%) from the alumina matrix. The addition of methanol to the sample before extraction raises the average yields to around 70% for both classes. The methanol addition effected the acids more than the base neutral compounds. Methanol is a weak Lewis acid. During extraction, it competed for the same adsorptive sites as other Lewis acids, thus enhancing recovery. The addition of BSTFA improves the extraction of the base-neutrals to 86% recovery. Presumably, this is due to elimination of surface hydroxyls to which the Lewis base probe compounds were adsorbed.

Methanol acted on the surface moieties to which the phenols were adsorbed, thus improving the extraction efficiency of the acids. BSTFA acted on the both the surface moieties and the phenols themselves. Both actions disrupted the adsorptive analyte-matrix interactions. The 30% of the probes which remained on the matrix when alumina was extracted with methanol modified carbon dioxide were presumably too strongly adsorbed to be displaced by the methanol. The analyte-matrix interactions were greater than the modifier-matrix interactions.

Extraction from the silica phase matrix benefited from the

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addition of either modifier. The nature, reactive or non-reactive, of the modifier made no difference. This was attributed to the weaker adsorption strength of the probes to the surface then seen with alumina. When the probes are weakly adsorbed, hydrogen bonding of methanol to the adsorptive moiety of the surface is sufficient to displace the analyte. The BSTFA reacts readily with the silanol groups of the silica, eliminating the adsorptive character of the sorbent. The methanol weakly hydrogen bonds to the base-neutral analytes and to the sites where the phenols are adsorbed, thus disrupting the analyte-matrix interactions.

Considering the phenyl and cyanno matrices, which are inert to BSTFA, the carbon dioxide solvent eluted 61% of the probes from the phenyl matrix. This retention is in large part due to the electrophlic character of both the matrices and sorbed analytes. The acid probes were more retained (53% recovery) by the cyanno phase than the base-neutrals (75% recovery). The acids have the ability to hydrogen bond to the nitrogen of the cyanno group, while the base neutrals have little attraction to the cyanno matrix, which is a Lewis base itself. The interaction is stronger with cyanno groups than phenyl due to the difference in electronegitivity between the phenyl π-cloud and the nitrogen of the cyanno moiety.

Methanol also interacts with the both the phenyl phase and the cyanno phase through hydrogen bonding. Methanol is a

hydrogen bonding donor, thus interacts well with electronegative surface moieties such as those containing O, N and to some extent π-clouds. This interaction is extensive enough to enhance the recovery of both probe classes to quantitative yields, 97% with methanol-modified CO_2 and 100% with BSTFA-modified CO_2. When BSTFA is present the phenols are converted to the TMS esters, leaving relatively weak induction forces of the phenol phase's aromatic rings as the primary mode of analyte-matrix interaction. This explains the slightly retention of the derivatized phenols (78% recovery) from the phenyl matrix and the quantitative extraction from the cyanno matrix when BSTFA was used as a extraction solvent modifier.

The amino matrix is both a hydrogen bonding acceptor, a base, and reactive towards BSTFA. Like the base phases described above recoveries were enhanced by the addition of either methanol or BSTFA. However, the acids did elute more efficiently when BSTFA was present than when methanol was used. This is attributed to the conversion of the acids to TMS derivatives which have little affinity for the amino or TMS-amino matrix.

Thus far, only homogenous sample matrices have been considered in this study. Fly ash was investigated as an example of a adsorptive and non-homogenous real-world sample matrix. The high adsorptivity of the fly ash was attributed to the oxidized surface of the fly ash resulting from the oxidizing

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atmosphere where it was produced. The interaction of the methanol with the oxidized surface of the fly ash is, presumably, not large enough to interrupt the strong analyte matrix adsorption and displace the analytes from the adsorptive sites of the matrix. The BSTFA interacts, indeed reacts, with oxidized moieties such as hydroxyl and acid groups to a much greater extent than does the methanol. The covalent interaction, which is many times stronger than a hydrogen bond, makes BSTFA the stronger displacing agent.

Precision. The effect of the reactive modifier on precision was determined using the amino matrix. The amino matrix was chosen because the matrix reacts with the reagent as well as the acid probe analytes spiked on to it, thus adding the modifier has the greatest effect on the system. The results of four replicate extractions are given in table V. The modifier increased the average overall extraction yield of the eight probe compounds from 54% to 103% while not significantly effecting the precision which remained around 10% RSD in both cases. Dividing the analytes into chemical classes, phenolic acids and the base neutral compounds, no difference was seen in recoveries or precision when the modifier was present. Considering the pure carbon dioxide extractions, yields of both classes were much lower, however yields of the acids showed a 7% RSD and the base neutrals a much higher 20% RSD. The high uncertainty in the base neutral data is primarily due to the

recovery of dichlorobenzene. If this value is omitted from the average the RSD of the base neutral compounds recovery is a reasonable 9% RSD. The use of this modifier does not adversely effect the precision.

Rate of Recovery. Figure 1 shows the cumulative recovery of phenol-D5 spiked which was spiked onto the five homogenous matrices. The upper three traces indicate the extraction profile of phenol extracted with pure carbon dioxide. The lower three traces indicate data obtained with carbon dioxide modified with the reactive modifier BSTFA. Two, or more, cell volumes were needed to reach exhaustive recovery when carbon dioxide alone was used to extract from silica or alumina. However, when BSTFA was present, quantitative recovery of the phenol took just over one cell volume. The total amount extracted was distributed over several three minute fractions when eluted by pure carbon dioxide.

Figure 2 shows the same data plotted as amount extracted verses time for phenol-D5 from the silica gel matrix. The trace resembles chromatographic elution. However, a distinct difference is apparent between the elution with pure carbon dioxide and modified carbon dioxide. In addition to the much larger and earlier eluting peak in the case of modified CO_2, extraction with modified solvent yields a much sharper peak than with pure carbon dioxide. Both the retention time and the peak width are related to desorption of the analyte from the sample

matrix.

Using the equation given in the introduction, the desorption rate constant of the phenol from the matrix surface can be determined. Figure 3 shows the logarithmic version of this function $\ln\{(m_o-m)/m_o\}$ plotted against void volumes (t/t_o) for phenol-D5 extracted from the silica matrix with pure CO_2. The time axis is normalized to the dead time (t_o) of the extraction cell. The slope of this line is the rate constant of desorption (k_d). The data indicates the rate constant of desorption (k_d) has the value $0.37/t_o$. Data obtained for extraction from the same phase with BSTFA-modified carbon dioxide gave a rate constant that approached infinity. This implies that the phenol is unretained, or is only very slightly retained, by the silica and elutes with the dead volume. The desorption rate constant in the presence of the BSTFA modifier is very large and therefore implies desorption is no longer a limiting factor in the extraction of phenol from silica gel.

Other matrices showed similar results, which are listed in table VI. The rate of desorption from the alumina matrix was ten times higher with pure carbon dioxide then with modifier present. The effect was less dramatic when the phenol was extracted from the cyanno matrix, two times higher when BSTFA was used. This is attributed to the inertness of the matrix moieties to the reagent modifier. In the case of little or no interaction with the surface, the increased desorption speed

must, at least in part, be attributed to the conversion of the phenol to its TMS derivative. Correlation was observed between the rates of desorption given in table VI and the yields listed in table, I and III.

The extractions discussed thus far have considered analytes spiked onto a matrix. To investigate the interaction of carbon dioxide and carbon dioxide modified with BSTFA with sample matrices and native analytes, the extraction of fluoranthrene from the standard reference material SRM 1941 was investigated. The extraction yielded 530 ng/g with pure CO_2 and 1080 ng/g with BSTFA modified CO_2 of fluoranthrene, which correspond to 47% and 92% recovery respectively compared to the NIST certified value of 1220±240 ng/g. The elution profile of fluoranthrene with pure carbon dioxide and BSTFA modified carbon dioxide are shown in figure 4. As in the homogenous matrices studied the elution profiles are markedly different. The carbon dioxide extraction profile is broader and later eluting than elution with modified solvent.

Figure 5 shows the results of plotting the data obtained from SRM 1941 as $\ln\{(m_o-m)/m\}$ versus t/t_o. The slope derived for the modified solvent data is much steeper than the that from the pure carbon dioxide extraction. This indicates fluoranthrene's rate of constant of desorption (k_d) was larger when modifier was present. The values for k_d obtained were $0.11/t_o$ and $0.44/t_o$ with unmodified and modified solvent

respectively.

An SFE experimental system lends itself well to being viewed as a chromatographic system; the extraction solvent as the mobile phase, the extraction cell as the chromatographic column and matrix acting as a stationary phase. However, some differences are apparent. The two systems are compared in figure 6. In a chromatographic model the zone containing the analyte is placed in a narrow band at the top of the chromatographic column. In an extraction system the analyte is spread throughout the extraction cell either adsorbed to, or absorbed in, the stationary phase. Thus, the eluted zone of an extraction is very wide compared to that of a chromatographic zone. The stationary phase of a chromatographic system is analogous to the sample matrix of a extraction system. In the chromatographic system the mobile phase solvent brings the analyte to the stationary phase. However, in the extraction system the reverse is true, the analyte is on, or in, the stationary matrix from which it is removed by the mobile extraction solvent. Regardless of these differences, the analytes' migration rate in both systems is limited by the desorption rate from the stationary matrix into the mobile solvent. Only very rarely, and by definition never in trace analysis, is the solubility of the analyte in the solvent the limiting factor in an extraction.

In chromatography, the entire analyte zone elutes from the

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system, this is not true in extraction. In extraction fractional recovery is common, while in chromatography this indicates irreversible adsorption which would suggests a problem. A simple chromatographic model would seem to indicate that longer extraction times are sufficient to quantitatively extract all analytes from the sample since the only limiting parameter is the desorption of the analyte. The desorption of the analyte requires breaking matrix-analyte associations, or even weak chemical bonds. An analyte adsorbed to the matrix must obtain a threshold energy to be released from the matrix and move into the extraction solvent. The analyte must gain enough energy from its surroundings to overcome the potential well in which it is trapped. In the case of weakly adsorbed analytes this energy can be provided by the solvation strength of the extraction fluid. Most analytes have sufficient solubility in supercritical fluids to be readily solvated. This is especially true at trace levels where even quantitative extraction of a analyte would only constitute a small mole fraction in solution. For more strongly adsorbed analytes a component of the solvent with an affinity for the adsorptive moiety can displace the analyte form the surface. This lowers the energy by interrupting the matrix-analyte interaction. The greater the affinity modifier has for the adsorptive moiety, the greater the disruption and the greater the effect.

CONCLUSIONS

Pure Carbon dioxide insufficiently disrupts analyte-matrix interactions to achieve quantitative extraction of both native and probe analytes. The addition of either reactive or non-reactive modifiers is sufficient to extract probe analytes from homogenous manufactured phases. However, the effect of methanol is insufficient to obtain quantitative yields from strongly adsorptive real-world samples such as incinerator fly ash. The reactive modifier, BSTFA, acts on the analyte-matrix interaction enough to affect quantitative yields of both compounds which are reactive and inert to reaction with BSTFA.

Analytes in a sample are ether entrained in the matrix or adsorbed to its surface. Assuming sufficient solubility of the analyte in the extraction fluid, the efficiency of the extraction will be controlled by either diffusion through or desorption from the matrix. In the case of diffusion, the analyte must diffuse through the matrix media to the surface where it can be solvated by the extraction fluid and carried out of the vessel. If the analyte molecule is adsorbed to the matrix surface, extraction is controlled by desorption of the analyte from the matrix surface. In the latter case the analyte-matrix interaction must be overcome for solvation to occur. In the case of a weakly adsorbed molecule, solvation energy of the extraction fluid may be sufficient to overcome the desorption

energy barrier. But in many cases the analyte is too strongly adsorbed for the non-polar solvents employed in SFE to overcome the analyte-matrix energy and solvate the analyte molecule.

Polar, both non-reactive and reactive, solvent modifiers not only increase the overall solvent strength of the solvent mixture, but also compete for adsorptive sites on the sample matrix to which analytes are adsorbed. Effective modifiers have affinity for the same adsorptive sites as the target analytes; thus occupying the sites and displacing the analytes from the matrix surface. The extent of this displacement will depend on the relative strength of the modifier-matrix interaction and the analyte-matrix interactions. The greater the modifier-matrix interaction relative to the analyte-matrix interaction the greater the partitioning of the analyte off the matrix into the solvent. Shifting this partition equilibrium can be further exploited by the addition of a modifier which interacts more strongly with the matrix than the non-reactive modifies employed in studies thus far. Non-reactive modifiers only form temporary, dispersive, induction or hydrogen bonding interactions, with the matrix. A strong hydrogen bond, such as a methanol modifier might from, is only a fraction of the strength of a covalent bond. Therefore, forming a covalent bond to the active site of the matrix is energetically favored over the weaker, non-covalent, analyte-matrix interaction. Reactive modifiers form covalent bonds to some adsorptive matrix moieties

such as hydroxyls, thus eliminating hydrogen bonding. Thus, the partition equilibrium favors the reactive modifier bonded to the surface and the analyte displaced off the surface and into the extraction fluid. Further, this action of the modifier on the analyte-matrix interaction lowers the desorption energy allowing the analyte to pass over the desorption barrier and escape the matrix quicker. Thus, faster extraction times are observed when modified solvents are used.

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FIGURE CAPTIONS

Figure 1. Cumulative fraction of phenol (m/m_o) extracted from selected adsorbents as a function of the void volumes (t_o). The material was extracted at 400 atm 100 °C, with pure carbon dioxide and BSTFA modified carbon dioxide. After an initial reaction/static extraction period of 5 min., the flow rate of carbon dioxide through the cell was 0.1-0.3 mL/min. at 400 atm measured at the pump. The flow restrictor was a 20 cm 50μm i.d. fused silica capillary. The extract was collected in methanol.

Figure 2. Extraction of phenol from silica gel, Amount extracted versus time. The sharper trace is data obtained with BSTFA and carbon dioxide. The broader trace is data obtained with pure carbon dioxide. Extraction conditions are the same as figure 1.

Figure 3. $Ln\{(m_0-m)/m_o\}$ as a function of void volumes of carbon dioxide passing through the cell for phenol extracted from the silica gel sorbent.

Figure 4. Amount extracted versus time for fluoranthrene from SRM 1941. The upper sharper is data obtained with BSTFA and carbon dioxide. The broader trace is data obtained with pure carbon dioxide. The material was extracted at 400 atm 100 °C, with pure carbon dioxide and BSTFA modified carbon dioxide. After an initial reaction/static extraction period of 5 min., the flow rate of carbon dioxide through the cell was 0.1-0.3 mL/min. at 500 atm measured at the pump. The flow restrictor was a 20 cm 50μm i.d. fused silica capillary. The extract was collected in methanol.

Figure 5. Plot of the function ln((mo-m)/m) versus time for fluoranthrene extracted from SRM 1941. Extraction conditions are the seam as thoes given for figure 4

Figure 6. Comparison of the chromatographic process and the extraction process.

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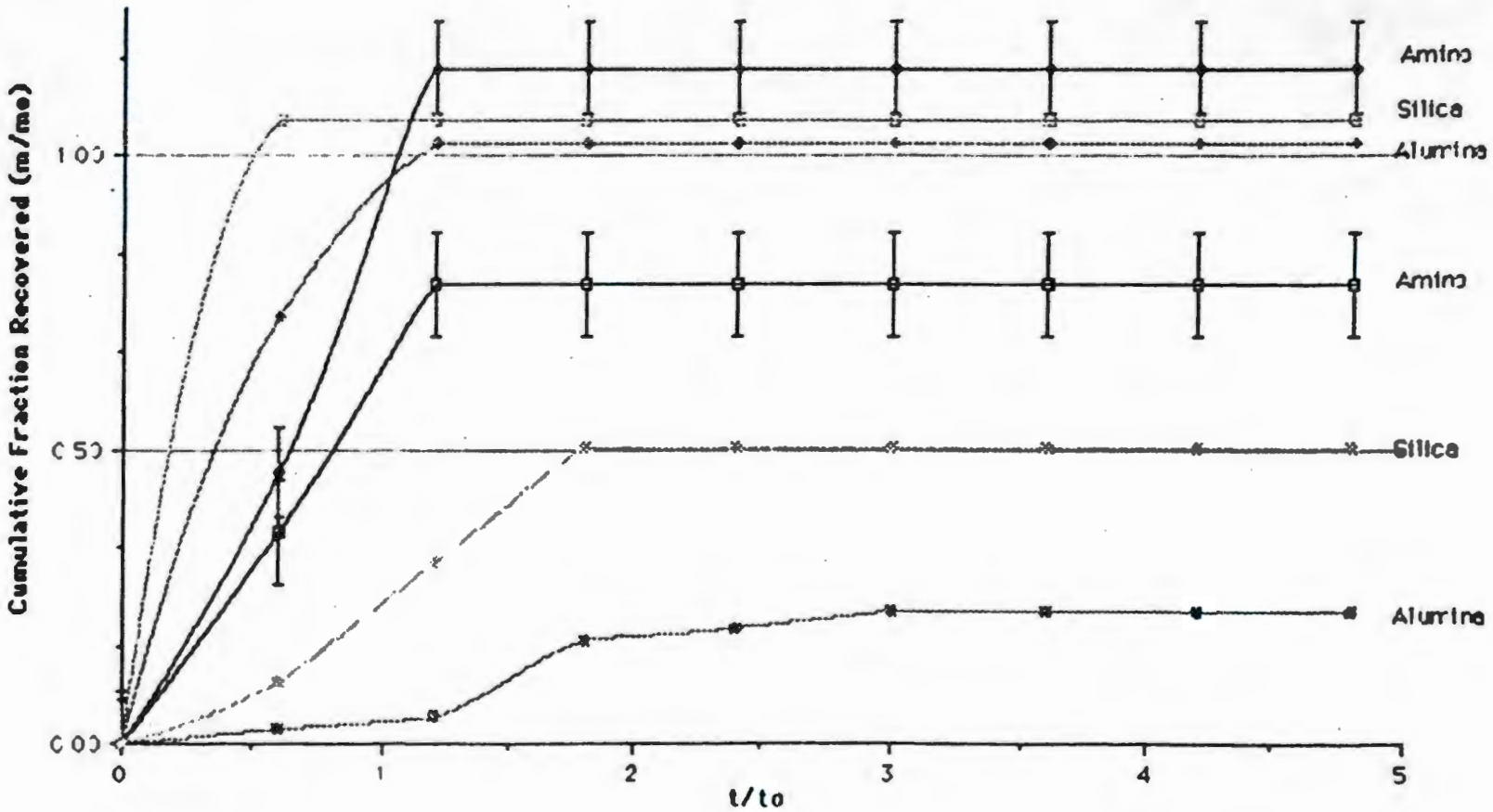
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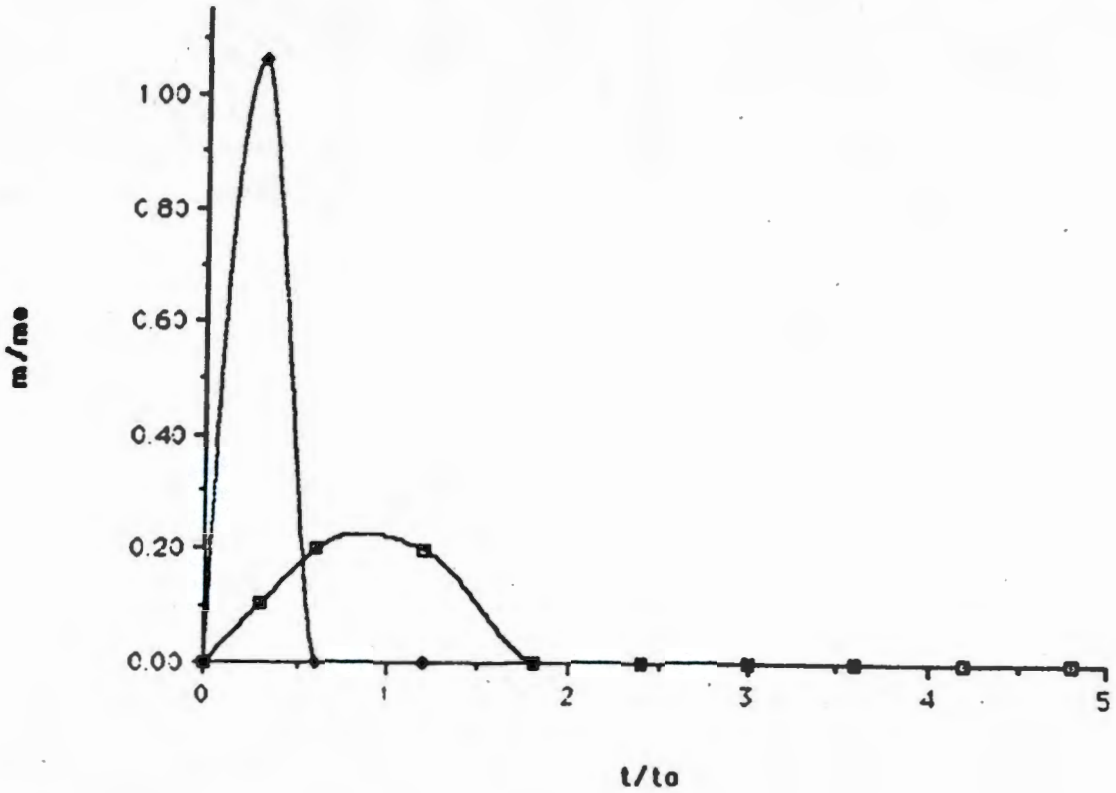
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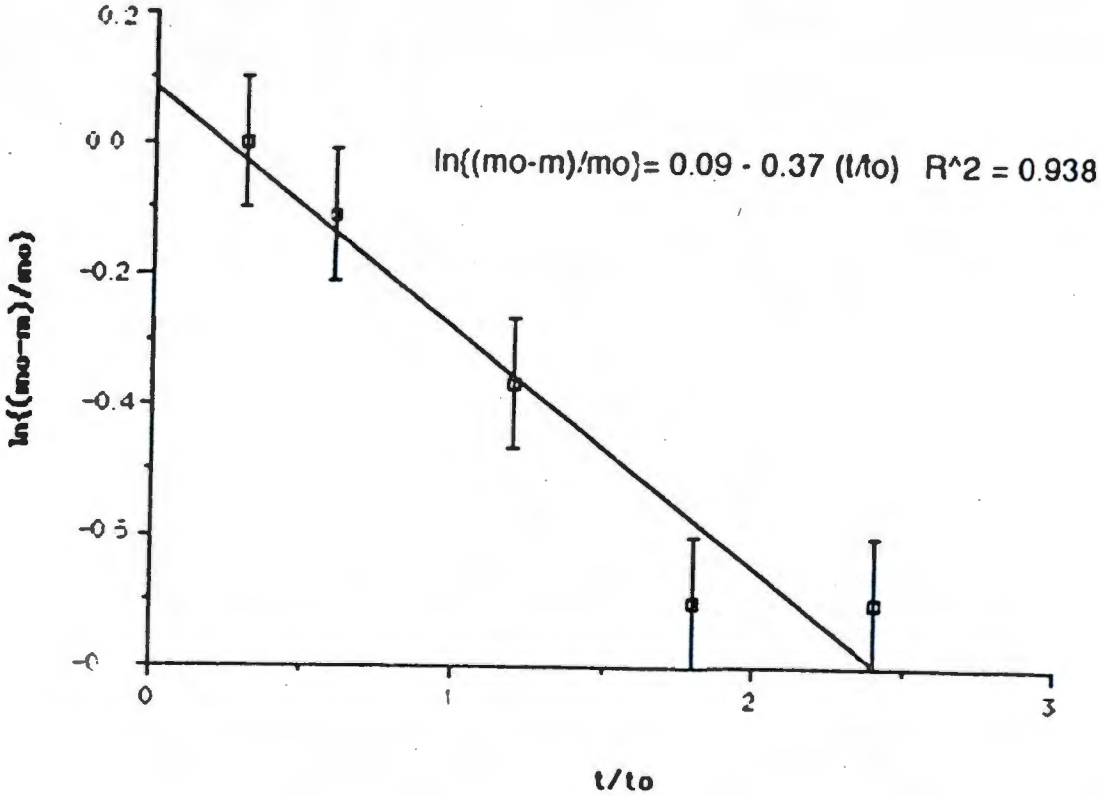

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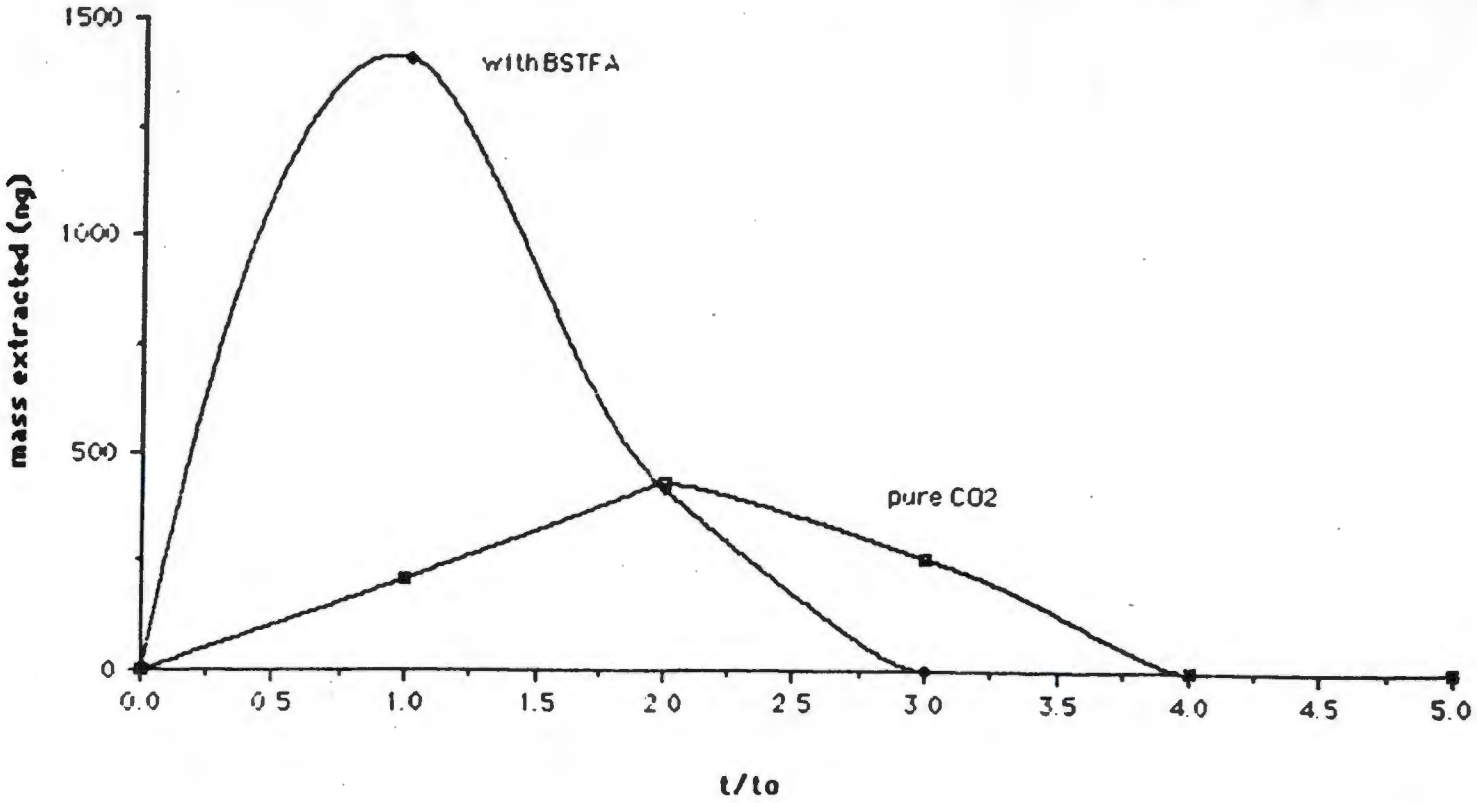

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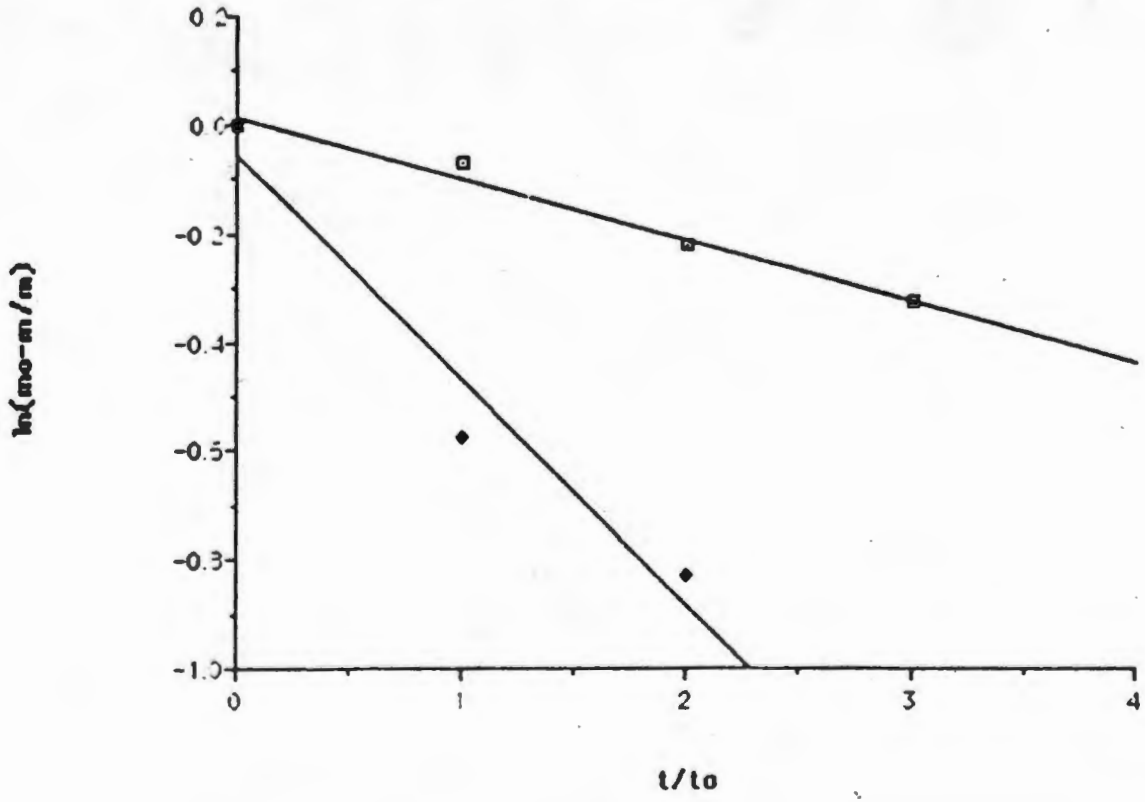

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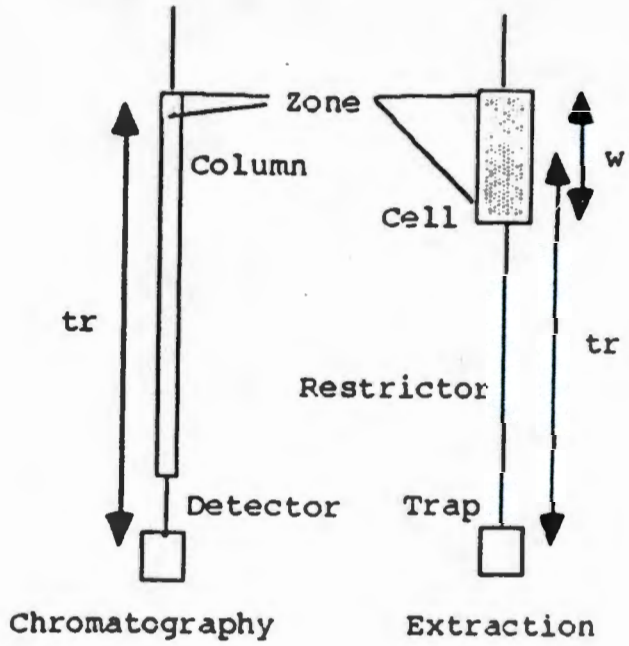
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Table I. Relitive Recoveries from Adsorbents with Carbon Dioxide (400 atm, 100 °C).

	Alumina	Silica	Amino	Phenyl	Cyanno
2-Fluorophenol	0.22	0.54	0.76	0.47	0.41
Phenol-d5	0.17	0.50	0.78	0.79	0.61
2-Chlorophenol-d4	0.43	0.51	0.96	0.65	0.58
1,2-Dichlorobenzene-d4	0.60	0.42	0.41	0.67	0.62
Nitrobenzene-d4	0.44	0.41	0.15	0.75	0.73
2-Fluorobiphenyl	0.58	0.43	0.91	0.71	0.65
2,4,6-Tribromophenol	0.16	0.46	0.32	0.53	0.54
Terphenyl-D14	0.13	0.44	0.13	0.33	1.02
Acids	0.24	0.50	0.70	0.61	0.53
Base-Neutral	0.44	0.43	0.40	0.62	0.75
Overall	0.34	0.46	0.53	0.61	0.64

Table II. Relitive Recoveries of Analytes from Adsorbents with Carbon Dioxide (400 atm, 100 °C) and 250 μL Methanol Modifier.

	Alumina	Silica	Amino	Phenyl	Cyanno
2-Fluorophenol	0.61	0.93	0.76	0.79	0.80
Phenol-d5	0.71	0.94	0.86	1.02	0.80
2-Chlorophenol-d4	0.91	1.12	1.07	1.20	1.07
1,2-Dichlorobenzene-d4	0.77	0.87	0.85	0.82	0.92
Nitrobenzene-d5	0.65	1.03	0.92	0.99	1.34
2-Fluorobiphenyl	0.78	1.05	0.90	0.89	0.99
2,4,6-Tribromophenol	0.54	0.95	0.62	0.99	1.19
Terphenyl-D14	0.64	0.84	0.99	1.04	0.86
Acids	0.69	0.98	0.82	1.00	0.96
Base-Neutral	0.71	0.95	0.91	0.94	1.03
Overall	0.70	0.97	0.87	0.97	1.00

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Table III. Relitive Recoveries of Analytes from Adsorbents with Carbon Dioxide (400 atm, 100 °C) and 250 μL BSTFA Modifier.

	Alumina	Silica	Amino	Phenyl	Cyanno
2-Fluorophenol	0.74	0.99	0.98	0.81	1.10
Phenol-d5	1.02	1.05	1.15	0.86	1.07
2-Chlorophenol-d4	0.91	1.04	1.00	0.84	1.12
1,2-Dichlorobenzene-d4	1.01	0.87	1.02	0.65	1.10
Nitrobenzene-d5	0.96	1.16	1.05	0.75	1.20
2-Fluorobiphenyl	0.96	1.12	1.00	0.80	1.01
2,4,6-Tribromophenol	0.65	1.01	0.83	0.63	0.82
Terphenyl-D14	0.52	1.06	0.97	0.62	0.36
Acids	0.71	1.02	0.99	0.78	1.03
Base-Neutral	0.86	1.05	1.01	0.71	0.92
Overall	0.79	1.04	1.00	0.74	0.97

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Table IV. Relative Recoveries of Analytes from Fly Ash Matrix.

	Pure CO_2	%RDS	CO_2 W/ MeOH	%RSD	CO_2 W/ BSTFA	%RSD
Phenol-d5	0.69	11	0.80	4	1.00	3
2-Chlorophenol-d4	0.65	3	0.35	1	0.86	20
1,2-Dichlorobenzene-d4	0.69	12	0.55	21	1.02	4
Nitrobenzene-d5	0.38	53	0.05	3	1.03	5
2-Fluorobiphenyl	0.75	7	0.62	26	1.16	5
2,4,6-Tribromophenol	0.35	19	0.62	14	0.48	17
Terphenyl-D14	0.27	9	0.04	2	1.06	2
Average	0.54	20	0.43	10	0.94	8

Table V. Reprodcibility of Recoveries with Pure and Modified Carbon Dioxide from the Amino Matrix.

	Pure CO_2	%RDS	CO_2 W/ MeOH	%RSD
2-Fluorophenol	0.758	10.1	0.978	14.8
Phenol-d5	0.780	8.9	1.15	7.7
2-Chlorophenol-d4	0.956	2.1	1.00	4.7
1,2-Dichlorobenzene-d4	0.406	52.4	1.02	9.4
Nitrobenzene-d5	0.152	7.5	1.05	5.7
2-Fluorobiphenyl	0.906	2.9	1.00	3.8
2,4,6-Tribromophenol	0.322	6.8	0.827	14.0
Terphenyl-D14	0.129	16.0	0.969	21.7
Acids	0.659	7.0	0.989	10.3
Base-Neutral	0.398	19.7	1.01	10.2
Overall	0.529	13.3	0.999	10.2

Table VI. Desorption Rate Constants and Retention times from Several Adsorbent Matrices

	kd	tr
Alumina (pure CO2)	0.11*	2.0*
Alumina (Modified)	1.0	2.0
Silica (pure CO2)	0.37	2.1
Silica (Modified)	large	1.2
Cyano (pure CO2)	0.64	1.5
Cyano (Modified)	1.2	1.5
Amino (pure CO2)	0.25	0.3
Amino (Modified)	3.0	0.7
Phenyl (pure CO2)	0.36	1.3
Phenyl (Modified)	large	0.4
SRM 1941 (pure CO2)	0.11	2.2
SRM 1941 (MOdified)	0.44	1.1

*All values are reported in void times (t_o).

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