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CHARACTERIZATION OF POLYIMIDE SORBENTS BY USING TRACER PULSE CHROMATOGRAPHY

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SUMMARY

A modification of tracer pulse chromatography was used to rapidly evaluate four novel polyimide sorbents for use in air sampling. This technique utilized probe molecules with different functional groups to evaluate the surface retention characteristics when the sorbents were highly loaded by these chemicals and humidity. The evaluation of the sorbents indicated the polymer subunits of each must have multiple sorption sites which is consistent with their chemical makeup. Some comparisons between the polyimides and Tenax-GC were made.

INTRODUCTION

The use of sorbents for air sampling or organic compounds has been done successfully for many years. One of the major sorbents in use is Tenax-GC (hereafter Tenax) which, when used with thermal desorption and cryofocussing in the analytical step, can allow very good sensitivity for many organic compounds^{1,2}. A major advantage of Tenax in this regard is its low retention of water. This alleviates any problems from subsequent analysis steps such as obstruction of the cryofocussing trap, high mass spectrometer pressures, etc. A major disadvantage of Tenax has been the poor retention of polar organics at ambient temperatures which prevents the collection of many of the toxic and carcinogenic compounds of interest.

To improve this situation we have previously investigated polyimide sorbents that we have prepared³ to determine their suitability for collection of a broad range of organic compounds from air including the volatile polar compounds. Among those initially tested, four polyimides were found suitable for further testing⁴.

To further characterize the four polyimide sorbents, we choose to probe the competitive effects on sorption for selected organic compounds and water. By examining the competition between various organic compounds and water the surface characteristics of the sorbents can be elucidated. One approach is to use the technique of tracer pulse chromatography as developed by Parcher^{5,6}. This gas chromatography (GC)–mass spectrometry (MS) technique involves continuously feeding a known, fixed concentration of an analyte into a carrier gas stream through a sorbent of interest. Once equilibration of the analyte with the sorbent is established, an injection

of a deuterated analogue of the analyte (probe) is made. This is carried out while the sorbent is maintained at a constant temperature. The procedure is repeated for different equilibration levels of the undeuterated analogue with the sorbent. The retention times of the probe thus provide information about the capacity of the sorbent for a given compound.

The method we have employed to evaluate these sorbents is a dynamic form of the tracer pulse chromatography technique which uses a mixture of analytes instead of one analyte at a time. This approach provided the advantages of better mimicking the collection of chemicals from air and of providing faster data collection.

EXPERIMENTAL

The polyimides were synthesized in-house by using a simple reaction between pyromellitic dianhydride and the appropriate aromatic diamine³. The polymer resin was dried and sieved to obtain 40–60 mesh particles. The Tenax used was 40–60 mesh and was obtained from Alltech Associates–Applied Science Labs. (Deerfield, IL, U.S.A.). The deuterated organic compounds were obtained from MSD Isotopes (Montreal, Canada). All other compounds were obtained from Aldrich (Milwaukee, WI, U.S.A.). Dichlorodimethylsilane (DCDMS)-treated glass wool was obtained from Alltech.

The GC–MS–computer (COMP) instrument used was an LKB 2091 magnetic sector mass spectrometer (LKB, Bromma, Sweden) interfaced to a Varian 3700 gas chromatograph (Palo Alto, CA, U.S.A.) and a Digital Equipment PDP 11/04 computer system (Maynard, MA, U.S.A.). For later stages of the work (model compounds), a Teknivent 802 MS interface (St. Louis, MO, U.S.A.) using a Tandy 3000 microcomputer (Fort Worth, TX, U.S.A.) was used for data acquisition. A gas jet separator (Becker-Ryhage type) for the mass spectrometer was used since the column flow-rate was 10 ml/min for each sorbent. The mass spectrometer was operated in the electron impact mode under the following conditions: electron beam energy, 70 eV; accelerating voltage, 3.5 kV; trap current, 50 μ A; and temperatures of ion source and Becker-Ryhage separator, 180°C. The glass columns used had dimensions sufficient to accommodate an *ca.* 80 cm \times 2 mm I.D. sorbent bed and were silanized by using DCDMS. DCDMS-treated glass wool was used to plug the ends of the sorbent bed. The polyimide sorbents were used as prepared. The Tenax was extracted with methanol and pentane and then dried before use.

A diagram of the interface which generated the organic and water vapors in the helium stream is shown in Fig. 1. The flow controller and flow meter used were Tylan FC-260 and FM-360 (Carson, CA, U.S.A.). The organic vapor generator was an enclosed vessel containing a mixture of the analytes for the introduction of the organic vapors into the sorbent column. The flows through the organic vapor generator and the humidifier were adjusted to provide the correct levels of organics and water vapor. The humidifier was optionally removed for experiments not involving water vapor. The gas lines from the organic vapor generator and humidifier to the GC–MS–COMP system were heated to *ca.* 100°C.

The 4-port valve allowed the interface to be operated in two modes. The initial mode of operation was with helium carrier gas valved directly to the GC–MS–COMP system; the second mode was with organics and water vapor introduced from the

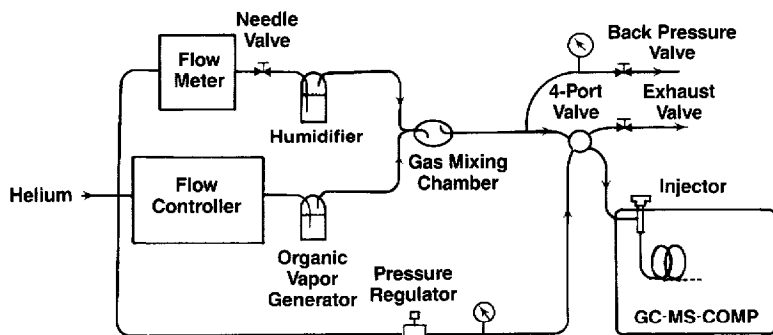


Fig. 1. Schematic of the continuous vapor introduction apparatus.

organic vapor generator and the humidifier, respectively. The pressure of the interface was maintained at 13.6 p.s.i.g. by using the back pressure valve, which was matched to the pressure regulator. The exhaust valve was set to match the flow resistance of the sorbent column.

Molecular probe studies

The actual experiments involved the use of 5 probe compounds plus water vapor. The probe compounds were ethanol, *n*-hexane, benzene, butanone, and nitromethane. These probes represent H-bonding, dispersion forces, π - π interactions and dipole interactions in a similar fashion to interactions described by McReynold's constants. This approach would most effectively provide information about the surface features of the polymer studied.

The experiments each involved five injections of a vapor mixture of the deuterated probe compounds. The deuterated compounds were: [2,2,2- $^2\text{H}_3$]-ethanol; [$^2\text{H}_{14}$]-*n*-hexane; [$^2\text{H}_6$]-benzene; [1,1,1,3,3- $^2\text{H}_5$]-butanone and [$^2\text{H}_3$]-nitromethane. The liquid mixture was prepared to provide approximately equal molar proportions of vapors. The mixture was maintained in a septum vial at 25°C. Headspace injections of this mixture consisted of *ca.* 5 μg for each compound. Injections were made at 10-min intervals starting at -10 min and ending at 30 min, where 0 min is the time at which the continuous stream of all undeuterated analytes was introduced (and optionally water vapor). The sorbent was maintained at an appropriate isothermal condition so that the most retained compound eluted approximately 30 min after injection. The 30-min period was sufficiently long to allow the changes in the retention time of the least retained compound to be evaluated. It was not so long as to cause undue band broadening of the last eluting compound. The 10-min injection interval was sufficient to evaluate changes in retention prior to an equilibrium state, therefore providing an insight into retentions on a sorbent before breakthrough of any of the frontal streams. The injection intervals (10 min) were constant to avoid minor errors due to competitions solely from the deuterated compounds. Table I shows the sorbent temperatures and the retention times of the probe compounds for each sorbent. The retention time of water was determined from its elution front.

The native (undeuterated) chemicals were also prepared as a vapor mixture for introduction into a continuously flowing stream. The organic vapor generator was

TABLE I

SORBENT TEMPERATURES AND RETENTION TIMES OF PROBE COMPOUNDS AND WATER

<i>Probe compound</i>	<i>Retention time (min)</i>				
	<i>PI-119</i>	<i>PI-109</i>	<i>PI-115</i>	<i>PI-149</i>	<i>Tenax</i>
Water	2.7	2.4	5.3	3.3	0.7
Ethanol	12.0	9.9	16.5	7.7	2.3
Nitromethane	17.6	16.5	30.8	29.6	8.0
Butanone	26.8	26.5	10.7	ca. 19.4	14.4
Benzene	10.9	15.7	5.1	ca. 13.1	28.4
<i>n</i> -Hexane	3.3	4.8	0.9	0.7	12.9
Temperature, °C	135	135	90	120	85

used for this and was maintained at 25°C for this group of compounds. Its operation was based on Raoult's law by using a gas stream passing through a liquid mixture of the organics. These compounds and water vapor were continuously introduced through the sorbent bed at the desired levels beginning at time $t = 0$ min of each experiment. Through a combination of eliminating the organic vapor generator, changing the organic mixture ratios, or changing the flow-rate through the humidifier (when present) various challenge conditions were created.

The organic vapor mixture that was continuously fed was nominally introduced at a level which would just show a small decrease in retention time if each chemical were introduced individually. This was accomplished by injecting larger and larger amounts of an individual compound until a retention time decrease was noted. This would imply the compound would be occupying a substantial number of the surface sites of the sorbent. This was found to be about 100 nmol/min for each compound in the vapor mixture and is the "1 ×" level used. For a 1 × experiment all organics were at this level. When added, water vapor was introduced at a level of 22 Torr, which was a higher level than for the organic compounds. This humidity level was chosen to approximate the higher ambient levels expected in actual field sampling conditions instead of being based on sorbent capacity.

The above setup essentially describes one experiment or GC-MS run. The GC-MS system was operated in the full-scan mode during the experiment. A typical experiment showing the chromatogram of the benzene front (m/z 78) and the corresponding chromatogram of the [$^2\text{H}_6$]benzene injections (m/z 84) is presented in Fig. 2.

By approaching the sorption capacity of the multi-functional sorbent with the probe molecules and water vapor (1 ×), additional loading of the sorbent with organics should show, with good sensitivity, the sorption characteristics of the polymer. This was tested by elevating the concentration of one of the organic chemicals in the continuously fed vapor mixture 10-fold to 1 μmol/min (10 ×) while maintaining the levels of the other chemicals in the mixture at 100 nmol/min (1 ×). This elevated-level experiment was conducted for each compound in separate experiments while the other compounds were continuously introduced at the nominal level (1 ×). All chemicals were also continuously introduced at 0.4 × and 0.1 × levels, to verify if the retention time reductions of the 1 × experiment were in a reasonable range, and to

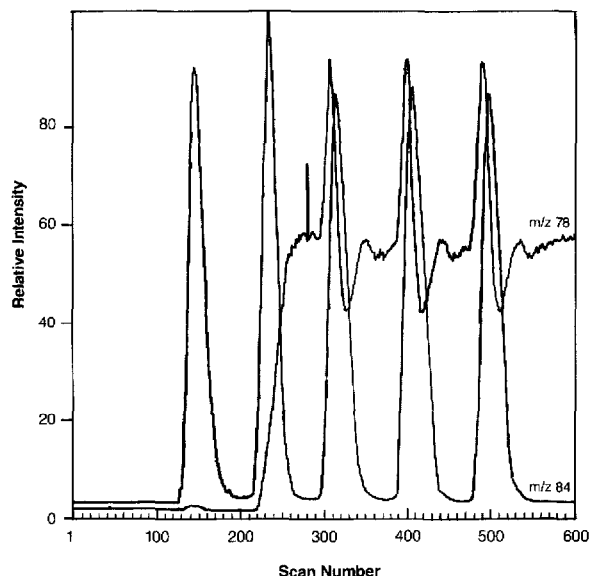


Fig. 2. Superimposed ion chromatograms showing the simultaneous elution of the benzene front (m/z 78) and the multiple $[^2\text{H}_6]$ benzene injections (m/z 84) through the PI-109 polyimide sorbent.

test if changes occurred. The deuterated compounds were injected at the same levels at all times in all of the experiments, thus they did not play a role in the variable loading of the sorbents. The relative levels of the individual compounds continuously introduced are shown in Table II for reference. In the table a value of 1 indicates a feed-rate of 100 nmol/min, 10 indicates 1 $\mu\text{mol}/\text{min}$, etc. As shown, experiments were carried out by testing the overall capacity of the sorbent and the effects of humidity. Half of the experiments was carried out with humidity, though the control experiment

TABLE II

RELATIVE LEVELS OF ORGANIC VAPORS INTRODUCED INTO THE SORBENT — MOLECULAR PROBE STUDIES

These experiments were carried out with water vapor continuously fed at 22 Torr and also at 0 Torr. The level of organics is normalized so that a level of 1 indicates 100 nmol/min, 10 indicates 1000 nmol/min, etc.

Experiment	Level of frontal loading				
	Ethanol	<i>n</i> -Hexane	Benzene	Butanone	Nitromethane
Control	0	0	0	0	0
1	1	1	1	1	1
2	10	1	1	1	1
3	1	10	1	1	1
4	1	1	10	1	1
5	1	1	1	10	1
6	1	1	1	1	10
7	0.4	0.4	0.4	0.4	0.4
8	0.1	0.1	0.1	0.1	0.1

used for comparisons did not have humidity added. The control is discussed further in a later section.

Model toxic compounds

The same general procedures were followed in carrying out dynamic tracer pulse chromatography for two additional sets of model toxic compounds. These experiments with additional chemicals were carried out on the PI-119 sorbent to further characterize it and to corroborate the results by using the probe compounds.

The first set of injected compounds included [$^2\text{H}_6$]benzene, [$^2\text{H}_3$]acrylonitrile, [$^2\text{H}_4$]dichloroethane, and [$^2\text{H}_5$]ethyl acetate. Their undeuterated analogues were introduced continuously as in frontal chromatography. As before, five vapor phase injections were made of the deuterated mixture at 25°C, however, the injections were made at 8-min intervals starting at -8 min and ending at 24 min. The PI-119 sorbent was maintained at 130°C in the gas chromatograph so the most retained compound eluted within 24 min after an injection. As was conducted for the probe compounds, the organic vapor generator for continuously feeding the analytes was maintained at 25°C. The scheme for the relative levels of the continuously fed chemicals is shown in Table III. The same absolute levels for the continuously fed chemicals were used (*e.g.* "1 ×" indicates 100 nmol/min per compound, etc.). The humidity levels and all other parameters were also unchanged.

The second set of compounds included [$^2\text{H}_{22}$]*n*-decane, [$^2\text{H}_7$]*n*-propylbenzene, [$^2\text{H}_4$]*o*-dichlorobenzene, and [$^2\text{H}_5$]benzonitrile as the injected compounds, and native chemicals as the frontal streams. Five discrete injections per experiment were made, but were done at 10-min intervals as was carried out with the probe compounds. The vapor-phase injected sample was maintained at 70°C. A syringe and the septum vial of the deuterated mixture were kept in an oven, quickly loaded and injected into the GC-MS apparatus to maintain sufficient vapor pressures of the constituents. The organic vapor-phase generator for the continuous feeding of vapor was also maintained at 70°C. The GC temperature of the PI-119 sorbent was maintained at 195°C

TABLE III

RELATIVE LEVELS OF ORGANIC VAPORS INTRODUCED INTO PI-119 — MODEL TOXIC COMPOUNDS

These experiments were carried out with water vapor continuously fed at 22 Torr and also at 0 Torr. The level of organics is normalized so that a level of 1 indicates 100 nmol/min, 10 indicates 1000 nmol/min, etc.

<i>Experiment</i>	<i>Level of frontal loading</i>			
	<i>Benzene</i>	<i>Acrylonitrile</i>	<i>1,2-Dichloroethane</i>	<i>Ethyl acetate</i>
Control	0	0	0	0
1	1	1	1	1
2	10	1	1	1
3	1	10	1	1
4	1	1	10	1
5	1	1	1	10
6	0.4	0.4	0.4	0.4
7	0.1	0.1	0.1	0.1

for these experiments. The continuously fed levels used were the same as for the first set of model toxic compounds, as were the levels used for the humidity.

RESULTS AND DISCUSSION

Conceptual model of experiment

A simplified representation of the technique we employed is shown in Fig. 3. The injection of the deuterated analyte occurs at the initial time point and the front stream (of a faster eluting compound) is introduced later as indicated by "front" in this example. Other combinations of continuously fed compounds and deuterated compounds can be examined also. As indicated, a retention time decrease for the deuterated analyte may occur as a result of competition(s) with the undeuterated analyte in the frontal stream. By making an injection without a frontal stream present, a control case is generated which can be used for comparison. The retention time decrease is measured and compared to the control where no competition exists. Also, by taking account of the sweep time of the deuterated pulse, a % deviation in the retention time can be determined from $[(t'_{\text{unk}}/t'_{\text{con}}) - 1] \cdot 100$, where t' is the corrected retention time for an unknown (unk) or control (con). Corrected retention time is $t' = t - t_{\text{sweep}}$. Also, it is important that the concentration level of an analyte stream is set (nominally) just under the capacity level at which any greater sorbent loading by the analyte causes a significant reduction in its retention time. Therefore, any additional loading by the same compound, or another which competes for the same surface functional groups, will provide a much more sensitive measure of the surface effects.

Therefore, the deuterated analyte is injected before or during the frontal stream migration of the native chemicals to measure the effects of competition. It should be pointed out that using a native analyte in an injection is less desirable since a concen-

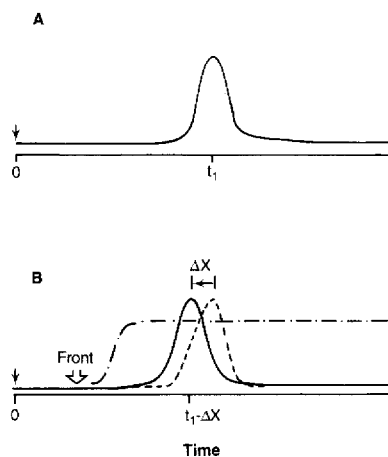


Fig. 3. Representations of the chromatography using dynamic tracer pulse chromatography. (A) The control case with a single compound injected. (B) The same compound is injected but its retention by the sorbent is affected by the front. The front is introduced after $t = 0$ and is a faster eluting compound in this example.

tration pulse does not migrate at the same rate as the actual molecules injected^{7,8}. Also, as a practical matter, identification of the injected analytes is more easily accomplished.

The method we used involved 4–5 organic compounds introduced simultaneously, where each represented a different functional group. Water was optionally introduced. By pulsing (injecting) the deuterated analogues at various time points as the different frontal streams migrated, a picture of the processes in effect at the sorbent surface were seen.

Molecular probe studies

Because of the large amounts of data generated by the experiments, only selected experiments will be presented in detail. In reviewing the results for all polymers tested, including Tenax, it was quite clear that water vapor affects breakthrough volumes (BVs). BV is the flowing gas volume required to elute a compound from a sorbent bed at a given temperature. The BV curve has been typically determined in the absence of water vapor. However, at least 50% humidity is almost always present during field sampling. The BVs for some compounds were found to be over 50% lower on some of the polymers tested in the presence of humidity. This can have a substantial impact on collection efficiency if a BV is approached for a given compound of interest in the field.

The general effects of water vapor across the polyimides and Tenax are shown in Fig. 4. The effect of water vapor on the retention of ethanol on the polyimide sorbents was quite significant, while the effect was much less on Tenax. This suggests that sorption on polyimides is affected when the retention of an analyte depends on H-bonding. For Tenax the changes were less apparent. Regardless of humidity, the retention of many volatile polar compounds is poor to begin with so humidity is not of any practical consequence. Differences between the two polyimides were also observed. Overall, continuously introducing organics into the sorbent bed provided better retention for ethanol by using PI-109 when water vapor was present than when it was not present (AA *versus* BB). On the other hand a further reduction in retention for ethanol occurred by using PI-119 under the same circumstances (CC *versus* DD). For PI-109 a large decrease in retention of ethanol occurred when the water vapor was introduced alone (AA), but subsequent injections indicated small increases. This suggests that the deuterated organics from the injections themselves may be coating the surface to a certain extent, either blocking the sorption of water or aiding in sorption of other organics by serving as stationary phase. This phenomenon was not as pronounced with PI-119.

These data illustrate the utility of the technique. The apparent H-bonding in this case shows the ability of the technique to determine any functional group effects on the retention. It also provides information about other effects which may not normally be expected such as the modification of the surface characteristics by the organics. The use of multiple injections helps to observe these more subtle effects which are prior to a steady-state equilibrium.

In the experiments involving water vapor, the retentions of nitromethane can be examined across the different polymers as shown in Fig. 5. In contrast to ethanol, water vapor did not significantly affect the retention of nitromethane on Tenax. However, all of the polyimides exhibited 10–30% reductions in retention times for

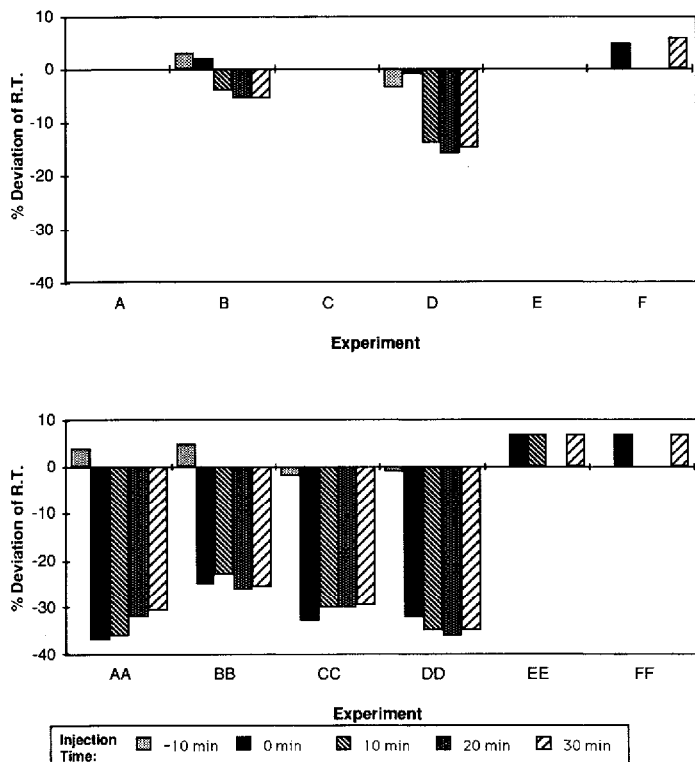


Fig. 4. Percent deviation of the retention time of $[^2\text{H}_3]$ ethanol on three sorbents. Sorbents tested were: PI-109 (A,B); PI-119 (C,D); Tenax (E,F). Experiments A, C and E were cases where no organic frontal streams were introduced. Experiments, B, D and F were cases where all organic frontal streams were introduced at the $1 \times$ level. Double letters indicate the additional presence of a water vapor frontal stream to the corresponding experiments.

nitromethane. This water vapor effect apparently was not altered upon adding the organic frontal streams for PI-115, PI-119 and Tenax, and was unchanged for PI-149. Only for PI-109 did addition of the organics change (increase) the retention of nitromethane substantially. As for ethanol on PI-109, the organic compounds in the frontal streams apparently aided in the retention of nitromethane.

The surface characteristics of the sorbents were evaluated effectively when one of the five organic frontal streams was elevated 10-fold. This provided a high loading of the sorbent with a frontal compound of a specific functionality. Therefore, changes in retention of a deuterated probe compound would indicate competition with the elevated compound in the frontal stream for the same sites on the sorbent. In Fig. 6, the experiments on PI-119 involving each of the elevated ($10 \times$) frontal streams in the absence of water vapor is shown. The $0 \times$ and $1 \times$ experiments are also shown for reference. The retention of $[^2\text{H}_6]$ benzene was not substantially affected by the increased level of hexane (B *versus* C). This suggests that the two compounds interact with different sites on the sorbent surface. An expected change in retention occurred for the frontal stream containing elevated levels of benzene as indicated by a simple

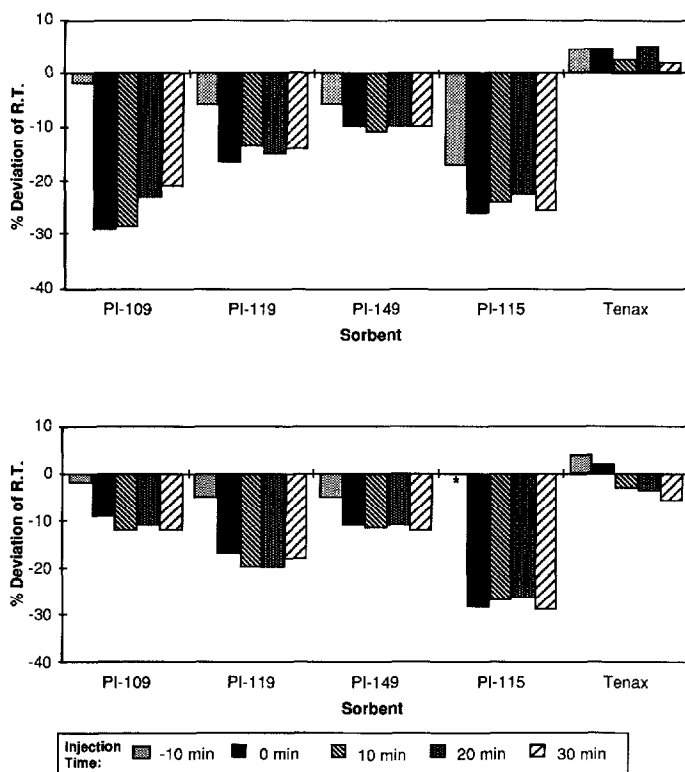


Fig. 5. Percent deviation of the retention time (R.T.) of $[^2\text{H}_3]$ nitromethane in the presence of water vapor on the tested sorbents. The top frame shows experiments with no organic frontal streams introduced. The bottom frame shows experiments with $1\times$ level organic frontal streams introduced. * = No data.

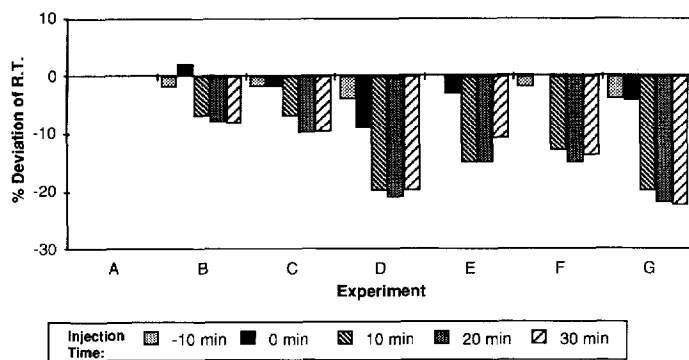


Fig. 6. Percent deviation of the retention time of $[^2\text{H}_6]$ benzene without water vapor on PI-119. A = $0\times$ case, B = $1\times$ case, C = $10\times$ hexane case, D = $10\times$ benzene case, E = $10\times$ ethanol case, F = $10\times$ nitromethane case, G = $10\times$ butanone case.

competition for the same site. A similar effect occurred for the elevated butanone experiment which paralleled the effects observed with benzene. This may indicate one or more sites on the sorbent's molecular subunit which involve inductive (π - π) effects or dipole-dipole interactions. This is consistent with the structure of polyimides. Where ethanol and nitromethane were at elevated levels in the continuously fed fronts, some additional competitive effects with [$^2\text{H}_6$]benzene occurred, but to a lesser extent for butanone. At the 30-min injection, the elevated ethanol experiment (E) resulted in an increase in retention from the 20-min injection. This effect is probably due to a modification of the sorbent surface by the accumulated butanone based partly on the compounds' retention times. That is, this "new surface" sorbs [$^2\text{H}_6$]benzene in a manner which becomes less sensitive to the competitive effects of ethanol.

Based on these and other results, each polyimide appears to possess 2-3 different sites or functionalities which are responsible for the phenomenon of adsorption. Also, perhaps more than half of the retention characteristics are attributable to the common part of the polymer derived from pyromellitic dianhydride. This similarity in retention characteristics is indicated by the overall similarity in the retention data that was obtained throughout the experiments. The differences are clearly related to the different diamines used to synthesize the different polymers, and perhaps to the stereochemistry of the polymer subunits. Results from the $0.4\times$ and $0.1\times$ experiments provided only attenuated effects of the $1\times$ case.

Model toxic compounds

These two sets of compounds were used to further evaluate the PI-119 sorbent's functional groups involved in the adsorption process. Sorbent characteristics were further probed by using many compounds with different functionalities. Some compounds such as benzonitrile have more than one functional group providing the potential for participation in adsorption by more than one mechanism.

The first set of toxics had retention times in the control experiment (without water vapor) of 15.0 min of benzene, 17.2 min for acrylonitrile, 17.6 min for 1,2-dichloroethane, and 18.6 min for ethyl acetate. By using the expression for % deviation of retention time, the data shown in Fig. 7 were generated. The data in this figure

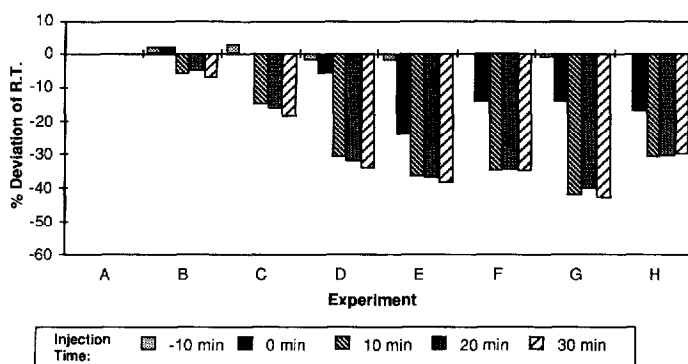


Fig. 7. Percent deviation of the retention time of [$^2\text{H}_6$]benzene without water vapor on PI-119. A = $0\times$ case, B = $0.1\times$ case, C = $0.4\times$ case, D = $1\times$ case, E = $10\times$ benzene case, F = $10\times$ acrylonitrile case, G = $10\times$ dichloroethane case, H = $10\times$ ethyl acetate case.

indicate, as in the previous figure, that chemicals which are retained longest do not *a priori* affect the retention of another chemical with a shorter retention time when more than one mechanism of sorption is operative. This is in contrast to the sorbent with only one functional site, where $\Delta H_{\text{sorption}}$ would indicate that more highly retained compounds are more successful at occupying a site. For two or more sites it is possible for one site on the sorbent subunit to be highly retentive for the most retained compound (ethyl acetate) and the other(s) to be less retentive for this compound. When 1,2-dichloroethane was continuously introduced at high levels, the weaker sites for ethyl acetate were presumably saturated while the strong site for ethyl acetate was not appreciably affected. $[^2\text{H}_6]$ Benzene would be expected to be more highly retained by the sites which more weakly adsorb ethyl acetate. The net effect is an apparent irregularity in $\Delta H_{\text{sorption}}$ which is a reflection of the different operative sites.

This is also evident in Fig. 8 which demonstrates that the retention of the second set of toxics is affected by high levels of *o*-dichlorobenzene or benzonitrile. In the control experiment the retention times were 1.4 min for *n*-decane, 4.5 min for *n*-propylbenzene, 12.3 min for *o*-dichlorobenzene, and 30.4 min for benzonitrile. Water eluted at 0.7 min. On this basis, the results showed that the elevated ($10\times$) *o*-dichlorobenzene frontal stream affected $[^2\text{H}_7]$ *n*-propylbenzene, $[^2\text{H}_4]$ *o*-dichlorobenzene and $[^2\text{H}_5]$ benzonitrile retentions more than the elevated ($10\times$) benzonitrile frontal stream did in the presence of water vapor. This would not occur for a mono-functional sorbent since again the magnitude of $\Delta H_{\text{sorption}}$ of the individual compounds were reversed. For $[^2\text{H}_{22}]$ *n*-decane the benzonitrile frontal stream did cause the greater drop in retention time relative to the effect of the *o*-dichlorobenzene frontal stream. This is what would be expected in a simple single-site adsorption model, and may suggest this is the case of *n*-decane on the PI-119 sorbent.

CONCLUSIONS

We have demonstrated that dynamic tracer pulse chromatography provides a relatively effective means of evaluating a sorbent. The technique is particularly rele-

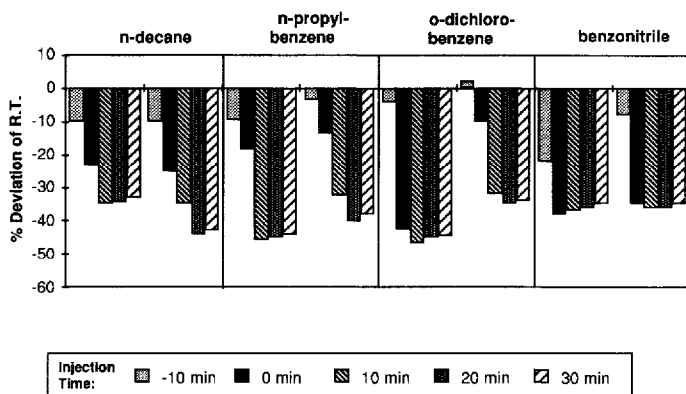


Fig. 8. Percent deviation of the retention times of the deuterated toxic compounds. The first set of bars for each compound is the elevated *o*-dichlorobenzene case with water vapor. The second set is for the elevated benzonitrile case with water vapor.

vant in that it simulates the way an air sample is collected, particularly when the sorbent is challenged by water vapor and high levels of organic compounds, which can be present at occupational levels. Water may be the only major challenging compound when sampling at environmental levels since organic levels will typically be lower.

This technique can address which functional groups of the polymer play a part in adsorption and to what extent, however, it cannot address precisely the mechanisms of adsorption or other effects due to the complexity of the elutions. The technique has also demonstrated the effect of a surface modification by organics through either coating the surface or blocking of water sorption providing some detail of the sorption process.

The information which can be gathered by this technique demonstrates the importance of humidity and high levels of organics on the BVs of a sorbent. It cannot be assumed that BVs obtained under dry conditions can be related to BVs under actual field conditions. This is most important for sorbents when retaining polar chemicals at sampling volumes which approach their BVs.

It has also been shown that the polyimides tested have good characteristics for air sampling purposes. The multifunctional polymers have tended to provide good retention volumes for a broad range of chemical classes. These polyimides do retain water more than Tenax which is a compromise for this better retention of polar organic compounds.

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