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Project Summary

Further Characterization of Sorbents for Environmental Sampling—II

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This report describes the continuation of a systematic study of the behavior of solid sorbents used to collect organic vapors from gaseous media. The studies were conducted using an elution analysis chromatographic method. The report deals with a series of experiments. Sorbents not used in earlier studies were examined to determine their specific retention volume and the percent recovery. Organometallics, as a chemical class not previously used, were studied to determine their retention volumes on some sorbents. The effect of methane on the recovery and the effect of mixed sorbents were also examined.

The resins used included Tenax-GC; XAD-2 and -7; Ambersorb 340, 347, and 348; and Florisil. One (Ambersorb 348) was found to be thermally unstable and was not recommended.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

This work involved the systematic study of the use of solid sorbents to collect organic vapors from gaseous media. The use of an adsorbent-filled cartridge has become increasingly popular for sampling organic vapors. The technique is used to sample source emissions and for ambient air concentrations. The use of these sorbents for environmental assessment studies has been adopted by EPA/IERL-RTP's Technical Support Staff by incorporating a sorbent trap in the EPA Source Assessment Sampling System (SASS) train. To support this application and gain a quantitative data base to guide in applications of the method, Arthur D. Little, Inc. has been carrying out research for several years in this area.

This report is the fourth in a series related to the use of sorbents for environmental sampling. The aims here were to:

- Determine the applicability of other resins in terms of capacity, effectiveness, and general usefulness.
- Investigate the recovery of several chemical classes from various resins.
- Investigate a mixture of sorbates on a resin.
- Determine the behavior of organometallics (particularly tetraethyllead and diethylmercury) on various resins.
- Determine the effect of a mixed atmosphere containing CH_4 on the specific retention.

These studies were conducted on various resins to determine their behavior using the elution analysis chromatographic method described in earlier reports.[1,2,3]

Approach

Experimental Technique

The chromatographic method used in this study was that of elution analysis. In elution analysis, a small quantity of adsorbate is injected onto the sorbate cartridge in a very short time. The specific retention volume, V_g^T, the fundamental retention constant in gas chromatography, can be determined for a sorbate on a particular sorbent from the resultant elution peak.

Knowledge of the value of V_g^T permits an estimation of the retention volume of a solute at another temperature or for a different sorbent cartridge size. Thus, V_g^T, determined from conventional gas chromatographic columns, can aid in the design of sorbent sampling modules.

Experimental Apparatus

The basic apparatus used to determine elution volumes, V_g^T, in this study was reported earlier.[2] Principal components of the apparatus are: the sorbent cartridge, gas chromatograph, and pressure, flow, and temperature measuring systems. The sorbent cartridges were proportionally scaled down to 0.5 cm I.D. from the typical cross-section of a SASS train sorbent resin canister. The two gas chromatographs used in this study were a Varian Model 1200 (a single-column instrument employing a flame ionization detector) and a Gow-Mac 550 (a dual-column instrument employing a thermal conductivity detector).

The sample introduction technique used in the elution analysis studies consisted of: taking up a small amount (<0.5 μL) of liquid sorbate in a 10 μL syringe, expelling the liquid, and pumping the syringe 50 or more times. This allowed generation of a reproducible dilute sorbate vapor concentration. With the resulting low concentration samples (<10 ppm), the experiments could be conducted in the Henry's Law region.

Three to five replicate elution experiments were run for each set of chromatographic conditions.

Recovery Studies

As in previous studies, the breakthrough volume was measured to determine V_g^{20} values. Since the sorbents are to be used for air sampling, the percent recovery of sorbates from the resins was determined for each sorbate. Recovery experiments were conducted using the sorbates, decane, ethanol, and n-butanol on six solid sorbents: XAD-2, Tenax-GC, charcoal, Florisil, XE-340, and XAD-7. The percent recovery of the sorbate from the sorbent was determined by challenging the sorbent with a known concentration of sorbate in air for a given amount of time. The sorbents were desorbed in appropriate solvents which were analyzed to determine the quantity of sorbate recovered from the resin. The quantity of the sorbate recovered from the resin is compared to the quantity which would have been collected (concentration in mg/m^3 x sampling rate in m^3/min x time in minutes). V_g data were used to calculate the recommended sampling volume to collect the sorbate at 10 ppm on the various sorbents with no breakthrough.

Effects of Methane Atmosphere on XAD-2

In the previous work,[3] studies were done to determine the effect of two major gas components — H_2O and CO_2 — on the resin. The effect of methane, found in stack gases at a concentration of thousands of ppm, is investigated here. Retention volumes were determined for four sorbates — n-pentanol, n-butanol, n-octane, and n-hexane —on XAD-2 at different column temperatures and two different atmospheres, with or without 1.1% methane in helium. The sorbates were selected to represent the classes of compounds which had major differences in elution behavior.

Effects on V_g of a Sorbate Mixture on XAD-2

In additon to the effect of other gases on the sorbate, it is useful to know the resin's behavior in the presence of a mixture of sorbates whose elution behavior is considerably different from each other. The sorbates used in this experiment were n-heptane, ethylbenzene, and n-butanol.

Retention Volumes of Organometallics

One of the Kiselev classes is organometallics, Group C. To date, it was the only group not investigated. Tetraethyllead and diethyl mercury, both stable in air, were used to investigate this group. The retention volumes for these two compounds were determined on XAD-2.

Results and Conclusions

The work reported here was designed to address several specific topics which resulted from previous studies. In this experimental investigation, two to three compounds each from a number of compound categories were used as models to investigate retention and recovery phenomena in various sorbent: sorbate systems. Several conclusions can be developed on the basis of these data.

Uncertainty in V_g Values

Review of cumulative sets of data on V_g^T for the same sorbate: sorbent system indicates that uncertainties in values of V_g^{20}, extrapolated from measurements at two or three elevated temperatures, may be as high as a factor of five. This uncertainty should be taken into account when comparing data for different sorbate: sorbent systems and in designing sampling systems with appropriate margins of safety to ensure quantitative collection of a given sorbate.

Alternative Sorbents

Florisil is comparable to XAD-2 and Tenax-GC in terms of its volumetric capacity for collection of the alkanes, alcohols and chlorinated aromatics tested. Florisil showed very much higher (about 10,000 times) capacity for the chlorinated aliphatic species (dichloroethane, dichloropropane) tested than either XAD-2 or Tenax-GC. It may be the sorbent of choice for collection of volatile chlorinated organics in applications, such as ambient air monitoring, in which large volumes must be sampled to meet detection limit constraints. The low blank values obtainable by thermal activation of Florisil are also an advantage for such applications.

Limited data obtained for aliphatic hydrocarbon sorbates suggest that recovery from Florisil may be less than quantitative. Also, the possible effects of moisture on Florisil V_g's should be investigated to determine its suitability for stack sampling.

Ambersorb XE 340[3], XE 347, and Amberlite XAD-7 have substantially greater capacity for collection of low molecular weight alcohols than do XAD-2 and Tenax-GC. Recovery of alcohols from Ambersorb XE 340 was also found to be satisfactory (75-88%); recovery from charcoal and from XAD-7 was less than 50% in several tests. Ambersorb XE 340 and 347 are therefore suggested for applications involving sampling specifically for volatile alcohols.

Organometallics

The volumetric capacity of XAD-2 was found to be adequate for collection of

two organometallic compounds tested — tetraethyllead and diethyl mercury. Values of V_g^T for organometallics on XAD-2 are very similar to those of organic species with similar boiling points, measured at the same temperature.

Effects of Methane Atmospheres on V_g^T for XAD-2

Data for aliphatic hydrocarbon and alcohol sorbates indicate no effect of 1.1% (11,000 part per million) methane on the volumetric capacity of XAD-2.

Effects of Mixtures of Sorbates

Data for an aliphatic, an aromatic hydrocarbon, and an alcohol show no evidence of competitive effects on V_g^T when several species are present at parts per million concentrations in the same sample.

References

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The complete report, entitled "Further Characterization of Sorbents for Environmental Sampling—II," (Order No. PB 82-234 667; Cost: $7.50, subject to change) will be available only from:

National Technical Information Service
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