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Project Summary

Investigation of 2,4-Dinitrophenylhydrazine Impregnated Adsorbent Tubes for the Collection of Airborne Aldehydes

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The objective of this study was to investigate the use of 2,4-dinitrophenylhydrazine (DNPH) impregnated adsorbents for sampling airborne aldehydes. Investigation focused primarily on the Sep-Pak C_{18} adsorbent material because it has been used in the past by researchers to sample airborne aldehydes and it is available as a commercially prepared cartridge. Experimental results using a 17 m^3 environmental chamber and various spiked amounts of aldehyde material (low ppb levels) showed that the DNPH-coated cartridge and the DNPH/acetonitrile impinger methods gave equivalent results. Blank levels of the DNPH-coated cartridges were studied as a function of storage time using various containers and temperature conditions. Canisters pressurized with zero-grade nitrogen provided the best storage device. Lower blank levels were also obtained when the cartridges were stored at lower temperatures. Blank levels appear to equilibrate after six days of storage. Significant batch-to-batch differences in blank levels were observed. To assure that quality data will be obtained, cartridges should be grouped according to batch number and blank levels should be determined prior to any field monitoring effort. Blank cartridge levels should be an order of magnitude lower than the sample cartridge level. Adjustment in sampled volume should be made accordingly. High performance liquid chromatography with UV detection proved to be a sensitive and stable analytical method for the DNPH derivatives. Three laboratories employing the above sampling and analysis methodology reported similar results after analyzing an eight component aldehyde derivative standard (2 ng/μl). Results of field sampling demonstrated that low ppb levels of airborne aldehydes can be determined with good analytical precision.

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This Project Summary was developed by EPA's Environmental Monitoring Systems 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

The determination of aldehydes and other carbonyl compounds in the atmosphere is of interest because of their importance as precursors in the production of photochemical smog, as photochemical reaction products and as a major source of free radicals in polluted environments. Additionally, short-term exposures to aldehydes such as formaldehyde, acetaldehyde, acrolein and crotonaldehyde are known to result in irritation of the eyes, skin and mucous membrane of the upper respiratory tract.

These carbonyl species are emitted into the atmosphere either directly from certain industrial processes or as secondary products from combustion sources. In rural areas, concentrations of 0.6 to 1.3 ppb formaldehyde have been reported. In urban environments, formaldehyde levels range from several ppb to over 50 ppb depending upon location and meteorological conditions. Acetaldehyde levels 20 to 50 percent of formaldehyde concentrations are generally found. Very little ambient air data exist, however, for the other carbonyl species.

The limited amount of speciated aldehyde data is largely due to the lack of a simple, sensitive, and selective analytical method. Derivatization techniques utilizing 2,4-dinitrophenylhydrazine (DNPH) reagent are currently being evaluated and will likely replace the earlier analytical methods—chromatropic acid, pararosaniline, and direct *analysis via gas chromatography*. With the DNPH technique, a derivative is formed by the reaction of DNPH with the carbonyl compound in the presence of acid to form the corresponding hydrazone derivative. Initially, the DNPH derivatives were separated and identified using packed column gas chromatographic techniques. More recently, high performance liquid chromatography (HPLC) has been employed by researchers to more easily separate and elute the DNPH derivatives. Quantitation of the hydrazone derivatives using HPLC is accomplished with a UV detector.

Sampling for carbonyl species is generally accomplished with either impinger or solid adsorbent techniques. With impinger methods, aqueous or organic solvents (or mixtures of both) have been used to prepare the DNPH absorbing solution. The use of DNPH/acetonitrile solutions permit the direct analysis of the adsorbing solution using reversed phase HPLC. The DNPH/acetonitrile impinger technique has simplified sampling efforts, but it is not ideally suited for extended sampling periods (solvent evaporation) nor for field use when samples are to be stored and shipped to a central laboratory for analysis. The use of adsorbent traps coated with DNPH circumvents some of the short-comings of the impinger technique. Adsorbents that have been impregnated with DNPH include XAD-2, silica gel, glass beads, commercially packaged plastic cartridges (e.g., Sep-Pak C_{18}), and glass fiber filters.

The objective of this study was to further investigate the use of DNPH impregnated adsorbent for sampling airborne aldehydes. Specific areas that were examined include:

- determination of collection and recovery efficiency of adsorbent tubes versus impingers
- design of leak-tight sample storage devices/improvement of adsorbent tube design
- improvement of sampling/analysis accuracy and precision for ambient aldehydes
- investigation of alternative detection schemes.

Procedures

A Varian model 5000 liquid chromatograph served as the primary analytical tool. A Hewlett Packard model 5890 gas chromatograph coupled to a flame ionization and an electron capture detector was also employed to determine if better selectivity and sensitivity for the hydrazone derivatives could be achieved. A third method, a continuous monitoring analyzer (CEA, Inc.), was tested for its selectivity and sensitivity for formaldehyde.

DNPH material showed unacceptable impurity levels and was purified by a crystallization process. The purified crystals were then accurately weighed-out and dissolved in acidified acetonitrile solution to form the stock adsorbing solution. Carbonyl-DNPH derivatives were prepared by adding the individual carbonyl compound to an acidified saturated solution of DNPH. The colored precipitate was filtered and washed with HCl/H_2O mixture and dried. The derivative was recrystallized in methanol if the purity level was unsatisfactory. A standard stock solution of each aldehyde derivative (20 mg/L) was prepared and checked throughout the study for possible degradation. Working calibration standards (2 mg/L) were prepared from the stock mixtures. These working standards were used on a daily basis.

Sep-Pak cartridges were used as the primary sampling devices. The coating procedure for these adsorbent sampling tubes involved adding 10 ml absorbing solution (gravity feed), draining the excess solution and then drying the cartridges with clean N_2 gas. After drying, the tubes were sealed with aluminum end caps and placed in a storage vessel.

Three types of storage containers were tested to determine the effect of blank levels versus time. These containers include: a stainless steel canister pressurized with N_2, an aluminum can containing a bed of charcoal and a glass vial with a Teflon-lined screw-cap. Temperature effects during storage were also examined. Coated cartridges were stored at room temperature, in the refrigerator and in the freezer.

Blank levels from several batches of the Sep-Pak cartridges were examined. Likewise silica gel, Tenax, and Maxiclean cartridges (Alltech) were also coated and tested to determine if lower blank levels could be achieved.

Impinger samples were collected at a nominal flow rate of 1 L/min using a single impinger containing 10 ml of the DNPH solution. Cartridge samples were collected at nominal flow rates ranging from 0.06 to 0.80 L/min. The cartridges were sampled either individually or in tandem.

A Teflon-lined aluminum 17 m^3 environmental chamber was used to facilitate the evaluation of the CEA formaldehyde analyzer and to carry out the impinger/cartridge comparison studies.

Results

Experimental results using a 17 m^3 environmental chamber and various spiked amounts of aldehyde material (39 to 236 ppb) showed that the DNPH coated Sep-Pak cartridge and the DNPH/acetonitrile impinger methods gave equivalent results. Cartridge/impinger ratios $\geq$ 0.85 were obtained for most of the tested aldehydes (acrolein ratio = 0.74). Based on the calculated chamber concentrations, both sampling methods showed absolute recoveries greater than 80 percent for formaldehyde, acetaldehyde, butyraldehyde and benzaldehyde. Acrolein recoveries ranged from 28 to 44 percent. For crotonaldehyde, recoveries of 127 to 159 percent were found.

Blank levels of the DNPH-coated Sep-Pak cartridges were generally 1 nanogram or less (formaldehyde derivative). However, one batch of Sep-Pak cartridges exhibited 8-fold higher blank levels. Alternative adsorbents, such as silica gel, Tenax, and Maxiclean-coated cartridges, showed blank levels similar to the latter batch of Sep-Pak material.

Canisters pressurized with nitrogen provided the best storage container for the coated Sep-Pak cartridges. Storage in a refrigerator or freezer also resulted in lower blank levels than storage at room temperature. Test results showed that cartridge blank levels did not appear to increase significantly after the sixth day of storage.

Results from samples (in triplicate) collected at a suburban location showed good analytical precision and low blank levels. Aldehyde concentrations ranged from 0.34 to 7.04 ppb and four of the five measured compounds showed standard deviation values less than 10 percent. Acetone's S.D. values averaged ~23 percent. For the sample blanks, formaldehyde averaged 0.15 ppb, acetone averaged 0.10 ppb and the remaining aldehydes were not detected.

High performance liquid chromatography was shown to be a sensitive and stable analytical method for the hydrazone derivatives. The system was able to detect 0.2 nanograms of formaldehyde derivative (injected on-column with a 10 μl sample size). Very good precision (<4 percent RSD) was obtained from the analyses of an eight component standard (2 ng/μl) over a two month period. Results from the analyses of the eight component standard by three laboratories agreed very well. Although gas chromatographic methods using an electron capture detector gave better sensitivity, a considerable number of extraneous peaks prohibited acceptable identification and quantitation of the aldehyde derivatives.

The continuous monitoring analyzer was able to detect $\geq$ 8 ppb formaldehyde and was nonresponsive to ppb levels of other aldehydes. The unit was also compared with the impinger and cartridge sampling methods. At a chamber loading of 57 ppb, an average formaldehyde reading of 63 $\pm$ 6 ppb was obtained with all three methods. An average value of 197 $\pm$ 19 ppb was found at a chamber loading of 221 ppb.

Conclusions and Recommendations

Based on the results of this work, it is concluded that the DNPH-coated Sep-Pak cartridges provide the researcher with a simple yet accurate means for sampling airborne aldehydes. Furthermore the analysis of the hydrazone derivatives is facilitated by the use of high performance liquid chromatographic methodology. Specific conclusions and recommendations are given below:

1. Experimental results using a 17 m^3 environmental chamber and various spiked amounts of aldehyde material showed that the DNPH-coated Sep-Pak cartridge and the DNPH/acetonitrile impinger methods gave equivalent results. Cartridge/impinger ratios of $\geq$ 0.85 were obtained for most of the tested aldehydes (acrolein ratio = 0.74). Based on the calculated chamber concentrations, both sampling methods showed absolute recoveries greater than 80 percent for formaldehyde, acetaldehyde, butyraldehyde and benzaldehyde. Considering the generated concentration levels and the adsorptive nature of these compounds, the above absolute recovery is quite acceptable. However for acrolein, recoveries ranged from 28 to 44 percent. For crotonaldehyde, recoveries of 127 to 159 percent were found. Both compounds are olefinic aldehydes and it is likely that these species undergo additional chemical reactions during the sampling and analysis process. We do not recommend using the cartridge sampling approach for these two carbonyl species.

2. Blank levels of the DNPH coated Sep-Pak cartridges were investigated as a function of storage time using various containers and temperature conditions. Canisters pressurized with nitrogen provided the best storage device. Storage in a refrigerator or freezer also resulted in lower blank levels than storage at room temperature. Coated cartridges showed no detectable amount of the aldehyde derivatives when analyzed within several hours of preparation. However, we found measurable levels after six days of storage. Blank levels did not appear to increase significantly after the sixth day. During these tests, several different batches of the Sep-Pak cartridges were housed within the same storage device. We observed an eight-fold difference in blank levels. This batch-to-batch difference may significantly affect the quality of data collected during a monitoring study. To assure that quality data will be obtained, cartridges should be grouped according to batch number and blank levels should be determined prior to any field monitoring effort. We recommend that the blank cartridge level be an order of magnitude lower than the sample cartridge level (i.e., adjust sampled volume accordingly).
3. High performance liquid chromatography was shown to be a sensitive and stable analytical method for the hydrazone derivatives. Very good precision was obtained from the analyses of an eight component standard (2 ng/μl) over a two month period. Although gas chromatography methods were also examined and gave better sensitivity, a considerable number of extraneous peaks prohibited acceptable identification and quantitation of the aldehyde derivatives.
4. Good interlaboratory agreement was obtained from the analysis of an eight component standard (2 ng/μl). These results demonstrate that the hydrazone derivatives can be prepared accurately at the lower ng/μl level and are stable in solution for at least four months.
5. Aldehyde samples collected at a suburban location showed good analytical precision and low blank levels. These results demonstrate that low ppb levels of airborne aldehydes can be determined with the sampling and analysis methodology discussed in this report.
6. A continuous monitoring analyzer was evaluated and exhibited good sensitivity and selectivity for formaldehyde. The unit was able to detect $\geq$ 8 ppb formaldehyde and was nonresponsive to ppb levels of other aldehydes.

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The complete report, entitled "Investigation of 2,4-Dinitrophenylhydrazine Impregnated Adsorbent Tubes for the Collection of Airborne Aldehydes," (Order No. PB 88-220 223/AS; Cost: $14.95, subject to change) will be available only from:

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