



Project Summary

Analysis of Aldehydes and Ketones in the Gas Phase

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Carbonyl compounds, especially aldehydes and ketones, play a key role in the photochemical smog-forming process. Because of this, their analysis has received considerable attention. In this Project Summary, some of the details of the testing and use of the 2,4-dinitrophenylhydrazine-acetonitrile (DNPH-ACN) method for the determination of aldehydes in ambient air are discussed. A discussion of interferences, the preparation of calibration standards, High Performance Liquid Chromatograph (HPLC) column evaluation, analytical testing, dicarbonyl-DNPH analysis, fluorescence methods, preliminary cartridge testing, and the results of atmospheric sampling in Schenectady, NY, and atmospheric and cloudwater sampling on Whiteface Mountain in Wilmington, NY, are included.

This Project Summary was developed by EPA's Atmospheric Sciences 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

Carbonyl compounds are an important constituent of photochemical smog. They are emitted from the tailpipes of automobiles; they are produced during the photooxidation of hydrocarbons, and they are active participants in free radical-chain reactions. Computer models simulating the chemical reactions in urban atmospheres require a knowledge of formaldehyde and other aldehyde concentrations.

Because of the key role of aldehydes and ketones in atmospheric chemistry,

their analysis has received considerable attention. Recent advances in high performance liquid chromatography (HPLC) techniques have prompted the development of a number of methods that depend on derivatization of the aldehydes and HPLC separation of the derivatives. One of these techniques involves the reversed-phase separation of 2,4-dinitrophenylhydrazine (DNPH) aldehyde derivatives. Another technique involves an extraction method based on DNPH derivatization followed by HPLC analysis and uv detection. Another more recent development involves the use of 2-diphenylacetyl-1,3-indandione-1-hydrazone (DAIH) to form fluorescent azine derivatives of the aldehydes; this is followed by HPLC separation of the derivatives and detection of the derivatives by fluorescence emission at 525 nm. Another adaptation of the DNPH-acetonitrile (ACN) method has recently been reported. In that work, a DNPH-ACN solution was used to coat a C₁₈-based cartridge that was then used for atmospheric sampling. The cartridge is leached out with acetonitrile after the air sampling and the leachate is analyzed.

In this Project Summary, some of the details of the testing and use of the DNPH-ACN methods are discussed. Included are a discussion of interferences, the preparation of calibration standards, HPLC column evaluation, analytical testing, dicarbonyl-DNPH analysis, fluorescence methods, preliminary cartridge testing, and the results of atmospheric sampling in Schenectady, NY, and atmospheric and cloudwater sampling on Whiteface Mountain in Wilmington, NY. Also, one of the potential applications of the various aldehyde-ketone analysis techniques is to the analysis of C₂-C₄ dicarbonyl compounds such as glyoxal,

methylglyoxal, and biacetyl. Previous work had shown that DNPH derivatives could be formed and detected under the conditions of the analysis. There was, however, ambiguity about whether the material being detected in the analysis was the mono- or the di-DNPH derivative of the dicarbonyls and whether there was some analytical interaction among the dicarbonyl compounds. An effort was made in this study to resolve these ambiguities.

Procedure

Authentic samples of the DNPH derivatives of a representative collection of aldehydes and ketones were synthesized. The samples served as calibration standards and aided in the development of optimal HPLC conditions for analysis.

In order to resolve the ambiguities in the chromatographic behavior of the mono- and di-DNPH derivatives of the C2-C4 dicarbonyl compounds, two approaches were used. In the first approach, solutions were made with large and small dicarbonyl-to-DNPH ratios. In the second approach, attempts were made to isolate authentic solid samples of the mono and di-DNPH derivatives.

The use of DAIH and 1-dimethylaminonaphthalene-5-sulfonylhydrazine (dansyl hydrazine) as analytical reagents for aldehyde determination was also tested. The preparation of the appropriate carbonyl compound derivatives was performed and their chromatographic behavior determined. A comparison of that behavior with that of the DNPH derivatives was made. Some preliminary experiments were also performed to compare the impinger DNPH method to a previously-developed cartridge method. The method allows for sampling with a cartridge coated with silica-C18 impregnated with a DNPH-ACN phosphoric acid mixture. The technique not only promises a simplified procedure, but it also has the potential of increasing sensitivity.

To provide information on ambient aldehyde levels and to test out the DNPH method under field conditions, three projects were undertaken. In the first, air in Schenectady, NY, was monitored daily during July and August of 1983. The second project consisted of sampling air at the State University of New York at Albany's (SUNYA) Atmospheric Sciences Research Center (ASRC) on Whiteface Mountain in Wilmington, NY, for one week during August 1983. In the third project, a variation of the DNPH method was used during July-August 1984 for

aldehyde and ketone determinations in cloudwater atop Whiteface Mountain.

Results

The synthetic samples of the DNPH derivatives of the simple aldehydes and ketones were determined by HPLC to be in excess of 99% pure. The chief impurity in each case was a small amount of the unreacted DNPH reagent itself. The uv detector response to each of the solutions at two wavelengths (254 nm and 360 nm) was evaluated. For all the derivatives the calibration curves were linear.

Two columns were evaluated in this study: a Varian MCH-10 (C-18), 25 cm x 4.6 mm, 10 microns and an Alltech C-18 column, 25 cm x 4.6 mm, 10 micron. The Alltech column was found to give the best separation and allowed for the resolution of several pairs of components that were of identical molecular weight but different structures. In particular, acrolein, acetone, and propanal could be resolved with this column.

Cross comparison of the DNPH method and chromotropic acid (CA) assay method for formaldehyde was performed in the concentration range 60 to 1400 ppb. The formaldehyde source was a permeation tube that consisted of solid paraformaldehyde encased in a Teflon tube held at a constant temperature. Within about ten percent, the results of the DNPH method and the CA method were found to be in agreement.

Four DNPH reagent solutions were prepared and stored in different types of containers. Periodically, samples from each of the solutions were withdrawn and analyzed by HPLC. After two weeks there was no detectable contamination in Teflon- or glass-stoppered containers. In the plastic-capped vial, however, there was a noticeable buildup of a peak having the same retention time as the benzaldehyde DNPH derivative. After two weeks, a steady buildup of impurities was observed in the reagent regardless of the container if acid had been added. In unacidified reagent there was no increase in contamination until acid was added. In addition, the stability of solutions after atmospheric sampling was determined. Samples of the Schenectady, NY, air were taken by passing 90 liters of air through the DNPH-acetonitrile solutions in the standard fashion. The resulting solutions, stored in Teflon-capped vials in a refrigerator were periodically analyzed. The results for the analysis of the stored DNPH-ACN solutions showed

that the solutions appeared to be stable for as long as three weeks after collection.

Limits of detection (LOD) and limits of quantification (LOQ) for the DNPH-acetonitrile technique were also determined. The LOD was defined as a signal that was greater than three standard deviations from the average background signal. The LOQ was defined as a signal greater than ten standard deviations from the average background signal. The LOD and LOQ for formaldehyde were 0.10 ppb and 0.32 ppb, respectively, and for acetaldehyde were 0.16 ppb and 0.53 ppb, respectively, for a 90 liter air sample. With the exception of acetone, the other aldehydes and ketones gave about the same instability in baseline as the acetaldehyde and their detection limits were about the same (0.16 ppb LOD and 0.53 ppb LOQ for a 90 l sample). Acetone was found in the reagent at exceedingly high and unstable concentrations. The contamination of the reagent, apparently due to the impurity in the acetonitrile, led to the inability to monitor acetone levels.

Efforts were also made to determine the chromatographic behavior of the mono- and di-DNPH derivatives of the C2-C4 dicarbonyl compounds. Two approaches were used. In the first approach solutions were made with large and small dicarbonyl-to-DNPH ratios. In the second approach attempts were made to isolate authentic solid samples of the mono and di-DNPH derivatives. The experiments at high dicarbonyl-to-DNPH ratios showed short retention times for polar C2-C4 mono-DNPH materials. Two peaks were observed in the high ratio run for methylglyoxal, one at 4.2 min and the other at 4.5 min comprising 20% and 80% of the mixture, respectively. The two peaks presumably represent the two isomers of methylglyoxal. In contrast, the experiments at low ratios, where di-derivatization is likely, show longer retention time materials (7.9-15.1 min). These longer retention time materials are, presumably, the di-DNPH derivatives. The preparation of the mono-DNPH derivatives was successful only for biacetyl. The solids isolated for glyoxal and methylglyoxal showed significant contamination with the di-DNPH derivative. Preparation of the di-DNPH derivatives went smoothly and HPLC analysis showed that the materials were reasonably pure (>95%). The solid derivatives were used to make up a solution to calibrate the HPLC responses. Also, estimates of the HPLC responses for the mono-DNPH derivatives of glyoxal and methylglyoxal were calculated from the dicarbonyl-to-DNPH ratio

experiments described before. There were some correlations in the response factors of the various DNPH derivatives by functional group class. The most sensitive measure of the functional group class appeared to be the 360 nm/254 nm uv response ratio. The large ratio (1.0) given by the dicarbonyl di-DNPH derivatives was easily distinguished from the corresponding ratio for simple monocarbonyl DNPH derivatives (0.49).

The method for determination of aldehydes based on the reaction DAIH followed by HPLC separation and fluorescence detection was examined. After comparing detection limits for this method with that of uv absorption and the DNPH method, the DAIH method was found to be inferior. Both the uv method and the DNPH method were about 25 times more sensitive. Preliminary results obtained with the dansyl hydrazine method also suggest that this method is inferior to the DNPH method. The more complex HPLC separations and the lack of reactivity with aromatic aldehydes suggest that this reagent may require sophisticated HPLC techniques and careful interpretation of the results.

A comparison of the cartridge method with that of the impinger DNPH-ACN method was also performed for formaldehyde. The results were very encouraging. Not only were the values for each dilution run comparable, but it appeared that the cartridge technique was more efficient. The chromatograms for the second cartridge in the series of two were cleaner than the chromatograms for the second of the two impinger in the solvent-based method. The average absolute error was about 7% and there appeared to be no systematic bias.

The July-August 1983 sampling data from Schenectady, NY, principally showed formaldehyde and acetaldehyde. All the data for formaldehyde were in the quantification range and went from a low of 0.70 ppb to a high of 30.5 ppb with an average daily concentration of 7.6 ppb. Although there was a large variation in the daily data, there was a general trend toward lower formaldehyde concentrations over the course of the summer. The concentration of acetaldehyde was always significantly below that of formaldehyde. When the amount of acetaldehyde was detectable, the ratio of formaldehyde to acetaldehyde averaged about 14:1. Since acetaldehyde was below its detection limit of 0.16 ppb in the vast majority of samples, the average ratio for those samples was greater than 48:1. The variation on formaldehyde over the

course of the day was explored by sampling every three hours for 36 hours. There were two peaks in the formaldehyde concentration over the course of the day. The first occurred about 7:00 - 10:00 a.m. and the second about 6:00 - 10:00 p.m. The peaks seemed to be clearly correlated with commuting automobile traffic. The daily minimum occurred at about 3:00 a.m. Over a 24-hour period, the range of formaldehyde concentrations was 1.7-8.1 ppb.

The work at the SUNYA ASRC station was done over a period of one week (August 14-20, 1983). No significant quantities of any aldehydes other than formaldehyde and acetaldehyde were detected. Formaldehyde concentrations ranged from 0.6-2.6 ppb. Acetaldehyde levels ranged from below the LOD of 0.16 ppb to a barely measurable 0.80 ppb. It was apparent that there was a tendency for the aldehydes to rise and fall with the ozone. Formaldehyde concentrations were found to reach a peak between 10:00 - 12:00 in the evening. The daily minimum occurred about 12:00 - 2:00 in the afternoon. Presumably the pattern reflects the fact that the chief mechanism for loss of formaldehyde is photolysis.

Not unexpectedly, the formaldehyde levels observed at Whiteface were significantly less than the levels in Schenectady. During the same week the work was performed at Whiteface, the levels of formaldehyde in Schenectady averaged 6.7 ppb and ranged from 3.2-9.5 ppb. Schenectady is about 90 miles south of Wilmington, NY, and during that week was influenced by the same weather systems. The average level of formaldehyde at Whiteface was about 1.3 ppb and ranged from 0.6-2.6 ppb. The formaldehyde levels differed by roughly a factor of five. The acetaldehyde data is difficult to interpret with any certainty. The data from each location are limited. There is, however, some indication that acetaldehyde, when detectable, is at about the same level on Whiteface Mountain as in Schenectady, NY.

In the cloudwater work during the July-August 1984 period, samples were taken directly from the cloud water collectors atop Whiteface Mountain every one to two hours during a cloud cover event. The samples were added to the DNPH reagent solution within ten minutes. The resultant solutions were then refrigerated for subsequent analysis. The maximum delay time between reagent mixing and analysis was five days; the majority of analyses were done within two days. Aqueous-based reagents showed significant

changes in formaldehyde and acetaldehyde concentrations with time while the acetonitrile-based reagent showed changes of no more than about 15%. The stability of the actual cloudwater samples was also determined to be more than a week. All samples taken using the ACN solution yielded quantifiable results above blank levels. There were consistently only three carbonyl compounds present. Formaldehyde ranged in concentration from 0.33-14.8 micromolar. Acetaldehyde and acetone were usually detected at levels that were comparable to these of formaldehyde.

Conclusion

The DNPH method of trapping and quantifying aldehydes in ambient air appears to be efficient and accurate. The method is not sensitive to interferences by common atmospheric contaminants. An Alltech C-18 HPLC column is recommended for rapid, efficient analytical separations of the C1-C4 aldehydes. The uv detection of the derivatives should be done at 360 nm but the 360/254 area ratio may aid in the determination of the nature of unknown materials and serve to confirm identifications made on the basis of retention times.

The DNPH reagent is stable when kept in glass- or teflon-capped containers for up to four weeks. If no acid is added to the reagent, it appears to be stable for several months. It is recommended that acidified reagent be used within two weeks. The sampled reagent appears to be stable for at least three weeks after sampling if it is refrigerated. It is recommended that analyses be performed within two weeks of sampling and that the samples be stored in teflon-sealed vials under refrigeration. The LOD and LOQ for the DNPH method are such that formaldehyde is readily determinable even in "clean" air, but information on the other carbonyl compounds may be limited to urban areas.

Analysis of dicarbonyl compounds with the DNPH method requires special care because of the extreme insolubility of the di-DNPH derivatives. In particular, sampling times have to be carefully adjusted based on anticipated concentrations so as not to exceed the solubility limits for the derivatives. In addition, the HPLC analysis should be done at higher ACN levels than the standard analysis to avoid column precipitation and to shorten the retention times.

Although the DNPH-ACN method is useful for the determination of aldehyde levels where there are laboratory facilities available, it is inconvenient for field

sampling. The necessity of handling a volatile, flammable, regulated organic solvent limits the kinds of situations suitable for DNPH-acetonitrile sampling. Preliminary testing of a DNPH cartridge technique has shown it to be accurate and more convenient than solvent-based alternatives. It is recommended that future work be devoted to the use of DNPH cartridge sampling for aldehyde determinations. Methods based on other hydrazine chromophores (DIAH and dansyl hydrazine) appear to offer no substantial advantages over DNPH while suffering from more difficult and longer analyses and inefficiencies in derivatization.

DNPH-ACN reagent solutions with subsequent HPLC analysis may prove useful for sampling rain and cloudwater for aldehydes. The preliminary work reported here indicates that the levels of acetaldehyde and acetone are comparable to that of formaldehyde.

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Marcia Dodge is the EPA Project Officer (see below).

The complete report, entitled "Analysis of Aldehydes and Ketones in the Gas Phase," (Order No. PB 85-181 865/AS; Cost: \$10.00, subject to change) will be available only from:

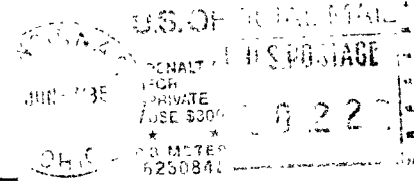
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