



Project Summary

Development and Validation of a Test Method for Formaldehyde Emissions

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Formaldehyde has been identified as a suspect carcinogen and may be regulated in the future as a hazardous air pollutant under Section 112 of the Clean Air Act. The full report details the field validation of a test method for sampling and analyzing formaldehyde emissions from stationary sources. Three potential source methods were evaluated. One method, the basic peroxide impinger/ion chromatography (IC) method is based upon the dissolution and oxidation of formaldehyde in the impinger reagent to form formate ion, which is measured by IC. The second method is a dinitrophenylhydrazine-coated (DNPH) cartridge/high performance liquid chromatography (HPLC) method, which is based on the reaction of formaldehyde with 2,4-DNPH and subsequent analysis of the hydrazone derivative by HPLC. The third method, the DNPH impinger/HPLC method extends the range of the cartridge method through the use of higher capacity DNPH impinger solutions.

Field testing of the methods were conducted at two different sites. At a formaldehyde manufacturing plant, where formaldehyde levels were high (> 100 mg/cu m), samples were collected using the basic peroxide impinger method and the DNPH impinger method. At a formaldehyde user facility, where formaldehyde

levels were low, samples were collected using the DNPH-coated cartridge method and the DNPH impinger method.

A statistical evaluation indicates that the DNPH impinger method is acceptable for determining both low and high concentrations of formaldehyde. Because of its range, this method is recommended as the reference method for determination of formaldehyde in source emissions.

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This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment 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

Formaldehyde has been identified as a suspect carcinogen and may be regulated in the future as a hazardous air pollutant under Section 112 of the Clean Air Act. The U. S. Environmental Protection Agency (USEPA) has an ongoing program to evaluate and

standardize source testing methods for hazardous pollutants, such as formaldehyde, in anticipation of future regulations. As a part of the program, the Research Triangle Institute (RTI) was contracted by the USEPA to perform an evaluation and field validation of potential source methods for formaldehyde.

Methods Evaluated

Three potential source methods were evaluated. The first of these, the basic peroxide impinger/ion chromatography (IC) method, is based upon the dissolution and oxidation of formaldehyde in the impinger reagent to form formate ion, which is measured by IC. The impinger reagent is a solution of 3% hydrogen peroxide/0.025 N sodium hydroxide. After sampling, the impinger solution is allowed to stand overnight before dilution and analysis in order for oxidation to be complete. The second method to be evaluated is a 2,4-dinitrophenylhydrazine (DNPH) impinger solution/high performance liquid chromatography (HPLC) method, which is based on the reaction of formaldehyde with DNPH, and subsequent analysis of the hydrazone derivative by HPLC. The impinger solution is prepared by diluting 25 mL of saturated DNPH solution to 100 mL with acetonitrile (ACN) and acidifying with 1.0 mL of 3.8 M perchloric acid; each impinger was charged with 20 mL of the solution. The impinger solutions were analyzed using an HPLC with a Zorbax-ODS column and variable wavelength detector set at 365 nm. The third method evaluated was a DNPH-coated cartridge/HPLC method. Sep-Pak cartridges are coated with acidified DNPH and used for sample collection. The hydrazone formed is extracted using ACN and measured using HPLC. The HPLC method used for this third method was identical to that used for the DNPH impinger method.

Sample Collection

Sample collection was performed at two sites, a formaldehyde manufacturing facility and a furniture factory (i.e., a user site). The DNPH and hydrogen peroxide methods were tested at the manufacturing site; the coated cartridge sampler was not suitable for this site because of the high levels encountered. The DNPH impinger and coated cartridge samplers were tested at the user site. The peroxide impinger was not tested at this site because it was found not to work well at low levels of formaldehyde. The source gas at each site was pulled from the source outlet and pumped through a

glass manifold using a metal bellows pump. Four of each type of sampler were attached to outlets on the manifold for each run. Back-up impingers of both types were used for all sampling at the manufacturing site; back-up impingers and cartridges were used only on select samplers at the user site because of the much lower concentration and much smaller chance of breakthrough. Source gas was drawn through the samplers using personal sampling pumps. Flow rates for these pumps were 75 mL/min for the DNPH impingers and 500 mL/min for the peroxide impingers at the manufacturing site and 200 mL/min for the DNPH impingers and 100 mL/min for the Sep-Pak cartridges at the user site. Four runs on each of three different days were made at each site; the runs were 45 minutes in duration at the manufacturing site and 60 minutes in duration at the user site. At the manufacturing site, pure water was used in certain impingers to collect formate (if present) as this material would yield a positive bias to the peroxide method. Select DNPH impingers were spiked with known amounts of DNPH-formaldehyde derivative prior to sampling in order to test for recovery.

Sample Analysis

For one pair of DNPH impingers from each quadruplicate set of samples, the front and back impinger samples were analyzed separately to ensure that there was no significant breakthrough. For the remaining impinger pairs, the contents of the impingers were combined and diluted to a known volume using acetonitrile. Dilutions were performed as necessary and samples were analyzed by direct injection into a Varian 5000 HPLC equipped with a 20- μ L sample loop and a Varian UV-50 variable wavelength detector set at 365 nm.

The DNPH-coated Sep-Pak cartridges were eluted in reversed direction by gravity feed using 6 mL of ACN. The eluate was collected in 5 mL volumetric flasks and diluted to the mark. Measurements were made using the HPLC system described above. The peroxide impinger samples were allowed to stand overnight prior to preparation for analysis. These peroxide impinger samples were then tested separately and/or combined like the DNPH impinger samples. Dilutions were performed as necessary and samples were analyzed using a Dionex Model 14

ion chromatograph equipped with an 800 μ L sample loop and a conductivity meter.

Results and Discussion

The levels of formaldehyde found at the manufacturing site varied from approximately 50 to 700 mg/cu m. A statistical test of the DNPH impinger/HPLC data showed that the standard deviation of the data, which varied from 1 to 19 percent RSD, varied in proportion to the mean (i.e., the highest values for the standard deviation are associated with the highest values for the mean and similarly, the lowest values of the standard deviation are associated with the lowest value for the mean). Statistical treatment of the peroxide impinger/IC data could not confirm this same proportionality due to the extensive data scatter. Examination of the peroxide impinger data revealed that, at formaldehyde concentrations greater than 600 mg/cu m, oxidation of the formaldehyde to formate ion appeared to be incomplete. This was confirmed through addition of fresh impinger solution to aliquots of the field samples, which resulted in increased apparent formaldehyde concentration. Statistical operations were performed to compare the DNPH impinger/HPLC and peroxide impinger/IC methods. The pooled coefficients of variation of the DNPH and peroxide data sets were calculated to be 7 and 11 percent, respectively. A comparison of the means using analysis of variance for a two-way classification indicated the methods to be significantly different at the 95 percent confidence level. The difference was 19 percent, with the peroxide impingers yielding higher results than the DNPH impingers. There is no obvious explanation for this difference. Formate background was found to be insignificant and the DNPH-formaldehyde derivative spiked into select impingers showed good recovery, i.e., greater than 98 percent. A likely explanation for the difference is the presence of an interferent formed by reaction with the peroxide.

The levels of formaldehyde found at the user site varied from approximately 0.75 to 1.9 mg/cu m. A statistical test of the DNPH impinger/HPLC data showed that the standard deviation did not increase as the mean value increased; rather, the average RSD for these data was 5.7 percent with a range of 0.7 to 15.2 percent. The standard deviation of the DNPH-coated cartridge/HPLC data also did not increase as the mean value

increased. The average RSD for these data was 1.9 percent with a range of 0.9 to 3.9 percent. The respective, pooled standard deviations for the impinger and cartridge data were calculated to be 4.9 and 2.1 percent. A comparison of the means again using analysis of variance indicated the methods to be significantly different at the 95 percent confidence level. The average difference was calculated to be 0.079 mg/cu m or 7.5 percent, with the DNPH cartridges producing demonstrably higher values. Several parameters which collectively may have contributed to this difference include slightly lower collection efficiency in the impingers, loss from the impingers (in the form of aerosol), and some minor interferent or formaldehyde background on the cartridges. The average recovery for the DNPH-formaldehyde derivative spike at the user site was 92 percent, which supports the first of the two possible reasons given for the difference between the methods.

Conclusion

The best precision was obtained with the DNPH-coated cartridge/HPLC method, which had a pooled standard deviation of 0.023 mg/cu m. The method was also the easiest to use, with no possibility of sample containers breaking or reagents spilling in the field. However, the capacity of the cartridge was exceeded quickly at the high concentrations (> 100 mg/cu m) of formaldehyde generally present at the formaldehyde manufacturing facilities.

The DNPH impinger/HPLC method was tested at both the formaldehyde manufacturing site and the formaldehyde user site. A statistical evaluation indicates that this method is acceptable for determining both low and high concentration levels of formaldehyde. Because of its poor detection limit, the basic peroxide impinger/IC method was found to be unsuitable for the determination of very low levels of formaldehyde (0.5 to 5 mg/cu m) such as those found at formaldehyde user sites.

The method also yielded unacceptable results for the very high concentrations of formaldehyde (> 500 mg/cu m) sometimes found at formaldehyde manufacturing facilities, because the formaldehyde is not completely oxidized to formate ion. The method does show potential at intermediate levels (50-300 mg/cu m), and, because the reagents used are safer and easier to prepare in the field than those used for the DNPH impinger method, it is recommended that the oxidation reaction be studied further.

The major objective of the study was to develop and recommend a single method for sampling and analysis of formaldehyde over a wide range of concentrations (< 1 mg/cu m to > 500 mg/cu m). The DNPH impinger/HPLC method meets this requirement and is therefore recommended as the reference method. However, in view of the excellent precision obtained for the DNPH-coated cartridge method and its ease of use, it is recommended that this method be approved as an alternate when low levels of formaldehyde are expected.

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Jimmy C. Pau is the EPA Project Officer (see below).

The complete report, entitled "Development and Validation of a Test Method for Formaldehyde Emissions," (Order No. PB-90-183-419AS; Cost: \$17.00 subject to change) will be available only from:

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