



## Project Summary

# Laboratory Evaluation of an Impinger Collection/Ion Chromatographic Source Test Method for Formaldehyde

E. Estes, P. Grohse, W. F. Gutknecht, and R. K. M. Jayanty

**An impinger collection/ion chromatographic source test method for formaldehyde was developed and evaluated. An impinger solution of 3% hydrogen peroxide/0.025 N sodium hydroxide was used to oxidize known amounts of formaldehyde to formate ion, which is readily analyzed by ion chromatography. After standing overnight, samples were diluted 1:5 and then analyzed on a Dionex Model 14 ion chromatograph having a standard anion separator column, an anion suppressor column, and a conductimetric detector. Using 0.0025 M  $\text{Na}_2\text{B}_4\text{O}_7$  as the eluent and mass transfer, by volatilization, of para formaldehyde directly into collection impingers as the formaldehyde-atmosphere generation technique, recoveries of 85 to 90 percent were achieved.**

Unlike colorimetric methods for formaldehyde, ion chromatography is not subject to interference from phenol, which is present with formaldehyde in many source emissions. In addition, interferent tests showed that the ion chromatographic method is not subject to interference from trioxane, a stable formaldehyde polymer, or from hexamethylene tetramine, a frequently used source of formaldehyde in industrial processes.

*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

Formaldehyde has been linked to eye and upper respiratory tract irritations, headaches, drowsiness, and gastrointestinal problems. In anticipation of the regulation of formaldehyde by the U.S. Environmental Protection Agency's Office of Toxic Substances, this project was undertaken to evaluate and standardize a source test method for the chemical.

Laboratory evaluation of a chromatographic acid method for measuring formaldehyde in the effluent of formaldehyde manufacturing plants was originally planned. However, a literature review indicated that this method is subject to interference from phenol, which is present with formaldehyde in many source emissions. Laboratory efforts were therefore concentrated on ion chromatographic analysis, which is not subject to phenol interference.

An absorbing solution of 3% hydrogen peroxide/0.025 N sodium hydroxide (pH 9.2) was used to oxidize known amounts of formaldehyde to formate ion, which is readily analyzed by ion chromatography. Samples were collected at 1 L/min using two midget impingers in series, each containing 20 mL of absorbing solution. After standing overnight, the two impingers were combined and diluted 1:5 and then analyzed on a Dionex Model 14 ion chromatograph having a standard anion separator column, an anion suppressor column, and a conductimetric detector. With 0.0025 M  $\text{Na}_2\text{B}_4\text{O}_7$  as the eluent,

the peroxide and formate peaks were well separated, eliminating any analyses problems resulting from alkaline hydrogen peroxide interference.

Three methods of generating atmospheres of known concentrations of formaldehyde for sampling were evaluated. The first method, a permeation system, was unsatisfactory because the permeation rate of the tube fluctuated, averaging about twice the rate certified by the manufacturer. The second approach, involving volatilization of formaldehyde into a Teflon bag, resulted in low recoveries, possibly because of formaldehyde loss to the walls of the bag (Teflon is a registered trademark of E. I. du Pont de Nemours & Co., Wilmington, DE). The third approach, which was the most effective, involved the mass transfer, by volatilization, of paraformaldehyde from a heated glass tube directly into impingers containing the absorbing solution (Figure 1).

Two compounds that potentially could be oxidized to formate were tested as possible interferents to the ion chromatographic method. S-trioxane was tested as an example of a stable formaldehyde polymer. Hexamethylene tetramine, a frequently used source of formaldehyde in industrial processes, was also tested. Samples of 20, 50, and 100  $\mu\text{g}/\text{mL}$  of each were prepared by diluting stock solutions in 3%  $\text{H}_2\text{O}_2/0.025 \text{ N NaOH}$ . After standing overnight, the samples were diluted 1:5 before analysis on the ion chromatograph.

## Results

In a final series of tests, in which samples collected using the mass transfer system were carefully observed to ensure that the paraformaldehyde was completely volatilized, a mean recovery of 86.5 percent was achieved. Control samples prepared by dissolving known quantities of paraformaldehyde in the impinger solution yielded a mean recovery of 98 percent.

Linear regression analysis was performed to determine if the percent recovery was level-dependent. The variation of percent recovery with quantity of formaldehyde vaporized,  $0.011 \pm 0.003$  percent per microgram formaldehyde, was small but significant at the 99 percent confidence level. Sampling precision, also obtained from the regression analysis, ranged from 7 percent for the smallest quantity of formaldehyde vaporized to 5 percent for the highest quantity. Thus, there is evidence that recovery may become less efficient at lower formaldehyde concentrations. On the other hand, the control samples gave excellent conversions and recoveries so that the formaldehyde generation process may have been the real problem. Geisling et al.\* experienced similar inconsistencies in generating formaldehyde from paraformaldehyde and found that other compounds are released when this method is used. Con-

sequently, they developed a generation system using vapor-phase depolymerization of trioxane, with reported conversions to formaldehyde of essentially 100 percent.

In the interferent tests, only small formate peaks, possibly due to impurities, were observed for trioxane and hexamethylene tetramine, indicating little or no interference from these compounds.

## Conclusions and Recommendations

The impinger collection/ion chromatographic source test method for formaldehyde was determined to be suitable for field applications. A field test at a plant with formaldehyde emissions is recommended to verify the test method. In future studies of the source test method, depolymerization of trioxane is recommended as the formaldehyde-generation method.

\*Geisling, K. L., Miksch, R. R., and Rappaport, S. M. Generation of Dry Formaldehyde at Trace Levels by the Vapor-Phase Depolymerization of Trioxane. *Anal. Chem.* 54(1):140-42, 1982.

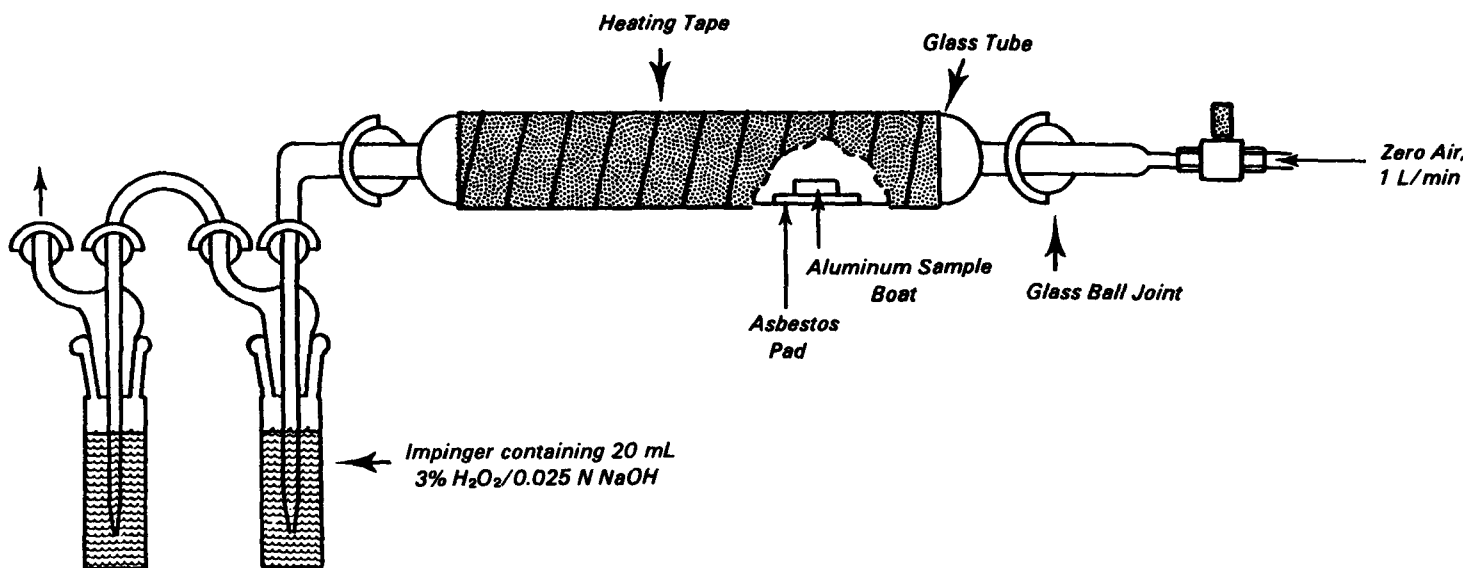


Figure 1. Formaldehyde-generation system: mass transfer.

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*The complete report, entitled "Laboratory Evaluation of an Impinger Collection/Ion Chromatographic Source Test Method for Formaldehyde," (Order No. PB 83-225 326; Cost: \$8.50, subject to change) will be available only from:*

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