# STATEMENT

Synopsis of Research Report 149

HEALTH EFFECTS INSTITUTE

# Development and Application of a Sensitive Method for Determination of Acrolein Concentrations in Ambient Air

## BACKGROUND

Acrolein is a reactive aldehyde that injures the airways in humans and other species, and the U.S. Environmental Protection Agency lists it among the mobile-source air toxics that pose the greatest health risk. Information on the acrolein concentrations to which people are exposed is an important prerequisite for assessing the risk to human health. Despite some technological improvements, it remains difficult to accurately measure acrolein at low levels because, upon collection, it rapidly forms unstable intermediates that are difficult to differentiate and quantify.

In 2001 Dr. Judith Charles of the University of California–Davis responded to HEI Request for Preliminary Applications 00-3 with a proposal to develop a new method for measuring low levels of acrolein, crotonaldehyde, and other unstable aldehydes and apply the new method to assess exposure of tollbooth attendants in the San Francisco Bay area. The Research Committee believed that the method proposed by Charles and colleagues might be useful to accurately measure low levels of acrolein and recommended the study for 2 years of funding with a focus on the development of the sampling and analytic method to determine whether the proposed approach would be successful. During the middle of the second year, Dr. Charles became ill, and Dr. Thomas Cahill replaced her as the principal investigator and completed the study.

## APPROACH

The investigators proposed to evaluate a sampling method that relies on the collection of acrolein in an aqueous medium containing sodium bisulfite, with which it forms a stable chemical reaction product. The overall aim of the study was to develop and optimize a method for the collection and analysis of acrolein and to evaluate the performance of the method by three different measures. One measure was collection efficiency, calculated as the concentration of acrolein in the first of two mist chambers in series relative to that in the second chamber, expressed as a percentage. The second measure was "spike recovery" (also defined as the mass balance), a measure of the overall carbonyl recovery, from collection to analysis. It was determined by adding a known carbonyl mass to a "spiking tube" placed upstream of the mist chamber and delivering it to the chamber by blowing pure nitrogen through the tube to simulate ambient collection conditions. Recovery was calculated as the percentage of the carbonyl mass in both chambers and remaining in the spiking tube relative to the mass added initially. The third measure was retention of deuterated acrolein-$d_4$ that had been added directly to the bisulfite solution as an internal standard before sampling, expressed as a percentage of the initial amount.

The investigators also measured acrolein levels in two field studies and compared the results with those obtained by other sampling methods.

## RESULTS AND INTERPRETATION

**Methods Development and Evaluation** The sampler developed by Charles and Cahill, with Dr. Vincent Seaman, consists of a custom-built glass mist chamber in which air enters at a high flow rate and carbonyls are trapped in a solution of sodium bisulfite as carbonyl-bisulfite adducts.

This Statement, prepared by the Health Effects Institute, summarizes a research project funded by HEI and conducted by Dr. Thomas M. Cahill, Department of Integrated Natural Sciences, Arizona State University, Phoenix, Arizona, and colleagues. The complete report, *Development and Application of a Sensitive Method to Determine Concentrations of Acrolein and Other Carbonyls in Ambient Air* © 2010 HEI, can be obtained from HEI or our Web site (see next page).

This reaction is rapid (on the order of seconds) for all the carbonyls tested, and its rate is dependent on the concentration of bisulfite. The optimal sampling time for acrolein and the other carbonyls is 10 to 30 minutes at a flow rate of approximately 20 L/min at 21°C, and the optimal setup is two mist chambers in series. Longer sampling times, lower flow rates, and different temperatures were not evaluated. After collection, hydrogen peroxide is added to free the carbonyl from the adduct, and a derivatizing agent is added to form a carbonyl derivative suitable for gas chromatography with mass spectrometry. The calculated minimum detection limit for acrolein varied between experiments and ranged from 0.012 μg/m$^3$ (0.005 ppb) to 0.035 μg/m$^3$ (0.015 ppb), values well below the detection limits of other existing methods.

The collection efficiency of the mist chamber methodology was determined to be 80% in the laboratory and 71% in the field. Assuming that the collection efficiency is the same in the two chambers, it would be approximately 91% for the whole system in the field. This is only a relative measure of collection because it does not consider the initial amount of acrolein. Using the spike-recovery approach, the investigators found that 97% of the acrolein mass was recovered. For this test acrolein was dissolved in solvent and volatilized into a nitrogen stream. Although this approach was designed to simulate sampling in the field, it may not reflect entirely the actual conditions to which acrolein is exposed when sampled in ambient air. The test using the deuterated internal standard showed that, once the acrolein was trapped, 93% was retained throughout the analytic process. Because the deuterated species was dissolved in the bisulfite solution in the mist chamber, rather than bubbled into the solution in an air stream (as it would be under ambient sampling conditions), the measure of internal standard retention does not evaluate the efficiency with which the carbonyl in the ambient air stream is trapped in the mist chamber solution. Overall, the Review Committee—in its independent evaluation of the study—thought that these analyses were useful and showed a high level of acrolein recovery under laboratory conditions. However, the dynamic processes that lead to absorption of acrolein in the field may vary.

**Field Studies** The first field study, conducted at the Peace Bridge in Buffalo, New York, was an opportunity to compare the mist chamber method with two methods conventionally used to measure acrolein: the dansylhydrazine-based passive sampler and Occupational Safety and Health Administration Method 52. Comparison of the methods is difficult, however, because sampling times varied widely, with the mist chamber sampling for 10 minutes (sequential measurements were averaged over 12 hours) and the other two samplers sampling continuously for 12 to 24 hours. Nevertheless, the results showed that the mist chamber methodology can detect lower concentrations of acrolein than the other two devices. The second field study, conducted using multiple mist chamber systems in three locations in California, showed that the results of the method were reproducible and detected differences in concentrations at sites that had different carbonyl sources nearby.

## CONCLUSIONS

The mist chamber methodology offers greater sensitivity for measuring acrolein than other existing methods. The analytic steps allow good separation of several carbonyls. The investigators evaluated chamber performance using three different approaches; however, they did not discuss the expected relationships among them. The approach of measuring the total recovery of acrolein from collection to analysis yielded a value of 97%.

Some limitations that might prevent the use of the method in population exposure studies are that the mist chamber has to be custom-built and is quite costly and that the method is labor-intensive, requiring a number of steps in the field. Development of more practical and less expensive approaches will be important if it is to be more widely used. The method performs optimally with very short sampling periods (10 minutes). The investigators provide a good rationale for having a sampler with a short sampling time to track short-term changes in acrolein concentrations. The Review Committee thought that a sampler with a wider range of sampling times would be more useful for measuring variations in ambient levels and personal exposures, without the need to combine data from repeated measurements taken over very shorts periods. Despite its potential limitations, the Investigators' Report shows that the mist chamber methodology can provide useful information when detailed temporal characterization of acrolein concentrations is needed.

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