



# STATEMENT

Synopsis of Research Report 153

HEALTH  
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## Improved Source Apportionment and Speciation of Low-Volume Particulate Matter Samples

### BACKGROUND

As particulate air pollution has increasingly been associated with adverse human health effects, interest has been growing in studying the chemical composition of inhalable particulate matter (PM) and how exposures to its specific constituents are associated with health effects. Much of the general characterization of the composition of PM has been performed on specimens collected by high-volume samplers. Personal sampling, although it improves exposure estimation, makes use of small-scale equipment that traditionally could not collect a sufficient volume of airborne PM for proper speciation analysis. In the current report, Dr. James J. Schauer and his team detail the methods they developed for the detection and quantification of a wide range of trace metals and nonpolar and polar organic species in low-volume PM samples.

### APPROACH

The investigators' aims were to develop multiple chemical analysis methods for the measurement of concentrations of organic compounds, trace metals, trace-element isotopes, and oxidation states of selected elements in samples of  $PM \leq 2.5 \mu m$  in aerodynamic diameter ( $PM_{2.5}$ ) collected using personal sampling equipment and to analyze existing personal exposure samples from various epidemiologic studies.

Schauer and colleagues developed a number of variations on gas chromatography-mass spectrometry (GC-MS) analysis as well as wet-chemical methods for more economical spectrophotometric analysis of selected metals (iron [Fe], manganese [Mn], and chromium [Cr]) and quantification of the relative proportions of their oxidative states.

The investigators applied rigorous clean-chemistry concepts to their methods development in order to

address the three pillars of quantitative trace-element analysis, namely the control and minimization of background values using blanks; the maximization of sensitivity; and the control, isolation, and removal of interferences.

The following methods were developed or fine-tuned: (1) acid digestion for trace-element characterization, (2) GC-MS techniques for the quantification of organic compounds, (3) wet-chemical spectrophotometric analysis techniques for the analysis of selected metals, and (4) x-ray absorption near edge structure (XANES) spectroscopy for the quantification of the valence states of Fe. The investigators then tested several real-world applications of the methods they had developed in order to demonstrate their utility for low-volume PM samples in a variety of circumstances:

- Using various types of co-located personal samplers, substrate combinations, and ambient samplers, the investigators compared samples from sites in East St. Louis, Illinois, and at the University of Southern California at Los Angeles.
- Samples from sites in East St. Louis; Waukesha, Wisconsin; and the Rancho Los Amigos National Rehabilitation Center, in the Los Angeles Basin, California, were subjected to simulated atmospheric aging for 0 to 10 days to measure changes in Fe oxidation states.
- The investigators undertook a study of Mn speciation in airborne wintertime PM samples from Toronto, Canada (where methylcyclopentadienyl manganese tricarbonyl [MMT] had been used extensively as an octane booster in gasoline prior to 2004).
- Personal samples of PM aerosols were obtained from a large, ongoing cancer study (led by Eric

Garshick of Harvard) of dockworkers, mechanics, and drivers at a truck terminal in St. Louis, Missouri. The samples were compared with samples obtained in each of four work areas in the terminal and at a nearby urban background monitor, measuring concentrations of elemental carbon, organic carbon, polycyclic aromatic hydrocarbons, steranes, and hopanes.

- The team obtained and compared indoor, outdoor, and personal PM samples from a study of coronary heart disease (led by Ralph Delfino of the University of California–Irvine) in elderly nonsmokers living at a retirement home in the Los Angeles Basin.

### RESULTS AND INTERPRETATION

The team reported good agreement between the size-resolved total PM mass concentrations collected by the co-located PM<sub>2.5</sub> personal samplers in East St. Louis and Los Angeles. Size-resolved trace-metal concentrations for six metals differed by site but showed better agreement within sampler type than between co-located samplers. In the Fe aging study, the greatest changes occurred in the first 6 days, when soluble Fe(II) increased in the coarse fraction over the first day and then decreased steadily. Because the greatest changes occurred in the brief period after sampling, the results were believed to indicate that atmospheric aging could have a substantial effect on exposure to soluble Fe in PM aerosols.

In the wet-chemical analysis of Mn, the greatest concentrations of soluble Mn were found in the coarse fraction of the samples, with decreasing concentrations as particle-size fractions decreased. Compared with speciation results for the East St. Louis samples used in the sampler intercomparison, air concentrations of Mn in Toronto were lower overall. Soluble oxidized Mn was detectable only in the PM<sub>2.5</sub> fraction of the Toronto samples.

Consistency of sampling results for the St. Louis truck terminal was found to vary by job classification and work area. Jobs that included high exposure variation within a job and work area indicated cases where exposures were more highly affected by individual job and personal activities than by area or background air quality.

No relationship was found between air concentrations from the indoor, outdoor, and personal samples for the retirement home residents for all analyzed trace elements except copper. The investigators thought this indicated that the personal exposure samples were not measuring exposure to the same pollutant sources as those represented in the indoor and outdoor samples.

According to the investigators, this study has advanced the PM speciation of personal exposure samples in three key areas: the development of (1) specialized GC–MS methods to measure organic tracers, (2) specialized high-resolution inductively coupled plasma mass spectrometry methods to measure trace elements, and (3) wet-chemical methods to speciate Fe and Mn. The investigators estimated that the cost of the analyses ranged from a high of \$250 per sample for the thermal desorption GC–MS method to a low of \$10 per sample for the wet-chemical method.

The HEI Health Review Committee noted that the description of the methods development and experimental analyses fully addressed the aims proposed at the beginning of the study. Schauer and his team have also demonstrated that their methods are well suited to PM samples collected for health studies.

The Committee noted, however, that the investigators were not able to meet certain goals. They did not test or expand much on their methods for the analysis of polar organic compounds, because the materials caused repeated instrument failures. The investigators also had difficulty measuring Cr(VI), an oxidation state of Cr, because of the extremely small amounts of Cr(VI) present in the PM aerosol found in most environments.

### CONCLUSIONS

Schauer and colleagues have developed methods that have sufficiently high sensitivity and sufficiently low detection limits to measure trace metals, nonpolar organics, and polar organics present in low-volume PM samples, such as those collected by personal sampling equipment. The team has successfully adapted wet-chemical methods for the extraction and quantification of Fe, Mn, and Cr in various oxidation states of interest to researchers.

Results from the St. Louis truck terminal indicated that personal activities, such as smoking and job tasks, had large effects on exposures. Results from the retirement home indicated that trace elements measured in personal PM samples were different from those measured in indoor and outdoor air samples (although the reasons for these discrepancies were not clear). These results indicate the broad suitability of the investigators' methods for use in studies of PM exposure and human health. Further work remains to be done on methods for the analysis of polar organic compounds and for improving detection of Cr(VI) from ambient air samples taken with personal samplers.