EQUIPMENT FOR PERSONAL AND PORTABLE AIR MONITORING:
A STATE-OF-THE-ART SURVEY AND REVIEW

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Abstract

The Harvard School of Public Health and the Energy and Environmental Policy Center of the Kennedy School of Government, under the auspices of the Electric Power Research Institute and the Gas Research Institute, conducted a "Workshop on Evaluation of Monitoring Equipment for Personal Exposure Assessment". On December 5-7, 1983, 45 indoor air quality researchers convened in Cambridge, Massachusetts to discuss new methods and instruments for measuring personal exposure to indoor and outdoor air pollution. This paper presents a summary of the presentations and discussions at that workshop.

Aerosols

William Turner of Harvard University discussed the Harvard/EPRI personal monitor, which consists of a 10-mm nylon cyclone into which the filter cassette is placed, a flow pulsation damper, a motor/pump assembly, a noise muffler, a 12-volt battery pack, and electronic circuitry for flow control and battery charging (9). The sampler was designed in 1978 to overcome many of the problems inherent in available samplers, namely, noise, flow rate variability, battery cycle time, capability to operate from 110 volts AC, ease of operation, and motor life. Ninety-nine samplers initially constructed have been successfully used in three major personal monitoring studies and a number of minor investigations. Modifications have been made to lighten the package weight and to improve the battery life. The pump motors have proven highly reliable with virtually no failures.

The National Bureau of Standards has developed a sampler designed to provide well-characterized size cuts and collection efficiencies, substantial collected sample mass, homogeneous sample deposition, quiet performance and energy-efficient operation (1). It uses an impactor inlet to remove particles with aerodynamic diameters greater than 15 um. A 6.8-um pore size, Nuclepore membrane coarse filter retains large particles and passes the respirable particles to a second-stage, fine filter. The package is contained in a 10 x 10 x 18 cm aluminum case and weighs about 1.6 kg. The sampler fills an void in the need for a portable particulate sampler capable of quietly collecting large amounts of material. By operating at 6 liters per minute (1pm), the unit processes over three times the amount of air handled by the Harvard/EPRI monitor.

The GCA Corp. has developed a new personal monitor, the MINIRAM Aerosol Monitor, Model PDM-1, which incorporates a miniature nephelometer to analyze air entering a chamber by diffusion. It provides both real-time and integrated data. It is silent (has no air pump), small (10 cm x 10 cm x 5 cm) and lightweight (less than 0.5 kg). The nephelometer senses particles between 0.1 and 20 um aerodynamic diameter and electronically converts the signal into a mass concentration. Among the potential problems are stray light sources (GCA provides a sunshield accessory), temperature effects, and humidity interferences. The currently available units have a lower detectable limit of 0.01 mg/m³. For personal and indoor monitoring, the electronics would require modification.

Radon

Eberline Instrument Division, Thermo Electron Corporation, manufactures a portable radon daughter analyzer, the Model WLM-1 Eberline Working Level Monitor. This device is capable of measuring and logging hourly and weekly average Working Levels. As particles are deposited on a membrane filter, alpha particles emitted by the radon decay products are measured with a silicon diffused junction detector. Counting continues from the time of collection until four hours after the end of the sampling period so that any residual radon decay products on the filter can be used to correct the reading. One need know only the alpha counting efficiency of the detector and the air flow rate to determine the Working Level. Evaluation data indicate excellent measurement precision, with a coefficient of variation for each WLM-1 of about 2%.

Researchers at Lawrence Berkeley Laboratory have constructed and deployed a device, called the Aardvark system, that simultaneously measures radon concentration and air exchange rates (8). The radon is detected with a scintillation flask and photomultiplier tube. The air exchange rate is measured by injecting sulfur hexafluoride (SF₆) in the structure and then monitoring its concentration over time. The Aardvark system gives 90-min-averaged air exchange data and 180-min-averaged radon concentrations.

Organic Compounds

Two portable gas chromatographs suitable for in-building field surveys are the Photovac and the HNU, both of which use a photoionization detector. The Photovac was found to be more sensitive than the HNU and was used in EPA field tests. Its sensitivity to 3 chlorinated hydrocarbons was in the parts-per-billion range for 1 cm air samples.

Integrated samples for volatile organic compounds can be collected on polyurethane foam (PUF) and PUF with TENAX GC polymer resin as trapping mediums for organics in a portable sampling system. The compounds were solvent-extracted and analyzed by gas chromatography. The minimum detectable level was 0.1 ug/m at an airflow of 4 1/min for most compounds tested (5).

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can be collected er resin as ystem. The hromatography. ow of 4 1/min for Researchers at the Bell Laboratories use thermal desorption methods for analyzing organic compounds adsorbed onto aerosols. About 100 ug of sample on a Teflon membrane filter was needed for gas chromatographic and mass spectrometric analysis. Thermal desorption was used to avoid the artifacts which often accompany solvent extraction of particles. The Teflon membrane filter was heated to a temperature between 100°C and 900°C for 1-20 s. After volatilization, the compounds were analyzed by GC/MS. Typically, temperatures near 250°C produced sufficient volatilization with minimal sample degradation. Some fragile organic compounds will be decomposed by this technique, however, and other compounds may be formed or lost during sampling.

Two screening techniques for samples suspected to contain PNA have been developed at Oak Ridge National Labs. In synchronous luminescence, the sample is ultravioletly excited and the excitation and analysis wavelengths are scanned simultaneously while a fixed-wavelength difference is maintained between them. Selectivity is improved when the wavelength difference corresponds to a resonance of the molecule of interest. The second technique, room-temperature phosphorescence, is used for rapid screening of samples. The large phosphorescence wavelength shifts allow discrimination against background fluorescence. The sample solution is spotted on a filter paper treated with a heavy-atom salt such as thallium acetate, lead acetate, cesium iodide or sodium bromide to enhance phosphorescence quantum yields of specific PNA compounds. The samples' phosphorescence is then measured with a conventional spectrofluorometer. In tests, the smallest detectable quantities of PNA compounds were in the nanogram range (10).

Researchers at Aerodyne Research, Inc. use a pattern recognition technique to analyze FTIR spectra of complex organic mixtures. In this technique, the principal components of pure compound spectra are analyzed to generate a set of representative spectra for each chemical class which is sufficiently cohesive (3). A small subset of these representers for each class is used to approximate an unknown mixture spectrum using a constrained, nonlinear, least-squares error-minimization algorithm. The results are given in terms of the chemical class fraction in the mixture. Tests run on numerically generated mixtures show that the procedure correctly recognizes mixtures containing roughly equal contributions from the current maximum of 21 classes. Although tests to date have involved gas-phase spectra, the technique can be used for spectra in any phase. For adsorbed species on particles, 50-100 ug samples should suffice.

Argonne National Lab researchers are working on a multipollutant monitoring device using multiple sensors and pattern recognition to analyze the results. Sensors include a variety of electrochemical cells and semiconductor diodes. While no one sensor is selective by itself, the whole array's pattern of response can be unique for a compound. In tests, ratios of the three largest responses from sixteen different sensors were calculated and assigned to one of five 'bin' levels, with up to 125 unique patterns available. It has been calibrated for 25 gases including formaldehyde and benzene and should be able to detect gases in amounts as low as 1 ppm.

An IR spectral correlation (SCORE) device is being developed by Aerodyne Research, Inc. The first application will be as a formaldehyde detector but it can be used for any gas with an infrared spectrum. The instrument consists of an infrared light source, a multipass sample cell, a monochromator, a detector and a focal plane spectral mask optimized to correlate positively with the formaldehyde absorption spectrum at 3.4 mm and negatively with interfering species such as water vapor and hydrocarbons. Minimum detectable levels will be about 500 ppb for a 1-min integration time.

Researchers at Oak Ridge National Laboratories have worked with several formaldehyde sampling and analysis techniques. Most of which use pararosaniline rather than chromotropic acid. Formaldehyde can be sampled with impingers, molecular sieve sorbents (7), or passive permeation samplers (8). The passive permeation sampler has a dimethylsilica membrane that dissolves formaldehyde vapor and passes it to a water-filled chamber below. The detection limit for the molecular sieve sampler is 25 ppb at 2 1/min for 15 min. The detection limit for the passive permeation sampler is 25 ppb for a 24-hr sampling period.

Lawrence Berkeley Laboratory has developed a passive formaldehyde sampler using a filter paper impregnated with NaHSO3. The minimum detectable, time-weighted average concentration for a 1-wk sampling period was 0.018 ppm using chromotropic acid analysis (5).

A novel personal sampling badge for formaldehyde, containing a polystyrene substrate coated with 10 stripes of p-hydroxybensoic acid hydrazide crystals is under development at Crystal Diagnostics, Inc. Formaldehyde diffuses through 1 of 2 entry holes, the choice of hole determining the sampling rate appropriate calibration range. When the formaldehyde contacts the hydrazide crystals, they are converted, one by one, to the hydrazone. A saturated solution of the hydrazone is then injected into the badge. Crystals grow on the hydrazone stripes causing them to change color. Time-weighted average exposure is read by counting the colored stripes. The minimum detectable level is 0.5 ppm-hr and the maximum detectable level is 30 ppm hr. Interferences occur from other low-molecular weight aldehydes.

Carbon Monoxide

Electrochemical CO monitors have been commercially available for some time and are sufficiently sensitive and interference-free so they can be used for indoor monitoring. Some monitors have an accessory data logger to obtain time-averaged and real-time data.

Other portable CO monitors use nondispersive infrared (NDIR) spectrophotometry. A recent improvement of the Luft NDIR monitor uses a single CO-filled detector instead of a divided detector (TECO). A rotating filter wheel is placed between the infrared source and the sample cell. One-half of the filter wheel is filled with an infrared nonactive gas and the other half is filled with enough CO to produce virtually 100% absorption at the center of the CO lines. When the filter wheel rotates, it modulates the radiation falling on the detector.

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Lawrence Berkeley Laboratory is developing a passive, personal CO monitor, similar to the Palmes tube, but loaded with palladium compounds instead of triethanolamine. Reactions involving CO produce Pd metal and change the sampling medium's reflectance. Hydrogen sulfide ($\rm H_2S$) and ethylene ($\rm C_2H_4$) interfere with this monitor. The limit of detection should be 5 ppm for a 1-wk exposure.

Nitrogen Dioxide

Electrochemical methods for the determination of NO_2 are similar to those for CO except that the NO_2 is reduced rather than oxidized. Commercially available instruments have a minimum detectable level of about 20 ppb according to the manufacturers.

Energetic Sciences has packaged an electrochemical NO₂ monitor, called the Ecolyzer Hipster, as a prototype personal monitor. whose minimum detectable level was designed to be 10 ppb. When compared to a chemiluminescent NO₂ monitor, the Ecolyzer Hipster was found to be nonlinear in the 50-300 ppb range, although more recent data from the manufacturer indicates that the response is reasonably linear. When 1000 ppm of CO was present, the Ecolyzer Hipster had a negative 0.5 ppm response. CO₂ and NO presence had no effect.

Palmes tubes have been further evaluated by Lawrence Berkeley Laboratory (4). Because TEA undergoes a liquid-solid phase transition at 21°C, the effect of temperature on tube performance was evaluated. It was found that capture efficiency at 15°C was 15% less than at 27°C. A similar decrease in tube performance occurs when the air velocity is reduced from 100 cm/sec to 0 cm/sec. Users of this sampler must therefore be cautious.

University of Denver researchers are attempting to use the chemiluminescent reaction of NO₂ with luminol in a personal continuous analyzer (11). In this monitor, a filter paper transports the luminol solution past a photomultiplier tube where it encounters the sampled air. The reaction of luminol and NO₂ produces light which is detected on the photomultiplier tube. The limit of detection for this instrument is about 4 parts-per-trillion (ppt) with no interferences except peroxyagetyl nitrate (PAN). This interference may not be serious because PAN is also an important air pollutant. A personal version of this monitor may be available by the end of 1984.

Thermo Electron Corp. is developing a single-sorbent cartridge for the simultaneous determination of NO₂, formaldehyde and air exchange. The instrument pumps air through a tube containing a Thermosorb absorbent treated with morpholine. This converts NO₂ in the air to N-nitrosomorpholine. A 1-min sampling time at a concentration of 1 ppb gives good data. After sampling, the nitrosomorpholine is extracted from the cartridge, resolved by gas chromatography, and detected in a chemiluminescent analyzer. No humidity effects and no interferences have been found.

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