New Trends in Monitoring Methods

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Air Toxics Exposure Assessment Workshop
San Francisco, CA
June 25- 27, 2002

EPA United States Environmental Protection Agency
Office of Research and Development
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Background

- Clean Air Act lists 188 HAPs
- Urban Air Toxics Strategy identified 33 urban air toxics from the list of 188 HAPs believed to present the greatest risk to public heath

- Monitoring deficiencies exist for a number of these compounds making widespread monitoring both at ambient sites and for human exposure studies difficult

- Efforts are being made to fill some of these monitoring gaps

- US EPA - ORD has a limited research budget for development of Air Toxics methods

- Because of limited budgets, method development must be targeted

- Whenever possible, resources will be used to coordinate methods development that can be used for both ambient and personal/residential monitoring

- Currently, there are approximately 300 ambient sites nationwide collecting ambient data on selected HAPs and other air toxics through a combination of Federal, state and local monitoring programs

- EPA will also be conducting air toxics human exposure studies.

Issues to Consider for Developing Monitoring Methods

- Analytical issues
- Economic issues
- “Ease of use” issues

Analytical Issues or Method Deficiencies

- Insufficient limits of detection or sensitivity
- Problems with compound stability and/or poor recoveries from sampling media
- Methods not sufficiently proven
- Poor comparability with other methods
- Poor reliability
- Unavailability of NIST or other standards
- Lack of practical, easy to implement, analytical methods

Economic Issues to Consider

- Initial purchase cost of monitoring equipment
- Ongoing cost to maintain monitoring equipment
- Initial cost of analytical equipment
- Per sample cost of analysis
- Data reduction and database costs

“Ease of use” Issues to Consider

- Labor intensity and skills required to set-up and operate monitoring equipment
- Calibration ease or complexity
- Applicability to ambient, personal, and residential monitoring
- Data turnaround time

Specific Examples

- US EPA in conjunction with the states, and local agencies are in the process of implementing a National Air Toxics Monitoring Network

- Pilot sites are initially monitoring 18 “core” VOCs, carbonyls and metals identified in the April 2000 Grant Guidance

“Core” Pollutants Monitored in the Pilot Sites of the National Air Toxics Network

Benzene
1,3 Butadiene
Carbon Tetrachloride
Chloroform
1,2 -Dichloropropane
Methylene Chloride
Tetrachloroethylene
Trichloroethylene
Vinyl Chloride

Arsenic and compounds
Beryllium and compounds
Cadmium and compounds
Chromium and compounds
Lead and compounds
Manganese and compounds
Nickel and compounds

Acetaldehyde
Formaldehyde

- An additional 9 pollutants were identified in the Grant Guidance as desired for inclusion on the “Max” list but current problems associated with these methods keeps them off the “core list”

Compounds of Interest Listed in the 2000 Grant Guidance for Air Toxics Pilot Project that Need Method Development

1,3-Butadiene 1,2-dibromoethane 1,2-dichloroethane	TO14A/15	Sensitivity issues False highs due to < MDL
acrylonitrile	TO-14A/15	NIST standard needed, recovery problems
Ethylene oxide	None /NIOSH 1614	Poor storage stability
1,1,2,2-Tetrachloroethane	TO-15	NIST standard needed
Arsenic and compounds	IO-3	Sensitivity issues, filter contamination, resource intensive
Beryllium and compounds*		Resource intensive, XRF sensitivity issue
Mercury and compounds	IO-3	Requires special equipment
acrolein	none	TO-11A results in unstable derivative, poor recovery
2,3,7,8-tetrachlorodibenzo-p-dioxin	TO-9A	Resource intensive

*Beryllium appears in both tables

Current Efforts to Address Monitoring Needs

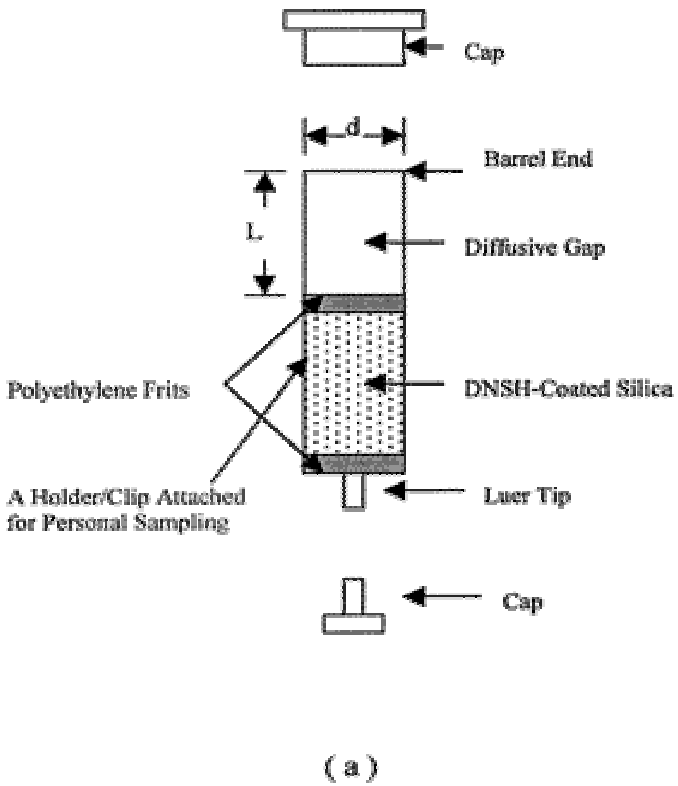
- Acrolein – effort to develop PAKS for ambient and personal/residential air
- Formaldehyde – effort to develop semi-continuous HCHO monitor for ambient air
- 1,1-Dichloroethane and other VOCs – efforts to improve detection limits for ambient air based on TO-15 method

PAKS (DNSH) Method for Acrolein

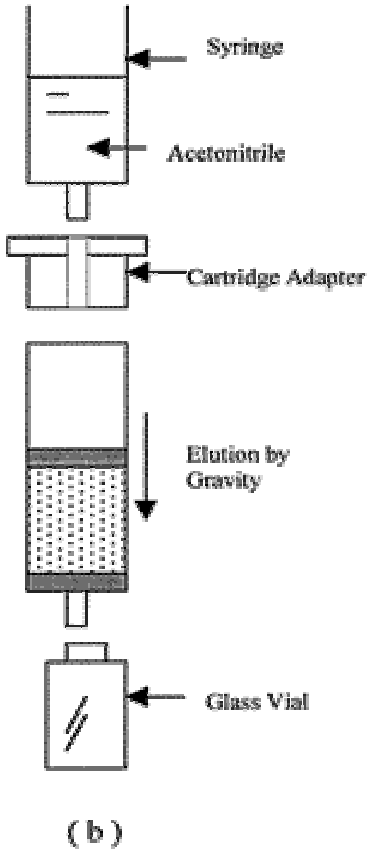
- PAKS - **P**assive **A**ldehyde and **K**etone **S**ampler
- Developed by EOHSI as a passive aldehyde and ketone sampling method for personal and residential monitoring in the RIOPA Study

- PAKS method uses C_{18} media coated with dansylhydrazine (DNSH) packed in a polypropylene syringe barrel
- Passive diffusion sampler
- Extracted with acetonitrile
- Analyzed by HPLC-Fluorescence

PAKS Cartridge



Sampling



Extraction

Source: J.Zhang, EOHSI

PAKS Advantages

- Passive sampler – no pumps required
- More sensitive than DNPH- Lower LODs
- Inexpensive – comparable to DNPH
- Better recoveries of acrolein (60% vs. 20%) and crotonaldehyde compared to DNPH
- Formaldehyde, acetaldehyde, and other carbonyls comparable to DNPH method
- Ozone does not appear to cause interference

PAKS Disadvantages

- Acrolein recovery lower than desired
- Stability on cartridge needs to be improved

PAKS Ongoing Development

- Working on improving acrolein recovery (>85%)
- Working on improving on cartridge stability (> 10 days)
- Once improvements are made – conduct field verification alongside DNPH at ambient sites – 4 season, 4 locations

Semi-Continuous Formaldehyde Monitor- Basis of Operation

- Developed with EPA support by Texas Tech University
- System captures HCHO from the air on the wall of a permeable Nafion tube through which water is flowing
- The HCHO enters the water as it permeates through the Nafion tube
- The HCHO/water is mixed with a second stream of water containing a reaction compound

- The resulting product compound is illuminated by light from a set of LEDs and molecular fluorescence occurs
- The derivitized fluorescence is detected using a photomultiplier tube to provide the analytical signal
- Details of the method are described in Anal. Chem. 1994, 66, 551-556.

Semi-Continuous Formaldehyde Monitor – Project Objectives

- Develop and evaluate semi-continuous formaldehyde monitor for application to toxics monitoring and photochemical modeling
- Develop and evaluate semi-continuous formaldehyde monitor for experimental testing of photochemical models (diagnostic testing)

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Features of the Semi-Continuous Formaldehyde Monitor

- Working range formaldehyde concentrations: 0.1 to 50 ppbv
- Working temperature range when operated in an environmentally controlled area:

  10 to 30 °C
- Time resolution, one complete cycle:

  10 minutes

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Features (cont).

- System operates for 7 days without need for consumables
- System includes provisions for generation of zero air from ambient air
- Every 10 minute cycle includes a zero air reading
- Literature indicates selectivity factor of 306 to 1 for most significant interfering compound (acetonitrile)

Calibration of the Semi-Continuous Formaldehyde Monitor

- Established using a compressed gas cylinder of trace formaldehyde in N_2 which is diluted with zero air to obtain different calibration levels

Example Output from Semi-Continuous Formaldehyde Monitor

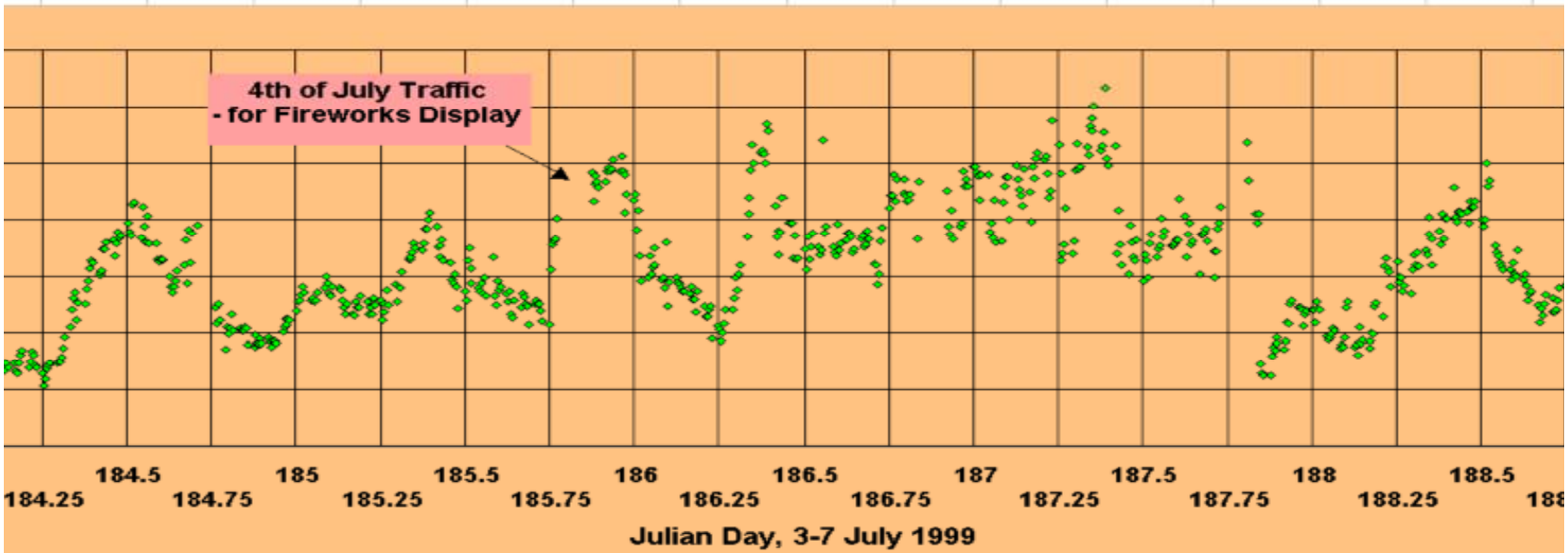

Figure 1 - Four Day Monitoring Sequence for HCHO on top of the Polk Bldg., Nashville

Semi-Continuous Formaldehyde Monitor – Advantages

- Less expensive to operate
- Less labor intensive
- Allows collection of more data points for modeling purposes

Semi-Continuous Formaldehyde Monitor – Disadvantages

- due to size and power requirements it is applicable for ambient site or stationary monitoring only
- Compound specific – monitors for only one compound

Improvement of Monitoring Capabilities for 1,1-DCE and Selected VOCs

- Regional Monitoring Initiative (RMI) for EPA Region 8

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Improvement of Monitoring Capabilities for 1,1-DCE and Selected VOCs

- RMI Objectives
  - Write TO-15 supplement for attaining lower detection limits for 1,1-Dichloroethane and other NATA list VOCs using Colorado Dept. of Pub. Health (CDPHE) guidelines and NERL in-house research results

Improvement of Monitoring Capabilities for 1,1-DCE and Selected VOCs

- Objectives (continued)
  - Review and confirm viability of canister based sampling and analysis methods for NATA list of VOCs

List of VOCs Targeted for Monitoring Capabilities Improvement

Vinylchloride	1,2-Dichloropropane	Hexachlorobutadiene
1,1-Dichloroethene	Trichloroethene	Acrylonitrile
Dichloromethane	cis and trans-1,3-Dichloropropene	1,3-Butadiene
Chloroform	1,1,2-Trichloroethane	Ethylene oxide
1,2-Dichloroethane	1,2-Dibromoethane	
Benzene	Tetrachloroethlene	
Carbon tetrachloride	1,1,2,2-Tetrachoroethane	

Improvement of Monitoring Capabilities for 1,1-DCE and Selected VOCs

- Results to date
  - Method detection limits for 1,1-DCE determined to be approximately 6 pptv
  - Results from a 53 day preliminary storage stability check for 10 – 200 pptv of 1,1-DCE in humidified zero air using three different canister types indicate stability within ±25% for 2 of the 3 canister types tested

Summary

At this time ORD has a limited air toxics monitoring methods program but we are trying to address some key issues

Summary – Key Issues

- Need to develop new methods or modify current methods to address known deficiencies
  - Lower detection limits for compounds that are presently observed at or below current limits of detection
  - Increase stability and recoveries for compounds known to be unstable or have low recoveries
  - Develop NIST standards for compounds for which there are no NIST standards

Summary – Key Issues

- Need to develop methods that are economically viable
- Need to develop methods that are less labor intensive
- Need to coordinate development of methods that can be used for both ambient site monitoring and personal or residential monitoring

Summary – Key Issues

- Need to continue the search for the relationships between ambient site measurements, personal, and residential measurements