United States
Environmental Protection
Agency

National Exposure
Research Laboratory
Research Triangle Park, NC 27711

Research and Development | EPA/600/SR-96/091 | August 1996

EPA

Project Summary

Evaluation of CAAA Compounds: Approaches for Stationary Source Method Development

Denny E. Wagoner, Raymond G. Merrill, Jr., James F. McGaughey and Joan T. Bursey

Abstract

A literature search-based study was performed to evaluate a selected subset of the 189 analytes listed in Title III of the Clean Air Act Amendments of 1990 for certain criteria. The overall objective of this program was to acquire sufficient information about physical properties and chemical characteristics of the compounds to suggest a technical approach for the sampling and analysis of these compounds from stationary sources. A database of the selected Clean Air Act Amendments compounds was prepared in spreadsheet format with detailed physical properties, chemical characteristics, and a summary categorizing the compounds in terms of potential sampling and analytical approaches. Recommendations for the sampling and analytical methodology for selected compounds or compound classes are also included where no methods have been documented or evaluated.

This Project Summary was developed by the National Exposure Research Laboratory's Air Methods Research Division, 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

Title III of the Clean Air Act Amendments (CAAA) of 1990 contains 189 entries as substances to be regulated. Far more than 189 individual chemicals are to be regulated, for some of the entries encompass hundreds of individual compounds: e.g., dibenzofurans as a category include 135 individual compounds, and polychlorinated biphenyls include more than two hundred individual compounds. The EPA has developed or is evaluating methods for many of the major chemical classes of these 189 compounds. Stationary source sampling and analytical methods for these compounds are under various stages of development or evaluation. In this program, compounds requiring further investigation have been identified and searches of the literature have been performed to gather information and evaluate a selected subset of the 189 CAAA entries for certain criteria. Physical properties and chemical characteristics of the compounds have been evaluated in order to propose a technical approach for the sampling and analysis of these compounds form stationary sources.

The CAAA analytes fall into several categories:

- Compounds which should perform reasonably well with existing methodologies because they meet the suggested method criteria such as boiling point. However, minimal method evaluation data are available for the CAAA analytes, so the performance of the methodology for the analytes must be evaluated.
- Compounds which should perform reasonably well when existing methodology is modified (i.e., compounds which must be derivatized before gas chromatographic analysis, compounds which require a specialized gas chromatographic column, or compounds which will require use of high perfor-

mance liquid chromatography rather than gas chromatography for analysis).

- Compounds for which a completely new sampling and analytical approach must be developed and evaluated.

The study of the literature and evaluation of existing data clearly indicate that the general sampling and analytical techniques that are commonly utilized (i.e., VOST, Method 18, Method 0010/Method 8270, Method 0011) provide adequate monitoring capability for many of the volatile and semivolatile organic compounds listed in the CAAA. However, the complexity of the chemical behavior of CAAA compounds will require the development of many new and/or modified sampling and analytical techniques for successful monitoring.

The mandate of this study was restricted to selected compounds from the total of 189 entries from the Clean Air Act Amendments. The families of metallic compounds were excluded from consideration, as were the families of compounds such as polycyclic organic matter (POM). Also excluded from consideration were compounds for which development of specific methods is presently in progress under EPA Contract 68-D1-0010, including the application of VOST to volatile halogenated organic compounds and Method 0010/8270 for semivolatile halogenated organic compounds.

Procedure

The information used to develop the spreadsheet of chemical information was derived from a variety of sources, including:

- Internal sources such as various investigators who have been involved in the development and evaluation of sampling and analytical methodology for a wide variety of organic and inorganic compounds;
- "Screening Methods for the Development of Air Toxics Emission Factors," an EPA report prepared under EPA Contract number 68-D9-0054 (EPA-450/ 4-91-021);
- "Handbook of GC/MS Data and Information for Selected Clean Air Act

Amendments Compounds," an EPA report prepared under Contract number 68-D1-0010;

- CRC Handbook;
- NIOSH;
- HON Database;
- Merck Index;
- The Environmental Monitoring Methods Index System (EMMI), which includes information on more than 2,600 analytes from over 80 regulatory and nonregulatory lists and more than 900 analytes from the Clean Water Act (CWA), Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), Superfund Amendments and Reauthorization Act (SARA), Resource Conservation and Recovery Act (RCRA), Safe Drinking Water Act (SDWA), the Clean Air Act (CAA), and analytes from other EPA and State lists;
- Material Safety Data Sheets for individual compounds;
- Agrochemical Handbook;
- Environmental Science and Technology; and
- Handbook of Toxic and Hazardous Chemicals.

An Appendix to the report includes a summary of physical and chemical properties for the compounds of interest, including structures for the compounds.

When sampling or analytical methodology is required for a compound, there are usually several choices:

- On the basis of physical parameters such as boiling point, an analyte is assigned to a methodology, and the performance of this methodology for this analyte has been demonstrated to be effective in previous evaluation of the methodology;
- An analyte is conditionally assigned to a methodology on the basis of physical parameters, chemical judgment, and experience, but no data are available to define the performance of the assigned methodology;
- An existing methodology does not work or does not work well for a given analyte, but a modification of the methodology (i.e., substitution of HPLC/MS for GC/MS, substitution of basic impingers for sorbent in a sampling train) can produce acceptable performance for a given analyte when the modified methodology is evaluated; or
- No known sampling/analytical methodology has a reasonable expectation of successful performance; a completely new sampling/analytical method must be developed to obtain test data for the analyte.

Existing methodology must be evaluated for a wide variety of Clean Air Act Amendments analytes, to determine the range and limitations of existing methodology. To evaluate existing methodology the following steps are required:

- Establish a successful analysis. The applicability of the sampling methodology and the sample recovery cannot be evaluated until a given compound can be analyzed accurately and reproducibly.
- Evaluate the recovery of the compound of interest from the proposed collection media. Once the compound analysis is established, the ability to recovery the compound from the collection media can be evaluated and new recovery procedures developed, if required.
- Establish the collection ability of the proposed collection media. For example, if a sorbent is proposed as the collection medium and successful recovery from the sorbent and successful analysis of the analyte have been established, the ability of the sorbent to quantitatively collect the compound of interest must be evaluated. The collection ability of the medium can be established by dynamic spiking of the sampling train, incorporating as many of the characteristic source variables as possible. For example, if hot, wet, acidic sources are expected, this source environment can be created in the laboratory or located in the field, and dynamic spiking into replicate sampling trains with recovery and analysis will demonstrate that the sampling train does indeed collect the compound of interest quantitatively.

Results and Discussion

Compounds expected to be amenable to existing methods are shown in Table 1. Compounds expected to require development of specialized methodology or major modification of existing methodology are shown in Table 2, with the expected problem areas. Other analytes are discussed on an individual basis, to formulate suggestions for sampling and analytical approaches which may provide effective sampling/analysis for the analyte, e.g., diethanolamine.

Diethanolamine

Diethanolamine is a water-soluble compound used as an emulsifier and dispersing agent. Diethanolamine should be collected in a Method 0010 XAD-2®/water collection system. Because of the water solubility of diethanolamine, aqueous impingers may constitute a better collection system. Extraction of diethanolamine

Table 1. *Compounds Expected to be Amenable to Existing Methods without Modification Currently Being Tested in the Methodology Indicated*

SemiVOST (Method 0010/8270[1])	*VOST (Method 0030/5041)*	*Method 0011*
acetophenone	*acetonitrile*	*acetaldehyde*
2-acetylaminofluorene	*acrylonitrile*	*acetophenone*
benzidine	*benzene*	*acrolein*
biphenyl	*carbon disulfide*	*2-chloroacetophenone*
b9s(2-ethylhexyl) phthalate	*1,1-dimethylhydrazine*	*formaldehyde*
catechol	*1,4-dioxane*	*hydroquinone*
chlordane	*1,2-epoxybutane*	*isophorone*
2-chloracetophenone	*ethyl acrylate*	*methyl ethyl ketone*
cresols	*ethyl imine*	*methyl isobutyl ketone*
o-cresol	*hexane*	*propionaldehyde*
m-cresol	*methyl ethyl ketone*	*quinone*
p-cresol	*methyl isobutyl ketone*	
cumene	*methyl methacrylate*	
DDE	*methyl tert-butyl ether*	
dibenzofuran	*propylene oxide*	
di-n-butyl phthalate	*1,2-propyleneimine*	
dichlorvos	*triethylamine*	
N,N-dimethylaniline	*2,2,4-trimethylpentane*	
N,N-diethylaniline	*vinyl acetate*	
3,3'-dimethoxybenzidine		
dimethylaminoazobenzene		
3,3'-dimethylbenzidine		
dimethyl phthalate		
4,6-dinitro-o-cresol		
2,4-dinitrophenol		
2,4-dinitrotoluene		
1,4-dioxane		
ethylbenzene		
ethyl carbamate		
ethylene thiourea		
heptachlor		
hexamethylene-1,6-diisocyanate		
hexamethylphosphoramide		
hydroquinone		

Table 1. *Compounds Expected to be Amenable to Existing Methods without Modification Currently Being Tested in the Methodology Indicated (continued)*

SemiVOST (Method 0010/8270[1])	*VOST (Method 0030/5041)*	*Method 0011*
isophorone		
lindane		
maleic anhydride		
methoxychlor		
4,4'-methylene bis(2-chloroaniline)		
4,4'-methylenedianiline		
naphthalene		
nitrobenzene		
4-nitrobiphenyl		
4-nitrophenol		
N-nitrosodimethylamine		
N-nitrosomorpholine		
parathion		
phenol		
p-phenylenediamine		
phthalic anhydride		
1,3-propane sultone		
propoxur		
quinoline		
quinone		
styrene		
styrene oxide		
2,4-toluenediamine		
o-toluidine		
trifluralin		
xylenes		
m-xylene		
o-xylene		
p-xylene		

[1] Use of Method 8270 for an analytical method does not imply that all of the analytes listed in Method 8270 can be sampled successfully by Method 0010 or quantitatively extracted from XAD®. Method 8270 analytical conditions are applicable to a far wider range of analytes than the analytes amenable to the SemiVOST method.

Table 2. *Compounds Expected to Perform Poorly in Existing Methodology*

Compound	*Problem*
acetamide	*Very polar; chromatographs poorly*
2-acetylaminofluorene	*Polar; high molecular weight; solubility problems*
acrylamide	*Very polar*
acrylic acid	*Polar and reactive; does not chromatograph well on most GC columns*
acrylonitrile	*Very polar*
4-aminobiphenyl	*Polar; high molecular weight; solubility problems*
benzidine	*Polar and reactive; does not chromatograph well on most GC columns*
bis(chloromethyl)ether	*Polar, reactive; reacts with water*
1,3-butadiene	*Very volatile, very reactive*
caprolactam	*Very polar; chromatographs poorlyy using GC techniques*
captan	*Polar; chromatographs poorly by GC*
carbaryl	*Polar; reactive; chromatographs poorly ; poor GC/MS response*
carbon disulfide	*Volatile; polar; water-soluble*
carbonyl sulfide	*Reactive gas*
catechol	*Very polar and water-soluble; chromatographs very poorly on most GC columns*
chloroacetic acid	*Polar; reactive; reacts with water; chromatographs very poorly on most GC columns*
2,4-D, salts and esters	*Not all amenable to GC techniques; polar and reactive*
DDE	*Very reactive*
diazomethane	*Very reactive; polar; cannot be chromatographed as diazomethane*
3,3'-dichlorobenzidine	*Very polar; chromatographs poorly on most GC columns*
dichlorvos	*Polar; chromatographs poorly on most GC columns*
diethanolamine	*Very polar; chromatographs poorly on most GC columns*
diethyl sulfate	*Very reactive; chromatographs poorly on most GC columns*
3,3'-dimethoxybenzidine	*Very polar: high molecular weight; chromatographs poorly on most GC columns*
dimethylaminoazobenzene	*Very polar; chromatographs poorly on most GC columns*
3,3'-dimethylbenzene	*Very polar; chromatographs poorly on most GC columns*
dimethyl carbamoyl chloride	*Very polar; not amenable to GC techniques*
N,N-dimeylformamide	*Very polar; chromatographs very poorly on most GC columns*
1,1-dimethylhydrazine	*Very polar; reactive; chromatographs very poorly on most GC columns*
dimethyl sulfate	*Very polar; reactive; chromatographs poorly*
4,6-dinitro-o-cresol and salts	*Very polar; not all amenable to GC techniques*
2,4-dinitrophenol	*Very polar; reactive; chromatographs poorly on most GC columns*
1,2-diphenylhydrazine	*Very polar; reactive; decomposes to azobenzene in the injector port of the GC*
epichlorohydrin	*Very polar; water-soluble; reacts with water; chromatographs poorly on most GC columns*

Table 2. *Compounds Expected to Perform Poorly in Existing Methodology (continued)*

Compound	*Problem*
1,2-epoxybutane	*Polar; water-soluble*
ethyl acrylate	*Polar; water-soluble*
ethyl carbamate	*Polar; chromatographs poorly; poor MS response*
ethylene glycol	*Polar; water-soluble; chromatographs poorly on most GC columns*
ethyleneimine	*Polar; water soluble; reactive*
ethylene oxide	*Polar; water-soluble; reac ive; mass 44 difficult to analyze by GC/MS*
ethylene thiourea	*Polar; water-soluble; chromatographs poorly on most GC columns*
hexamethylphosphoramide	*Polar; chromatographs poorly on most GC columns; poor MS response*
maleic anhydride	*Polar; water-soluble; chromatographs poorly on most GC columns*
methanol	*Polar; water-soluble; volatile; mass 32 is difficult to analyze by GC/MS; requires a special column for good chromatography*
methoxychlor	*Polar; chromatographs poorly on most GC columns*
methyl hydrazine	*Polar; water-soluble; reactive*
methyl methacrylate	*Polar; water-soluble; volatile*
4,4'-methylene bis (2-chloroaniline)	*Polar; chromatographs very poorly on most GC columns*
4,4'-methylenedianiline	*Polar; chromatographs very poorly on most GC columns*
4-nitrobiphenyl	*Polar; chromatographs very poorly on most GC columns*
4-nitrophenol	*Polar; chromatographs very poorly on most GC columns*
2-nitropropane	*Polar; not amenable to GC analysis*
N-nitrosodimethylurea	*Very polar; chromatographs poorly on most GC columns*
N-nitrosodimethylamine	*Very polar*
N-nitrosomorpholine	*Very polar; chromatographs poorly on most GC columns*
p-phenylenediamine	*Polar; chromatographs poorly on most GC columns*
phthalic anhydride	*Very polar; reacts with water; chromatographs poorly on most GC columns; poor MS response*
1,3-propane sultone	*Very polar; chromatographs poorly on most GC columns*
ß-propiolactone	*Polar; reactive*
propoxur	*Polar; chromatographs poorly on most GC columns*
propylene oxide	*Polar; water-soluble; volatile*
1,2-propyleneimine	*Polar; water-soluble; volatile*
styrene	*Semivolatile, but styrene is a component of the XAD-2® polymer. Sampling styrene with Method 0010 may require a special polymer.*
2,4-toluenediamine	*Polar; water-soluble; chromatographs poorly on most GC columns*
o-toluidine	*Polar; water-soluble; chromatographs poorly on most GC columns*
toxaphene	*Multicomponent pesticide (at least 50-60 components); will require very sensitive and specific analysis, with pattern recognition*
triethylamine	*Polar; water-soluble; volatile; chromatographs poorly on most GC columns*
trifluralin	*Polar; chromatographs poorly on most GC columns; poor MS response*
vinyl acetate	*Polar; water-soluble; volatile*

from water by either an organic solvent or solid phase extraction techniques should be explored as an alternative to analysis by direct aqueous injection, because direct aqueous injection has high detection limits. The inability to perform GC/MS analysis of diethanolamine under Method 8270 analytical conditions has been demonstrated. Use of a polar gas chromatographic column may improve the analysis, or HPLC or HPLC/MS may be required for analysis of this analyte.

Individual evaluations of more than 90 Clean Air Act Amendments analytes are provided.

Conclusions and Recommendations

The following conclusions can be drawn from the literature studied for this program and from available method evaluation data:

- Performance of a given sampling/analytical methodology for a given analyte is strongly matrix-dependent. Availability of excellent method evaluation data at one particular source category does not establish that the methodology will always perform successfully for the analyte at any source. The only way to establish with complete certainty that a given methodology will perform successfully for a given analyte at a particular source is to demonstrate the efficacy of the methodology for the analyte, using some kind of field spiking technique.
- Because of the chemical properties of many of the Clean Air Act Amendments analytes (such as polarity or water solubility), standard analytical conditions such as those used in Method 8270 or Method 5041 will not provide an adequate analysis. New analytical approaches must be considered and evaluated.
- Multistep analytical procedures will be required for the broadest possible extension of the applicability of a given sampling methodology. For example, analytes collected on XAD-2® may be extracted by use of a sequence of solvents, extracts may be divided so an aliquot can undergo a derivatization procedure, sequential analysis on different chromatographic columns may be required, analysis by both GC/MS and HPLC/MS may be required. The alternative to multistep analytical procedures is the collection of multiple samples for individual analytical procedures.
- Alternative extraction techniques such as supercritical fluid extraction should be considered for Tenax® and XAD-2®, the most commonly used collection sorbents.
- Creative new sampling and analytical approaches are required to resolve the sampling and analytical problems posed by polar water-soluble compounds.
- The ultimate demonstration of a successful overall sampling/analytical method is the application of dynamic spiking procedures in a field test. The analyte(s) must be introduced as close to the tip of the probe of the sampling train as possible throughout the duration of the sampling process. In many cases for the compounds of interest, dynamic spiking procedures need to be developed and/or evaluated before they can be applied in the field.
- The applicability of broad-based methods such as VOST and Method 0010/8270 should be evaluated for the widest possible range of analytes to determine the range and limitations of these methods prior to the development of multiple methods for individual analytes.

Denny E. Wagoner, Raymond G. Merrill, Jr., James F. McGaughey, and Joan T. Bursey are with Radian Corporation, Research Triangle Park, NC 27709.
***Merrill D. Jackson** is the EPA Project Officer (see below).*
The complete report, entitled "Evaluation of CAAA Compounds Approaches for Stationary Source Method Development," (Order No. PB96-193206; Cost: $41.00, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Air Methods Research Division
National Risk Management Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

United States
Environmental Protection Agency
National Risk Management Research Laboratory (G-72)
Cincinnati, OH 45268

Official Business
Penalty for Private Use $300

EPA/600/SR-96/091

BULK RATE
POSTAGE & FEES PAID
EPA
PERMIT No. G-35