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Project Summary

Candidate Sampling and Analysis Methods for 21 Suspect Carcinogens in Combustion Emissions

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The report identifies candidate sampling and analysis methods for 21 suspect carcinogens in conventional coal and fuel oil combustion emissions. The methods were selected from an extensive review of existing techniques used to determine the substances in air and other matrices. In addition to identifying specific methods for each suspect carcinogen, the report describes a comprehensive sampling and analysis protocol which can be used to determine 13 of the suspect carcinogens. Costs for the separate candidate methods and for the comprehensive protocol are also provided.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, 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

The U.S. EPA's Office of Air Quality Planning and Standards (OAQPS) has listed 21 substances as having a high probability of being carcinogenic. The formation of these suspect carcinogens in combustion processes could consequently pose a significant health hazard. The presence of the 21 substances in combustion emissions must therefore be evaluated. The substances are:

acrylonitrile
arsenic
asbestos
benzene
beryllium
cadmium
diethylnitrosamine
dimethylnitrosamine
2,3,7,8-tetrachlorodioxin
ethylene dibromide
ethylene dichloride
ethylene oxide
formaldehyde
nickel
N-nitroso-N-ethyl urea
N-nitroso-N-methyl urea
perchloroethylene
polynuclear aromatic hydrocarbons (PAH)
trichloroethylene
vinyl chloride
vinylidene chloride

This report identifies candidate sampling and analysis methods which can be used to determine 21 substances in conventional coal and fuel oil combustion emissions. The sampling and analysis methods in this report provide an excellent reference basis for conducting this work.

The report presents a collaboration of independent efforts conducted by Battelle's Columbus Laboratories and Arthur D. Little, Inc. Each contractor had prepared a separate report describing the findings of their individual investigation to identify methods for determining the suspect carcinogens in combustion emissions. The information presented in the two separate reports is compiled in this report.

The report presents an overview of existing methodology used to determine the 21 substances and identifies the methods selected from this overview as appropriate for the sampling and analysis of the suspect carcinogens in combustion emissions. Additional material presented includes an evaluation of the combustion formation potential of the suspect carcinogens, a description of a comprehensive protocol for determining 13 of the substances in a single field study, and an estimation of costs for conducting each separate method on a single compound and for implementing the comprehensive protocol for determining 13 of the substances. Appendices supplement the overview of existing methodology in the body of the report by individually describing specific sampling and analysis procedures for the suspect carcinogens.

Summary

Combustion Formation Potential

The purpose of this initial effort was to determine the potential of the 21 suspect carcinogens for formation in combustion processes. Eight of the substances (trichloroethylene, formaldehyde, 2,3,7,8-tetrachlorodibenzodioxin, PAH, arsenic, beryllium, cadmium, and nickel) have been reported as being present in coal and fuel oil combustion emissions. The combustion formation potential of the remaining 13 substances was evaluated on the basis of thermodynamic stability, organic synthesis chemistry, and combustion conditions. The presence of acrylonitrile, benzene, vinyl chloride, and vinylidene chloride in combustion emissions was deemed reasonably or highly probable. Asbestos was also assessed as having a high probability of being present in combustion emissions since many older furnaces have exposed asbestos linings. The remaining eight substances were evaluated and determined to have a minimal potential for formation in combustion processes.

Overview of Existing Methodology

Existing sampling and analysis methodology for the 21 suspect carcinogens was reviewed to provide a basis for selecting candidate procedures for determining the substances in combustion emissions. Based on general requirements for air sampling, the features and previous applications of three major methods—EPA's Source Assessment Sampling System (SASS), EPA's Method 5 sampling train, and grab sampling—were reviewed. Each method was found to be successful for sampling one or more of the substances under consideration. Analytical methods reviewed included EPA Level 1 Environmental Assessment Procedures and other documented EPA methods. Additional analytical techniques reviewed included NIOSH procedures and several literature methods. Numerous methods were identified for determining the suspect carcinogens in water, soil, sediment, sludge, and other matrices. Few methods, however, had been specifically designed or validated for application to combustion emissions. Sampling and analysis procedures for asbestos were considered separately. Existing asbestos techniques were found to be time-consuming and often unvalidated.

Specific Sampling and Analysis Recommendations

Comparison and evaluation of the reviewed sampling and analysis techniques led to the selection of candidate methods for determining the 21 suspect carcinogens in combustion emissions. Precedence was given to previously validated methods. Recommendations for candidate sampling methods were restricted to proven air sampling methods since techniques for sampling water, soil, or other matrices would not apply. For the candidate analytical methods, techniques successfully used to determine the suspect carcinogens in other matrices were recommended when techniques had not been verified for analysis in air emissions.

The specific sampling and analysis methods recommended for the suspect carcinogens are listed in Table 1. Sampling recommendations primarily involved variations of EPA's SASS train, Method 5 train, and grab sampling methods. Separate procedures were recommended for arsenic and formaldehyde. Several sampling methods were suggested for asbestos since the reliability of any one method has yet to be proven. For analysis of the organic compounds, gas chromatography (GC), combined gas chromatography/mass spectrometry (GC/MS), and high performance liquid chromatography (HPLC) methods were included in the recommendations. Atomic absorption spectroscopy (AAS) was suggested for inorganic elements. For asbestos, analysis with transmission electron microscopy was recommended. The recommended sampling and analysis methods have not, in most cases, been subjected to necessary laboratory and field validations; however, the methods should provide reliable analyses of the concentrations of the suspect carcinogens in combustion emissions if employed with adequate quality control.

Comprehensive Sampling and Analysis Protocol

The candidate sampling and analysis methods are similar for several of the suspect carcinogens. To reduce the amount of effort required for determining the complete group of substances in a single source emission, combinations of redundant techniques were considered. A sampling and analysis protocol for a comprehensive field study was developed incorporating these combinations. The comprehensive protocol only accommodates those 13 suspect carcinogens which have been reported to exist or which have a reasonable to high probability of being formed in combustion emissions as determined in this report.

The sampling system for the comprehensive field study protocol is shown in Figure 1. The sampling system for the comprehensive field study protocol incorporates all EPA standard methods: (1) a SASS train or a high volume Method 5 train with an organic adsorbent column, (2) a midget impinger train similar to Method 6, and (3) an evacuated Tedlar bag sampling train similar to Method 106 with a bypass charcoal tube. Dioxin, PAH, the four metals, and asbestos are collected by the SASS or the Modified Method 5 train. Subsequent analysis would include combined GC/MS for dioxin and PAH, AAS for the metals, and electron microscopy for asbestos. The midget impinger train collects formaldehyde by derivatization with 2,4-dinitrophenylhydrazine. Analysis is conducted by GC or HPLC. The Tedlar sampling bag train collects the volatile organics and acrylonitrile. GC with flame ionization detection (FID) would be used to analyze these compounds.

An alternative to the comprehensive field study sampling and analysis protocol was also developed. This second protocol incorporates features to provide Level 2 environmental assessment information. The sampling system would be collected in a Tenax-GC sampling tube instead of a Tedlar bag. Analytical modifications include the use of GC/MS (for the volatile organics and formaldehyde) and GC with alkali flame detection, rather than FID (for acrylonitrile). The alternative protocol would provide a higher precision and accuracy than the original comprehensive field study protocol; however, the tech-

Table 1. Recommended Sampling and Analysis Procedures for 21 Suspect Carcinogens in Combustion Emissions

Compound	Sampling Method	Analytical Procedure
ORGANICS		
Acrylonitrile	*Charcoal Tube*	*GC/FID or GC/MS for specificity*
Benzene	*Tedlar bag/Gas bulb*	*GC/FID*
Diethylnitrosamine	*SASS Train/Sorbent*	*GC/FID*
Dimethylnitrosamine	*SASS Train/Sorbent*	*GC/FID*
Dioxin	*SASS/Modified Method 5 Train*	*GC/MS*
Ethylene Dibromide	*SASS Train/Sorbent*	*GC/FID*
Ethylene Dichloride	*Gas Bulb*	*GC/ECD*
Ethylene Oxide	*Charcoal Tube*	*GC/FID*
Formaldehyde	*Impinger (DNPII)*	*HPLC, GC, or GC/MS for identification*
Nitrosoethylurea	*SASS Train/Sorbent*	*HPLC with UV detection*
Nitrosomethylurea	*SASS Train/Sorbent*	*HPLC with UV detection*
Perchloroethylene	*SASS Train/Sorbent*	*GC/ECD*
PAH	*SASS/Modified Method 5 Train*	*GC/MS*
Trichloroethylene	*Tedlar bag/Gas bulb*	*GC/FID*
Vinyl Chloride	*Tedlar bag/Gas bulb*	*GC/FID*
Vinylidene Chloride	*Tedlar bag/Gas bulb*	*GC/FID*
INORGANICS		
Arsenic	*Method 5 Train/Modified Aerotherm HVSS system*	*Hydride Generation AAS*
Beryllium	*Method 5 train*	*AAS*
Cadmium	*Method 5 train*	*AAS*
Nickel	*Method 5 train*	*AAS*
ASBESTOS	*Filter*	*Transmission Electron Microscopy*

niques in the alternative protocol are not all EPA-approved.

Cost Model

Separate costs were calculated for individual analyses conducted on a single sample. In addition, a detailed cost model for the Level 2 comprehensive field study protocol was developed. The model was derived by establishing the labor, instrumentation, and laboratory capabilities needed to conduct each activity of a comprehensive field study such as planning, pre-site survey, sampling, sample delivery, data evaluation, and reporting. A cost matrix of capabilities versus activities was then generated which itemized each cost element and summarized the total costs.

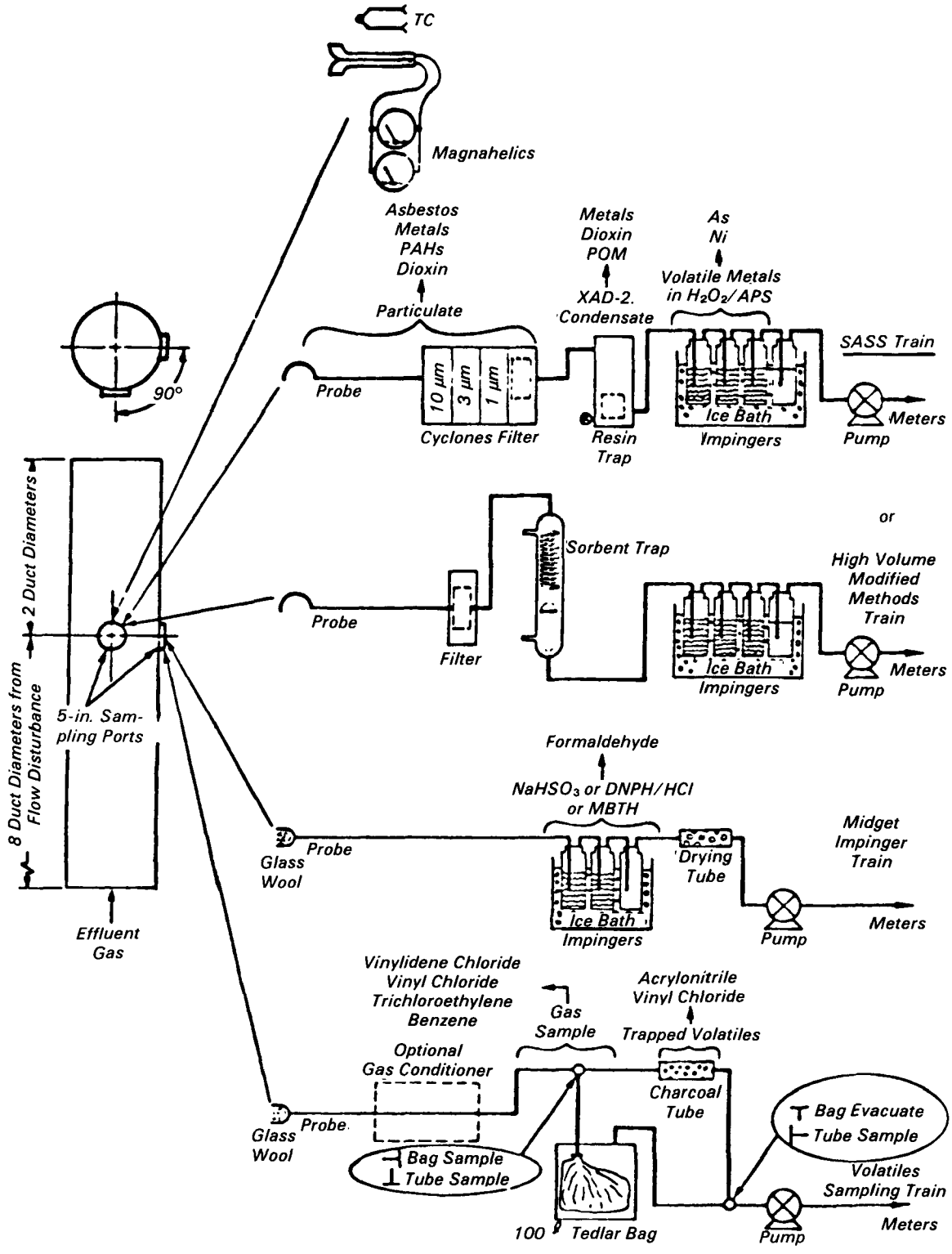

Figure 1. *Sampling system for comprehensive field study protocol.*

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The complete report, entitled "Candidate Sampling and Analysis Methods for 21 Suspect Carcinogens in Combustion Emissions," (Order No. PB 84-224 401; Cost: $17.50, subject to change) will be available only from:
National Technical Information Service
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