



Project Summary

A Literature Review on Occurrence and Methodology for Determination of Nickel, Chromium, Manganese, and Arsenic Species in Air

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A critical literature review of the state of the art for speciation of four metals in atmospheric samples was performed. The four metals of concern were arsenic, chromium, manganese, and nickel. Instrumental and wet chemical techniques for distinguishing the compound forms and valence states of these metals were critically assessed. Advantages and limitations of the various speciation approaches were addressed and recommendations are provided for future research to develop speciation procedures.

Three basic types of speciation procedures identified were: a) direct analysis of particulate matter, b) speciation of inorganic compounds after dissolution, and c) sequential or selective extraction. Direct analysis techniques offer the possibility of determining specific compounds. However, such techniques are often limited in terms of sensitivity and frequently only surface concentrations can be determined. The latter two techniques cannot determine specific inorganic compounds because of the inclusion of a dissolution step. However, such techniques may give useful information and are more generally applicable than direct analysis techniques. In a few cases (e.g., arsine), compounds may exist in the gas phase

and can therefore be readily distinguished from other compound forms of the element.

The literature review included manual searches of Chemical Abstracts, Citations Index, Analytical Abstracts, Air Pollution Abstracts, and selected environmental journals. Literature from the period 1968-1983 was included in the survey.

This Project Summary was developed by EPA's Environmental Monitoring Systems 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

There is an increasing awareness by environmental scientists of the importance of analytical methodologies which differentiate and determine the chemical forms of metal pollutants in the ambient atmosphere and near point emission sources. This is due to the great differences in health effects of different forms of the same element, e.g., As(III) and As(V). Potentially the trace metals of interest can be present in compound forms in the gaseous phase and in both compound and nonstoichiometric solid

phases. The latter are much more common for the elements of concern in this study, i.e., As, Cr, Mn, and Ni. However, nickel carbonyl, arsine (AsH_3), and cyclopentadienyl manganese tricarbonyl might be found in the gas phase near some specific sources.

Speciation of environmental samples is a very difficult inorganic analytical problem for several reasons. The chemical compositions of atmospheric pollutant samples are very complex, containing some 70 to 80 detectable elements which may combine to form hundreds of chemical compounds and thousands of mixtures. The concentrations of the trace elements in the atmosphere are low, e.g., at $\mu\text{g/g}$ levels in particulate matter, thus frequently taxing sampling and analytical capabilities to provide reliable determinations of even the total elemental content. The commonly used analytical methods are designed to provide elemental analyses, not information on compound type or valence states. Other techniques yield information on types of ions present. However, both ionic and elemental techniques commonly break down the inorganic forms into their ionic or atomic states by procedures that change the chemical forms of the sample to facilitate the determination of the total concentration of the element. Until recently there has been little substantive interest in funding the development of analytical efforts necessary to differentiate between trace metal compound species in any media, particularly in air samples. Finally, atmospheric samples often contain components that can interact rapidly with each other necessitating use of sampling methodologies that would minimize such interactions and preserve the integrity of the components as they exist in the ambient air or source emissions. In general, covalent inorganic species exist as discrete compounds, are frequently volatile at ambient temperature, and may be determined by techniques used in organic analysis. These species will be found predominantly in the gas phase or perhaps adsorbed on particulate matter. However, the majority of the metal species of interest will be found in ionic compounds or nonstoichiometric mixtures in the particulate matter. Some of these ionic compounds and mixtures are not soluble in mild solvents and very strong reagents are required to dissolve them.

Despite the difficulties cited above, some efforts have been made to develop and apply methodologies for the determination of metal species in atmospheric

samples. It was the objective of this program to conduct a comprehensive and critical review of the relevant information in the published literature on the subject of certain metal species occurring in the air and methods for determining these species. The metals of interest are As, Cr, Ni and Mn. Some specific compounds, deemed of particular interest by the U.S. EPA Project Officer, were included in the review. Determinations of both the valence states (oxidation states) of these metals and the type of metallic compounds are of interest.

Conclusions and Recommendations

The most significant conclusion of this study is that very few analytical techniques show promise for the determination of specific inorganic compounds in ambient air. Indeed, the most reliable compound methods would apply only to volatile species (e.g., gas chromatography). Instead, one must rely on less specific methods which provide information concerning valence state (e.g., solubility in various extractive media), to infer the inorganic compound originally present. In virtually all cases cation and anion analysis data (e.g., by atomic absorption spectroscopy, ion chromatography) must be gathered to aid in the interpretation of data from speciation techniques.

The speciation methods described in the literature can be roughly classified into three groups as summarized below:

- (a) Direct analysis of the particulate material.
- (b) Speciation of inorganic components after dissolution.
- (c) Sequential or selective extraction and analysis.

Direct analysis techniques include X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA), X-ray diffraction (XRD), and secondary ion mass spectroscopy (SIMS). The direct analysis techniques offer the possibility of determining specific inorganic compounds whereas the other two approaches cannot due to the dissolution process. However, most of the direct analysis techniques suffer from one or more of the following limitations: (a) detection of only surface compounds, (b) poor sensitivity, (c) detection of only crystalline materials, and (d) poor discrimination between similar inorganic compounds. Some direct analysis applications have been reported for Cr, Mn, and Ni compounds. However, much more re-

search must be conducted to establish whether or not such approaches could be applied to ambient air analysis.

Speciation procedures for dissolved inorganics, particularly in water samples, have been widely reported for arsenic, and these methods appear to warrant further study. The particular extraction process preceding the application of these techniques must be validated using authentic compounds with known valence states to ensure preservation of the original form of the element of interest.

Selective and/or sequential extraction procedures have been widely applied to solid samples but have not been validated. These schemes appear to be promising due to their simplicity and relevance to health effects, but require extensive validation of the methodology.

On the basis of the findings of this study, the areas which appear most promising for speciation of the elements of interest are:

As—Solution phase procedures such as electrochemistry and chromatography have considerable promise for arsenic speciation. Further studies need to be conducted to develop and evaluate extraction procedures which can dissolve the arsenic compounds completely without altering their form (e.g., valence state).

Cr—X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) shows some promise for Cr speciation but is limited in that only surface analysis data are obtained. Solution phase techniques suffer from the difficulty encountered in attaining quantitative dissolution of Cr in the sample. Various colorimetric and electrochemical procedures are suitable for distinguishing Cr(III) and Cr(VI), if suitable dissolution procedures can be identified. Further research should be conducted to compare the performance of several of these methods for ambient air analysis. The extraction approach employed would also require validation using authentic compounds of interest.

Mn—Very few promising approaches are available for Mn speciation. Negative ion secondary ion mass spectroscopy (SIMS) may warrant further evaluation. Electron spin resonance (ESR) and nuclear magnetic resonance (NMR) are also worthy of at least cursory evaluation. Solution phase speciation methods do not appear promising. Consequently,

sequential and/or selective extraction is probably the most useful area for further research. Several such schemes have been reported and should be further evaluated and/or refined using authentic Mn compounds of interest.

Ni—Selective and/or sequential extraction appears to be the most promising area for further research. A few direct analysis methods such as X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS) and solution phase speciation procedures such as high performance liquid chromatography (HPLC) after complexation may also warrant further study.

In view of the lack of routine, validated methods for the inorganic compounds of interest, any further work in this area should apply several alternate approaches to determine the validity of the data. In addition, elemental and anion data must be collected to aid in the interpretation of data from speciation procedures.

There are more effective techniques available for speciation of volatile inorganic compounds than for the non-volatile species. Volatile metal carbonyls can be separated from particle bound metal compounds during the sampling process. Instrumental methods such as chemiluminescence, mass spectrometry, and gas chromatography with element specific detection appear to offer good sensitivity for these volatile species. These methods warrant further evaluation and refinement.

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The complete report, entitled "A Literature Review on Occurrence and Methodology for Determination of Nickel, Chromium, Manganese, and Arsenic Species in Air," (Order No. PB 84-172 105; Cost: \$10.00, subject to change) will be available only from:

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