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REVIEW OF A WORKSHOP ON
X-RAY FLUORESCENCE ANALYSIS OF AEROSOLS
April 4-6, 1973
Battelle Seattle Research Center
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J. A. Cooper,
Chairman

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June 1, 1973

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REVIEW OF A WORKSHOP ON
X-RAY FLUORESCENCE ANALYSIS OF AEROSOLS

PREFACE

The utility of X-ray fluorescence will be determined by its applicability to current problems and its analytical merits relative to other possible methods of analysis. Aerosol analysis is a current problem area where X-ray fluorescence is clearly applicable. However, the capabilities and limitations of general X-ray fluorescence analysis have not been well established for this particular application and the relative merits of energy dispersive X-ray fluorescence analysis are just beginning to be understood.

A small group of investigators actively involved with quantitative X-ray fluorescence analysis of aerosol trace elements met for a three day workshop at the Battelle Seattle Research Center on April 4, 1973 to discuss X-ray fluorescence analysis of aerosols. The major objectives were to define the boundary conditions within which X-ray fluorescence can produce reliable quantitative information, define future innovations which would significantly improve the technique's capability, and suggest ways to improve the general acceptance of X-ray fluorescence.

This report summarizes the workshop results and is a product of the efforts of all the participants.

J. A. Cooper,
Chairman

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REVIEW OF A WORKSHOP ON
X-RAY FLUORESCENCE ANALYSIS OF AEROSOLS

SUMMARY

Twenty-eight participants attended and contributed to a three day workshop on X-Ray Fluorescence Analysis of Aerosols. Aerosol sampling techniques, methods of X-ray excitation and analysis, quantitative procedures, and other independent methods of analysis were discussed.

It was generally agreed that of the energy-dispersive X-ray fluorescence techniques, mono-energetic photon and proton excitation offer the best detectabilities. Proton excitation appears to offer greater sensitivity for the analysis of small quantities of material on thin backings while photon excitation appears more versatile and applicable to thicker samples. Wavelength-dispersive X-ray fluorescence seemed to have better detectability for low atomic-number elements and is generally applicable to aerosol analysis.

It was also generally accepted that X-ray fluorescence analysis has demonstrated an ability to provide definitive quantitative analysis for up to 18 elements in urban aerosols (Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sr, Zr, Mo, Cd, Sn, Ba and Pb) and semi-quantitative analysis for up to 9 low atomic-number elements (Na, Mg, Al, Si, P, S, Cl, K and Ca). Membrane filters were generally preferred for X-ray fluorescence analysis. Standards and correction factors used are adequate for most elements but must be established for elements below Ti. Current computer programs are adequate for the more abundant elements, but further work is required for effective analysis of low intensity and complex peaks. The publication of additional quantitative results and quantitative intercomparison studies would greatly advance the general acceptance of X-Ray fluorescence as a quantitative tool for aerosol analysis.

INTRODUCTION

Suspended particulate matter in air is recognized as a major pollutant which can have a pronounced effect on health and the environment. Toxic trace elements such as Be, F, V, As, Se, Cd, Sb, Hg and Pb are associated with air pollutants and are derived from a wide spectrum of natural and anthropogenic sources. Many of these pollutants are generated in localized urban areas and may produce serious regional effects, while others are carried great distances and contribute to the hemispheric and worldwide air-pollution problems. If abatement efforts and the ecological and health effects of atmospheric trace elements are to be accurately understood and evaluated, it is essential that their baseline concentration, origin, transport and ultimate fate be investigated and monitored. The number of practical aerosol trace element investigations has been limited because they require multielement analysis of large numbers of samples. Monitoring activities of the Environmental Protection Agency and state agencies are likely to require the analysis of several hundred thousand samples each year while other agencies, programs and investigations collectively may require a similar number of analyses.

Although none of the available analytical techniques is capable of measuring all elements of interest in their normal concentration ranges, X-ray fluorescence (XRF) can provide definitive measurements for many of these elements and can place relatively small upper limits on many other elements required. It also has the potential of providing the rapid, nondestructive, low-cost multielement analysis capability required to monitor and investigate the behavior of atmospheric pollutants. Although extensive aerosol analysis programs using XRF have been initiated in the last year, there is little published information to aid in choosing the particular instrumentation, standards and other analytical parameters required to measure a particular group of elements on a specific type of aerosol collection media.

This report is a review of the workshop discussions which covered many of the current problems related to quantitative XRF analysis of aerosols.

DISCUSSION

SAMPLING TECHNIQUES, COLLECTION MEDIA AND SAMPLE PREPARATION

The lower limits of detection (ng/m^3) and the quantitative capability of XRF analysis of aerosol trace elements are strongly dependent on the sampling procedure. These detection limits depend primarily on the volume of air sampled per cm^2 of collection substrate and the substrate mass per cm^2 . The detection limits of other analytical techniques such as instrumental neutron activation analysis (INAA) and atomic absorption spectrometry (AAS) are determined mainly by the total volume of air sampled and blank interference levels. The ability of XRF to quantize an element is related to the depth of deposition within the sampling media and aerosol loading per cm^2 . The quantitative analysis of filters and particle-sized aerosol samples from impactors was discussed in terms of the sampling technique's ability to quantitatively collect aerosols and the ability of XRF to quantitatively analyze the resulting samples.

FILTERS

The various types of filters discussed included glass fiber, Whatman 41, IPC, Millipore, Gelman cellulose ester, and Nuclepore. Although glass fiber filters have good aerosol sampling properties such as strength, efficiency, reproducible tare weight, and flow-rate capabilities, they were considered unacceptable for non-destructive XRF analysis because of the high concentrations of trace elements in the blank and its high mass per cm^2 . Whatman 41, currently being used in many urban aerosol analysis programs, has one of the lowest trace element contents but its areal density is relatively high (8 mg/cm^2). It has poor efficiency at low face velocities and the aerosol can deposit at varying depths within the filter, seriously reducing the accuracy of analysis for measuring elements below V because of uncertainties in the X-ray absorption correction. The IPC filter commonly used for high-altitude aerosol sampling where its filtering efficiency is high at the high face velocities used, has low efficiencies at low face velocities and similar negative characteristics to Whatman 41.

It was generally felt that Millipore, Gelman cellulose ester

and Nuclepore membrane filters are the most desirable for XRF analysis. These membrane filters have the advantages of low areal densities and minimum X-ray absorption due to substrate. Millipore filters have good filtering efficiencies even at low face velocities but somewhat higher blank elemental content than either Nuclepore or Whatman 41. The Millipore blank levels are usually not high enough, however, to cause serious interferences with typical urban aerosol samples. Nuclepore would probably be preferred when detectability is a problem because of its low areal density (1 mg/cm^2), minimum X-ray absorption and low trace element content. However, a high face velocity must be achieved to assure a high aerosol collection efficiency.

Quantitative XRF analyses, verified by independent methods, have been obtained for aerosols on Whatman 41 for elements down to V using thin film assumptions while verified quantitative results have been obtained down to Ti using Millipore. It is expected that with good X-ray absorption corrections, quantitative results will be attainable down to about Cl on membrane filters.

PARTICLE-SIZE SAMPLERS

The types of particle-size samplers discussed included the Andersen, Scientific Advances and Lundgren impactors. An untested sampler by Environmental Research was also considered which is designed to separate particles according to aerodynamic characteristics similar to Andersen impactors. Instead of impacting on a surface, the particles pass through a hole into a chamber and are drawn through filters providing a uniform deposit that could be readily analyzed by XRF. The only other impactor capable of providing a uniform deposit is the Lundgren impactor. If the excitation beam diameter is small, the Lundgren can yield information on the time of deposition. The Scientific Advances instrument produces deposits less than 1 cm in diameter which can be analyzed directly by XRF. The Andersen forms a large number of dots on each stage which are difficult to analyze by XRF without some sample preparation. Although the Scientific Advances impactor has lower flow rates, it was considered to have sharper particle size cutoff values and lower wall losses than the Andersen and Lundgren impactors. The Lundgren was the only impactor capable of giving a continuous

time variation with a uniform deposit. Jerry Wesolowski presented convincing evidence which clearly established the need to coat impaction surfaces with a sticky material to minimize particle bounce off.

Recommendations

1. The potential sensitivity and detectability of XRF could be improved if a low mass filter can be developed with a low trace-element blank and appropriate sampling parameters such as high efficiency and high flow rate.

2. Significant improvements in particle-sized analysis of aerosols by XRF could be realized with improved impactors having sharper particle size cutoff diameters, and uniform deposits.

METHODS OF X-RAY EXCITATION AND ANALYSIS

The different methods of X-ray fluorescence analysis discussed are outlined in Figure 1. Each category is distinguished by either:

FIGURE 1 - METHODS OF XRF EXCITATION AND ANALYSIS

the method used to excite the characteristic sample X-rays and/or the method used for their analysis. While wavelength-dispersive X-ray fluorescence (WDXRF) has been evolving as an analytical tool over the past 25 years, energy dispersive X-ray fluorescence (EDXRF) has only recently been applied extensively as an analytical tool because of the improved resolution performance of solid state detectors. It is often difficult to make a knowledgeable decision as to the optimum method for a particular problem because of the many variations of this general technique. The object of this session was to discuss the relative merits of the various methods of XRF analysis as applied to trace element analysis of aerosols.

It was the general consensus that of the EDXRF methods discussed, mono-energetic photon excitation and proton excitation demonstrated the best general sensitivities, alpha particle and bremsstrahlung excitation were considered less sensitive while electron excitation was not considered competitive for trace element analysis. Mono-energetic photon and proton excitation techniques have demonstrated detectabilities equivalent to about 1 ng/m^3 of air. There is some uncertainty as to which of the two techniques is optimum for specific applications. There is, however, a general feeling that photon excitation is more versatile and applicable to analysis of thick filters where maximum counting rates can be achieved. Proton excitation is considered better for the analysis of thin samples for which current photon technology is unable to provide high enough excitation intensities. Some of the participants thought protons could provide better sensitivities for elements below about Ca.

The 3σ interference-free detection limits for 5-minute analyses of material deposited on 5 mg/cm^2 filter media were compared for many of the analytical variations. The minima in the detectability vs atomic-number curves for all methods occurred between 1 and 10 ng/cm^2 . These minima could be moved to other atomic-number regions by using different secondary exciters, energy particles, or crystal-target arrangements. The WDXRF systems appeared to have the best detection limits for low atomic-number elements (<21) because of low bremsstrahlung background interference and high resolution; however, the lower limits of detection increased as much as tenfold for higher atomic-number elements because of increased bremsstrahlung

interference, reduced bremsstrahlung excitation intensity and decreased resolution. The radioisotopic exciters when limited to a 5-minute analysis exhibited a relatively poor detectability minimum because of their limited excitation intensity. Other mono-energetic photon-excitation sources are currently unable to attain maximum detectabilities per unit time with thin samples such as Nuclepore filters because of limited excitation intensities. The detectabilities discussed are for interference-free sensitivities which should be reasonable for WDXRF systems but may not be representative of EDXRF systems where unresolved lines are common. In addition, the 5-minute counting intervals used to calculate the sensitivities will be significant only when there are either too many samples to analyze in the allotted time or when increased exposures significantly increase the cost, or damage the sample.

One unique capability of particle-excitation systems discussed was their ability to form a highly collimated beam which could be used to study single particles or spatial characteristics such as the time-related deposits on a Lundgren impactor drum.

The estimated cost of an urban aerosol analysis, yielding definitive, quantitative results for 10 to 18 elements ranged from \$2 to \$15 per sample. However, many of these estimates were based on a hypothetical annual program of about 100,000 samples and were not based on long standing experience of analyzing routine samples.

Recommendations

1. Although a new appreciation was obtained for the relative capabilities of WDXRF and EDXRF analysis, as well as for photon and proton excitation, further studies are required to define each technique's optimum area of application. Probably the best method for establishing these relative capabilities is the analysis and publication of verified results for a large number and variety of typical aerosol samples.

2. Development of a high-powered, pulsed, mono-energetic photon source would provide a significant improvement in the capability of EDXRF analysis.

QUANTITATIVE ANALYSIS

SPECTRAL ANALYSIS AND COMPUTER AUTOMATION

One of the main advantages of the EDXRF analysis method is its rapid data accumulation rate. This capability cannot be fully utilized unless data analysis (spectral analysis and quantitative calculations) is short relative to accumulation rate. A variety of computer-based data analysis programs are currently being used.

Simple Peak Stripping routines consisting of two-point peak integrations with background subtraction and elemental interference compensation are being routinely used. Although it is difficult to analyze low-intensity peaks with overlapping lines, it provides acceptable accuracy for the more intense lines and can be adequately implemented with a minicomputer.

Library Techniques that reference an elemental response library are being used. The simplest approach is to strip the background and the single-element response spectra. This technique currently is being used successfully but it has the disadvantage that a complete high precision library must be measured and changes in detector resolution may cause anomalies. Errors are accumulated and not minimized during the stripping procedure.

A more general approach is to fit the measured spectrum with library response functions using a least squares regression method. Errors in the library, gain shifts, resolution broadening, and other effects propagate as errors in the fitted results; however, this seems to be a useful and powerful technique and may be readily implemented using available software for either large or small-scale computers.

Peak Fitting computer codes which use complex peak-fitting techniques such as those developed for gamma-ray analysis offer the most general approach to spectrum analysis. Application of these methods to the analysis of X-ray spectra is in an early stage of development, but show considerable promise.

Recommendations

1. Compare the various stripping and library techniques and improve their efficiency for use on a minicomputer.

2. The large-scale techniques using Gaussian peak and complex background fitting require much additional work to achieve operational status. Automated means of background estimation and multiple peak stripping by this technique need to be studied and verified.

3. Develop spectral analysis procedures for accurate determination of low intensity and overlapping peak areas.

ENHANCEMENT, ABSORPTION, PARTICLE SIZE AND LOADING EFFECTS

Enhancement of characteristic X-rays by higher energy characteristic X-rays, self-absorption of characteristic X-rays in the particulate deposit and collection substrate, and errors due to particle size and particle composition variation were discussed. These are the main sources of error in quantitative analysis of air particulates. The objective was to discuss methods of reducing such errors.

It was generally agreed that enhancement effects are negligible; whereas absorption, particle size and loading effects can be large for elements below about Ca. The filter material is the dominant source of characteristic X-ray absorption for aerosol particulates deposited at varying depths within glass and cellulose fiber filters and may be significant for elements below Fe. Whatman 41 absorption correction factors for solution standards have been estimated to be 1.4 for V and 20 for Al; urban aerosols which deposit preferentially toward the front surface of the substrate would require smaller correction factors. Absorption in the substrate is negligible for mylar and membrane media since the particles are deposited essentially on the surface. Self-absorption in the actual aerosol deposited is small for elements above K for deposits less than a few hundred $\mu\text{g}/\text{cm}^2$. Methods of minimizing these errors ranged from using theoretical absorption-correction factors to making multicomponent standards duplicating as near as possible the aerosol-filter matrix.

Particle-size and composition effects are expected to be small for elements above Ca. For lower atomic-number elements, the effect may be large and may vary considerably with the composition of the particles. Particle-size effect models presented by both Birks and

Rhodes suggest significant problems for the determination of elements around S. The actual seriousness of the size effects has yet to be demonstrated by comparison of quantitative XRF results with those obtained by other analytical techniques.

Recommendations

Detailed quantitative intercomparisons with other techniques are needed to elucidate the magnitude of absorption, particle size and composition effects as functions of exciting radiation, substrate and characteristic X-ray energy.

STANDARDS

Standardized samples for XRF analysis of aerosols should closely approximate the actual sample to minimize possible absorption and particle size differences. A variety of uniformly deposited standards of known mass per cm^2 , however, have been shown to be adequate for quantitative analysis of elements above Ca, whereas low atomic-number element standards have yet to be established and verified. The diversity of excitation sources and geometries, the large variety of collection surfaces used for aerosol sampling, the lack of availability of standard reference material, the relatively large effort required to perfect a method involving preparation of powdered deposits and poor communication between investigators have hindered the adoption of a single standard preparation procedure.

A variety of primary gravimetric standards, standard reference samples and their methods of preparation were discussed and are summarized below.

Solution Evaporation consists of the deposition of gravimetrically determined quantities of elements by solution evaporation on filters. Such variations as "single spot," "multiple spot," and "freeze-dried spot" are descriptive of methods used to provide a uniform deposit. All of these standards have been demonstrated to be adequate for the quantitative determination of high atomic-number elements. These standards, however, should not be applied to elements below about Fe without corrections for absorption differences, since the standard elements are uniformly deposited throughout the filters while aerosols may be deposited on the surface of a membrane filter or in

nonuniform manner in a fibrous filter.

Vacuum Deposition of inorganic compounds as thin films on mylar has been shown by several laboratories to be adequate for determination of aerosol trace elements.

Other standard preparation techniques discussed included aqueous filtration of uniformly dispersed insoluble salts and pellet preparation from a cellulose mixture of inorganic salts. Although these were considered adequate for some elements, they were not considered as desirable as either solution evaporation or vacuum deposition.

Standard Samples consist of reference materials deposited on aerosol collection substrates to simulate aerosol samples. The particles are transferred to the collection media by either the puff deposition technique proposed by Bob Giaugue or the method of collection from artificial aerosol chambers proposed by John Rhodes. Although standard aerosol samples are useful, there can be uncertainties in the composition of the deposited material due to possible variations in particle collection efficiencies.

Recommendations

1. Standardization procedures for low atomic-number elements should be emphasized with special attention to problems associated with particle-size and chemical-composition variations.
2. The National Bureau of Standards should prepare enough simulated aerosol samples for multiple laboratory comparisons.
3. To be of maximum benefit for XRF, future NBS standardized samples simulating aerosols should closely approximate the composition, particle size, and deposition pattern of actual aerosol samples.
4. Another workshop should be held in August during the Denver X-Ray Conference to discuss standards and intercomparison results.

COMPARISON OF QUANTITATIVE RESULTS

Results of a rough intercomparison study were reported and discussed. The purpose of the intercomparison was to help establish

the elements that can be quantitatively measured by XRF, to establish their accuracy and precision, and to provide a foundation for the discussion of quantitative problems related to the analysis of aerosols on different collection substrates. The samples analyzed included: (1) San Francisco Bay area aerosol on Whatman 41, (2) high altitude aerosol on Kronisol-treated IPC 1478, (3) St. Louis aerosol on Kronisol-treated IPC 1478, (4) Japanese basalt on millipore, (5) multielement solution standard on Whatman 41, (6) Corpus Christi aerosol on Whatman 41, (7) Richland aerosol on 1/4 mil mylar Lundgren 4th stage, (8) Richland aerosol on 1/4 mil mylar Lundgren 3rd stage, (9) Richland aerosol on Nuclepore, and (10) Pacific aerosol on Nuclepore. Although these samples were not ideal, most of them were real samples similar to ones routinely analyzed.

The samples were shipped to three laboratories, analyzed and then returned to the first laboratory for reanalysis; they were then divided into thirds and redistributed to the other laboratories. Although nine groups reported results for most of the ten samples, the study was incomplete since not all participants analyzed the samples and not all samples were analyzed by those reporting results. This intercomparison must be considered a rough study because of the incomplete analysis and because sample integrity was not rigorously maintained; the results, therefore, reflect the errors in the intercomparison method as well as errors in the analytical techniques.

Results were reported for INAA, AAS, WDXRF and EDXRF using proton and alpha-particle excitation, secondary and transmission tube excitation and radioisotopic sources. Some of the samples lost small amounts of material during shipment, different pieces of the same filter were sometimes analyzed, and many of the analyses were made under far from optimum conditions. The results, however, were usually within 20 percent and rarely deviated more than 40 percent for the more abundant elements.

The aerosol elements detected and quantitatively measured by XRF are listed in Tables I and II. Of the 18 elements listed in Table II as having been quantitatively measured in typical urban aerosol samples (see Appendix C) by XRF, 7 are either questionable, highly

interfered with by other elements or only occasionally observed, leaving 11 elements which are routinely measurable under current conditions. As XRF instrumentation and quantitative techniques progress, not only will it be possible to routinely measure more of the 18 elements listed in Table II, but more of the low atomic-number elements listed in Table I will be included in Table II as quantitatively measurable.

TABLE I. ELEMENTS DETECTED IN URBAN AEROSOLS BY XRF BUT NOT QUANTITATIVELY MEASURED

Na	S (Pb)
Mg	Cl
Al	K
Si	Ca

() Common interfering elements

TABLE II. ELEMENTS QUANTITATIVELY MEASURED IN URBAN AEROSOLS BY XRF

Ti	Cu	Zr
V (Ba, Ti)	Zn	Mo*
Cr	As (Pb)	Cd?
Mn	Se?	Sn*
Fe	Br	Ba
Ni*	Sr	Pb

* Measured occasionally

? Detection questioned

() Common interfering elements

Recommendation

A more refined and controlled intercomparison of gravimetric standards and standard samples should be conducted to test the present state-of-the-art in quantitative analysis. (John Rhodes has already begun this intercomparison by mailing sets of well characterized standards to workshop participants and other interested investigators. The results will be presented and discussed in August at the Denver X-Ray Conference).

OTHER METHODS OF AEROSOL ANALYSIS:
INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS
AND ATOMIC ABSORPTION SPECTROMETRY

The sensitivity of standard flame AAS compares favorably with XRF and INAA for many elements and has higher sensitivities for some light elements and particularly Cd; however, it requires the sampling of large volumes of air ($\sim 100 \text{ m}^3$). A preliminary cost and time analysis suggests that a multielement analysis by AAS would be comparable to INAA but would require a longer time and cost more than XRF. In addition, AAS is a destructive technique and there are more difficulties in sample preparation than with either XRF or INAA. Although flameless AAS has greater sensitivity, it was not considered a routine analytical tool which would be acceptable to multielemental analysis of large numbers of aerosol samples.

INAA does not have the matrix and absorption difficulties that are common to XRF; it also has much higher sensitivity for most elements with the notable exceptions of Cd and Pb. Although INAA can routinely provide positive measurements for 25 to 35 elements in urban aerosols, the cost per analysis is higher than for XRF and its turn-around time for a complete analysis is longer. If only the elements measured with short-lived activities are reported, INAA can provide positive information on about ten elements at a considerably reduced cost and at a comparable turn around time to XRF.

ACKNOWLEDGEMENTS

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LIST OF APPENDICES

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APPENDIX B WORKSHOP PARTICIPANTS

APPENDIX C URBAN AEROSOL TRACE ELEMENT RANGES
AND TYPICAL VALUES

APPENDIX D SELECTED REFERENCES AND X-RAY FLUORESCENCE
AND AEROSOL TRACE ELEMENTS

APPENDIX A

WORKSHOP PROGRAM

Wednesday, April 4

8:10 - 8:30

8:30 - 9:15

Welcome: J. A. Cooper
Introduction of Participants and Review
of Laboratory Programs and Facilities

Session Moderator:

R. Stevens

9:15 - 10:15

Standards I

Topic Introduction: N. Bonner

10:15 - 10:35

Break

10:35 - 12:00

Standards II

12:00 - 1:30

Lunch

Session Moderator:

R. B. Moler

1:30 - 3:00

Spectral Analysis and Computer Automation

Topic Introduction: J. Rhodes

3:00 - 3:20

Break

3:20 - 5:30

Absorption, Enhancement, Particle-Size
and Loading Effects

Topic Introduction: J. Rhodes

Thursday, April 5

Session Moderator:

J. A. Cooper

8:15 - 10:10

Comparison of Quantitative Results, I

Topic Introduction: J. Cooper

10:10 - 10:30

Break

10:30 - 12:00

Comparison of Quantitative Results, II

12:00 - 1:30

Lunch

1:30 - 3:30

Methods of Excitation and X-Ray Analysis, I

Topic Introduction: L. Birks

3:30 - 3:50

Break

3:50 - 5:30

Methods of Excitation and X-Ray Analysis, II

Friday, April 6

Session Moderator:

J. A. Cooper

8:15 - 10:00

Aerosol Sampling Techniques, Collection
Media and Sample Preparation for Optimum

X-Ray Fluorescence Sensitivity, I

Topic Introduction: T. Cahill

10:00 - 10:20

Break

10:20 - 12:00

Aerosol Sampling Techniques, Collection
Media and Sample Preparation for Optimum

X-Ray Fluorescence Sensitivity, II

12:00 - 1:30

Lunch

1:30 - 3:00

Other Methods

3:00 - 3:20

Break

3:20 - 5:30

Preparation of Summary

APPENDIX B

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APPENDIX C

URBAN AEROSOL TRACE ELEMENT RANGES AND TYPICAL VALUES

The elements for which an analytical tool can provide positive results are of prime concern when evaluating its application to a particular problem. To complete this evaluation, ranges and typical concentrations in the samples of interest must be known in addition to sensitivities and interferences of the analytical technique.

Trace element ranges and typical concentrations found in urban aerosols are illustrated in Figure C-1, constructed from the references listed. This information, the sensitivities (Section II) and the elements already detected and measured (Table I, Section IV-D) can be used to predict those elements which should be measurable by XRF.

FIGURE C-1

URBAN AEROSOL TRACE ELEMENT RANGES AND TYPICAL VALUES

REFERENCES FOR FIGURE C-1

1. Aras, N. K., W. H. Zoller, G. E. Gordon, G. J. Lutz, "Instrumental Photon Activation Analysis of Atmospheric Particulate Material". Preprint from G. E. Gordon, Univ. of Maryland, College Park, Maryland (January 1973).
2. Anthanassiadis, Yanis C., "Air Pollution Aspects of Phosphorus and its Compounds," Litton Systems, Inc., Bethesda, Maryland, Clearinghouse for Federal Scientific and Technical Information, PB-188-073, U. S. Department of Commerce (September 1969).
3. Anthanassiadis, Yanis C., "Air Pollution Aspects of Vanadium and its Compounds," Litton Systems, Inc., Bethesda, Maryland, Clearinghouse for Federal Scientific and Technical Information, PB-188-093, U. S. Department of Commerce (September 1969).
4. Anthanassiadis, Yanis C., "Air Pollution Aspects of Cadmium and its Compounds," Litton Systems, Inc., Bethesda, Maryland, Clearinghouse for Federal Scientific and Technical Information, PB-188-086, U. S. Department of Commerce (September 1969).
5. Anthanassiadis, Yanis C., "Air Pollution Aspects of Zinc and its Compounds," Litton Systems, Inc., Bethesda, Maryland, Clearinghouse for Federal Scientific and Technical Information, PB-188-072, U. S. Department of Commerce (September 1969).
6. Cooper, J. A., Battelle-Northwest, Richland, Washington. Personal Communication (January 1973).
7. Dams, R., J. A. Robbins, K. A. Rahn, and J. W. Winchester, "Nondestructive Neutron Activation Analysis of Air Pollution Particulates," Anal. Chem. , 42, 861 (1970).
8. Durocher, N. L., "Air Pollution Aspects of Beryllium and its Compounds," Litton Systems, Inc., Bethesda, Maryland, Clearinghouse for Federal Scientific and Technical Information, PB-188-078, U. S. Department of Commerce (September 1969).
9. Eisenbud, M. and T. J. Kneip, "Trace Metals in the Atmosphere," Technical Paper No. 16, New York State Department of Environmental Conservation (1971).

10. Gordon, G. E., W. H. Zoller, E. S. Gladney and A. G. Jones, "Trace Elements in Urban Atmosphere," American Nuclear Society Topical Meeting on "Nuclear Methods in Environmental Research," University of Missouri, Columbia, Missouri (August 1971).
11. Giaugue, R. D., F. S. Goulding, J. M. Jaklevic, and R. H. Pehl, "Trace Element Analysis with Semiconductor Detector X-ray Spectrometers," Anal. Chem., 45, #4, 671, (April 1973).
12. Henry, W., and E. R. Blosser, Battelle-Columbus, Columbus, Ohio. Private Communication (January 1973).
13. Hwang, Jae Young, "Trace Metals in Atmospheric Particulates and Atomic Absorption Spectroscopy," Anal. Chem., 44, 20A (1972).
14. Kneip, T. J., M. Eisenbud, C. D. Strehlow, and P. C. Freudenthal, "Airborne Particulates in New York City," J. Air Pollution Cont. Ass., 20, 144 (1970).
15. Moyers, J. L., W. H. Zoller, R. A. Duce, and G. L. Hoffman, "Gaseous Bromine and Particulate Lead, Vanadium, and Bromine in a Polluted Atmosphere," Environ. Sci. Tech., 6, 68 (1972).
16. Rahn, K., J. J. Wesolowski, W. John, and H. R. Ralston, "Diurnal Variation of Aerosol Trace Element Concentrations in Livermore, California," J. Air Pollution Cont. Ass., 21, 406 (1971).
17. Rancitelli, L. A., Battelle-Northwest, Richland, Washington, Personal Communication (January 1973).
18. Rhodes, J. R., A. H. Pradzynski, C. B. Hunter, J. S. Payne, and J. L. Lindgren, "Energy Dispersive X-Ray Fluorescence Analysis of Air Particulates in Texas," Environ. Sci. Tech., 6, 922 (1972).
19. Stahl, Quade R., "Air Pollution Aspects of Selenium and its Compounds," Litton Systems, Inc., Bethesda, Maryland, Clearinghouse for Federal Scientific and Technical Information, PB-188-077, U. S. Department of Commerce (September 1969).
20. Sullivan, Ralph J., "Air Pollution Aspects of Iron and its Compounds," Litton Systems, Inc., Bethesda, Maryland, Clearinghouse for Federal Scientific and Technical Information, PB-188-088, U. S. Department of Commerce (September 1969).

21. Sullivan, R. J., "Air Pollution Aspects of Manganese and its Compounds," Litton Systems, Inc., Bethesda, Maryland, Clearinghouse for Federal Scientific and Technical Information, PB-188-079, U. S. Department of Commerce (September 1969).
22. Sullivan, R. J., "Air Pollution Aspects of Arsenic and its Compounds," Litton Systems, Inc., Bethesda, Maryland, Clearinghouse for Federal Scientific and Technical Information, PB-188-071, U. S. Department of Commerce (September 1969).
23. Sullivan, R. J., "Air Pollution Aspects of Nickel and its Compounds," Litton Systems, Inc., Bethesda, Maryland, Clearinghouse for Federal Scientific and Technical Information, PB-188-070, U. S. Department of Commerce (September 1969).
24. Sullivan, R. J., "Air Pollution Aspects of Chromium and its Compounds," Litton Systems, Inc., Bethesda, Maryland, Clearinghouse for Federal Scientific and Technical Information, PB-188-075, U. S. Department of Commerce (September 1969).
25. Zoller, W. H., and G. E. Gordon, "Instrumental Neutron Activation Analysis of Atmospheric Pollutants Utilizing Ge(Li) γ -Ray Detectors," Anal. Chem., 42, 257 (1970).
26. "Air Quality Criteria for Particulate Matter," U. S. Department of Health, Education and Welfare; Public Health Service, Consumer Protection and Environmental Health Service; National Air Pollution Control Administration, Washington, D. C. AP-49, 16 (1969).

APPENDIX D

SELECTED REFERENCES ON X-RAY FLUORESCENCE

AND

AEROSOL TRACE ELEMENTS

- Bertin, E. P., "Principles and Practice of X-Ray Spectrometric Analysis," Plenum Press, New York, 1970.
- Billings, C., W. Matson, "Hg Emissions from Coal Combustion," Science 176, 1232 (1972).
- Birks, L. S., J. V. Gilfrich, P. G. Burkhalter, "Development of X-Ray Fluorescence Spectroscopy for Elemental Analysis of Particulate Matter in the Atmosphere and in Source Emissions," EPA-R2-72-063, November 1972.
- Birks, L. S., and J. V. Gilfrich, "Development of X-Ray Spectroscopy for Elemental Analysis of Particulate Matter in the Atmosphere and in Source Emissions; Phase II: Evaluation of Commercial Multiple Crystal Spectrometer Instruments," NRL Report 7617, June 1973.
- Birks, L. S., "X-Ray Spectrochemical Analysis," 2nd. Edition., Interscience, New York, 1969.
- Bove, J., S. Siebenberg, "Airborne Pb and CO at 45th Street, New York City," Science 167, 986, 1970.
- Brar, S., D. Nelson, J. Kline, P. Gustafson, E. Kanabrocki, C. Moore, D. Hattori, "Instrumental Analysis for Trace Elements Present in Chicago Area Surface Air," J. Geophys. Res. 75, 2989 1970.
- Cahill, T. A., FINAL REPORT, "Cyclotron Analysis of Atmospheric Contaminants," Project Clean Air PCA-038, October 31, 1972.
- Cahill, T. A., R. Sommerville and R. Flocchini, "Elemental Analysis of Smog by Charged Particle Beams: Elastic Scattering and X-Ray Fluorescence," Trans. Amer. Nucl. Soc., 15, 70, 1972.
- Chow, T., J. Earl, "Pb Aerosols in the Atmosphere: Increasing Concentrations," Science 169, 577, 1970.
- Chow, T., J. Earl, C. Snyder, "Pb Aerosol Baseline: Concentration at White Mountain and Laguna Mountain, Calif.," Science, 178, 401 1972.
- Cooper, J. A., "Comparison of Particle and Photon Excited X-Ray Fluorescence Applied to Trace Element Measurements of Environmental Samples," Nucl. Instr. and Methods 106, 525, 1973.

- Dams, R., J. A. Robbins, K. A. Rahn, J. W. Winchester, "Nondestructive Neutron Activation Analysis of Air Pollution Particulates," Anal. Chem., 42, 861, 1970.
- Duce, R. A., J. W. Winchester, T. Van Nahl, "I, Br, Cl in Winter Aerosols and Snow from Barrow, Alaska," Tellus 18, 238, 1966.
- Duce, R. A., A. Woodcock, J. Moyers, "Variation of Ion Ratios with Size Among Particles in Tropical Oceanic Air," Tellus 19, 369, 1967.
- Flocchini, R. G., P. J. Fenney, R. J. Sommerville, T. A. Cahill, Nucl. Instr. and Methods 100, 397, 1972.
- Foote, R., "Hg Vapor Concentrations Inside Buildings," Science 177, 513, 1972.
- Giauque, R. D., F. S. Goulding, J. M. Jaklevic, R. H. Pehl, "Trace Element Determination with Semiconductor Detector X-ray Spectrometers," Anal. Chem. 45, 671, 1972.
- Gilfrich, John V., "Applications of X-Ray Analysis to Environmental and Biomedical Studies," Advances in X-Ray Analysis, Vol. 16, Plenum Press, New York, 1973.
- Gilfrich, J. V., L. S. Birks, P. G. Burkhalter, "X-Ray Spectrometry for Particulate Air Pollution: A Quantitative Comparison of Techniques," Anal. Chem., In Press, 1973.
- Goulding, F. S., J. M. Jaklevic, B. V. Jarrett, D. A. Landis, "Detector Background and Sensitivity of Semiconductor X-Ray Fluorescence Spectrometers," Advances in X-Ray Analysis, Plenum Press, vol. 15, 470, 1972.
- Goulding, F. S. and J. M. Jaklevic, "X-ray Fluorescence Spectrometer for Airborne Particulate Monitoring," Report prepared for the Environmental Protection Agency, EPA-R2-73-182, April, 1973.
- Goulding, F. S. and J. M. Jaklevic, "Photon-Exited Energy Dispersive X-ray Fluorescence Analysis for Trace Elements," to be published in Annual Review of Nuclear Science, 1973.
- Hammerle, R. H., R. H. Marsh, K. Rengan, R. D. Giauque, J. M. Jaklevic, "A Test of X-ray Fluorescence as a Method for Analysis of the Elemental Composition of Atmospheric Aerosols," In Press, 1973.
- Hunter, C. B. and J. R. Rhodes, "Particle Size Effects in X-Ray Emission Analysis: Formulae for Continuous Size Distributions," X-Ray Spectrometry, Vol. 1, 107-111, 1972.
- Jaklevic, J. M. and F. S. Goulding, "Detection of Low Energy X-rays with Si(Li) Detectors," IEEE TRANS. on Nucl. Sci., NS-18, No. 1, 187, 1971.
- Jaklevic, J. M., R. D. Giauque, D. F. Malone, and W. L. Searles, "Small X-ray Tubes for Energy Dispersive Analysis Using Semiconductor Spectrometers," Advances in X-Ray Analysis, Plenum Press, vol. 15, 266, 1972.

- Jaklevic, J. M. and F. S. Goulding, "Semiconductor Detector X-ray Fluorescence Spectrometry Applied to Environmental and Biological Analysis," IEEE TRANS. on Nucl. Sci., NS-19, No. 3, 384, 1972.
- Jaklevic, J. M., F. S. Goulding, and D. A. Landis, "High Rate X-ray Fluorescence Analysis by Pulsed Excitation," IEEE TRANS. on Nucl. Sci., NS-19, No. 3, 392, 1972.
- Jaklevic, J. M. and F. S. Goulding, "Applications of X-ray Fluorescence Techniques to Measure the Elemental Composition of Particles in the Atmosphere," Proceedings of Dallas Symposium on Analytical Methods Applied to Air Pollution Measurements, (R.S. Stevens and W. Herget, eds.) published by Ann Arbor Science, 1973.
- Jenkins, R. and J. L. DeVries, Practical X-Ray Spectrometry, Springer-Verlag, New York, 1967.
- Joensun, O., "Fossil Fuels as a Source of Hg Pollution," Science 172, 1027, 1971.
- Johansson, T. B., R. Akselsson, S.A.E. Johansson, "Proton-Induced X-Ray Emission Spectroscopy in Elemental Trace Analysis," Advances in X-Ray Analysis, vol. 15, Plenum Press, New York, 373, 1972.
- Johansson, T. B., R. Akselsson, S.A.E. Johansson, "X-Ray Analysis: Elemental Trace Analysis at the 10^{-12} g Level," Nucl. Instr. and Methods, 84, 141, 1970.
- Kneip, T. J. and G. R. Laurer, "Isotope Excited X-Ray Fluorescence," Anal. Chem., 44, 57A, 1972.
- Landis, D. A., F. S. Goulding, R. H. Pehl, J. T. Walton, "Pulsed Feedback Techniques for Semiconductor Detector Radiation Spectrometers: IEEE TRANS on Nucl. Sci., NS-18, No. 1, 115, 1971.
- Landis, D. A., F. S. Goulding and B. V. Jarrett, "Some Aspects of X-ray Fluorescence Spectrometers for Trace Element Analysis," Nucl. Instr. and Methods 101, 127, 1972.
- Lee, Jr., R. E., and S. Goranson, "National Air Surveillance Cascade Impactor Network. I. Size Distribution Measurements of Suspended Particulate Matter in Air," Environ. Sci. and Techn. 6, 1019, 1972.
- Lee, Jr., R. E., "The Size of Suspended Particulate Matter in Air," Science 178, 567, 1972.
- Liebhafsky, H. A., H. G. Pfeiffer, E. H. Winslow, P. D. Zeman, "X-Rays, Electrons, and Analytical Chemistry," Wiley-Interscience, New York, 1972.
- Luke, C. L., T. Y. Kometani, J. E. Kessler, T. C. Loomis, "X-Ray Spectrometric Analysis of Air Pollution Dust," Environ. Sci. and Techn. 6, 1105, 1972.

- McMullen, T. B., R. B. Faoro, G. B. Morgan, "Profile of Pollutant Fractions in Nonurban Suspended Particulate Matter," J. Air Poll. Cont. Ass., 20, 369, 1970.
- Moyers, J. L., W. H. Zoller, R. A. Duce, G. L. Hoffman, "Gaseous Bromine and Particulate Lead, Vanadium and Bromine in a Polluted Atmosphere," Environ. Sci. Tech. 6, 68, 1972.
- Moyers, J. L., W. H. Zoller, R. A. Duce, "Gaseous I Measurements and their Relationship to Particulate Pb in a Polluted Atmosphere," J. Atmos. Sci., 28, 95, 1971.
- Müller, R. O., "Spectrochemical Analysis by X-Ray Fluorescence," trans. by K. Keil, Adam Hilger, London, 1972.
- Murozumi, M., T. Chow, C. Patterson, "Chemical Concentrations of Pollutant Pb Aerosols, Terrestrial Dusts and Sea Salts in Greenland and Antarctic Snow Strata," Geochim. et Cosmochim. Acta, 33, 1247, 1969.
- Patterson, C., "Contaminated and Natural Pb Environments of Man," Arch. Environ. Health, 11, 344, 1965
- Perry, S. K. and F. P. Brady, "A Comparative Study of Alpha and X-Ray Induced X-Ray Emission for Elemental Analysis," Nucl. Instr. and Methods 108, 289, 1973.
- Rahn, K., J. J. Wesolowski, W. John, H. R. Ralston, "Diurnal Variation of Aerosol Trace Element Concentrations in Livermore, California," J. Air Poll. Cont. Ass. 21, 406, 1971.
- Rhodes, J. R., "Design and Application of X-Ray Emission Analyzers Using Radioisotope X-Ray or Gamma Ray Sources," ASTM Special Technical Publication No. 485, 243-285, 1971.
- Rhodes, J. R., A. Pradzynski, R. D. Sieberg, T. Furuta, "Application for a Si(Li) Spectrometer to X-Ray Emission Analysis of Thin Specimens," Application of Low Energy X- and Gamma Rays, (C. A. Ziegler ed), 317-334, Gordon & Breach, Publ., 1971.
- Rhodes, J. R., A. H. Pradzynski, C. B. Hunter, J. S. Payne, James L. Lindgren, "Energy Dispersive X-Ray Fluorescence Analysis of Air Particulates in Texas," Environ. Sci. & Techn., vol. 6, 922-927, 1972.
- Rhodes, J. R., A. H. Pradzynski, R. D. Sieberg, "Energy-Dispersive X-Ray Emission Spectrometry for Multielement Analysis of Air Particulates," ISA Trans. vol., 11, #4, 1972.
- Rhodes, J. R. and C. B. Hunter, "Particle Size Effects in X-Ray Emission Analysis-Simplified Formulae for Certain Practical Cases," X-Ray Spectrometry, vol. 1, 113-117, 1972.
- Rhodes, J. R., "Energy Dispersive X-Ray Spectrometry for Multielement Pollution Analysis, American Laboratory, In Press, 1973.

- Tanemura, T. and H. Suita, "Air Pollution Analysis by the Energy Dispersive X-Ray Spectrometry Using Radioisotopes," Radioisotopes 21, 641, 1972.
- vonHevesy, G., Chemical Analysis by X-Rays and Its Application, McGraw-Hill, New York, 1932.
- Watson, R. L., J. R. Sjurseth, R. W. Howard, "An Investigation of the Analytical Capabilities of X-ray Emission Induced by High Energy Alpha Particles," Nucl. Instr. and Methods 93, 69, 1971.
- Weiss, H., M. Koide, E. Goldberg, "Se and S in a Greenland Ice Sheet: Relation to Fossil Fuel Combustion," Science 172, 261, 1971.
- Weiss, H., M. Koide, E. Goldberg, "Hg in a Greenland Ice Sheet: Evidence of Recent Input by Man," Science, 174, 692, 1971.
- Winchester, J. W., W. H. Zoller, R. A. Duce, C. Benson, "Pb and Hallogens in Pollution Aerosols and Snow from Fairbanks, Alaska," Atmos. Environ., 1, 105, 1967.
- Winchester, J. W. and R. A. Duce, "Neutron Activation Analysis of Pb Halide Pollution Aerosols," Nucl. Activation Tech. in Life Sciences, 631, 1967.
- Winchester, J. W., "Trace Metal Associations in Urban Airborne Particulates," Bull. Am. Meteor., 54, 94, 1973.