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16. Abstract

Increasing reliance on coal as the future source of energy has spurred great interest in improved techniques for the measurement of heavy metals in effluents from various types of coal plants. There are several sensitive techniques currently used for the measurement of trace metals in environmental specimens. These can be divided into four major categories: (1) Atomic Absorption/Emission Spectroscopy, (2) Nuclear Techniques, (3) X-ray Spectroscopic Methods, and (4) Chromatography/Mass Spectrometry. Atomic Absorption technique is especially suited for aqueous sample analysis. However, the technique does not lend itself easily to multielement analysis. Nuclear techniques include Charged-Particle Scattering, Charged-Particle Activation Analysis, and Instrumental Neutron Activation Analysis. Charged-Partical Scattering and activation techniques are usually appropriate for the determination of lighter elements, most of which cannot be readily determined by other analytical methods. Neutron Activation Analysis is a widely utilized technique for fly/bottom ash elemental analysis, though certain critical elements (Be, P, S, Tl, Pb) cannot be easily determined. X-ray spectroscopic techniques provide simultaneous, sensitive multielement analyses and lend themselves readily to depth profiling, which has become increasingly important in aerosol studies. Chromatography/Mass Spectrometry methods, although quite sensitive, are not appropriate for aerosol analysis.

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SUMMARY

Trace metals constitute an important component of all fossil fuels, including coal. Increasing reliance on coal as the future source of energy has spurred great interest in improved techniques for the measurement of heavy metals in effluents from various types of coal plants. There are several sensitive techniques currently used for the measurement of trace metals in environmental specimens. These can be divided into four major categories: (1) Atomic Absorption/Emission Spectroscopy, (2) Nuclear Techniques, (3) X-ray Spectroscopic Methods, and (4) Chromatography/Mass Spectrometry. Atomic Absorption Spectroscopy is widely used in such diverse fields as biochemistry, metallurgy, and air/water analysis. It is especially suited for aqueous sample analysis. However, the technique does not lend itself easily to multielement analysis and is destructive of the test specimen. Nuclear spectroscopic techniques include Charged-Particle Scattering, Charged-Particle Activation Analysis, and Instrumental Neutron Activation Analysis (INAA). Charged-Particle Scattering and activation techniques are usually appropriate for the determination of lighter elements, most of which cannot be readily determined by other analytical methods. INAA is a widely utilized technique for fly/bottom ash elemental analysis, though certain critical elements (Be, P, S, Tl, Pb) cannot be easily determined. X-ray spectroscopic techniques include X-ray fluorescence and charged-particle-induced X-ray emission methods. A discussion of these last two methods constitutes the main subject of this review. Besides providing simultaneous, sensitive multielement analyses, these techniques lend themselves more readily to depth profiling, which has become increasingly important in aerosol studies. The gas/liquid chromatographic and gas-chromatographic/mass-spectrometric methods are rather slow (although quite sensitive), destructive of the sample, and inappropriate for airborne particulate analysis.

INTRODUCTION

Until a few years ago, the main environmental quality monitoring effort was concentrated on the measurement of gaseous components - such as oxides of carbon, nitrogen, sulphur, and hydrocarbons - emitted from coal-fired power plants and coal processing facilities. Recently, other effluents - such as aerosol/fly ash, bottom ash, and sludge from stack scrubbers - have also received increasing emphasis. Special attention has been paid to the trace metal components of these effluents. It has been found that most volatile compounds in coal are emitted as gases or parts of aerosols emanating from the plant stacks. Some of the trace elements are also left in the bottom fly ash.

In this review, special consideration is given to the measurement of composition of aerosols emitted from coal plants. Several authors report (refs. 1 and 2) that these aerosols exhibit elemental fractionation. Certain potentially toxic elements have been found to be preferentially concentrated in finer

aerosols ($\leqq 2$ μm). This is particularly significant in view of the fact that the finer aerosols are not efficiently filtered in the nasal passages of the human respiratory system.

There are several techniques for trace-element determination in the environmental specimens. These can be broadly grouped into four different categories:

1. Atomic Spectroscopic Techniques

    a. Atomic Absorption/Emission Spectroscopy

    b. Atomic Fluorescence Spectroscopy

These techniques are excellent for samples in liquid form.

2. Nuclear Techniques

    a. Charged-Particle Scattering

    b. Charged-Particle Activation

    c. Neutron Activation

    d. Photon Activation

These techniques are all nondestructive and well suited for analyzing solid samples.

3. X-ray Spectroscopic Techniques

    a. X-ray Fluorescence

    b. Charged-Particle-Induced X-ray Emission

        (1) Proton-Induced X-ray Emission and Heavy-Ion-Induced X-ray Fine Structure

        (2) Electron-Excited X-ray Emission

These techniques are nondestructive (or can be nondestructive) and are excellent for solid samples, though liquids as well as gases can also be analyzed.

4. Miscellaneous Techniques

    a. Gas/Liquid Chromatography

    b. Ion-Probe Mass Spectrometry

    c. Photoelectron Spectroscopy

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Since all of these techniques are standard, no detailed explanation of the experimental methods is given for any of them. Only the strong features of various techniques and their limitations have been discussed, except in the case of heavy-ion-induced X-ray fine-structure technique, which is discussed in somewhat greater detail. X-ray spectroscopic techniques (and, to a lesser extent, nuclear techniques) have been given major attention, not necessarily because they are amongst the most sensitive, but because they are suitable for nondestructive multielement aerosol analysis and also lend themselves readily to depth profiling, which is becoming increasingly important in aerosol studies.

A review of the type presented in this report is relevant to NASA programs, as information about the morphology and the elemental composition of aerosols in the troposphere and the stratosphere is needed in several ongoing NASA studies. This review also provides a suitable vehicle for transferring some NASA-developed technology to the private sector.

SYMBOLS AND ABBREVIATIONS

AA   Atomic Absorption

AE   Atomic Emission

AF   Atomic Fluorescence

CPAA   Charged-Particle Activation Analysis

CPS   Charged-Particle Scattering

EC   Electron Capture

ESCA   Electron Spectroscopy for Chemical Analysis

EXAFS   Extended X-ray Absorption Fine Structure

HPLC   High-Performance Liquid Chromatography

INAA   Instrumental Neutron Activation Analysis

IPAA   Instrumental Photon Activation Analysis

LAMMA   Laser Microprobe Mass Analyzer

PIXE   Proton-Induced X-ray Emission

XRF   X-ray Fluorescence

E_{in} incident proton energy

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E_p	energy of proton
E_{scat}	elastically scattered proton energy
E_γ	energy of gamma ray (photon)
Ge(Li)	lithium-drifted germanium detector
$N_x(K\alpha)$	number of $K\alpha$ X-rays
$N\gamma$	number of gamma rays
n	neutron
d	deuteron
p	proton
p_L	L-shell vacancy fraction
z	atomic number
α	alpha particle
β^+	positron
β^-	electron
γ	primary gamma ray
γ'	secondary gamma ray
θ_{lab}	proton scattering angle in laboratory coordinates
λ	wavelength of photon, Å
σ	standard deviation

DISCUSSION OF VARIOUS TECHNIQUES

Atomic Spectroscopic Techniques

A brief discussion of elemental detection capabilities of atomic spectroscopic techniques is first given for the sake of completeness of the review. These techniques are widely used in such diverse areas as geochemistry, metallurgy, and air/water analysis.

In principle, all elements can be detected by Atomic Absorption (AA) since atoms of all elements are capable of radiation absorption. However, the measurement of elements with resonance lines below 2000 Å becomes difficult with normal instruments due to incipient absorption by oxygen as well as increased absorption of lenses, low reflectance of mirrors, and low photomultiplier sensitivities. The attractiveness of the AA technique stems from its rather low cost, high sensitivity for trace elements in solution, reasonable through-put rate, and flexibility of operation (such as flame AA or nonflame AA). In Atomic Emission (AE) spectroscopy, the sample is subjected to high-energy thermal environment (electric arc, flame, or plasma) in order to produce excited-state atoms capable of emitting light. This may lead to background emission from the sample matrix and consequently affect the detection limits in emission spectroscopy. The main advantages lie in quick multielement detection capability and effective analysis of rare earths and refractory materials.

Atomic Fluorescence (AF) is an extension of Atomic Absorption. It is produced by the deexcitation of atoms which have been excited with radiation of a suitable frequency. The intensity of Atomic Fluorescence - and consequently the achievable sensitivity and detection - is dependent on the number of atoms in the ground state and the intensity of the exciting light source. For this reason, studies in Atomic Fluorescence have closely parallelled the development of newer and more intense light sources, such as lasers. Atomic Fluorescence spectroscopy has a potential advantage over AA because lower .detection limits may be achievable by increasing the radiation intensity of the exciting light source.

The sensitivities of atomic spectroscopic techniques (refs. 3 to 5) for most elements of interest are summarized in table I. These techniques, in spite of their excellent sensitivities, are not convenient for simultaneous multielement analyses and are destructive of the test specimens.[1] Atomic spectroscopic techniques are not considered any further in this review.

Nuclear Techniques

Charged-Particle Scattering (CPS) techniques include elastic and inelastic scattering and are more appropriate for lighter elements which constitute most of the mass of the finer aerosols. Figure 1 shows how the energy of the elas-tically scattered protons is expected to change with scattering angle for

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[1]Some attempts at simultaneous multielement analyses by Atomic Absorption, using multielement sources and multichannel approaches have recently been made. However, the sensitivities reported in these studies are considerably worse than conventional Atomic Absorption/Atomic Fluorescence studies. Atomic Emission Spectroscopy, of course, can provide simultaneous multielement analysis, but its sensitivity is considerably lower than that of Atomic Absorption Spectroscopy for most elements of interest.

various elements.[2] It is clear that the energy differences in the background directions for protons scattered from neighboring light elements are sufficiently large to make them easily resolvable. Figure 2 shows a typical spectrum (ref. 6) of elastically scattered protons from an aerosol sample at $\theta_{lab} = 135°$. In the inelastic scattering studies, it is usually the first excited state of the pollutant nucleus that is significantly excited. Determination of the pollutant nuclei (atoms) can be made either on the basis of inelastically scattered proton groups or simultaneously emitted gamma rays. (For example, see Na^{23} inelastic peak in fig. 2.) Charged-Particle Activation Analysis (CPAA) is also appropriate for the determination of lighter elements, most of which cannot be determined by other analytical methods, except the elastic/inelastic scattering reactions just discussed. Some typical reactions (ref. 7) for light-element detection by CPAA are listed in table II(a). For elements with $Z \geqq 10$, CPAA is quite complementary to Instrumental Neutron Activation Analysis, though it has not been used much except for the elements that cannot be determined by thermal neutrons. Some examples (ref. 7) of heavier element detection by CPAA are summarized in table II(b). Interferences can present a problem in CPAA studies. However, use of several incident energies, coupled with an appropriate choice of reactions, often proves quite useful. For example, $N^{14}(p,\alpha)C^{11}$ and $B^{11}(p,n)C^{11}$ reactions can be resolved because their relative cross sections change from 1/2 to 1/10 as the proton energy decreases from 15 MeV to 5 MeV. An even better technique of resolving boron and nitrogen interferences may depend on $B^{10}(d,n)C^{11}$ and $N^{14}(d,\alpha n)C^{11}$ reactions whose relative cross-section ratio changes from 30 to infinity as the deuteron energy decreases from 10 MeV to 5.9 MeV.

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[2]The energy of the elastically scattered protons is given by the following expression:

$$(E_{scat})^{1/2} = \frac{M_1}{M_1 + M_2}(E_{in})^{1/2} \cos\theta + \left[\frac{M_1^2 E_{in} \cos^2\theta}{(M_1 + M_2)^2} + \frac{(M_2 - M_1)E_{in}}{(M_1 + M_2)}\right]^{1/2}$$

where

M_1 proton mass

M_2 mass of scattering atom

θ proton scattering angle

E_{in} incident proton energy   } Measured in laboratory coordinates

E_{scat} energy of scattered proton

Instrumental Neutron Activation Analysis (INAA) technique has been used extensively for nondestructive analysis in several fields - including aerosol analysis - though certain critical elements (such as Be and Pb) cannot be easily determined. Interferences due to threshold reactions are very rare under normal irradiation conditions where the thermal neutron flux far exceeds the fast neutron flux. The few reactions of concern include F^{20} (formed by neutron capture in F^{19} as well as $n\alpha$ reaction in Na^{23}) and Mg^{27} (formed by neutron capture in Mg^{26} as well as np reaction in Al^{27}). Spectral interferences resulting from finite gamma-ray detection system resolution do present some problems. Some such interferences are: Mg^{27} (844 keV) and Mn^{56} (846 keV); Se^{75} (121 keV) and Eu^{152} (122 keV); Hg^{203} (279.1 keV) and Se^{75} (279.6 keV); Cu^{64} (511 keV) and annihilation radiation.

Sometimes it may be more convenient to use fast neutron-induced activation, particularly when cross sections for (n,p) and (n,α) reactions of interest are accurately known. (See ref. 8.) For example, Si^{28}(n,p)Al^{28} reaction with 14.5 MeV neutrons at a flux of 10^9 n/cm^2-sec easily allows silicon concentration determinations as low as 50 ng/m^3.

Typical detection limits for several pollutant elements using the INAA technique (refs. 9 and 10) are summarized in table III. Because of the general availability of nuclear reactors and large thermal neutron-capture cross sections for many nuclei, the greater part of activation work has been done with thermal neutrons where sensitivities of the order of 10^{-9} g are not at all unusual.

Some elements - such as Be, C, N, O, F, and Pb - which are not highly activated with thermal neutrons can be studied with Instrumental Photon Activation Analysis (IPAA). For beryllium, detection of photoneutrons is used as the criterion for elemental detection. For elements C, N, and O, the photoactivation products decay exclusively by β^+-emission and the associated annihilation radiation serves as the basis for their detection. For elements heavier than oxygen, the A(γ,n/p)B reaction products are identified by their characteristic γ-ray spectra detected with a Ge(Li) detection system. Sometimes interferences experienced in INAA can be avoided by using the IPAA method. For example, determination of nickel may be complicated by Ni^{64}(n,γ)Ni^{65} and Cu^{65}(n,p)Ni^{65} interferences in the INAA spectrum. However, the photonuclear reaction product Ni^{57} produced in Ni^{58}(γ,n)Ni^{57} cannot be produced from any other element at photon bombarding energies less than 45 MeV. IPAA technique is equally applicable to biological, geochemical, and oceanographic samples. Like other nuclear techniques, interferences occur in IPAA also. But they can usually be avoided by appropriate choices of photon energies and judicious choices of irradiation and cooling times. Cu, Zn, Zr, and Ag are amongst the elements determined in this way in complex metal ores. Interferences between F^{19}(γ,n)F^{18} and Na^{23}(γ,αn)F^{18} can be avoided by using a 22-MeV beam since Na^{23}(γ,αn)F^{18} reaction has a threshold of 23 MeV. Thus, IPAA may be better than INAA for detecting trace elements in the presence of large quantities of Na^{23} (as is the case for marine aerosols). Also, Na^{23} can be studied via Na^{23}(γ,n)Na^{22} as opposed to Na^{23}(n,γ)Na^{24}, which produces an overwhelming 2.76-MeV gamma ray. IPAA also has some interesting

applications in forensic studies. For example, IPAA has been used to measure lead content of whiskey by $Pb^{204}(\gamma,n)Pb^{203}$ reaction to determine its contraband origin!

Sometimes IPAA is based on the excitation of metastable isomers via (γ,γ') reactions. Although (γ,γ') sensitivities are rather low, their specificity is very good. If the irradiation is conducted at suitably low energies ($E_\gamma < 8$ MeV), the only activation produced in IPAA is that due to the production of isomeric nuclides.

Although IPAA is not generally as sensitive as INAA, it can be used to measure concentrations of several elements that are difficult (or impossible) to measure by INAA - especially toxic elements like Ti, Ni, As, I, and Pb. The combined effect of the electron bremsstrahlung spectrum and the excitation function for photonuclear reactions as a function of target atomic number leads to a general increase in photonuclear reaction cross section with increasing Z-value. This result makes it possible to detect low quantities of high Z-elements in the presence of much greater quantities of low Z-material. Table IV summarizes limits of detectability for several elements in urban aerosols for IPAA and INAA techniques. (See refs. 11 and 12.) Sometimes it may be preferable to use $K\alpha$ X-rays from (γ,n) reaction products - particularly when $N_x(K\alpha)/N_\gamma$ is much greater than 1. A comparison of IPAA and X-ray spectroscopic analysis following the photon activation is given in table V. (See refs. 13 and 14.)

X-ray Spectroscopic Techniques

X-ray spectroscopic techniques include X-ray Fluorescence and charged-particle-induced X-ray emission (both electron-induced and heavy-particle induced). They can deal with samples in all physical forms though they are not frequently used for gaseous and liquid samples. X-ray Fluorescence (XRF) can be conducted with radioactive sources as well as tube-excited X-rays. The XRF detection limits can be improved with secondary targets in the path of the main X-ray beam. Prominent X-ray fluorescers are: Ti($K\alpha$) = 4.5 keV; Mo($K\alpha$) = 17.5 keV: Sm($K\alpha$) = 40.0 keV: and W($K\alpha$) = 59.3 keV. By choosing appropriate secondary targets, most elements can be analyzed to the ng/m^3 sensitivity range. The use of a pulsed-beam operation, coupled with an anti-coincidence guard-ring detection system for X-rays, helps improve elemental sensitivities. Sometimes, the use of polarized X-rays may also be desirable since it can minimize X-ray scattering effects. In this context, the use of monochromatized synchrotron radiation would be especially helpful. Desirable features of the XRF technique are (1) it is rapid, (2) it provides simultaneous multielement analysis, (3) it is nondestructive and needs no special sample preparation, (4) samples can be very small (1 mg or so), and (5) it lends itself to automation for large sample throughput rates.

Experimental detection limits (ref. 15) for routine trace-element concentrations in environmental samples, using the tube-excited pulsed X-ray fluorescence system, are summarized in table VI. The problem of elemental spectral interferences in XRF analysis can be just as severe as in other analytical procedures. Some of the interferences encountered in aerosol

analysis are summarized in table VII. It is obvious that Ti and S suffer really bad interferences from Ba and Pb, respectively, if the latter elements are present in significant quantities. Fortunately, this is not always the case. Determination of K is also affected by the presence of Cd and Sn in the specimen. The XRF analysis of air particulate samples has to be corrected for the following effects: (1) matrix effects (particle size and interelement interference effects), (2) particle penetration into substrate (when collected on filter papers), and (3) bremsstrahlung background produced in the target. A number of matrix correction procedures (ref. 16) have been devised which require the use of samples of known composition. In the empirical approach, one obtains influence coefficients from a multiple regression calibration involving a large number of standards, which are then used to calculate the corrected concentrations of each element in the unknown sample. The minimum number of calibration standards required generally equals twice the number of elements to be analyzed. In the theoretical procedure, one corrects for matrix effects using theoretical relations involving known values of absorption coefficients and the fluorescence yields of the elements involved as well as an explicit form of the excitation radiation spectrum and arrives at the corrected elemental concentrations by iterative calculations. The substrate penetration correction factor is obtained by analyzing both sides of the collection filter. The most obvious physical cause of background in the XRF spectra is the bremsstrahlung radiation produced by the secondary electrons in the sample. However, most of the experimentally observed background does not seem to originate in the sample. The integrated number of background counts is 2 to 8 percent of the "high-energy" counts (incident radiation scatter peaks), depending on the secondary target. This background appears to be the result of yet unknown processes (ref. 17) in the detector. Once the physical mechanism responsible for this background is understood, it may be possible to minimize or eliminate it.

The Proton-Induced X-ray Emission (PIXE) technique has been used extensively (refs. 18 and 19) for multielement characterization of aerosols. Monoenergetic protons of energy ranging from 1 to 5 MeV as well as equivalent alpha particles can be used as projectiles, though the former have been used more frequently. The analysis is usually performed at two different proton energies for uniform sensitivities over the entire elemental range. Elements with atomic numbers 11 to 30 are analyzed with lower energy protons ($\approx$2 MeV), whereas elements heavier than zinc require higher proton energies ($\approx$4 MeV). A typical PIXE spectrum of an urban aerosol sample analyzed at Langley Research Center is shown in figure 3. Spectrum a was obtained with 2-MeV protons, and 4-MeV protons were used for spectrum b. The results of a routine PIXE analysis of aerosol samples collected downwind from two oil-fired heating plants at Langley Research Center (ref. 20) are summarized in table VIII. The use of an appropriate "funny filter" (ref. 21) between the aerosol samples and the detector also permits reasonably uniform sensitivity for medium to heavy elements in the presence of more abundant lighter elements. Detection limits below 1 ng/m^3 are easily achieved for most elements. PIXE technique is rapid and lends itself easily to pulsed automated operation with improved elemental sensitivities for routine aerosol analysis.

Goulding and Jaklevic (ref. 17) have calculated PIXE performance data for 2- and 4-MeV protons (100 nanoamps for 200 seconds at each energy) incident on a 5-mg/cm^2 sample containing 1 ppm by weight of several elements. The detector

geometrical efficiency was assumed to be 0.3 percent. Using the 3σ criterion for limit of detection, the calculated detection limits for various elements are summarized in table IX. Calculations for an XRF system are summarized in table X. In these calculations, Ti, Mo, and Sm fluorescers have been used to cover roughly the same range of atomic numbers as in PIXE analysis. The counting time per sample has been kept equal in XRF and PIXE analyses. It is apparent that the two techniques are quite comparable in elemental sensitivities and are indeed complementary to each other. PIXE technique is superior to XRF in the following respects: (1) It has microbeam capability for individual particle analysis, and (2) it admits of depth profiling, using ion microprobes. However, PIXE analysis is more sensitive to sample matrix than XRF, making the latter preferable when measuring moderately thick samples such as filter papers or larger aerosols.

PIXE analysis is often conducted in concert with elastic scattering because elastically scattered particles provide useful information about lighter elements ($Z \leqq 11$) which cannot be detected by X-ray techniques.

Electron-excited X-ray spectrometry is not as sensitive as XRF or PIXE, mainly because of large bremsstrahlung noise produced by the primary electron beam in the sample. However, it has excellent spatial resolution. Electron microprobe analyzers and scanning electron miscroscopes provide effective tools for individual aerosol analysis.

None of the X-ray techniques discussed so far provide any information about the chemical forms of the elements, yet the chemical form is of extreme importance in toxicology. One variant of PIXE can, however, lead to (or at least has the potential of leading to) the chemical form of the pollutant atom. This involves the use of heavier ions as the projectiles. The X-ray spectra produced in such ion-atom collisions cannot be resolved with conventional Si(Li) detectors, but wavelength-dispersive X-ray detectors can provide some very good results. Recent studies (refs. 22 to 24) have shown that the intensity distribution of the $K\alpha$ satellites produced in heavy ion-atom collisions is quite sensitive to the projectile energy and the chemical form of the target atom. As long as $Z_{projectile}$ is less than Z_{target}, the relative intensities of the nth satellite peak $f(n)$ of the $K\alpha$ X-ray satellites appear to be given by the following binary expression:

$$f(n) = \binom{8}{n} p_L^n (1 - p_L)^{8-n} \tag{1}$$

where p_L, the average L-shell vacancy fraction, is given by

$$p_L = \frac{1}{8} \sum_{n=1}^{7} n f(n) \tag{2}$$

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The best results are obtained for energy per atomic mass unit of the projectile in the range 0.5 to 2.0 MeV/amu. Some typical results (refs. 22 and 23) are shown in figures 4 and 5. Figure 4 shows the $K\alpha$-Satellite Spectra of Si, S, and Cl atoms for several chemical forms of them under bombardment with 32.4-MeV oxygen ions. Notice the changes in p_L values for different chemical forms of the same elements. Figure 5 shows the relationship between p_L and the "effective charge" (defined as the product of oxidation number and bond ionicity) for several silicon and chlorine compounds. It is clear from this figure that p_L decreases with increasing effective charge, which suggests that all of the valence electrons which happen to be localized about the target atom at the time of the collision are ionized. The definite correlation observed between the L-shell vacancy fraction p_L and the effective charge on the target atom strongly supports the conclusion that interatomic processes must contribute to the deexcitation of multiply ionized states following heavy ion-atom collisions. Although changes in p_L from compound to compound are rather small, it is possible that further developments in $K\alpha$-Satellite Spectrometry could provide a useful means for obtaining information about the chemical form of the target elements in special situations (i.e., a large variety of compounds of third-row elements). (See ref. 24.) Because this technique provides information relative to the bulk conditions of the sample, it is complementary to Electron Spectroscopy for Chemical Analysis (ESCA) which provides information concerning the conditions at the surface only. Figure 6 illustrates how ESCA is used to infer chemical states of elements of interest on aerosol surfaces. (See ref. 25.) This figure shows the spectrum of Al 2p bonding states on the surfaces of aerosols collected from a space vehicle launch rocket exhaust.

Another technique of great promise is a variation of XRF wherein photoelectron fine structure - rather than characteristic X-ray spectra - is measured following appropriate incident X-rays. Extended X-ray Absorption Fine Structure (EXAFS) refers to the oscillations in the X-ray absorption coefficient extending out to several hundred electron volts on the high energy side of an X-ray photoelectron edge. (See refs. 26 and 27.) These oscillations are believed to arise from the scattering of the ejected photoelectrons by atoms surrounding the absorbing atom and are intimately related to the chemical form of the scattering element. Like heavy-ion-induced X-ray fine structure, EXAFS can also provide chemical speciation information about the target material. Availability of intense and energetic synchrotron radiation sources may, in the future, make EXAFS a practical technique for bulk chemical speciation of air pollution samples.

X-ray spectroscopic techniques, in conjunction with electron or heavy-ion streams continually exposing fresh surfaces, can provide depth profile of trace elements in aerosols. Since depth profile in aerosols is expected to be independent of aerosol sizes, such analyses should be considered for larger (≥ 25 μm) aerosols.

Miscellaneous Techniques

Chromatographic techniques are very sensitive for gas/liquid analysis, but they have certain inherent limitations. Gas chromatography is restricted to gases or compounds that can be vaporized without chemical dissociation (i.e.,

Atomic weights $\leq$ 200 amu), whereas liquid chromatography requires liquid sample preparation and consequently suffers from the danger of inadvertent sample pollution. Furthermore, High-Performance Liquid Chromatography (HPLC) imposes considerable operational problems - such as application of very high pressures (10 MPa to 30 MPa) and specially designed pumps to provide a constant flow of the order of a few milliliters per minute through the packing column. (See refs. 28 and 29.) Ion-probe mass spectrometry, like chromatographic techniques, is also destructive of the sample, though it is a sensitive technique for depth profiling of selected elements in aerosol samples. The Laser Microprobe Mass Analyzer (LAMMA) is the latest form of an ion-probe mass spectrometer. It has excellent sensitivity (10^{-18} to 10^{-20} g) and is essentially nondestructive. (See refs. 30 and 31.) However, LAMMA is essentially a surface instrument since it analyzes the microplasma created by a short laser pulse which vaporizes about 10^{-13} g of the sample surface and simultaneously ionizes it. Photoelectron spectroscopy provides quite useful information about elemental oxidation states in the 20- to 25-Å-thick surface layer of solid specimen. However, this technique (ref. 32) requires sample introduction into high vacuum (100 µPa) and cannot provide bulk chemical speciation information, except by a continual destructive etching with a positive argon ion stream to expose fresh surface.

CONCLUDING REMARKS

Various analytical techniques used for trace-element measurements in environmental specimens have been discussed. Atomic Absorption (AA) techniques are most suitable for aqueous solutions and can routinely attain sensitivities of the order of ng/ml for most elements, with a few exceptions such as F, P, and S. Even though AA analysis can be quite fast (Regular flame AA $\approx$ 6 sec/sample; Graphite furnace AA $\approx$ 2 min/sample), special precautions are necessary against inadvertent sample contaminations. The various nuclear techniques are quite sensitive, rapid, and nondestructive, as well as amenable to automation. (For example, a 2- to 5-mg/cm^2 sample requires an irradiation time of about 3 minutes at a thermal neutron flux of 10^{12} ng/cm^2-sec, followed by a cooling period of 3 minutes and counting time of 6 minutes for elements with half lives $\leq$ 10 minutes to provide detection sensitivity in the ng/m^3 range. For elements with half lives of 10 minutes to 15 hours, a cooling period of 15 minutes followed by a counting time of 30 minutes is required for similar results by Instrumental Neutron Activation Analysis (INAA). For Instrumental Photon Activation Analysis (IPAA) the irradiations have to last several hours because far less activity per unit irradiation time is produced with bremsstrahlung than with moderate flux reactors.) However, they do require rather expensive nuclear sources (a neutron reactor for INAA; a betatron or linac for IPAA; and a Van de Graaff generator or a cyclotron for Charged-Particle Activation Analysis (CPAA)). Amongst the most sensitive and rapid nondestructive trace-metal detection techniques are those based on characteristic X-ray emission from elements of interest. (For example, a total irradiation time of 6 to 7 minutes is usually quite adequate to provide sensitivities of the order of a few ng/m^3 for the entire range of elements present in 2- to 5-mg/cm^2 aerosol samples analyzed by X-ray spectroscopic techniques.) These techniques include X-ray Fluorescence and Proton-Induced X-ray Emission (PIXE). Usually, the excitation radiation

sources for these techniques are much less costly than those needed for nuclear techniques. However, chemical speciation of trace elements in aerosols will require rather expensive dedicated radiation facilities (a heavy-ion accelerator for PIXE and $K\alpha$ fine structure spectroscopy and a variable-energy intense monochromatic photon source for Extended X-ray Absorption Fine Structures).

In summary, it seems that no single technique is equally good for analyzing all types of environmental specimens. Gas chromatography and mass spectrometry are quite appropriate for analyzing gaseous samples. Atomic Absorption and high-performance liquid chromatography are appropriate for analyzing liquid samples, though solids can also be analyzed with equal sensitivity by using appropriate solvents. Solids may be sensitively analyzed by nuclear and X-ray spectroscopic methods, particularly when nondestructive techniques are required. EXAFS and $K\alpha$-Satellite Spectrometry appear to be the most viable candidate techniques for nondestructive bulk chemical speciation in aerosols. For depth profiling of trace elements in solids, Laser Microprobe Mass Analyzer and X-ray spectroscopic techniques (in conjunction with heavy-ion streams continually exposing fresh surfaces) would be appropriate. It is recommended that, whenever feasible, two or more complementary techniques should be used for analyzing environmental samples.

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TABLE I.- SUMMARY OF ELEMENTAL DETECTION LIMITS BY ATOMIC

ABSORPTION/EMISSION SPECTROSCOPIC TECHNIQUES

Element	Flameless atomic absorption (ref. 3)		Laser induced flame atomic fluorescence (ref. 4)		Plasma emission spectroscopy (ref. 5)
	λ, Å	2σ, ng/ml	λ, Å	3σ, ng/ml	2σ, ng/ml
Ag	3280.68	0.005	3281	4	4
Al	3961.53	.02	3944/3961	.6	1
Ba	5535.55	.15	5537	8	1
Bi	3067.72	.10	3068	3	50
Ca	4226.73	.05	4227	.08	.1
Cd	2288.02	.003	2288	8	5
Co	3453.50	.10	3474/3575	1000	2
Cr	3578.69	.01	3593	1	1
Cu	3247.54	.02	3247	1	1
Fe	3734.00	.02	2967/3735	30	2
In	4511.32	.30	4104/4511	.2	25
K	7664.91	.02	----------	-------	10
Mg	2852.13	.004	2852	.2	.1
Mn	4030.76	.01	2795	.4	1
Mo	3798.25	.07	3798	12	1
Na	5889.95	<.5	5890	<.1	1
Ni	3414.76	.20	3524/3610	2	1
Pb	4057.83	.05	2833/4058	13	15
Sr	4607.33	.2	4607	.3	1
Ti	3998.64	1	3999	2	2
Tl	3519.24	.1	3776	4	----
V	4739.24	.2	3704/4112	30	5
Zn	2138.56	.001	----------	-------	2
S	1807.31	5000	----------	-------	----
[a]Hg	1849.68	.10	----------	-------	----

[a]Flameless limits are given for 100 microliters of solution.

TABLE II.- SUMMARY OF SELECTED DETECTION LIMITS BY

CHARGED PARTICLE ACTIVATION ANALYSIS (REF. 7)

(a) Light element

Element	Nuclear reaction	Sensitivity and comments
B	$B^{11}(p,n)C^{11}$ at $E_p = 14.5$ MeV	0.5 ppb (polycrystalline silicon matrix) 3 ppb (monocrystalline silicon matrix)
	$B^{10}(d,n)C^{11}$	1 to 10 ppb
C	$C^{12}(He^3,\alpha)C^{11}$	0.3 ppm 0.01 ppm (if C/O ratio is not too unfavorable)
N	$N^{14}(p,\alpha)C^{11}$	1 ppb (requires irradiation with two proton energies to separate boron and nitrogen)
	$N^{14}(d,n)O^{15}$	1 to 10 ppb
O	$O^{16}(He^3,p)F^{18}$	Several ppb (in favorable matrices)
F	$F^{19}(He^3,2p)F^{20}$	70 ppb (normalized to a beam of 100 μA on a 100 mg/cm^2 matrix and 1.63-MeV gamma-ray detection efficiency of 10 percent)

(b) Heavy element

Element	Matrix	Reaction	Sensitivity	Interference
S	Fe Al	$S^{34}(p,x)Cl^{34m}$	0.1 ppm	$Cl^{35}(p,pn)Cl^{34m}$
Ca	Si Al Mg	$Ca^{40}(He^4,p)Sc^{43}$	.3 ppb	$K^{41}(He^4,2n)Sc^{43}$
V	Al	$V^{51}(p,n)Cr^{51}$	36.0 ppb	----------------
Tl	Glass	$Tl(p,xn)Pb^{203}$	1.0 ppb	$Pb^{204}(p,pn)Pb^{203}$
Pb	Pd Ta Glass	$Pb^{206}(p,n)Bi^{206}$	10.0 ppb	----------------
Bi	Glass	$Bi^{209}(p,3n)Po^{207}$	1.0 ppb	----------------

TABLE III.- SUMMARY OF DETECTION LIMITS FOR SEVERAL TRACE ELEMENTS

BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (REFS. 9 AND 10)

Element	Detection limit (24-hour urban sample),[a] ng/m^3	Element	Detection limit (24-hour urban sample),[a] ng/m^3
Ag	1	K	7.5
Al	8	Mg	600
Ba	40	Mn	.6
Bi	-------------	Mo	----------
Br	Br^{80m}(4)	Na	40
Br	Br^{82}(0.5)	Ni	20
Ca	200	Pb	----------
Cd	5	S	5000
Cl	100	Si	----------
Co	.02	Sr	----------
Cr	.20	Ti	40
Cu	5	Tl	----------
F	-------------	V	.2
Fe	20	Zn	Zn^{65}(1.0)
In	In^{116m}(0.04)	Zn	Zn^{69m}(20.0)

[a]Thermal neutron flux = 2.6×10^{12} n/cm^2-sec   (24-hour sampling with high-volume sampler).

TABLE IV.- COMPARISON OF DETECTION LIMITS BY IPAA AND INAA TECHNIQUES

FOR SELECTED ELEMENTS IN URBAN AEROSOLS (REFS. 11 AND 12)

(1) It is assumed that the aerosol samples were collected from 1000 m^3 air.
(2) IPAA performed with bremsstrahlung from 50-µA beam of 35-MeV electrons.
(3) INAA performed with neutrons at a flux of 6×10^{13} n/cm^2-sec.
(4) Gamma rays detected with 55-cm^2 Ge(Li) detector.

Element	Detection limit, ng/m^3		Element	Detection limit, ng/m^3	
	IPAA (ref. 11)	INAA (ref. 12)		IPAA (ref. 11)	INAA (ref. 12)
As	0.2	--------	Na	2	0.002
Br	30	0.005	Ni	.05	.25
Ca	30	2	Pb	12	-----
Ce	.4	2×10^{-5}	Sb	.3	2×10^{-5}
Cl	.4	.05	Ti	.9	--------
Cr	4.5	4×10^{-5}	Zn	3	4×10^{-5}
I	.17	--------	Zr	.2	--------

TABLE V.- COMPARISON OF CONVENTIONAL IPAA AND X-RAY SPECTROSCOPIC

ANALYSIS FOLLOWING PHOTON ACTIVATION (REFS. 13 AND 14)

Element	Reaction	$\dfrac{N_X(K\alpha)}{N_\gamma}$	Detection limits, μg (a)	
			γ-rays	X-rays
Cu	$Cu^{65}(\gamma,n)Cu^{64} \xrightarrow[\text{12.8 hr}]{EC/\beta^+} Ni^{64}$	120	32	0.28
As	$As^{75}(\gamma,n)As^{74} \xrightarrow[\text{17.9 days}]{EC/\beta^+} Ge^{74}$	.6	.7	1.1
Zr	$Zr^{90}(\gamma,n)Zr^{89} \xrightarrow[\text{78.4 hr}]{EC/\beta^+} Y^{89}$	1.1	.27	.24
Pd	$Pd^{104}(\gamma,n)Pd^{103} \xrightarrow[\text{17.0 days}]{EC} Rh^{103}$	4.3	5.5	1.3
Sn	$Sn^{118}(\gamma,n)Sn^{117m} \xrightarrow[\text{14.0 days}]{\gamma(M_4)} Sn^{117}$	.18	2.2	12
Cd	$Cd^{116}(\gamma,n)Cd^{115} \xrightarrow[\text{53.5 hr}]{\beta^-} In^{115m} \xrightarrow[\text{4.5 hr}]{\gamma(M_4)} In^{115}$	.7	.7	1.0
Hg	$Hg^{198}(\gamma,n)Hg^{197m} \xrightarrow[\text{24 hr}]{\gamma(M_4)} Hg^{197} \xrightarrow[\text{65 hr}]{EC} Au^{197}$	2.8	.9	.3
Pb	$Pb^{204}(\gamma,n)Pb^{203} \xrightarrow[\text{52.1 hr}]{EC} Tl^{203}$	.7	.8	1.2

[a] Calculated assuming 6 hours decay time (from the end of irradiation) and 10^3 as minimum number of counts in 12 hours.

TABLE VI.- EXPERIMENTAL LIMITS OF DETECTION FOR TRACE ELEMENTS USING

AUTOMATED PULSED X-RAY FLUORESCENCE SYSTEM (REF. 15)

[12-hour samples at $3m^3/hr$]

Secondary target	Element	Minimum detectable limits (3σ), ng/m^3	Secondary target	Element	Minimum detectable limits (3σ), ng/m^3
Ti (elements analyzed for 93.6 sec)	Al	40	Mo (elements analyzed for 83.4 sec)	Zn	1.06
	Si	11.78		Ga	.76
	P	6.58		As	.62
	S	5.88		Se	.52
	Cl	5.32		Br	.54
	K	1.83		Rb	.56
	Ca	1.54		Sr	.76
Mo (elements analyzed for 83.4 sec)	Ti	6.26		Hg	1.20
	V	4.44		Pb	1.82
	Cr	3.32	Sm (elements analyzed for 153 sec)	Cd	1.18
	Mn	2.70		Sn	1.56
	Fe	2.36		Sb	1.62
	Ni	1.24		Ba	6.20
	Cu	1.30			

TABLE VII.- EXAMPLES OF COMMON INTERFERENCES ENCOUNTERED

IN XRF AEROSOL ANALYSIS

Element a	X-ray energy for element a, keV	Element b	X-ray energy for element b, keV	Interference coefficient[a] between elements a and b, α_{ab} (ref. 15)
K	3.314 (Kα)	Cd	3.367 (Lβ)	0.36 ± 0.05
K	3.590 (Kβ)	Sn	3.708 (Lβ)	0.24 ± 0.04
Ca	3.692 (Kα)	Sn	3.708 (Lβ)	0.23 ± 0.04
Mn	6.490 (Kβ)	Fe	6.404 (Kα)	0.017 ± 0.001
Ti	4.932 (Kβ)	Ba	4.852 (Lβ)	0.52 ± 0.03
V	4.952 (Kα)	Ba	4.852 (Lβ)	0.28 ± 0.02
S	2.308 (Kα)	Pb	2.346 (Mα)	0.50 ± 0.03

[a] $C_a' = C_b - \Sigma \alpha_{ab} C_b$ where C_a' = Corrected concentration of element a, C_b = True concentration of element b (standard), and

$$\alpha_{ab} = \frac{\text{Apparent concentration of element a}}{\text{True concentration of element b}}, \text{ or } \frac{C_a}{C_b}.$$

TABLE VIII.- ELEMENTAL CONCENTRATIONS OBSERVED IN FINE AEROSOLS

(0.43 TO 0.65 μm) COLLECTED DOWNWIND FROM TWO OIL-FIRED

HEATING PLANTS AT LANGLEY RESEARCH CENTER (REF. 20)

[24-hour samples at 1.7 m^3/hr]

Element	Concentration in heating plant number 1, ng/m^3	Concentration in heating plant number 2, ng/m^3
V	128.11 ± 10.27	30.33 ± 10.09
Mn	≦20.61	2.70 ± 3.02
Fe	14.99 ± 1.12	40.22 ± 4.30
Ni	17.49 ± 0.54	4.43 ± 0.52
Cu	5.44 ± 0.36	23.10 ± 0.98
Zn	33.72 ± 0.55	91.06 ± 3.47
As	0.19 ± 0.44	4.43 ± 1.85
Se	0.91 ± 0.18	0.76 ± 0.15
Br	1.80 ± 0.28	13.22 ± 0.64
Rb	≦0.67	0.67 ± 0.29
Sr	≦0.69	0.75 ± 0.21
Mo	1.74 ± 0.50	1.32 ± 0.39
Ag	4.22 ± 1.52	5.64 ± 1.33
Cd	≦4.53	5.33 ± 1.55
Sn	24.66 ± 4.84	45.66 ± 5.24
Ba	≦32.58	27.20 ± 10.34
Pb	16.52 ± 1.09	53.55 ± 2.49

TABLE IX.- CALCULATED LIMITS OF DETECTION FOR SELECTED

ELEMENTS IN A PIXE ANALYSIS SYSTEM USING

2-MeV AND 4-MeV PROTONS (REF. 17)

Element	Limits of detection, ppm for 20 microcoulombs	
	E_p = 2 MeV	E_p = 4 MeV
S	0.24	----
Ca	.27	----
Fe	.05	----
Zn	.04	----
Br	.07	0.05
Mo	.26	.06
Cd	1.23	.13
Pb($L\alpha$)	.24	.21

TABLE X.- COMPARISON BETWEEN CALCULATED AND MEASURED

ELEMENTAL DETECTION LIMITS FOR AN AUTOMATED

PULSED XRF ANALYSIS SYSTEM (REF. 17)

Secondary target	Element	Detection limit, ppm	
		Calculated	Measured
Ti (100 seconds)	Al	8.2	8.2
	S	2.7	2.6
	Ca	1.7	---
Mo (100 seconds)	Fe	1.3	1.8
	Zn	.6	1.1
	Br	.4	.5
	Pb($L\alpha$)	.9	1.5
Sm (200 seconds)	Mo	1.0	---
	Cd	.7	0.9
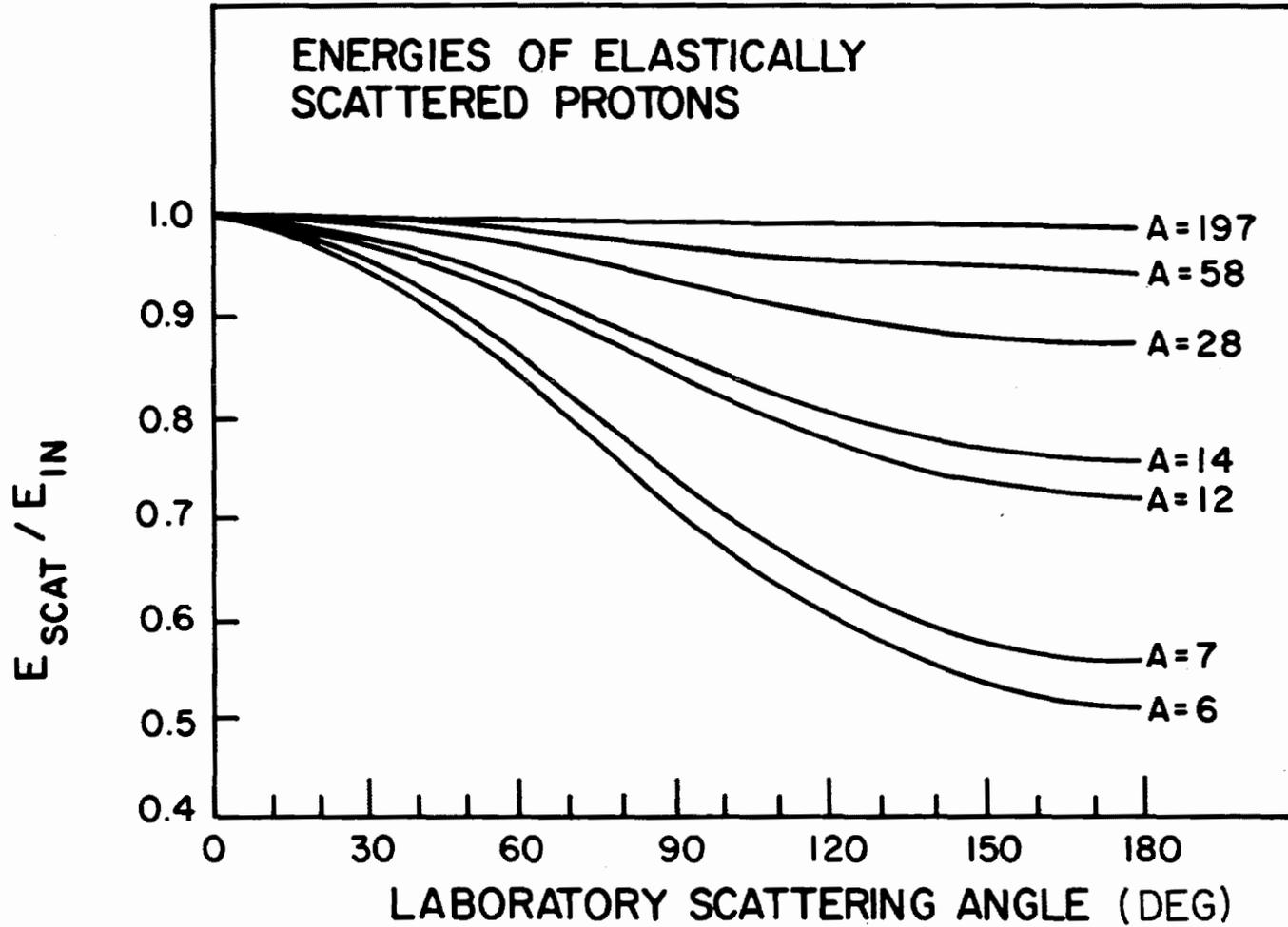
Figure 1.- Dependence of elastically scattered proton energies on angle and scatterer atomic weight.
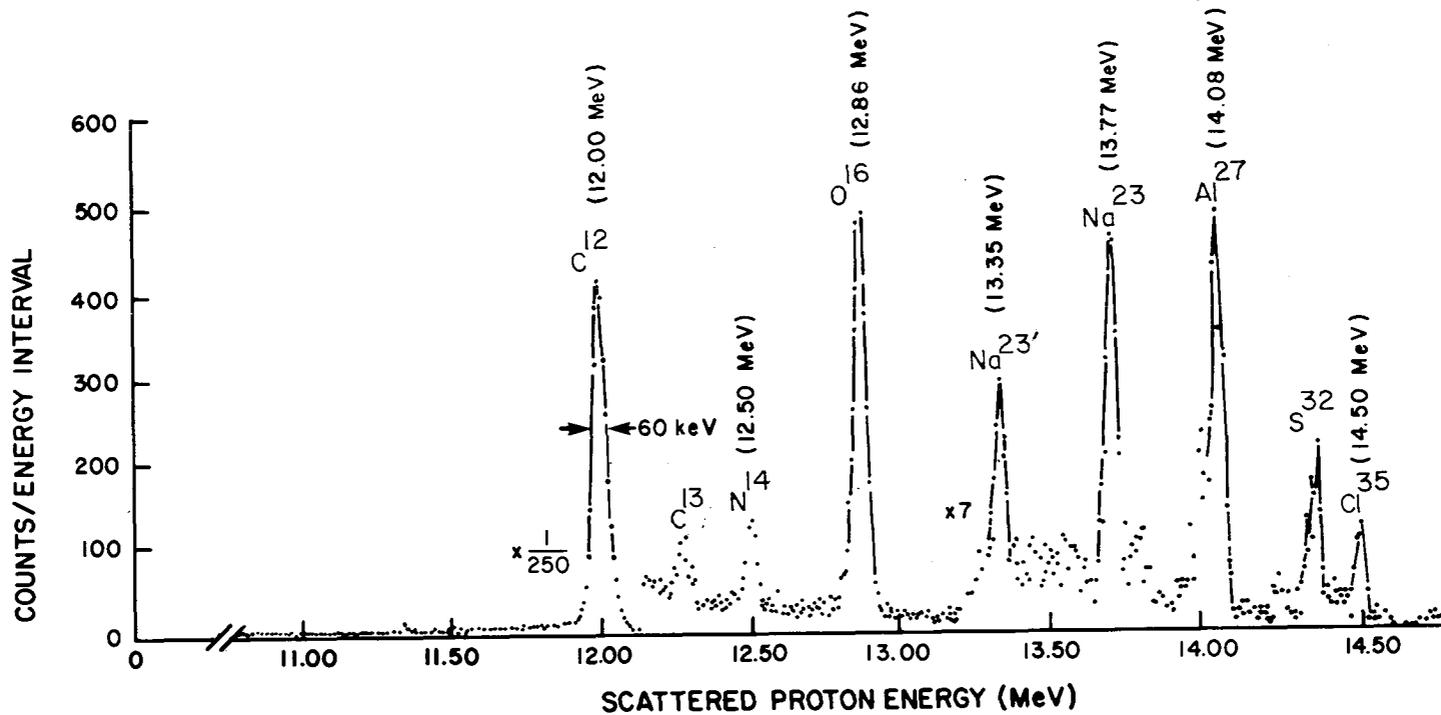
Figure 2.– Spectrum of 16-MeV protons scattered from an aerosol sample at $\theta_{lab} = 135°$ (Integrated incident proton charge = 4 microcoulombs); adapted from reference 6.
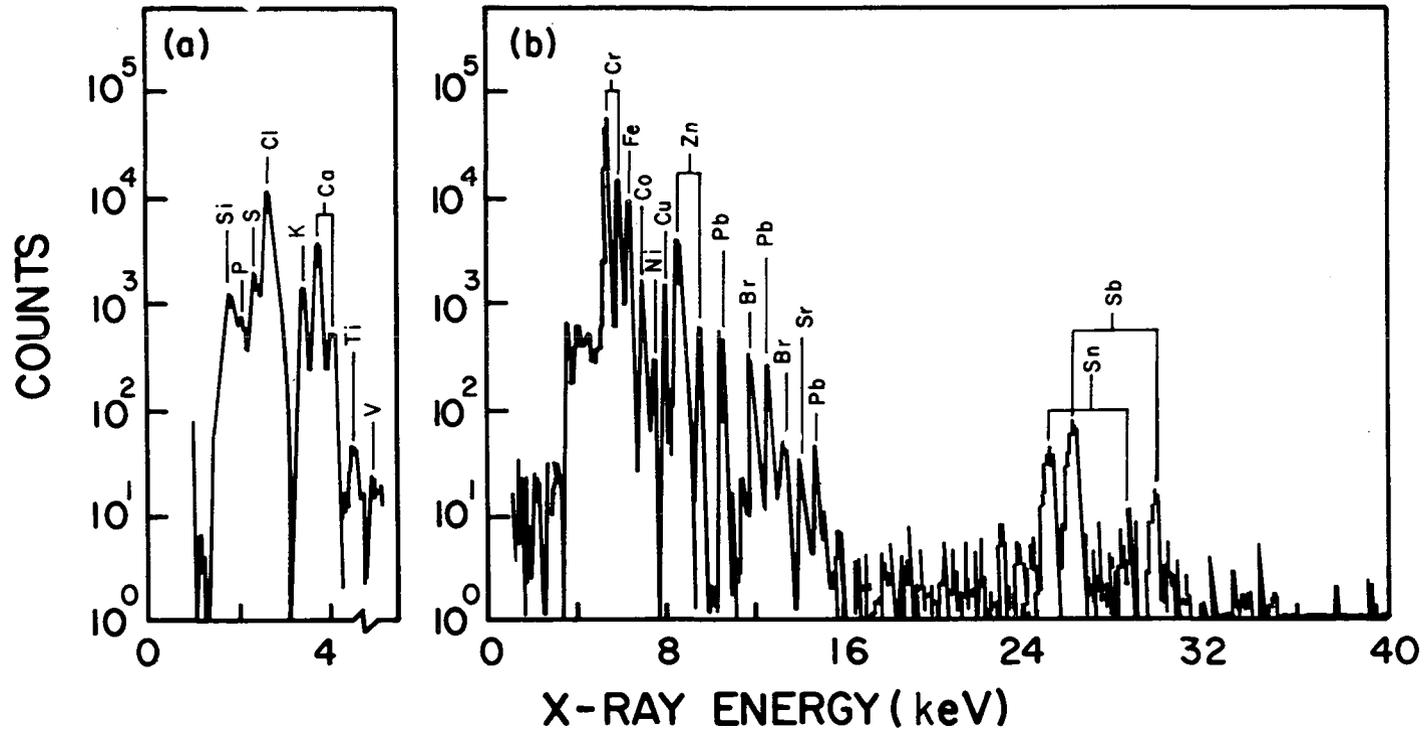
Figure 3.- Typical X-ray spectra from an aerosol sample. Spectrum a was obtained with 2-MeV protons, and 4-MeV protons were used for spectrum b.
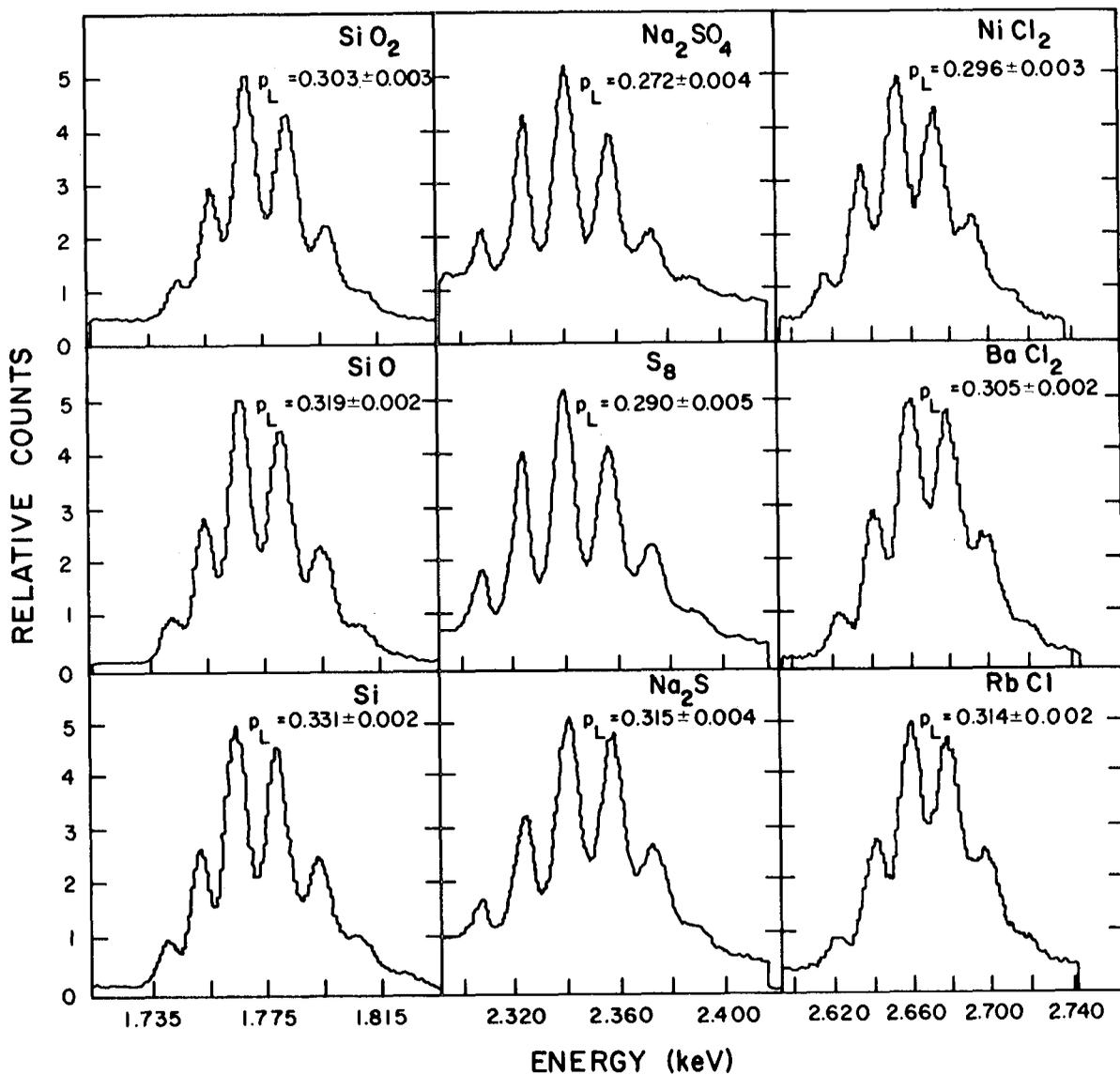
Figure 4.- Sample Kα-Satellite Spectra for several Si, S, and Cl compounds showing the variation of the relative satellite intensities with chemical environment. These spectra were all taken with 32.4-MeV oxygen ions. (Adapted from refs. 22 and 23.)
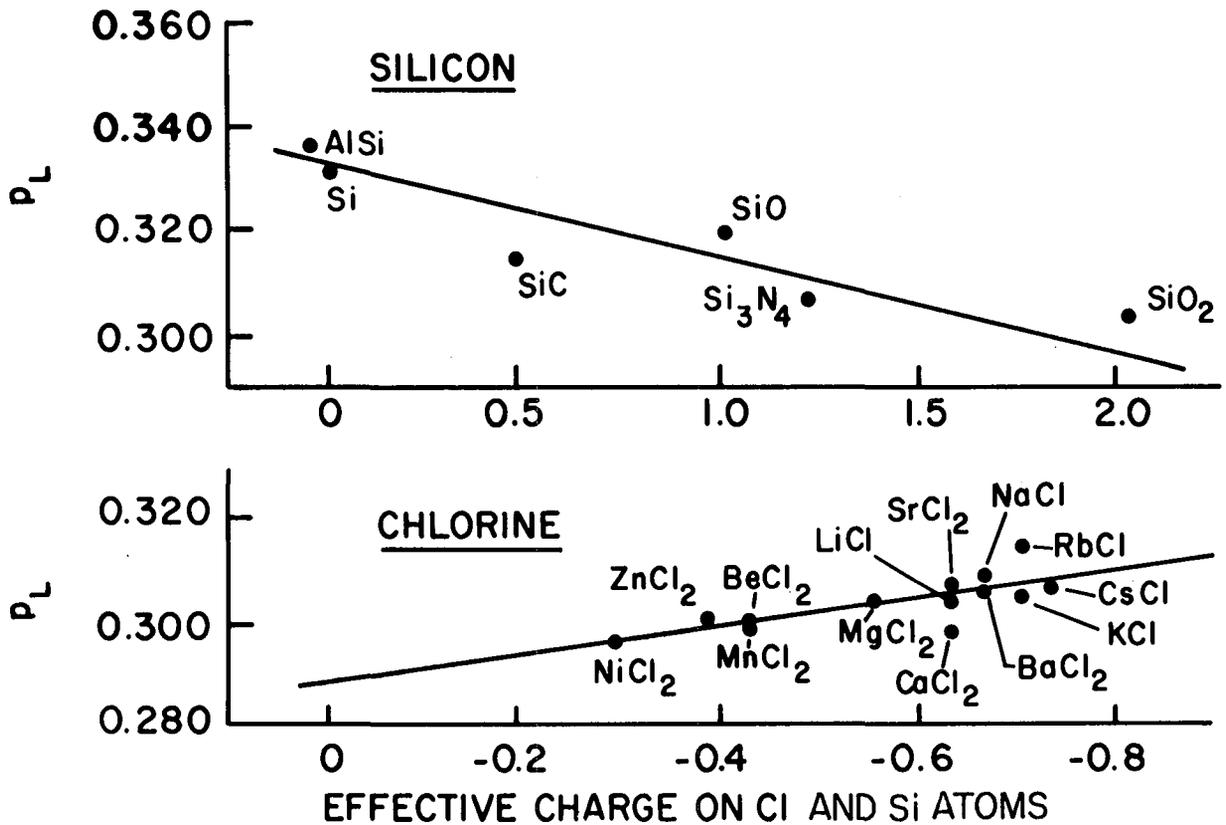
Figure 5.- Variation of p_L with effective charge for simple compounds of silicon and chlorine. (Adapted from refs. 22 and 23.)
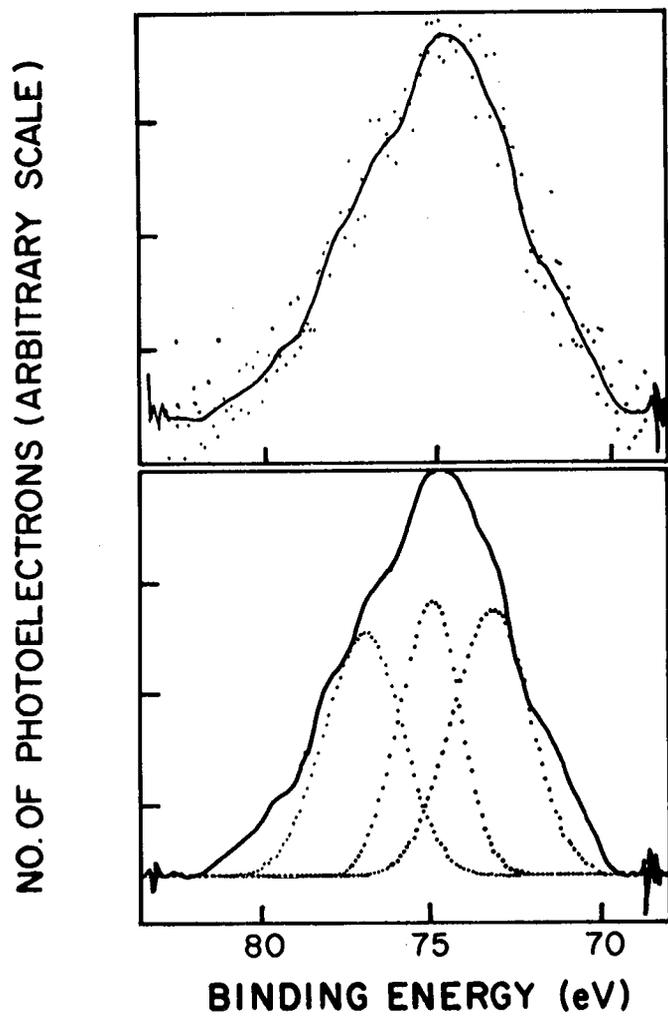
Figure 6.- Al 2p photopeak spectrum of aerosol sample 75-A-47;
raw data and deconvoluted components (ref. 25).

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15. Supplementary Notes

16. Abstract

Increasing reliance on coal as the future source of energy has spurred great interest in improved techniques for the measurement of heavy metals in effluents from various types of coal plants. There are several sensitive techniques currently used for the measurement of trace metals in environmental specimens. These can be divided into four major categories: (1) Atomic Absorption/Emission Spectroscopy, (2) Nuclear Techniques, (3) X-ray Spectroscopic Methods, and (4) Chromatography/Mass Spectrometry. Atomic Absorption technique is especially suited for aqueous sample analysis. However, the technique does not lend itself easily to multielement analysis. Nuclear techniques include Charged-Particle Scattering, Charged-Particle Activation Analysis, and Instrumental Neutron Activation Analysis. Charged-Partical Scattering and activation techniques are usually appropriate for the determination of lighter elements, most of which cannot be readily determined by other analytical methods. Neutron Activation Analysis is a widely utilized technique for fly/bottom ash elemental analysis, though certain critical elements (Be, P, S, Tl, Pb) cannot be easily determined. X-ray spectroscopic techniques provide simultaneous, sensitive multielement analyses and lend themselves readily to depth profiling, which has become increasingly important in aerosol studies. Chromatography/Mass Spectrometry methods, although quite sensitive, are not appropriate for aerosol analysis.

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