

THE APPLICATION OF X-RAY FLUORESCENCE SPECTROMETRY
FOR MULTIELEMENTAL ANALYSIS OF AIR PARTICULATE SAMPLES

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Abstract

The performance of XRF spectrometer as a tool for multielemental analysis of air pollution samples was discussed. The non-destructive couples with multielemental nature of the technique and satisfactory sensitivity for most elements were the most important characteristics for its popularity as a method of analysis. Thus, the technique promises a significance reduction in cost and time of analysis. As a result, more extensive and revealing air particulates survey should be possible, with consequent improvements in the discovery and positive identification of particulate pollution sources.

Introduction

An analysis of the elemental composition of particulate matter can be very useful in determining the sources of pollution. The chemical characterization of particulate pollutants in the environment has been greatly facilitated by the development in recent years of a number of instrumental multi-element analytical procedures. A rapid and inexpensive analytical technique is sought for if there are large numbers of air particulate samples need to be analyzed. With such technique, surveillance could be established over wide areas where air pollution is a problem.

The four techniques most widely used for elemental analysis of airborne particulate samples are optical emission spectroscopy (ES), atomic absorption spectroscopy (AA), Neutron activation (NA) and x-ray fluorescence (XRF). Each of these methods has definite advantages and disadvantages, though none is applicable

to all elements.

Emission spectroscopy¹ and atomic absorption spectrophotometry² are at present the most widely used methods in air pollution control laboratories. Emission spectroscopy is a multi-elemental technique but requires careful sample pretreatment and is not considered to be very precise. Its sensitivity varies significantly from element to element and in fact it has insufficient sensitivity to detect such important pollutants as Se, Hg, As and Cd.³

Atomic adsorption spectrophotometry is strictly a single element analytical technique, but the modern instruments have been equipped with interchangeable lamps for sequential analysis of up to six elements per sample. A standardized 8x10 inch air particulate filter may not be large enough for sequential analyses of many elements, especially when the more accurate method of standard addition is used. This technique may have insufficient sensitivity for As, Hg and Se.³

Application of neutron activation for analysis of air particulates has been demonstrated by a few workers, e.g., Zoller and Gardon, 1970;⁴ Dams, *et al.*, 1971.⁵ This method is very sensitive for some elements while quite insensitive for others in particular lead. It requires an access to a nuclear reactor if it is to cover the whole range of elements of interest to study. A long time between sample irradiation and measurement must be allowed, from several hours up to a few weeks for some elements.⁵ Thus, this method can be used for special cases but is not practical for routine application.

X-Ray Fluorescence Spectrometry

Presently, X-ray fluorescence analysis has emerged as a very powerful technique for the elemental analysis of environmental samples. The use of x-ray fluorescence is noticeably increasing because a number of attributes make it especially attractive.

for the analysis of airborne particulate matter. These features include (1) direct analysis of filter deposits with no need of sample preparation, (2) the nondestructiveness of the method, which permits samples to be retained for further analysis of future reference, (3) fairly uniform detectability across the periodic table, with the ability to analyze all elements from atomic number, 9 (fluorine) upward, and (4) the availability of commercial instruments that permit the analysis of samples for a large number of elements in relatively short intervals and at low cost. Once loaded with samples, the apparatus can operate unattended.

Briefly, an XRF technique consists of exciting inner electrons in atoms of an unknown material. On returning to the ground state, the electrons give up their energy in the form of x-rays. Thus, the characteristic of x-ray energies identify the element present in the material. The schematic view of x-ray fluorescence spectrometer is shown in Figure 1. Exciting radiation provided by an x-ray tube impinges upon the filter medium or impactor film containing the collected particulate matter. A fraction of the photons, if of sufficient energy, produce vacancies in the inner shells of atoms within the specimen, and in turn characteristic x-rays are emitted. These x-rays are detected by a detector sorted by their energies and the elemental concentrations are determined from the intensities of the x-rays.

There are two general approaches to sorting x-rays of different wavelength dispersion, in which the x-rays are identified after the original beam has been spread out by an analyzing crystal, and by energy dispersion, in which the undispersed x-rays are sorted into 100 to 1000 energy groups by means of a high-resolution frequency-sensitive semi-conductor detector coupled to a multi-channel analyzer.

Birks and coworkers⁶ at the Naval Research Laboratory carried out an EPA supported laboratory study to develop XRE as

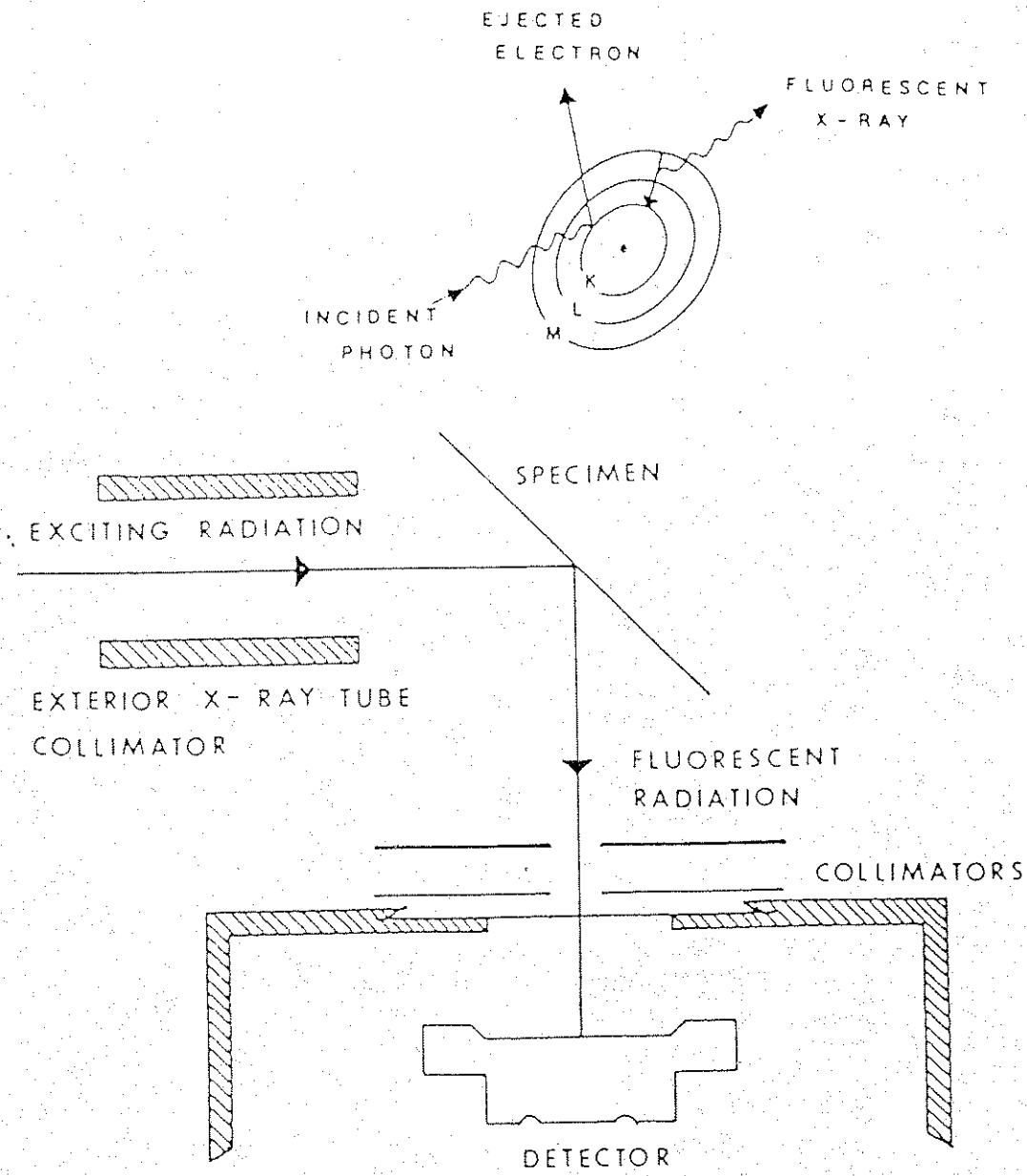


Figure 1
Schematic of X-Ray Fluorescence Analysis Technique

a method for routine multi-elemental analysis of filter-deposited particulate samples. The study compared various XRF techniques, including the options available for both excitation and detection of the fluorescence. Among the main conclusions were the following :

1. The single-element limit of detection, where interferences are absent or negligible, is about the same for either wavelength or energy dispersive.
2. Atmospheric particulates samples and the sample from the power plants, incinerators and other source emissions typically contain many elements at widely different concentrations. Energy-dispersive XRF spectra for such samples show significant interferences between neighboring elements, particularly the elements from sulfur to nickel in the periodic table, and require mathematical unfolding to determine the x-ray intensities. For such real pollution samples, the use of wavelength dispersion spectrometers with their high-resolution capability is a distinct advantage; their use requires considerably less data manipulation, thus avoiding what can be in many instances a major source of error.
3. For routine analysis of large number of samples in which elements of interest can be specified in advance, the use of multi-channel wavelength spectrometers appears as the most practical solution, inasmuch as these instruments combine two important features, i.e. high spectral resolving power and simultaneous measurement of a large number of elemental concentrations.

Figure 2 shows the comparison of the spectrum obtained for a CaCl_2 -KCl mixture using the wavelength dispersive and energy dispersive XRF. The K_β potassium line, which is easily separated by the wavelength dispersive XRF, is evident in the

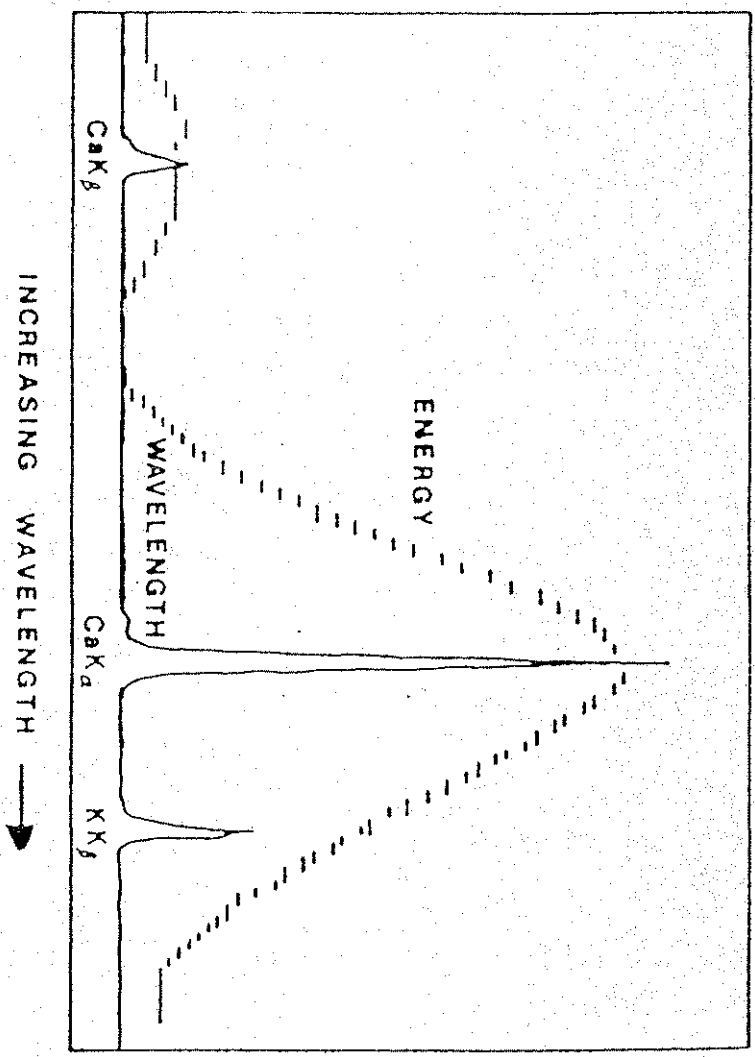


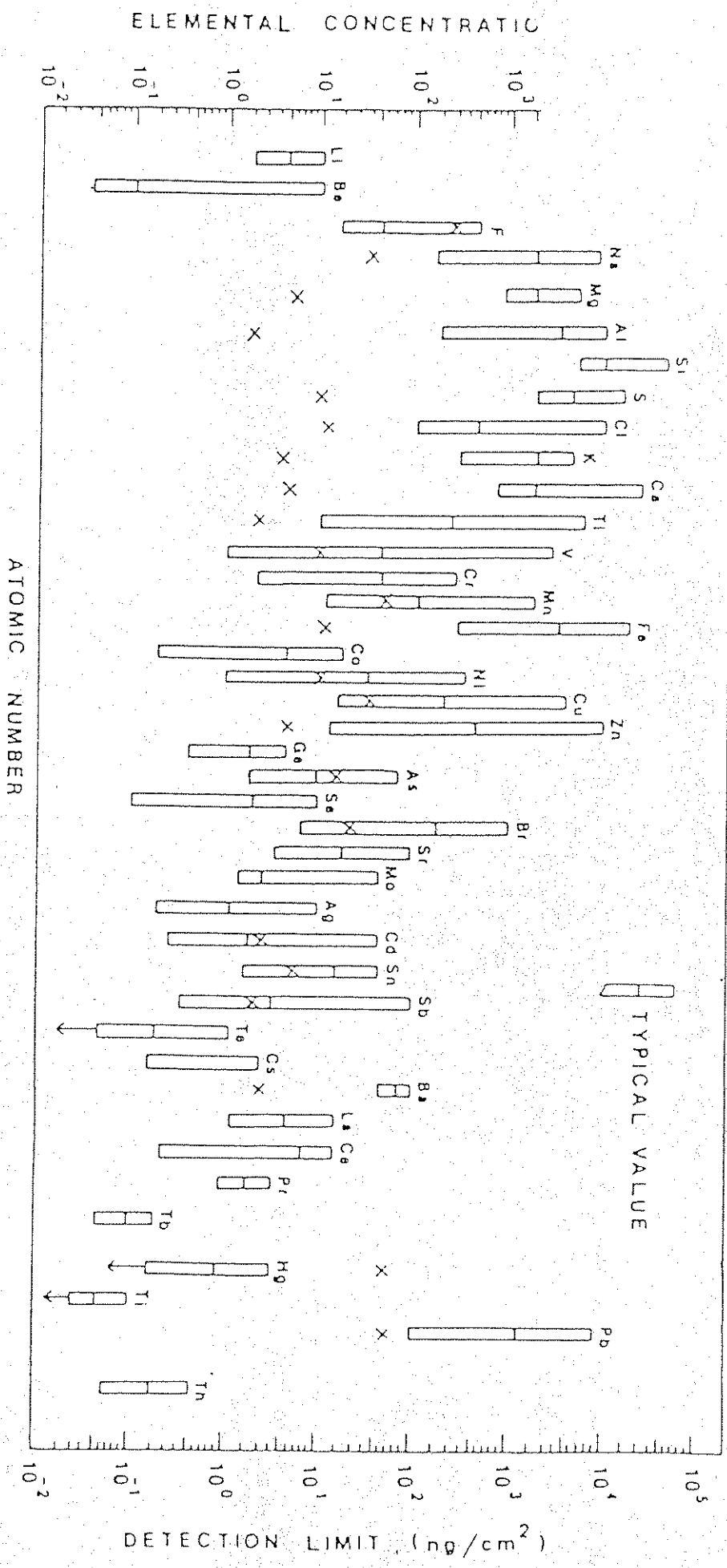
Figure 2
Comparison of X-Ray Spectra Obtained With Energy and Wavelength Spectrometers
on a Calcium-Potassium Sample

energy-dispersive spectrum only as slight distortion in the right side of the calcium K_{α} peak. The wavelength dispersion offers superior resolution for most elements, higher count rate per element, better peak-to-back ground ratio, and is applicable to the low-energy x-ray region where chemical effects (balance, coordination) can be measured using high-resolution x-ray spectroscopy.

The ability of the wavelength dispersive XRF system to detect a wide variety of elements in the atmosphere is illustrated in Figure 3 which is a plot of the ranges and typical values of the concentrations of various elements in urban air.⁷ The detection limits represented by the crosses (3 sigma peak areas above background) for x-ray fluorescence are superimposed on the plot. The detection limits are expressed in ng/cm^2 for each element assuming that it is deposited on a cellulose membrane filter which has a mass per unit area of $5 mg/cm^2$. The detection limits can be converted to units of mass per unit volume by dividing the values of Figure 3 by the air volume sampled per unit area of filter.

For x-ray analysis it is necessary that the particles be collected on a filter having very low level of impurities. Clean glass fiber filters containing a large amount of impurity are unacceptable for x-ray fluorescence, whereas teflon membrane filter with a polyethylene backing are found to be excellent for x-ray fluorescence analysis. The x-ray analysis may also be effected by the thickness of the specimens. The use of thin specimens minimizes matrix effects in x-ray fluorescence analysis. The preparation of thin uniform specimens usually eliminates the tedious procedure of either preparing sets of standards similar to the specimens to be analyzed, or adding internal standards to correct for matrix effect. When employing thin specimens, matrix enhancement effects are normally very small. Similarly, particle size effects caused by significant absorption or enhancement of required fluorescence radiation within a single grain may also deter the x-ray analysis.

something like this



Minimum Detectable Limits for the Wavelength Dispersive SRF System
 With Upper and Lower Ranges of Concentration for Urban Aerosols.

Figure 3

Even though the average mass per unit area of the particulate deposit conforms to that for a thin specimen, individual grains may be large enough to produce these effects.

The Performance of XRF Techniques

The XRF techniques have been used in many air pollution studies lately. Rhodes, *et al.*³ used radioisotope sources for excitation with a Si (Li) detector for energy-dispersive spectrometry and a minicomputer for data reduction and automatic instrument control in order to determine the heavy metal constituents of air particulates collected on a filter paper at various locations in Texas. Eighty-nine samples were collected and seventeen elements per sample were determined. Twelve of the samples were also determined with AA analysis for comparison as shown in Table 1. It was concluded that XRF spectrometer has proved itself capable of use for multi-elemental air particulate survey measurements and for pollution source location.

Dzuby, *et al.*,⁸ analyzed size fractionated aerosol sample collected in St. Louis using XRF technique for twenty two elements. The results of the analysis is given in Table 2. It was found that the small particles contain at least 75 percent of the S, Zn, Br and Pb at the sampling site. At least 75 percent of the Si, Ca, Ti and Fe is contained in the large particles size. The concentration listed in Table 2 for V, Cr, Mn, Ni, Cu, Zn, Rb, and Sr are significantly lower than the typical urban values in Figure 3. This may be due to the residential value of the sampling site and to the relatively clean air conditions at the time of measurements.

Trace metals collected on filter by a hi-volume air sampler for 24 hours were analyzed using XRF method by Dittrich and Cothern.⁹ A gamma ray exciting source (^{241}Am) and a Bremstrahlung exciting source (^{147}Pm) were both used to produce the x-ray. Several metals including Ti, Fe, Cu, Zn, Pb, Cd and Sn were

Table 1
 Comparison of Results of Atomic Absorption Analysis and X-Ray Fluorescence in Texas
 (Rhodes, *et al.* 3)

($\mu\text{g}/\text{m}^3$)

	Mn		Fe		Cu		Zn		Pb	
	AA	XRF	AA	XRF	AA	XRF	AA	XRF	AA	XRF
Amarillo	0.02	0.05	1.48	1.5	0.10	0.12	0.20	0.15	0.35	0.32
Beaumont	0.03	0.04	0.65	0.4	0.13	0.23	0.11	0.01	0.46	0.44
Clute	0.03	0.01	0.98	1.0	0.03	0.01	0.13	0.11	0.55	0.60
Corpus Christi	0.08	0.09	4.41	10.0	0.16	0.16	1.37	1.77	0.75	0.80
El Paso	0.10	0.11	2.61	3.4	0.80	0.96	1.55	1.66	2.73	2.56
Fort Worth	0.05	0.05	1.53	1.3	0.01	0.01	0.69	0.23	0.66	0.54
Harlingen	0.02	<0.03	1.24	1.2	0.20	0.02	0.20	0.02	0.12	0.04
Lubbock	0.16	0.17	2.59	8.6	0.03	0.01	0.22	0.05	0.34	0.26
Dallas	0.01	0.01	0.75	0.7	0.02	0.02	0.10	0.01	0.66	0.67
Houston	0.02	<0.03	0.65	0.6	0.22	0.22	0.19	0.14	0.92	1.03
Matagorda	NA	<0.02	0.28	0.2	0.31	0.36	0.37	0.005	0.08	0.04
San Antonio	0.01	<0.02	0.62	0.1	0.06	<0.01	0.51	0.07	0.46	0.33

Table 2

Analysis of St. Louis Aerosol by Energy-Dispersive
X-Ray Fluorescence (Dzubay, *et al.*⁸)

Element	Fine. * (ng/m ³)	Coarse. * (ng/m ³)
Si	600 ± 160	2000 ± 700
S	3700 ± 600	600 ± 200
K	160 ± 60	240 ± 80
Ca	110 ± 40	1700 ± 300
Ti	64 ± 7	210 ± 30
V	4 ± 2	<3
Cr	<3	<3
Mn	5 ± 2	6 ± 2
Fe	130 ± 14	400 ± 40
Co	<2	<2
Ni	<2	<2
Cu	<3	<3
Zn	45 ± 6	15 ± 2
As	20 ± 10	<4
Se	7 ± 2	<2
Br	114 ± 12	30 ± 4
Rb	<1	<1
Sr	<2	4 ± 2
Cd	<13	< 13
Sn	<14	< 14
Ba	<30	< 30
Pb	460 ± 50	110 ± 12

*The collected size ranges are 0-2 μm for fine particles
and 2.5 - 10 μm for coarse particles.

detected. It was found that the element in the Periodic Table between Ti and Cs were seen to have a sensitivity limit of $0.5 \mu\text{g}/\text{m}^3$ of air. Thus, the method provides a potentially useful technique for the determination of trace metallic air contaminants.

Stevens, *et al.*¹⁰, had applied XRF and source apportionment methods to determine the origin of the ambient aerosols that effect the visibility in the forested area of Shenandoah Valley. They calculated that 90% of visibility degradation in the valley was caused by fine particles ($<2.5\mu\text{m}$) and sulfates account for 63% the fine particle mass.

Wagman, *et al.*,¹¹ had carried out an experiment in order to make a comparison between XRF and AA analysis. The samples consisted of particle emissions collected on high-purity quartz filters from a controlled combustion source fueled with oil spiked with known amounts of organometallic compounds. The calculated values (shown in Table 3) for the five metals analyzed are based upon the amount of spiked fuel consumed and the known fraction of total emissions collected on the filter. They found that XRF concentrations are in remarkably good agreement with the calculated values with the exception of the cadmium value, which is about 10 percent low. This was probably due to the attenuation of some of the relatively low-energy cadmium fluorescence resulting from only partial penetration of collected aerosol into the interstices of the quartz fiber filter.

The performance of the XRF spectrometer as a method for the analysis of the elemental composition of the atmospheric aerosols were also studied by Hammerle and coworkers.¹¹ Ten elements Ca, Ti, Mn, Cr, Fe, Ni, Cu, Zn, Br and Pb that are present in typical air pollution samples were detected by the XRF spectrometer using a single excitation radiation (MoK α). As a comparison, Neutron Activation was also used to determine all of these elements except Pb, which was analyzed by Atomic Absorption

The elemental composition of the collected particulate matter as

Table 3

Comparison of XRF and AAS Analyses of Particulate Samples from a Simulated Combustion Source (Wagman, *et al.*)¹¹

Element	Total Collected, mg		
	Calculated Value*	Atomic absorption	X-ray fluorescence
Pb	202	228	212
Mn	182	195	183
Co	182	193	183
Cd	183	187	166
V	216	159	230

* Based on analysis of fuel oil spiked with organometallic compounds

determined by the two methods are shown in Table 4.

Table 4

Comparison of x-ray Fluorescence and Neutron Activation Analysis* (Hammerle, *et al.*, 1973)¹²

Element	XRF	NAA
Co	45 ± 2	48 ± 14
Ti	2.0 ± 0.2	Not seen
Cr	0.92 ± 0.08	1.2 ± 0.3
Mn	3.62 ± 0.14	3.44 ± 0.08
Fe	52.5 ± 0.3	55.7 ± 4.3
Ni	0.47 ± 0.03	0.40 ± 0.24
Cu	1.59 ± 0.06	1.22 ± 0.78
Zn	5.50 ± 0.20	5.50 ± 0.18
Br	5.04 ± 0.20	2.56 ± 0.15
Pb	28.5 ± 1.1	26.7 ± 1.4**

* mass is given in µg
 ** analyzed by atomic absorption

In summary, the performance of non-destructive x-ray fluorescence analysis systems has demonstrated the applicability of this technique to large-scale air sampling networks. Its sensitivity and accuracy is more than adequate for most air pollution studies.

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