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COMPARISON OF MINIMUM DETECTABLE LIMITS
AMONG X-RAY SPECTROMETERS

Joseph M. Jaklevic and Richard L. Walter

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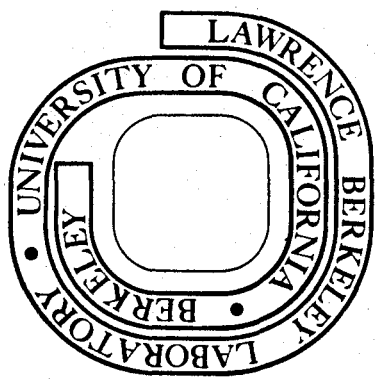
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X-RAY FLUORESCENCE ANALYSIS OF ENVIRONMENTAL SAMPLES

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COMPARISON OF MINIMUM DETECTABLE LIMITS AMONG X-RAY SPECTROMETERS

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INTRODUCTION

Methods for applying the various X-ray techniques to air particulate samples have been under development over the past several years at a number of laboratories. In some cases the technology has progressed beyond the experimental prototype stage to the construction of complete analysis facilities capable of processing large numbers of samples on a routine basis. It therefore seems appropriate that the capabilities of the various methods be compared on the basis of these existing facilities.

The comparison is based on measurement of minimum detectable limits for single elements for each of three X-ray fluorescence methods. These limits are derived from measured sensitivities and background counting rates. It is assumed that the background fluctuations are determined solely by random Poisson counting statistics. The peak-to-background ratio achieved at the detectable limit is also derived from these quantities. This parameter is of interest in assessing the susceptibility of the measured concentration to small changes or drift in the background levels such as might be introduced in certain types of spectral analysis.

The emphasis on minimum detectable limits as a parameter for comparison does not imply that it is the only governing factor in determining the utility of a given analytical method. The ultimate goal of any analytical measurement is to either determine the concentration of a given element to a desired degree of accuracy or to make a decision whether or not a particular element is present at some specified level. The single element detectabilities quoted in this discussion represent optimistic predictions regarding the statistical accuracy of any such measurement. Possible systematic errors or erroneous background determinations could increase the detectable limits over those quoted. Analysis of realistic samples can further complicate the picture because of interelement interferences, X-ray absorption and enhancement effects, and possible changes in the background characteristics. Each of these affects the various methods in different ways so that a simple comparison can no longer be made.

Three multielement X-ray fluorescence methods were considered:

(1) wavelength dispersive analysis using 16 fixed crystals and 1 scanning channel, (2) energy dispersive analysis using a series of discrete energy photon sources and a Si(Li) spectrometer, and (3) energy dispersive analysis using 3-MeV proton excitation and a Si(Li) X-ray spectrometer.

DEFINITION OF PARAMETERS

The expression used for the minimum detectable limit is based on the derivation used by Currie.¹ Using his Equation 2 we define the detection limits for a given method

$$C_D = 3.29 \sigma_o \quad (5.1)$$

where σ_o is the standard deviation of the observed result. This represents a 95% confidence level of detection at the decision limit C_c , which is defined as¹

$$C_c = 1.64 \sigma_o \cong C_D/2 \quad (5.2)$$

If we assume that the standard deviation at the minimum detectable limit is determined solely by the Poisson distributed counting statistics in the background under the X-ray peak, then Equation 5.1 becomes

$$C(\text{mdl}) = 3.29 (R_b/t)^{1/2}/S \quad (5.3)$$

where R_b is the background counting rate in counts/sec under the X-ray peak, t is the time interval of the measurement, and S is the sensitivity of the instrument for that specific element expressed as counts/sec per $\mu\text{g}/\text{cm}^2$ of concentration.

The peak-to-background ratio at the minimum detectable limit is given by

$$\text{PBR}(\text{mdl}) = S \cdot C(\text{mdl}) / R_b = 3.29 / (R_b t)^{1/2} \quad (5.4)$$

This parameter can be used to appraise the influence of random errors in the measurement of the background. In many forms of X-ray spectral analysis, the background level under a peak is inferred from background measurements over widely separated regions of the spectrum. The possibility exists that this estimate could be slightly in error as the sample form or composition is varied.

In order to include this effect in discussions of minimum detectable limit it is useful to consider an expanded limit as follows:

$$C'(\text{mdl}) = C(\text{mdl}) \left[1 + \frac{\epsilon}{\text{PBR}(\text{mdl})} \right] \quad (5.5)$$

where ϵ is a fractional uncertainty in the background brought about by systematic errors above the random errors included in $C(\text{mdl})$. If we assume, for example, that the estimated background is 10% less than the actual background, *i.e.*, $\epsilon = 0.1$, subsequent analysis will leave residual concentration for that element equivalent to 10% of the actual background. The value of this false measurement would be equal to the minimum detectable limit if $\text{PBR}(\text{mdl}) = 0.10$. Since typical $\text{PBR}(\text{mdl})$ can range from 0.05 to 2, this illustration emphasizes the importance of valid background subtraction methods for low-level detection.

RESULTS

Data are presented for three specific systems. The first system is a wavelength dispersive XRF unit that contains 16 fixed crystal spectrometers and 1 crystal with scanning capabilities.² Excitation is provided by the direct output from Cr or Rh anodes. Wavelength systems are commercially available from a number of manufacturers, and this particular one was purchased from Siemens. At least one company provides a system with about twice as many fixed crystals as the one referred to here.

The second XRF system is the pulsed Lawrence Berkeley Laboratory (LBL) unit for energy dispersive analysis described by Jaklevic.³ It employs secondary fluorescers of titanium, molybdenum or samarium for generating the exciting radiation. Because the fluorescent radiation from the samples is detected with a Si(Li) detector, the technique possesses all the advantages and the disadvantages of recording and analyzing a continuous spectrum of the X-ray yield. The predecessor to this system

was also developed at the Lawrence Berkeley Laboratory and has been described previously.⁴ This latter system is not pulsed and operates at lower counting rates (*i.e.*, approximately 5000 counts per second, with minimum detectable limits ranging from 2 to 10 times higher than the newer pulsed system). Commercial energy-dispersive units are also available from several firms, and these units can perform at minimum detectable limits comparable to the older LBL system. At least one significant difference concerning detection limits exists between both LBL systems in comparison to the wavelength system above and the PIXE system described below. The two energy-dispersive XRF systems operate with the samples in a helium atmosphere and thereby avoid the complications (and losses) of dealing with vacuum chambers. However, some of the background counts accumulated for very thin samples can be attributed to the X-ray scattering from the helium.

For the comparison, detectable limits from two particle-induced X-ray emission analysis (PIXE) systems will be considered. These are the 5-MeV and 3-MeV proton-beam systems operated at the Florida State University⁵ (FSU) and Duke University,⁶ respectively. Since the data were intended to represent optimum single element detectabilities, absorbers were used to reduce the low-energy continuum background in the case of measurement for the elements with higher energy K_{α} lines. This is analogous to the use of multiple fluorescent X-ray energies in the case of photon-excited fluorescence. In routine analysis a compromise between using absorbers is to employ a leaky absorber, that is, one which has a small hole that permits a few percent of the soft X-rays to reach the Si(Li) detector. The primary advantage is that only one irradiation is necessary per sample, but one pays the price of having a fairly complicated continuous background to take into account.

The results for the three types of systems are presented in Tables 5.1, 5.2 and 5.3 for a range of elements. The sensitivity (in units of counts/sec per $\mu\text{g}/\text{cm}^2$) is given in the left hand column and is the same regardless of the substrate on which the material is deposited. The background counts correspond to the counts occurring within the wavelength or energy window selected for the devices for counting or intergrating the "peaks." For the energy dispersion systems, the area of integration is restricted to the central region of the peak, which contains about 70% of the total area, for optimal signal to noise ratio. Values of R_b are included in the tables using the following notation:

- R_{b0} = Background count rate (counts/sec) under peak of element Z when no sample or substrate is present.
- R_{bs} = Background count rate (counts/sec) under peak of element Z when a clean sample substrate is present.

Table 5.1 EPA Wavelength Dispersive System

Element	S	No Membrane			Mylar			Nuclepore			Millipore		
		R _{bo}	C(mdl) ^a	PBR	R _{bs}	C(mdl) ^a	PBR	R _{bs}	C(mdl) ^a	PBR	R _{bs}	C(mdl) ^a	PBR
Al	130	0.3	1.3	0.63	0.5	1.7	0.49	0.4	1.7	0.50	0.8	2.2	0.38
Si	100	1.1	3.4	0.31	2.4	5.1	0.21	103	33	0.03	2.7	5.4	0.20
S	320	21	4.9	0.07	24	5.1	0.07	36	6.3	0.05	41	6.7	0.05
K	1200	43	1.8	0.05	45	1.8	0.05	45	1.8	0.05	210	3.9	0.02
V	160	1.5	2.4	0.27	4.0	4.0	0.17	9	6.0	0.11	23	9.5	0.07
Fe	140	25	12	0.06	29	13	0.06	34	14	0.06	51	17	0.05
Zn	180	1.1	2.0	0.31	2.6	2.9	0.21	4.5	3.9	0.16	14	6.9	0.09
As ^b	130	5.8	6	0.14	10	7.9	0.11	15	10	0.08	43	17	0.05
As ^c	40	7800	318	0.004	7900	320	0.004	8100	325	0.004	8400	330	0.004
Se	230		12										
Sr													
Cd	180	1.2	2.0	0.31	1.5	2.2	0.27	2.1	2.7	0.23	3.1	3.3	0.19
Ba	220	0.3	0.8	0.60	1.5	1.8	0.27	1.9	2.0	0.24	4.9	3.2	0.15
Sn	140	0.4	1.4	0.56	1.2	2.6	0.30	4.0	4.8	0.16	3.9	4.7	0.17
Pb	160	250	32	0.02	300	35	0.02	390	40	0.02	700	53	0.01

^aC(mdl) is in units of ng/cm². Data represent 100-second analysis.

^bScanning crystal results. Set for K_α line.

^cFixed crystal results. Set for K_β line.

Table 5.2 LBL Energy-Dispersive System

Element	S	No Membrane			Millipore		
		R _{bo}	C(mdl) ^a	PBR	R _{bs}	C(mdl) ^a	PBR
Al ^b	4.0	3.9	160	0.16	25.7	417	0.065
Si	11.2	4.4	62	0.16	28.7	157	0.061
S	63.5	8.3	15	0.12	53.6	38	0.045
K	227	12.3	5.1	0.09	79.7	13	0.037
V ^c	37.3	1.7	11.0	0.24	6.2	22	0.13
Fe	75.9	1.5	5.3	0.27	5.5	10	0.14
Zn	149	2.2	3.3	0.22	8.0	6.2	0.12
As	210	1.0	1.6	0.34	3.7	3.0	0.17
Se	233	0.9	1.3	0.34	3.3	2.6	0.18
Sr	321	3.2	1.8	0.18	11.7	3.5	0.096
Cd ^d	95.6	1.1	3.6	0.31	2.9	5.9	0.19
Sn	94.4	1.8	4.7	0.25	4.5	7.4	0.15
Ba	59.8	20.2	25	0.074	48.7	38	0.047
Pb ^e	110	2.3	4.5	0.215	8.8	8.9	0.111

^aC(mdl) is in units of ng/cm². Data represents 100-second analysis for each of three secondary fluorescers.

^bThe elements aluminum through calcium in the periodic table are measured by their K_α X-rays using a titanium fluorescer.

^cElements titanium through strontium are measured by K_α X-rays using a molybdenum fluorescer.

^dElements zirconium through barium are measured by K_α X-rays using a samarium fluorescer.

^eHeavy elements are measured with L_α or L_β X-rays using a molybdenum fluorescer.

Values of R_{bs} are tabulated for the following substrates: 5 mg/cm² Millipore esters of cellulose filter, 1 mg/cm² Nuclepore polycarbonate filter, 0.5 mg/cm² Mylar film, and ultrathin Formvar film. The minimum detectable limits in Table 5.1 are somewhat lower than the values in the report by Wagman *et al.*² and represent more recent measurements.⁷

The counting times were 100 seconds for each of three fluorescers for the case of the secondary fluorescer system and 100 seconds total for each of the other methods. The quantities C(mdl) and PBR(mdl) are derived from the sensitivity and background measurement using Equations 5.3 and 5.4 respectively. Values for C(mdl) are expressed in units of ng/cm².

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Table 5.3 Duke PIXE System

Element	S	No Membrane			Formvar			Nuclepore			Millipore		
		R _{bo}	C(mdl) ^a	PBR	R _{bs}	C(mdl) ^a	PBR	R _{bs}	C(mdl) ^a	PBR	R _{bs}	C(mdl) ^a	PBR
Al													
Si													
S	1.9	0.018	23	2.5	0.5	123	0.46	90	1650	0.03	43	1100	0.05
K	260	0.018	0.17	2.5	0.9	1.2	0.35	120	14	0.03	460	27	0.02
V	530	0.020	0.09	2.3	0.3	0.34	0.60	50	4.4	0.05	180	8.4	0.02
Fe	410	0.025	0.13	2.1	0.14	0.30	0.88	6	1.9	0.13	22	3.7	0.07
Zn	190	0.020	0.25	2.3	0.025	0.28	2.1	0.3	1.0	0.6	1.6	2.2	0.25
As	90	0.018	0.50	2.5	0.025	0.6	2.1	0.06	0.9	1.3	0.18	1.6	0.80
Se	70	0.018	0.60	2.5	0.018	0.6	2.5	0.04	0.9	1.7	0.14	1.7	0.90
Sr	28	0.013	1.3	2.9	0.013	1.3	2.9	0.015	1.4	2.7	0.07	3.1	1.2
Cd	2.3	0.010	14	3.3	0.010	14	3.3	0.018	19	2.4	0.02	21	2.2
Ba													
Sn													
Pb ^b	14	0.018	2.5	2.5	0.018	3.2	2.5	0.02	3.3	2.3	0.06	5.8	1.3

^aC(mdl) is units of ng/cm². Data represents 100-second analysis at 3 MeV proton energy and 70 nA beam current.

^bThe analysis of Pb is based on the L β line. The K α line is used for all other elements.

The results for these systems are also plotted in Figures 5.1, 5.2 and 5.3. Here the C(mdl) values (right-hand scale) for each system are compared to the relative abundances for aerosol pollutants as quoted by Cooper⁸ and represent typical values and upper and lower levels for urban elemental concentrations in ng/m^3 (left-hand scale). The conversion factor from ng/m^3 to ng/cm^2 depends on the volume of air sampled per unit area of filter. For a typical Millipore membrane filter operating in an aerosol sampler, the upper limit before the filter becomes clogged is about $10 \text{ m}^3/\text{cm}^2$. In designing an aerosol sampler, one allows for variations in pollutant levels above this typical urban value, so we might expect that systems will operate with an allowable limit of $3 \text{ m}^3/\text{cm}^2$. In Figures 5.1, 5.2 and 5.3 the normalization chosen between the left- and right-hand scales is the somewhat conservative value of $1 \text{ m}^3/\text{cm}^2$.

One general comment about Figures 5.1, 5.2 and 5.3 is that each of the three systems is capable of determining the abundances of many elements present in typical aerosols. Certain elements such as selenium, cadmium and mercury are more difficult to detect except when present in elevated concentrations or when longer sampling times are used.

The normal filter media used in aerosol sampling would be represented by either the Nuclepore ($1 \text{ mg}/\text{cm}^2$) or Millipore ($5 \text{ mg}/\text{cm}^2$) substrates. The values of R_{b0} represent a lower limit of the method, assuming a minimum possible backing. The values quoted for Mylar and Formvar are included as representatives of detectability that can be achieved with other sample forms appropriate for the respective methods.

The wavelength dispersive system appears to be better for detecting elements ranging from fluorine to sulfur. The data shown in Figure 5.2 represents the C(mdl) for 28 elements, but the present EPA system can only measure 16 elements conveniently with the fixed crystals and would need to measure the others successively with the scanning crystal spectrometer. The wavelength dispersive method is capable of the best resolution, which reduces the number of cases where interelement interferences are important. If no crystals are used to measure the background levels, then it may be difficult to make accurate determinations of concentrations near the minimum detectable limit when the peak to background ratio is small.

The secondary fluorescer system with an energy dispersive Si(Li) detector can obtain information on about 45 elements in a 300-second analysis when all three fluorescers are used. According to Figure 5.2, about 25 elements from a typical urban atmosphere could be analyzed above the minimum detectable limits. An additional 20 elements would normally be reported as not detected but would be analyzed when a pollution episode causes their concentration to rise above the minimum detectable limit.

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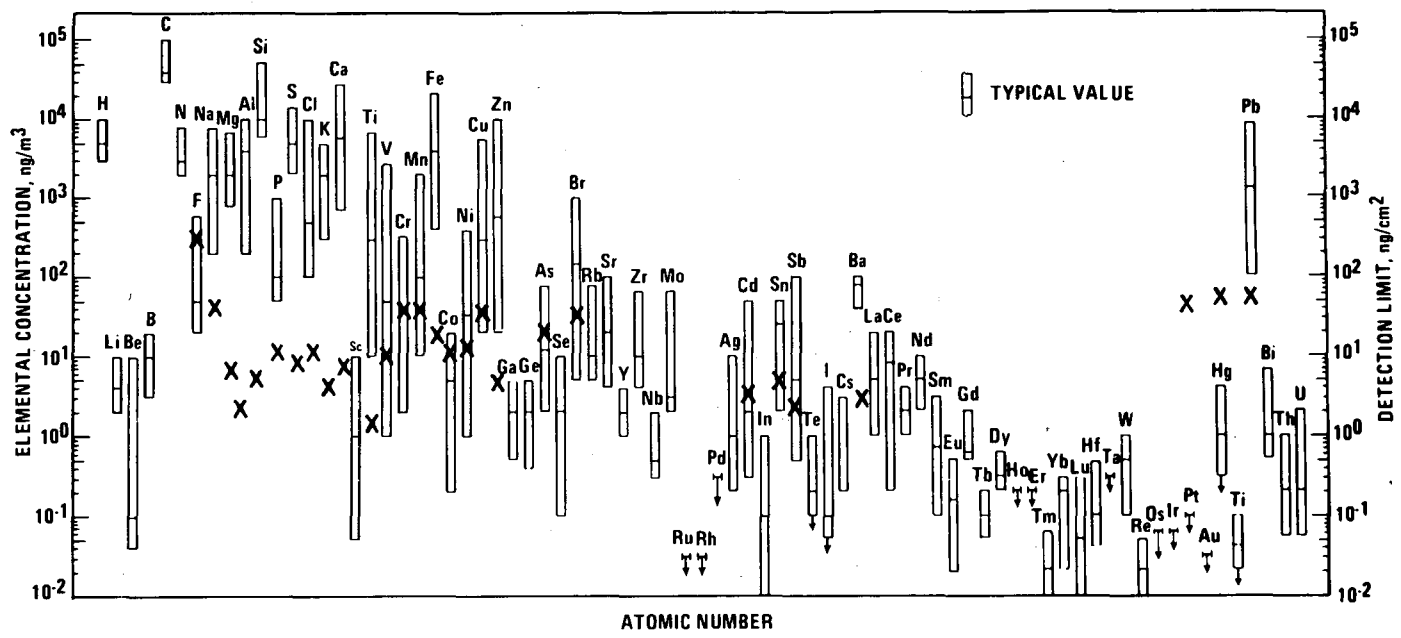


Figure 5.1 Minimum detectable limits in ng/cm² for the wavelength dispersive XRF system described in text are represented by the crosses. See text for discussion of conversion to ng/m³ for aerosol elemental concentrations according to right hand scale. The rectangles illustrate upper and lower ranges of concentrations for urban aerosols as reported in reference 8. Typical values are represented by the horizontal bars inside the rectangles.

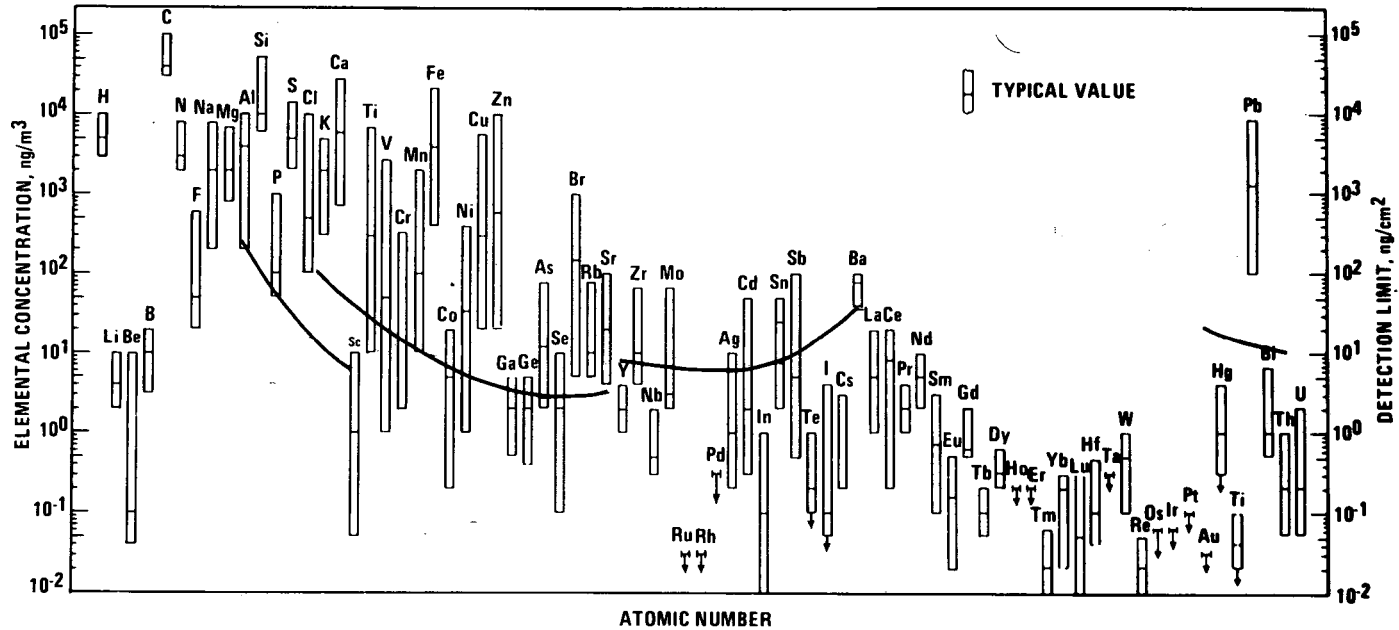


Figure 5.2 Minimum detectable limits in ng/cm^2 for the energy dispersive XRF system described in text. The curves are for the secondary fluorescers titanium, molybdenum and samarium (left to right) and for molybdenum (far right).

See caption of Figure 5.1 for additional explanation.

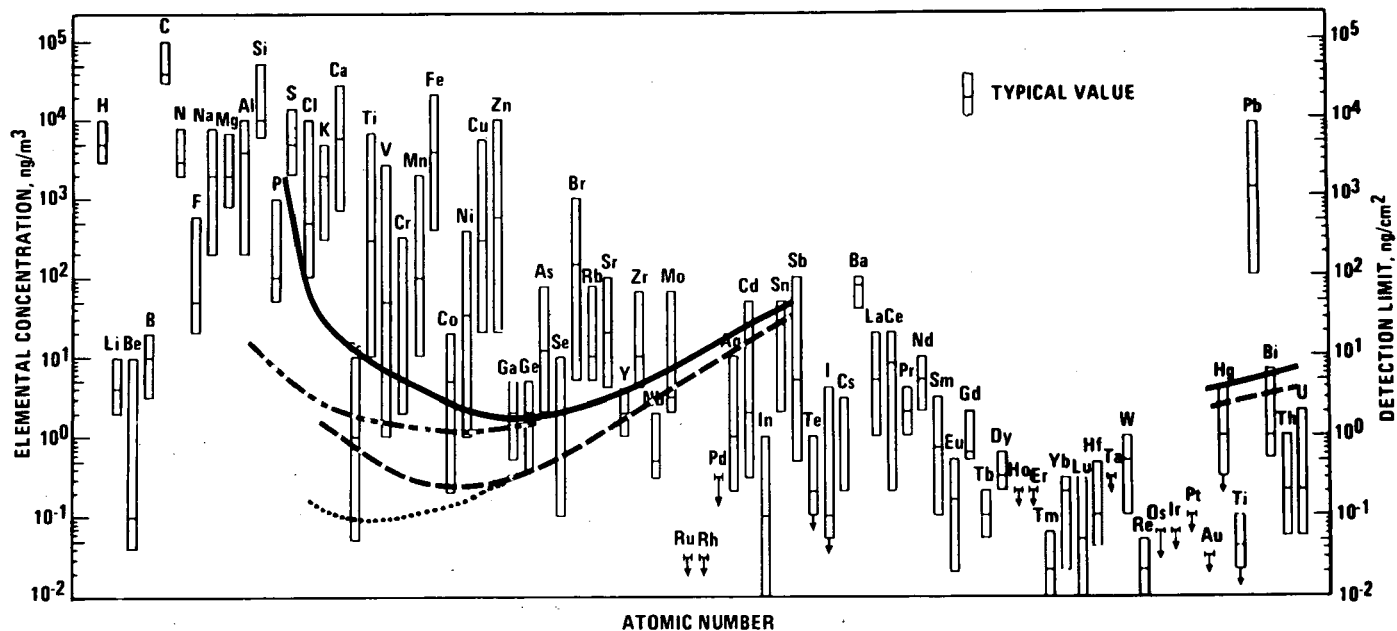


Figure 5.3 Minimum detectable limits in ng/cm^2 for the Duke and the FSU PIXE systems described in text. The curves illustrate the detection limits for the following situations: — Millipore substrate (Duke), --- Nuclepore substrate (FSU), -.- Formvar substrate (Duke), ... no substrate (Duke). See caption of Figure 5.1 for additional explanation.

According to Tables 5.1 and 5.2, the single element minimum detectable limits are comparable within a factor of 2 for elements with atomic numbers between 23 and 50. It should also be pointed out that in energy dispersive systems, the heavy elements from zinc to barium are measured using the high energy K_{α} radiation to avoid the interference in the L X-ray region that is discussed by Birks in Chapter 4 of this volume.

For the PIXE results in Table 5.3, the Duke system employed an absorber comprised of 0.13 mm of Mylar. The FSU results were obtained with a 0.7-mm Mylar absorber that had a hole amounting to 9% of the Si(Li) detector area.⁵ This enhanced the sensitivity for light elements, as can be seen in Figure 5.3. The FSU results for the heavier elements are slightly worse than the Duke values. Both systems utilized about 70 nA of beam with an irradiation area of only about 0.5 cm². This small area is of practical significance because it allows one to employ miniature air samplers or air filter devices of small orifices as have been constructed at FSU.⁵ The appropriate match between the area of irradiation and the sample deposit is essential if minimum detectabilities are to be achieved.

SUMMARY

On the basis of this comparison it is established that each of the three methods is capable of performing reasonable analytical measurement on air particulate samples. For each method, there are still possible improvements in techniques and instrumentation which could further enhance the capabilities of that technique. More detailed comparisons between the three XRF methods are difficult to make since additional factors such as accuracy, convenience, cost and reliability must enter into any practical considerations. The additional information presented in the accompanying chapters will contribute to an understanding of some of these factors.

ACKNOWLEDGMENTS

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