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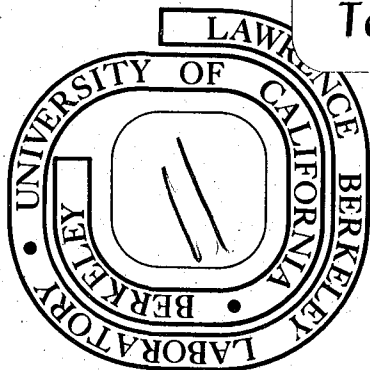
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AUTOMATED ELEMENTAL ANALYSIS USING ENERGY DISPERSIVE X-RAY FLUORESCENCE ANALYSIS

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comprehended outputs such as plots, averages, and statistical correlations were devised and adapted for use with the data file. At the core of the final data handling system is 40 million word disk file which permits immediate access to any of the analytical results generated in the study.(12)

ABSTRACT

The application of energy dispersive x-ray fluorescence analysis to the measurements of air particulate samples has been described in several recent publications. Among its many advantages, the possibility of automatic analysis for large scale monitoring programs has not been widely discussed. We describe the completion of a program in which a total of 34,000 air particulate samples have been collected and analyzed over the past two years. An automatic photon-excited energy dispersive spectrometer was used to obtain elemental concentrations for 27 elements on each sample. The sensitivity of the system is adequate to detect quantities of 10 ngm/cm² or less in a measurement time of approximately six minutes per sample. The precision and accuracy of the results will be compared to statistical analyses of the data set.

Summaries of the results are presented and the implications for air particulate monitoring discussed.

INTRODUCTION

Several laboratories are currently involved in programs which rely upon the x-ray fluorescence (XRF) method for the elemental analysis of aerosol particulate samples.(1-5) Intercomparison studies have validated the results obtained with this technique and have demonstrated its advantages over other analytical methods in many instances.(6-8) The non-destructive nature of XRF is especially important where it is desirable to perform a number of measurements on a specific environmental sample.

Photon-excited, energy-dispersive x-ray fluorescence analysis is particularly well suited for use in large scale studies of air particulates because of its multiple element capability, high sensitivity for most elements of interest including S and Pb, stability of calibration, and ease of automation. The normal air particulate sample consists of a thin deposit of particulates on a uniform filter backing and is an ideal sample for this analysis method.

In this study, we have taken advantage of these features to construct a complete sampling network and associated analysis facility which are designed for use in large scale monitoring programs. Previous publications have described portions of the system in great detail.(9-11) In the present paper, we describe the operating experience acquired during three years of operation of the complete system. During that period, we have acquired and analyzed over 34,000 air particulate samples. Results for total particulate mass and the elemental concentrations for 27 elements were obtained for each sample. We will report observations on the long-term stability of the system and reproducibility of the results.

One of the more challenging aspects of the program involves the manipulation of the large data files during the data analysis and the subsequent sorting of the analytical results to correspond to specific sampling sites and times. Formats for more easily

DESCRIPTION OF PROGRAM

The samples are collected as a part of the Environmental Protection Agency (EPA) sponsored Regional Air Pollution Study (RAPS) in St. Louis, Missouri. Ten automatic dichotomous samplers (11) were operated continuously at ten selected sites in the St. Louis' area. These sites are a part of a larger air quality monitoring network in which a number of quantities of interest in air pollution modeling were continually measured as a part of the RAPS program. The use of dichotomous samplers enabled us to acquire size fractionated samples in which the fine (<2 μm) and coarse (>2 μm) aerosol particles were collected separately on 37 mm diameter membrane filters. These filters are mounted in individual plastic holders which in turn are packed in 36 slide photographic cartridges for convenient automatic cycling through the sampler and the analysis equipment. When the ten site network is operated on a twelve hour sampling schedule, a total of 15,000 filters are collected per year. Over the course of the present study, a more frequent schedule was maintained at two of the urban sites resulting in a total of 34,000 samples over a two year period.

In order to analyze these samples for both total mass and elemental composition, it was necessary to devise automatic methods for sample handling, analysis, and data storage. Mass measurements were performed using a beta-particle attenuation method; elemental analyses for 27 selected elements were performed using an energy dispersive x-ray spectrometer with pulsed x-ray excitation.

Figure 1 shows a flow diagram for the study. The mounted filters are individually labeled and loaded into the photographic slide trays for subsequent handling in the automatic equipment. They are then "weighed" in the beta-gauge and the tare weight

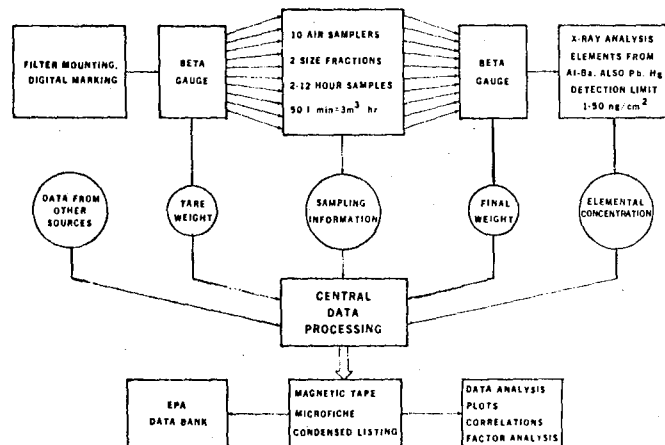


Fig. 1 - Flow chart of aerosol sampling and analysis program

written on magnetic tape. The slide trays are then sent to the monitoring site where they are exposed in the dichotomous samplers.(13) Upon return they are again analyzed in the beta-gauge and the results compared with the earlier measurement.

Finally, the elemental concentrations are measured in the XRF spectrometer and the results written in the data file. At the time of the XRF analyses, the information regarding the location, date, time, and duration of the individual filter samples is entered into the computer system. This information is obtained both from data written on the individual slide trays and redundant information in an accompanying log book.

As the data from various measurements are accumulated, they are entered onto the disk file from the magnetic tapes, sorted according to time and location, and stored in the proper sequence in the main data file. During the data sorting procedure, we apply a number of mathematical corrections which reduce the data to its final form.

BETA-GAUGE MASS MEASUREMENTS

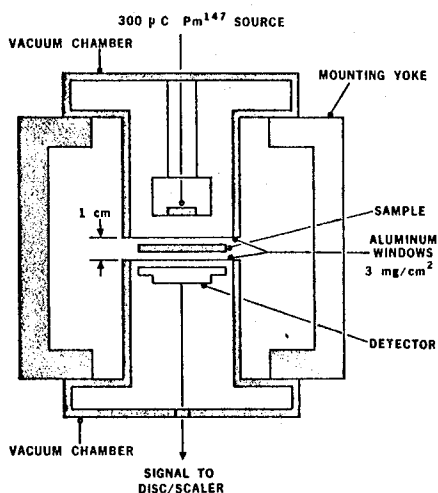


Fig. 2 - Schematic of beta-gauge

Figure 2 is a schematic of the beta-gauge showing a ¹⁴⁷Pm source mounted in the upper vacuum chamber with a 2.5 cm diameter cooled Si(Li) semiconductor detector in the lower chamber. The source strength is shown to be 300 µc, although, more recently we have employed a 4 mC source for higher counting rates. The large area detector and large source to detector distance results in a more uniform sensitivity over a larger area of the filter. The measurement consists of inserting the membrane filter into the region between the source and detector and observing the change in the total counting rate. The measured counting rate can be related to the mass per unit area of the sample by the following:

$$I = I_0 e^{-\mu x} \tag{1}$$

where I_0 and μ are the source intensity and mass absorption coefficient, respectively, I is the observed counting rate and x is the mass per unit area in mg/cm^2 .

Although the measurement is straightforward in principle, the use of beta-attenuation in the present study is complicated by the high precision required. A typical measurement consists of determining the mass accumulated a $4 \text{ mg}/\text{cm}^2$ filter to a precision of

accumulated a $4 \text{ mg}/\text{cm}^2$ filter to a precision of $\pm 10 \text{ } \mu\text{g}/\text{cm}^2$. This requires that each mass measurement be accurate to $\sim 0.1\%$. The elapsed time between the measurements of the tare weight and the exposed weight might be several months, during which time it is likely that the measuring apparatus has been subject to deliberate or accidental changes.

Our procedures employ frequent calibrations to eliminate many of the problems associated with system instability. A series of carefully weighed polycarbonate film standards which span the mass region of interest are measured with the beta-gauge and the resulting count rates determined. To achieve adequate statistical accuracies, scaler counts are accumulated for 100 second intervals at a counting rate of $\sim 10^5$ counts/second. The resulting data of mass (mg/cm^2) versus counts/second are then fitted to Equation 1 by the least square method. The resulting calculated values of I_0 and μ are then used to calculate the unknown masses of the membrane filters.

Since the experimental behavior of Equation 1 is not expected to be valid to a high degree of accuracy over a wide range of mass, the mass region covered by the thin-film standards is limited from $3 \text{ mg}/\text{cm}^2$ to $5 \text{ mg}/\text{cm}^2$. Typical values are $\mu = 0.145 \text{ cm}^2/\text{mg}$ and $I_0 = 1.53 \times 10^5$ counts/second. The average deviations of the gravimetric masses to the least square calculations was $\pm 3 \text{ } \mu\text{g}/\text{cm}^2$ for 70 consecutive calibrations.

Following the calibration run, two slide trays (36 samples each) are then automatically cycled through the beta-gauge with a 30 second counting interval per sample. At the end of this one hour cycle, the system is recalibrated and the cycle repeated.

Two sources of error which cannot be eliminated by frequent calibration are relative humidity variations and filter porosity effects. The mass of the cellulose membrane filters used in the present study are known to depend slightly upon the ambient relative humidity. By carefully measuring a large number of blank filters over a range of relative humidities encountered in a laboratory, we have established an experimental correction factor representing a $1.80 \pm 0.02 \text{ } \mu\text{g}/\text{cm}^2$ change in mass for each percent change in relative humidity. The correction is used to refer all measurements to the same value of relative humidity.

The filter porosity effects are manifested as a differences in apparent absorption per unit mass due to the difference in structure of the membrane filter relative to the continuous films used in calibration. Normally, this correction is not necessary if the configuration of the beta-gauge is not changed between successive measurement on the same filter. However, if the apparent μ has been altered due to a change in source chamber vacuum window, for instance, then the discrepancy between porous filters and the films can be changed. In order to correct for this, a series of clean filters whose masses have been previously measured are kept on hand to recalibrate the system in the event of unscheduled changes in the mass absorption coefficient.

When operated in the mode discussed above, the beta-gauge is capable of measuring a particular sample to an accuracy of $\pm 4 \text{ } \mu\text{g}/\text{cm}^2$. After the difference between the two successive measurement is calculated and the correction factors applied, the accuracy of the mass measurement is estimated to be $\pm 10 \text{ } \mu\text{g}/\text{cm}^2$. The characteristics of the dichotomous samplers require a flow of $50 \text{ l}/\text{min}$ distributed over an area of approximately 7 cm^2 on the membrane filter. The accuracy of the mass measurements then corresponds to $\pm 11 \text{ } \mu\text{g}/\text{m}^3$ for a two hour sample and $\pm 2 \text{ } \mu\text{g}/\text{m}^3$ for a twelve hour sample.

X-RAY FLUORESCENCE MEASUREMENT

The energy dispersive x-ray fluorescence spectrometer was specifically designed for use in this project. It consists of a low-background Si(Li) semiconductor detector spectrometer operated in a close coupled geometry with the sample and x-ray tube. Fluorescence excitation is provided by a low-power pulsed x-ray tube and a series of three secondary fluorescence targets. The advantages of pulsed excitation include increased sensitivity for analysis due to higher output counting rate and the reduction of pulse pile-up.(14) The use of secondary fluorescence targets allows a wider range of elements to be covered with optimum sensitivity. The three fluorescers used in the present study are Ti, Mo, and Sm. Using these, a total of 27 elements ranging in atomic numbers from Al through Ba together with Pb and Hg are measured at detectabilities of 10 ngm/cm² or less.

The x-ray spectrometer employs an anti-coincidence guard-ring detector operated with a pulsed-light feedback amplifier. This type of detector has been designed to reduce the background in photon excited XRF applications.(15) When operated in conjunction with the pulsed x-ray tube, output counting rates of 14000 cps can be achieved with a pile-up probability of 2% and energy resolutions of 195 eV at 5.9 keV. At this counting rate, the total analysis time for all three fluorescers was approximately six minutes.

An automatic sample changer was used to manipulate the filter holders and to sequence the secondary target during the analysis cycle. An on-line mini-computer was used to control the analysis sequence, acquire the pulse height analyzer spectrum, and perform the spectral stripping of the fluorescence data.

CALIBRATION PROCEDURES

The calibration factors are determined using a series of thin-film standards which closely replicate the membrane filter samples. These standards are either uniform deposits of individual elements whose mass has been determined gravimetrically or multiple element standards in which the ratio of elemental concentrations is accurately known.(16) Calibration factors for elements for which standards are not available are derived from interpolation between near by atomic numbers.

Table 1 is a list of the 27 elements reported in the study giving the minimum detectable limit (3 σ) and sensitivity as determined from the calibration procedures. To convert detectabilities to ng/m³ for a 12 hour sample, divide the values in column three by 5; for example, the detectable limit for S is 6 ng/m³ for a twelve hour sample. The errors quoted for some of the sensitivities reflect the uncertainties associated with the thin-film calibration.

Once the data from all three fluorescence and the total mass measurement are available, they are entered into the large disk file where additional corrections are made. These include corrections for particle size effects, interelement interference of x-ray lines in the XRF spectrum and the penetration of particles into the filter. Finally, the results are converted from ng/cm² on the filter to ng/m³ referred to the air volume sampled using the known flow characteristics of the dichotomous samplers.

Particle size effects are due to the absorption which the fluorescent x-rays experience within discrete particle on the filter. Like all absorption effects, they are more severe for the light elements where the lower energies of the characteristics x-rays are in the region of greatest absorption. The particle size effect are corrected using the method described Dzubay and Nelson.(17) They assume uniform spheres

Table 1 - Detectable Limits and Sensitivity for Energy Dispersive X-ray Fluorescence Analysis

ELEMENT	ATOMIC NUMBER	MINIMUM DETECTABLE LIMIT (ngm/cm ²)	SENSITIVITY (counts/sec per μ gm/cm ²)
Al ^{a)}	13	200	7.40
Si	14	58.9	25.3 \pm 5.3
P	15	32.9	48.0
S	16	29.4	83.8 \pm 1.5
Cl	17	26.6	125
K	19	9.14	272
Ca	20	7.7	411 \pm 7.0
Ti ^{b)}	22	31.3	28.8
V	23	22.2	37.8
Cr	24	16.6	49.3 \pm 1.0
Mn	25	13.5	59.8 \pm 1.0
Fe	26	11.8	76.4 \pm 1.2
Ni	28	6.2	112 \pm 1.8
Cu	29	6.5	128 \pm 2.3
Zn	30	5.3	148 \pm 2.1
Ga	31	3.8	166
As	33	3.1	209
Se	34	2.6	234
Br	35	2.7	258
Rb	37	2.8	304 \pm 2.5
Sr	38	3.8	320
Hg	80	6.0	109
Pb	82	9.1	109 \pm 1.9
Cd ^{c)}	48	5.9	75.5 \pm 1.9
Sn	50	7.8	75.7 \pm 7.7
Sb	51	8.1	74.6
Ba	56	31	62.1 \pm 1.7

- a) Elements analyzed for 93.6 seconds, Ti secondary target.
- b) Elements analyzed for 83.4 seconds, Mo secondary target.
- c) Elements analyzed for 153 seconds, Sm secondary target.

ELEMENT	FINE PARTICLES	COARSE PARTICLES
Al	0.91 \pm 0.09	0.41 \pm 0.12
Si	0.93 \pm 0.07	0.48 \pm 0.15
P	0.95 \pm 0.05	0.58 \pm 0.24
S	0.97 \pm 0.03	0.64 \pm 0.22
Cl	0.98 \pm 0.02	0.70 \pm 0.20
K	0.99 \pm 0.01	0.78 \pm 0.15
Ca	0.99 \pm 0.01	0.81 \pm 0.13
Ti		0.87 \pm 0.10
V		0.90 \pm 0.08
Cr		0.92 \pm 0.07
Mn		0.93 \pm 0.06
Fe		0.94 \pm 0.05
Ni		0.96 \pm 0.03
Cu		0.94 \pm 0.06
Zn		0.95 \pm 0.05

Table 2 - Particle Size Attenuation Corrections for the Light Elements

of composition approximating that of typical aerosol particles. Table 2 is a list of these values for the two size ranges of interest. We can see that the fine particles are very slightly affected.

Interelement interferences due to x-ray lines which overlap in the pulse height spectrum are corrected by first measuring the magnitude of these interferences and apply a correction according to the following:

$$C_i = C_j - \sum \alpha_{ij} C_j \quad (2)$$

where the C_j are the observed concentrations, C_i is the corrected concentration, and α_{ij} is the influence of element j and the concentration of i. It is measured by analyzing a thin-film standard of element j using the spectral stripping procedure appropriate for element i; α_{ij} is then the ratio of the apparent concentration of i to the known concentration of element j in the standard.

In practice the number of overlaps is few, a list of the ones currently used in the data analysis is given in Table 3. It should be noted that the interference of Pb L_{α} and As K_{α} is not included since this problem is handled directly in the spectral stripping program by removing the complete Pb L x-ray spectrum before the As analysis is performed. The largest interelement corrections is due to the Pb M x-ray overlap with the S K_{α} . However, since typical S concentrations in St. Louis were an order of magnitude larger than Pb, the correction is normally 5% or less.

Element i	X-ray Line	Element j	X-ray Line	α_{ij} a)
K	K	Cd	L	0.36 ± 0.05
K	K	Sn	L	0.24 ± 0.04
Ca	K	Sn	L	0.23 ± 0.04
Ca	K	Sb	L	0.28 ± 0.04
Mn	K	Fe	K	0.017 ± 0.001
Ti	K	Ba	L	0.52 ± 0.03
V	K	Ba	L	0.28 ± 0.02
S	K	Pb	M	0.50 ± 0.03
Hg	L	Pb	L	0.010 ± 0.002

Table 3 - Interelement Interference Corrections

Penetration of the particulates into the filter does not normally require sizeable corrections. However, it has been observed that under certain meteorological conditions, a significant penetration of S particulates into the cellulose filter matrix can occur. (18) In that instance large absorption corrections may be necessary. In order to identify these occurrences and derive the appropriate correction, an additional measurement of the S concentration is performed with the sample inverted. In this situation, the aerosol deposits on top of the sample and facing away from the detector instead of underneath as would normally be the case. By observing variations in the ratio of the two S measurements, an estimate of the particulate penetration can be obtained and a correction applied to the data. Because of the larger uncertainty associated with this correction, the error assigned to the light element determination is appropriately increased.

Some idea of the accuracy and long-term stability of the system can be gained from Tables 4, 5, and 6. Table 4 gives the results of a comparison of analyses of ambient air samples acquired by three dichotomous samplers operated side by side. One of the samplers has been in field use for two years without recalibration prior to the comparison. The average deviations among the results represent the combined precision of the air sampling and XRF measurement. Since S and Pb are predominantly in the fine particle fraction, the errors of 0.5 and 1.2% should be representative of the fine particle sampling error whereas the 4.6% error in the measurement of coarse particulate Fe reflects the uncertainty associated with the sampling of coarse particles.

The precision of the XRF measurement over the long-term are given in Table 5. Here we list root mean square deviations obtained from successive analysis of the same filter over a three month period. No

Element	Particle Size	Mean Concentration (ng/m ³)	Average % Deviations
S	Fine	1218	0.5%
	Coarse	250	2.5%
Pb	Fine	1154	1.2%
	Coarse	369	2.9%
Fe	Fine	208	2%
	Coarse	1622	4.6%

Table 4 - Reproducibility of Air Samplers Measured Side by Side Sampling

Element	Average Concentration (ng/cm ²)	Deviation (ng/cm ²)	% Deviations
Al	740	33	4.5
Si	2397	40	1.7
P	217	15	6.9
S	11693	189	1.6
Cl	298	9.2	3.1
K	515	7.7	1.5
Ca	3959	55	1.4
Ti	123	18	14.6
Mn	48.1	5.5	1.1
Fe	1930	18	0.9
Cu	123	5.9	4.8
Zn	519	29	0.6
Br	126	2.0	1.6
Pb	653	5.5	0.9
Sr	12.9	1.1	8.5
Cd	24.8	1.6	6.4
Sn	34.8	2.1	6.0
Sb	6.8	2.0	29
Ba	102	5	4.9

Table 5 - Root Mean Square Deviations of Analyses of Identical Samples Over a Three Month Period

Element	Sample 1		Sample 2	
	A	B	A	B
K	30600 ± 610	33700 ± 670	14100 ± 280	15169 ± 303
Ca	739 ± 136	770 ± 7	1264 ± 141	1517 ± 10
Ti	698 ± 62	820 ± 56	1853 ± 73	2136 ± 20
V	78 ± 25	79 ± 9	95 ± 25	43 ± 21
Cr	29 ± 19	20 ± 7	70 ± 20	70 ± 8
Mn	27 ± 15	8 ± 6	27 ± 15	6 ± 4
Fe	49 ± 12	76 ± 6	173 ± 14	195 ± 12
Ni	1185 ± 17	1190 ± 5	3980 ± 19	3975 ± 20
Cu	15 ± 4	18 ± 3	33 ± 5	47 ± 2
Zn	79 ± 5	63 ± 7	87 ± 6	121 ± 8
As	499 ± 8	482 ± 2	3634 ± 19	3534 ± 14
Se	43 ± 12	0 ± 8	28 ± 4	9 ± 6
Br	24 ± 3	24 ± 2	8 ± 2	8 ± 2
Sr	301 ± 5	318 ± 6	174 ± 4	185 ± 3
Hg	11 ± 4	5 ± 1	10 ± 3	7 ± 2
Pb	17 ± 6	19 ± 3	0 ± 5	5 ± 5
	1759 ± 18	1751 ± 32	1012 ± 15	992 ± 9

Table 6 - Comparison of Our Analyses with Independent XRF Measurements. Values listed are in ng/cm². Errors are 1 σ for counting statistics only. Column A are the results from Giauque, B are from the present work.

adjustment in the calibration was made during this interval and the normal analysis procedure was followed. The results show a reproducibility of better than 1% for the major elements Fe and Pb. This should represent the combined uncertainties due to x-ray tube stability, sampling positioning error, etc. The larger percent of errors associated with less abundant element reflect statistical counting accuracy in the individual measurements.

Table 6 is a comparison of our results using the automatic procedure with results obtained in the same samples by an independent XRF measurement at LBL. The reference measurements were performed by R. Giauque using a separate XRF system calibrated by a different series of standards and validated by numerous inter-comparison studies. The excellent agreement validates the accuracy and stability of the calibration as implemented in the present study.

RESULTS

As noted earlier, the final stage in the data analysis process is the ordering of the results in the large data file according to sampling time and place.

If we include the data for 27 elements with associated errors, ten sampling sites, two size ranges and each 6 or 12 hour sampling interval over a two year period then this constitutes well over 10^6 pieces of information available for examination by the experimenters.

Several formats for presenting this data set are currently available. These include time sequence plots of selected elements, scatter plots of correlated pairs of measurements, matrices listing correlation coefficients between pairs of observables, and averages of various measurement over extended periods.

Figure 3 shows some examples of plots of elemental concentrations obtained from two hour samples and presented as a function of time for a typical urban site in the RAMS network. All results are from the fine particulate aerosol fraction and represent a 20 day interval in July in 1975. The S concentration exhibits a slowly varying profile characteristic of long-term meteorological trends as opposed to Lead and Bromine which are strongly correlated and exhibit diurnal patterns characteristic of their common automotive origin. Note in the early portion of these plots there are incidents of high Pb concentration which correlate with Zn rather than with Br. This is probably indicative of a non-automotive source for the Pb.

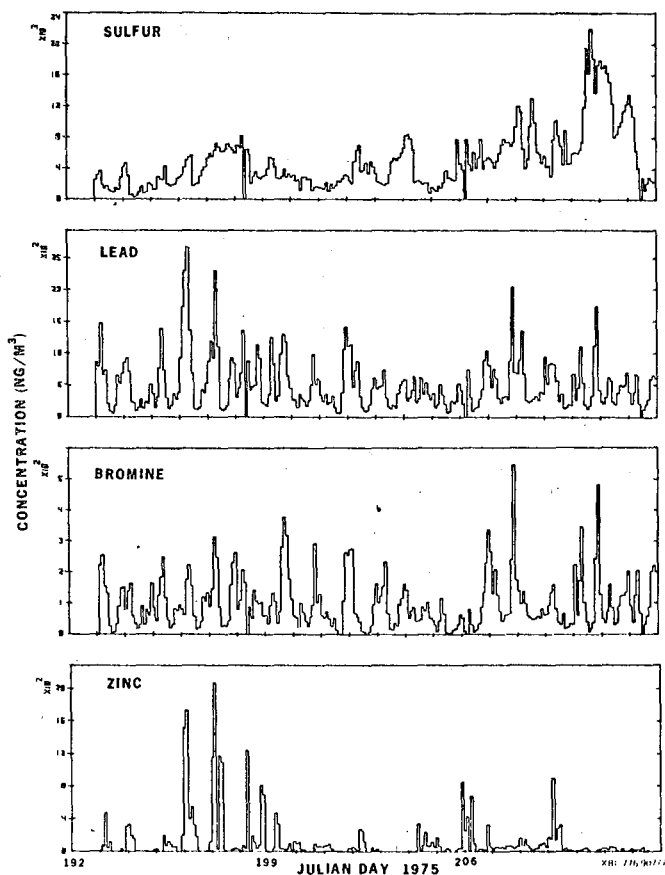


Fig. 3 - Plot of elemental concentration of fine particle S, Pb, Br and Zn. Sampling interval is 2 hours.

Figure 4 is a scatter plot showing the correlation of fine particulate S with the fine particulate mass measurement. A linear regression analysis between these variables indicates that as much as 12% of the total fine particulate mass is elemental S which would represent 36% of the mass if it were in the sulfate form as expected. (19)

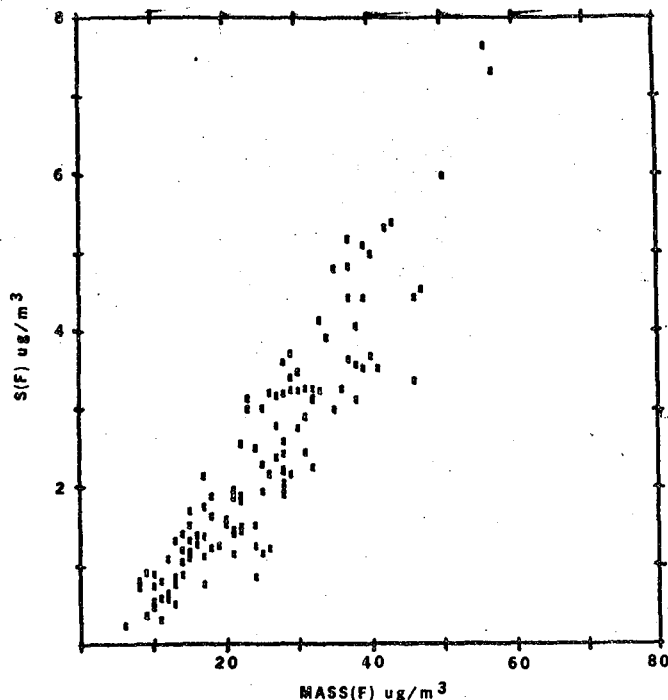


Fig. 4 - Scatter plot of fine particle sulfur vs. fine particle mass.

SULFUR (FINE) (ng/m³)

STATION	103	105	106	108	112	115	118	120	122	124
JULY	5663	5786	5427	4726	5277	5531	4940	4646	3954	3967
AUG.	4900	4455	4142	3698	3719	3760	2818	3619	3607	3045
SEPT.	3776	3793	3158	2761	3037	2626	2627	2684	2181	2916
OCT.	2986	2818	2705	2196	2584	2301	2100	2205	1721	1972
NOV.	2352	2228	2128	2093	2055	1911	1496	1789	1843	1470
DEC.	2818	2748	2589	2576	2716	2492	1961	2397	2196	1584
SIX MO. AVERAGE	3733	3638	3358	3008	3231	3104	2657	2890	2584	2492

MASS (FINE) (ug/m³)

STATION	103	105	106	108	112	115	118	120	122	124
JULY	55.6	50.0	48.6	36.3	50.0	42.3	34.5	36.2	33.0	27.4
AUG.	46.8	31.2	29.4	28.1	29.4	25.6	18.3	21.2	27.1	18.7
SEPT.	31.7	28.9	27.2	23.7	22.4	19.5	17.7	25.6	20.3	20.6
OCT.	43.4	37.2	25.7	25.5	24.2	20.0	15.1	24.5	23.2	16.5
NOV.	20.8	27.0	20.1	25.3	22.1	17.3	12.8	23.6	16.9	17.3
DEC.	24.1	26.6	20.6	23.2	21.3	19.7	15.6	21.5	17.5	13.5
SIX MO. AVERAGE	37.1	33.5	28.6	27.0	28.2	24.1	19.1	25.4	23.0	19.0
S(F)/M(F)	0.10	0.11	0.12	0.11	0.11	0.13	0.14	0.11	0.11	0.13

Table 7 gives the averages for the fine particulate S and Pb for the ten stations used in the study. A yearly cycle in S concentrations is observed at all stations with a maximum in July. It should be noted that stations 122 and 124 are far removed from the city whereas stations 103, 106, and 113 are located close to the downtown area. The relatively high concentrations at the remote sites indicate the widespread nature of the sulfate distribution.

Preliminary use of the data file will include more extensive listing of the results in the forms described above. Due to the ease of access of the data for

larger data processing programs, it is probable that more sophisticated multivariate analysis will be performed in the future. These will include data from other sources such as meteorological observations and gaseous pollutant measurements.

CONCLUSIONS

We feel that we have demonstrated the effective use of beta-gauge mass measurements and energy-dispersive x-ray analysis in large-scale applications. The sensitivity and accuracy of the measurement are more than adequate for most air monitoring applications. The special attention devoted to the problem of sulfur analysis has resulted in accurate XRF determinations at this environmentally important element. The full value of the program will become established as more extensive data interpretation is performed.

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