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CHARACTERIZATION OF AEROSOLS IN CALIFORNIA BY X-RAY INDUCED X-RAY  
FLUORESCENCE ANALYSIS

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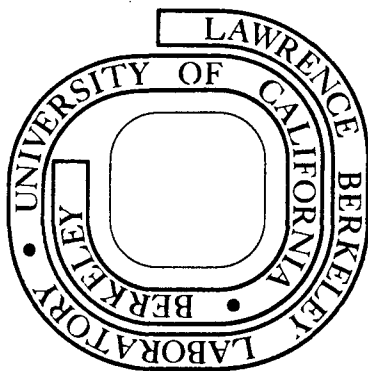
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CHARACTERIZATION OF AEROSOLS IN CALIFORNIA BY X-RAY  
INDUCED X-RAY FLUORESCENCE ANALYSIS\*

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ABSTRACT

X-ray induced x-ray fluorescence analysis was employed to determine elemental concentrations in aerosols collected on impactor films and filter media during Phase I of the "Characterization of Aerosols in California" study. Elemental diurnal patterns were established for aerosols collected over two hour periods. Elemental distributions were correlated with particle size distributions. Occurrences in the formation of aerosols were easily detected. Sensitivities routinely attainable within a twenty minute counting interval corresponded to less than  $10 \text{ ng/m}^3$  of air for twelve of the twenty elements measured.

## INTRODUCTION

Elemental analyses of aerosols, coupled with meteorological and particle size distribution data provide information which correlates the contribution of primary and secondary sources to the total airborne particulate matter.<sup>1,2</sup> From such data, evaluations of the contributions of anthropogenic sources may be made. Possible control strategies may then be established to reduce air pollution with considerable emphasis placed on the portions of the aerosols which can affect visibility and the human respiratory systems. To determine what technique should be employed for the elemental analyses the following are some criteria that should be considered.

- (1) The technique should permit the analyses of a broad range of elements, with emphasis placed on certain elements.
- (2) High sensitivities must be attainable ( $\text{ng}/\text{m}^3$  level).
- (3) The procedure should be relatively rapid (minutes). This permits preliminary evaluations from which future studies may be prudently established.
- (4) The analyses must be quantitative and the costs should be small.
- (5) The technique should be non-destructive so that future measurements may be made.

A technique that satisfies these criteria is x-ray induced x-ray fluorescence analysis.

## DISCUSSION

General Technique

Figure 1 illustrates the technique employed for x-ray fluorescence analysis. Exciting radiation provided by an x-ray tube impinges upon the

filter media 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 semiconductor detector, sorted by their energies, and the elemental concentrations are determined from the intensities of the x-rays.

In addition to the photoelectric interactions, a portion of the exciting radiation is scattered either coherently or incoherently. For analyses of aerosols collected on typical filter media or impactor films, the intensity of the scattered x-rays is often quite large compared with that of the characteristic x-rays. In order to obtain high sensitivities, monochromatic exciting radiation is employed and is selected of an energy slightly greater than the K or L absorption edge energies of the elements to be analyzed, but of sufficient energy that the incoherently scattered radiation does not produce considerable overlapping background. Using this procedure, high efficiencies are obtained for producing photoelectric interactions and high x-ray peak intensities with respect to background are achieved. A molybdenum transmission x-ray tube<sup>3</sup> produced the monochromatic exciting radiation employed to obtain the data reported in this paper. High sensitivities for most of the elements in the periodic table may be obtained by employing an x-ray tube with secondary fluorescers,<sup>4</sup> or different characteristic x-ray tubes.

#### Equipment and Characteristics

For the experiments discussed in this paper, a guard-ring detector<sup>5</sup> with pulsed-light feedback electronics and a 512 channel pulse-height analyzer were employed. The total resolution of the system, FWHM, was 225 eV at 6.4 keV

(FeK $\alpha$  x-ray energy). Excitation was provided by a molybdenum transmission x-ray tube with combined anode plus window thickness of 0.010 cm. The x-ray tube was operated at 42 KV and 300  $\mu$ A. The x-ray tube, specimen, detector geometry is shown in Fig. 1. The total area of the specimens used varied from 1 to 3 cm<sup>2</sup> depending upon the external tube collimation employed. Correction for system dead time resulting either through pile-up rejection or analyzer dead time was made using a gated clock that measured the total system live time.

Calibration Method

Aerosols collected on filter media or impactor films can in general be considered as thin specimens. For most analyses the concentrations of an element is directly proportional to the intensity of its characteristic x-rays. Matrix enhancement effects are essentially negligible. Although matrix absorption effects are usually quite small for most analyses, corrections are sometimes necessary when lower energy x-rays are employed for analyses. For the data reported in this paper, no corrections were necessary, hence, compensations for matrix absorption effects will not be discussed.

Since the intensity of an x-ray line from an "infinitely" thin specimen is directly proportional to the concentration,  $m_j$  ( $\mu$ g/cm<sup>2</sup>) of the element, the intensities and elemental concentrations may be expressed as:

$$I = I_0 G K_j m_j \tag{1}$$

where  $I_0$  is the exciting radiation intensity, G a geometry factor, and  $K_j$  (cm<sup>2</sup>/ $\mu$ g) is a factor which relates the ability to excite and detect an x-ray from the element j. As previously reported,<sup>6</sup> the value of  $I_0 G$  can be

determined from a single element thin-film standard and the relative values of  $K_j$  for characteristic x-rays from other elements are obtained by calculating the relative probability of fluorescence excitation and detection of x-ray lines as a function of  $Z$ . The thin-film standard is prepared by evaporation of the element onto a thin substrate. The standard is prepared thin enough that absorption effects are negligible (around  $100 \mu\text{g}/\text{cm}^2$ ). Calculated values of  $K_j$  for x-ray lines from eight elements have been reported to agree within several percent of measured values from evaporated thin-film standards.<sup>6</sup> In effect, standardization for exciting radiation intensity and total system geometry is made with the single element thin-film standard and factors converting counts/sec to  $\mu\text{g}/\text{cm}^2$  for the other elements are calculated.

#### Analysis Program

X-ray spectra of the collected aerosol specimens are recorded on magnetic tape and the analytical computations are made by a Control Data 6600 computer. Although our program has been established for the analyses of many types of specimens, much less than 50 K of core space would actually be required for the analyses of only aerosols. The analysis program is performed in three steps. First, the x-ray spectrum background due to the scattered exciting radiation is removed, secondly, the interferences due to overlapping x-ray lines are unfolded, and thirdly, the concentrations of the elements in the original air sampled are calculated from the intensities of the appropriate x-ray lines employed for analysis.

The shape of the scattered exciting background is simply determined by employing a blank filter of mass similar to that of the filters used for the aerosol collections. The scattered x-ray background within various energy



0 0 0 0 0 9 0 0 0 0 4

ranges to be employed for analysis are ratioed to the intensities of the incoherent plus coherent scattered exciting MoK $\alpha$  radiation. These scattered radiation background factors are employed for analyses. This procedure was possible since the typical aerosol loadings contributed only a couple of percent to the total mass of the filter plus collected aerosol. Also the loadings were of average effective atomic number similar to that of the collection media.

Fixed sets of channels corresponding to preselected energy ranges are employed for analyses. Although the spectrometer is stable over widely varying conditions, one of the more intense x-ray lines is used to compensate if a base-line shift occurs. To obtain high statistical accuracies between 70 to 80 percent of the total peak areas are employed for analyses. The peak fractions used are established from elemental thin-films. Corrections for overlapping x-ray lines are also determined from the elemental thin-films by establishing relationship between individual x-ray peak shapes and intensities. In effect, a series of simultaneous equations are established which compensate for overlapping x-ray lines occurring over the preselected energy ranges.

The concentrations of the individual elements present in the aerosol are then calculated from the individual x-ray line intensities using Eq. (2).

$$\frac{\mu g(j)}{m^3} = \frac{C_j}{C_s} \times \frac{m_s}{V} \times \frac{1}{K_j} \quad (2)$$

where

$C_j$  and  $C_s$  are the characteristic x-ray count rates from element  $j$  and the standard

$m_s$  is the standard mass ( $\mu\text{g}/\text{cm}^2$ )

$V$  is the volume of air sampled ( $\text{m}^3$ ) per  $\text{cm}^2$  of collection media

$K_j$  is defined by Eq. (1).

### Sampling

Sampling of aerosols was carried out during the summer of 1972 by the Air and Industrial Hygiene Laboratory of the California Department of Public Health as a part of the extensive aerosol characterization program sponsored by the California Air Resources Board. Several types of aerosol collection devices which used filter media and impactor films were employed. We limit the results reported in this paper to data obtained on some of aerosols collected over two hour intervals for a period of 24 hours. Specifically, results obtained on total aerosols ( $< 20 \mu$ ) or aerosols collected with a Lundgren four stage impactor which provided particle size distributions of the elements are reported. Analyses were performed on particulate matter collected on stages 3, 4 and the after filter of the Lundgren impactor. The respective 50% cut points for these stages were 1.5, 0.5, and  $< 0.5 \mu$ . Emphasis was placed on the analyses of particulate matter collected on stage 4 and the after filter since these contain particles of the size range which affect visibility and are efficiently trapped in the human respiratory system.

Various collection media that were suitable for different types of instrumental analyses were employed during this study. These media were also used to evaluate bounce-off problems associated with the use of Lundgren impactors.<sup>7</sup> Either washed  $0.8 \mu$  GA-1 Gelman filters or silver membrane filters were employed for the total and after filters. Although dry or sticky Mylar or Teflon were used for the four impactor stages, only the dry Mylar impactor

films were analyzed by x-ray fluorescence. Typical two hour collections corresponded to  $0.75 \text{ m}^3/\text{cm}^2$  for the total and after filters, and to  $2.50 \text{ m}^3/\text{cm}^2$  for the impactor stages.

## RESULTS

For most specimens, the concentrations or limits of detection of twenty elements were determined in twenty minutes or less. Table I lists the sensitivities attained for two types of collection media employed. The minimum detectable amount is defined as that quantity which gives a line intensity above background equal to three times the square root of the background for counting times not to exceed 1000 sec. The values listed in Table I include the background due to the Ca, Fe, Cu, and Zn impurities in the Gelman filters and the Zn impurity in the Mylar film.

Figure 2 shows the spectrum and results obtained on a aerosol collected over a two hour interval on .0006 cm Mylar on the 4th stage of a Lundgren impactor. The results reported are in  $\text{ng}/\text{cm}^2$ . Since the volume of air sampled was  $2.50 \text{ m}^3/\text{cm}^2$  of impactor film, the concentrations of the elements in the original air were two-fifths the values listed. Figures 3-9 illustrate a few of the diurnal patterns established during this study. When these data are united with meteorological, particle size distribution, and other chemical data they provide considerable insight into the formation of aerosols. We will initially discuss possible interpretations from the x-ray data alone.

For the Fresno data, the diurnal patterns for K, Fe, Ti, and Mn are very similar for the total filter. These four elements are most likely produced by a mechanical process such as wind blown soil (larger particles) since their concentrations were an order of magnitude lower for the after filter. The Ca was also present almost entirely in the large particles and is probably from a

mixture of soil and cement particles. Approximately  $3/4$  of the Pb and Br is present in the  $< 0.5 \mu$  range. (This is within the size range of particles which are trapped with a high efficiency in the respiratory system,  $0.05-1 \mu$ .) The Pb and Br arises from auto emissions and the Pb/Br ratio indicates the Pb and Br are most likely from an aged aerosol. (The Pb/Br ratio from a fresh aerosol is less than 3.0.) Over half the Zn was present in the  $< 0.5 \mu$  range. The diurnal patterns established for Zn during this study usually did not correlate well with any of the other elements determined. Zinc is often thought to be associated with tire dust. During these studies, several episodes of high Zn concentrations as is illustrated in the Fresno data at 2200 have occurred. The Zn in these cases was predominately present in the small particle size range,  $< 0.5 \mu$  and occurred during late evening or early morning hours. The Zn in these cases could be due to combustion sources, possibly from incineration of tires or tin cans. As shown in Fig. 4, only  $1/10$  of the total Fe was present in the small particles ( $< 0.5 \mu$ ). The diurnal patterns for Fe and Pb were somewhat similar indicating that possibly the Fe in the small particles had come from the same area as the auto emissions.

The Pomona data of 10/24-10/25 illustrated in Figs. 5-7 is interesting in that three different particle size cuts  $1.5$ ,  $0.5$ , and  $< 0.5 \mu$  were analyzed. The diurnal patterns for Pb and Br were similar for the three size cuts. However, the ratio of Pb present was  $1:5:10$  for the 3rd, 4th stages, and after filter respectively, again illustrating the Pb and Br were present in the small particles. For stage 3, the diurnal patterns for Fe, Ca, and Ti are also similar to those of Pb and Br suggesting that possibly these elements in the  $0.5-1.5 \mu$  range originated from the same area. Very large amounts of S were detected on stage 4. The S values for stage 4 were typically 10 to 20 times larger than those for stage 3. Novakov has shown this S is present as  $SO_4^{=8}$ .

The S was quite likely due to a secondary aerosol. Also, the Pb/Br ratio which was over 7/1 between 0100 and 0700 for the 4th stage indicates that in this particle size range the Pb is from an aged aerosol. The concentration of Zn successively increased with decreasing particle size. Also, the diurnal patterns for Zn for the three particle size ranges were different. The Fe concentration was generally several times higher in the two larger particle size ranges than for those particles  $< 0.5 \mu$ .

The Los Angeles Harbor Freeway specimens collected on 9/19-9/20 were from the heaviest smog episode during the entire study. Figure 10 contains a plot of the data obtained from the particles collected on the total filter (silver membrane). Also included in this plot are the condensation nuclei count (CNC) and the wind direction determined by the Whitby Group.<sup>8</sup> The mobile laboratory was stationed approximately one block from the freeway and the aerosols were collected from the direction of the freeway when the wind direction was above  $180^\circ$ . The two high Pb peaks episodes correspond to the heavy morning and evening traffic and to two of the broad CNC maxima. The wind direction shifted towards the freeway between 0700 and 0900, hence the episode peaked at the somewhat early hour of 0600. The high CNC between 1000 and 1600 is thought to be possibly due to a secondary aerosol. This is consistent with the fact that aged automotive emissions are detected during this period as is evident by the increase in the Pb/Br ratio of the somewhat larger particles,  $0.5-1.5 \mu$ , collected on 4th stage of the Lundgren impactors. Also the diurnal patterns for Fe and Ca for this stage were very similar. The Fe and Ca may be due to the same source, possibly of sedimentary origination. The bulk of the Fe and Zn were present in the larger particles  $> 0.5 \mu$ . The diurnal patterns for these two elements were very similar for the total filter, suggesting that the majority of the Fe and Zn originate from the same area, and possibly from the same source.

During these studies aerosols were collected at San Jose on five separate days. On three of these days the Sr levels in the aerosols increased dramatically (the largest change being from  $< 0.012$  to  $0.180 \mu\text{g}/\text{m}^3$ ) between the hours of 0000 and 0400. Most of the Sr was in particles  $< 0.5 \mu$ , indicating it came from an anthropogenic source. The Sr could possibly be attributed to the manufacture of fireworks or highway flares.

Although the data discussed in this report are only a fraction of the results obtained, they serve to illustrate some of the contributions x-ray fluorescence analysis can make in the study of aerosols. This data has been combined by Hidy et al.<sup>8</sup> with a wealth of other chemical, physical, and meteorological data obtained by other experimenters during this study.

#### ACKNOWLEDGEMENTS

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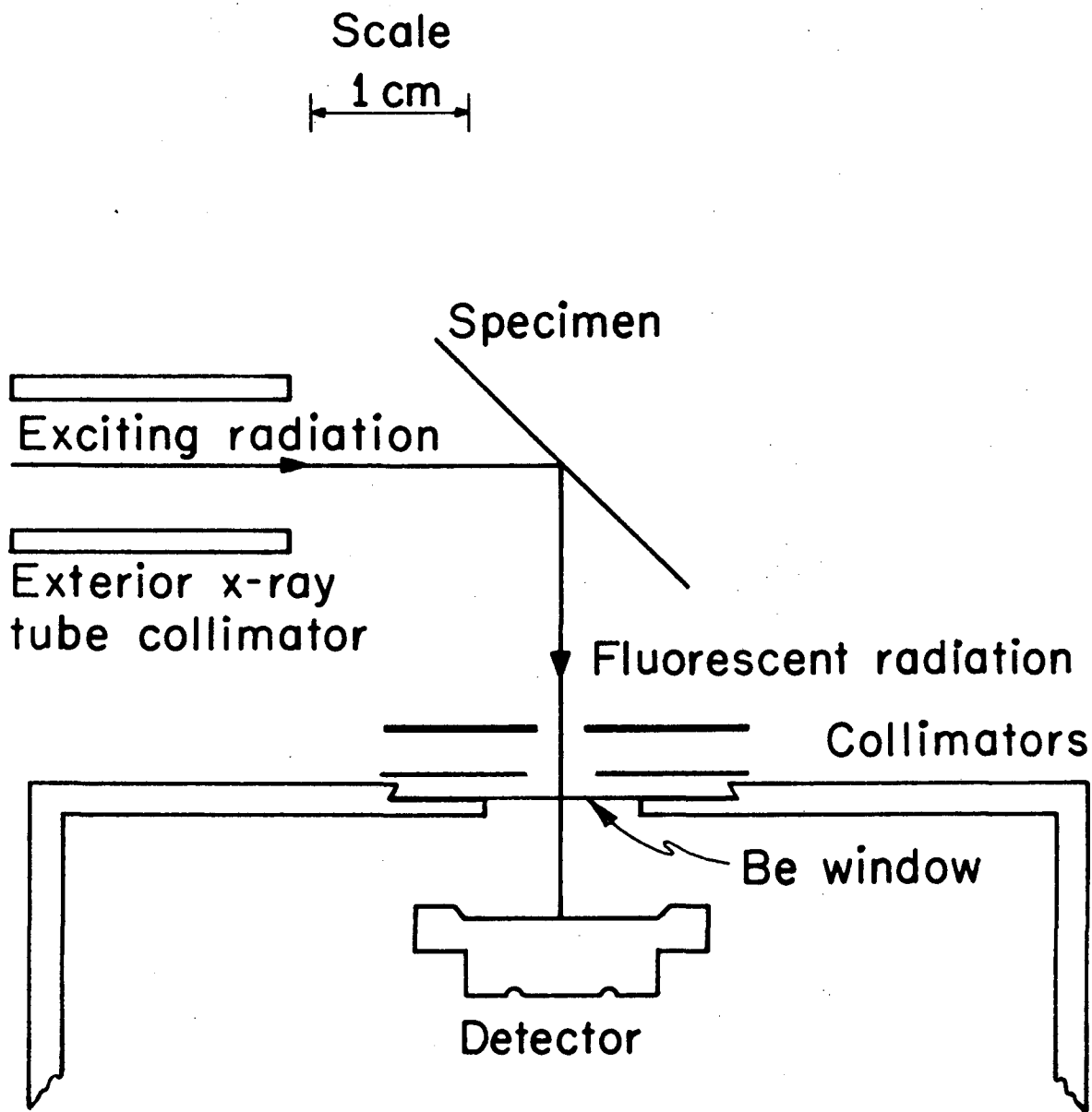
Table I. Theoretical Limits of Detection

Media	Gelman filter	.0006 cm Mylar
Mass ( $\text{mg}/\text{cm}^2$ )	5.0	0.9
Air volume sampled ( $\text{m}^3/\text{cm}^2$ )	0.75	2.50
Area analyzed ( $\text{cm}^2$ )	3	1
Element and spectral line		
SK $\alpha$	—	160 $\text{ng}/\text{m}^3$
ClK $\alpha$	—	80
KK $\alpha$	110 $\text{ng}/\text{m}^3$	36
CaK $\alpha$	50	15
TiK $\alpha$	20	5
VK $\alpha$	16	4
CrK $\alpha$	13	3
MnK $\alpha$	9	3
FeK $\alpha$	10	2
NiK $\alpha$	4	1
CuK $\alpha$	6	1
ZnK $\alpha$	4	2
GaK $\alpha$	3	1
AsK $\alpha$	4	1
SeK $\alpha$	4	1
BrK $\alpha$	5	2
RbK $\alpha$	8	2
SrK $\alpha$	9	3
HgL $\alpha$	7	2
PbL $\alpha$	7	2
PbL $\beta$	18	5



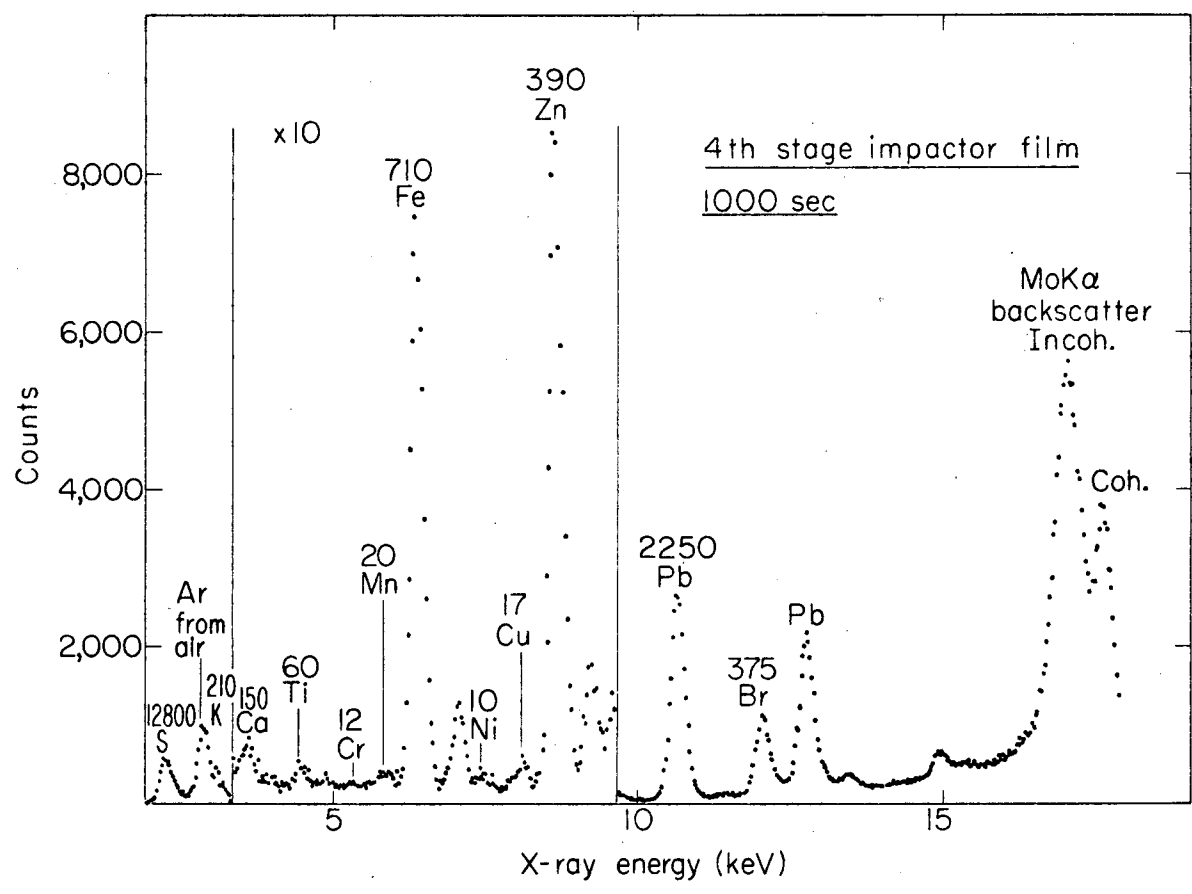
## FIGURE CAPTIONS

- Fig. 1. Schematic of x-ray fluorescence analysis technique.
- Fig. 2. Spectrum of aerosol collected over a two hour interval on dry .0006 cm Mylar on the 4th stage of a Lundgren impactor.
- Fig. 3. Diurnal patterns for elements collected on total filters at Fresno on 8/31-9/1.
- Fig. 4. Diurnal patterns for elements collected on after filters at Fresno on 8/31-9/1.
- Fig. 5. Diurnal patterns for elements collected on 3rd impactor stage at Pomona on 10/24-10/25. (One specimen was missing, hence the void in the data.)
- Fig. 6. Diurnal patterns for elements collected on 4th impactor stage at Pomona on 10/24-10/25.
- Fig. 7. Diurnal patterns for elements collected on after filter at Pomona on 10/24-10/25.
- Fig. 8. Diurnal patterns for elements collected on 4th stage at Los Angeles Harbor Freeway on 9/19-9/20.
- Fig. 9. Diurnal patterns for elements collected on after filter at Los Angeles Harbor Freeway on 9/19-9/20.
- Fig. 10. Diurnal patterns for elements collected on total filter (silver membrane) at Los Angeles Harbor Freeway on 9/19-9/20. Also included are CNC and wind direction data.



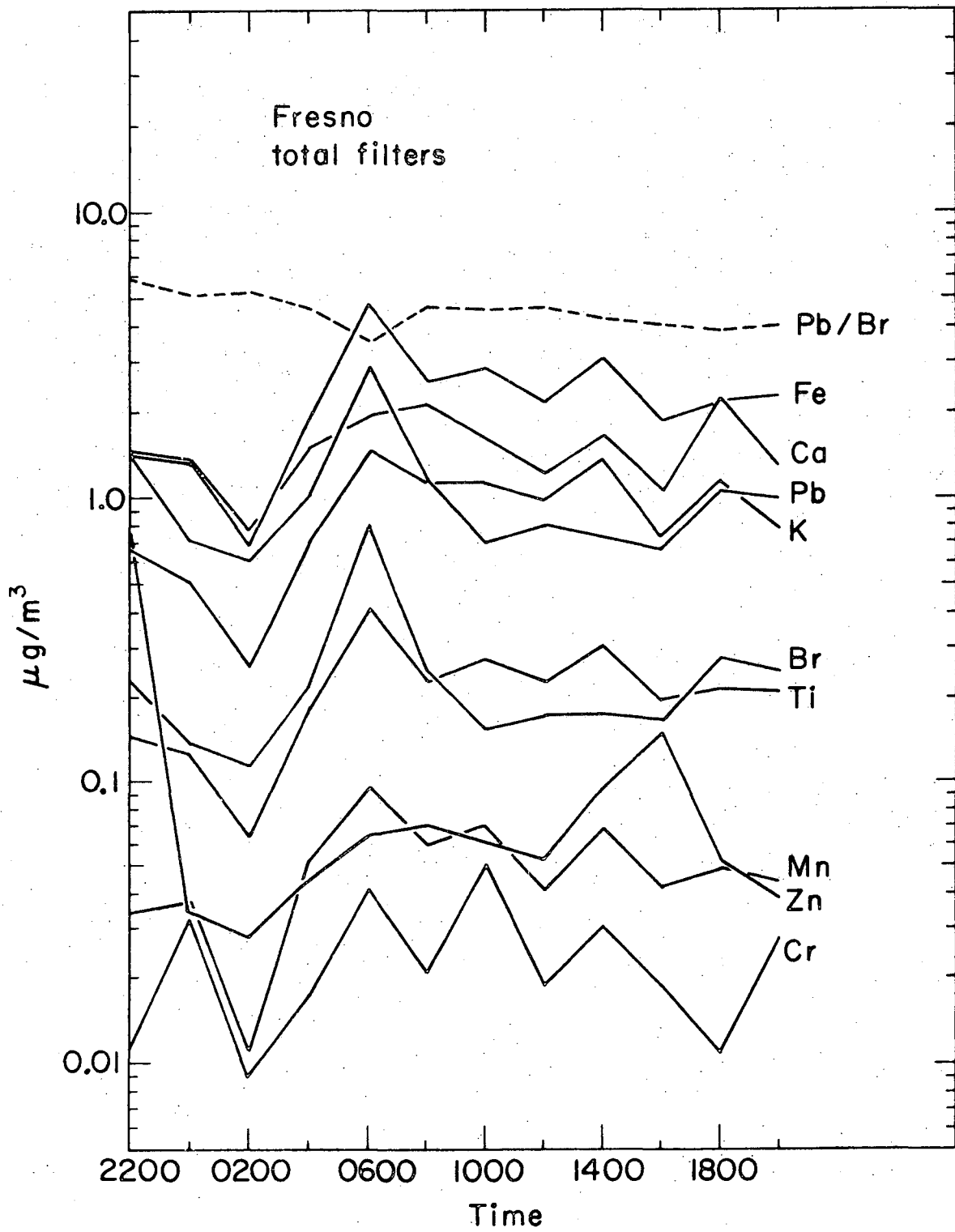
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Fig. 1



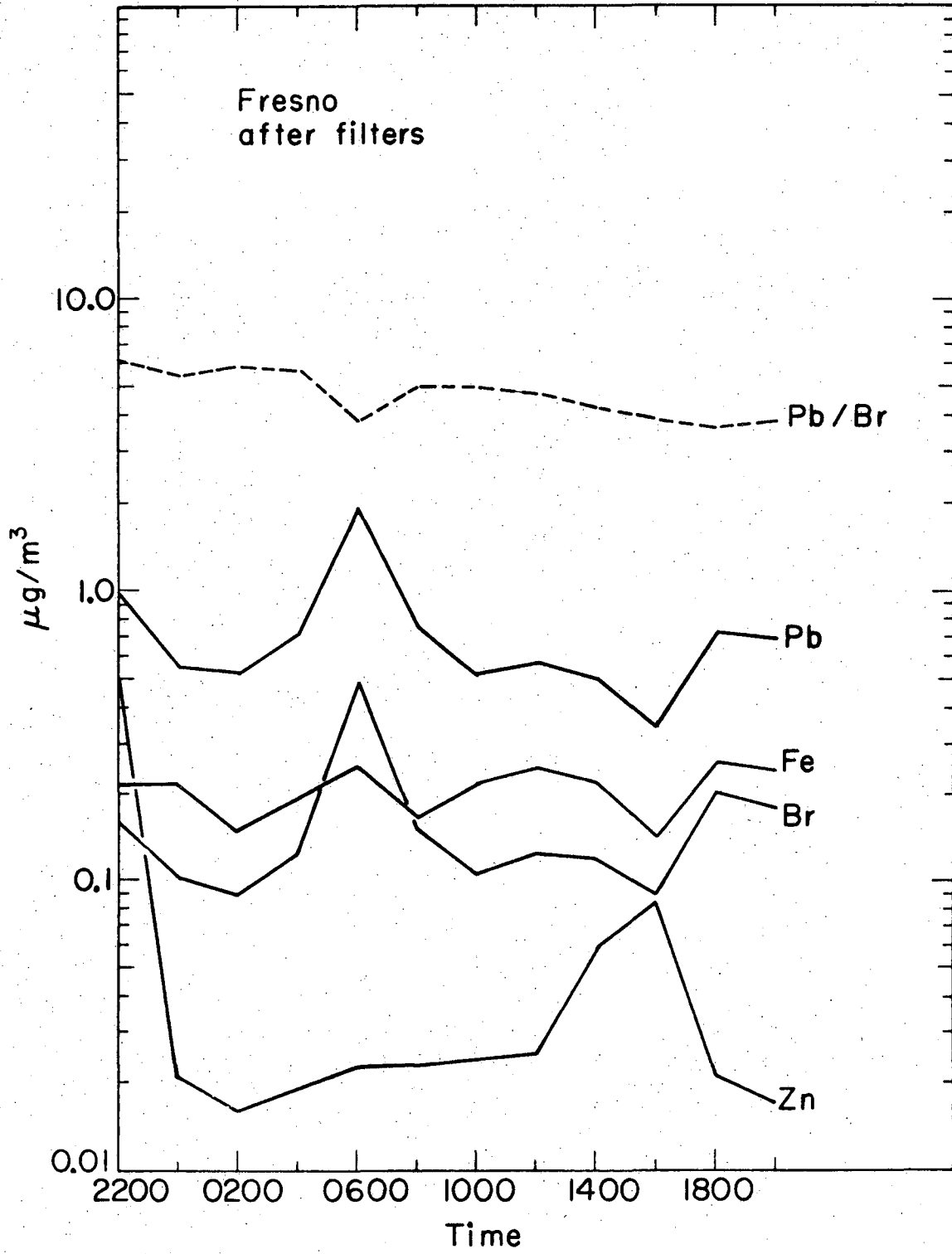
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Fig. 2



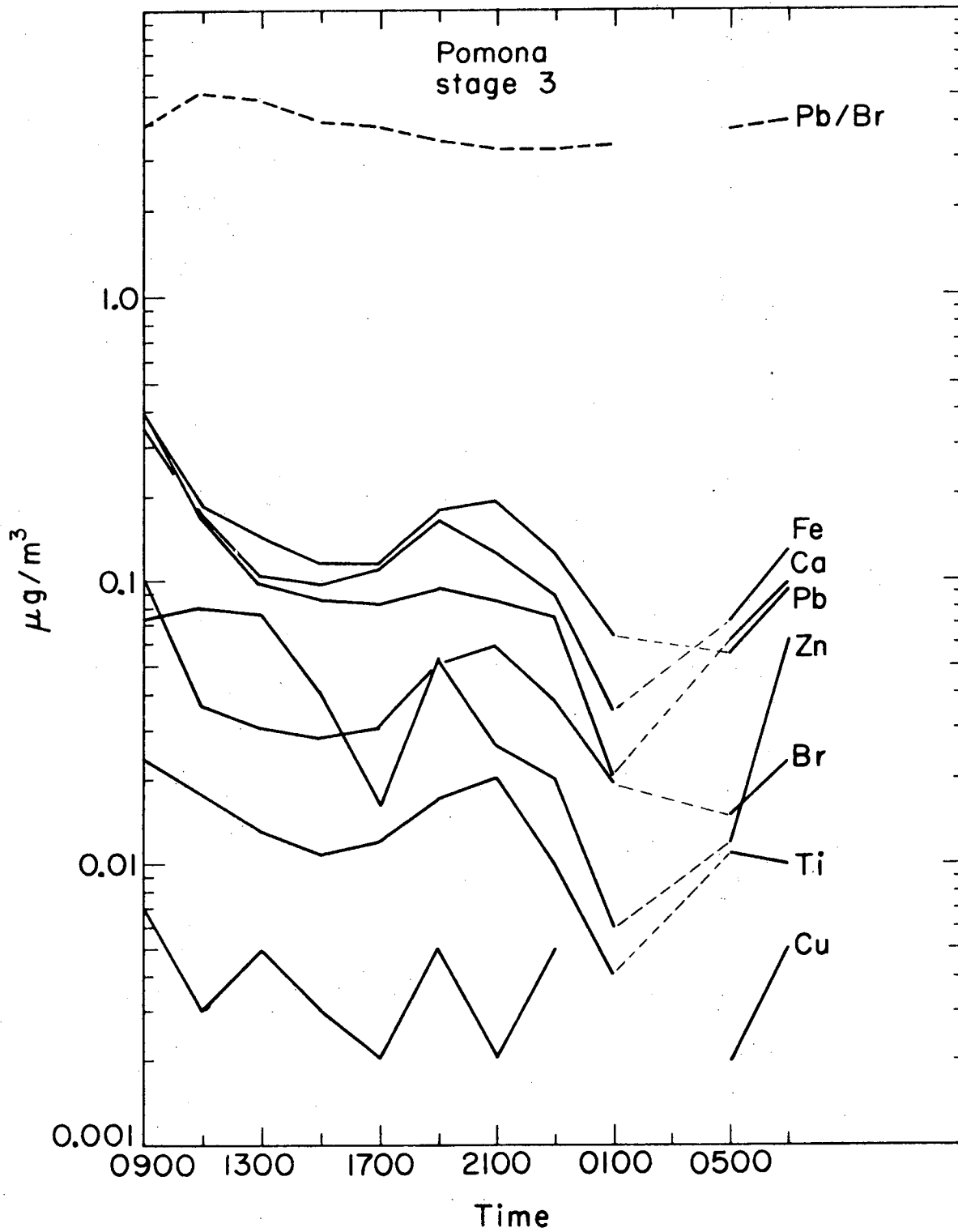
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Fig. 3



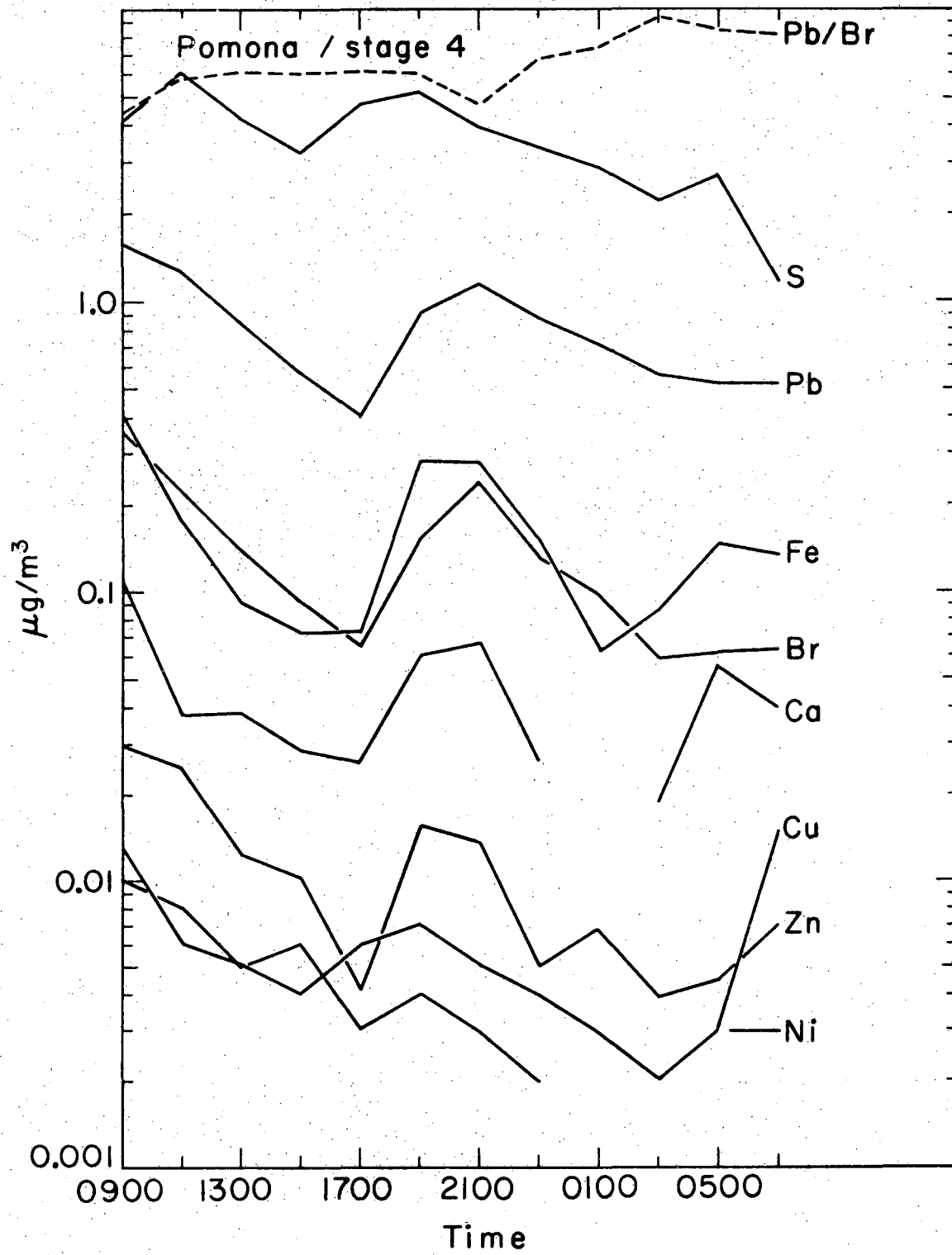
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Fig. 4



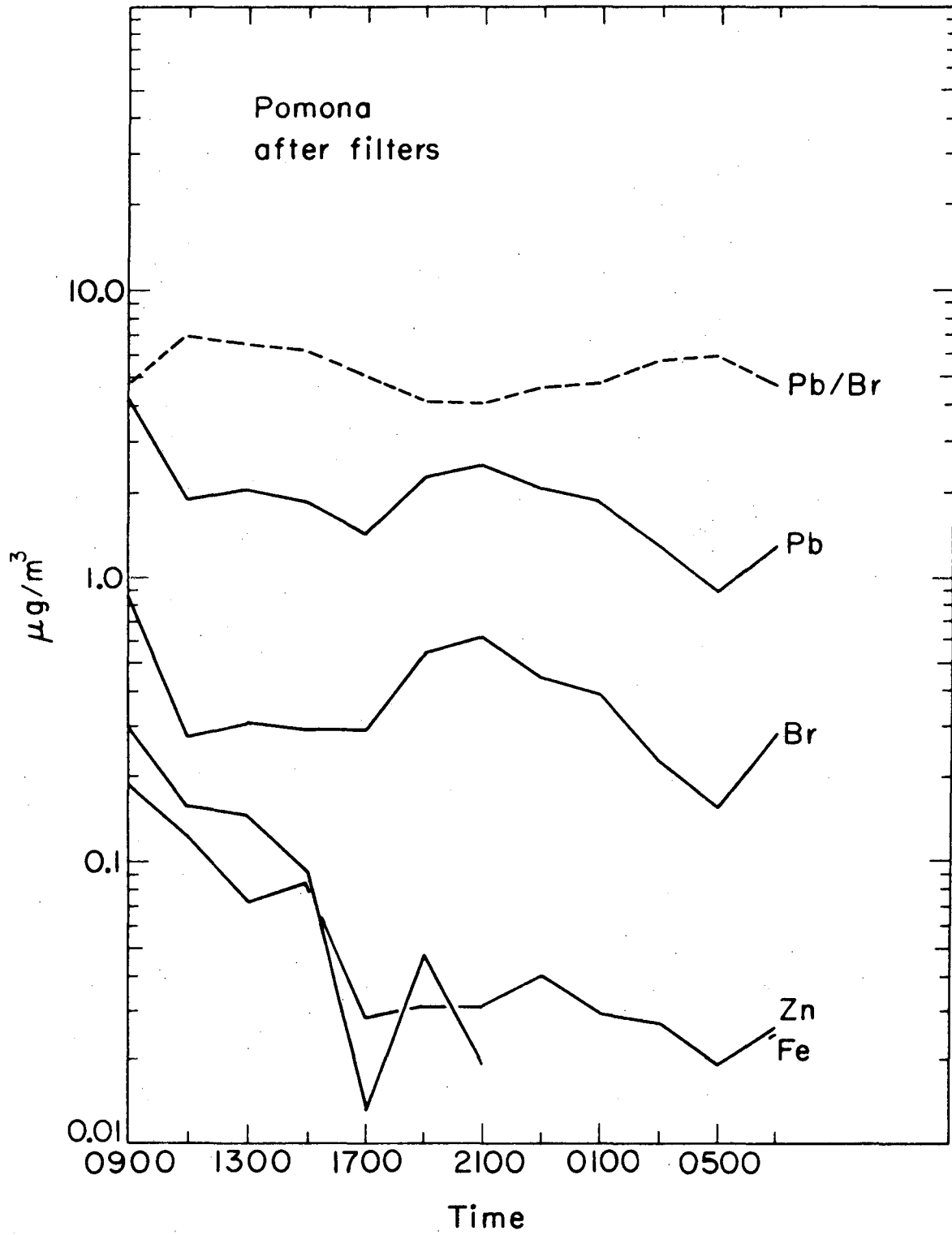
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Fig. 5



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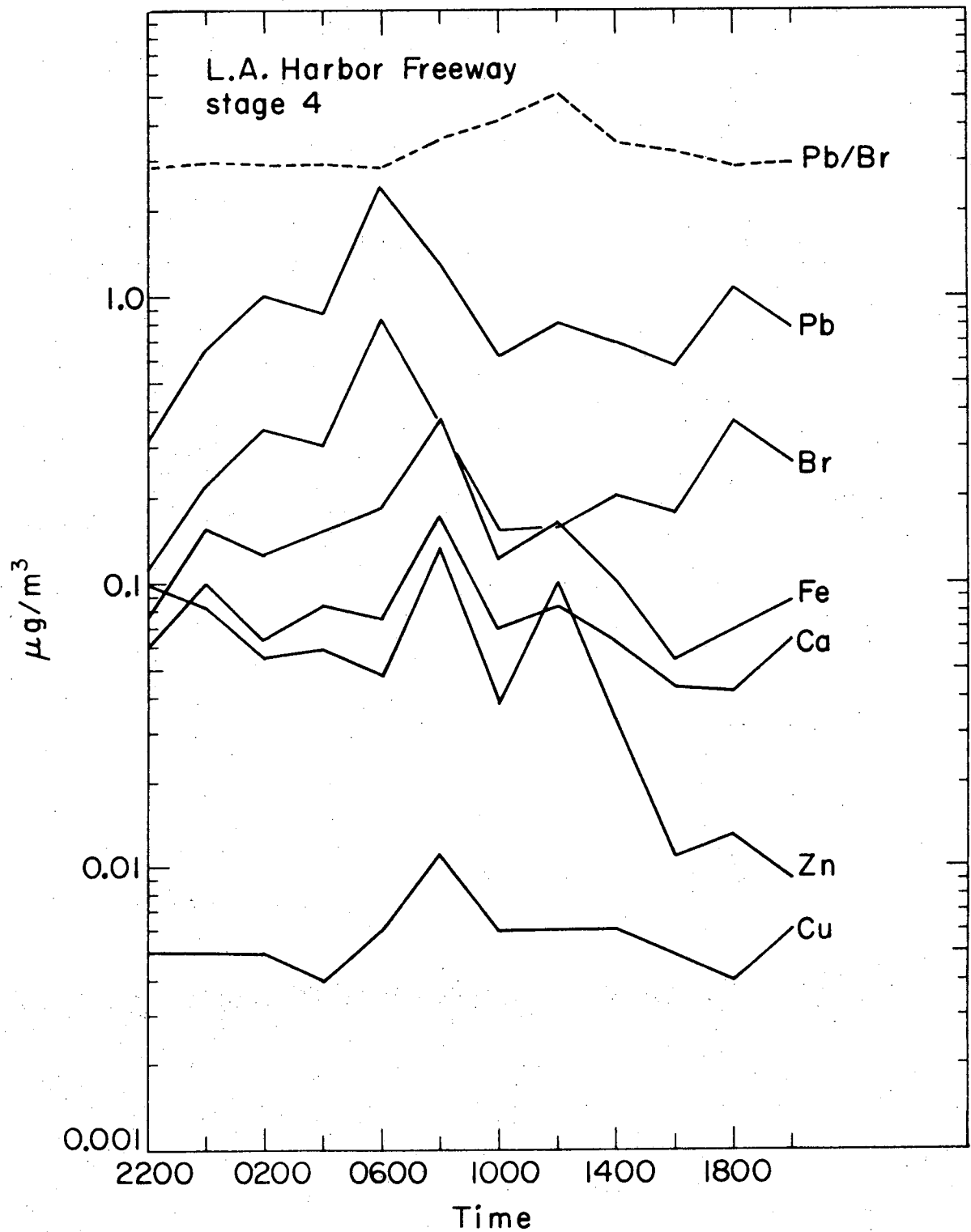
Fig. 6



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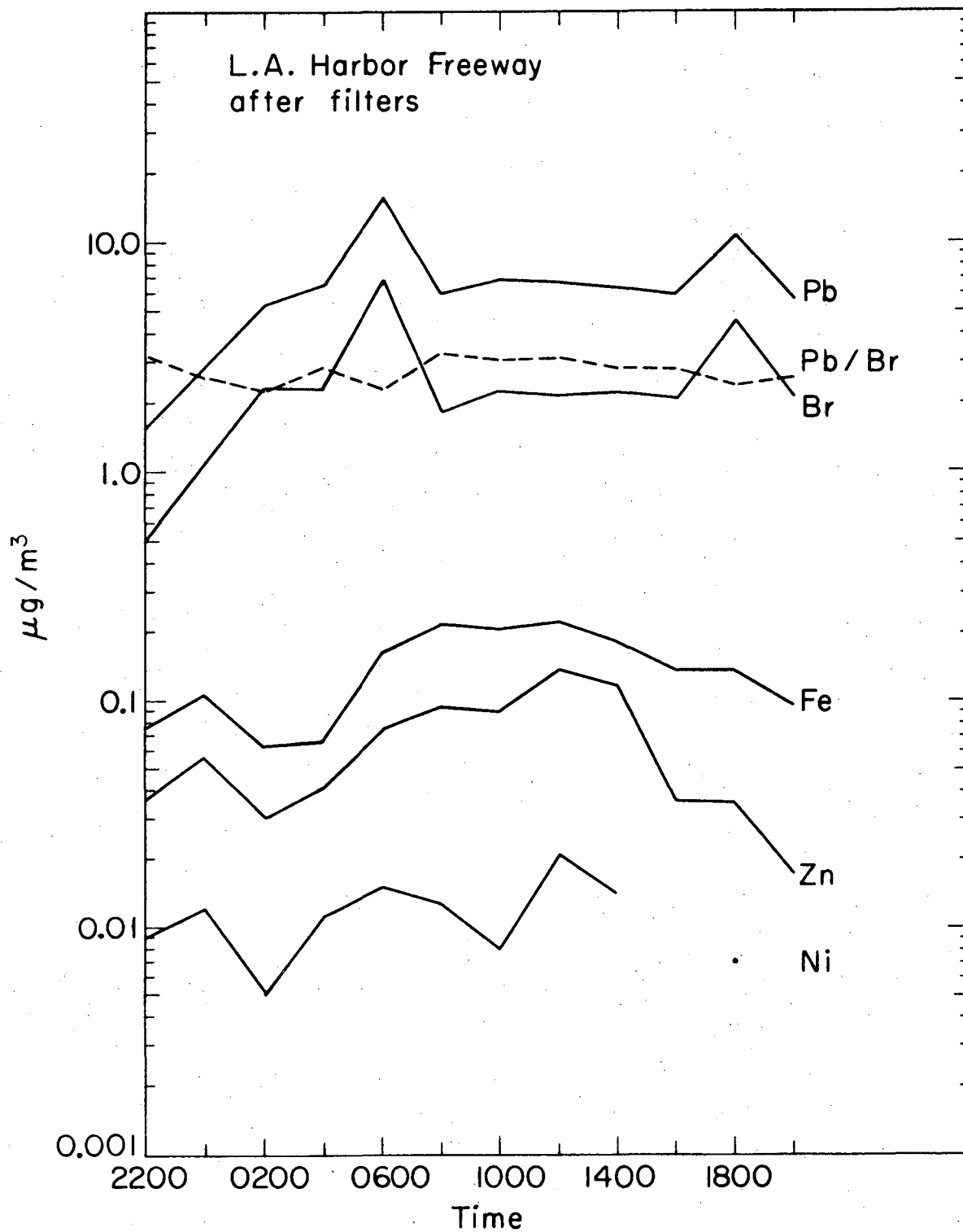
Fig. 7





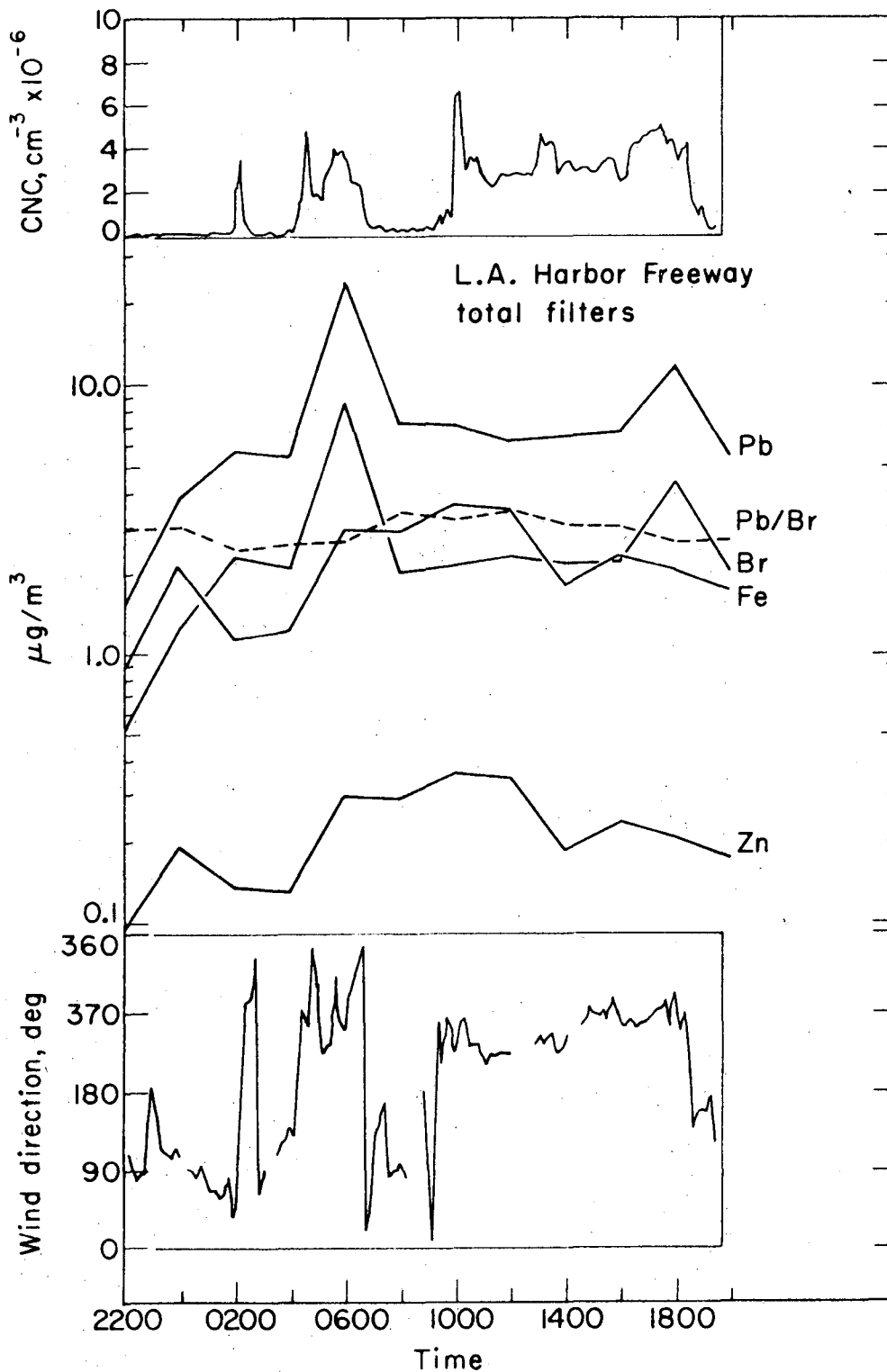
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Fig. 8



XBL 735-2924

Fig. 9



XBL 735-2930

Fig. 10

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