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ATMOSPHERIC LEAD AND BROMINE CONCENTRATION IN BERKELEY, CALIF.
(1963-1970)¹

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April 1971

Abstract

Lead and bromine aerosols collected in downtown Berkeley, Calif., for one-week periods over the past eight years, have been analyzed using non-dispersive x-ray fluorescence analysis. Typical analysis times were 2 minutes. The results suggest that x-ray fluorescence is a practical technique for routine lead monitoring, and that continuous monitoring stations are feasible.

Seasonal lead variations similar to those found in the San Diego area were observed and appear to be correlated to data for wind and wind direction. The ratio of bromine-to-lead collected on filters appears to be higher in Berkeley than in the six other U. S. cities previously reported.⁴

Introduction

The present study was undertaken to determine if non-dispersive x-ray fluorescence analyses² for lead, bromine and other elements can be made rapidly enough that continuous sampling by remote automated monitoring systems would be possible.

Earlier measurements on filter papers using x-ray fluorescence analysis with difference-filter techniques³ as well as those using a mass-spectrometer⁴ usually concentrated on a single element in a single analysis, whereas the present method is capable of a multi-element analysis in a single run.

In this study, work has been limited to just lead and bromine aerosols because of the complications introduced by the relatively high concentrations of iron and zinc present in HV 70 filter paper fabric. The use of low-ash filter paper for collection purposes eliminates some of these problems.

Sample Collections

A series of filter papers was collected weekly over the past eight years in downtown Berkeley, California by the safety-service department of the Lawrence Radiation Laboratory as part of an environmental survey system.⁵ The downtown sampling station is located on a busy street (Shattuck Avenue between Hearst and Berkeley Way), and the air intake to the system is located about eight feet from the curb and about 7 feet above the street level facing the street. The air was filtered through HV 70 filter paper at an average flowrate of 4 ± 0.5 cfm, and the aerosols were collected on an open area of ~ 196 cm².

Counting Assembly and Procedure

Each of the over 400 filter papers was analyzed for two minutes on the x-ray fluorescence spectrometer shown in Fig. 1. The filter papers were folded twice (to increase by a factor of 4 the effective lead and bromine seen by the x-ray detector) and placed in a holder that compressed the papers and held them at a fixed geometry with respect to the x-ray fluorescence system.

A source-target-assembly similar to one described by Giaque⁶ was used and is shown in Fig. 2. The main advantage of the source-target two-step excitation method is that it allows one to choose the x-ray energy which is used to excite the sample, and thereby optimize the measurement. The target material used here was zirconium metal. The primary radiation was a 100 mc source of ¹²⁵I.

Eight hundred channels of pulse-height information were taken on each two minute run and stored on magnetic tape in digital form at the end of each run. Figure 3 shows the lead - bromine region of the spectrum for a sample collected over a 7-day period in December of 1969 and counted for 2 minutes. The data could be processed by hand or, more quickly, by a computer or a pulse-height analyzer with summing capability. A blank piece of HV 70 filter paper showed negligible lead and bromine but significant amounts of iron and zinc.

Each filter paper was analyzed twice, once with a slow amplifying system for which count rate corrections were needed, and a second time with a high-rate pulsed optical feed-back amplifying system⁷ for which count-rate corrections were negligible. The results from both sets of runs agreed, with an average reproducibility of better than 5%.

The lead and bromine concentrations were obtained by summing a number of channels over the Pb L α and Br K α peaks, subtracting the nearly negligible background and comparing the results to standards treated in the same manner.

Calibration

A number of techniques were used to calibrate the filter papers for lead and bromine. These included: analyses of weighed amounts of lead metal and of KBr which had been vaporized onto Al foils; wet chemical analyses of foils and some filters; and independent x-ray fluorescence analyses of some of the filters by R. D. Giaque. The lead and bromine results agreed within standard deviations of 7 and 13 percent, respectively.

Results

The atmospheric lead and bromine concentrations for the years 1963 to 1970 are plotted on Fig. 4. The seasonal variations are similar to those reported for San Diego by Chow and Earl for lead,⁴ and correlate very well with climatological data for wind direction and speed. In the summer the San Francisco Bay Area has winds of average speed of nine to ten miles per hour and these winds are from the Pacific Ocean. The winter winds average five to seven miles per hour and have no predominant direction. The higher-speed winds from the cleaner areas of the ocean result in the cleansing of the Bay Area and as a result the lead and bromine concentrations are lower in the summer. There seems to be no correlation with rainfall.

Table I shows the average lead and bromine concentrations for each of the 8 years. The averages are essentially constant over the 8 years, within a standard deviation of 5% for lead and 7% for bromine.

TABLE I
Daily average of $\mu\text{g}/\text{m}^3$ for bromine and lead

Year	Bromine	Lead
1963	0.75	2.8
1964	0.75	2.8
1965	0.83	3.0
1966	0.85	3.0
1967	0.90	3.1
1968	0.90	3.2
1969	0.84	3.0
1970	0.82	2.9

An average bromine-to-lead weight ratio of 1:60 has been reported for six cities of the United States.⁸ Our study indicates a ratio of 1:3.2. We have no explanation for this difference.

In order to determine which additional elements could be detected, a one-week collection (Jan 1971) was made on Whatman #40 paper. In addition to the lead and bromine, iron and zinc were detected in a 2 minute x-ray fluorescence analysis. The spectrum is shown in Fig. 5. The air volume was 11,884 cubic feet.

Summary

The analysis of lead and bromine aerosols collected over 7 day periods on air monitoring filter papers appears to be particularly suited to non-dispersive x-ray fluorescence analysis. Lead and bromine concentrations can be determined in many cases in 2 or 3 minute runs. The technique is non-destructive so that the papers can be reanalyzed if needed or saved for future reference.

With a combined increase of less than an order of magnitude in the air flow and the excitation source and no folding of the filter paper, results comparable to those reported here would be obtained with 2 hour collections and 2 hour counts. A system of continuous air-monitoring could be installed in which the data from many remote locations could be fed to a single central computer, which could give bihourly concentrations of lead, bromine, iron, and zinc at any of the remote locations. As the equipment is easily made portable,⁹ temporary stations could also be established.

Acknowledgments

We thank Jim Haley for suggesting the analyses and Dr. R. M. Latimer, J. Young, and H. P. Cantelow, all of the Safety Services Dept., for supplying the filter papers. R. D. Giaugue, Ray Clem, and Gordon Steers helped in the calibrations and A. F. Minter, G. E. Schleimer, and G. F. Garabedian changed the filter papers between counts. L. Y. Goda did the plotting and made many calculations.

Footnotes and References

- (1) Work performed under the auspices of the U. S. Atomic Energy Commission.
- (2) H. R. Bowman, E. K. Hyde, S. G. Thompson, and R. C. Jared, *Science*, 151, 562 (1966).
- (3) P. L. Sciaraffa and C. A. Ziegler, *Isotopes and Rad. Tech.*, Vol. 8, No. 2, 164, Winter (1970-71).
- (4) T. S. Chow and J. L. Earl, *Science* Vol. 169, August 1970.
- (5) H. P. Cantelow, J. S. Peck, A. E. Salo, and P. W. Howe, UCRL-10255.
- (6) R. D. Giaque, *Anal. Chem.*, 40, 2075 (1968).
- (7) D. A. Landis, F. S. Goulding, R. H. Pehl, and J. T. Walton, to be published in *I.E.E. Transaction on Nuclear Science*, Vol. 18, 1971.
- (8) E. R. Blossen and R. J. Thompson, paper presented at Pittsburgh Conf. An. Chem. and Applied Spectroscopy, March 4, 1971.
- (9) J. Frierman, H. R. Bowman, I. Perlman, and H. York, *Science*, 164, 588 (1969).

Figure Captions

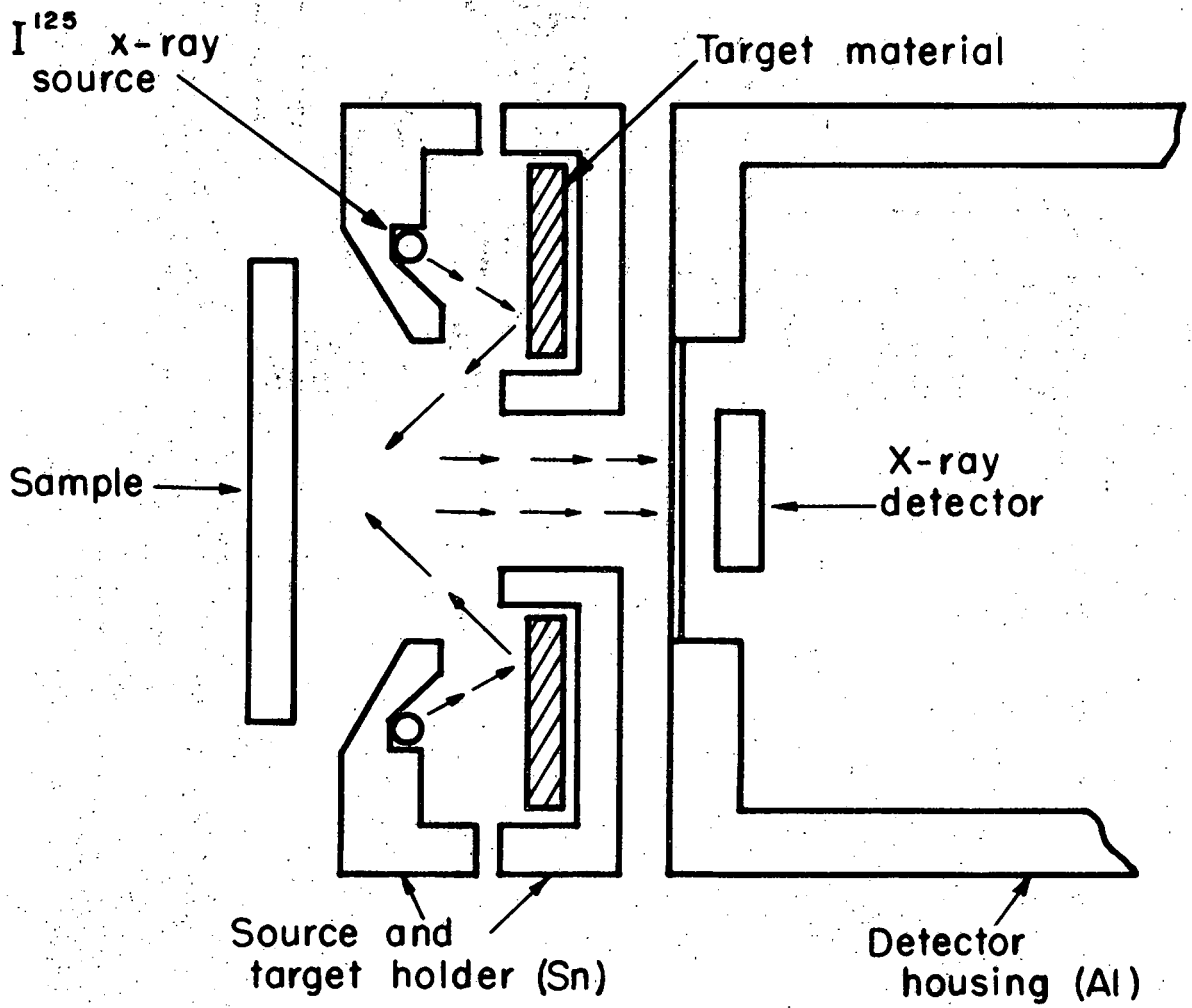
- Fig. 1. The non-dispersive x-ray fluorescence spectrometer with filter paper holder assembly.
- Fig. 2. The source-target-assembly. The primary radiation from a 100 m.c. ^{125}I source produces target K x-rays (Zr) which are used to excite characteristic x-rays in the filter paper samples.
- Fig. 3. The lead and bromine intensity distribution measured in a filter paper using a multichannel pulse height analyzer. Background has not been subtracted.
- Fig. 4. Atmospheric lead (upper solid line) and bromine (shaded area) concentrations in downtown Berkeley (1963-1970).
- Fig. 5. X-ray spectrum from aerosols collected on Whatman #40 filter paper.



XBB 712-752

Fig. 1

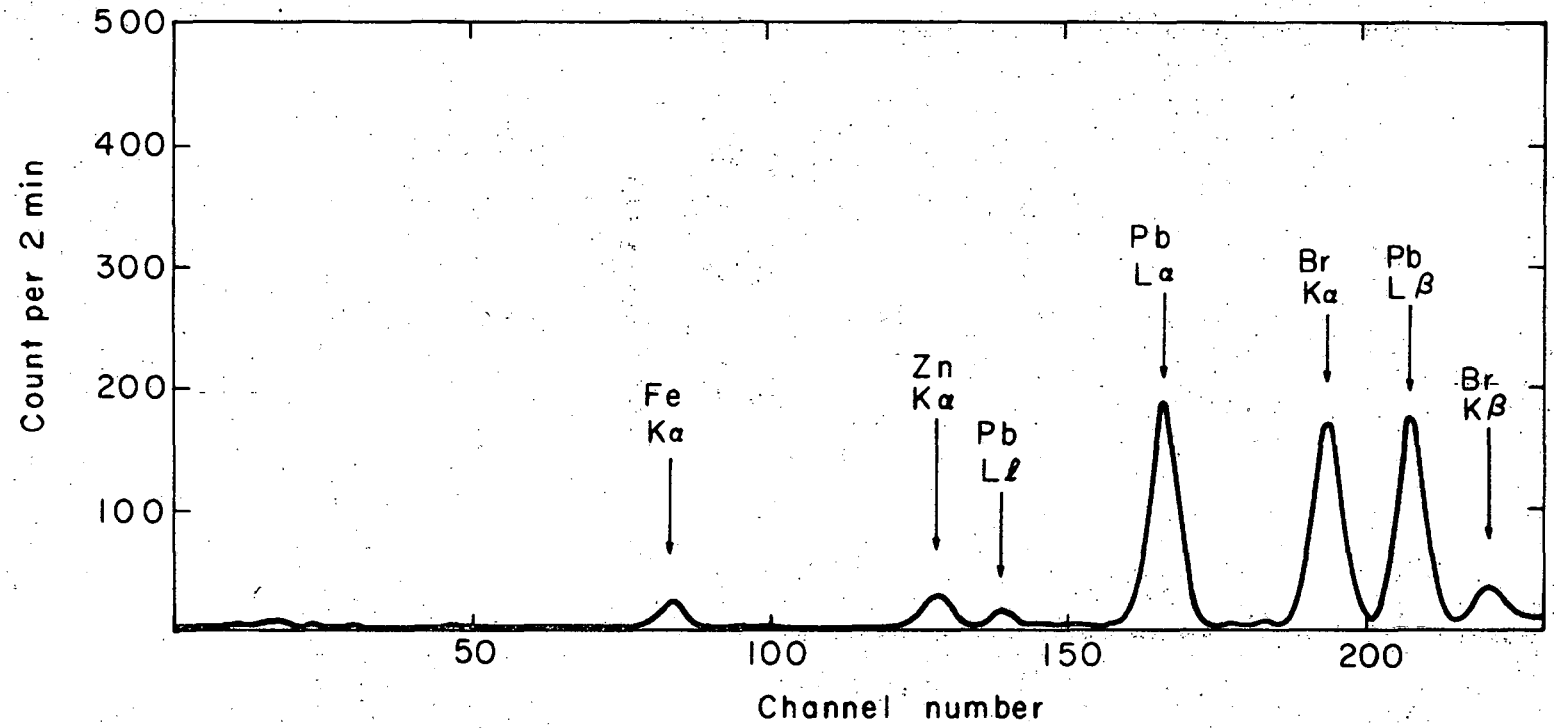
Source-Target Assembly



XBL670-5398

Fig. 2

Fig. 5



XBL714-3236

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