

ANALYSIS OF NASHVILLE AIR POLLUTION II¹

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ABSTRACT

Studies of a Nashville air pollution sample have been conducted using a two component system. One system employing source excited x-ray fluorescence analysis (SEF) has been used for qualitative determinations and another, atomic absorption spectroscopy (AA), has been used to make quantitative determinations. A brief description is given of the principles involved and results are compared with those of a previous paper dealing with Nashville air pollution.

INTRODUCTION

The application of existing knowledge or ideas to atmospheric pollution studies can be an important part of existing programs aimed at solving environmental problems. An important part of any program will necessarily include a method of rapidly obtaining, at minimal cost, a quantitative assay of atmospheric constituents or environmental pollutants. Though the assay may be accomplished by neutron activation analysis utilizing a reactor or by charged particle induced x-ray fluorescence using an accelerator, the instrumentation is in most cases prohibitively expensive. However, the superior sensitivity of these techniques may, in most cases, be unnecessary. In such cases, a compromise may lie in the use of a combination of x-ray fluorescence and atomic absorption. In such a situation, the cost is not prohibitive and the sensitivity is still sufficiently high for many applications. For the detection of light element pollutants such as NO₂, results have been reported utilizing laser induced molecular fluorescence which seem promising (Sinclair, 1972).

In what follows, we shall discuss a two component system for rapid assay of elements lying beyond Na in the periodic table. A rapid qualitative determination is performed via gamma-induced x-ray fluorescence and is followed by a quantitative assay using atomic absorption spectroscopy. A brief description will be given of the principles involved and the results will be compared with those of a previous paper (Carlton & Lehman, 1971).

X-RAY FLUORESCENCE SPECTROSCOPY

Characteristic x-rays may be produced in a substance via the photo-electric effect, wherein a collision occurs between a quantum of energy and a bound electron. If

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the gamma quantum has an energy greater than the binding energy of the electron, the electron may be ejected with a kinetic energy

$$E_k = h\nu - E_b$$

where $h\nu$ is the energy of the incident gamma quantum and E_b is the binding energy of the electron. One then has a vacancy in one of the innermost electron shells which will then be filled by one of the outer electrons. In the process an amount of energy is released in the form of x-rays or Auger electrons. The ratio of x-rays emitted to electron vacancies is called the fluorescence yield and is a function of atomic Z , increasing with increasing Z . As a consequence, the Auger effect is the predominant mode of energy release for light elements, and x-ray fluorescence becomes inefficient for elements lighter than sodium. For elements heavier than sodium the technique is useful and has definite advantages over other methods due to the characteristic nature of the x-ray energies. For analysis systems with sufficient energy resolution, this means that elements can be simultaneously identified in one spectrum in a non-destructive manner. In the few cases where an ambiguity might arise, one can rely on the well known intensity ratios for the various x-ray components of a given atom.

The selection of a fluorescing source is important from the standpoint of maximizing the efficiency of the technique in elemental identification. The characteristic of primary importance in this regard is the gamma ray energy. To understand this one must consider the energy dependence of the mechanism responsible for atomic vacancies. The photoelectric absorption cross section, which expresses the probability of a vacancy being created in a collection of atoms, is given approximately by an expression of the form

$$\sigma \propto Z^5 / E$$

where Z is the atomic number of the atom and E is the incident photon energy. From this it can be seen that in order to maximize the probability of vacancy creation, the energy must be as small as possible and still exceed the binding energy of the electron which is to be ejected. Since the binding energy of k-shell electrons is a function of Z , one would ideally desire a photon source of variable energy in order to achieve maximum sensitivity for simplicity and economy. Thus one may select three radioactive gamma emitters with an energy span equivalent to the binding energy range of the atoms under investigation. The strength of the radioactive source is another factor to consider in

maximizing sensitivity and in general, an increase in source strength will result in an improved sensitivity up to the point where background becomes intolerable. Other factors exclusive of the source can also affect the sensitivity such as detector efficiency, geometry and sample characteristics.

The basic components of an x-ray fluorescence spectrometer are:

- 1) Source and shielding
- 2) Detector
- 3) Data acquisition

For rapid qualitative analysis, the detector should be of the Si(Li) type, which provides the resolution capabilities necessary for the simultaneous assay of a number of elements. The cost of such a detector, depending upon the resolution desired, lies in the \$5,000-\$10,000 range.

The data acquisition system is simple and provides for pulse amplification and pulse height analysis. Prices may range from \$5,000-\$15,000.

A complete source excited fluorescence analyzer is commercially available for under \$20,000. A typical experimental configuration is shown in Figure 1.

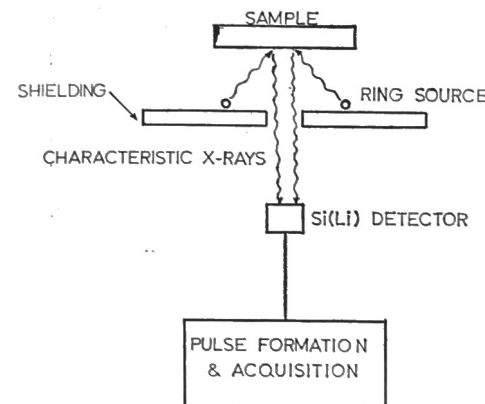


FIG. 1 Source excited fluorescence, analyzer, schematic representation

The present application of the technique has been the qualitative determination of the atmospheric pollution elements in a sample of Nashville air. The particular sample used in this part of the report consisted of pollutants collected on filter paper by means of a high volume suction pump.

The pulse height spectrum obtained from this sample is shown in Figure 2, along with the energy calibration of the system. The results are tabulated in Table 1 giving the channel location in the analyzer and the energies of the various peaks, together with the identification made on the basis of energy determination. It should be pointed out that some elements appeared in this spectrum which did not show up in the previous

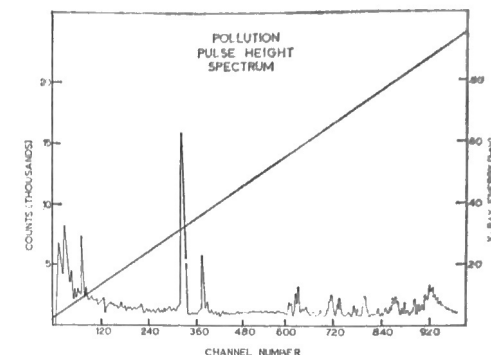


FIG. 2. Pulse height spectrum analysis of elements in a sample of Nashville air

work and this is due to the improved sensitivity of this technique over the previous technique for those particular elements.

TABLE 1. The elements present in an air pollution sample based upon source-excited x-ray fluorescence spectroscopy (SEF)

Channel Number	x-ray	Element	Energy (kev)
20	K _α	Ca	3.72
31	L	Ba	4.72
49	K _α	Fe	6.35
56	K _β	Fe	6.98
75	K _α	Zn	8.70
84	K _β	Zn	9.59
332	K _α	Ba	31.96
382	K _β	Ba	36.45
720	K _α	Au	67.07
776	K _α	Pb	74.28

ATOMIC ABSORPTION SPECTROSCOPY

The principle underlying atomic absorption spectroscopy has been extensively described in the literature, having been in wide use as a research tool in spectroscopy for many years. The instrument used in the present study was a Beckman Dual Beam Grating Spectrometer. In the case of the air pollution sample under investigation in this part of the report a previously investigated sample (using neutron activation analysis) was placed in solution to be used in the spectrometer. Although the intensity I received by the photomultiplier is not directly proportional to the concentration C of the element, the quantity $\log I$ is approximately proportional to the quantity $\log C$ in certain regions. The present pollution sample was low enough in concentration to be in the region of direct proportionality.

Most of the metals and a few of the non-metals are sensitive to this type of measurement. The sensitivity of the technique to various elements is shown in Table 2. The technique is relatively free of interference

and is readily adaptable to routine analysis of large numbers of samples in the case where quantification of a known element is desired.

TABLE 2. *Practical detection limits (parts per million) for numerous elements using atomic absorption spectroscopy (AA)*

Element	Practical Limits (ppm)
Ag	0.2
Al	1
Cd	0.01
Cr	0.1
Cu	0.05
Fe	0.1
Hg	2
K	0.05
Mg	0.02
Mn	0.1
Na	0.02
Pb	0.2
Zn	0.01

Herein lies the need for a supplementary technique for rapidly determining the elements present in a sample. To do this with absorption spectroscopy would be indirect and time consuming. Quantitative analysis of the sample was made by comparing the intensity of light passing through the sample to that passing through a standard sample. Light sources were used which were suggested by the previous technique (x-ray fluorescence) and then other available light sources were used to check for other elements. The results are shown in Table 3 where the concentrations of the various pollutants in the air sample are expressed as parts per million (ppm) of the pollution sample, previously subjected to soxhlet extraction. Due to the method of collection of the air sample, the ppm of the total volume of air sampled would be small indeed.

TABLE 3. *Results of atomic absorption spectroscopy applied to a pollution sample which had been extracted from filter papers*

Element	Concentration (ppm)
Zn	6.6
Mg	0.083
Ca	0.142
Cu	3.3
Na	31.0
K	13.6

CONCLUSION

The two techniques discussed are seen to be complimentary in that source-excited x-ray fluorescence, (SEF) while not as sensitive as atomic absorption, (AA) allows a simultaneous assay of all components of a sample, and one can thus know which light sources to use in the atomic absorption studies. It can be seen that, through some trial and error, we were able to detect elements present in the sample by (AA) which were not detected by (SEF). For the elements K, Mg and Na, the (SEF) technique was insensitive due to absorption of the x-rays in a Be window before entering the sensitive volume of the detector. The same is true of the elements shown in Table 4 which were detected by neutron activation analysis in a previous study but were not detected by (SEF).

TABLE 4. *Elements detected in an air pollution sample by the various techniques employed: neutron activation analysis (NAA), source excited fluorescence (SEF), atomic absorption (AA)*

Element	Detection Method		
	NAA	SEF	AA
Na			X
Mg	X		X
Al	X		
Si	X		
P	X		
K			X
Ca		X	X
Fe		X	
Cu	X		X
Zn		X	X
Ba		X	
Au		X	
Pb		X	

Those elements detected by atomic absorption are not inclusive in that light sources for all elements were not available. This explains the failure to detect by (AA) some of the elements detected by (NAA). Thus there seems to be consistency among the various techniques when differing regions of sensitivity are taken into consideration.

LITERATURE CITED

- Carlton, R. F. and A. J. Lehman, Jr. 1971. *TJAS*. 46(2): 63 p.
Sinclair, T. F. 1972. *Indus. Res.* 14(2): 26 p.