Determination of Al, Mn, Na, V, Cl, and Br in Air Borne Particulate Using Instrumental Neutron Activation Analysis

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Abstract—Instrumental neutron activation analysis employing lithium- drifted Ge-γ ray detectors has been used successfully to measure the concentration of 6 elements (mostly metals) in atmospheric aerosol of south of Baghdad. Samples were collected by pumping air through membrane filters connected to electric vacuum pump. Samples were irradiated for 5 min at neutron flux density of 6×10^{12} n/cm^2.s, and were measured on multichannel 4096 analyzer. Gama-ray spectra were analyzed and concentrations of many elements were measured and results were discussed.

Keywords—Instrumental Neutron activation analysis, atmospheric aerosol, elements concentration.

INTRODUCTION

Because of national concern regarding air pollution we tried to determine the concentrations of elements in the atmosphere of urban area. It is difficult to study the particulate material in the atmosphere because of many problems involving the collection and analysis of the samples and the interpretation of the results. In this study we report a quite sensitive suitable analytical technique to deal with air pollution problems.

Work on atmospheric aerosols has employed samples collected on filters then dissolution of the samples followed by chemical or instrumental analysis. The problem with such method it may introduce large errors by loss of material or contamination of the sample [1], [2].The errors in determination of trace metals by ion exchange with glass or plastic containers could be very severe with use of strong acids [3] . Matrix effects in many of the common analytical methods may be severe if particulate material and / or interfering ions are present [4]-[8]. Most of these difficulties are avoided by the method presented in this study in that the standard filters irradiated with neutrons prior to any treatment. Neutron activation analysis offers excellent sensitivities that are superior to other analytical techniques in performing identification and quantitative elemental analysis [9].

This study involves collection of aerosols from air on a filter, then irradiation of the filter with thermal neutrons, and observation of γ-rays from samples with lithium-drifted germanium [Ge (Li)] detectors. Gamma rays from irradiation product of many elements can be observed and their intensities measured, allowing one to compute the concentrations of those elements. The field of instrumental neutron activation analysis (INAA) in which no chemical separation are performed, has been greatly extended by the development of Ge(Li) γ-ray detectors. It is now possible to resolve $\gamma - rays$ of many radioactive nuclides from complex mixtures of activities. Many Workers [10]-[13] demonstrated that the concentrations of more than 25 elements could be determined by (INAA) with the use of Ge(Li) detectors. The pioneering work of activation analysis was done by Winchester and co-workers[14] and Dudey et- al.[15]when they observed lines from irradiation products of about 23 elements in Ge(Li) γ-ray spectra of marine aerosol samples afrer chemical removal of Na and additional ion- exchange steps. Generally, because of lower ratio of Na to another elements in nonmarine atmosphere, it is possible to measure concentration of quite number of elements from polluted urban areas, by high-resolution Ge(Li) γ-ray spectrometry without any chemical separation[16]. Examination of many types of cellulose, polystyrene and polyvinylchloride filters has shown that the blank activity levels are quite acceptable for most applications of this type [17]-[27].

Experimental and Results

A membrane filter pump calibrated at 2 liters per minute was used and connected to 37mm filter paper. The sampler was placed about 3m above the ground and the total sampling time was at least 8 hours. Ambient air samples analyzed in this study were collected from suburban region called Jisr-diyala located in the south eastern of Baghdad, the capital city as shows in Fig.1. The suburban region is located several kilometers from a heavy-traffic intersection and not far away from industrial complex.

Fig. 1. Location area of sampling

Meteorological conditions such as temperature, humidity and wind velocity obtained from the Hourly Weather Forecast (wundergrond.com) were recorded regularly on April during the collection of the samples and as shows in Table 1. Experiments conducted in 1991 and for many obstacles, the data have not been published to date.

Table 1. Metrological condition on April

	Max.	Min.	Avg.
Temperature (C^o)	36	26	31
Humidity %	48	12	22
Sea Level Pressure (hPa)	1019	1002	1010
Wind (Km/h)	37	0	11
Rain (mm)	0.0	0.0	0.0
Cloud cover %	35	4	20
Visibility (Km)	10	2	6

Whatman filter paper (cellulose)was chosen for use throughout this study as the collection surface because of its low impurity content, stability for INAA and acceptable strength , dry or wet. Our scanning electron microscope examination showed that Whatman filter paper has fibrous structure Fig.2. with average porosity of 0.53 μm. It is collection efficiency as a particle filter was reported in pervious work by Paciga and Jervis[28] to be not less than 80% and by Neustadter and others[29] to be greater than 83% for

most particle size. In table 2 we list the amount of various elements that we found in clean Whatman filters by neutron activation. The filter has very small blanks for the elements observed except Cl.

Fig. 2. SEM image shows the fibrous structure of Whatman filter paper used in this work.

Table 2. Amounts of impurities in clean Whatman filter paper

Elements	Amount (μg) in the whole filter
Na	0.52
Al	0.065
Cl	0.65
V	0.0019
Mn	0.0025
Br	0.065

The amount of particles dislodged from the filter during normal handling was estimated by washing the inner surfaces of the samplers with 0.5% Triton aqueous solution. The elements of this solution were measured by electro thermal atomic absorption spectrometry after nitric acid digestion. The average amount of elements found on the internal walls of the samplers was 8% of total aspirated elements. This shows that losses on the internal collector surfaces may be a major source of error in measurements of aerosol contaminants if this sample fraction is neglected. Also S. Hotland showed similar result [30].

The collected samples and the standards were put in polyethylene containers and were irradiated for 5 min. and delay time for 3 min. at neutron flux density of $6x10^{12}$ n/cm^{-2}s at 14 July reactor in Baghdad. The samples and the standers were measured for 10 min. counting time on a multichannel 4096 analyzer in combination with a Ge / Li / detector / 2.5 Kev resolutions at energy level of 1.333Mev for Co^{60}

isotope. In table 3 we give detailed information on the energies and intensities of □-ray emitted by some of the species observed in this work.

Table 3. Energies and intensities of observed γ-ray emmited by some of neutron-irradiation products

Nuclide	Halftime	E_γ (Kev)Ref[31]	$^aI_\gamma$ (%) Ref[31]	Best time for counting after irradiation Ref[16]
Al[28]	2.3 min	1778.9 ± 0.2^b	100	0-20 min
Cl[38]	37.3 min	1642.0 ± 0.2^b 2166 ± 0.2^b	38 45	20-60 min
V[25]	3.77 min	1434.4 ± 0.2^b	100	0-20 min
Br[80]	17.6 min	616.2 ± 0.2 665.6 ± 0.2	6.8 1.1	1-4 min

a Absolute photon intensities, [b]Ref. 32

To minimize confusion, we have listed only those rays that are strong enough to be observed in the irradiated filter samples. Even with the excellent resolution of Ge(Li)detectors there are some doublets that some rays cannot be clearly resolved[16]. In the work reported here we have generally been able to avoid the problem of interference by using the strongest "Clean" line of each species for the essay.

Fig.3. shows gamma-ray spectra after 5 min irradiation. Radioactive nuclides were identified on the bases of energies and high lives of peaks, and we must emphasize the importance of accurate determination of γ-ray energies. Gamma-ray energies of nearly all (n, γ) products of reasonable half life have been determined nearly to$\pm$ 0.5 Kev.
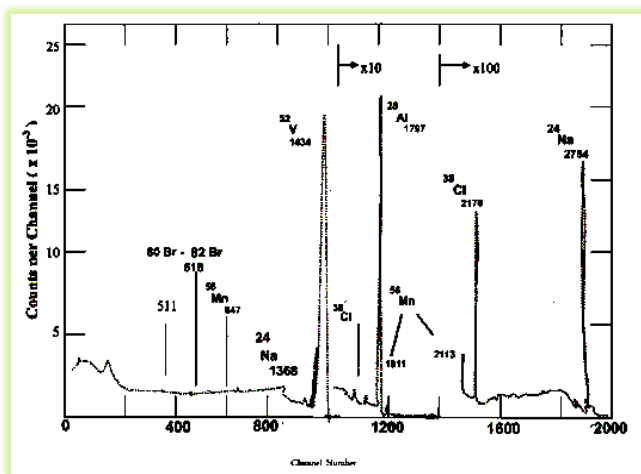

Fig. 3. Gamma-ray spectra taken after 5-min. irradiation of filter sample

Determination of Elements Concentrations

We used the peak area to calculate the quantity of any element in a sample and were computed from the ratio of the peak areas in the sample to the areas of corresponding peaks for the elements irradiation products in the monitor spectrum. Because of variation in background under the peaks and possible changes in peak width; one must use peak area rather than peak heights for quantitative assays.

We determine the areas of the photo peaks by summing the counts in the channels of the peaks and subtracting a smooth background determined from the channels on each side of the peaks. When the peaks were identified, we were able to use special computer programme to determine the areas of strong peaks on smooth background if they are separated from other peaks in the spectrum. Computer analysis was particularly useful for □-ray of short lived species present in spectra taken with a few minutes after irradiation, as the case of our work. Most of the species prominent at this time have rays that are widely spaced and which extend up to moderately high energies. Thus we were able to determine the amounts of Al, V, Mn, Br, Cl, and Na in these short runs. The results in table 4 show concentrations of the various elements observed in the samples taken from south-eastern of Baghdad.

Table 4. Atmospheric concentrations of several elements observed in the aerosol samples.

Elements	Concentration (μgm^3)
Na	0.7
Al	0.8
Cl	0.5
V	0.58
Mn	0.02
Br	0.16

Discussion

In our experiment, in relatively short time we measured the concentrations of six elements. Also one can measure the concentration of more than 20 elements if gamma ray spectra of each sample were taken at longer time after irradiation.

After INAA analysis is complete, the same samples can be used to measure additional elements, like Pb by other techniques. We made some preliminary studies and we measured the concentration of Pb and we found strong correlation between Pb and Br in air, both of which originate largely from automobile exhaust. Whinchester et- al. found similar correlation in air [14].

The INAA method is fast and convenient for elements having highly active, short- lived irradiation products, like Na, Al, Cl, Br, V and Mn. The time from receipt of sample unitl concentrations are available can be under 1 hour. The sampling time in our system is about 8 hours, but collection time could be reduced to 1 hour with high- volume pump. This would allow us to monitor the development of air pollution in short time.

We think that Al, Br, and V are indicators of pollution from automobile exhaust and heavy fuel oils. In the present results, elements representative of crustal materials and soils arose from near industrial site, which was also near a major express way and heavily traveled arterial road. The elements Br, Cl, and V considered to arise from anthropogenic sources and from industrial sites. Mn and Ca might arise from sewage sludge and other light industries.

Some experiments were carried out on the physical and chemical characterization of ambient aerosol. This was performed by direct examination and size classification of individual particles collected on filter paper through scanning electron microphotography (SEM) and Instrument Neutron Activation Analysis (INAA) among about 200 particles per filter paper. From the scan of the SEM images (not shown here), particle size distribution are compiled, such as those shown in Fig. 4.
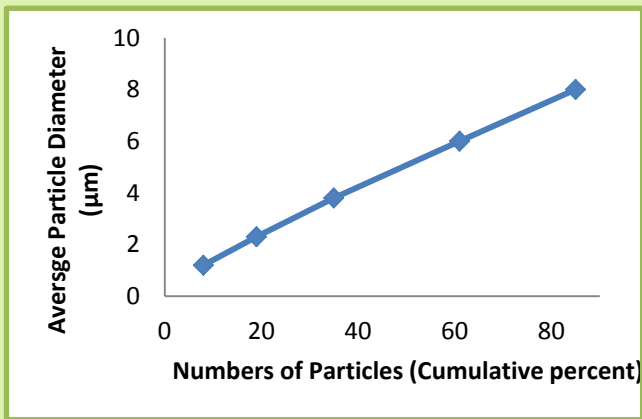

Fig. 4. Particle size distributions are compiled from the scan of the SEM images

Due to the importance attached to measurement sensitivity as a criterion for evaluating any given trace analysis method; it is worthwhile to consider this point in connection with the samples analyzed in this study. Experimental sensitivity values have been reported for almost all elements which can be measured by means of neutron activation analysis [33], [34]. In a set of experiments, the ratio of level of an element measured to the minimum detectable level of the element in a given sample, R, have been computed [23]. Table 5. gives average R values for some elements which are more commonly observed in air filter samples with INAA.

Table 5. Detectability (R) of elements common in air filter samples

Elements	R
V	4.10
Al	121.9
Br	33.5
Mn	28.4
Na	13.2
Cl	27.8

It is clear from pervious tables that almost all elements investigated are present at concentrations above their detection limits and below threshold limit value (TLV) which considered being 5000 $\mu g \text{m}^{-3}$ of air.

Neutron Activation Analysis is still used successfully in air pollution [35], nutrition pollution [36]-[38] and other fields [39]-[41] since its discovery in 1936 by Hevesy and Levi.

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