PRNC- 186

PUERTO RICO NUCLEAR CENTER

TOXIC METALS IN THE ATMOSPHERE

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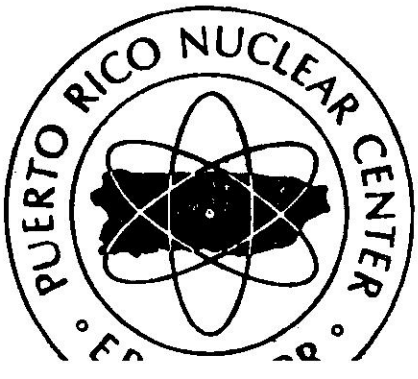

TOXIC METALS IN THE ATMOSPHERE

by

Fausto J. Muñoz-Ribadeneira, Tin Mo, and M.J. Canoy

PART I

NONDESTRUCTIVE MULTIELEMENT INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF TOXIC METALS IN THE ATMOSPHERE OF SOUTHERN PUERTO RICO

by

Tin Mo and M.J. Canoy

Part I

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INTRODUCTION

During the past several years there has been increasing concern with environmental problems. These problems were ushered in by a rate of technological progress not in harmony with nature. In the attempt to cope with the demands for improved standards of living, sound ecological planning was overlooked. In particular, the quality of the air necessary for the sustenance of life has suffered from the encroachment of industrialism and urbanization. For this reason, techniques to measure toxic compounds in the atmosphere have been developed.

Malignancies and other deleterious effects induced by the carcinogenic and synergistic action of varying levels of different metals on humans are discussed in detail by Hamilton (1934), Elkins (1959), and Lee (1972). Data on the levels of these pollutants in the air are necessary before they can be judged hazardous. After collection of these data, their relation to statistical data on public health problems in Puerto Rico can be studied.

This study is concerned with the metallic elements Ni, V, Mn, Sb, Se, Hg, Pb, Cd, and Cr. These metals are being introduced into our atmosphere by industry, automobile exhaust emissions, the burning of municipal wastes, building construction, and agricultural insecticides, and are considered hazardous when they reach certain levels of concentration.

The study of aerosols and atmospheric particulates is not an easy task because of problems in the collection and analysis of samples and in the interpretation of results. No single analytical method can cope with all the problems involved, including sufficient speed to deal with air pollution emergencies. The instrumental neutron activation analysis (INAA) method that is being adopted and developed in our laboratory is described. This method is quite accurate and sufficiently sensitive for the determination of almost all the metals with which we are concerned. This technique has great potential usefulness, particularly as several metal concentrations (V, Mn, Al, etc.) can be determined within about an hour after receipt of the samples. Thus, the method can be applied rapidly to indicate pollution crises and to suggest the most serious contributors to the crisis.

For most studies of atmospheric particulates, samples are collected on filters or in particulate impactors. Many of the analytical methods require dissolution of the sample followed by chemical and instrumental analyses. A serious shortcoming of such methods is that dissolution and subsequent wet chemical steps may introduce large errors, either by loss of material or contamination of the sample. The sample materials themselves, especially pollution aerosols, are generally insoluble in water since the majority of them are carbonaceous and may even be refractory (Junge 1963). West and coworkers (1966) stated that even with the use of strong acids, ion exchange of trace metals with glass and plastic containers may be quite severe. West (1968) and Christian (1969) showed that matrix effects in many of the usual analytical methods (e.g. emission spectrography, atomic absorption, or microchemical techniques) may be serious if particulate material and/or interfering ions are present.

Activation analysis has not been commonly used in atmospheric studies. The pioneering work was done mostly by Winchester and coworkers (1967) who applied

radiochemical techniques to study mainly the halogens Na, V, and Cu in the atmosphere, ocean, rain, and snow. Brar et al. (1969) used NaI(Tl) detectors without chemical separations to measure the concentrations of several elements in aerosols from the Chicago metropolitan area. Dudey et al. (1969) observed gamma rays from irradiation products of about 23 elements in Ge(Li) gamma ray spectra of marine aerosol samples after chemical removal of Na and additional ion exchange steps. Dams et al. (1970, 1971), Gordon et al. (1971), and Tuttle et al. (1971) then successfully applied a nondestructive multielement neutron activation analysis procedure to determine up to 33 elements in air pollution.

EXPERIMENTAL METHODS

The method adopted follows quite closely the procedures employed by Dams et al. (1970). This method involves collecting aerosols from 5 to 15 m^3 of air on a filter and irradiating the filter with nuclear reactor thermal neutrons to determine concentrations of all metals under study, except nickel. To measure Ni concentrations, the fast neutrons of the reactor were used to effect the ^{58}Ni (n,p) ^{59}Co reaction. The ^{58}Co gamma rays were detected to determine nickel concentration. The gamma rays from all the irradiated samples were observed with high resolution lithium-drifted germanium, or Ge(Li), detectors.

Sampling Procedures

Eight air tape sampling machines (Bendix Corporation Model No. 23000 paper tape samplers) were placed at six different locations around the south coast of Puerto Rico. The sampling stations were diverse with respect to the density of population, industrial plants, and automobile traffic. The exact locations were given in the Aguirre Power Project Environmental Studies Annual Report for 1971 and are shown in Figure 1.

Atmospheric aerosols were collected on a filter paper tape by drawing air through an electric vacuum pump. Air particulates were collected on a circular spot (1.27 cm^2) on the filter paper. The filter paper used (Bendix Corporation Catalog No. 6102, acid-washed paper, type W-41) has high collection efficiency for particulate material down to the 0.1 range. The paper also has fine chemical quality and purity, so that the interferences or contributions from superfluous background concentrations of the trace metals in the blank samples are kept to a minimum or essentially to zero.

Each paper tape sampler had an automatic tape advance and clamping system. The machine cycle was adjusted so that every two hours the incoming air would pass through a fresh part of the air tape assuring an average air flow of 11 liters/minute. The amount of pollutants collected during periods of 8, 12, and 24 hours made up a sample for neutron activation analysis. In this way it was possible to observe variations in the concentrations of the contaminating metals within one day and to measure the average daily concentrations of the contaminants in the air at different sampling stations and under varying meteorological conditions.

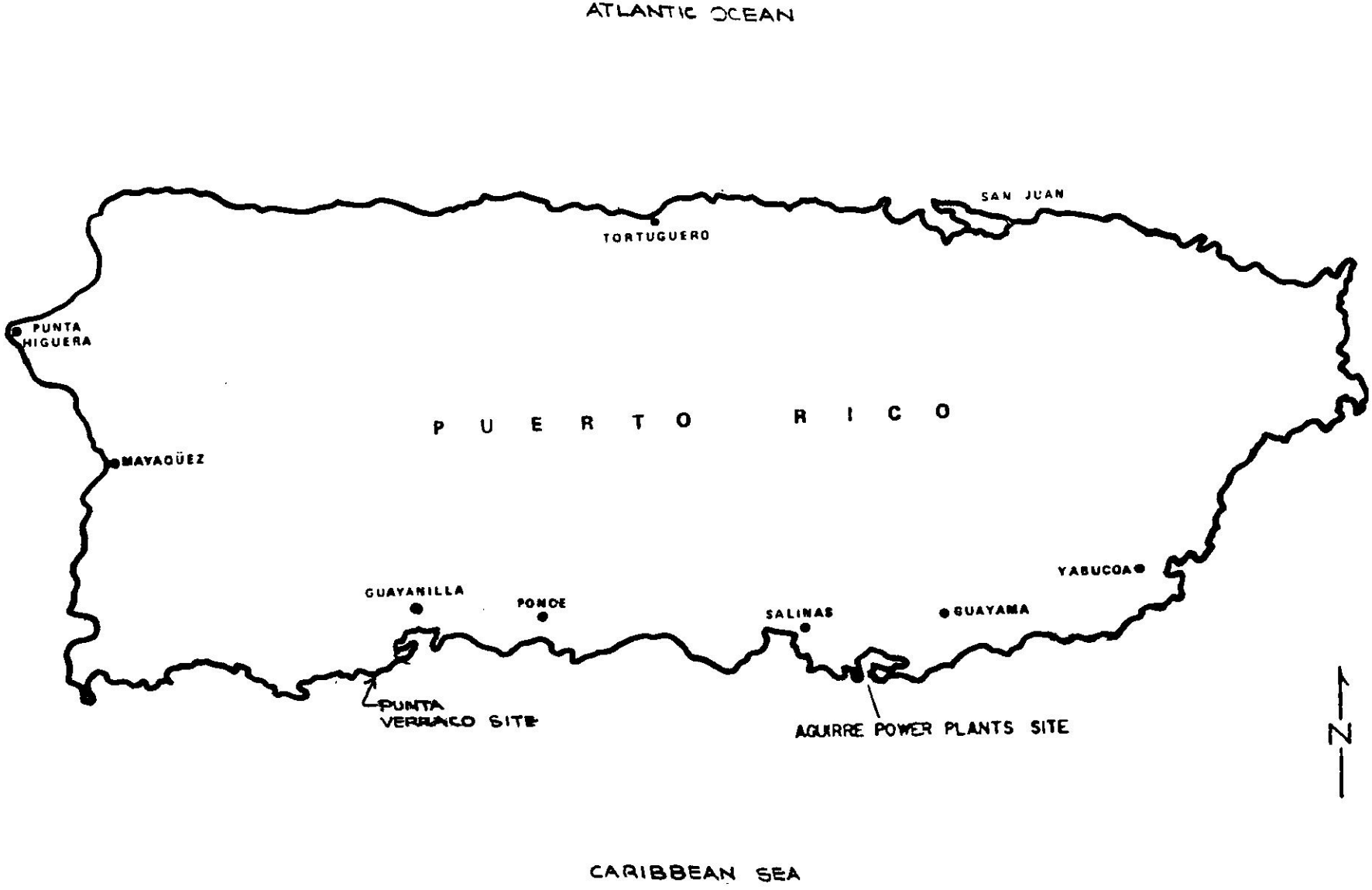


FIGURE 1. Air particulate sampling stations, 1971 - 1972

Laboratory Procedures

Preparation of Samples for Irradiation

Samples. Plastic gloves and stainless steel surgical scissors were used to cut out a piece of the air tape containing four spots of air particulates (corresponding to 8 hours flux of air or 5.28 m^3 of air collected). The sample was then placed in a 7 cm diameter Petri dish and dried under a heat lamp. After cooling in a desiccator, the sample was weighed and sealed in a small polyethylene snaptop irradiation vial (10 mm x 25 mm, Bel Art Plastics Co., Pequannock) which had been washed with a warm 1:1 nitric acid-sulphuric acid solution and de-ionized distilled water. The polyethylene vial was then heat-sealed with a heated quartz tube. The outside of the vial was washed with warm nitric acid-sulphuric acid and de-ionized water and wiped dry. The sample was then placed inside a clean plastic bag.

Blanks. Blank samples were prepared in the same manner.

Standards. Fifty microliters each of two well balanced mixtures of the appropriate elements were deposited on each piece of clean paper tape (approximately the same length as the samples and blanks), allowed to dry and cool, then weighed and sealed inside the irradiation vials. One standard consisted of 0.1 micrograms each of the elements vanadium and manganese which gave short-lived radionuclides upon neutron irradiation. Another standard consisted of 0.1 micrograms each of arsenic, chromium, selenium, mercury, nickel, cobalt, and zinc which yielded longer-lived radioactive species upon neutron irradiation.

Irradiation and Counting Procedures

The irradiation and counting scheme given by Dams et al. (1970) was followed. For the analysis of elements giving rise to short-lived isotopes, samples, standards, and blanks were irradiated for five minutes in a flux of about 10^{13} neutrons/cm^2/second in the Puerto Rico Nuclear Center reactor's fast transfer rabbit irradiation facility. Because the neutron flux from one irradiation to the next could not be assumed to be constant, an accurately weighed titanium standard wire was co-irradiated with each sample to serve as a flux monitor. These wires were taped to the sides of the irradiation vials before they were encapsulated inside the outer irradiation rabbit.

The short-lived gamma ray nuclides ^{28}Al, ^{62}V, and ^{68}Mn were detected in the irradiated samples about three minutes after irradiation by counting for 400 seconds live-time with a large, co-axial detector of effective volume 26 cm^3 (Canberra) coupled to a 1024 channel analyzer (Packard). The flux monitors were counted for 20 seconds each. Then the samples were counted again for 1000 seconds live-time 15 minutes after the end of irradiation.

Another set of samples with appropriate standards and blanks was irradiated for five to eight hours and counted at decay-times of one to two days for 2000 seconds live-time to determine the elements As, Cu, Zn, and Br. To determine the elements Ni, Co, Zn, Hg, Se, Cr, As, Sb, Sc, and Fe (which give rise to long-lived nuclides), the same samples were counted for either 100 minutes live-time (high activity samples) or for 1000 minutes live-time (low activity samples) after 20 to 30 days of cooling. For the long irradiation, all irradiation vials were

encapsulated inside an aluminum canister provided with a screw cap and lowered into the irradiation position on the periphery of the reactor core. The aluminum canister was rotated during irradiation to effect normalization of the neutron flux received by the samples.

After irradiation and cooling, the paper samples were transferred from the snaptop vials to clear plastic vials to be counted for different live-times on the Ge(Li) detector. The resolution of the Ge(Li) detector used in this study was 2.3 kev full-width at half maximum (FWHM) of the photopeak produced by 1332 kev gamma rays from ^{60}Co. The peak to Compton ratio was about 16.

DATA REDUCTION

Presence of Isotopes

Radioactive nuclides were identified solely on the basis of energies and half-lives of the photopeaks. Comparison of the gamma ray spectrum of the unknown sample with that of the standard sample and prior calibration of the gamma spectrometer with standard sources of known energies facilitated the identification of radioactive nuclides in the irradiated unknown samples. Most radioactive species emit several gamma rays, so the intensity pattern of the several gamma rays can be utilized for very clear identification in those cases. The importance of accurate determinations of gamma ray energies must be emphasized. Gamma ray energies of nearly all (n,p) products of reasonable half-life have been accurately determined, nearly always to ± 0.5 kev and often much better (Table III in Gordon et al. [1968] and Table 1 in this report). If one can determine the gamma ray energies of photopeaks in spectra of the unknowns to ± 0.5 kev or better, there is little ambiguity in the assignments of the gamma rays to particular radioactive nuclides. For identification of species, the spectra were analyzed by hand, in which case it was assumed that the energy versus channel number calibration curve is linear over small energy regions.

Figure 2 represents the gamma ray spectrum of an air particulate sample irradiated for three minutes and at five minutes decay-time from the end of irradiation. The spectra were dominated by 2.3 minute ^{28}Al, 3.8 minute ^{52}V, 17.6 minute ^{80}Br, and 2.58 hour ^{56}Mn.

Figure 3 shows the gamma ray spectra of air particulate and blank samples (which were co-irradiated for five hours in a flux of about 10^{12} neutrons/cm^2/second) and at a decay-time of 24 hours from the end of irradiation. The 35.3 hour ^{82}Br and 15.0 hour ^{24}Na photopeaks dominate the spectrum of the irradiated air particulates. The gamma ray spectrum of the irradiated blank samples shows no photopeaks of appreciable magnitude corresponding to those in the air particulate sample except for the 511 kev annihilation and 1368 kev ^{24}Na peaks. This attests to the fine chemical quality and purity of the paper tapes used for collecting aerosol samples.

Photopeaks produced by nuclides with half-lives up to 12 years (^{152}Eu) are observed in the spectrum of Figure 4, taken 36 days after a long irradiation (five hours) of an air particulate sample. Even though most of the peaks are well

Element	Target Isotope	Isotopic abundance %	Product nuclide	Effective (N_{th}, δ) (barns)	Best photopeaks for determination; kev	Best time after irrad. for counting
Short Runs						
Al	^{27}Al	100	2.3 min ^{28}Al	0.23	1779	0-20 minutes
V	^{51}V	99.75	3.77min ^{52}V	4.9	1434	0-20 minutes
Mn	^{55}Mn	100	2.58 hr ^{56}Mn	13.3	847, 1811	1-4 hours
Cu	^{65}Cu	30.9	5.1 min ^{66}Cu	2.3	1039	0-20 minutes
Long Runs						
Se	^{74}Se	0.87	120 day ^{75}Se	30.0	265	1 month
Hg	^{202}Hg	29.80	47 day ^{203}Hg	3.8	279[b]	1 month
Cr	^{50}Cr	4.31	27.8day ^{51}Cr	17.0	320	1 month
Sb	^{121}Sb	57.25	2.8day ^{122}Sb	6	564	1 week
	^{123}Sb	42.75	60 day ^{124}Sb	3.3	603	1 month
Ni	^{58}Ni	67.8	71 day ^{58}Co	(n,p)	810	1 month
Zn	^{64}Zn	48.9	245 day ^{65}Zn	0.46	1115	1 month
	^{69}Zn	18.57	13.7 hr ^{69m}Zn	0.075	439	1 day
Fe	^{58}Fe	0.31	45 day ^{59}Fe	1.1	1098, 1292	1 month
Sc	^{45}Sc	100	84 day ^{46}Sc	23.0	888	1 month
Co	^{59}Co	100	5.26 yr ^{60}Co	37.0	1173, 1332	1 month

Data obtained from Lederer et al. (1967)
The monoenergetic ^{203}Hg(279.1 kev) is interfered with by ^{75}Se(279.6 kev), but a correction based on the spectrum of pure ^{75}Se can be applied in most cases.

TABLE 1. Production and decay characteristics of nuclides of metals of interest observable with Ge(Li) detectors in neutron irradiated atmospheric aerosols

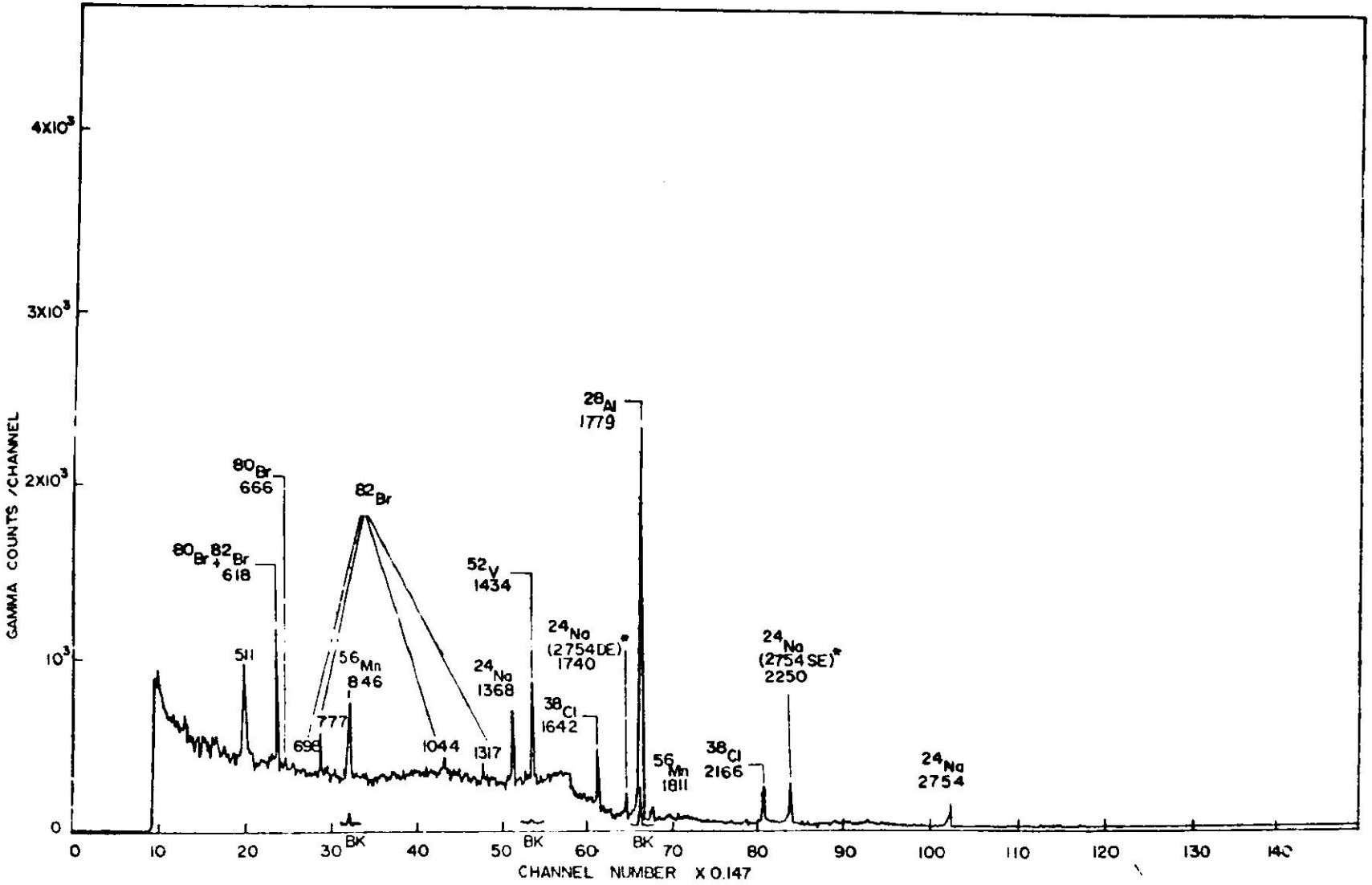


FIGURE 2. Gamma ray spectra of irradiated air particulate sample five minutes after irradiation

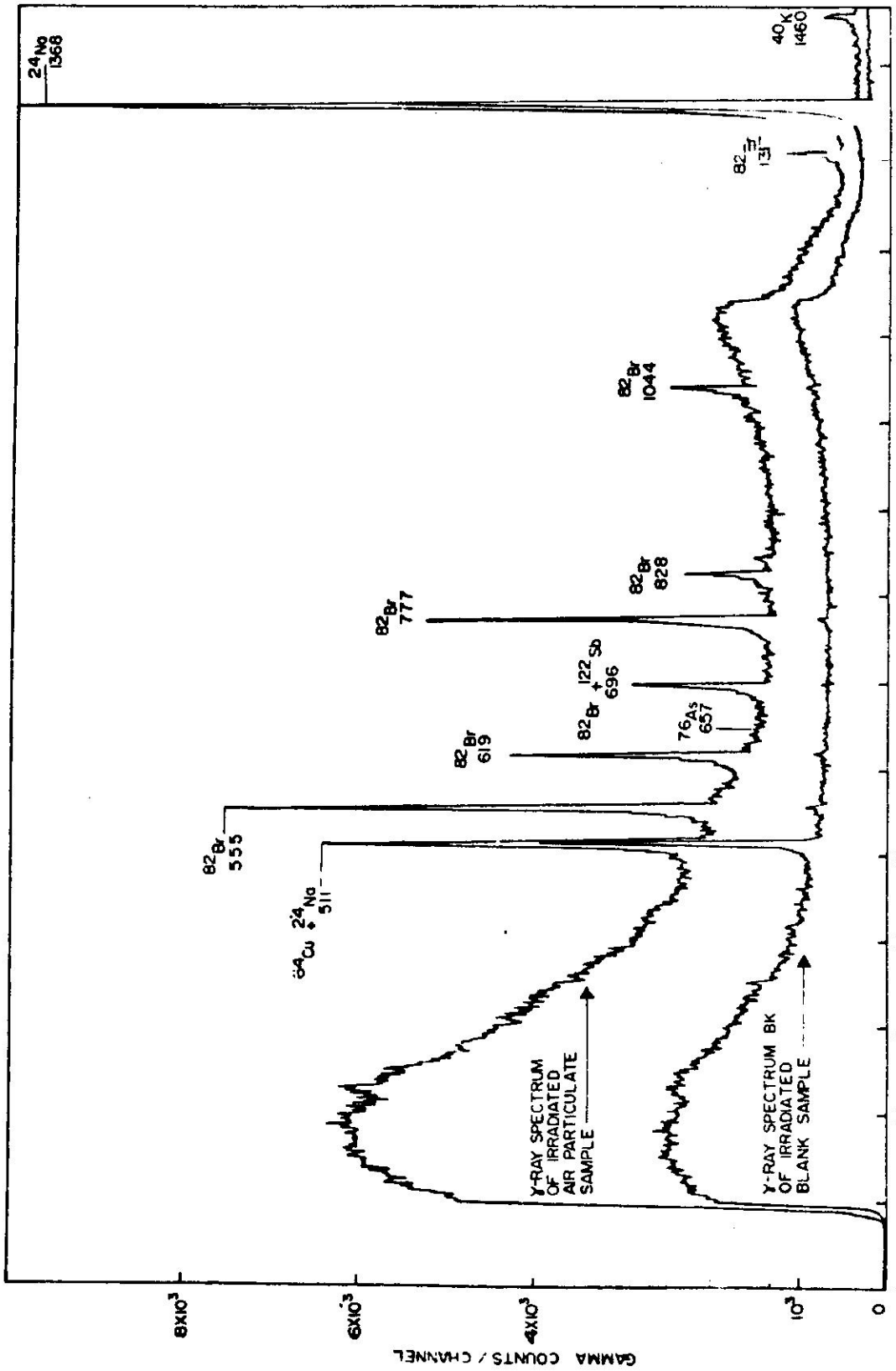


FIGURE 3. Gamma ray spectra of irradiated air particulate sample one day after irradiation

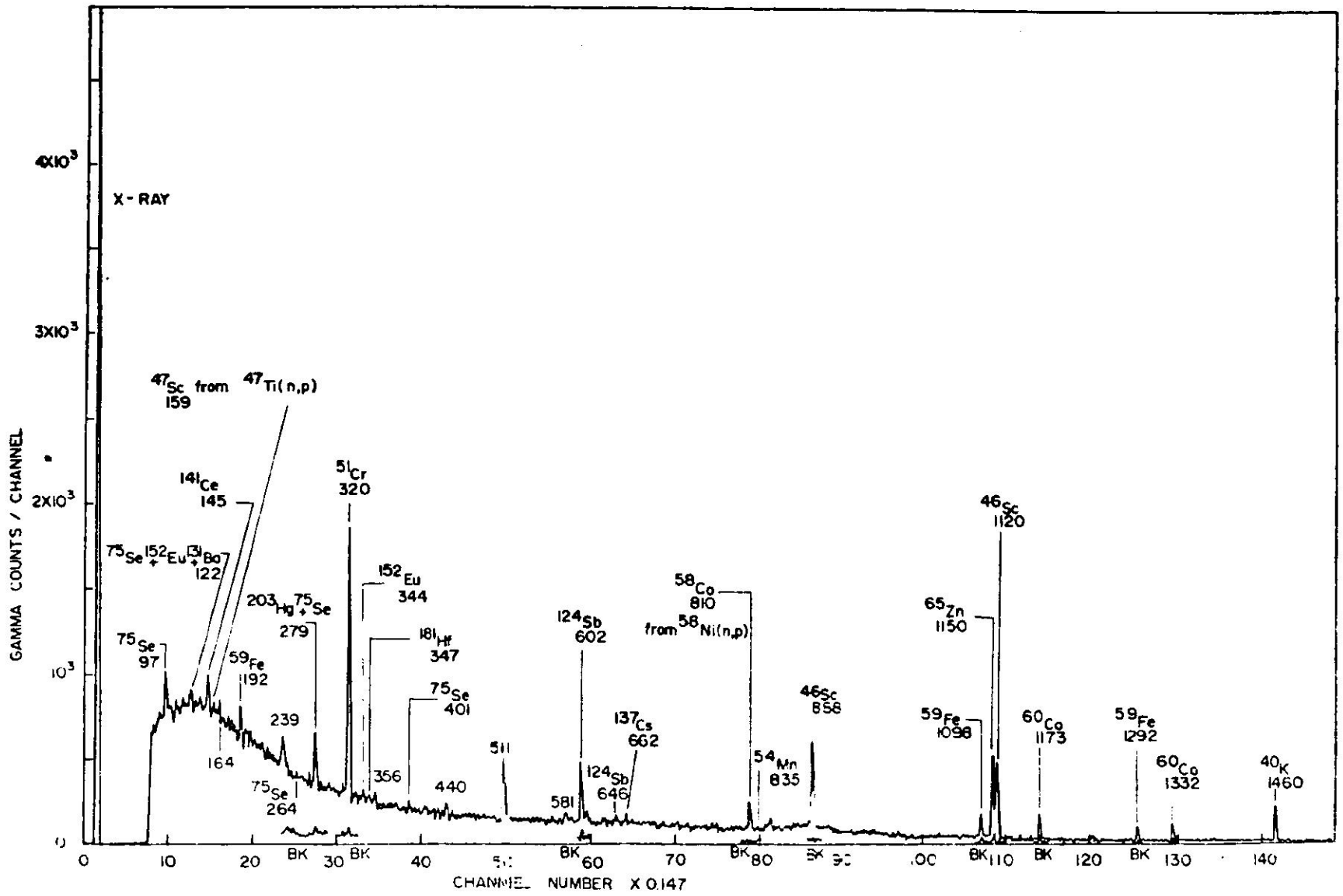


FIGURE 4. Gamma ray spectra of irradiated air particulate sample one month after irradiation

resolved, the spectrum is quite complicated up to 347 kev. The strongest peak in the low energy part of the spectrum is the 320 kev line of ^{51}Cr. The predominant peak in the medium energy part of the spectrum (500 to 800 kev) is the 602 kev ^{134}Sb photopeak. In the high energy region (800 to 1500 kev) ^{49}Sc, ^{59}Fe, ^{60}Co, and ^{65}Zn dominate the spectrum.

Calculation of Net Peak Areas

Areas of the photopeaks were determined 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 (Covell 1959).

Conversion of Peak Areas to Weights of Trace Metals

The amount of a given element in a sample was calculated from the ratio of the peak areas in the sample spectrum to the areas of the corresponding peaks for the element's irradiation products in the standard sample's spectrum. Because of variations in background activity under the peaks and possible changes in peak width due to high count rates or gain shifts, net peak areas rather than peak heights were used for quantitative assays. Corrections were applied for decay between the counting times of samples and standards. As often as possible attempts were made to deposit amounts of standard solution on comparison standard paper tape that gave counting rates similar in order of magnitude to the samples. This enabled the use of the same counting positions at about the same counting rates for both samples and monitors. It was reported by Gijbels et al. (1968) that errors on the order of 10% can result from coincidence summing and other geometrical effects if the various samples are counted in different positions, even if one attempts to use an efficiency versus position curve. The same authors stated that errors can also arise from large differences in count rates, about 10% for count rates differing by a factor of three if the dead-time fraction is high. This is because analyzers do not necessarily correct accurately for dead-time losses even in the live-time mode.

Calculations of Metal Concentrations

The concentration of C_x of a metal x in air is computed by the formula:

$$\frac{\text{Weight of metal}}{\text{Volume of air sampled}} = C_x = \frac{A_x}{A_s} \cdot \frac{W}{V} \quad \frac{m_s}{m_x} \qquad \ldots\ldots\ldots(1)$$

where A_x = net gamma counts under the photopeak (at the end of irradiation) corresponding to a certain energy gamma ray of a nuclide of element x present in aerosol sample; A_s = net gamma counts under the photopeak of the same energy as for A_x and corresponding to the same nuclide of element x present in the standard sample (corrected for decay also to the end of irradiation); W = weight of element x present in the standard sample, usually expressed in micrograms or nanograms; V = volume of air (usually expressed as m^3) sampled to collect the aerosol sample; m_x = weight of paper sample with air particulates; and m_s = weight of paper sample with standards.

Subtraction of Analytical Blanks

The net activities or counts due to the sample and standard, A_X and A_S, respectively, are further defined by equations (2) and (3):

$$A_X = A_{GX} - A_{BKX} - A_{BL} \quad \text{.....(2)}$$

$$A_S = A_{GS} - A_{BKS} - A_{BL} \quad \text{.....(3)}$$

where A_{GX} or A_{GS} = gross counts under photopeak; A_{BKX} or A_{BKS} = total counts due to the background in channels containing the photopeak; and A_{BL} = net counts under the photopeak of the same nuclide in the aerosol sample. (A_{BL} is shown experimentally to be essentially zero in most cases for the paper tape used in this study and can be neglected.) All the quantities on the left side of equations (2) and (3) should be values obtained after extrapolation to the time at the end of irradiation. The values should also be corrected for differences in weights of the blank, sample, and standard paper tapes.

Calculation of Errors

The error reported in this study for a single determination of metal concentration in a single aerosol sample is the standard deviation σ due to counting statistics (Friedlander et al. 1964). The standard deviations σ_X and σ_S due to counting statistics for net counts A_X and A_S respectively are defined as:

$$\sigma_X = (\sigma_{GX}^2 + \sigma_{BKX}^2 + \sigma_{BL}^2)^{1/2} \quad \text{.....(4)}$$

$$\sigma_S = (\sigma_{GX}^2 + \sigma_{BKS}^2 + \sigma_{BL}^2)^{1/2} \quad \text{.....(5)}$$

where σ_{GX} or $_{GS}$ = standard deviation due to counting statistics of gross counts under the photopeak; σ_{BKX} or $_{BKS}$ = standard deviation due to counting statistics of background in channels containing the photopeak; and σ_{BL} = standard deviation due to counting statistics of net counts under the photopeak in the blank sample which corresponds to the photopeak of a common nuclide in the aerosols and standards.

The standard deviation due to counting statistics σ_C for the calculated concentration of the metal in air is computed by the following relation (Mo 1971):

$$\sigma_C = C_X (\sigma_X^2/A_X^2 + \sigma_S^2/A_S^2)^{1/2} \quad \text{.....(6)}$$

C_X is defined in equation (1). However, when duplicate determinations are made of the metal concentrations, the average value is reported together with the relative standard deviation calculated from the spread of the individual values.

DISCUSSION

Air Pollution in San Germán, Puerto Rico during November 1972

The data given in Table 2 for eight hour average concentrations of the polluting elements for morning, daytime, and night, in the air of San Germán are plotted in Figure 5. The graph illustrates the variations in the metal concentrations within one day during the period 10 through 23 November 1972. For each of the trace metals and for Bromine, the concentrations in the air reached their maxima from about 8:00 a.m. to 4:00 p.m. A fraction of the Br found may be of maritime origin, but most of it probably indicates pollution from automobile exhaust emission (Winchester 1967).

The aerosol samples were collected before the burning of sugar cane began in January. The major sources of pollution might be a combination of exhaust emission from cars, dusting and spraying of herbicides on major crops like sugar cane or pineapple, and earth moving and excavating activities. Most of the terrain around San Germán consists of serpentinite, which has high Cr (~1000 ppm), Ni (~1000 ppm), and Co (~100 ppm) content (Wedepohl 1971). The dust stirred up by automobiles, earth movers, and wind may contribute to the peaking of these elements during the day. Figure 4 clearly indicates that the concentrations of the trace metals and Bromine were highest during the day when traffic, construction, and wind turbulence were at the maximum. It is also possible that some of the trace metals may have been transported from the industrial operations in the southern part of the island.

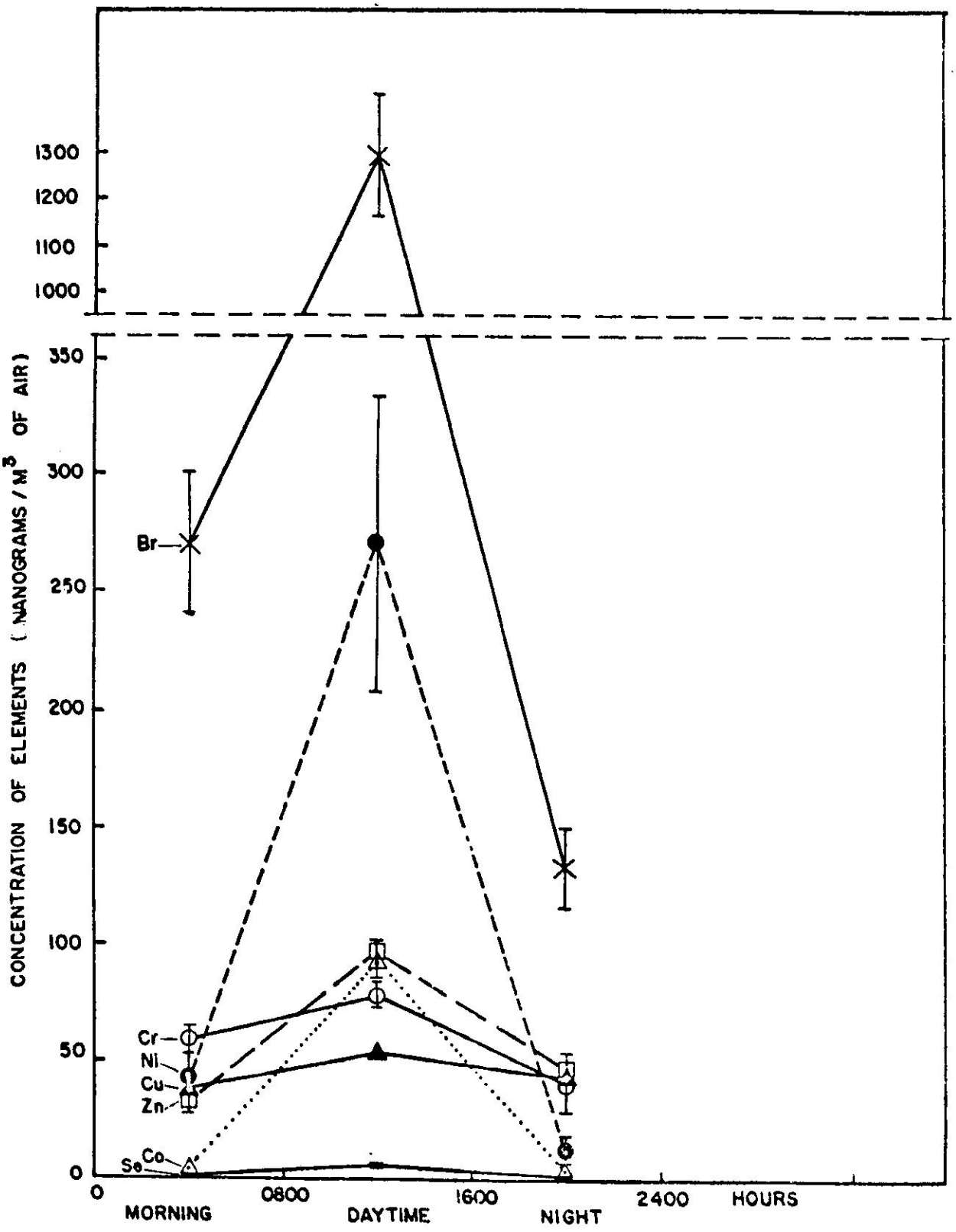
The multielement ratios in different brands of gasoline should be obtained and fuel oils used in power plants analyzed by the INAA technique for Br and other trace metals to ascertain the origin of pollution. The aerosol samples collected during the sugar cane burning season should also be analyzed for trace elements to appraise the extent of pollution from metal compounds contained in herbicide residues released during the combustion process.

Instrumental Neutron Activation Analysis (INAA)

It has been shown in this preliminary study and elsewhere (Salmon and Creevy 1971, Dams et al. 1970, Hoffman et al. 1969, and Pillay and Thomas 1969) that the INAA technique is potentially useful for the study of atmospheric pollution. With the INAA method one can determine simultaneously the concentrations of up to 33 elements with high precision and sensitivity without destroying the sample. After the INAA process has been completed, the same samples can be used to confirm results or to measure additional elements by other techniques. Determination of many elements simultaneously also enables one to look for correlations among elements that are largely emitted from a common source of pollution. The INAA technique can be used to determine the concentrations of most elements in suspected sources of pollution. The main advantage of the INAA method is the security against contamination or loss of material.

The INAA method is fast and convenient. For elements having highly active, short-lived irradiation products (Al, Br, V, and Mn), the time from receipt of sample until the concentrations are available can be under one hour. With high volume pumps mounted on mobile collecting units (a truck and/or small aircraft),

FIGURE 5. Variations within a day* of elemental concentrations in the atmospheric aerosols of San German, Puerto Rico



* Time period: 10-23 November 1972

sample collection time could be reduced considerably and the most serious contributors to a pollution crisis could be discovered with some additional groundwork. Such a system would enable public health and environmental agencies to issue warnings about developing air pollution emergencies.

Most of the steps in the INAA technique can be automated and assisted by a computer (Fite et al. 1961). With computer analysis for species emitting intense gamma rays, very little manpower per sample would be required. Without a computer, a trained technician could manually calculate the results from a short irradiation (three samples and one standard) in about one hour. The manual computations for the elements observed in a long run would take about two hours per sample.

The PRNC nuclear reactor has been modified to provide several irradiation sites with higher thermal neutron fluxes (10^{13} neutrons/cm^{-2}/sec^{-1}) and fast neutron fluxes. Better fluxes of neutrons, increased time of irradiation (up to eight hours), and increased sample size (up to 15 m^3 of air sampled during 24 hours) would greatly improve the sensitivity and precision of the INAA method in future experiments.

Important pollutant metals like cadmium, lead, boron (as hydrides), and platinum (as ammonium chloroplatinate dust) cannot be measured by the INAA technique. Excellent facilities for atomic absorption spectrophotometry exist at PRNC, and the technique and methodology are being developed by Muñoz-Ribadeneira to determine Pb, Cd, Cu, and Zn by this method.

The INAA and atomic absorption and emission spectrophotometry methods will not yield any information about the molecular form of air pollutants, e.g., the important organic constituents and the various compounds of sulphur and nitrogen. Therefore, these methods must be considered complements to other techniques in current use for general air pollution studies since INAA and AAS can detect only elemental concentration data. However, the INAA method can and will contribute substantially to our understanding and control of air pollution in Puerto Rico.

PART I

REFERENCES

Brar, S.S., D.M. Nelson, D.M. Kanabraocki, et al., 1969. In Modern Trends in Activation Analysis (J.R. DeVoe, ed.). National Bureau of Standards, Washington, D.C.

Christian, G.D., 1969. Anal. Chem. 41: 24A.

Covell, D.F., 1959. Anal. Chem. 31: 1785.

Dams, R. et al., 1970. Nondestructive neutron activation analysis of air pollution particulates. Anal. Chem. 42: 861-867.

Dams, R. et al., 1971. Nondestructive multielement neutron activation analysis of air pollution particulates. In Nuclear Methods in Environmental Research. Proc. Am. Nucl. Soc. Top. Meeting, August 23-24. University of Missouri.

Dudey, N.D. et al., 1969. In Modern Trends in Activation Analysis (J.R. DeVoe, ed.). National Bureau of Standards, Washington, D.C.

Elkins, H.B., 1959. The Chemistry of Industrial Toxicology, 2nd ed. John Wiley and Sons, New York.

Fite, L.E., D. Gibbons, and R.E. Wainerdi, 1961. Texas Engineering Experiment Station Report No. TEES-2671-1.

Friedlander, G., J.W. Kennedy, and J.M. Willer, 1964. Nuclear and Radiochemistry, 2nd ed. John Wiley and Sons, New York.

Gijbels, R., J.C. Dran, H. Erten, W. Zoller, J. Fasching, and G. Gordon, 1968. In Chemistry progress report, MIT 905-133. MIT Laboratory for Nuclear Science.

Gordon, G.E., 1971. Trace elements in the urban atmosphere. Proc. Am. Nucl. Soc. Top. Meeting, August 23-24. University of Missouri.

Gordon, G.E. et al., 1968. Geochim. Cosmochim. Acta 32: 369.

Hamilton, A., 1934. Industrial Toxicology. Hoeber, New York.

Hoffman, G.L., R.A. Duce, and W.H. Zoller, 1969. Environ. Sci. Technol. 3: 1207.

Junge, C.E., 1963. Chapters 2 and 5. Air Chemistry and Radioactivity. Academic Press, New York.

Lederer, C.M., J.M. Hollander, and I. Perlman, 1967. Table of Isotopes, 6th ed. John Wiley and Sons, New York.

Lee, D.H.K., 1972. Metallic Contaminants and Human Health. Academic Press, New York.

Lowman, F.G., 1973. Personal communication to Tin Mo. Puerto Rico Nuclear Center, Mayaguez.

Mo, T., 1971. Uranium concentrations in marine sediments. Ph. D. dissertation, Texas A and M University.

Muñoz-Ribadeneira, F.J., 1973. Personal communication to Tin Mo. Puerto Rico Nuclear Center, Mayaguez.

Pillay, K.K.S., and C.C. Thomas, Jr., 1969. Report No. WNY-046. Western New York Nuclear Research Center, Buffalo.

Puerto Rico Nuclear Center, 1971. Aguirre Power Project Environmental Studies Annual Report 1971, PRNC-153.

Ríos, O.P., 1973. Personal communication to Tin Mo. Puerto Rico Nuclear Center, Mayaguez.

Salmon, L. and M.G. Creevy, 1971. In Nuclear Techniques in Environmental Pollution. IAEA, Vienna.

Tuttle, R.F., 1971. Neutron activation analysis of trace elements in airborne particulates. In Nuclear Techniques in Environmental Pollution. IAEA, Vienna.

Wedepohl, K.H., 1971. Geochemistry. Holt, Rinehart, and Winston, New York.

West, F.K. and P.W. West, 1966. Anal. Chem. 38: 1566.

West, P.W., 1968. Chapter 19. In Air Pollution, Vol. II, 2nd ed. (A.C. Stern, ed.). Academic Press, New York.

Winchester, J.W., W.H. Zoller, R.A. Duce, and C.S. Benson, 1967. Atmos. Environ. 1: 105.

PART II

SUMMARY REPORT

APPLICATIONS OF ATOMIC ABSORPTION SPECTROPHOTOMETRY FOR THE ANALYSIS OF TOXIC METAL CONCENTRATIONS IN THE ATMOSPHERE OF THE SOUTH AND WEST COASTS OF PUERTO RICO

by

Fausto J. Muñoz-Ribadeneira

PART II

LIST OF TABLES

INTRODUCTION

During 1971 and 1972 air tape particulate samples were collected in different towns on the south and west coasts of Puerto Rico. The studies focused on the determination of concentrations of Cr, Mn, Co, Ni, Cu, Zn, and Pb by Atomic Absorption Spectrophotometry (AAS). This report summarizes the methodology developed for preparation of air filter paper tape samples for AAS and the inventory of metal concentrations in the aerosols retained by filter paper tapes at different sampling stations.

A review of the literature indicated that several elements in chloride form can be volatilized at high ashing temperatures (430 to 450°C) and that sulfatation can reduce this volatilization, increasing the recovery of metals. However, salts of these metals form more insoluble compounds with glass beakers under the influence of high ashing temperatures (HAT).

First Experiment

In order to test the results of these investigations, twenty replicate air tape samples (10 cm x 2.54 cm) were cut from a paper tape roll (Type W-41, Bendix Environmental Division) and placed in 100 ml Pyrex beakers which had been washed three times with hot HCl $2\bar{N}$, rinsed with de-ionized distilled water, and dried. Standards of the metals were added to the paper tapes with a certified micropipette. The concentrations of the standards were chosen to obtain an easily readable percent of absorption (>5%). The standards were in chloride form with lead as nitrate. The samples were then slowly dried under an infrared lamp.

Data from Table 1 show the low recoveries of the chlorides of Zn, Cd, Cu, and lead nitrate and indicate the tendency of these compounds to volatilize at the muffle temperatures used in these investigations. The value of wetting samples with H_2SO_4 prior to ashing is evident by the increased yield of metal, as shown in Table 1.

Under the influence of the heat treatment, more insoluble compounds were formed between the traces of the metals and the Pyrex glass of the beakers. In most cases, an increase in metal recuperation resulted from samples having been submitted to several washing-extractions by hot HCl. In order to inquire into the statistical meaning of this increase, Student's "t" test with equal number of degrees of freedom and different variance was carried out. It was hypothesized that if "t" theoretical distribution for 95% probabilities ($t_{0.05}$) was smaller than "t" calculated (t_c), the difference would be significant, and this favorable difference in metal recovery would be determined by the repetition of the hot HCl $2\bar{N}$ washing-extraction. Results indicate the value of repeating the HCl treatment of the calcination residue of the paper tape samples (Table 2).

Results obtained from samples submitted to the H_2SO_4 treatment showed even better metal recuperation. The substances formed by the treatment between the residues of the air tapes and the Pyrex beakers were more easily extracted by the hydrochloric acid (when the samples were in sulfate form) prior to the heat treatment in the muffle.

TABLE 1. Average percent of trace metal recovery from paper tape samples* after dry ashing at high temperatures

Element	Without H_2SO_4 Treatment		With H_2SO_4 Treatment	
	Washed once with HCl	Washed three times HCl	Washed once with HCl	Washed three times HCl
Chromium	95.2 ± 3.5 (3.68)	94.8 ± 2.8 (2.94)	96.2 ± 4.5 (4.68)	92.3 ± 5.5 (6.01)
Manganese	88.5 ± 10.2 (11.60)	98.5 ± 1.0 (1.13)	97.6 ± 1.5 (1.54)	94.1 ± 1.8 (1.91)
Cobalt	80.0 ± 13.2 (16.25)	93.6 ± 3.8 (4.07)	98.8 ± 0.3 (0.30)	95.8 ± 2.0 (2.15)
Nickel	37.1 ± 6.7 (18.01)	71.7 ± 18.9 (26.19)	88.9 ± 1.6 (1.82)	94.9 ± 3.0 (3.16)
Copper	63.4 ± 15.0 (23.72)	89.6 ± 6.2 (7.15)	94.3 ± 4.0 (4.26)	97.7 ± 0.5 (0.52)
Zinc	32.1 ± 6.4 (20.02)	57.6 ± 12.5 (21.72)	57.3 ± 22.7 (39.70)	82.2 ± 14.4 (17.5)
Cadmium	16.3 ± 3.0 (18.85)	26.2 ± 14.5 (55.46)	80.6 ± 5.3 (6.61)	89.0 ± 3.9 (4.32)
Lead	37.1 ± 6.7 (18.01)	31.7 ± 8.9 (35.53)	100.0 -	100.0 -
Total Averages	56.2 ± 17.2 (30.67)	70.4 ± 28.2 (40.08)	89.2 ± 15.4 (17.27)	93.2 ± 6.2 (6.65)

* Average of five replications
\+ Standard deviation from mean
( ) Standard deviation from mean percent

TABLE 2. Statistical analysis of effect of extracting calcination residues of air filter paper tape samples by hot HCL $2\bar{N}$ and comparison of results between single and triple extraction by HCl $2\bar{N}$.

Element	Samples without H_2SO_4		Samples with H_2SO_4	
	t_c	Statistical significance	t_c	Statistical significance
Cr	0.019	None	1.207	None
Mn	2.182	Yes	6.682	Yes*
Co	3.110	Yes	9.279	Yes*
Ni	3.859	Yes	7.906	Yes
Cu	3.609	Yes	3.771	Yes
Zn	4.561	Yes	4.144	Yes
Cd	1.577	None	5.709	Yes
Pb	1.085	None	-----	----

"t" (Student) distribution function at 95% probability and 8 degrees of freedom = 2.306.

* Favorable to samples washed only once with hot HCl $2\bar{N}$

Other Experiments

Other experiments were designed with these conditions:

a) 95% recovery of the metals would be acceptable;

b) 5% standard deviation from the mean would be considered reasonable;

c) hydrogen peroxide should be used instead of perchloric acid, and Pyrex beakers should be used rather than Teflon beakers and/or platinum crucibles;

d) acid inventory should be kept as low as possible; and

e) organic matter should not be present in the metal solution to avoid enhancement of the signal in the spectrophotometric detector.

It was agreed that the acid inventory could be reduced if the air tape samples were burned with alcohol prior to their acid dissolution. Table 3 shows the variables taken into account in the design of the experiments for this new phase of the investigation.

TABLE 3. Experimental design to test effects of different variables used in chemical preparation of air tape samples*

Experiment Code	Variables			
	Alcohol Burning	Chemical Treatment(1)	Muffle Heating	Chemical Treatment(2)
P	**	**	**	**
Q	**	**	0	**
R	0	**	0	**
T	0	**	**	**

* Five replications for each code set of samples
** Presence of Variable
0 Absence of Variable

Notes to Table 3

1. Alcohol burning. After the addition of the standards, the samples were dried as in previous experiments, wetted with 2 ml of alcohol of spectroscopic quality, and burned.

2. Chemical Treatment(1). To each of the samples, 6 ml of inverse aqua regia (3HNO_3-1HCl) was added. The beakers were covered with watch glasses 7 cm in diameter and put on a hot plate for slow boiling. The watch glass permits some reflux of the acids, so the reaction may last until the paper tape dissolves. The samples were then boiled rapidly, and the evaporation was continued almost to dryness. Then 4 ml of concentrated HNO_3 and 1 cm^3 drop of H_2O_2 (30% per volume) were added. The samples were again boiled, first slowly and then at higher temperatures. When the samples were almost dried, 3 drops of concentrated H_2SO_4 was added to test the presence of organic matter, found to be negligible or nonexistent. Samples were then evaporated up to complete disappearance of SO_3 fumes. Samples Code P and T were submitted to the heat treatment in the muffle oven following these procedures.

3. Chemical Treatment(2). The residues from the calcination and other chemical treatments were extracted three times with hot HCl 2$\bar{N}$. The results obtained in these experiments are presented in Table 4.

TABLE 4. Average percent metal recovery from filter paper tape samples submitted to different chemical treatments

Elements	Variables involved as indicated in Table 2 P	Q	R	T
Chromium	87.5	94.0	99.1	90.0
σ	10.3	5.5	0.6	7.8
σ %	11.43	5.85	0.60	8.67
Manganese	90.2	91.9	97.5	96.2
σ	6.4	4.6	2.3	4.1
σ %	7.09	5.04	2.35	4.26
Cobalt	91.5	98.7	98.0	94.5
σ	6.0	1.0	1.6	4.3
σ %	6.55	1.01	1.63	4.55
Nickel	81.7	87.5	98.0	92.4
σ	7.9	6.7	0.8	4.7
σ %	9.67	7.66	0.82	5.08
Copper	82.9	90.0	95.5	97.6
σ	10.5	6.0	2.3	1.8
σ %	12.66	6.67	2.41	1.84
Zinc	46.0	57.0	96.5	90.4
σ	8.4	8.7	2.0	5.9
σ %	18.26	16.26	2.07	6.52
Cadmium	36.5	35.0	94.5	88.6
σ	3.0	5.7	3.8	6.0
σ %	8.21	16.28	4.02	6.77
Lead	55.0	63.0	100.0	100.0
σ	10.1	8.5	------	------
σ %	18.15	13.49	------	------
Total Average	71.5	77.0	97.1	93.7
σ	22.8	22.7	1.8	4.0
σ %	32.09	29.48	1.90	4.26

In order to evaluate the results obtained from samples submitted to different chemical treatments, Student's "t" test was applied to data from Table 4. The summary of these calculations is presented in Table 5 and includes the comparison of data obtained by different chemical treatments for each one of the elements under study.

TABLE 5. Statistical analysis on data obtained by atomic absorption spectrophotometry from samples submitted to different chemical treatments

Elements	PQ	PR	PT	QR	QT	RT
Cr	1.244(N)	2.517(Y)	0.432(N)	2.061(N)	0.937(N)	2.601(Y)
Mn	0.255(N)	2.326(Y)	1.765(N)	3.044(Y)	1.850(N)	0.703(N)
Co	2.647(Y)	2.701(Y)	0.908(N)	0.829(N)	2.127(N)	1.705(N)
Ni	1.252(N)	4.590(Y)	2.603(Y)	1.822(N)	1.338(N)	2.626(Y)
Cu	1.312(N)	2.621(Y)	3.086(Y)	1.914(N)	2.713(Y)	1.608(N)
Zn	2.034(N)	13.078(Y)	9.672(Y)	9.895(Y)	7.105(Y)	2.189(N) (90%)
Cd	0.411(N)	26.789(Y)	17.434(Y)	19.423(Y)	14.402(Y)	2.613(Y)
Pb	1.363(N)	(Y)*	(Y)*	(Y)*	(Y)*	(N)

"t" Student Distribution Function at P (0.05) and 8 degrees of freedom = 2.306

(N) No statistical significance
(Y) Statistical significance at P (0.05) confidence level
* The difference is so large that it is accepted as significant.

Samples submitted to treatments P and Q show the lowest percent of metal recovery, but Table 5 indicates no statistical difference between their results. Both sets of samples were submitted to alcohol burning prior to other treatments. The statistical comparison between P and T is significantly favorable for T for Ni, Cu, Zn, Cd, and Pb (Table 5). These sets of samples were submitted both to the H_2SO_4 treatment and later to the effects of heating at high temperatures in the muffle, but T did not receive alcohol burning. As observed in Table 4, there was a significant statistical difference in the results, especially for the more easily volatilized elements. Their low recovery could be attributed to the high temperatures associated with flaming in alcohol burning.

For all the elements studied there were significant favorable statistics for samples R compared to samples P (Table 5). Samples R received the aqua regia-HNO_3 - H_2O_2 treatment (ANH) and were not submitted to alcohol burning or the muffle.

The statistical comparison of data between Q and R and Q and T also indicates significant differences in favor of samples R and T in chemical elements that could be more easily volatilized at high temperatures. Samples R and T were not submitted to alcohol burning and the negative effects of flaming.

Table 4 shows that metal recovery from samples submitted to the ANH method was higher than from those submitted to the H_2SO_4 muffle heating. Also, the overall percent of metal recovery was higher and the variations in the data were smaller. If the same statistical analysis is applied to the data from samples R and T, the differences between them are statistically significant at P (0.05); (t_c = 2.953). In data from Table 5 these differences are statistically significant

for Ni, Cd, and Cr, because Ni and Cd were volatilized by muffle treatment and Cr, under heat effects, was retained in the Pyrex beaker and extracted with more difficulty by HCl 2N. Recovery is improved when samples are submitted to wet ashing compared to ashing at high temperatures, even when samples first receive the H_2SO_4 treatment.

Application of Chemical Treatments to Natural Aerosol Samples

The two most successful chemical treatments, sulfatation of the samples coupled with HAT and the wet digestion of samples by the ANH method, were used to determine toxic metal concentrations from air tape samples obtained at Mayaguez, Puerto Rico. These investigations will be reported later in 1975 (Muñoz-Ribadeneira, F.J., 1975. Preparation of air filter paper tape samples for multielement analysis by atomic absorption spectrophotometry, in preparation.)

PART III

PRELIMINARY SURVEY OF THE CONCENTRATIONS OF TRACE METALS IN THE ATMOSPHERE OF EIGHT SELECTED SITES IN SOUTHWESTERN PUERTO RICO

by

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PART III

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Barnett, W.B., 1972. Acid interferences in atomic absorption spectrophotometry. Anal. Chem. 44(4): 695.

Beyer, M., 1969. Preparation of metallic air pollutants for atmospheric absorption analysis. Atom. Abs. News. 8(1): 23.

Kometani, T.Y., 1966. Effect of temperature of volatilization of alkali salts during dry ashing of tetrafluoroethylene fluorocarbon resin. Anal. Chem. 38(11): 1597.

Kometani, T.Y. and J.L. Bove, 1972. Dry ashing particulate matter on paper and glass filters for trace metal analysis by AAS. Env. Sc. Techn. 6(7): 617.

Lee, D.H.K., 1972. Metallic Contaminants and Human Health. Academic Press, New York.

Romo, L.A., 1964. Métodos de Investigacion Cientifica. Editorial "Tip Cat Casals", Barcelona.

Thompson, R.J., G.B. Morgan, and L.J. Purdue, 1970. Analysis of selected elements in atmospheric particulate matter by atomic absorption. Atom. Abs. News. 9(3): 53.

U.S. Dept. of Health, Education and Welfare, 1969. Air Quality Criteria for Particulate Matter. Publ. No. AP-49. Washington, D.C.

U.S. Environmental Protection Agency, 1971. A Mathematical Model for Relating Air Quality Measurements to Air Quality Standards. Publ. No. EPA 49-89.

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