

CYCLOTRON ANALYSIS OF AUSTRALIAN ATMOSPHERIC

CONTAMINATION BEFORE AND AFTER THE 1974

FRENCH NUCLEAR TESTS IN THE PACIFIC \*

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Abstract

Atmospheric particulates collected, around East Coast Australian cities and Port Moresby, just before and after the French Atomic Test Series of 1974 in the Pacific have been analysed by proton activation using the Melbourne University Cyclotron. A number of elements, namely S, Ca, Ti, Cr, Fe, Ni, Cu, Zn, Se and Hg, ranging in concentrations from .001  $\mu\text{g}/\text{m}^3$  to up to 3.27  $\mu\text{g}/\text{m}^3$  have been detected. The changes observed in the concentrations of these elements in the two sets of samples, taken just before and just after the Atomic Tests, are attributed to Synoptic rather than Nuclear Fall-Out effects.

Introduction

In the event of any possible fall-out from nuclear tests not only would the radioactive contamination in the atmosphere increase but also the concentrations of various stable isotopes would change. Therefore, an analysis of the elemental composition of the atmospheric particulates taken from an area just before and after nuclear tests should give some indication about the extent of fall-out in that particular region.

France carried out an extensive series of nuclear tests in the Pacific between June and September, 1974. It was widely feared that some of the nuclear fall-out would reach Australia and New Guinea, especially the East Coast cities.

The Commonwealth Scientific and Industrial Research Organization (C.S.I.R.O.) has a number of continuously operating high volume air samplers, collecting particulates in polystyrene filters, stationed in various locations in and around Australia for atmospheric research. Therefore, it was decided to analyse the aerosol particulates collected by these samplers in the time period just before and after the French tests in order to investigate the extent and nature of any fall-out.

Conventional analytical techniques such as gravimetry, colorimetry, emission spectroscopy and atomic absorption spectrophotometry can usually supply the required sensitivity for medium atomic weight elements but they are quite time consuming and are destructive in that the sample must be dissolved, which is not always convenient, especially for these historical samples. The wet chemical preparations can also lead to additional sources of error from the reagents used. These techniques may also suffer from incomplete recovery of the elements from the solution. So a non-destructive method of analysis with adequate sensitivity was needed in this case.

Chaudhri and Batra<sup>1</sup> have shown that sensitivities of up to ppb levels are obtainable through thick target activation analysis using charged particles. With the Melbourne University Cyclotron, we have shown that proton activation analysis is capable of being applied to a vast range of matrices for elemental determination in the sub ppm region. Recently, Debrun and Barrandon<sup>2</sup> have also published detection limits ranging from few tens of ppm to up to 1 ppb for a number of elements between  $Z = 3$  to  $Z = 82$  through activation analysis by 10 MeV protons. We applied thick-target proton activation to analyse non-destructively the polystyrene filters containing atmospheric matter, using the Melbourne University Cyclotron.

Experimental Procedure

The particulate samples were collected from various cities along the eastern coast of Australia as well as in New Guinea by the C.S.I.R.O. Division of Atmospheric Physics. These cities were Port Moresby, Townsville, Brisbane, Sydney, Melbourne and Hobart. In each case, approximately 5000 cubic metres of air was pumped through a 0.2 micron polystyrene filter in a high volume sampler for one week during June, 1974 (just before the French tests - Set A). Another was obtained in a similar way during September, 1974 (after the French tests - Set B). This allowed any possible difference in the elemental/isotopic composition due to the fall-out to be determined.

Sample preparation involved cutting a 1 cm square piece from each filter, originally about 15 cm square, placing it in a recessed groove in the aluminium target holder and covering it with a thin piece of aluminium foil. Great care had to be taken with the samples so as not to introduce any contaminants. Handling was done using various instruments that were thoroughly cleaned and rinsed in multiply distilled water. The aluminium foil was in turn held down with a brass bracket.

A standard was prepared by placing a blank piece of filter paper of known dimensions into a solution containing compounds of the elements of interest dissolved in multiply distilled water. The compounds used were  $\text{CaCO}_3$ ,  $\text{TiO}_2$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{ZnO}$ ,  $\text{SeO}_2$ ,  $\text{ZrNO}_3$ ,  $\text{HgCl}_2$ ,  $\text{SrO}$ ,  $\text{Sc}_2\text{O}_3$ ,  $\text{As}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{PbF}_2$  and  $\text{V}_2\text{O}_5$ . The filter was then allowed to dry in free air and irradiated under the same conditions as the other samples. A number of blank filters were also used to determine their elemental contributions.

Each sample was irradiated with 8.5 MeV protons for 1 hour at a current of 1  $\mu\text{A}$ . During each run, the target assembly was cooled with liquid nitrogen, the volume contained in the target arm being more than adequate for the 1 hour. Each filter appeared intact at the end of the irradiation period with no evidence of scorching. After a waiting period of 1 hour, each sample was counted with the Ge(Li) detector and PDP-9 computer system. This delay was necessary in order to reduce the high count rates due to the induced short lived, mainly positron, activities.

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Analysis

The analysis of the spectra was performed with a semi-automatic program developed by us for use on a Digital PDP-9 computer in 16K configuration. The 4096 channels of data are firstly smoothed by a third order convolution process acting on groups of 5 channels. Next, the peaks are located, their exact energies found from a fitting function, and their areas calculated. A printout is obtained giving all the required parameters.

At the proton energies of interest here, the (p,n) reaction is the dominant one with usually insignificant contributions from (p,2n) and (p,d) reactions<sup>3</sup>. Quantitative analysis was based on the thick target theory of Ricci and Hahn<sup>4</sup>. This states that under the same experimental conditions, the concentration of the elements in the sample and standard are related by

$$\frac{Y}{Y_s} = \frac{C}{C_s} \cdot \frac{Q}{Q_s} \cdot \frac{R}{R_s} \quad (1)$$

where Y is the yield of gamma rays from the activation of the element considered, C is the concentration of that element in any convenient unit, Q is the integrated charge and R is the range of the protons in the target. Values appropriate to the standard have the subscript s. For the equation to be valid, the matrices of both the sample and standard should be similar, that is, have similar densities and average atomic weights. Moreover, the element to be determined must of course be homogeneously distributed. Both these conditions were met in our experiments.

The composition of the polystyrene filter material has been determined to be 7.5% H, 88% C, 2.5% O and 0.3%N.<sup>5</sup> From this, the range of the protons in the filter can be calculated from the Bragg Additivity Rule which has only a small error at the energies of interest here<sup>6</sup>.

For convenience, Equation 1 can be rewritten in the form

$$\frac{Y}{Y_s} = \frac{C'}{C'_s} \cdot \frac{m}{m_s} \cdot \frac{A_s}{A} \cdot \frac{Q}{Q_s} \cdot \frac{R}{R_s} \quad (2)$$

where C' is the concentration (e.g. ppm) of element Z in the particulate mass, C'<sub>s</sub> is the concentration of element Z in the standard compound, m is the mass of the particulate on the filter, m<sub>s</sub> is the total mass of the infused standard compound, A<sub>s</sub> is the effective mass area of the filter, that is, the area exposed to the particulates and A is the area of the standard filter.

Results and Discussion

A gamma spectrum of an irradiated filter is shown in Figure 1. The nuclides which, after activation, give rise to various gamma peaks in the spectrum have been identified and labelled accordingly. From the areas of the gamma peaks in the spectrum, the concentrations of various elements can be calculated using Equation 2.

The elemental concentrations of the air samples from various locations in the two sets are shown in Table 1. The elemental contributions of the blank filters was more than an order of magnitude smaller than

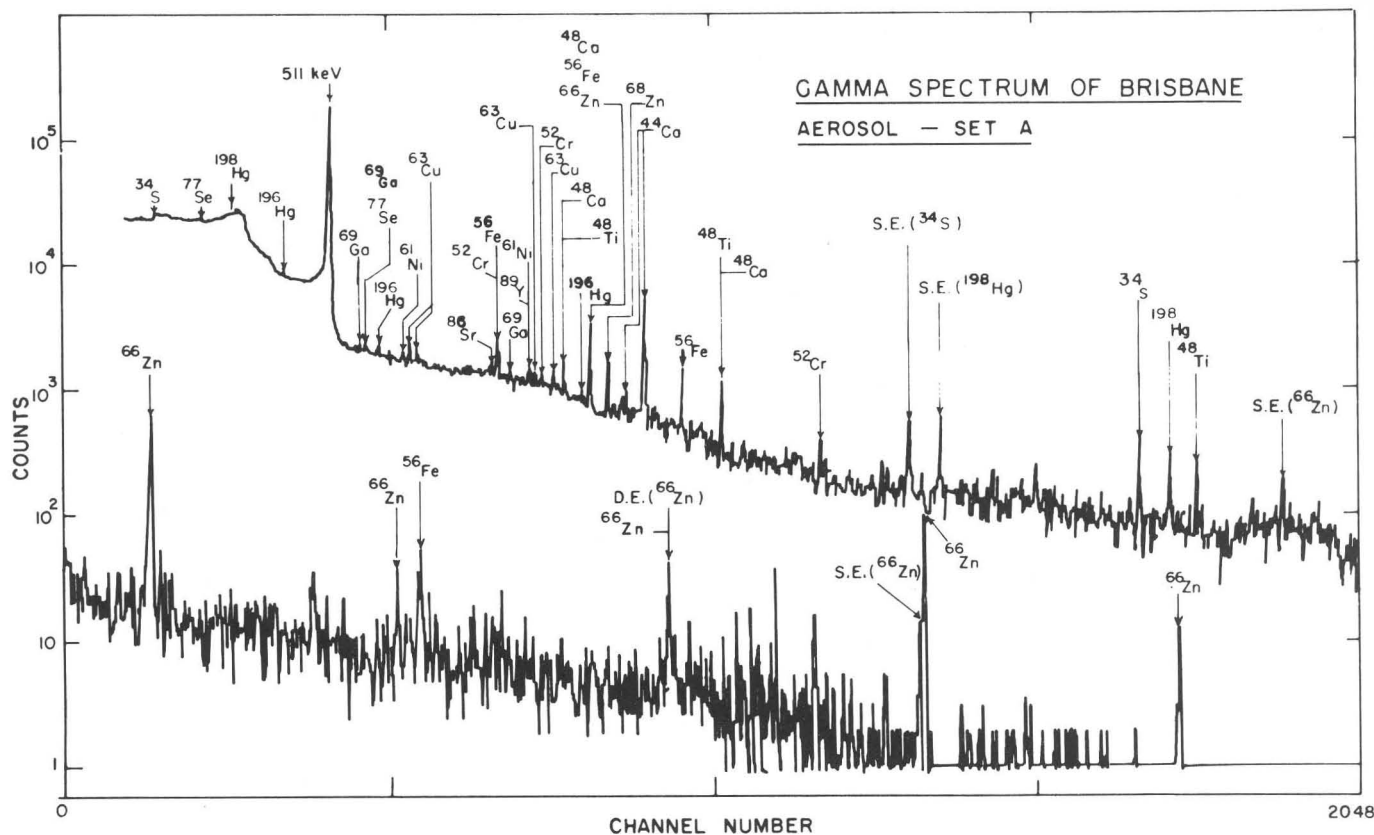


Fig. 1: Gamma spectrum of the activities induced by 8.5 MeV protons in the filter containing Brisbane air particulates. The lower curve is the continuation of the upper curve.

TABLE I

Results of the analysis of atmospheric particulates. Concentrations are in $\mu\text{g}/\text{m}^3$ of air <sup>b</sup> .											
City	TSP <sup>a</sup>	S	Ca	Ti	Cr	Fe	Ni	Cu	Zn	Se	Hg
Port Moresby	23.9	0.002	0.10	0.05	<0.003	0.29	<0.004	0.008	0.001	0.002	0.06
	34.7	0.01	0.19	0.06	0.002	0.39	0.02	0.13	0.03	0.002	0.02
Townsville	51.7	0.004	0.31	0.18	0.04	1.92	0.02	0.29	0.16	0.05	<0.15
	41.3	0.06	0.42	0.27	0.02	2.21	0.15	0.41	0.13	0.03	<0.001
Brisbane	25.7	0.07	0.73	0.41	0.12	1.46	0.09	0.41	0.25	0.18	0.35
	51.4	0.15	2.00	0.63	0.11	3.26	0.16	0.53	0.41	<0.12	<0.01
Sydney	22.9	0.05	0.12	0.06	0.03	1.04	0.07	0.24	0.11	0.05	0.06
	39.7	0.06	0.47	0.33	0.05	2.80	0.10	0.40	0.22	<0.11	0.27
Melbourne	50.5	0.13	1.62	1.18	0.05	3.27	0.13	0.79	0.44	0.04	0.36
	31.8	0.05	0.97	0.81	0.05	2.43	0.12	0.39	0.29	0.11	0.30
Hobart	42.0	0.05	0.84	0.28	<0.008	0.48	0.58	0.26	0.25	0.07	0.05
	26.5	0.02	0.17	0.22	<0.003	0.31	0.04	0.04	0.08	0.01	0.08

(a) Total Suspended Particulates (b) All errors are typically < 10%

those in the samples. Nevertheless, it was still taken into consideration when calculating the values given in the Table.

The first line of each city are the results for the first set of samples (Set A) while the second line are the results for the second set (Set B). The total particulate concentrations are generally below those of North America and Europe which are in the range 50-200  $\mu\text{g}/\text{m}^3$ .<sup>7,8</sup> Despite this, levels of Ni and Cr are generally similar while Cu, Fe, Ti, Se and Hg are higher. During the three month period between the taking of Sets A and B, the elemental concentrations at Port Moresby, Townsville, Brisbane and Sydney, the four cities to the North, generally increased whilst those at Melbourne and Hobart both decreased. This, however, is not regarded as coming from the fall-out but suggests major synoptic effects such as prevailing southerly winds or a series of strong low pressure regions with their centres located between Sydney and Melbourne. This would have the tendency to blow inland dust into the four Northern cities, and ocean air over the two Southern ones. Goodman et al<sup>9</sup>, using the atomic absorption method, found an unusually high level of Ni (0.85  $\mu\text{g}/\text{m}^3$ ) in the atmospheric particulates collected over Hobart at the beginning of July, 1974. This striking rise is also present in our results of Set A (0.58  $\mu\text{g}/\text{m}^3$ ) taken at the end of June, 1974, indicating a good agreement.

To investigate possible common sources of elements, linear correlation coefficients were computed between all possible pairs of elements as follows:

$$r_{xy} = \frac{\overline{xy} - \bar{x}\bar{y}}{\{(\bar{x}^2) - (\bar{x})^2\}^{1/2} \{(\bar{y}^2) - (\bar{y})^2\}^{1/2}}$$

where x and y represent the concentrations of any two elements to be correlated. The most significant correlations are listed in Table 2.

These figures were studied further by drawing clusters showing elements which are highly correlated, and their form was based on the "Domain Sampling Theory" of Tyron<sup>10</sup> originally intended for psycho-

logical studies. The cluster for Set A showed that most elements correlated well except for Ni which does not correlate with any element, suggesting that it is a possible pollutant. The cluster for Set B showed that all elements correlated well except for Hg, suggesting that this is also a possible pollutant.<sup>11</sup>

TABLE II

Linear Correlation Coefficients					
SET A			SET B		
x	y	r <sub>xy</sub>	x	y	r <sub>xy</sub>
Zn	Ca	0.97	Cu	Fe	0.98
Ca	Ti	0.96	Zn	Cr	0.97
Cu	Zn	0.95	Ca	Cr	0.96
Cu	Ti	0.95	S	Cr	0.95
Cu	Fe	0.92	Zn	Ca	0.94
Zn	Ti	0.92	S	Ca	0.93
S	Cu	0.91	Ni	Cu	0.93
Cu	Ca	0.90	Se	Zn	0.92
S	Zn	0.89	Se	Fe	0.90
S	Ca	0.89	Ni	Fe	0.90
S	Ti	0.89	S	Zn	0.89
Se	Cr	0.87	Fe	Zn	0.88
Fe	Ti	0.85	Se	Cr	0.88
Hg	Cu	0.82	Zn	Ti	0.87
Hg	Cr	0.81			

The absolute concentrations of various elements observed, and their variations between the two Sets, suggest that the atmospheric composition around east coast Australian cities was not noticeably affected by the French Atomic Test Series of 1974, in the Pacific. However, there may well be some other elements present which could not be detected in the present experiment,

and whose concentrations might have been influenced by the Tests.

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\*\* DISCUSSION \*\*

W. SCHULTE: You give an error of 10%. Is that the error of one measurement, or is that because you took a number of different samples in the same area at different times and calculated the error from that?

M. CHAUDHRI: This 10% is the total error, comprised of the errors (1) due to the statistics and background subtraction, (2) due to the non-uniformity of the particulate concentrations at different locations on the filter, (3) in the range-energy tables used. To obtain the absolute concentration of a particular element, we used a number of samples and also different locations on each filter for averaging.