

CYCLOTRON ANALYSIS OF AUSTRALIAN ATMOSPHERIC

CONTAMINATION BEFORE AND AFTER THE 1974

FRENCH NUCLEAR TESTS IN THE PACIFIC *

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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 Batra¹ 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 Barrandon² 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 CaCO_3 , TiO_2 , $\text{K}_2\text{Cr}_2\text{O}_7$, Fe_2O_3 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, ZnO , SeO_2 , ZrNO_3 , HgCl_2 , SrO , Sc_2O_3 , As_2O_3 , Sb_2O_3 , PbF_2 and V_2O_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 μA . 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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TABLE I

Results of the analysis of atmospheric particulates. Concentrations are in $\mu\text{g}/\text{m}^3$ of air ^b .											
City	TSP ^a	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 $\mu\text{g}/\text{m}^3$.^{7,8} 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 al⁹, 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 Tyron¹⁰ 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.¹¹

TABLE II

Linear Correlation Coefficients					
SET A			SET B		
x	y	r_{xy}	x	y	r_{xy}
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.

References

1. M. A. Chaudhri and G. J. Batra. Charged particle activation analysis with cyclotrons. Paper presented at the International Conference on the Uses of Cyclotrons in Chemistry, Metallurgy and Biology, Oxford, 1969.
2. J. L. Debrun and J. N. Barrandon. Activation Analysis with particles from a cyclotron: determination of trace oxygen in metals by He-3 activation, multi-elemental trace analysis by proton activation. Proc. 7th Int. Conf. on Cyclotrons and their Applications (Birkhaeuser, Basel, 1975). P. 507-510.
3. N. B. Gove and A. W. Wapstra. Nuclear reaction Q-values. Nucl. Data Tables 11, 127-280 (1972).
4. E. Ricci and R. L. Hahn. Theory and experiment in rapid, sensitive He-3 activation analysis. Anal. Chem. 37, 742-748 (1965).
5. Australian Microanalytical Service, C.S.I.R.O. Analysis Report - Ref. No. 490.
6. L. C. Northcliffe and R. F. Schilling. Range and stopping-power values for heavy ions. Nucl. Data Tables A7, 233-463. (1970).
7. U.S. Department of Health, Education and Welfare, NAPCA Report No. AP-49, P.12 (1969).
8. C.E. Junge. Air Chemistry and Radioactivity. Academic Press, New York and London, 1963, P.359.
9. H.S. Goodman, B. N. Noller, G. I. Pearman and H. Bloom. The heavy metal composition of atmospheric particulates in Hobart, Tasmania. Clean Air 10, 38 (1976).
10. R. C. Tyron and D. Bailey. Multivariate Behavioural Res., 1, 95 (1966).
11. M. M. Lee. Some applications of charged particle activation analysis. Thesis, University of Melbourne, 1977 (unpublished).

** 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.