

TRACE ELEMENT DETERMINATION IN AEROSOLS FROM THE ANTARCTIC PENINSULA BY NEUTRON ACTIVATION ANALYSIS

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(Received July 29, 1991)

The knowledge of the composition of atmospheric aerosols in remote areas, like the Antarctic Peninsula is of great importance for the study of long-range transport of atmospheric contaminants and also from the climatological point of view. Instrumental neutron activation analysis was applied in the present work to determine the elements Al, V, Mn, Na, Cl, Ca, Au, Br, Sb, Sc, Fe, Zn, K, Th and La in aerosol samples collected in the Brazilian Antarctic Station "Comandante Ferraz" (62° S, 58° W) located on King George Island in the Antarctic Peninsula. The sources of the aerosols were investigated by means of Enrichment Factors and Principal Factor Analysis. Both methods yielded similar results. Sea and soil were identified as the major sources of aerosols, in the samples collected at the Brazilian Station.

Introduction

Recently much interest has grown in the determination of the composition of atmospheric aerosols in remote areas, like the South Pole and the Antarctic Peninsula. This is due to the fact that this kind of knowledge is of great importance to the study of long-range transport of atmospheric contaminants and also from the climatological point of view.

Aerosols interact with solar radiation, absorbing and scattering light and also affect the micrometeorological processes, since they behave like water vapor condensation nuclei.¹ Atmospheric aerosols interfere not only in the energy balance, but also in the climate of the Earth.

The Antarctic Continent is one of the most remote regions on Earth. It is far from the main anthropogenic sources, so it is particularly adequate for the analysis of natural atmospheric aerosols.² A considerable extension of the Continent is constantly covered with ice, except for some coastal regions and also the nunataks (hill or mountain peaks situated over the glacial surfaces).

According to HIDY,³ in remote areas the total concentration of particulate matter varies between 0.5 to 30 $\mu\text{g}/\text{m}^3$. Since the elemental concentrations found in these areas are extremely low, very sensitive analytical methods have to be employed, such as neutron activation analysis, particle induced X-ray emission spectroscopy (PIXE), ion chromatography, atomic absorption or emission spectrophotometry.

Neutron activation analysis, which is the method employed in the present work, has been used by several authors for the multielemental analysis of aerosol samples from remote areas. In some cases, AANI was utilized in combination with other analytical techniques.

ZOLLÉR et al.⁴ determined 22 elements in suspended particulate matter collected at the Amundsen-Scott Station on the South Pole (90° S), 2800 m above sea level. The methods used were NAA and AAS and two sources were identified for these elements: oceanic and crustal.

BOUSTRON and LORIUS⁵ determined 12 elements in Antarctic ice by AAS. The enrichment found for the elements Pb, Cd, Cu, Zn and Ag was attributed by the authors to a volcanic process.

MAENHAUT and ZOLLER² quantified 36 elements by INAA in samples collected at the South Pole, showing that this method is very well suited for multielemental determinations in samples collected in remote areas. The highest concentrations were found for Na, Cl and S.

In a later work, MAENHAUT et al.⁶ discussed the possible sources responsible for the anomalous enrichment of certain elements. Sources like extraterrestrial dust and volcanism were suggested.

IWASHIMA et al.⁷ analyzed aerosols collected in the Japanese Syowa Station and determined arsenic contents by NAA followed by a radiochemical separation procedure.

KOIDE et al.⁸ measured seven elements (Na, Cl, Br, Mg, Cu, Al and K) by AANI and observed the predominance of the marine aerosol in the station.

In the summer 1983 – 1984 the Brazilian Antarctic Program, PROANTAR, was effectively started and the Brazilian Antarctic Station “Comandante Ferraz”, located on King George Island in the Antarctic Peninsula (62° S, 58° W). Figure 1 shows the map of the Southern Hemisphere, with the location of the Brazilian Station.

MOREIRA – NORDEMANN et al.⁹ examined rain water collected at the Station during the summers of 1985 to 1987, measuring the pH and determining the Na and Mg concentrations by AAS and also sulfate, nitrate and chloride by ion chromatography. The authors concluded that the origin of the ions is essentially marine.

ARTAXO et al.¹⁰ determined 21 trace elements by PIXE in aerosols collected at the Brazilian Station. The total concentration of the particulate was determined by gravimetry. The data obtained were analyzed by Absolute Principal Factor Analysis.

PEREIRA et al.¹¹ started in 1986 to collect systematically aerosol samples in the Brazilian Station in order to measure atmospheric radioactivity by alpha-spectrometry. Radon-222 is a natural atmospheric tracer and it is used for the study of long distance transport processes in the troposphere.¹¹⁻¹³

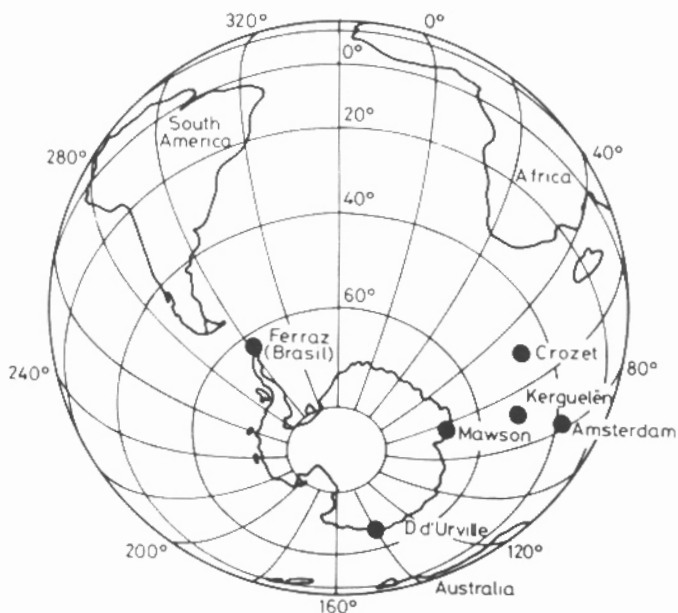


Fig. 1. Map of the Southern Hemisphere showing the localization of the Brazilian Station „Comandante Ferraz”

After the measurements by alpha-spectrometry, the samples were submitted to INAA, for determination of the elements Al, V, Mn, Na, Cl, Ca, Au, Br, Sb, Sc, Fe, Zn, K and La, in the present work. The data obtained were analyzed by means of calculating Enrichment Factors and by Principal Factor Analysis.

Experimental

Sample collection

The aerosol samples were collected in the years 1986 and 1987, in the Brazilian Antarctic Station “Comandante Ferraz”(62° 05' S, 58° 23,5' W).

The sampling site was carefully chosen so as to avoid any anthropogenic contribution coming from the Station itself. Only about 5% of the winds that strike the

Atmospheric Sciences Laboratory, where the collection was made, come from the direction where the core of the station is localized.

The aerosols were collected by means of filtration through a membrane filter Millipore-MF, type HA, with a diameter of 47 mm and a pore size of 0.47 μm . A membrane pump with a flow-rate monitor was used for filtration and each sampling cycle lasted one week. The flow rate was about 5 liters/min.

The nylon sampler containing the filter was placed over the Laboratory, at 6 m above the ground (30 m above sea level).

In order to avoid that rain or snow would also pass through the filters, the sampler was placed inside a PVC cover.

Instrumental neutron activation analysis

Multielemental standard preparation: since the multielemental comparator method of neutron activation analysis was utilized, special care was taken in preparation of standards.

First the stock solutions were prepared by dissolution of the p.a. or spectroscopically pure metals or compounds in bidistilled acids and further dilution in deionized and distilled water. Then convenient mixtures were prepared and aliquots of 50 to 100 μl of the synthetic standards were pipetted onto sheets of Whatman No. 42 filter paper of about 1.5 cm^2 area. The sheets were dried under an infrared lamp and inserted and sealed inside plastic envelopes, previously washed with p.a. ethyl alcohol.

Irradiations: each sample was irradiated twice, together with the convenient synthetic standards, under a thermal neutron flux of about $10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$.

The short irradiations of 5 minutes allowed determination of the elements Mn, V, Al, Na and Cl and the long irradiations of 24 hours allowed determination of Br, Au, K, La, Na, Ca, Sb, Sc, Fe, Zn and Th.

Gamma-ray spectrometric measurements: the irradiated aerosol samples and standards were measured using an ORTEC Ge(Li) detector, with a resolution of 2.7 keV at the 1332 keV peak of ^{60}Co . The detector was coupled to a 6240B ORTEC 4096-channel analyzer and associated electronics. Data reduction was carried out using a PDP 11/04 minicomputer and the GAMMA 2 routine of the GELIGAM ORTEC Program.

Cooling times varied from 3 to 100 minutes for the short irradiations and from 2 to 20 days in the long irradiations. Measurement times were from 3 to 30 minutes for the short irradiations and of 15 hours in the case of long irradiations.

Results and discussion

Before analyzing the aerosol samples, the precision and the accuracy were checked for the reference materials Bowen's Kale (IUPAC) and W-1 (USGS).

The relative standard deviations and relative errors obtained were generally lower than 5% for both of them.

Special attention was dedicated to the analysis of the blanks of the Millipore-MF type A filter utilized for aerosol collection. Corrections for blank were carried out for all of the elements analyzed. Chromium, for instance, was only detected in the blank and it was not determined in the aerosols.

Table 1 presents the average elemental concentrations, in ng/m^3 , obtained for the short irradiations of 5 minutes in which the elements Na, Al, Cl, V and Mn were quantified.

Table 2 presents the average elemental concentrations in ng/m^3 of the above elements according to the season of the year; winter-86, summer 86/87, winter 87. In Table 2 are also included the radon activities, in Bq/m^3 , determined by PEREIRA.¹³

Table 1
Average elemental concentrations, in ng/m^3 , of the elements analyzed with 5-minute irradiation

Element	Year of collection of filters			
	1986		1987	
	Range min - max	Average concentration	Range min - max	Average concentration
Na	227.9 - 2161.1 (38)*	1076.2 \pm 467.9	327.1 - 2991.3 (40)	1033.5 \pm 684.1
Al	12.07 - 49.10 (38)	24.86 \pm 8.20	3.02 - 29.21 (40)	10.08 \pm 5.42
Cl	410.6 - 4347.2 (38)	1969.6 \pm 875.2	597.1 - 5428.3 (40)	1912.4 \pm 1246.5
V	0.10 - 0.96 (36)	0.30 \pm 0.14	-	-
Mn	0.07 - 0.99 (36)	0.33 \pm 0.22	0.03 - 2.44 (40)	0.26 \pm 0.41

*Number of determinations is indicated in parentheses.

In Table 3 are presented the average concentrations of the elements K, Ca, Sc, Fe, Zn, Br, Sb, La, Au and Th, in ng/m^3 , obtained from the long irradiations of 24 hours.

It can be observed from Table 2 and Figure 2, mainly for the elements Na, Cl and Mn, that the concentrations found attained lower values in winter. This was already expected, since in winter the sea and soil are covered with snow or ice in the Antarctic Peninsula, causing a decrease in the input of aerosols in the atmosphere.

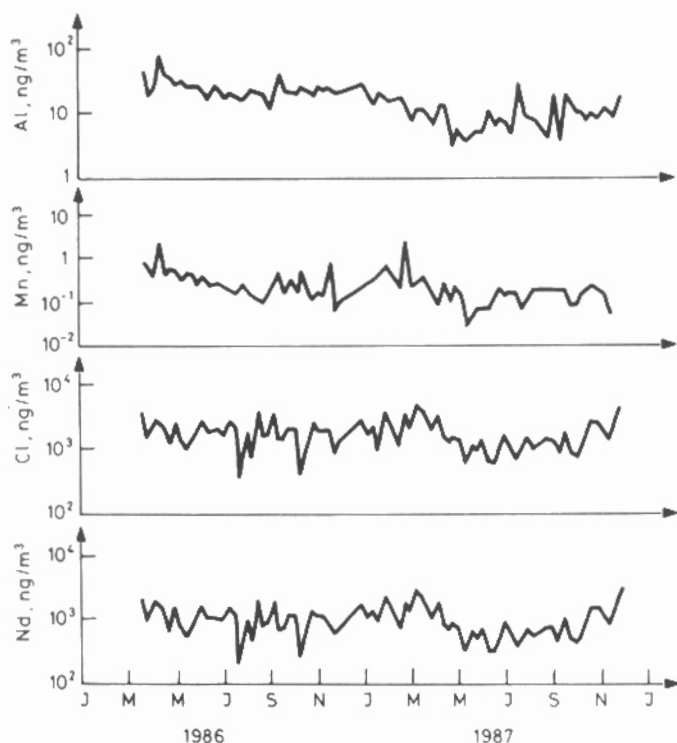


Fig. 2. Temporal variation of the concentration (ng/m^3) of the elements determined by means of 5-minute irradiations, in 1986 and 1987

Table 2
Average elemental concentrations, in ng/m^3 , of the elements determined by 5-minute irradiation according to the season

Element	Winter-86	Summer-86/87	Winter-87
Na ng/m^3	Range: 227.9 – 2161.1 (34) Average: 1082.9 \pm 470.9	711.1 – 2991.3 (9) 1726.9 \pm 725.8	327.1 – 2838.9 (33) 865.8 \pm 537.3
Al ng/m^3	Range: 12.07 – 49.1 (34) Average: 25.15 \pm 8.52	7.28 – 29.2 (9) 15.08 \pm 6.36	3.02 – 29.21 (33) 9.54 \pm 5.65
Cl ng/m^3	Range: 410.6 – 4347.3 (34) Average: 2001.4 \pm 882.4	1120.2 – 5428.3 (9) 3093.3 \pm 1388.4	597.1 – 5300.9 (33) 1613.9 \pm 980.0
V ng/m^3	Range: 0.1 – 0.96 (34) Average: 0.30 \pm 0.14	- -	- -
Mn ng/m^3	Range: 0.1 – 0.99 (34) Average: 0.35 \pm 0.21	0.22 – 2.44 (7) 0.68 \pm 0.80	0.03 – 0.28 (26) 0.15 \pm 0.07
Rn Bq/m^3 **	Range: 0.014 – 0.049 Average: 0.026 \pm 0.018	- -	0.008 – 0.024 0.014 \pm 0.008

*Number of determinations is indicated in parentheses.

**Data of PEREIRA (1989).

It can be observed from Tables 1 and 2 that the marine aerosol is predominant in the region of sample collection, which was expected, due to localization of the Station. The Cl/Na ratio found in the aerosol (1.8) is in agreement with the ratio found in seawater, which confirms the marine origin of the elements.

Table 3
Average elemental concentrations, in ng/m^3 , of the elements determined in samples of 1986, with 24 hours irradiation

Element	Range min - max		Average concentration
K	29.94 - 655.82	(17)*	116.94 ± 151.56
Ca	40.78 - 1003.92	(31)	224.47 ± 174.45
Sc*	1.74 - 6.79	(33)	3.39 ± 1.23
Fe	8.71 - 46.82	(34)	24.81 ± 7.36
Zn	0.1 - 24.8	(21)	5.17 ± 7.22
Br	1.03 - 8.36	(34)	4.07 ± 2.20
Sb**	1.4 - 62.85	(33)	15.79 ± 14.57
La**	5.41 - 84.34	(27)	30.01 ± 18.67
Au**	0.68 - 13.6	(34)	3.44 ± 2.75
Th**	1.54 - 12.09	(18)	5.50 ± 2.84

*Number of determinations is indicated in parentheses.

** pg/m^3 .

With relation to the other elements, determined by long irradiations, it was not possible to study their seasonal behavior, since the data obtained refer mainly to the winter of 1986.

Enrichment factor analysis

Enrichment factors were calculated by utilizing the results reported by MASON¹⁴ for the average composition of the earth's crust and of seawater.

Aluminium and sodium were utilized as reference elements for the calculations of EFs for soil and sea, respectively.

The analysis of the EFs obtained allow the following conclusions: (1) the sea is responsible for the presence of the elements Na, Cl, K, Ca and Br in the atmosphere of the region of the Antarctic Peninsula studied; (2) soil contributes to the emission of the elements Al, Sc, V, Mn, Fe, La and Th found in the aerosols; and (3) the elements Zn, Sb and Au are enriched in relation to the sources investigated. Other authors have also observed the enrichment of these and other elements in the Antarctic region.

Principal factor analysis

The elemental concentrations obtained were analyzed by Principal Factor Analysis, excluding the elements K, Ca, Mn, La and Th due to the fact that the concentrations determined in these aerosols were close in many cases to the detection limits.

The ten elements that were considered for the PFA statistical treatment: Na, Al, Cl, Sc, V, Fe, Zn, Br, Sb and Au could be divided into three factors, which explain 73.3% of the variability of the data: (1) in factor 1 are the elements Na, Cl and Br, which are typically of marine origin. So this factor can be associated to the sea as a source; (2) in factor 2 are present the elements Al, Sc, V and Fe, which can be related to soil as a source; and (3) the elements Zn, Sb and Au, which were found to be enriched in the enrichment factor treatment were retained in Factor 3. Since these elements are not tracers of natural sources, it was not possible to identify this factor.

The origin of the these anomalously enriched elements is not well defined and they could be natural or anthropogenic as well. In the Brazilian Station Comandante Ferraz, their origin would be preferentially natural, since similar enrichments were found in other places in the Antarctic.

„The authors wish to thank the Brazilian financing agencies: FAPESP, FINEP, CNPq and also the PROANTAR Program (Subproject n° 9586) for their support.”

References

1. E. MÉSZÁROS, Atmospheric Chemistry – Fundamental Aspects, New York, Elsevier, 1981.
2. W. MAENHAUT, W. H. ZOLLER, J. Radioanal. Chem., 37 (1977) 637.
3. G. M. HIDY, Aerosols – An industrial and environmental science, New York, Academic Press, 1984.
4. W. H. ZOLLER, E. S. GLANDNEY, R. A. DUCE, Science, 183 (1974) 198.
5. C. BOUTRON, C. LORUIS, Nature, 277 (1979) 551.
6. W. MAENHAUT, W. H. ZOLLER, R. A. DUCE, J. Geophys. Res., 84 (1979) 2421.
7. K. IWASHIMA, M. FUJITA, T. ABIKO, N. YAMAGATA, Antarctic Record, 59 (1977) 2.
8. T. KOIDE, T. ITO, N. YANO, T. KOBAYASHI, Mem. Natl. Inst. Polar Res. Spec. Issue, 19 (1981) 152.
9. L. M. MOREIRA-NORDEMANN, M. C. FORTI, A. W. SETZER, Annals of the 1st Seminar on Atmospheric and Space Sciences in Antarctic, São José dos Campos, April 27–29, 1988, p. 193.
10. P. ARTAXO, F. ANDRADE, A. W. SETZER, Annals of the 1st Seminar on Atmospheric and Space Sciences in Antarctic, São José dos Campos, April 27–29, 1988, p. 117.
11. E. B. PEREIRA, D. J. R. NORDEMANN, M. B. A. VASCONCELLOS, An. Acad. Brasil Cienc., 58 (1986) 182.
12. E. B. PEREIRA, A. W. SETZER, I. F. A. CAVALCANTI, Rad. Protec. Dosim., 24 (1988) 85.
13. E. B. PEREIRA, Tellus, 42B (1) (1990) 39.
14. B. MASON, Princípios de geoquímica, São Paulo, Polígono, 1971.