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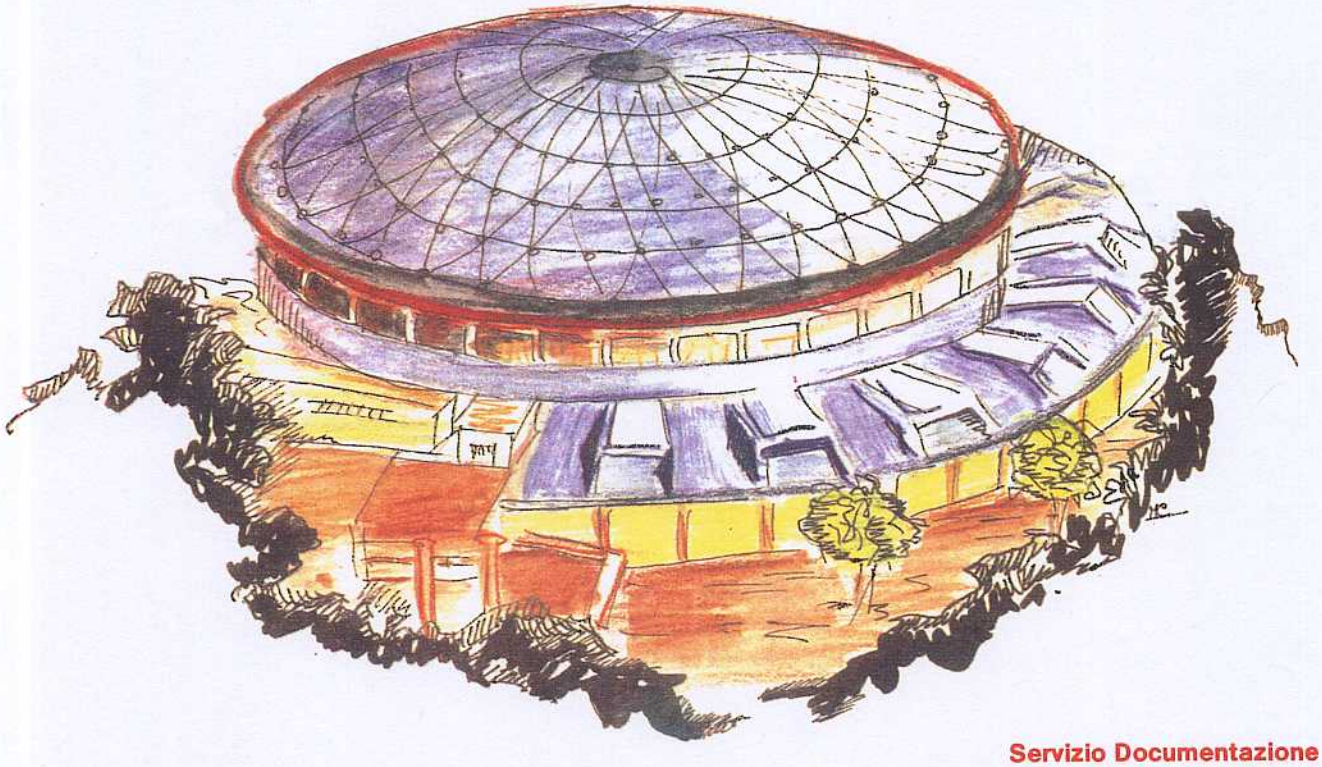

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XRF ANALYSIS OF VOLCANIC ASH USING SYNCHROTRON RADIATION

Emilio Burattini
Laboratori Nazionali di Frascati (INFN), Gruppo PWA,
P.O. Box 13, 00044 Frascati, ITALY,

Alberto Riveros, Marcelo Rubio,
Héctor Jorge Sánchez and Renzo Sartori
Facultad de Matemática, Astronomía y Física (UNC),
Laprida 854, CP 5000 Córdoba, ARGENTINA

Abstract

XRF quantitative analyses of volcanic ash were carried out in the Mycroanalysis station of the PWA Group of the Frascati National Laboratories. Very accurate and interesting results were obtained using a conventional XRF arrangement. These results are confronted with the ones obtained by mean of Chemical Analysis in a different laboratory.
Qualitative analyses using a total-reflection setup were performed obtaining optimal spectra and precise determination of new elements present in the samples.

1 INTRODUCTION

During August 1991 the Hudson volcano situated in the southern part of the Andean Cordillera erupted and remained active for about one month. The volcano is situated near the Argentina/Chile border (on the Chilean side) at about 50° S in the southern part of the S. American continent (Patagonia).

While there was no consequence due to the initial eruption, a large area in the Patagonian sector was affected by the later emission of ash, so much so that the towns and villages (e.g., Perito Moreno and Los Antiguos in Argentina, and Puerto Ibañez and Chile Chico in Chile) within a 100 km radius of the volcano were declared disaster areas.

The rain of ash reached the northern part of Patagonia, as far as the cities of Viedma in Argentina and Valdivia in Chile, both more than 1000 km from the volcano.

Up to 15 cm of ash was deposited in the immediate neighborhood of the volcano over agricultural land, resulting in the loss of crops and the death of farm animals and wildlife.

The initial fear concerned the chemical composition of the volcanic material and the percentage of elements that could be harmful for biological systems, such as Fl, Cl, S, As, and Pb. In addition, some biological laboratories stressed the fact that if there was a high concentration of silicon, it could cause the loss of teeth of the animal population, resulting in eventual death from starvation.

With the aim of obtaining an accurate analysis of the ash composition, two samples coming from different geographical areas near the volcano were analyzed in the Micro-analysis Station of the PWA Group of the Frascati National Laboratories (Italy).

2 EXPERIMENTAL

2.1 Method

The XRF (X Ray Fluorescence) analysis differs from other similar methods, such as PIXE (Proton Induced X-ray Emission), neutron activation, or EPMA (Electron Probe Micro Analysis), in that the photoexcitation has less effect on the sample, even for a large volume of irradiated area. The sensitivity of this method (and the other methods, too) depends on the signal–to–noise ratio, i.e., on the background of the measured spectra. This background is greatly reduced in the case of Synchrotron Radiation excitation, mainly due to the intrinsic and nonintrinsic characteristics of this kind of radiation, e.g., collimation, polarization, monochromatization possibilities, etc[1].

2.2 Apparatus

The apparatus consist of an experimental chamber allowing conventional XRF (SRXRF) and total–reflection X–ray fluorescence (TRXRF).
The conventional system consists of a sample holder (3×6 cm) that can be positioned along the X,Y axis with a precision of 5 μm. The geometry of measurement is 90° with 45° of incident and take–off directions. At the entrance of the chamber two slits allow an orthogonal collimation.
The detecting system consists of a solid–state detector with a Si(Li) crystal (Silena), a high voltage source (ORTEC 478), an amplifier (ORTEC 572), and a multichannel analyzer (ORTEC 916).

The incident beam, coming from a six–pole wiggler (with a critical energy of 2.5 keV), is monochromatized by a two–crystal monochromator with a resolution of 3 eV. The beam intensity (about 10^{13} photons/sec mrad 0.1% b.w. for the critical energy) is monitored by a ionization chamber and a V/F converter.
Among the main characteristics of the whole system, we can mention the following: a detecting–system resolution of 180 eV for the K_α line of Mn, a sensitivity of 2 ngr/cm^2 for Fe, and a short dead–time of the electronic chain[2].

2.3 Measurements and Data Analysis

The samples consist of compacted disks and dust of ash from the cities of Perito Moreno (about 100 km from the volcano) and Puerto Deseado (about 400 km) without any drying treatment.
The compacted disks were used to perform the quantitative analysis by means of the conventional system, while the dust was used for qualitative analysis, using the total–reflection setup.
The samples were irradiated for 600 s, with an excitation energy of 10 keV. Pure samples of Zn, Ni, Fe, V, Ti, and Calcium Hydroxy Apatite [$Ca_{10}(PO_4)_6(OH)_2$] were measured in similar conditions in order to be used as standard samples.
The spectra were analyzed using the AXIL[3] package and the concentrations were calculated with the sensitivity method incorporated in the mentioned software.
Figure 1 shows the measured spectrum of the volcanic ash from Perito Moreno zone.

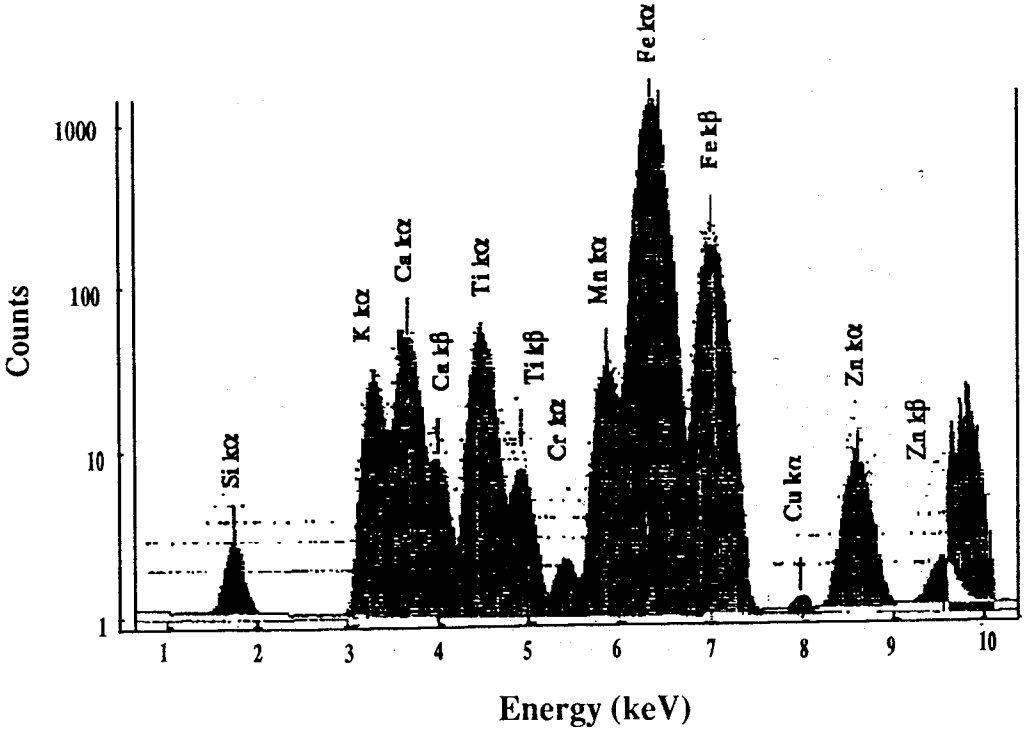

Figure 1: Measured spectrum of volcanic ash from the Perito Moreno area (about 100 km from the volcano) using the conventional setup

3 RESULTS

We should first mention that no appreciable difference between the concentrations of the two samples was observed. It could indicate a homogeneity in the concentration of the volcanic material deposited over different areas.

Table I shows the concentrations obtained, compared (column C) with the results from the Geochemical Laboratory of the University of La Plata (Argentina)[4].

As can be seen, the lowest detected element was Si, while the highest was Zn, which is immediately behind the excitation energy. Moreover, some elements in the low–energy region (Fl, Na, Mg, Al, P, and S) could not be detected while traces of Cu and Zn were found.

Table I: Elemental concentrations calculated in this work:
A - Sample from Perito Moreno (about 100 km from de volcano)
B - Sample from Puerto Deseado (about 400 km from de volcano)
C - Sample from Perito Moreno area analyzed using Chemical Analysis at the University of La Plata (Argentina)[4]
†No errors were reported.
‡Estimated by difference.

Element	Sample		
	A	B	C†
O (%)	69‡	64‡	47
Fl	–	–	365–320 ppm
Na (%)	–	–	4.1
Mg (%)	–	–	1.5
Al (%)	–	–	8.6
Si (%)	20 ±4	23 ±6	26.8
P	–	–	3400 ppm
S	–	–	1300 ppm
K (%)	3 ±1	4 ±1	1.5
Ca (%)	4 ±1	5 ±1	4.2
Ti (%)	1.2 ±0.4	1.4 ±0.4	1.0
Mn	800–400 ppm	800–300 ppm	1300 ppm
Fe (%)	2.2 ±0.8	2.2 ±0.8	4.6
Cu	< 10ppm	< 10 ppm	–
Zn	300–100 ppm	300–50 ppm	–

4 TOTAL–REFLECTION MEASUREMENTS

The spectrochemical analysis using the total–reflection technique[5] is increasingly adopted because higher sensitivities can be reached. The total–reflection setup of the PWA Lab. is mounted on the chamber of the conventional system, replacing the horizontal detector with a horizontal goniometric sample holder (with 4–min arc of precision) and installing a vertical solid–state detector (similar to the horizontal one) in the top part of the chamber.

Volcanic–ash dust (200 ngr/cm^2) was deposited on a silicon flat buffer. The buffer was placed on the sample holder (almost horizontally) in front of the beam with about 20–min arc of inclination in order to produce the total reflection of the 10–keV incident photons.

The fluorescent emission produced by the volcanic–ash dust deposited on the buffer was recorded for 300 s. This spectrum is shown if figure 2.

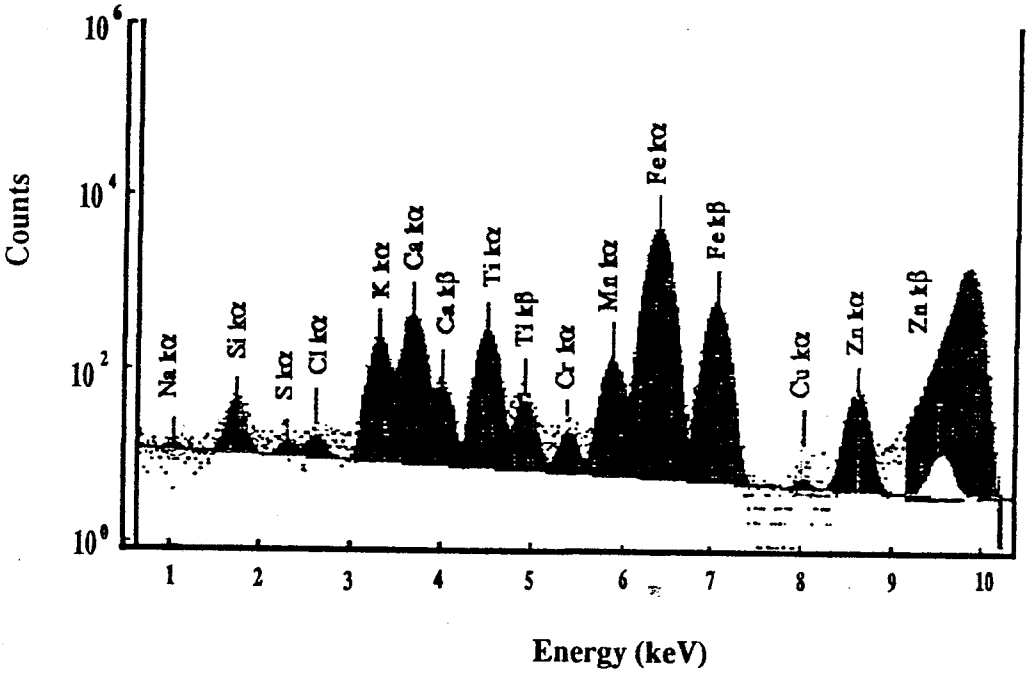

Figure 2: Measured spectrum of volcanic ash from the Perito Moreno area (about 100 km from the volcano) using the total-reflection setup

The difference between the conventional setup spectra and this one is clear. The signal–to–noise ratio is improved, such that new peaks in the low–energy range can now be clearly appreciated, e.g., Si, Na and Cl (this one not detected in previous measurements).

The high intensity of the scattering peak of the excitation line (comparing it with the conventional system peaks) is due to the geometrical configuration of the detection system in respect to the polarization of the incident photons[6].

5 FINAL COMMENTS

New and accurate results on the chemical composition of the volcanic ash were obtained. Some new elements were detected, e.g., Zn and Cu, that were absent in previous measurements.

The compositions obtained are very reliable, even though only a few standards were used and a simple method for data analysis was adopted.

The total–reflection measurements of the volcanic ash represent the first results obtained by means of a nonconventional system in the PWA Lab. With this technique new elements in the low–energy range were observed (e.g. Cl). Even if only qualitative analyses were carried out, the results show that the system capabilities promise well for the future.

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