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PIXE TECHNIQUE USED FOR CHARACTERIZATION OF HUMAN EXPOSURE TO MINERAL SANDS DUST PARTICLES

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ABSTRACT. The aim of this study was to characterize human exposure to mineral dust particles using PIXE (Particle Induced X ray Emission) and ^{252}Cf-PDMS (Plasma Desorption Mass Spectrometry) techniques. The dust particles were generated during the separation process of mineral sands to obtain rutile, ilmenite, zircon and monazite concentrates. The aerosol samples were collected at the village and during the ilemenite reprocessing phase. A cascade impactor with six stages was used to collect mineral dust particles with aerodynamic diameter in the range of 0.64 to 19.4 µm. The particles impacted on each stage of the cascade impactor were analyzed by PIXE (Particle Induced X ray Emission) and the elemental mass concentration and the MMAD (Mass Median Aerodynamic Diameter) were determined. By employing the ^{252}Cf-PDMS technique the chemical compound of the elements found in the mineral dust particles samples, in the cerium oxide samples and in the concentrate of monazite samples were identified. Cerium oxide and their clusters were identified in the cerium oxide samples while cerium phosphates were observed in the concentrate monazite samples. Molecules of thorium oxide were identified in monazite and cerium oxide samples. The mass spectra (^{252}Cf-PDMS technique) of dust samples showed the presence of the thorium silicate, thorite and zircon in the fine fraction of aerosol. The ^{252}Cf-PDMS technique was, also, used to characterize urine sample from a inhabitant of the village. The results show that Buena village inhabitants inhale monazite particles.
Keywords: PIXE, 252Cf-PDMS, Mineral sands dust particles, human exposure.

INTRODUCTION

People living in regions with high concentration of monazite can incorporate metals, specially thorium. The incorporation can be by ingestion (local foodstuff and coarse particles) and by inhalation of fine airborne particles. Workers involved in mineral concentration processes inhale mineral particles generated during the mineral processing [1, 2].

The most important Brazilian mineral sands deposit and processing plant are located in Buena, a seashore village with 300 inhabitants in the North of Rio de Janeiro states.

^{232}Th average concentration in feces and urine samples from a group of Buena village inhabitant were 6.7±1.6 mBq/g_{ash} and 1.5±0.5 mBq/L respectively [3]. ^{232}Th concentrations in two daily complete meals consumed by inhabitants were respectively 42.0 and 15.0 mBq/kg_{wet} [4]. The thorium concentrations in the meals do not explain the concentration of ^{232}Th observed in inhabitant's feces samples.

In order to evaluate the risk to the human beings due to dust particles inhalation, it is necessary to determine the deposition rate, the concentration and the kinetics of the particles flowing in the respiratory tract. Furthermore, the chemical composition, size and the elemental mass concentration of the particle in the respirable fraction of aerosol are necessary for evaluation of the worker's risk [5, 6, 7, 8].

EXPERIMENTAL METHOD

Urine samples of an inhabitant living in Buena village for more than 30 years, but not involved in the mineral concentration processes, were collected. This sample (1.4 L) was collected during 24 hours, homogenized and the aerosol samples were collected at the village and at the mineral sands processing plant during the reprocessing of ilmenite to obtain concentrates of ilmenite. The airborne particle samples were collected using a six-stage cascade impactor (CI) [9]. The air samplers were placed at 1.5 m from the ground, running 8 hours per day during 10 days (from 8:30 up to 16:30 h) the dry season. Airborne particles samples were analyzed by PIXE using 2 MeV proton beam obtained from the 4 MV van de Graaff accelerator at PUC-RIO. The X-Rays were detected by a Si-PIN detector with two geometries: one using 0.2 mm - thick aluminum foil as an X-Rays absorber and the second one without aluminum foil. The efficiency curve was determined using reference standard material. The X-Rays spectra were analyzed using an updated version of custom-designed software based on the stripping of a multi-elemental spectrum [9,10].

Urine samples of an inhabitant living in Buena village for more than 30 years, but not involved in the mineral concentration processes, were collected. This sample (1.4 L) was collected during 24 hours, homogenized and an aliquot of 750 mL was obtained and divided up to an aliquot of 35 mL, a volume of 10 µl was deposited on a stainless steel cube and dried at room temperature to produce a urine film. The urine film was analyzed using the ^{252}Cf-PDMS system of the Chemical Characterization Laboratory of the Texas A&M University (ATM) [11]. The aerosol collected at 6th stage of the cascade impactor, the concentrate of monazite and the cerium oxide were analyzed by ^{252}Cf-PDMS at PUC-Rio[12,13].

RESULTS AND DISCUSSION

The elemental mass concentrations and MMADs of the airborne dust particle samples collected at the plant and at the village (residences number 1, 2 and 3) are shown in Tables 1 and 2, respectively. The uncertainly associated to the mass concentration is about 10 % (volume and mass determination). The geometric standard deviation is lower than 3 for all MMAD values. At the plant, the highest Th concentration occurs during the electromagnetic separation process however the cerium concentration was below the detection limit of PIXE method (4.3 ng). These results suggest that monazite dust particles were not present in the respirable fraction of aerosol and that the thorium bearing particles were due to other aerosol source. The presence of Ti and Fe in the dust particle X ray spectra suggesting that rutile and ilmenite were the source of Fe and Ti bearing particles. At the village, the MMAD values were less than 2.5 µm and the elemental mass concentrations decreases depending on the relative plant to house distance and wind direction. This suggests the mineral sands plant the main source of airborne particles in the respirable fraction of the aerosol.

The mineral dust particles impacted on the 6th stage of the cascade impactor (particle with aerodynamic diameter in the range from 0.4 to 0.64 µm) during the electromagnetic separation process were analyzed by PDMS and the mass spectrum of positive ions showed that Th was associated to oxygen (ThO_n) and silicon ($ThSiO_4$), indicating that thorite, not monazite, was the source of airborne particles containing thorium. The presence of cerium compounds was not observed in this mass spectrum, showing that there were not monazite dust particles in the respirable fraction of aerosol.

The ions of Ti and Fe observed in the mass spectra (^{252}Cf-PDMS method) showed that ilmenite ($TiFeO_2$) was the source of Ti and Fe bearing dust particles. The presence of zircon airborne dust particles ($ZrSiO.H_2O$) was also observed in the mass spectra.

The elements Ca, Cr, Mn, Ni, Cu, Zn and Pb observed in the X-ray and in the mass spectra indicate the existence of other sources of aerosol besides the mineral sands. Some of these sources could be the mechanical wearing of equipment, particles of oil used to lubricate or the burning fossil. Besides these sources, there were particles from soil (Al, Ni, Si, Zn, Fe and Ca) and marine aerosol (Cl, Ca, Na, K, Zn and Fe), which were transported.

The ^{232}Th average concentration in 24 h urine samples from the Buena village inhabitant was 1.8 mBq/L [3]. This sample was analyzed by ^{232}Cf-PDMS. The ions present in the human urine (Na^+, Mg^+ and Ca^+), $NaCl^+$, $CaC_2O_4^+$ and the main organic compounds were identified in the mass spectrum of positive ions. The phosphates, sulphates, NHO_3^-, $C_5H_{11}O_5^-$ normally present in the human urine and the CN clusters, that characterize the organic compounds, were also observed in the negative ions spectrum. The urine mass spectra were compared to the mass spectrum of airborne particles collected during the ilmenite concentration [11,12] and to the mass spectrum of a sample of concentrate of monazite [12]. The $FeTi^+$ ions were identified in the mass spectra of some the of urine samples, indicating the presence of ilmenite. The identification of these molecular ions in the urine mass spectra shows that the inhabitants were exposed to ilmenite particles by inhalation, being probably part of ilmenite incorporated not dissolved by physiological processes. The Zr^+ and ZrO^+ were also identified in the spectra suggest that the inhabitant incorporate zirconite. The La^+, Ce^+, $LaPO_3^-$ and $LaPO_4^-$ were identified in the urine sample of the Buena inhabitant. The presence of yttrium oxide in the urine mass spectrum suggests that part of the yttrium incorporated is not metabolized. The thorium compound identified in the positive mass spectrum was $ThNH_4$, showing that the thorium present in urine was the product of thorium compound metabolized by the human body. The urine mass spectra suggest that thorium could be associated to a protein before it goes to urinary tract. The identification of La, Ce, Y and Th compounds in urine mass spectra shows that the inhabitant has incorporated the monazite by inhalation.

The mass spectra from inhabitant of Buena village were compared to mass spectra of one individual never exposed to monazite particulate (inhabitant of Rio de Janeiro city). The lines characterizing the monazite (La, Ce, Y and Th) were not identified in the mass spectrum of control.

Table 1. Elemental mass concentration in the respirable fraction of aerosol (μg/m^3)

Local	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Br	Zr	Ce	La	Pb	Th	Y
A	<dl	<dl	0.89	0.52	<dl	0.25	0.10	0.53	<dl	0.45	<dl	0.01	<dl	0.04	<dl	<dl	0.01	0.02	<dl
B	<dl	<dl	3.58	.03	<dl	2.42	0.11	3.81	<dl	0.03	2.36	0.46	<dl	8.23	<dl	<dl	0.09	0.14	<dl
C	<dl	<dl	3.75	5.77	<dl	1.59	0.14	5.25	<dl	0.03	<dl	0.03	<dl	0.36	<dl	<dl	0.05	<dl	<dl
	<dl	<dl	3.41	2.33	<dl	2.63	2.67	3.18	<dl	0.03	0.02	0.02	<dl	<dl	<dl	<dl	<dl	<dl	<dl
R1	1.6E5	710	270	1.78	0.08	0.03	0.05	4.56	0.03	0.01	0.01	0.05	5E-3	0.14	0.08	0.06	0.06	0.03	1E-2
R2	5.2 E4	350	210	1.43	0,03	0,06	0.08	2.34	0.02	0.02	0.01	0.04	<dl	0.08	0.07	0.05	0.04	0.03	1E-2
R3	3.3 E4	130	110	0.15	28	0.03	0.07	0.55	0.01	6E-3	2E-3	0.02	1E-3	0.08	0.01	7E-3	0.01	6E-3	3E-3

A= Inside the plant – step Drying; B= Inside the plant – step Electromagnetic Separation; C= Inside the plant – step Gravimetric Separation; R1= residence number 1; R2= residence number 2; R3= residence number 3; dl=detection limit

Table 2. Mass Median Aerodynamic Diameter (MMAD) of airborne particles containing metals (μm)

Local	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Br	Zr	Ce	La	Pb	Th	Y
A	-	-	1.7	1.7	-	1.5	1.4	1.6	-	1.6	-	2.1	-	2.2	-	-	1.6	1.7	-
B	-	-	1.5	1.4	-	1.3	1.0	1.3	-	1.5	1.5-	1.7	-	1.4	-	-	1.4	1.4	-
C	-	-	1.7	2.0	-	1.5	1.6	1.5	-	1.7	-	1.9	-	2.4	-	-	2.4	-	-
	-	-	1.6	1.5	-	1.0	1.1	1.4	-	1.3	2.4	1.6	-	-	-	-	-	-	-
R1	1.6	1.6	1.5	1.6	2.2	2.2	1.9	1.2	0.7	1.7	1.9	1.7	1.9	2.2	1.8	1.9	2.0	1.2	1.8
R2	2.0	1.3	1.7	2.1	1.3	1.3	1.4	2.1	1.0	1.3	0.8	0.8	-	2.3	0.7	0.8	0.7	0.6	0.9
R3	1.1	0.8	1.0	0.7	0.7	1.0	0.8	0.7	1.0	0.7	0.8	0.8	0.8	2.1	1.0	1.1	0.8	1.1	1.1

A= Inside the plant – step Drying; B= Inside the plant – step Electromagnetic Separation; C= Inside the plant – step Gravimetric Separation; R1= residence number 1; R2= residence number 2; R3= residence number 3

CONCLUSIONS

The airborne particles characterization suggests that inhabitants of Buena village and workers in the mineral processing plant are exposed to mineral sands particles, marine aerosols and particles from anthropogenic sources in the respirable fraction of aerosols. The sources of mineral sands particles are the mineral plant and natural deposit of mineral sands located in the village. The ^{252}Cf-PDMS results showed that although the plant processes mineral sands, the source of thorium bearing particles was thorite sand present in the soil of the region from which monazite is extracted. The ilemenite, zircon and thorite particles were identified in the fine fraction of aerosol. Based on the PIXE and PDMS analysis it was possible to conclude that there were other sources of aerosol, which produce airborne dust particles containing Th in the respirable fraction.

The mass spectra of the urine sample from a inhabitant of Buena village and of Rio de Janeiro city show the lines of molecules ions that characterize main compounds present in the human urine (NH_3, NaCl, oxalate acid, K, Mg, etc). The lines of TiFe, La, Ce, Zr, Y and $ThNH_4$ in the urine sample from the Buena inhabitant characterize metal incorporation probably by inhalation. These results suggest that the main source of metal in Buena village is the minerals sands and that the inhabitant inhales monazite particulate.

Results of urine sample from Buena by ^{252}Cf-PDMS technique agree with the results of aerosol characterization. These results suggest that thorium was metabolized and probably has been associated to a protein in the human body. However metals such as Y could be not metabolized and eliminated as oxide in urine. The employment of PIXE and ^{252}Cf-PDMS techniques for the analysis of enviromnetal and biological samples is an important tool for characterization of human and metal contamination. The knowledge of this information can provide the base for the identification of the sources of pollution and permit evaluation of the environment impact due to the industrial

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