

Evaluation of Trace Elements in Lung Samples from Coal Miners Using Neutron Activation Analysis

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ABSTRACT

In this study, instrumental neutron activation analysis was applied to the determination of Sc, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Th, and U in lung samples from miners working in coal mines located in the state of Santa Catarina, Brazil. These results were compared to those from a control group constituted of healthy individuals. The results showed that the elements determined exhibit considerable intersubject variability within a single group of individuals and the mean values of concentrations in miners' lungs were higher than those of normal individuals. Lung samples presented U concentrations varying from 11 to 890 µg/kg. Therefore, for some samples, the contribution of the uranium fission products in the analysis of La, Ce, Nd, and Sm was considered by determining the interference correction factors. The accuracy of the results was evaluated by analyzing certified reference materials.

Index Entries: Neutron activation analysis; lungs; lanthanides; scandium; thorium; uranium; hafnium; coal mine.

INTRODUCTION

The strong correlation between the increasing environmental and occupational contamination of the biosphere and its pathological effects

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for living organisms makes it a very important task for researchers to determine the trace element concentrations of biological materials.

Consequently, trace elements have been determined in lungs of a selected population group in several articles (1,2) for a comparative study and to investigate pulmonary diseases caused by toxic elements. Also, epidemiological studies (3,4) have been carried out in order to evaluate the risk of lung diseases and the harmful effects of various inhaled particles or gases.

The main objective of this study was to assess lung trace element concentrations of trace elements in lungs from individuals who had worked in a coal mine located in the state of Santa Catarina, Brazil as well as in lungs from healthy individuals (control group) and to make a comparison. Miners are considered to be one of the critical groups for occupational lung diseases as a result of the exposure and inhalation of toxic substances.

Also, the determination of trace elements in these samples is of interest in order to check the occurrence of pulmonary diseases caused by coal dusts because the X-ray exams of their lungs sometimes do not reveal anything.

The elements Sc, lanthanides, Hf, Th, and U were chosen for the analyses because most Brazilian coal samples have presented relatively high contents of these elements (5). The determination of these elements in lung tissues is very important in order to study the incidence of diseases associated to their abnormal accumulation because of the lack of investigation about the effects of these elements in the respiratory system.

As far as Sc, lanthanides, Hf, Th, and U are concerned, the literature for their determination in pulmonary tissues is scarce, especially in the case of nonexposed populations. However, there have been reports of occupational pulmonary diseases provoked by lanthanides. Pneumocoinosis has been reported in workers exposed to the inhalation of cerium oxide dust and in men handling rare earth concentrates (6). Lanthanides have caused vague symptoms (nausea and headache) in workers of lithographic industries (6).

The analytical method applied in this work was instrumental neutron activation analysis (INAA).

EXPERIMENTAL

Collection and Preparation of Lung Samples

Lung samples were obtained from two groups of adult males. Lungs from miners were obtained from subjects who have been exposed to the coal dusts in the course of their profession. They had worked in coal mines located in Criciúma in the state of Santa Catarina,

Brazil. Because samples from this group of individuals were collected from necropsies, the lobe tissue samples were obtained from the most affected area of the lung.

Control samples were obtained from healthy individuals in autopsies performed at the Institute of Forensic Medicine of the University of São Paulo. Control group pulmonary tissues were taken from right middle lobes.

The samples were freeze-dried for analysis and in this process a mean weight loss of about 80% was obtained. The dried samples were crushed with a Teflon pestle and homogenized. To avoid contamination of the samples, a series of precautions were taken. Handling of the samples was performed inside a class 100 laminar-flow hood and a Teflon spatula was used for their transfer.

Microscopy studies were also carried out using these lung samples embedded in paraffin.

Synthetic Standard of Elements

The synthetic standards were prepared by pipetting diluted standards solutions containing one or more elements onto pieces of Whatman No. 41 filter paper and dried at room temperature in a dessicator. Stock solutions of rare earth elements were previously prepared by dissolving their respective calcinated oxides (Johnson Matthey "Specure") with nitric acid, except for Ce. The Ce standard solution was provided from the National Institute of Standards and Technology (NIST, USA). The uranium standard solution was prepared by dissolving U₃O₈ No. 6 from the Compagnie Générale des Matières Nucléaires (COGEMA, France) with nitric acid. The Hf standard solution was provided by Spex Chemical. The quantity of the elements (in µg) in the irradiated standards were Sc = 0.10, La = 1.0, Ce = 4.0, Nd = 2.0, Sm = 0.50, Eu = 0.10, Tb = 0.150, Yb = 0.350, Lu = 0.150, Hf = 1.0, Th = 1.0, and U = 1.0.

Procedure for Lung Sample Analysis

About 150 mg of each dried tissue sample, weighed in a clean polyethylene envelope, were submitted to thermal neutron irradiation at the IEA-R1 nuclear reactor of the Instituto de Pesquisas Energéticas e Nucleares (IPEN). The comparative INAA method was used and the samples were irradiated with synthetic standards of elements. Irradiations were carried out for a period of 16 h under a thermal neutron flux of about 10^{12} n/cm²/s. The measurements of the induced gamma-ray activities were carried out with a GMX20190 hyperpure Ge detector, connected to an ADCAM 918^a Multichannel Buffer (EG&G ORTEC, Oak Ridge, TN) connected, in turn, to a microcomputer. The resolution (full width at half-maximum) of the system was 0.90 keV for the 122-keV gamma-ray peak of ⁵⁷Co and 1.90 keV for the 1332-keV gamma ray of

^{60}Co . Two series of measurements were carried out: the first one 5 d after irradiation, for determining La, Sm, Nd, Yb, Lu, and U, the second one, 20 d after irradiation, for determining Sc, Ce, Eu, Tb, Yb, Hf, and Th. The gamma-ray spectra were processed by VISPECT software developed by Dr. Denis Piccot, Centre d'Etudes Nucleaires de Saclay, France. Concentrations of the elements were calculated using comparative method and radioisotopes (with their respective gamma-ray energies and half-lives) used in these analyses were ^{46}Sc (889.3 keV; 83.81 d), ^{140}La (1595 keV; 40.27 h), ^{141}Ce (145.4 keV; 32.5 d), ^{147}Nd (91.4 and 531.0 keV; 11.06 d), ^{153}Sm (103.0 keV; 47.1 h), ^{152}Eu (1407.5 keV; 12.2 y), ^{160}Tb (879.4 keV; 73.0 d), ^{169}Yb (177.0 keV; 30.6 d), ^{175}Yb (197.8 and 396.1 keV; 101 h), ^{177}Lu (208.4 keV; 6.75 d), ^{181}Hf (482.2 keV; 42.4 d), ^{233}Pa (312.0 keV; 27.0 d), and ^{239}Np (106.1 and 277.6 keV; 2.36 d).

The interference factors due to the contribution of uranium fission products in the analyses of La, Ce, Nd, and Sm were experimentally determined. To obtain the correct concentrations of these elements, the amount of U was first determined and then multiplied by the interference factor. The interference contribution was then subtracted from the concentrations of the elements measured. The following values (in μg of element/ μg of U) were determined for interference factors: 0.017 ± 0.01 for ^{140}La for a decay time equal to 128.16 h, 0.29 ± 0.01 for ^{141}Ce , 0.21 ± 0.01 for ^{147}Nd , and 0.068 ± 0.007 for ^{153}Sm . Depending on the ratio between the concentrations of the lanthanide and U in the sample, this correction was negligible.

RESULTS AND DISCUSSION

For most of the elements analyzed, it was verified the analytical lung sample results are better represented by geometric means of concentrations. The geometric mean values, standard deviations, medians, and ranges for the concentrations of elements Sc, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Th, and U analyzed in lungs from control and miners groups are presented in Table 1. As may be seen in this table, results obtained indicated a variability of elemental concentrations within a single group of individuals. The control group presented standard deviations of the results lower than those obtained for coal miners; however, when taking into account the statistical *t*-test and calculating the 95% confidence interval, both of groups indicated an equally large variation. The mean values obtained for all the investigated elements were significantly higher in the lungs of the miners group in comparison to those of the control group. These findings indicated that Sc, lanthanides, Hf, Th, and U from coal dusts are retained in the lungs. All miners submitted to the present analysis had demonstrable disease in their lungs during histopathological studies. They had a picture designated as a coal worker's pneumoconiosis, which is characterized by deposits of particles, mainly dominated

Table 1
Concentrations of Elements in Lung Samples from Control and Coal Miner Groups

Element	Control Group (n=4)			Coal Miner Group (n=13)		
	$X_G \pm S_G$	Median	Range	$X_G \pm S_G$	Median	Range
Sc	2.56 \pm 1.7	3.10	1.20 - 3.8	93.7 \pm 4.1	111	12.8 - 830.4
La	39.0 \pm 1.8	41.1	20 - 74	354.3 \pm 3.6	391	75 - 2871
Ce	159.3 \pm 1.4	149	112 - 259	922 \pm 2.9	928	273 - 5481
Nd	122.9 \pm 2.1	125	62 - 288	358 \pm 3.5	347	40.5 - 2453
Sm	3.79 \pm 1.3	3.86	2.8 - 4.9	54.3 \pm 4.1	64.2	6.9 - 473
Eu	1.62 \pm 1.7	1.66	0.85 - 3.0	12.4 \pm 3.1	12.3	2.9 - 76
Tb	n.d.	n.d.	n.d.	17.0 \pm 2.9	19.9	2.1 - 68
Yb	n.d.	n.d.	n.d.	34.5 \pm 4.2	47.4	0.86 - 215
Lu	0.60 \pm 2.0	0.6	0.31 - 1.2	6.1 \pm 3.6	6.95	0.98 - 37.3
Hf	3.23 \pm 1.3	2.79	2.65 \pm 4.57	35.8 \pm 3.5	37.4	5.9 - 287.5
Th	10.1 \pm 1.6	9.6	6.1 - 18.9	98.1 \pm 4.1	113	12.3 - 892
U	19.2 \pm 4.2	42.9	3.7 - 44	67.0 \pm 3.0	68.5	8.75 - 356.2

Note: n = number of samples; $X_G \pm S_G$ = geometric mean and standard deviation; n.d. = not detected. Results are given in $\mu\text{g}/\text{kg}$ of dried weight.

Table 2
Concentrations of Elements in USGS W-1 Geological Reference Material

Element	This work			Ref. (8)
	Mean \pm s	S_R	E_R (%)	
Sc, ppm	32.7 \pm 0.7	2.3	6.6	35 \pm 2
La, ppm	10.6 \pm 0.8	8.0	2.7	10.9 \pm 1.3
Ce, ppm	22.4 \pm 2.3	10.	2.6	23 \pm 2
Nd, ppm	13.7 \pm 1.5	11.2	8.7	15 \pm 3
Sm, ppm	3.49 \pm 0.12	3.5	0.3	3.5 \pm 0.3
Eu, ppm	1.07 \pm 0.05	4.5	3.6	1.11 \pm 0.09
Tb, ppm	0.645 \pm 0.015	2.3	0.7	0.65 \pm 0.07
Yb, ppm	1.99 \pm 0.60	8.2	6.1	2.12 \pm 0.18
Lu, ppb	324 \pm 19	5.9	4.7	340 \pm 40
Hf, ppm	2.70 \pm 0.25	9.1	3.8	2.6 \pm 0.3
Th, ppm	2.25 \pm 0.10	4.4	6.2	2.4 \pm 0.4
U, ppm	0.551 \pm 0.031	5.7	3.1	0.57 \pm 0.07

Note: Mean \pm s = Arithmetic mean and standard deviation; S_R = relative standard deviation; E_R = percentage relative error; number of determinations = 6.

by carbon dust, in pulmonary interstitial space. These deposits elicit inflammatory response of variable intensity, ultimately leading to different degrees of pulmonary fibrosis.

There have been increasing applications of lanthanides in several technological and industrial fields, although little is known about the biological effect of this class of elements. It is not known whether the mechanisms responsible for the foregoing pathological processes are affected by the concentrations of lanthanides. Thus, the precautions for use and the effects caused by this class of elements need more investigations.

Analytical quality control of the results was previously evaluated by using reference materials: USGS W-1 (diabase) Rock and NIST 1575 Pine Needle. Results obtained for pine needles were published in a previous article (7). Geological reference material was analyzed, because the elements considered are not generally certified in biological reference materials. Results for W-1 geological reference material presented in Table 2 indicate a good precision and accuracy of the results obtained by the INAA procedure.

In conclusion, our results indicated that coal miners present significant concentrations of lanthanides in their lungs. This fact encourages the development of clinical studies focusing on the possible role of these elements in detecting pneumoconiosis.

ACKNOWLEDGMENTS

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico and Fundação de Amparo à Pesquisa do Estado de São Paulo from Brazil for financial support.

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