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Multielemental hair composition of Brazilian Indian populational groups by instrumental neutron activation analysis

M. B. A. Vasconcellos,[1]* P. Bode,[2] A. K. Ammerlaan,[2] M. Saiki,[1] G. Paletti,[1] M. G. M. Catharino,[1] D. I. T. Fávaro,[1] R. Baruzzi,[3] D. A. Rodrigues[3]

[1] Instituto de Pesquisas Energéticas e Nucleares, Caixa Postal 11049, CEP 05422-970, São Paulo, SP, Brazil
[2] Interfaculty Reactor Institute, Delft University of Technology, Mekelweg 15, NL-2629 JB, Delft, The Netherlands
[3] Department of Preventive Medicine, UNIFESP, Rua Pedro de Toledo, 675, CEP 04039-031, São Paulo, SP, Brazil

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In the present paper, for the first time the multielemental composition of hair samples of Indian populations living in the Xingu Park Reservation, in the Brazilian Amazonic region has been determined, by INAA. Irradiations were carried out at the Interfaculty Reactor Institute (Delft, The Netherlands) and, using a combination of different irradiation and decay times, about 40 elements could be determined in the hair. Previous analysis made at the Radiochemistry Division of IPEN/CNEN-SP (Brazilian Nuclear Energy Commission) of hair samples of a Brazilian control population allowed the determination of 20 elements, also by INAA. Comparison of the data obtained for the Indian populations and the controls showed very significant differences in elemental compositions for some elements, like Hg, Mn and Al while for others, like Cu and Zn, the concentrations were similar. A discussion of the differences found for other elements also is made in the present paper.

Introduction

Since the beginning of gold exploration activities using mercury amalgamation in the 1980's, in the Brazilian Amazon as well as in other Latin American countries like Venezuela, Colombia, Bolivia and others, a lot of effort has been put in analyzing several environmental compartments of the regions affected, in order to assess the impact caused by the mercury contamination.[1]

Many of these works focused on biomonitoring of mercury contamination by analysis of human hair samples, either of riverine populations that could accumulate mercury by fish consumption or of goldshop workers, exposed mainly to inorganic mercury during the amalgam burning.[2–4]

Soon it was recognized the importance of making also the mercury speciation in hair, as well as in other biological samples like blood and urine, due to the particular toxicity of this mercury compound and to its ability to surpass biological barriers like the placenta, making the fetus and the expecting mother a group at particular risk.[5]

In the present work, the study began with focus on the biomonitoring of mercury in Indian populations living in the Xingu Park, an area located in the Brazilian Amazonic Region. These populations consume fish as their main protein source and are thus subject to mercury exposure, although the region of the Park is not located in significant gold exploration areas.

Analysis of total mercury by instrumental neutron activation analysis, in thirteen Indian groups living in the Xingu Park has revealed very high concentrations of mercury in most of the hair samples of these populations, with arithmetic means, geometric means and medians rising up to about 20 times the mercury concentrations in hair of the control Brazilian population.[6–7]

The methylmercury contents were determined by CVAAS in hair of half of the Indian groups analyzed, focusing to the groups that presented the highest total mercury concentrations. Very high methylmercury concentrations were also found, comprising from 70 to 100% of total mercury,[8] which can be attributed to the high fish consumption of these populations.

On the other hand, many efforts have been made to use hair as a biomonitor for other toxic elements like cadmium and lead and also to establish a relationship between trace elements and nutritional status and/or occurence of several kinds of diseases in humans.[9] In many medical clinics, hair is being used as an additional biomonitor, together with blood and urine, to supply data for physicians in order to have more complete information about the health status of the patients.

One crucial problem in using hair as a clinical tool is the establishment of trace element concentration data that can be considered as representative of the "normal" or average concentration of a given populational group. In several countries, extensive data base have been collected of a great number of trace elements in human hair samples.

In Brazil, SAIKI et al.[10] have analyzed trace elements in hair samples of a populational group in São Paulo, using instrumental neutron activation analysis. The authors report the geometric means, arithmetic means and medians, as well as the ranges obtained, for the elements: Al, As, Br, Ca, Cd, Cl, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Sb, Sc, Se, V, Zn.

* E-mail: mbvascon@curiango.ipen.br

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In the present paper, for the first time are presented data obtained for multielemental trace element analysis of the hair samples of the Indian populational groups living in the Xingu Park, which are being exposed to methylmercury due to fish consumption, as revealed by data previously reported.[8]

The hair samples were the same as collected for total mercury and methylmercury analysis, by the physicians of the São Paulo School of Medicine.

The method utilized was instrumental neutron activation analysis and it was possible to determine the elements: Ag, Al, As, Ba, Bi, Br, Ca, Co, Cd, Cl, Cr, Cu, Fe, Hg, I, K, Mg, Mn, Mo, Na, Ni, Rb, Sb, Sc, Se, Si, Sr, Ta, Ti, V, Zn in hair of the Indians.

The results are compared with the Brazilian control population, which was reported by SAIKI et al.[10]

Experimental

Collection and washing of hair samples

Hair samples of Indian populational groups living in the Xingu Park and of the Brazilian control population were collected according to the protocol recommended by the International Atomic Energy Agency, IAEA.[11] The samples were cut using stainless steel scissors, from the occipital area of the head and as close as possible to the scalp in an amount corresponding to about 2 g.

The hair was then cut with the scissors into segments of about 0.5 mm long and transferred to a glass vial to be submitted to the recommended procedure of sequencial washing with acetone and water, followed by drying at room temperature.

Multielemental determination in hair samples by instrumental neutron activation analysis

About 50–70 mg of the hair samples were weighed in polyethylene capsules, for irradiation at the nuclear research reactor of the Interfaculty Reactor Institute of the Delft University of Technology (Delft, The Netherlands).

The analysis protocol consisted of short and long irradiations of 30 seconds and 5 hours, under thermal neutron fluxes of $1.45 \cdot 10^{17}$ n·m^{-2}·s^{-1} and $4.67 \cdot 10^{16}$ n·m^{-2}·s^{-1}, respectively, followed by gamma-ray measurements with different decay times, in a germanium detector coupled to associated electronics.

Using these conditions, the following elements could be determined: Ag, Al, As, Ba, Bi, Br, Ca, Co, Cd, Cl, Cr, Cu, Fe, Hg, I, K, Mg, Mn, Mo, Na, Ni, Rb, Sb, Sc, Se, Si, Sr, Ta, Ti, V, Zn.

Gamma-ray spectrum analysis

The gamma-ray spectrum analysis and interpretation has been carried out using the "holistic" software, developed at IRI.[12] In this software the gamma-ray spectrum is considered to be the linear sum of the gamma-ray spectra of all radionuclides present in the sample. Knowing the relative activities of the different radionuclides that may be produced by activation of a single element, a gamma-ray spectrum thus can be considered to be the linear sum of the spectra of the elements. All measured spectra (viz. the three spectra measured after different decay times) of a sample are being interpreted simultaneously. In the interpretation step all gamma-ray lines not just the characteristic peaks of all radionuclides, produced from each element are used simultaneously resulting in a list of elements and their concentrations. The gamma-ray lines and relative intensities[13] are consistent with the data published by BROWNE and FIRESTONE.[14] The quantitation is based on the single comparator method. This software, therefore, differs from traditional software in which usually radionuclides are being identified on basis of detection of only one or two gamma-ray lines, and only one radionuclide is used to determine an element.

Results and discussion

In Table 1 is presented a summary of the results obtained for the ranges and medians of the control group and of the Groups 2, 3, 4, 6 and 8 of Indians living in the Xingu Park. These groups were constituted of adult Indians, of both sexes, healthy and with high fish consumption. These results are also presented in Fig. 1 for better visualization.

It was possible to make a comparison for 20 elements only, which were determined by INAA in both cases: Al, As, Br, Ca, Cd, Cl, Co, Cr Cu, Fe, Hg, K, Mg, Mn, Na, Sb, Sc, Se, V and Zn, respectively, at IPEN/CNEN-SP (São Paulo, Brazil) and at IRI (Delft, The Netherlands).

One feature immediatily apparent is that, for practically all elements, with the exception of cobalt, the medians obtained for the five groups of Indians that are being analyzed are very similar, or at least of the same order of magnitude, which is not usual when different ethnic populational groups, comprising individuals of various ages and different genders are compared. Figures 1 and 2 illustrate this feature clearly.

If the concentrations found in the hair of the Indian groups are compared to controls, also some interesting conclusions can be drawn:

(1) The concentrations of mercury in hair of all the Indian groups were much higher than for the control group, as already reported in previous works.[6–7]

Table 1. Elemental concentrations in hair samples (in μg/g) from control and Xingu Park Indian populations by INAA

Element	Controls		Group 2		Group 3		Group 4		Group 6		Group 8	
	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median
Al	1.6–37.4	13.7	281–452	366.5	425–679	591.5	131–535	270	165–457	278.5	105–315	187
As	0.0067–0.126	0.022	0.0514–0.0846	0.0680	0.041–0.101	0.0763	0.0366–0.0804	0.0565	0.0228–0.0734	0.0391	0.0195–0.212	0.0291
Br	0.42–85.4	2.6	0.674–0.764	0.719	0.61–1.28	0.7925	0.467–2.28	0.6560	0.326 –1.06	0.5655	0.277–0.853	0.3495
Ca	118–1788	457	409–1400	904.5	775–1700	1053.5	543–1190	865.5	916–1420	1180	476–1020	894
Cd	0.0436–1.22	0.172	–	–	–	–	–	–	–	–	0.121–0.226	0.1735
Cl	40.7–1339	257	46.3–243	144.65	58.9–383	228.1	54.9–405	94.95	58.9–81.1	63.1	56–537	96.05
Co	0.0081–0.325	0.0259	0.0286–0.0942	0.614	0.0295–0.222	0.0899	0.0562–0.263	0.1775	0.0446–0.174	0.0706	0.0456–0.657	0.146
Cr	0.0682–0.753	0.163	–	–	–	–	–	–	–	–	–	–
Cu	4.0–56.1	14.9	–	–	7.61–15	9.6	8.92–63.6	12.8	9.11–10.1	9.59	8.84–10.9	9.85
Fe	7.2–36.8	14.0	131–205	168	186–488	271	72–201	132.4	79–269	131	35.2–117	80.9
Hg	0.08–4.75	1.16	11.6–15.7	13.65	7.99–11.7	8.99	12.1–21.3	14.65	8.86–23.3	15.75	9.73–18.9	14.55
K	0.53–25.7	3.50	41.5–149	95.25	–	–	48.3–352	112.95	–	–	21.6–422	112.8
Mg	7.7–267	54.5	–	–	245–296	270.5	333–571	350	310–490	427	166–422	300.5
Mn	0.105–2.50	0.359	10.7–115	62.85	14.4–55.6	33.15	80.3–117	90.85	35.4–107	72	17.8–67.7	40.1
Na	1.50–29.7	4.1	8.47–27	17.735	7.31–45.6	24.2	11.9–766	57.05	17.9–45.6	26.65	–	–
Sb	0.0031–0.848	0.0256	0.02–0.022	0.021	0.0426–0.373	0.0595	0.0167–0.147	0.0303	0.0193–0.0662	0.0362	0.0166–0.0874	0.0406
Sc	0.00118–0.0057	0.00153	0.0324–0.0533	0.0429	0.0551–0.144	0.0836	0.0204–0.0678	0.0441	0.0229–0.0568	0.0336	0.0117–0.0432	0.0234
Se	0.0091–0.869	0.425	0.377–0.395	0.386	0.267–0.332	0.2905	0.365–1.58	0.4455	0.274–0.375	0.3130	0.269–0.38	0.332
V	0.0015–0.054	0.0542	0.431–0.762	0.5965	0.593–1.45	0.9915	0.257–1.7	0.555	0.257–0.69	0.4695	0.16–0.576	0.332
Zn	106–264	157.8	121–142	131.5	–	–	104–138	125	–	–	109–155	131.5

– Element not detected.

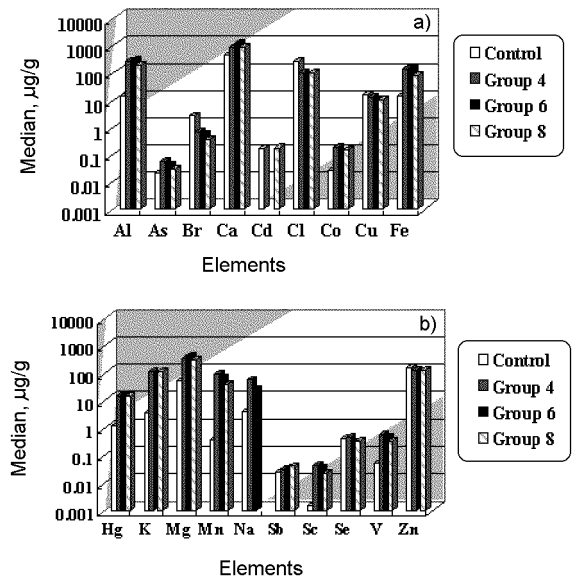

Fig. 1. Comparison of multielemental concentrations in the control population and in Indian groups living in the Xingu Park

(2) As already reported,[15] the Hg/Se molar ratios were very close to one in hair of the control populations and increased with mercury concentrations, which agrees with results found by other authors in organs of autopsies.

(3) The concentrations of nutritionally important elements like copper and zinc is very similar in both groups (Indians and controls). Cobalt and manganese, on the other hand, are much lower in the Indians hair.

(4) The concentrations of elements Al, Fe and Sc, whose origin generally is the soil, are much higher in the Indian hair.

One hypothesis that could provide an explanation is the constant use of natural pigments by the Indians, such as the red "urucum"extracted from a seed, to colour their hair and body.

Also it has to be pointed out that these Indian populations are constantly bathing in the rivers of the region, which accumulates suspended particulate matter in their hair, not totally eliminated by washing.

Conclusions

The analysis of 20 elements by INAA in hair of a control group of Brazilian residents of the region of São Paulo and in Indian populations living at the Xingu Park Indian reservation in the Amazonic region allowed an interesting comparison of multielemental concentrations between these groups.

The concentrations of most elements were remarkably similar between the Indian groups analyzed which is generally not the case between different ethnic groups. Toxic elements concentrations (Cd, Sb) were much lower in Indian hair, while soil originated elements (Al, Fe, Sc) were much higher. Mercury concentrations were much higher in the hair of all Indian groups as compared to control, probably due to their high fish consumption. Nutritionally important elements such as Cu and Zn were similar in Indians and controls while others (Co, Mn) are lower in the Indians.

This study will continue with analysis of more samples of the Brazilian control population and a more thorough examination of the differences found in the comparison with the Indians.

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