VALIDATION OF THE INSTRUMENTAL NEUTRN ACTIVATION ANALYSIS METHOD FOR MERCURY ANALYSIS IN HAIR SAMPLES USED FOR BIOMONITORING OF MERCURY ENVIRONMENTAL CONTAMINATION.

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Abstract

Environmental mercury contamination has become lately of widespread concern in Brazil due to the gold extraction activities in the Amazonic region and also to industrial activities.

It is estimated that tons of mercury are thrown in the rivers of the Amazonic region annually or are evaporated into open air due to the amalgamation procedure employed in gold extraction.

In the present work, as part of an IAEA CRP, three main populational groups were studied: a control group, of individuals with no suspicion of contamination by mercury; a group of people living near the Billings Dam, located in one of the most heavily industrialized parts of the country, and several Indian tribes living in the Xingu Park, an Indian reservation located in the Amazonic region.

An important part of the Project was the validation of the analytical methodology for the analysis of total mercury in the hair samples of the populational groups studied.

Instrumental neutron activation analysis was chosen for analysis of mercury in these samples. It has the advantage of being non - destructive, which can be quite convenient when dealing with a large number of samples, which is the case in epidemiological studies.

The experimental procedure consisted of irradiation of the hair samples in the IEA - R1 nuclear research reactor and measurement of the gamma radioactivity of ^{197}Hg.

For the validation of the analytical methodology, the following Reference Materials were analyzed: Fish Flesh Homogenate (IAEA), MA-A-2/TM; Chinese Human Hair, GBW 9101, (SHINR-HH) and the candidate reference materials IAEA-085 and IAEA-086 (Human Hair). The recently acquired reference material BCR-CRM 397 was also analyzed.

The accuracy and precision of the instrumental neutron activation method for analysis of these reference materials is discussed, as well as the applicability of the method to the analysis of mercury in hair of the populational groups studied.

1.INTRODUCTION

Contamination of the environment by mercury has become of general concern in Brazil in recent years, due to increasing industrial activities and mainly to gold extraction by amalgamation with mercury in the Central and Northern States of the country, mainly in the Amazonic region [1,2].

High levels of mercury in fish caught at the rivers of the region as well as in human hair and urine have been detected by different authors, in the Tapajós, Madeira and Negro Rivers Basins[3,4].

The Radiochemistry Divison of IPEN/CNEN-SP has recently been engaged in a similar kind of work, in the framework of the IAEA. CRP on Environmental Exposure to Mercury in Selected Human Populations as Studied by Nuclear and Other Techniques [5].

In this CRP, hair was chosen as the biological monitor, due to its ease of collection, stability during storage and due to the fact that it can trace the history of the contamination during the period of time in which it remains in the head [6].

In the case of the Brazilian Project, the main focus of the study was an Indian reservation located in the Xingu Park, in the Amazonic region, where several Indian tribes have lived for many years.

The Xingu Park is at a considerable distance of the gold exploration sites of the Amazonic region and initially it was supposedly free from mercury contamination.

The collection and analysis of hair of individuals from ten of these tribes have shown mercury concentrations several orders of magnitude higher than those found for a control population.

For analysis of total mercury in the hair samples, instrumental neutron activation analysis (INAA) was the method of choice, due to its non - destructive character and adequate sensitivity for the levels of mercury found in hair.

An important part of the Project was also the validation of the analytical methodology for mercury determination, which was very much stimulated during the CRP of the IAEA.

For this validation, the following reference materials were analyzed: Fish Flesh Homogenate, IAEA-MA-A-2/TM, Chinese Human Hair, GBW 9101 (SHINR-HH), and the candidate reference materials IAEA-085 and IAEA-086 (Human Hair). The recently acquired reference material BCR-CRM 397 was also analyzed.

2. EXPERIMENTAL

2.1. Collection and Washing of Hair Samples

The hair samples were collected and washed according to the protocol recommended by the IAEA [7].

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 grams.

The hair was then cut with the scissors into segments as short as possible and transferred to a glass vial, for washing with acetone. The samples were covered completely with the solvent and stirred at frequent intervals, for 10 minutes and the solvent carefully decanted. After drying of the solvent at room temperature, the hair was homogenized and washed three times with distilled water. A final washing step with acetone was then carried out and the samples were left to dry in the open, being at this point ready for analysis.

2.2. Determination of total mercury in hair and in reference materials, by instrumental neutron activation analysis (INAA)

Due to the need to analyze hundreds of hair samples for this study, it was considered as more convenient to use INAA for total Hg determination and to use polyethylene envelopes for irradiation, which are cheaper and easier to handle than quartz ampoules.

About 100 to 200 mg of the prepared hair samples and of the reference material were weighed in polyethylene envelopes previously washed with diluted nitric acid and desionized water.

Irradiations were carried out for a period of one hour, in a pneumatic station, under a thermal neutron flux of about 10^{12} n.cm^{-2} . s^{-1}, in the IEA - R1 research reactor.

The standards were prepared by pippeting about 1 μg of mercury, in the nitrate form, onto sheets of Whatman Nº 40 filter paper, previously impregnated with a solution of thioacetamide, to prevent mercury losses by volatilization before and during irradiation, as recommended by Noguchi et al [8].

After a decay period of about 70 hours, samples, reference materials and mercury standards were measured in a GMX 20195 ORTEC Ge detector, with a resolution of 1.9 keV

in the 1332 keV peak of ^{60}Co. The detector is coupled to an ADCAM 918A Multichannel Buffer and associated electronics.

Spectrum analysis was performed by means of the VISPECT2 software, developed by D. Piccot, from Saclay, France [9].

For calculation of mercury concentrations, the 69 and 77 keV peaks of ^{197}Hg ($t_{1/2}$ = 64.1 h) were used.

3. RESULTS AND DISCUSSION

In Table I are presented the results obtained for the analysis of total mercury by INAA in the reference materials: Fish Flesh Homogenate, (IAEA), MA-A-2/TM; Chinese Human Hair, GBW 9101; BCR - CRM 397 and in the candidate reference materials IAEA - 085 (Human Hair, elevated level) and IAEA - 086 (Human Hair, low level).

It can be observed that the relative errors obtained for the human hair reference materials were very good: 1.3% for the Chinese Human Hair and 2.8% for BCR - CRM 397. The relative error for the reference material of marine origin, Fish Flesh Homogenate, of 5.7%, was not so good as for the hair reference materials but still acceptable at this concentration level. This could be explained by the difference in matrix composition, since the materials of marine origin present high activities due to the high concentrations of elements such as sodium and bromine and consequently present more complex gamma - ray spectra, the hair matrix being cleaner for INAA.

The relative standard deviations present higher values than the relative errors and varyied between about 7 to 9%, which can also be considered as acceptable for analysis at the parts per million level.

Table II presents some of the results obtained for analysis of hair samples, in the framework of the CRP of the IAEA on Assessment of Environmental Exposure to Mercury in Selected Human Populations as Studied by Nuclear and other Techniques [10].

It can be observed that the means varyied from less than 1 ppm (group of residents at the Billings Dam, São Paulo, Brazil) to more than 20 ppm (Indian Group 6), which correspond approximately to the concentration range of the reference materials analyzed.

One important conclusion that arose from the CRP, apart from considerations about the validation of the methodology, was that all the Indian tribes analyzed present concentrations of mercury in hair much higher than the controls, which could mean that they are at risk of mercury intoxication. The most probable source of contamination is fish, which is the main source of protein for these populations, but further investigation has to be conducted in the region of the Xingu Park and materials other than hair have to be analyzed, such as fish, sediments, plants and aerosols.

The instrumental neutron activation analysis method can be considered as adequate for monitoring of total mercury in hair of the populations that were object of the study, as regards accuracy, precision and required sensitivity.

The procedure employed for INAA, with relatively short irradiation time, of 30 minutes to 1 hour and using mercury standards pipetted on filter paper impregnated with thioacetamide to avoid losses of mercury during irradiation was convenient to handle the number of samples involved in this kind of study. Up to the present moment about 400 hair samples have been analyzed and many more analysis will have to be done, since the study is being extended to other regions of Brazil where gold exploration occurs.

4. CONCLUSIONS

The analysis of several reference materials, mainly of human hair matrixes, have shown that the instrumental neutron activation analysis method was very adequate in terms of accuracy, precision and sensitivity, for monitoring of mercury levels in hair of several Brazilian populational groups.

The procedure adopted for INAA, using relatively short irradiation times and mercury standards pipetted on filter paper impregnated with thioacetamide and encapsulated in polyethylene envelopes allowed the determination of mercury in about 400 hair samples.

TABLE I. ANALYSIS OF MERCURY IN REFERENCE MATERIALS BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

REFERENCE MATERIAL	ppm Hg (CERTIFICATE)	ppm Hg (PRESENT WORK) **	RELATIVE ERROR (%)	RELATIVE STANDARD DEVIATION (%)
Fish Flesh Homogenate MA-A-2/TM	0.47 ± 0.02	0.50 ± 0.06	5.7	9.4
Chinese Human Hair, GBW 9101	2.16 ± 0.21	2.13 ± 0.05	1.3	7.8
IAEA - 085, Human Hair	*	26.8 ± 1.1	*	8.7
IAEA - 086, Human Hair	*	0.66 ± 0.04	*	9.5
BCR - CRM 397, Human Hair	12.3 ± 0.5	12.0 ± 0.9	2.8	7.2

* Material in the process of certification

** Confidence limits at the 95% level

TABLE II. SUMMARY OF THE RESULTS OBTAINED FOR MERCURY CONTENTS IN THE HAIR OF THE BRAZILIAN POPULATIONAL GROUPS STUDIED.

POPULATIONAL GROUP	$\bar{x}$	s	MEDIAN	$\bar{x}_G$	RANGE
CONTROLS	1.06	0.61	0.96	0.90	0.26 - 2.9
BILLINGS DAM	0.88	0.68	0.74	0.71	0.30 - 3.0
INDIAN GROUP 1	18.50	5.9	18.0	17.1	6.87 - 34.3
INDIAN GROUP 2	12.0	4.0	10.7	11.4	6.54 - 21.6
INDIAN GROUP 3	8.7	3.0	8.2	8.2	4.5 - 18.5
INDIAN GROUP 4	13.2	3.8	13.0	12.7	4.8 - 25.3
INDIAN GROUP 5	10.6	3.9	11.5	9.4	1.7 - 15.1
INDIAN GROUP 6	20.6	10.0	18.8	19.0	8.1 - 57.3
INDIAN GROUP 7	16.5	5.5	15.8	15.5	2.5 - 30.2
INDIAN GROUP 8	17.2	6.0	16.2	16.3	2.10 - 31.7
INDIAN GROUP 9	17.7	4.1	16.6	17.3	10.9 - 25.0
INDIAN GROUP 10	8.1	9.0	2.8	4.7	1.5 - 33.1

$\bar{x}$ = arithmetic mean

$\bar{x}_G$ = geometric mean

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