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DETERMINATION OF MERCURY IN HEAD HAIR OF BRAZILIAN POPULATIONAL GROUPS BY NEUTRON ACTIVATION ANALYSIS

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In the present work, determination of mercury in the head hair of populational groups living near a heavily industrialized region in São Paulo and of Indians living in the Xingu park in the Amazonic region, was carried out by instrumental neutron activation analysis. A control group of people with no suspicion of contamination by mercury was also studied. The range of mercury concentrations found up to now were: for the control group from 0.26 to 0 2.5 ppm; for the Indians from 6.9 to 34 ppm, and for the industrialized region inhabitants: from 0.30 to 3.0 ppm.

Human hair samples have received much attention lately for studying trace elements in vivo. They can be used for monitoring environmental exposure to pollutants as well as for evaluating poisoning by heavy metals.

Also the trace element composition of hair can be used for assessing nutritional status and can be related to human health or disease.

Hair samples have the advantage of being easier to collect and to prepare than other biological materials, like blood, urine, tissues, organs, and others.

Elements such as mercury are absorbed by hair and retained over a period of time they remain on the head, while blood and urine levels indicate transient concentrations[1].

Instrumental neutron activation analysis (INAA), due to its multi-elemental capabilities, has been applied by several authors to the trace analysis for many elements in hair. In the specific case of mercury, and other elements such as arsenic, selenium,and antimony, radiochemical separations have also been developed.

Lin et al.[2] analysed head hair of 32 dentists and 30 normal controls by INAA and compared the results with cold vapour atomic absorption (CVAAS) and NAA combined with $Pb(DCC)_2$

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preconcentration. The normal range was from 1.91 to 5.44 ppm, and the values for dentists were from 4.32 to 24.1 ppm.

Noguchi et al.[3] also analysed hair of 58 dentists from a public hospital and 50 dentists from private clinics, using INAA. The ranges were from 2.47 to 13.7 ppm for the dentists of the public hospital, and from 2.08 to 10.6 ppm for the dentists of the private institutions. The authors point out that these values are lower than in the past, which suggests that sufficient care is currently being taken by dentists in Japan in the handling of amalgams.

Lind et al.[4] used RNAA as the reference method for analysis of hair for quality control of four laboratories using CVAAS. The reference materials Ispra-I4 and IAEA HH-1 were analysed, as well as hair standards prepared at the laboratory.

Al Shahristani and Al-Haddad[5] analysed several hundred samples of human head hair, including both "normal" people and people who had ingested an organic mercury compound. The mercury contents in hair of "normal" people were from 0.1 to 12 ppm. People who had ingested mercury but showed no symptoms had hair mercury concentrations from a few to 300 ppm. Mild symptoms appeared with 120-600 ppm mercury levels in hair and severe with 400-600 ppm.

Muramatsu and Parr[6] studied the relationship between concentrations of some trace elements in hair, liver, and kidney from autopsy subjects. The elements Ag, Co, Cr, Hg, Sb, Se were determined by INAA in most cases. Hg and Se in some of the liver samples with very low levels of these elements were determined using a radiochemical procedure. It was concluded that, with the exception of mercury and to a lesser degree selenium, hair analysis did not provide a useful measure of the trace element status of the subjects included in the study.

Also in Brazil lately, the general population, the scientific community, and governmental authorities have shown much concern about contamination of the environment by mercury.

Gold extraction activities in the Central and Northern states of Brazil have had a disastrous environmental impact in these regions, since tons of mercury are thrown in the rivers annually or are evaporated into open air after the amalgamation of gold.

Also industrial activities and use in the past of organo--mercurial fungicides in the sugar cane plantations can give rise to public health problems due to contamination by mercury.[7,8]

In the State of São Paulo, which is the most heavily industrialized part of the country, one region that suffers the impact of industrial activities is that of the Billings Dam. Populations living in the villages near this Dam consume frequently fish caught there that could be contaminated by several pollutants including mercury.

The present work is part of a Coordinated Research Programme of the IAEA, in collaboration with the World Health Organization, on Environmental Exposure to Mercury in Selected Human Populations.

Experimental

Collection of the hair samples

Hair samples were collected from three main groups up to now:

1. Control group, of 25 people without any special suspicion of contamination by mercury, e.g., university students and friends.
2. Group of people living near the Billings Dam, in a small village called "Santa Cruz", of which 28 samples were collected up to now.
3. Group of Indians living in the Xingu Park, in the Amazonic region, of which 27 samples were collected up to now. This park is located along the course of the Xingu River, in the northern part of the State of Mato Grosso. The surface of the park is of about 25000 square kilometers and its population is of about 3000 Indians, divided in 17 tribes[9].

The samples of the three groups were being collected according to the procedure recommended by the IAEA[10]. During collection of the samples, questionnaires were filled which contained relevant data about the participants of the study group, such as sex, age, eating habits, weight, height, and hair treatments utilized.

Instrumental neutron activation analysis for total mercury

Preparation of mercury standards

Mercuric oxide, HgO, Aldrich Gold Label, 99.999% pure was dissolved in diluted nitric acid and taken up to a concentration of about 2 mg Hg/mL.

This stock solution was diluted to about 20 μg Hg/mL and 50 μL were pipetted onto Whatman No. 40 filter paper, impregnated with a solution of thioacetamide, to prevent mercury losses by volatilization before and during irradiation, as recommended by Noguchi et al.[11]

Treatment of hair samples

The hair samples were cleaned according to the procedure recommended by the IAEA[10], by cutting in very small pieces and washing several times with acetone and water. After the final washing with acetone, the hair was dried at room temperature and stored in black plastic containers.

Irradiation and measurement

About 100–200 mg of hair samples were weighed in polyethylene envelopes, which were sealed and encapsulated in outer envelopes. The standards pipetted on filter paper containing thioacetamide were also encapsulated in double polyethylene envelopes.

Reference materials were also irradiated, together with synthetic standards, for analytical quality control. Irradiations were carried out in a pneumatic station, for 1 hour under a thermal neutron flux of about 10^{12} $n.cm^{-2}.s^{-1}$.

After a decay period of about 70 hours, samples, reference materials, and mercury standards were measured with 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.

For calculation of mercury concentrations, the 77 keV peak of ^{197}Hg ($t_{1/2}$ = 64.1 h) was used. Experiments were carried out with tracer to check for self-absorption, which was not encountered for hair samples up to about 200 mg.

Results

Analysis of reference materials

Two different reference materials were analyzed to check the analytical procedure employed: Fish Flesh Homogenate, MA-A-2/TM, (IAEA) (Hg = 0.47 +- 0.02 ppm) and Chinese Human Hair RM, SHINR-HH (Hg = 2.16 +- 0.21 ppm). A minimum of six determinations were carried out for each RM, and the results obtained were: 5.7% relative error and 9.4% relative standard deviation for MA-A-2/TM, and 1.8% relative error and 6.9% relative standard deviation for SHINR-HH.

Table I presents a summary of the results obtained for the mercury contents in hair of the three populational groups studied: control group, group of Indians living in the Xingu Park, and group of people living near the Billings Dam in the State of São Paulo.

In Table II, a comparison is made between results obtained for total mercury in hair of control populations in the present work and the ones obtained by other authors, in Brazil and in other countries.

TABLE I

SUMMARY OF THE RESULTS OBTAINED BY INAA FOR MERCURY CONTENTS IN THE HAIR OF THE POPULATIONAL GROUPS STUDIED (in ppm).

POPULATIONAL GROUP	$\bar{x}$	s	MEDIAN	$\bar{x}_G$	s_G	RANGE
CONTROLS	1.06	0.55	0.96	0.93	1.71	0.26-2.5
INDIANS FROM XINGU PARK	18.5	5.9	18.0	17.6	1.38	6.9-34
POPULATION FROM THE BILLINGS DAM	0.88	0.68	0.74	0.71	1.85	0.30-3.0

$\bar{x}$ = arithmetic mean

s = standard deviation of the arithmetic mean

$\bar{x}_G$ = geometric mean

s_G = standard deviation of the geometric mean

TABLE II

COMPARISON OF THE RESULTS OBTAINED FOR THE DETERMINATION OF MERCURY IN HAIR, OF A CONTROL POPULATION IN THE PRESENT WORK AND BY OTHER AUTHORS (in ppm)

AUTHOR	ARITHMETIC MEAN	STANDARD DEVIATION	RANGE
PRESENT WORK	1.06	0.55	0.26–2.5
Camara et al.[7]	1.46	3.70	0.12–35.2
Carvalho et al.[8]	1.11	0.67	0.30–2.36
Mazzilli and Munita[13]	2.02	1.36	0.3–5.8

Discussion

The results obtained for the reference materials Fish Flesh Homogenate and Chinese Human Hair were in good agreement with literature values, showing relative errors below 6%.

The analytical procedure employed, using irradiations of 1 hour at a moderate neutron flux, allowed the use of polyethylene for encapsulating samples and standards instead of quartz ampoules, which made the procedure cheaper and quicker. This is very important when populational studies are involved, since the number of samples to be analyzed can be quite high.

The geometric mean of 0.93 ppm found for mercury concentrations of the control population in the present work can be considered as low if compared with some other countries, (3.8 for Japan, 1.8 for USA and 3.5 for England) and is close to the one found for Pakistan (1.2 ppm), according to Chatt and Katz.[12]

The arithmetic mean found for the controls in the present work, of 1.06 ppm, is very close to the one found by Carvalho et al[8], of 1.11 ppm. It is interesting to note that theregion of Brazil studied by Carvalho et al is completely different from São

Paulo in most aspects. The values found by Camara et al.[7] and Mazzilli and Munita[13] also in the state of São Paulo, 1.46 and 2.02 ppm, were higher than the ones obtained by us.

Regarding regards the two other populational groups that were studied, the concentration of mercury in the hair of the Indians from the Xingu Park was very much higher than in the controls, with arithmetic and geometric means of 18.5 and 17.6 ppm, respectively. This was quite surprising, because the region of the Park is still supposed to be free from mercury contamination arising from the gold extraction activities that are occurring in the Amazonic region. On the other hand, the Indians use several natural products, extracted generally from seeds, to treat their hair, that maybe could constitute sources of mercury.

Also it should be noted that the consumption of fish by the Indians is generally high, and this could mean that the waters where they are caught have been already contaminated by mercury.

The other populational group, that consumes fish caught in the Billings Dam, did not show any abnormality in the content of mercury in their hair, indicating that the group is probably not at risk in this sense.

The case of the Indians deserves further study, since the tribes from the Xingu Park have not been previously investigated as regards the content of mercury in hair. Samples from another group of Indians have been already collected and will be analyzed for mercury. This group has fish as its main source of proteins, always caught at the same site.

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