IAEA-TECDOC-330

HEALTH-RELATED MONITORING OF TRACE ELEMENT POLLUTANTS USING NUCLEAR TECHNIQUES

RESULTS OF CO-ORDINATED RESEARCH PROGRAMMES
ON NUCLEAR METHODS FOR HEALTH-RELATED MONITORING
OF TRACE ELEMENT POLLUTANTS
AND
HEALTH-RELATED ENVIRONMENTAL RESEARCH
USING NUCLEAR TECHNIQUES

A TECHNICAL DOCUMENT ISSUED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1985

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Printed by the IAEA in Austria
March 1985

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FOREWORD

In recent years there has been a considerable growth of interest in problems of environmental pollution from industrial and agricultural substances, and the harmful impact of such pollution on human health.

In 1977 the Agency created a special sub-programme on "Health-Related Environmental Research". The main purpose of this sub-programme is to promote the application of nuclear methods for assessing the contamination of man by environmental pollutants such as toxic heavy metals.

The following two Co-ordinated Research Programmes (CRPs) were organized concurrently by the Agency on this subject, and were finally phased out at the end of March 1984.

(I) CRP on Nuclear Methods for Health-Related Monitoring of Trace Element Pollutants, and

(II) CRP on Health-Related Environmental Research Using Nuclear Techniques (RCA Regional Project).

During the lifetime of these programmes, 31 different institutes from 29 countries have participated in them, 19 with research contracts and 12 with research agreements.

The elements of primary interest in these programmes were mercury, cadmium, arsenic, lead, selenium, copper and zinc. Several environmental samples such as hair, food and water were analysed. The main analytical methods used were instrumental neutron activation analysis (INAA), radiochemical neutron activation analysis (RNAA), X-ray fluorescence spectrometry (XRF), proton-induced X-ray emission spectrometry (PIXE) and atomic absorption spectrometry (AAS). In order to check the reliability of the analytical methods used in the participating laboratories, intercomparison studies were organized by the Agency. Animal experiments using radiotracer were also included in one of the programmes.

The final reports or abstracts (in the case of already published papers) submitted by the participants, as well as summary reports of both Co-ordinated Research Programmes, are compiled in this publication in order that they may be available to all interested persons.

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Part I

CO-ORDINATED RESEARCH PROGRAMME ON NUCLEAR METHODS FOR HEALTH-RELATED MONITORING OF TRACE ELEMENT POLLUTANTS

ANALYSIS OF POLLUTANTS IN HUMAN SCALP HAIR IN CAIRO

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Abstract

Scalp hair, urine and blood samples from volunteers selected from different areas surrounding Cairo were collected for study by neutron activation analysis (NAA) and conventional methods.

The results for 14 elements in hair show some variation between the different regions. Qualitatively there is a slight difference of abundance of the investigated elements. Broadly speaking the presence of major elements is dominant. No relationship was observed between the elemental composition of hair and urine.

1. INTRODUCTION

Recently enormous advances have been seen in the scope of trace element analysis providing reliable data for biological systems. The most important techniques now used are radioactivation analysis in combination with gamma spectrometry and atomic absorption spectrometry (1, 2). Among the samples analysed for pollution studies are nails, scalp hair, blood, urine and drinking water (3, 4, 5). Some investigators have claimed that concentrations of trace elements in hair and nail may differ with respect to non-essential elements, due to differences in trace element intake, dietary habits and drug abuse (5). Other authors claimed that such differences stem from the geographical location, environmental conditions, race and age of the subjects (6).

2. EXPERIMENTAL

2.1. Collection of hair

Small plastic bags were used to collect about 5 g of hair from each volunteer and the collection was carried out at random from subjects living in the above-mentioned areas. From each area about 60 samples were collected from subjects of different age and occupation.

2.2. Preparation of samples for irradiation

Washing of hair was done for decontamination purposes. A weighed amount of hair was taken for serial washing, starting with pure distilled water, then 0.1 N HNO_3 and finally with detergent and distilled water. The samples were dried in an oven for 15 min at 70°C; 5 mg amounts were placed in special plastic containers and irradiated at a flux density of $10^{12} n.cm^{-2}s^{-1}$ in the Cairo 2MW research reactor for 48 hrs. The

samples were then left to cool for 3 days to remove short-lived radionuclides and then subjected to counting. Replicate samples were treated similarly and sent to be irradiated in the Bandung Triga type 1MW reactor for further confirmation (7). The results were evaluated collectively as shown in table 1.

Table 1 Elements Traced in Human Scalp Hair Samples in Cairo Inhabitants, Expressed in μg/g Dry Hair Samples as Mean Value

Element	Province	High average	Province	Low average
As	Heliopolis	0.8	Giza	0.1
Cd	Nasr City	1080.0	Cairo Ind.	120.1
Co	Cairo Industrial area	250.0	Heliopolis	110.0
Cr	Giza	1.2	Giza	0.2
F	Giza	0.5	Sporadic	0.05
Fe	Sporadic	150.0	Port Said	50.0
Sb	Upper Egypt	510.0	Alexandria	58.0
Cs	Alexandria	280.0	Cairo City	56.0
I	Port Said	17.0	Upper Egypt	7.0
Mn	Giza	6.1	Alexandria	2.2
Mo	Cairo City	0.16	Giza	0.08
Se	Industrial	8.0	Heliopolis	2.0
Zn	Sporadic	180.0	Nasr City	30.0
Sc	Giza	40.0	Sporadic	12.0

2.3. Medical examination

For the medical examination, special medical sheets were prepared. A summary of the data is presented in table 3. Samples of urine were collected over 24 hours. Full reports were prepared for each individual. The data collected are summarized in table 2. This work is still going on. Further data will be published in a second report.

3. RESULTS

The following tables summarize the data obtained from volunteers selected at random from five areas in Cairo and its surroundings. Interpretation of the data was done on the basis of group analyses. Fig. 1. shows the location of the sampling areas.

The urine samples were collected from the same subjects and reports for 24 hrs are tabulated in table 2. Medical examination as well as clinical medical sheets are also described in table 3. The haemoglobin percent of each volunteer was determined using the spectrophotometric technique. The total blood counts for both red and white corpuscles were also determined and are reported in the same tables.

Table 2 List of Investigation of Urine and Blood Samples

Name	Sex	Urine												RBC		
		Colour	Volume in ml	Sp. gr.	Odour	Appearance	Sed	pH	Alb	Sugar	K.B.	Bile	Blood	Microscopical	in mill	Hb %	WBC
H.S.	M	yellow	100	1029	arom	clear	-	6	-	-	-	-	-	oxalate	5.1	93	3600
Gh.g	M	amber	120	.1028	arom	clear	-	6.2	-	-	-	-	-	ox,ur.	4.1	95	4200
A.H.	M	yellow	40	1025	arom	turbid	+	5.9	-	-	-	-	traces	urates	4.8	93	5400
A.K.	M	orange	80	1026	arom	clear	-	5.7	-	+	-	-	nil	cast	5.3	100	6300
E.S.	M	amber	190	1035	sweet	clear	+	6.1	-	+	+	-	nil	cast,ox.	4.5	95	6200
F.A.	M	yellow	80	1026	arom	clear	-	5.1	+	-	-	-	+	RBC,ur.	5.1	100	5400
H.F.	M	orange	130	1027	sweet	turbid	-	6.1	-	+	+	-	nil	cast,ur.	5.1	98	5200
M.E.	M	yellow	100	1025	arom	clear	-	5	-	-	-	-	traces	ox.ur.	4.6	98	6200
M.I.	M	orange	100	1031	ammon	turbid	+	5.4	-	-	-	-	absent	PO_4,ur.	4.5	100	5600
R.M.A.	M	watery	200	1017	putrif	turbid	+	5.4	-	-	-	-	traces	PO_4,pus	4.3	100	6500
E.A.	F	yellow	160	1031	arom	clear	-	6.3	-	-	-	-	nil	oxalate	4.6	89	4500
R.W.A.	M	orange	110	1032	arom	clear	-	5.1	-	-	-	-	nil	ur.ox.	4.8	83	6500
A.S.E.	M	yellow	130	1019	arom	turbid	+	6.0	-	-	-	-	traces	cast,RBC	5.1	96	5400
N.A.	F	yellow	50	1034	arom	turbid	+	7.0	+	-	-	-	traces	RBC,ox.	4.7	98	5400
N.A.M.	F	yellow	48	1031	arom	clear	-	6.8	-	-	-	-	nil	pus	4.8	100	6000
F.M.S.	F	yelllow	58	1028	arom	clear	-	5.8	-	+	-	-	-	ur.ox.	5.0	100	4500
Y.I.	M	orange	68	1026	arom	clear	-	6.1	-	-	-	-	-	ox.RBCs	4.2	92	6200
I.S.I.	M	yellow	78	1031	arom	turbid	+	5.4	+	-	-	-	-	ox.urate	5.1	98	7000
K.H.S.	M	yellow	100	1026	arom	clear	-	5.1	nil	-	-	-	-	ox.urate	6.1	100	6500

Table 3 Medical Examination (Summary)

Name	Age	Sex	Occupation	Residence Area	General Examination	Neck	Abdominal	Asthma	Build	Smoking habits
H.S.	23	M	carpenter	Giza	normal	clear	slight pain	nil	moderate	no
GH.G.	25	M	student	Shoubra	normal	tonsil	normal	-	-	no
A.H.	22	M	hair dresser	Nasr City	hernia	thyr +	pain	present	weak	smoker
A.K.	24	M	carpenter	Giza	normal	clear	normal	nil	moderate	no
E.S.	25	M	grocer	Heliopolis	headache	allergy	distention	+	strong	addict
F.A.	26	M	student	Nasr City	normal	clear	normal	nil	moderate	smoker
H.F.	24	M	carpenter	Alexandria	high bl.pr.	swall.	normal	+	well built	heavy sm.
M.E.	23	M	tailor	Cairo City	normal	clear	normal	nil	moderate	smoker
M.I.	20	M	carpenter	Ind. Prov.	normal	swall.	slight pain	nil	moderate	smoker
R.M.A.	22	M	student	Heliopolis	normal	clear	normal	+	weak	no
E.A.	24	F	tailor	Nasr City	normal	clear	normal	nil	moderate	smoker
R.W.A.	32	M	waiter	Giza	normal	swall.	distention	nil	moderate	no
A.S.A.	24	M	carpenter	Nasr City	normal	clear	normal	nil	moderate	no
N.A.	20	F	student	Heliopolis	normal	clear	normal	nil	weak	no
N.A.M.	23	F	student	Cairo City	normal	clear	normal	nil	moderate	no
F.M.S.	24	F	labourer	Ind.Prov.	headache	thry +	pain	+	moderate	addict
Y.I.	23	M	student	Heliopolis	normal	clear	normal	nil	weak	no

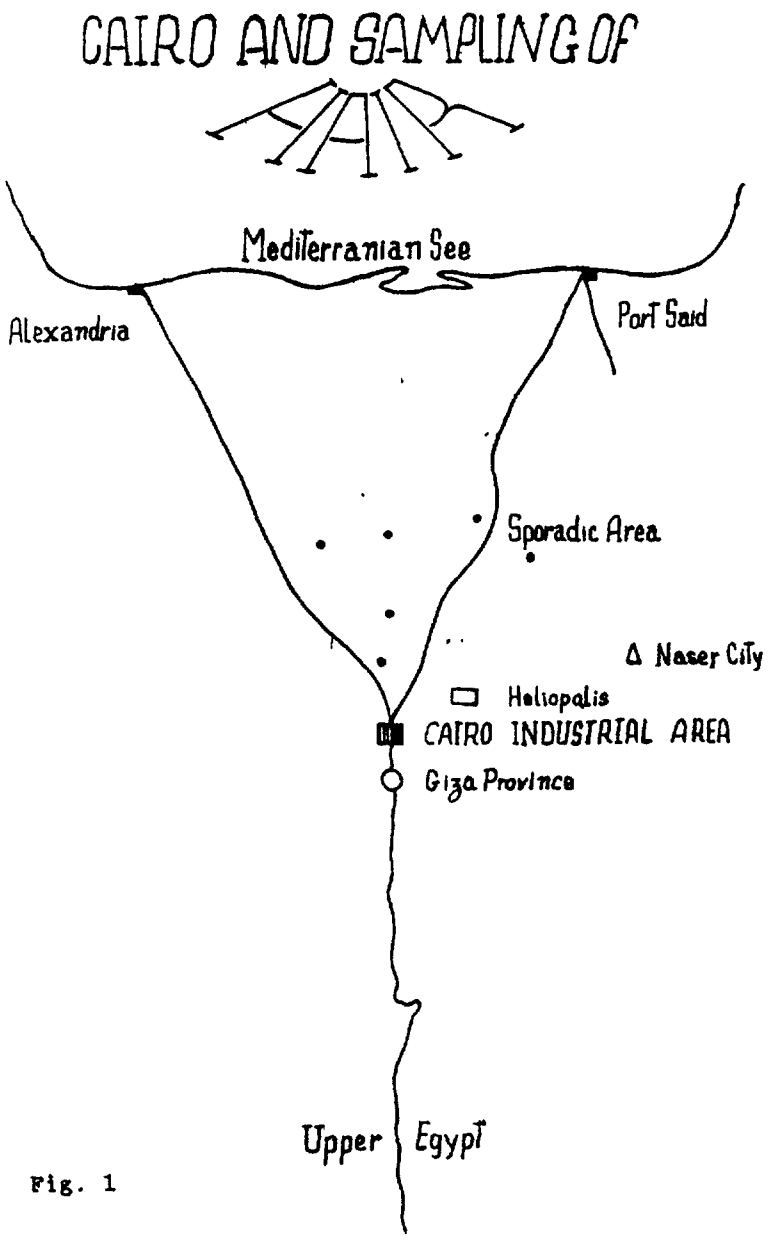

Fig. 1

4. DISCUSSION

A comparison of hair samples obtained from different locations in Cairo and its surrounding shows that elemental concentrations vary little between the different locations.

In this study, washing of hair by a standard method has been adopted for all the investigated samples. Thus, the concentration of each of the 14 elements is thought to reflect the actual composition. Previous authors have claimed that trace elements can be easily washed out of hair or incorporated into it during washing (1). To avoid such errors, all hair samples have been treated similarly using reference untreated samples. Our controls revealed no differences caused by washing, either qualitatively or quantitatively.

5. CONCLUSIONS

Inter-regional differences in the elemental composition of hair samples included in this study are mostly insignificant. For example, samples analysed to-date showed the presence of Cr, Mo, Sb and Cd at more or less similar concentrations. Sc, Co, Fe, Mn, Se and Zn are essential elements and, on the whole, minimum variations are seen in these elements among different regions. There is however a steady increase in the value of F from south to north. This observation may be explained according to the expected halogen increase in coastal areas. The iodine values behave similarly, but with some big differences moving from desert areas to the coast. Inhabitants of Alexandria and Port Said do not suffer from iodine deficiency goitre, a phenomenon known to happen in oases west of Cairo (8).

6. ACKNOWLEDGEMENT

The senior author wishes to thank the IAEA for its support under research contract 3003/RB. Thanks are also due to AEE in Cairo for irradiation facilities and continuous support.

The senior author also wishes to acknowledge the help of the PAIR BATAN of Bandung, Indonesia, for RNAA of some samples, and the Arab Drug Company (ADCO) for sampling and analysis of body fluids. Thanks are also due to ECN in Petten for their invaluable help and generosity during the meeting of May 1983.

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INVESTIGATION OF CONTENT OF ESSENTIAL ELEMENTS IN HUMAN TISSUES IN CONNECTION WITH VARIOUS DISEASES

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Abstract

The content of some trace elements in animal and human organs was determined, and their relation to biological activity in general and hypertonia and cancer in particular was studied. The following aspects of the present investigation are worth pointing out: (a) determination of "normal" element concentrations in organs and deviations therefrom in rats (Wistar) after thymectomy as a function of age; (b) determination of "normal" concentrations of trace elements in human tissues taken from organs of individuals without clinical pathology. Liver, kidney, heart, small and large intestines of rats from different age groups were analyzed: (a) healthy rats, age 3,6,9 and 12 months; (b) thymectomized at 3-month-age rats, 6,9 and 12 months old. The concentrations of 5 elements were considered. It was established that the concentration variations in kidney follow the change of blood pressure, and those in heart and liver follow the rate of change of blood pressure. A decrease of the concentrations of elements studied in organs at 3 months after thymectomy and a general tenedency to increasing after that age can be noticed.

1. INTRODUCTION

The investigations being carried out in the NAA Group at the Institute of Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences, Sofia, aim at studying the interconnection between trace elements and the most widespread diseases of today, the hypertonia and the cancer.

Since human materials are, as a rule, not readily available for analysis, our investigations are centred around laboratory animals used as models. The work on the present project encompasses two main aspects: (a) determination of trace elements in organs of laboratory animals (mice and rats) with and without pathological changes, (b) determination of these elements' content in the organs of persons without clinically-noticeable disease symptoms.

Although the presence of microelements in living organisms is well known, their role and functions are still the subject of intensive investigations. The comparative study of element composition in organs of healthy and sick animals contributes to the clarification of the problem.

Published data exist on the participation of certain elements in the processes which take place in an organism affected by cardio-vascular diseases. A risk factor in similar diseases is the hypertonia.

On the other hand, the thymus is one of the little studied glands; not much is known about its functions as a regulator of endocrinic processes. In addition, literature data indicate that the thymus has an influence on the blood pressure. The removal of thymus (thymectomy) leads to the appearance of a number of pathologic phenomena. One of those is the hypertonic reaction, i.e. the rise of the blood pressure.

2. GOALS, SCOPE, TECHNIQUES

The present investigation aims at:

- defining the normal concentrations of certain elements in the organs of laboratory animals (rats) and their age-dependent alterations,
- defining the concentrations of the same elements in thymectomized animals (thymus removed),
- establishing the deviations from the normal after a thymectomy had been effected,
- seeking for a correlation between the deviations resulting after the thymectomy and the hypertonic reaction.

140 male rats of the Wistar breed in the age of 3,6,9 and 12 months were investigated, 60 of those were subjected to thymectomy at the age of 3 months. During the whole experiment the rats obtained standard bricketted food. The experiment was carried out as follows:

- analysis of 3-month old rats;
- analysis of healthy 6-month old rats;
- analysis of 6-month old rats whose thymus was removed three months before;
- parallel analysis of healthy 9-month old rats and such thymectomized six months before;
- parallel analysis of healthy 12-month old rats and of such thymectomized nine months before.

Liver, kidney, heart, intestines and rectum were analyzed. The animals were slain at the age indicated, the organs were extracted, purified from fat and multiply washed in bidistilled water. The organs of 20 rats were mixed to form a sample representative of the respective age. All the samples underwent homogenization and were freeze-dried. Up to the irradiation they were kept in well closed glass vessels.

The instruments employed were made from titanium, stainless steel and teflon, they were cleaned by means of acids, bidistilled water and alcohol. The same procedure was applied to the vessels where the samples were kept and to the irradiation ampules.

The irradiation was carried out in plythene and quartz ampules. Two irradiation regimes were selected:

- t_{irr}= 1 min, t_d= 2 min, t_m= 5 min,
- t_{irr}= 1 min, t_d= 2h, t_m= 5 min.

Devices used: IRT-2000 reactor, pneumo-tube with and without Cd filter, thermal column, GeLi detectors, multichannel analyzers.

3. RESULTS AND DISCUSSION

The results obtained allow us to make certain conclusions on the changes of the elements studied, both depending on age and thymectomy-induced. Definite changes may be considered to be a consequence of thymectomy.

A number of elements behave conversely in normal and thymectomized animals. E.g., selenium in rectum, copper in heart and magnesium in kidneys increase with the age of healthy animals while decreasing with the age of thymectomized ones. On the contrary, the content of others (potassium in liver, vanadium in rectum) normally goes with the age while thymectomy inverts this tendency. Some elements show more intricate modifications (manganese in intestines, rectum and liver; magnesium and sodium in rectum): in healthy animals they first grow, then decrease, in thymectomized ones the direction of change is the opposite. For certain elements no thymectomy-dependent changes were observed (selenium and zinc in rectum, potassium in heart, magnesium and chlorine in liver).

Generally, lower concentrations of elements studied were observed at 6 months age (i.e. three months after thymectomy). Later, in older animals, a general increase of concentrations was established. This may be due to the capacity of the living organism to restore some normal life functions in the absence of a basic anzime regulator. The element behaviour in normal and thymectomized animals may be given a tentative interpretation. Literature data indicate that thymocites are DNA-carriers (Alekhina, 1967). The thymectomy eliminates this relevant DNA-source, and this may account for the changes of the heart-muscle activity. The reduced supply of DNA (an important oxidizer) to the heart might explain the lower manganese content therein. According to Shustov (1967), a high oxidating capacity is characteristic to manganese; hence, our results seem to justify the conjecture that hypertonia accompanied with hypertrophy takes place when oxidation processes are less intensive. The great variance of manganese content in normal and thymectomized rat's organs leads us to the assumption that the thymus is a basic manganese regulator in the organism (See Table 1).

An attempt was made to consider the ratios between some couples of elements studied. A constant potassium to sodium ratio was noted which corresponds to their balance in the organism. This holds in thymectomized animals, too. An exception to the rule is the rectum where this ratio varies strongly (see Table 2). It is an indicative fact that the normal (healthy) organs have a limited range of their own as far as the potassium to sodium ratio is concerned (Fig. 1).

TABLE 1. MANGANESE CONTENT IN RAT'S ORGANS, PPM

Organ	Age, months	Normal	Thymectomized
Small intestines	3	9.0 ± 0.5	
	6	10.8 ± 0.3	6.2 ± 0.3
	9	8.3 ± 0.5	7.0 ± 0.3
	12	4.1 ± 0.1	8.3 ± 0.4
Large intestines	3	11.6 ± 1.3	
	6	15.7 ± 0.6	8.2 ± 0.6
	9	19.9 ± 0.2	-
	12	5.6 ± 0.2	10.1 ± 0.5
Liver	3	10.9 ± 1.7	
	6	15.5 ± 0.4	9.5 ± 0.4
	9	12.8 ± 0.4	6.2 ± 0.6
	12	8.7 ± 0.5	8.8 ± 0.4
Heart	3	2.8 ± 0.5	
	6	4.6 ± 0.8	2.3 ± 0.3
	9	3.9 ± 0.2	less than 1.4
	12	2.8 ± 0.1	2.0 ± 0.3
Kidney	3	4.2 ± 0.6	
	6	7.4 ± 0.6	4.2 ± 0.4
	9	7.9 ± 0.2	4.4 ± 1.5
	12	4.6 ± 0.1	3.5 ± 0.5

TABLE 2.

age	organ									
	large intest.		small intest.		liver		kidney		heart	
	norm.	thym.	norm.	thym.	norm.	thym.	norm.	thym.	norm.	thym.
3	3.8		3.3		5.6		1.7		3.3	
6	2.1	3.2	2.7	2.9	5.4	4.1	1.8	1.7	2.7	4.3
9	1.9		2.4		5.3	5.1	1.6	1.8	2.5	3.4
12	6.9	2.2	2.7	2.4	4.8	3.9	1.4	1.4	3.1	3.7

An interesting conclusion which may be drawn out of the correlations considered is the existence of definite regularity between changes in kidneys and the blood pressure (Fig. 2). As to heart and liver, it was established that these organs react to the speed of blood pressure change after thymectomy (Fig. 3). Investigations of rats with innate (genetic) hypertonia were also carried out to compare the two sorts of hypertonic reactions. Since the elements studied showed different behaviour, it may be concluded that these two sorts of reactions go different ways. Unfortunately, only 12-month old animals were available for this study.

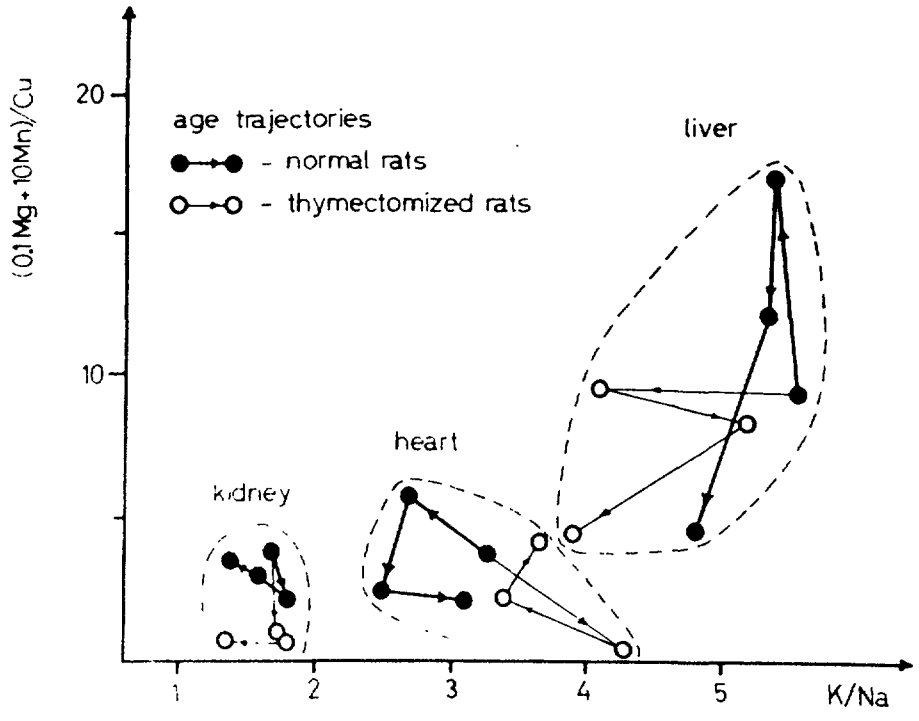
(0.1 Mg + 10Mn)/Cu
20
10
age trajectories
- normal rats
- thymectomized rats
liver
heart
kidney
1
2
3
4
5
K/Na

Fig. 1

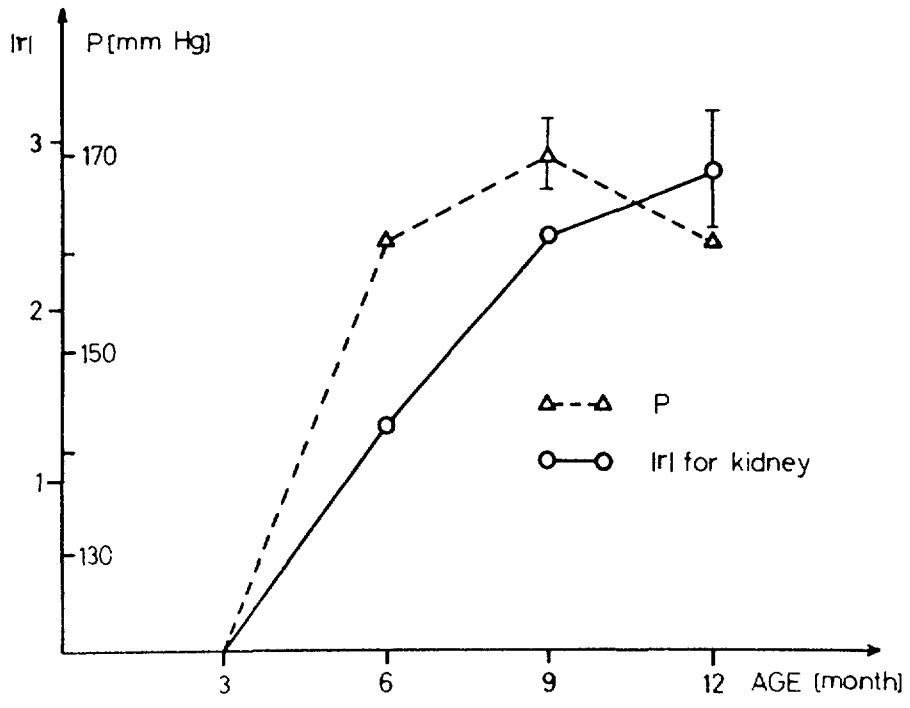
|r|
P [mm Hg]
3
2
1
170
150
130
P
|r| for kidney
3
6
9
12
AGE (month)

Fig. 2

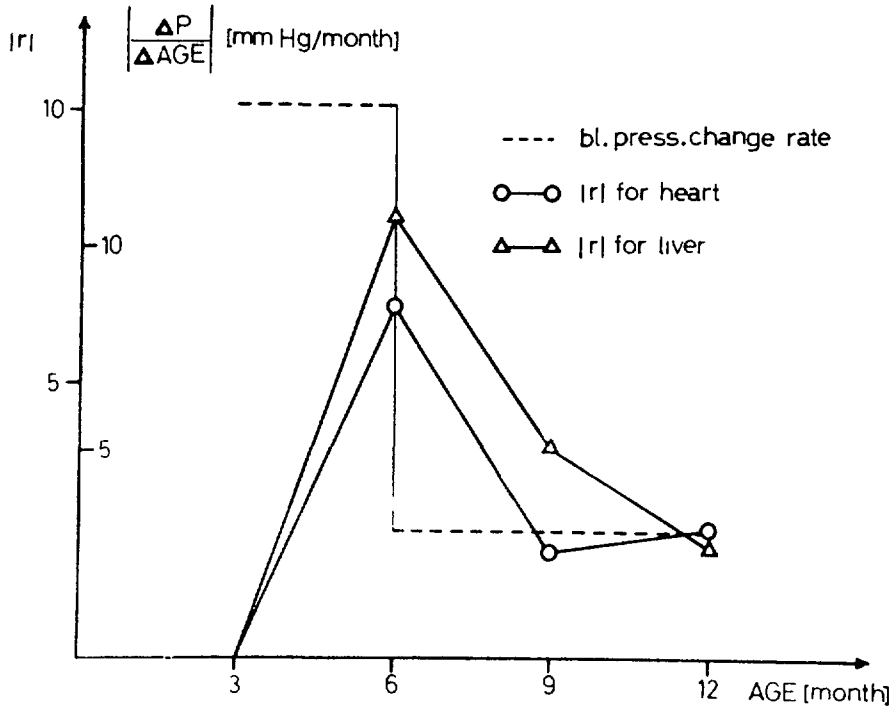

Fig. 3

4. CONCLUSIVE REMARKS

In our view, to explain both the processes which take place in the organism after thymectomy and the role of elements studied in these processes, the study of element ratios and the changes therein are of definite interest. To pursue this goal, it would be essential to broaden the faction of elements determined and to concentrate on their changes shortly after thymectomy when pathology is most acute. A subject of further studies would be thymosin-injected thymectomized rats at different post-thymectomy stages. Also, it would be of interest to carry on the comparative investigation of the two groups of animals (thymectomized and spontaneous hypertensive) for a better parallel between the two kinds of hypertonic reactions.

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CORRELATION OF TRACE METALS IN HAIR AND NAILS

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Abstract

Correlation of Cd, Cu, Hg, Pb and Zn was studied in 350 hair and nail samples of 12 persons. Determination was performed by atomic absorption spectrometry. Cd, Pb and Hg concentrations are fluctuating significantly in the specimens. Correlation was found for these elements in hair and finger nails and for Pb in hair and toe nails. Zn and Cu are more stable, the ratios of contents in corresponding samples are within a small range.

1. INTRODUCTION

Hair has been extensively described to be a good indicator for exposure to toxic elements. For some toxic and essential elements a proven clinical significance based on hair concentrations was found. Recommendations have been reported concerning standardization of hair analysis [1]. To study the significance of hair analysis for body burden the levels of trace elements have been compared with those in blood and urin [2-5]. By means of radiotracers the deposition of some of the toxic elements in hair and organs was studied in animals [6-7].

Until now, only a few papers are dealing with analysis of nails [8-12]. Therefore, a comparison of the levels of some toxic and essential elements in hair, finger and toe nails was planned to get more information about trace metal amounts in nails, the fluctuations in these specimens and the interrelations between hair and nails. The growing rate of hair is 1 - 1.5 cm/month, while growth of finger and toe nails is about 3 mm resp. 0.8 mm/month only [13]. If sampling is performed from all fingers resp. toes 1 to 2 months periods are necessary to get the next toe nail sample . For hair analysis it is suggested to use only the first 2.5 - 5 cm of recent growth. Nail clippings are comparable to the distal ends of long hair.

For this long term correlation study hair and nail samples were collected from 12 persons several times. Fluctuations of trace metal contens in the specimens were presumed. Therefore, it was expected to achieve more information about correlation of these materials by repeated sampling from a small group than from a large number of samples from different persons. For all members of the group environmental exposure during working hours is low. About half of the group is living in rural, half of them in an urban region. Persons working in laboratories,

workshops, physicists and an electronics engineer were selected for the group. For some of them generally or occasionally increased levels of the analytes had been expected due to handling materials containing the elements of interest.

2. EXPERIMENTAL

2.1. Sampling

Hair was cut close to the scalp from different locations of the head. The first 4 to 6 cm of recent growth were used for analysis. Nails were clipped from all fingers resp. toes. As far as possible, sampling of the 3 specimens was performed at the same day , resp. within at least 2 weeks. Period between sampling was 4 to 8 weeks depending an the individual growing rate of the toe nails.

2.2. Washing procedure

Hair samples were cleaned by stirring for 10 min periods with acetone, three times water and again acetone. For normal environmental or occupational exposed hair this method was found to remove external pollution completely. This was checked by leaching tests of 10 samples cleaned after the washing step by applying the procedure for nails described later.

Removement of external pollution was found to be the main problem in analysis of nails. About 110 samples were checked during this study. A more efficient cleaning was obtained first by application of an ultrasonic bath and 5 min contacts of the washing solutions [14] and second by replacing the water of the second washing step by a 2 % detergent solution (Deconex 11 NS, Borer Chemie, Switzerland). While the differences in the contents of Cu, Hg and Zn were not significant, most of the samples showed 15 - 70 % lower Cd and Pb concentrations applying detergent solution instead of water in the first washing step. For these tests nails were cut into small pieces and two subsamples were taken. Therefore, the following washing procedure for nails is proposed to remove external pollution: 5 min contacts in an ultrasonic bath with acetone, 2 % detergent solution (Deconex), 2 times water and again acetone. This method was used for all nail samples analyzed since 1981. The first 50 toe nail and 51 finger nail samples were cleaned with acetone and water in the ultrasonic bath.

2.3. Analysis

The cleaned samples were dried between filter paper for 24 h and weighed. 100 - 150 mg sample material was digested with 3 ml of 1:6 $HClO_4$: HNO_3 acid mixture at 110°C in closed teflon beakers for 45 min. After digestion the solutions were diluted to 100 ml and stored in polyethylene flasks. Electrothermal AAS was applied to analysis of Cd, Cu and Pb, cold vapor technique to determination of Hg and flame measurement for Zn using the conditions described earlier [15].

2.4. Samples

Samples were collected from 10 males and 2 females (No 9 and 11) working in the Austrian Research Centre. 5 persons are living in rural districts in Lower Austria (No 3, 5, 6 - near a main road, 9 and 12). All others are living in Vienna (No 2 in an industrial district). Higher concentration levels of pollutants were expected for those of the group working with solid (mainly No 4, 6, 7) and liquid (mainly No 1, 9 and 11) materials containing or consisting of the elements of interest.

3. RESULTS

3.1. Trace element contents in the hair and nail samples of the observed group.

In Tab. 1 and 2 the average trace metal contents of the hair and nail samples are summarized for each person.

Hair: In general, the levels in the hair samples of the group are relatively low, except the Cd and Pb contents in the samples of No 2. Code No 2 is living in an industrial district of Vienna, professional pollution should be neglectable (electronics engineer). This contamination was found in the hair samples only, showing a significant increase of Pb content between February and May 1981, then the concentration was decreasing slowly. The levels in toe nails are relatively low. To find out the reason for this contamination, hair samples of two members of No 2's family were analyzed. Cd and Pb contents of these samples were within the normal range. Therefore, the contamination could not be caused by industrial pollution of the living district. It was also supposed that the levels in hair are increased due to the hobby of No 2 (pistol shooting). Samples of another member of the club were analyzed and normal levels in hair and toe nails, slightly increased levels in finger nails were found. Probably two customs are responsible for the unusual ratio of No 2's hair and toe nails. Due to a very dry skin he is smearing the scalp with oil (in the oil no Cd and Pb was found) and is washing the hair in relatively long intervals.

Finger nails: Finger nails were available from 10 persons of the group only. In the samples of No 4, 6 and 7, persons frequently working in a workshop, higher Cd and Pb contents were found than in the samples of the other persons.

Toe nails: In relation to the other toe nail samples the Cd content in the samples of No 8 is very low. Toe nails of No 1 are indicating a Hg contamination. In December 1981 the Hg concentration increased significantly. A maximum was reached in February 1982, then the values decreased again. As for the Cd and Pb content of hair of No 2 these high Hg contents in some of the toe nails of No 1 are showing no correlation to the other specimens.

Tab. 1: Trace element contents in hair and nail samples of the observed group

Code No	Sample material	n	Mean values ($\mu g.g^{-1}$) Cd	Pb	Cu	Zn	Hg
1	Fingernails	11	0.83 ± 93 %	2.43 ± 42 %	9.17 ± 54 %	165.4 ± 22 %	1.46 ± 105 %
	Toenails	14	0.24 ± 119 %	1.89 ± 35 %	3.67 ± 29 %	154.1 ± 9 %	4.61 ± 146 %
	Hair	8	0.40 ± 27 %	4.15 ± 32 %	9.99 ± 17 %	189.0 ± 6 %	0.87 ± 62 %
2	Toenails	10	0.06 ± 34 %	1.01 ± 41 %	2.12 ± 21 %	80.3 ± 8 %	0.43 ± 53 %
	Hair	10	3.39 ± 67 %	44.95 ± 49 %	15.44 ± 44 %	106.0 ± 24 %	1.23 ± 55 %
3	Fingernails	9	0.60 ± 50 %	3.89 ± 56 %	10.68 ± 79 %	113.3 ± 23 %	0.56 ± 53 %
	Toenails	11	0.11 ± 75 %	0.91 ± 51 %	4.03 ± 58 %	102.0 ± 24 %	0.49 ± 59 %
	Hair	9	0.43 ± 90 %	2.46 ± 67 %	10.85 ± 23 %	169.7 ± 7 %	1.68 ± 67 %
4	Fingernails	8	1.66 ± 46 %	5.63 ± 37 %	8.90 ± 32 %	126.1 ± 21 %	0.47 ± 60 %
	Toenails	8	0.48 ± 111 %	5.52 ± 80 %	6.03 ± 36 %	108.5 ± 5 %	0.67 ± 173 %
	Hair	8	0.74 ± 134 %	7.57 ± 45 %	10.39 ± 37 %	159.6 ± 6 %	0.84 ± 67 %
5	Fingernails	11	0.34 ± 57 %	3.00 ± 64 %	5.28 ± 15 %	161.5 ± 8 %	0.82 ± 27 %
	Toenails	8	0.07 ± 32 %	1.12 ± 35 %	3.60 ± 12 %	122.5 ± 7 %	0.48 ± 30 %
	Hair	7	0.09 ± 50 %	0.87 ± 35 %	8.12 ± 19 %	167.3 ± 7 %	0.95 ± 52 %
6	Fingernails	7	1.08 ± 38 %	4.75 ± 53 %	8.54 ± 36 %	147.5 ± 8 %	0.54 ± 44 %
	Toenails	7	0.30 ± 30 %	2.55 ± 38 %	5.85 ± 28 %	135.3 ± 14 %	0.32 ± 50 %
	Hair	7	0.44 ± 32 %	4.80 ± 39 %	10.40 ± 18 %	210.0 ± 10 %	1.31 ± 45 %

Tab. 2: Trace element contents in hair and nail samples of the observed group

Code No	Sample material	n	Mean values ($\mu g.g^{-1}$) Cd	Pb	Cu	Zn	Hg
7	Fingernails	21	2.70 ± 52 %	15.38 ± 56 %	9.06 ± 38 %	143.2 ± 8 %	0.52 ± 51 %
	Toenails	15	0.24 ± 44 %	4.19 ± 50 %	4.71 ± 38 %	97.8 ± 13 %	0.34 ± 53 %
	Hair	15	0.80 ± 45 %	8.64 ± 46 %	10.47 ± 19 %	162.6 ± 10 %	1.33 ± 74 %
8	Fingernails	11	0.52 ± 49 %	2.71 ± 44 %	6.22 ± 16 %	141.4 ± 6 %	0.40 ± 15 %
	Toenails	10	0.02 ± 44 %	0.95 ± 36 %	2.57 ± 19 %	80.0 ± 9 %	0.34 ± 56 %
	Hair	10	0.25 ± 50 %	2.54 ± 76 %	10.67 ± 15 %	189.0 ± 4 %	1.00 ± 58 %
9	Fingernails	15	0.66 ±134 %	3.14 ±153 %	5.75 ± 28 %	129.0 ± 13 %	1.02 ± 37 %
	Toenails	15	0.07 ± 22 %	1.05 ±122 %	3.31 ± 29 %	118.2 ± 17 %	0.81 ± 77 %
	Hair	15	0.16 ±100 %	1.14 ± 40 %	8.39 ± 35 %	183.1 ± 4 %	1.33 ± 61 %
10	Fingernails	10	0.33 ± 67 %	2.18 ± 46 %	5.50 ± 21 %	120.3 ± 16 %	1.00 ± 40 %
	Toenails	9	0.09 ± 62 %	1.10 ± 32 %	2.66 ± 22 %	80.7 ± 11 %	0.70 ± 36 %
	Hair	8	0.10 ± 47 %	2.59 ± 33 %	9.17 ± 13 %	161.2 ± 9 %	1.80 ± 41 %
11	Toenails	11	0.15 ± 28 %	2.22 ± 55 %	3.16 ± 20 %	136.2 ± 13 %	0.80 ± 41 %
	Hair	11	0.24 ± 72 %	2.88 ± 34 %	15.97 ± 18 %	162.3 ± 6 %	1.00 ± 35 %
12	Fingernails	9	0.89 ± 83 %	3.48 ± 53 %	8.64 ± 22 %	130.7 ± 12 %	1.27 ± 68 %
	Toenails	9	0.07 ± 30 %	1.27 ± 25 %	4.29 ± 16 %	102.3 ± 5 %	0.94 ± 79 %
	Hair	9	0.33 ± 61 %	2.45 ± 38 %	11.64 ± 13 %	158.4 ± 8 %	3.27 ± 71 %

3.2. Fluctuation of trace element contents in hair and nails within the observation period.

Fluctuations of trace metal contents were found in hair and nails of all persons of the group. For some elements and some of the observed persons these variations are very high. In Tab 1 and 2 the relative standard deviations are listed in addition to the average trace metal concentrations. Precision of the analysis including measurement errors in the chemical preparation of the samples is in the range of ± 2 % to ± 8 % [15] and is less influencing these results. Zn and Cu contents in hair and nails of the group were relatively stable. Higher Cu fluctuations were found in two cases only, the finger nails of No 1 and finger and toe nails of No 3. Both persons are often handling Cu metal. Wide variations in Cd, Pb and Hg concentrations were found in samples of the persons working in the laboratory (No 1, 9) and in the workshop (No 4).

3.3. Ratio of trace metal contents in hair and nails

3.3.1 Ratio of the average contents. Comparing the average contents of trace metals in hair, finger and toe nails of each of the 12 persons the following results were obtained:

Cd, Pb, Cu, Zn, Hg	in fingernails	>	toe nails
Cd, Pb, Cu, Zn, Hg	in hair	>	toe nails
Cu, Zn, Hg	in hair	>	finger nails
Cd	in hair	<	finger nails
Pb [+]	in hair	≃	finger nails

[+]in average this ratio is about 1. For the observed persons ratios of 0.3 - 1.7 were found.

Except the unusual ratio of Hg in nails of No 1, only the relation of the Pb concentration in the hair and toe nails of No 5 are not fitting in these results. Among the persons of the group significant differences for the ratios were found mainly for the Cd and Pb ratio of hair and toe nails of No 2 and the Cd and Zn ratios of hair and toe nails of No 8. In relation to the Zn concentrations in these hair samples, the contents in the toe nail samples are relatively low. This could be influenced by a mycosis of the toe nails. Fig. 1 to Fig. 3 present the relations of the mean concentrations in the specimens of each person. Unusual ratios are marked by the code No.

FIG. 1: RELATION OF MEAN CONTENTS IN HAIR AND NAILS (PPM)

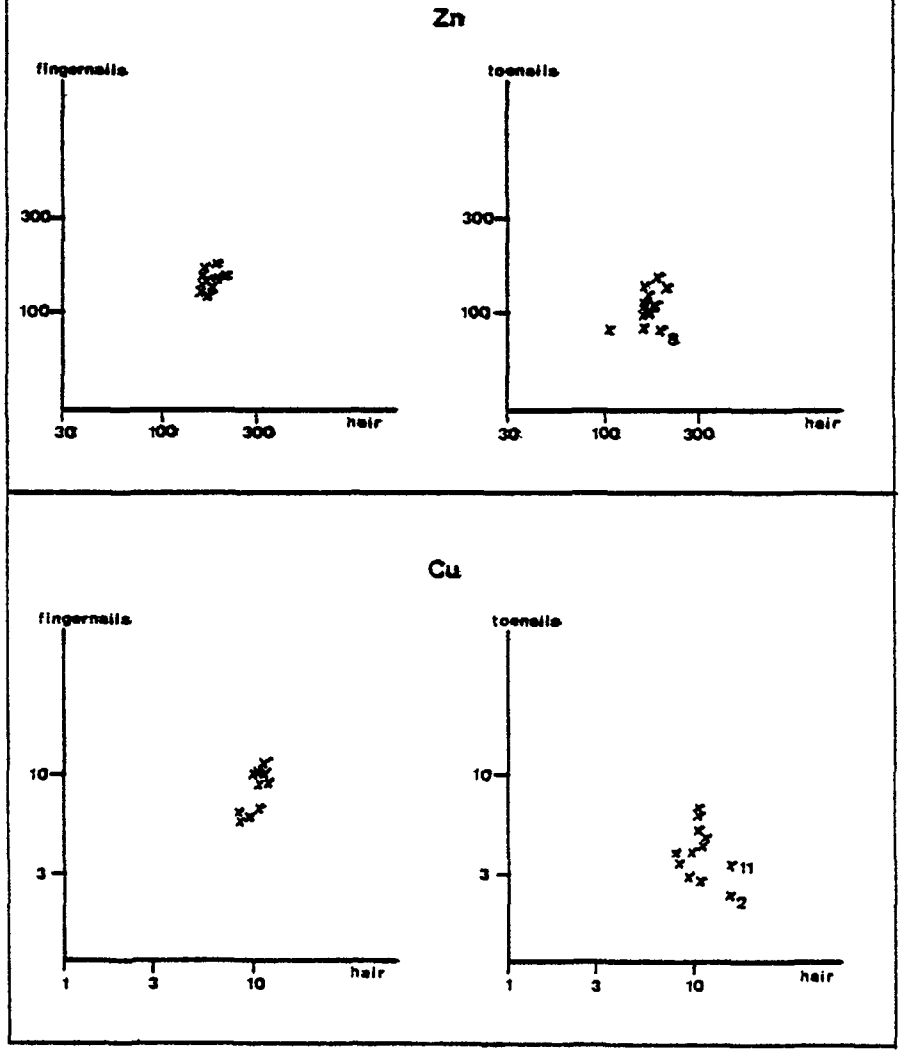
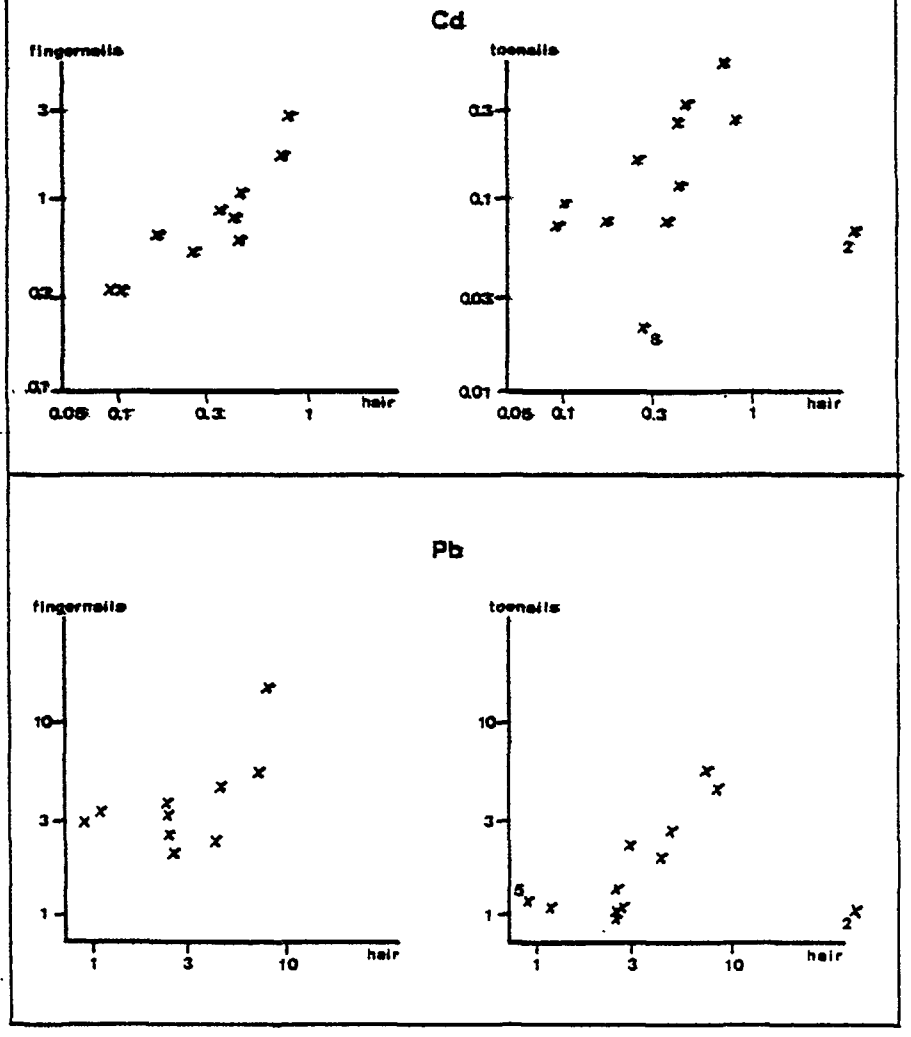


FIG. 2: RELATION OF MEAN CONTENTS IN HAIR AND NAILS (PPM)



In general, a trend was found that a decrease or increase in trace element contents in hair is often reflected by nails too. But there are also results like Hg and Pb in samples of No 1 and No 2 which are not indicating any relation between corresponding hair and nail samples. Moreover, in the calculation of the average ratios of contents in hair and corresponding nail samples (Tab. 3) high relative standard deviations were obtained in some cases. The deviations from the average values of the ratios are within a small range for Zn (6 values are out of ± 50%) and for Cu (more than 80% of the ratios are within ± 100%). For Cd, Pb and Hg, only 40% to 65% of the values are within ± 100%.

To judge the correlation between hair and nails a statistical evaluation of the correlation coefficient was carried out. Partly, the results were not meeting the terms for a Gaussian distribution. Therefore, the Spearman rank correlation coefficients were calculated. For the pollutants a correlation was obtained between hair and finger nails (Cd: 0.5, Pb: 0.47, Hg: 0.29) and finger and toe nails (Cd: 0.45, Pb: 0.65, Hg: 0.36), while hair and toe nails are showing a correlation for Pb only (Pb: 0.44). This result could not be influenced by replacement of outliers by 4 σ boundary values.

4. SUMMARY

Cd, Cu, Hg, Pb and Zn contents were analyzed in 350 hair and nail samples of 12 persons by atomic absorption spectrometry. While removement of external pollution from hair was done with acetone and water, for nails a more efficient cleaning with acetone, detergent and water in an ultrasonic bath had to be applied.

In average, contents of these analytes were found to be higher in hair and finger nails than in toe nails. Comparing hair and finger nails, higher Cu, Hg and Zn contents were obtained in hair and higher Cd concentrations in finger nails. Pb levels were similar in these two materials.

Cd, Hg and Pb concentrations were fluctuating in specimens of a person, while Zn and Cu were more stable. In two cases a contamination was reflected only by hair (Pb) resp. nails (Hg). Therefore, the relations of the mean values for these elements were significantly different to those of the others of the group. For one person an outlying Cd ratio, for another person unusual Pb and Zn ratios were found in the contents of hair and toe nails. For corresponding hair and nail samples the ratios of Zn and Cu contents are within a small range. Correlation was found for Cd, Pb and Hg between hair and finger nails and for Pb in hair and toe nails. For Cd and Hg in hair and toe nails the correlation coefficients were < 0.25.

In spite of the trend of nails to reflect often increased or decreased trace metal levels in hair, hair can be considered to be a more reliable indicator for uptake of pollutants.

Moreover, hair collection and cleaning is easier and sampling is not depending on the growing rate. Nail analysis seem to be often falsified by external pollution which could not be removed by the washing procedure. By the long contact of the nail clippings to environmental influences the results are not as evident as of hair samples taken from the first centimeters of recent growth. To get comparable results in the literature nail analysis, especially sampling and washing, should be standarized.

ACKNOWLEDGEMENTS

This work was done under a Research Contract with the International Atomic Energy Agency, Vienna. We are grateful for much assistance provided by colleagues, especially Mrs. A. Heinrich for sample pretreatment, Dipl. Ing. L. Riedlmayer for the statistical evaluation and Dipl. Ing. F. Helmreich (Department of Mathematics and Information) for the rank correlation.

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HUMAN SCALP HAIR AS AN EPIDEMIOLOGIC MONITOR OF ENVIRONMENTAL EXPOSURE TO ELEMENTAL POLLUTANTS

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Abstract

The suitability of using scalp hair as an epidemiological monitor of environmental exposure is being evaluated. Instrumental neutron activation analysis (INAA) methods using short-lived nuclides have been developed for simultaneous multielement determinations in scalp hair. Graphite furnace atomic absorption spectrometry (GFAAS) method has been used for measuring Pb and Cd. Precision and accuracy of the methods have been evaluated by analyzing standard reference materials and IAEA Intercomparison Hair Sample HH-1. A detailed study on different hair washing methods has been done and reported here. The effect of exogenous contaminants from shampoo on levels of certain elements has been studied. Variation of trace element levels along the longitudinal segments of hair strands has been investigated. The methodologies have been applied to screen population groups exposed to environmental arsenic and to study trichothiodystrophy.

1. INTRODUCTION

During the past 20 years or so various types of industry have become operational around the world - new processes and chemicals have been invented, and both their products and wastes have been discharged to the environment - to atmosphere, biosphere and hydrosphere. Many of these chemicals are known to contain toxic elements and other hazardous substances which are finding their ways to the central figure of environmental pollution problems - man himself. Toxic elements, either ingested or inhaled, from the environment can be translocated to scalp hair. The interest in hair trace element levels is evident from more than 500 papers published in open literature on this subject.

Scalp hair is being recognized as a tissue which incorporates elements into its structure during the growth process, after which it becomes separated from continual metabolic activity of the body (1). It is a stable material which is painlessly removed, generally discarded, readily collected, conveniently transported and easily preserved.

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Levels of most toxic elements in scalp hair are at least an order of magnitude higher than that found in other tissues and body fluids; consequently, hair samples of lower mass can be analyzed with better precision and accuracy. Less interferences are also encountered in most hair elemental measurement techniques. Obviously, there are many advantages in using scalp hair as an indicator for screening population groups exposed to environmental pollutants. Such usage of scalp hair is, of course, not free from opposing viewpoints. In this regard, two most commonly referred items are: (a) separation of endogenously deposited elements from exogenous contaminants in hair; and (b) ability of hair to reflect dose-response relationship. While we have attempted to resolve the first item by developing hair washing methods and comparing various available methods, the second item needs to be further evaluated by using animal models and/or autopsy samples.

During the tenure of this co-ordinated research program (CRP) organized by the International Atomic Energy Agency (IAEA), we have concentrated our efforts (a) to develop instrumental neutron activation analysis (NAA) methods using short- to medium-lived nuclides and graphite furnace atomic absorption spectrometry (GFAAS) methods for Cd and Pb; (b) to evaluate the quality (precision, accuracy and detection limit) of analytical data by analyzing the IAEA Intercomparison Hair sample and several other standard reference materials; (c) to compare available hair washing methods using in-house hair standards; (d) to examine the effectiveness of the washing methods by applying them to hair samples which have been treated with contaminants; (e) to study the variation of trace elements along the longitudinal segments of hair strands; and (f) to apply these methods for analyzing hair samples collected from a population group exposed to environmental arsenic and from individuals with neuroectodermal symptom complex.

2. DEVELOPMENT OF ANALYTICAL METHODS

Neutron activation analysis methods have been developed for the simultaneous determination of multielement concentrations in human scalp hair. Levels of Cd and Pb in hair have been measured using atomic absorption spectrometry.

2.1 Instrumental neutron activation analysis (INAA)

There are several elements which give long-lived (half-life 65 d) nuclides on thermal and resonance neutron activation. The sensitive detection of these nuclides normally require lengthy irradiation, decay, and counting periods. Some of these elements can also be determined through short-lived isomers of the long-lived nuclides and through alternate short-lived nuclides. At least 38 elements are known to produce both short- and long-lived neutron activation products (2). The application of short-lived nuclides in routine measurements can reduce total analysis time and provide superior detection limits in many cases. The objective of this study was to develop INAA methods for the simultaneous determinations of multielement concentration in human scalp hair using short- and medium-lived nuclides.

INAA methods based on the principles of conventional one-shot irradiation as well as cyclic activation were developed. The cyclic activation technique involves the irradiation of a sample for a short time, transferring it quickly to a detector counting the induced activities and repeating the process several times. During the early stages of our investigation on short-lived nuclides, a cyclic INAA (CINAA) method consisting of manual transfer of a sample was developed (3,4). A pneumatic, automated rapid transfer sample recycling system was later designed (5) and subsequently improved (3,4,6). A computer program was developed to theoretically calculate the optimum timing parameters for simultaneously determining a number of short-lived nuclides (7). A method was also developed to correct for coincidence losses in high count rate gamma-ray spectrometry (4,8).

The INAA methods were applied to human scalp hair. The nuclear data for the elements detected in hair are shown in Table 1. The timing parameters used and nuclides detected were as follows: (A) irradiation time (t_i) of 30 s, decay time (t_d) of 10 s, and counting time (t_c) of 20 s for ^{110}Ag, ^{28}Al, ^{80}Br, ^{49}Ca, ^{38}Cl, ^{20}F, ^{128}I, ^{27}Mg, ^{56}Mn, ^{24}Na, ^{86m}Rb, ^{46m}Sc, ^{77m}Se and ^{52}V; (B) t_i = 10 min, t_d = 5 min, and t_c = 5 min for ^{28}Al, ^{139}Ba, ^{49}Ca, ^{66}Cu, ^{128}I, ^{42}K, ^{27}Mg, ^{56}Mn, ^{24}Na, ^{37}S, ^{51}Ti, ^{239}U, ^{52}V and ^{69m}Zn; (C) t_i = 16 h, t_d = 2 d, and t_c = 3000 s for ^{76}As, ^{198}Au, ^{82}Br and ^{122}Sb; and (D) t_i = 16 h, t_d = 21 d, and t_c = 3000 s for ^{110m}Ag, ^{131}Ba, ^{60}Co, ^{51}Cr, ^{59}Fe, ^{203}Hg, ^{140}La, ^{86}Rb, ^{46}Sc, ^{75}Se and ^{65}Zn.

Table 1. NUCLEAR DATA FOR ELEMENTS DETECTED BY INAA

Element	Nuclide	Half-life	Photopeak used, keV
Ag	^{110}Ag	24.4 s	658
Al	^{28}Al	2.24 min	1779
As	^{76}As	26.3 h	559
Au	^{198}Au	2.7 d	412
Ba	^{139}Ba	82.9 min	166
Br	^{80}Br	17.6 min	617
Ca	^{49}Ca	8.72 min	3084
Cl	^{38}Cl	37.3 min	1642
Co	^{60}Co	5.27 a	1332
Cr	^{51}Cr	27.7 d	320
Cu	^{66}Cu	5.1 min	1039
F	^{20}F	11.2 s	1633
Fe	^{59}Fe	44.6 d	1099
Hg	^{203}Hg	46.8 d	279
I	^{128}I	25 min	443
K	^{42}K	12.4 h	1525
La	^{140}La	40.3 h	487
Mg	^{27}Mg	9.46 min	1014
Mn	^{56}Mn	2.58 h	1811
Na	^{24}Na	15.0 h	1369
Rb	^{86m}Rb	1.02 min	556
S	^{37}S	5.1 min	3102
Sb	^{122}Sb	2.68 d	564
Sc	^{46m}Sc	18.7 s	142
Se	^{77m}Se	17.4 s	162
Ti	^{51}Ti	5.8 min	320
U	^{239}U	23.5 min	74
V	^{52}V	3.76 min	1434
Zn	^{65}Zn	244 d	1115

2.2 Graphite furnace atomic absorption spectrometry (GFAAS)

Concentrations of Pb and Cd were measured using a GFAAS method. A Perkin-Elmer model 403 atomic absorption spectrometer in conjunction with a Perkin-Elmer HGA 2200 graphite furnace and autosampler AS-1 was used for this purpose.

The hair samples were digested in a TEFLON bomb at about 100 °C for 16h in 2mL ULTREX concentrated nitric acid. The volume was then made up to 10mL with Super-Q water. The experimental conditions for the analyses of Pb and Cd by GFAAS are given in Table 2.

Table 2. EXPERIMENTAL CONDITIONS FOR ANALYSIS OF CADMIUM AND LEAD BY GFAAS.

Parameters	Cadmium		Lead	
	time	temp.,°C	time	temp.,°C
Drying	20 s	90	20 s	100
Charring	10 s	300	15 s	400
Atomizing	4.5 s	2200	5 s	2200
Wavelength	227.6 nm		282.5 nm	
Slit width	4		3	
Flow time	3 norm		3 norm	
Gas supply	40		30	
Gas	argon		argon	
Linear range	DL - 5 ppb		DL - 10 ppb	

DL - detection limit

3. EVALUATION OF PRECISION AND ACCURACY

Precision and accuracy of the INAA and GFAAS methods were evaluated by analyzing replicate samples, in-house hair standards, standard reference materials (SRM), certified reference materials (CRM), and intercomparison samples. The SRM included the National Bureau of Standards (NBS) Bovine Liver (both 1577 and 1577a), Oyster Tissue, Orchard Leaves, Spinach, Tomato Leaves, Pine Needles and Citurs Leaves. Several CRM supplied by the IAEA were analyzed; these included Animal Muscle, Animal Bone, Fish Solubles and Milk Powder. The IAEA Intercomparison Hair Sample HH-1 (1980) was also analyzed by the INAA and GFAAS methods, and the results are presented in Table 3. Most of our results agree very well with those reported by M'Baku and Parr (9). The causes for apparent deviations of Au, Cu and Na concentrations are not fully known at this stage. It should, however, be pointed out that we have measured the Cu level of HH-1 as 10.6±1.0 ppm in recent experiments.

The GFAAS result of 2.6±0.3 ppm Pb compares favorably with that of 2.73 ppm in HH-1 reported by M'Baku and Parr (9). Our Cd value of 0.177±0.02 ppm by GFAAS is, however, lower than the certified value of 0.26 ppm. On the other hand, the Cd content

Table 3. ELEMENTAL CONTENT OF IAEA INTERCOMPARISON RUN HH-1 (1980)

Element	Individual Determinations[a]						Average ± r.s.d.[a]	IAEA value[a]
	1	2	3	4	5	6		
Ag	0.12	0.20	0.18	0.13	0.07	0.15	0.16±0.04	-
Al	5.8	6.6	6.5	6.2	7.1	6.9	6.5±0.5	-
As	0.052	0.053	0.059	0.052	0.053	0.054	0.054±0.003	0.053
Au[b]	0.150	0.162	0.155	0.154	0.154	0.157	0.155±0.004[b]	0.025
Ba	2.3	7.5	3.5	8.1	4.4	2.6	4.7±2.5	-
Ca	550	500	540	548	555	550	540±20	522
Cl	2070	1995	2010	1940	2030	1950	2000±50	2270
Co	5.76	5.79	5.93	5.76	5.91	6.08	5.87±0.13	5.97
Cu	9.4	7.5	8.5	10.4	8.0	7.3	8.5±1.2[d]	10.2
F	870	1000	840	970	800	890	900±85	-
Hg	1.71	1.77	1.81	1.74	1.80	1.76	1.77±0.04	1.70
I	24.2	22.9	23.7	24.8	23.8	24.3	24.0±0.7	-
K	10	10	9	11	9	8	10±1	-
Mn	0.92	1.2	0.59	0.86	0.52	0.98	0.85±0.25	0.85
Na	23.2	24.6	23.1	23.4	23.4	23.2	23.5±0.6	12.6
S[c]	4.34	4.20	4.24	4.00	4.00	4.25	4.22±0.11	4.9
Sb	0.028	0.025	0.027	0.024	0.026	0.025	0.026±0.001	0.031
Se	0.33	0.36	0.27	0.27	0.23	0.28	0.29±0.05	0.35
Zn	1.74	178	176	178	176	179	177±2	174

[a] All values are in ppm except otherwise mentioned
[b] in ppb
[c] in %
[d] see text for details

of NBS SRM-1577 Bovine Liver of 0.278±0.03 ppm measured in our laboratory agrees well with the value of 0.27±0.04 certified by the NBS, indicating the reliability of the GFAAS method for Cd.

4. CALCULATION OF DETECTION LIMITS

There are various methods to calculate limits of detection in INAA. We have used the method prescribed by Currie (10) for calculating critical limit (L_C), qualitative detection limit (L_D) and quantitative determination limit (L_Q) for several elements in IAEA Intercomparison Run HH-1 hair sample. These limits are presented in Table 4. Almost all elements measured in HH-1 were above their respective L_D values. The limits could be further improved by using a neutron flux higher than that was available for the present study, viz. 5×10^{11} n cm^{-2} s^{-1}. However, this may not be necessary.

5. COMPARISON OF HAIR WASHING METHODS

Since hair is inherently an oily tissue which is being constantly exposed to exogenous contaminants, any trace element analysis must take into account the possibility that what is measured may not all be elements deposited internally in hair tissue during the growth process within the hair scalp follicle. For this reason various hair washing procedures have been used in order to remove exogenous contaminants. IAEA has recommended a washing method of 10 min contacts with 25 mL portions of acetone, water, water, water and acetone, successively (11). However, different washing procedures are still being used, and controversy continues to brew.

Table 4. DETECTION LIMITS OF ELEMENTS IN IAEA INTERCOMPARISON RUN HH-1 (1980)

Element	Critical limit, L_C	Qualitative Detection Limit, L_D	Quantitative Determination Limit, L_Q
Ag	0.065	0.14	0.54
Al	0.81	1.6	5.2
As	0.023	0.046	0.15
Au	9.9×10^{-4}	2.0×10^{-3}	6.3×10^{-3}
Ba	3.6	7.6	23
Br	0.077	0.16	0.50
Ca	28	52	210
Cl	6	13	41
Co	0.047	0.097	0.35
Cu	1.9	3.8	12
F	11	23	100
Fe	35	73	250
Hg	0.10	0.20	0.68
I	0.13	0.26	0.84
K	8	16	53
Mg	47	95	310
Mn	0.37	0.75	2.4
Na	2.0	4.1	13
S,%	0.14	0.28	1.14
Sb	0.022	0.045	0.14
Sc	0.0016	0.0034	0.012
Se	0.078	0.16	0.56
V	0.032	0.065	0.21
Zn	1.7	3.5	12

All values are in ppm except for S which is in %

The purpose of this study was to investigate the effect of washing hair with ethylenediaminetetraacetic acid (EDTA), sodium dodecyl sulphate (SDS, an ionic detergent), Triton X-100 (TR, a non-ionic detergent), acetone, ether, ethanol, water, hydrochloric acid and sodium hydroxide on different elements commonly found in hair. The results of these washing methods were compared with that of IAEA. The efficacy of the suggested washing procedures in removing external contaminants due to the usage of certain shampoos was also studied. Details of the results will be published separately (12); the highlights of the investigation are described below.

5.1 Preparation of in-house hair standards

In order to compare different washing methods using a homogeneous hair sample, it was necessary to prepare about 50g of a hair standard. For this purpose, hair samples from two males were collected over a period of one year. None of these persons used any special hair treatment except ordinary shampoo; and they are normal healthy males residing in Halifax, NS, Canada, and working as academics.

The samples were first cut to small sections (0.5-0.7 cm) and homogenized thoroughly without treating them with any wash solution (even water). They were designated as "Stock A" and "Stock B" in-house hair standards.

Six samples of each of the hair standards were analyzed by both INAA and GFAAS methods for 18 elements. The results are presented in Table 5. It appears that both the standards are fairly homogeneous with respect to the elements measured.

Table 5. ELEMENTAL CONTENT OF UNWASHED IN-HOUSE HAIR STANDARDS

Element	Content[a]	
	Stock "A"	Stock "B"
Al	23.8±2.6	24.2±2.5
As	0.276±0.015	0.102±0.019
Au	0.015±0.001	0.12±0.008
Br	14.7±0.77	3.32±0.19
Ca	2008±54	1000±31
Cl	325±15	318±13
Co	6.70±1.64	---
Cu	21.4±1.35	12.9±2.6
Hg	2.36±0.19	2.46±0.13
I	0.27±0.036	0.40±0.04
Mn	0.98±0.08	0.69±0.05
Na	156±6	104±17
Pb	4.94±0.39	4.57±0.68
S[b]	4.43±0.2	4.20±0.18
Sb	0.302±0.09	0.260±0.08
Se	1.21±0.15	0.92±0.13
V	0.17±0.01	0.20±0.02
Zn	220±5.6	156±11

[a]All values are in ppm except otherwise noted; average of six determinations.

[b]in %

5.2 General procedure

The following reagents were selected as wash solutions: deionized water, acetone, ether, hexane, ethanol, 1% SDS, 1% TR, 1% disodium EDTA, 0.1M HCl and 0.1M NaOH. The volume of the washing reagent used was 20mL each time. Approximately 250 mg of the hair standards were placed with the wash solution in a 75mL polyethylene beaker and shaken in a wrist action shaker. The samples washed with detergents were further rinsed with water to remove sud. Each sample was subdivided and analysed by both INAA and GFAAS.

5.3 Comparison of pre- and post-irradiation washings

The extent of variation caused by different washing methods was studed by washing the in-house hair standards before and after irradiations. The hair samples were washed for 5, 10, 15 min, 1 and 24 h before the irradiation, and for 1, 3, 5, 15 min, 1 and 24 h after the irradiation. Only the nuclides with half-lives greater than 10 h (viz. those of Au, Br, Co, Hg, Na and Zn) were measured in post-irradiated and washed samples due to the time required to process the samples.

The results for post- and pre-irradiation washings of hair with water are shown in Fig. 1. Zinc and Hg are not effected by washing compared to the extent Au, Br, Co and Na are. In post-irradiation washing 80-90% Zn and 80-100% Hg are retained while 80-85% Zn and 80-90% Hg are held back in pre-irradiation washing. Cobalt is reduced to less than 2% in both washings. The degres of removal of Na and Br depends very much on the shaking time.

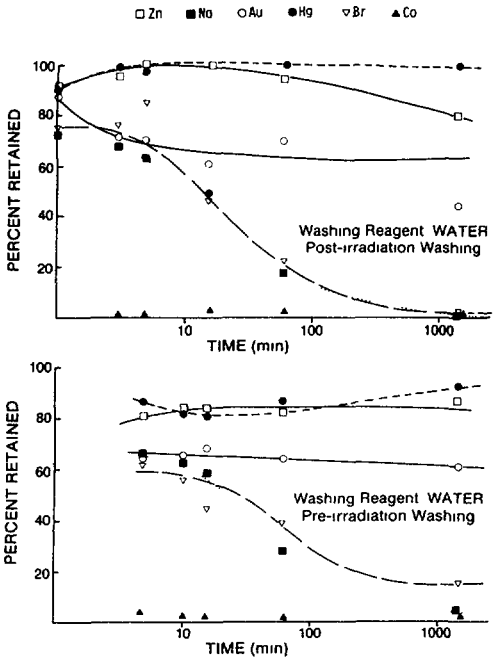

Fig.1. Comparison of post- and pre-irradiation washings of hair with water.

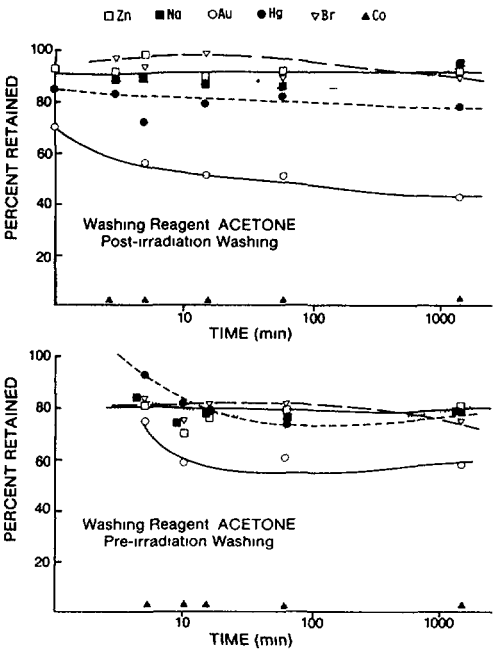

Fig.2. Comparison of post- and pre-irradiation washings of hair with acetone

Post- and pre-irradiation washings of a hair standard with acetone are graphically presented in Fig. 2. Cobalt is again reduced to 1-2% in both types of measurement. The leaching of Co and Au by acetone is similar to that by water. Levels of Na and Br are not reduced as much in acetone as in water. The results of washings with SDS and TR are very similar to each other.

Two conclusions can be drawn from the comparison of pre- and post-irradiation washings: (a) there is not much evidence of Szillard-Chalmer Effect; and (b) washing treatment, in general, does not introduce contamination with the exceptions of SDS, NaOH and EDTA where samples were contaminated with Na, and with Cl in case of HCl.

5.4 Comparison of different washing agents

Acetone, ether, Triton X-100, SDS, EDTA, deionized water, hydrochloric acid and sodium hydroxide were used to wash a hair standard prior to irradiation. The results are shown in Figs. 3 and 4 for Cu, Hg, Au and Zn. Acetone, ether, TR, SDS and water show similar behavior. There might be some leaching effect, however, it is not as drastic as in the case of EDTA, HCl and NaOH. Levels of Au, Hg and Zn are significantly reduced by HCl and NaOH washes. The effect of increased shaking time on percent reduction of certain elements such as Mn, Au, etc. in EDTA wash has been noted. Data on several other elements have shown that they can be leached out in considerable proportions from the hair shaft by washing with NaOH, HCl and EDTA. It should also be noted that these reagents and SDS contaminate the hair samples with Na and Cl which seriously interfere in the determinations of short- and medium-lived nuclides by INAA.

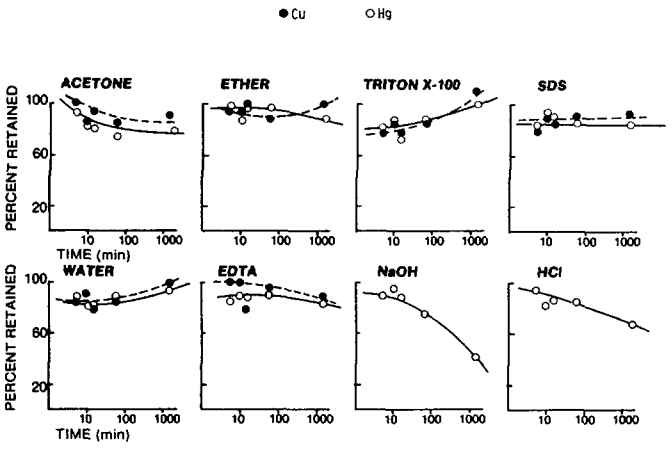

Fig.3. Effects of different washing agents and time on Cu and Hg content of hair.

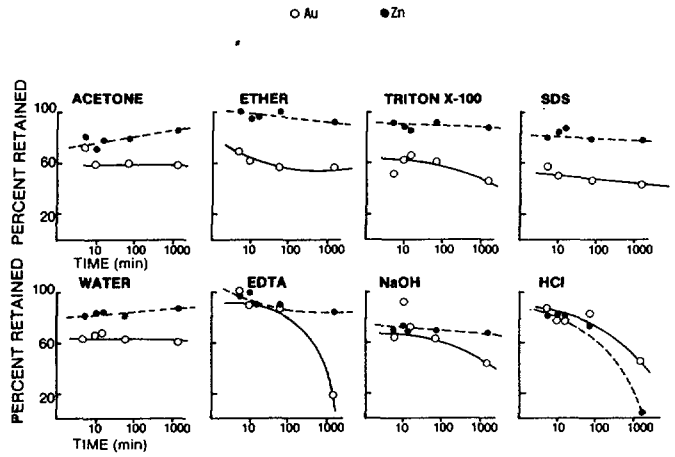

Fig.4. Effects of different washing agents and time on Au and Zn content of hair.

It is clear from the results obtained in this study that two factors are mainly responsible for the leaching of elements from hair strands, and these are (a) washing agent and (b) time of contact. In order to get reproducible results, the washing reagent and contact time must be selected such that the elemental concentration reaches a constant value, i.e. further washings should not change the concentratins of all the elements. Since different elements are affected by various reagents to different degrees, reproducible multielement hair levels can be obtained by short washing periods with a combination of different reagents. The following combination of washing reagents were selected for further studies: (a) acetone, water, water, water, acetone (the IAEA procedure); (b) ether, water, acetone (E-W-A); (c) Triton X-100, water, water (TR); (d) SDS, water, wter (SDS); (e) alcohol, water, hexane (A-W-H); and (f) alcohol, ether, water (A-E-W).

5.5 Comparison of combination of washing agents

The stock "A" hair standard was kept in contact for 10 min with 20mL of each of the above washing reagent. In order to obtain reproducible results, these washing procedures must bring the concentration of the elements to a constant level. To evaluate this, the hair samples were wshed one, two and three times using the washing reagents (a), (b), (c) and (d). The results for Al, Au, Cu, Hg, Na and Zn are presented in Fig. 5. Concentrations of Al, Au, Cu, Hg and Zn are fairly constant with the number of washings suggesting that the elements have reached a constant level after the first wash, and that further washing has no real effect.

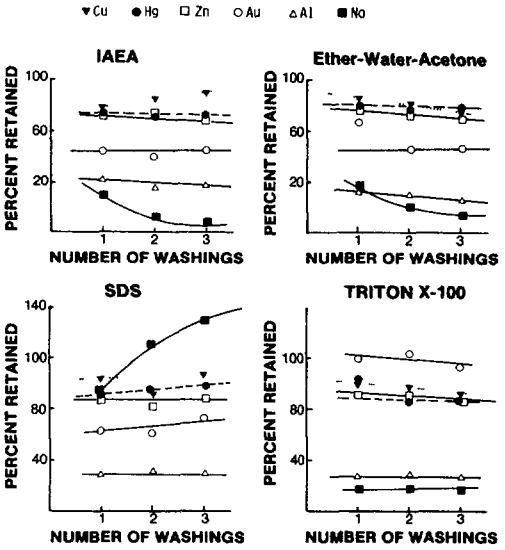

Fig.5. Effects of different washing procedures and number of washings on Al, Au, Cu, Hg, Na and Zn content of hair.

The effect of washing the Stock "A" hair standard with several combination of reagents on the multielement content is shown in Table 6. Concentrations of Au, Ca, Cu, Hg, I, Pb, S, Se, V and Zn are found to be essentially the same after being washed with several washing procedures. Values for As are not reproducible due to interference from the 554-keV gamma-ray of ^{82}Br on the 559-keV gamma-ray of ^{76}As. The large variation in Sb levels after washing by different procedures may be caused by inhomogeneity of Sb in the washed hair samples. The variation in Mn concentrations after washing cannot be contributed by the washing reagent contamination since these reagents were analyzed for multielement content and found to be fairly pure.

Table 6. COMPARISON OF DIFFERENT WASHING METHODS USING STOCK "A" HAIR STANDARD

Element	Content[a]				
	Unwashed	IAEA	SDS	TRITON-X	E-W-A
Al	23.8±2.6	9.34±0.29	6.21±0.73	7.80±0.83	6.99±0.75
As	0.276±0.015	0.031±0.01	0.044±0.02	0.020±0.01	0.072±0.02
Au	0.015±0.001	0.009±0.0001	0.0080±0.0001	0.0098±0.0015	0.0096±0.003
Br	14.7±0.77	6.63±0.58	5.48±0.34	5.24±0.33	9.13±0.32
Ca	2008±54	1715±63	1532±49	1575±55	1668±36
Cl	325±15	155±7	141±30	124±23	200±18
Co	6.70±1.64	0.128±0.02	0.11±0.01	0.119±0.04	0.127±0.003
Cu	21.4±1.35	19.93±1.06	20.6±2.6	22.24±1.9	21.5±2.75
Hg	2.36±0.19	2.37±0.19	2.32±0.22	2.21±0.20	2.40±0.22
I	0.27±0.036	0.26±0.037	0.264±0.03	0.287±0.018	0.252±0.04
Mn	0.98±0.08	1.29±0.12	1.76±0.03	2.70±0.40	1.80±0.54
Na	156±6	44±7.8	166±16	28.7±2.1	66±6
Pb	4.94±0.39	0.375±0.04	0.436±0.04	0.407±0.04	0.489±0.05
S[b]	4.43±0.2	4.32±0.18	4.5±0.13	4.48±0.09	4.45±0.24
Sb	0.302±0.09	0.26±0.11	0.23±0.11	0.078±0.02	0.26±0.11
Se	1.21±0.15	1.03±0.23	1.08±0.20	0.98±0.23	1.01±0.13
V	0.17±0.01	0.115±0.02	0.080±0.013	0.10±0.017	0.110±0.006
Zn	220±5.6	209±7.3	197±5.3	207±3.3	217±9.2

[a] All values are in ppm except otherwise noted; average of six determinations.

[b] in %

5.6 Effect of changing the order of reagents in a washing procedure

Hair strands, when washed with water, are known to swell to a certain degree. This swelling might affect the rate of removal of contaminants during the washing process. In order to evaluate this effect, hair samples were washed with the E-W-A procedure according to the following scheme: (i) ether-water-acetone; (ii) ether-acetone-water; and (iii) water-ether-acetone. The results reveal that there is no difference in the elemental content (with the exception of Mn) of the hair standard no matter which order is used as long as the same reagents and contact times are involved. It can therefore be concluded that swelling of hair by water does not affect the contamination removal efficiency of the washing procedure.

5.7 Comparison of hair-wash solution shaking techniques

In the past, hair samples were generally washed using wrist action shakers. With the availability of ultrasonic baths, a few workers have used them possibly thinking that these baths may be superior to wrist action shakers in removing loosely attached dust particles in hair strands.

The effect of different shaking techniques on the efficacy of a given washing procedure was evaluated in this study. Samples of the Stock "A" hair standard were washed by the IAEA washing procedure using a wrist action shaker and an ultrasonic bath, and then the multielement content of the samples were determined using the INAA and GFAAS methods. The results are presented in Table 7. Essentially the same elemental concentrations were obtained using the two shaking techniques.

Table 7. COMPARISON OF TWO WASHING TECHNIQUES USING THE STOCK "A" HAIR STANDARD AND IAEA WASHING METHOD

Element	Content[a]		
	Unwashed	Ultrasonic	Wrist Action
Al	23.8±2.6	12.5±1.6	9.34±0.29
As	0.276±0.015	0.035±0.01	0.031±0.01
Au	0.015±0.001	0.012±0.002	0.009±0.001
Br	14.7±0.77	7.37±0.79	6.63±0.58
Ca	2008±54	1787±41	1715±63
Cu	21.4±1.35	21.7±1.63	19.93±1.06
Hg	2.36±0.19	2.00±0.14	2.37±0.19
I	0.27±0.036	0.28±0.016	0.26±0.037
Mn	0.98±0.08	3.17±0.12	0.29±0.12
Na	156±6	44.2±3.45	43.9±7.8
Pb	4.94±0.39	0.377±0.04	0.375±0.04
S[b]	4.43±0.20	4.36±0.97	4.32±0.84
Sb	0.302±0.09	0.117±0.003	0.26±0.11
Se	1.21±0.15	1.14±0.24	1.03±0.23
V	0.17±0.01	0.116±0.006	0.115±0.02
Zn	220±5.6	203±5.7	209±7.3

Identical shaking time used; average of six determinations.

[a]All concentrations are in ppm except otherwise noted.

[b]in %

Exceptions to this conclusion were Al, Mn and Sb, of which the variations in Mn and Sb have been described above. The reason for the difference in Al levels is not clear at this stage.

5.8 Effect of shampoo on trace element content of hair

The objective of this study was to compare some of the washing methods for removing exogenous contaminants deposted on hair strands by the usage of shampoo. Preliminary results were presented in the first research progress report (13) and in a thesis (14). Trace element concentrations of 23 commonly used shampoos were determined by INAA. The "Head & Shoulders" and "Dan Gard" shampoos were found to contain 3.9 and 1.1 mgZn/g, and "Selsun Blue" had 3.9 mgSe/g of shampoo. Detailed studies on the effect of these shampoos on the hair Zn and Se content, and the efficiency of the washing methods to remove them from hair were carried out. Results obtained are briefly described below.

Five percent solutions of the "Head & Shoulders", "Dan Gard", "Selsun Blue" and "Old Spice" (which has a very low metal content) shampoos were prepared. Each hair sample was separately dipped in a shampoo solution (10mL) for 10 min. The samples were filtered and washed with deionized water until they were free from suds. These exposed samples were then washed with various washing procedures and analyzed by INAA.

The hair sample treated with "Selsun Blue" had 183% increased Se content. After washing it with various wash procedures, the Se content was not reduced to that of the untreated level and remained high. It appears that Se from "Selsun Blue" is irreversibly adsorbed on the hair strand and cannot be completely removed by any of the washing procedures used in this study.

The Zn concentration of the hair sample dipped in 5% "Head & Shoulders" shampoo solution increased, slightly by 22%, after rinsing with water. Only when the samples were washed with SDS, the Zn levels were reduced back to those of the untreated samples. The IAEA washing procedure gave a 13% increase in Zn levels.

In order to evaluate the efficiency of the IAEA and SDS washing procedures for removing Cu, Hg and Zn, 50 μg/mL of these elements were added to a 5% solution of the "Old Spice" shampoo. The standard hair samples were dipped in this solution for 10 min, and then rinsed with water to remove suds prior to washing them by the IAEA and SDS procedures. The added Cu and Zn were completely removed by both the above procedures. However, Hg could not be removed by either of the washing procedures.

It can be concluded from the above results that most of the elements exogenously deposited by shampoos can be quantitatively removed by both the IAEA and SDS washing procedures with the exceptions of Se and Hg. Extreme caution must be exercised in interpreting hair Se levels where a person uses Se-containing shampoo; however, this is not a serious handicap since such persons can be easily identified by filling up a well-designed questionnaire. Although it appears that Hg can be irreversibly adsorbed by keratin, no shampoo containing detectable amounts of Hg has yet been found indicating that the increase in hair Hg levels from the usage of shampoo is highly unlikely. However, the situation could be quite different where a person is occupationally exposed to high atmospheric Hg levels.

6. APPLICATION OF HAIR TRACE ELEMENT DATA

A number of hair samples were analyzed by INAA over the last few years for a number of purposes. The applications include environmental and occupational exposures, suspected poisoning cases, hair disease, and baseline level studies. A couple of applications are described below.

Scalp hair samples from the residents of Waverley, Nova Scotia, Canada, were analyzed for As levels in an epidemiological survey. Samples of water from several wells in the Waverley area were found to contain high amounts of As which might have come from the leaching of arsenopyrite ores. Hair As concentrations were determined by INAA in an attempt to measure the body burden of As arising from drinking As-contaminated well water. The results of this survey are shown in Table 8. Approximately 58% of the individuals tested had more than 1 ppm and about 37% had more than 2 ppm As in hair. It appears that even modest elevations in hair As over 1 ppm can cause electromyographic abnormalities. Intakes of As estimated from the concentration of contaminated well water suggested that a 1 g accumulative As intake would lead to a 2 ppm hair As level. (Ref. 64 in Ref. 15).

Table 8. ARSENIC CONTENT OF HAIR FROM WAVERLEY, NOVA SCOTIA RESIDENTS

Range, ppm	Distribution, %
> 0.5	33.3
0.5 - 1.0	8.34
1.0 - 1.5	8.34
1.5 - 2.0	12.5
2.0 - 2.5	12.5
2.5 - 3.0	4.17
3.0 - 3.5	0
3.5 - 4.0	0
4.0 - 4.5	4.17
4.5 - 5.0	8.34
5.0 - 5.5	0
5.5 - 6.0	0
6.0 - 6.5	4.17
> 6.5	4.17

Table 9. COMPARISON OF ELEMENTAL CONTENT OF NORMAL AND SULFUR-DEFICIENT HAIR (TRICHOTHIODYSTROPHY)

Element	Content[a]	
	Normal Hair	Sulfur-deficient Hair
Ag	1.2	0.3
Al	32	51
As	0.62	0.65
Au	1.25	0.51
Ba	9.4	4.9
Br	17.5	23.4
Ca	190	510
Cl[b]	1.09	0.813
Co	0.08	0.21
Cr	0.40	0.75
Cu	167	13
Fe	454	853
Hg	0.28	0.25
I	0.26	0.28
K	3460	2620
La	0.073	0.078
Mg	52	215
Mn	2.9	2.0
Na[b]	0.301	0.343
Rb	3.3	1.6
S[b]	3.46	1.29
Sb	0.25	0.12
Sc	0.023	0.0098
Se	0.15	0.21
Zn	95	98

[a] All concentrations are in ppm except those of Cl, Na and S.

[b] Concentrations are expressed in percentages.

Trichothiodystrophy, or sulphur-deficient brittle hair, was suggested (16) as a clinical marker for a "neuroectodermal symptom complex that usually features mental and physical retardation and may also include nail dystrophy, lamellar ichthyosis, ocular displasia, dental caries, and decreased fertility". Hair samples from a normal boy and a patient of the same age suffering from trichothiodystrophy (both are from the same town) were analyzed for trace elements (Table 9). Concentrations of several elements including Ca, Cu, Fe, Mg and S were found to differ significantly in these two hair samples. Amino acid analyses of hair and fingernails also showed considerable differences (16).

7. ELEMENTAL CONTENT OF LONGITUDINAL SECTIONS OF HAIR STRANDS

Since scalp hair is a progressively growing tissue and the growth rate is fairly constant at about 1.1±0.2 cm per month (17), sectioning of hair strands prior to analysis can provide information on the variation in body metal content over the period of time encompassed by the entire hair length, typically 16-18 months. It has also been suggested that sweat can translocate elements from root to the distal end along the hair shaft. In order to examine the fate of trace elements along the shaft, a hair sample was cut into 4 cm sections and analyzed by INAA. The results are presented in Table 10. Several trends can be identified. Further research in this area is being done.

Table 10. ELEMENTAL CONTENT OF SEGMENTS OF HAIR STRANDS[a]

Element	0-4 cm	4-8 cm	8-12 cm	12-16 cm	16-20 cm	20-24 cm	>24 cm
Al	23.6	21.2	16.4	18.6	16.8	34.1	61.5
As	0.052	0.013	0.044	0.010	0.014	0.027	0.086
Au	0.053	0.075	0.062	0.068	0.061	0.080	0.081
Br	5.64	3.88	1.66	1.65	4.60	18.0	38.2
Ca	567	1954	3131	3440	3489	5698	8350
Cl	2378	1157	404	311	2032	675	834
Co	0.365	0.605	0.530	0.890	0.630	0.708	1.68
Cu	20.1	30.3	34.1	43.4	58.6	76.2	144
Hg	1.17	1.29	1.60	2.19	2.48	2.22	2.28
I	n.d.	0.133	0.220	0.104	0.140	0.222	0.091
K	287	404	140	74.5	45.8	56.3	61.5
La	0.56	0.21	0.56	1.15	1.16	0.144	0.25
Mg	102	231	271	332	324	550	911
Mn	0.21	0.32	0.45	0.63	0.55	0.72	0.91
Na	326	647	304	167	104	97.7	124
S[b]	4.80	4.10	4.19	4.42	4.17	4.37	4.32
Sb	0.39	0.72	0.33	0.55	0.60	0.43	0.51
V	0.01	0.04	0.04	0.05	0.04	0.04	0.045
Zn	167	147	147	138	147	118	90.2

[a] All values are in ppm except where noted

[b] in %

8. CONCLUSIONS

The INAA methods developed here have been found to be very useful for the determination of trace multielement concentrations in scalp hair within a relatively short time. The elements which are routinely determined in human scalp hair in our laboratory through short-, medium- and long-lived neutron activation products include Ag, Al, As, Au, Ba, Br, Ca, Cl, Co, Cr. Cu, Fe, Hg, I, K, La, Mg, Mn, Na, Rb, S, Sb, Sc, Se, Ti, U, V and Zn. Precision, accuracy and sensitivity of measurements have been observed to be more than adequate for obtaining reliable data. The IAEA Intercomparison Hair sample HH-1 was the only hair reference material available and it was extremely useful for evaluating the methods developed in this study. The GFAAS method for the determination of Pb was adequate for measuring Pb levels in most hair samples. The GFAAS method for Cd needs to be significantly improved so that very low levels of Cd in hair can be reliably measured. Alternatively, a radiochemical NAA method developed earlier (18) can be used for Cd.

A very detailed study on hair washing methods has been carried out using in-house standards. The factors studied included evaluation of pre- vs. post-irradiation washings, efficiency of single reagents in removing exogenous contaminants, comparison of various washing procedures which use a combination of different reagents in sequence, effect of changing the order of reagents in a given washing procedure, and comparison of hair-washing solution shaking techniques. The IAEA and other washing procedures which utilize mild treatments with organic solvents, water and detergents have been found to be sufficient for removing exogenous contaminants such as oils,

laquers, loose dust particles, etc. More severe treatments with EDTA, NaOH and HCl have been observed to leach significant amounts of trace elements from hair with increasing times as well as number of washings. The effect of usage certain medicated shampoos containing large quantities of Se and Zn has been investigated. Most of the elements exogenously deposted by shampoos can be quantitatively removed by the IAEA and SDS washing procedures with the exception of Se. It has also been observed that externally applied Hg cannot be removed from hair by any of the available washng procedures.

A study on the variation of trace element content along the longitudinal sections of hair strands has shown some interesting trends. Further research needs to be done in this area. We have applied hair trace element data to few areas and found scalp hair to be a useful screening tissue for assessing community exposure to environmental inorganic pollutants.

9. FUTURE RESEARCH

Our future work on hair will include (a) study on dose-response relationship using animal models and/or autopsy samples; (b) refinement of the GFAAS method for Cd and Ni; and (c) completion of a book on hair trace elements. Other on-going research projects of environmental health interest in our laboratory include (a) studies on leaching of sewage sludge; (b) transfer of pollutants among the different environmental compartments; (c) protein-bound trace elements in biomedical samples; (d) occupational health parameters; (e) speciation of radionuclides; and (f) quality of drinking water with respect to trace toxic elements and their species.

*

This research was financially supported by a research operating grant from the Natural Sciences and Engineering Research Council of Canada.

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HAIR AND NAILS AS MONITORS OF EXTERNAL TRACE ELEMENT BURDENS

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The work done under this contract is described in detail in technical reports already published by ECN. Only the titles and abstracts are reproduced below.

The full length report is available directly from Dr. H.A. Das.

(I) Instrumental Neutron Activation Analysis of Human Hair and Related Radiotracer Experiments on Washing and Leaching

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Abstract

- This text summarizes the work done under the IAEA-contract 2440/RB.
- The aim was to develop a fast and reliable system for the determination of trace elements in human head hair by instrumental neutron activation analysis (INAA) and radiotracer washing experiments.
- The standardized procedure for INAA was applied to hair samples collected by the Coronel Laboratory of the University of Amsterdam. The correlation between trace element contents is considered.

CONCLUSION

- The elements N, Na, P, Cl, K, Cr, Mn, Fe, Co, Cu, Zn, As, Br, Ag, Sb, I, La, Eu, Au and Hg may be determined by INAA. The routine programme based on simultaneous irradiation of many samples for 12 h at a flux density of $5 \cdot 10^{12} cm^{-2} s^{-1}$ yields Na, Cr, Fe, Co, Cu, Zn, Br, Ag, Sb, La, Au and Hg.
- The elements Na, K and Br are easily washed out. They should be avoided if INAA is to be applied as a tool for discrimination. They may, however, be used to characterize the sample by their elution-curves.
- The most promising elements for discrimination seem to be Fe, Co, Ag, Cd and Au.
- There exists a similarity between the elution of trace elements from hair and nails.

(ECN-107, 1981)

(II) Determination of Arsenic, Selenium and Antimony by Neutron Activation Analysis. Application to Hair Samples

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Abstract

- A fast rabbit system for instrumental activation analysis with reactor neutrons is described. Its use in the determination of selenium in hair is discussed.
- A survey is given of the correction factors which are inherent to the use of short-lived radionuclides.
- An alternative to INAA is NAA based on the separation of arsenic, selenium and antimony by hydride evaporation and absorption on active carbon.
- Data for some Standard Reference Materials are given.
- This work was done under research contract 2440/RI/RB with the IAEA.

(ECN-131, 1983)

DEVELOPMENT OF HEALTH-RELATED ANALYTICAL TECHNIQUES

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Abstract

Related to the programme based on Nuclear Methods for Health-Related Monitoring of Trace Element Pollutants in Man initiated by I.A.E.A. in 1978, our laboratory (L.A.R.N.) has developped and optimized samples preparation techniques for hair analysis without dissolution and preconcentration or chemical separation, and PIXE non vacuum technique for measurement of biological samples such as liquids. The results obtained at L.A.R.N. have been compared with results obtained by other techniques, and it is found that PIXE can be used with reliability to analyse in a short time a lot of biological samples.

1. HAIR ANALYSIS.

Hair and nails can be analysed by conventional techniques (atomic absorption, neutron activation) but also by PIXE. The interest of PIXE is that it is possible to make multi-element analyses, all elements being determined at the same time and in the same experimental conditions. Even a single strand of hair can be explored for local anomalies (colour, shape, etc...).

Hair can be considered as an indicator of man's environment; the distance from the scalp being related to the growing time (datation), two possible origins of traces due to environment can be detected (exogenous and endogenous), and samples can be easily collected without special authorization.

During 1978, the activity was oriented towards the absolute determination of the chromium content of one hundred samples which came from a location in Mexico where environmental pollution was suspected. The PIXE method used for these analyses allows simultaneous detection of several trace elements that permits to search correlations between concentrations of pollutants and essential trace elements (like Fe, Zn) in hair.

Experimental conditions were set up so as to obtain good reliability and accuracy in the measurements, and to minimize the time spent for both the target preparation and measurement. The total length of hair is used in the sample preparation. After washing and drying, the hair is ground in an agate mortar at the liquid nitrogen temperature. A pellet of 12mm in diameter is pressed to obtain a 1/2 mm thick sample of circular shape. The proton beam is defocused to cover 80% of the target; this defocusing is obtained by passing the beam through an Al foil in front of the target.

The proton beam is monitored using a Ge(Li) detector to measure gamma-rays from (p,p'γ) reactions induced in the Al foil. Charge build up on the hair sample can be eliminated by setting a heated filament near the sample (electron spraying). In Fig.1 we have reproduced two spectra of X-ray detected during the irradiation of hair with a proton beam of 2 MeV. Different elements can be detected at the same time (K, Ca, Cr, Fe, Cu, Zn). Unfortunately there is a large background due to bremsstrahlung, but this background can be eliminated by using electron spraying (a heating filament emits electrons which neutralize the sample charge). Spectra shown in Fig.1a and 1b were obtained on the same hair sample, but with different experimental conditions : (1a) with electron spraying and (1b) without electron spraying.

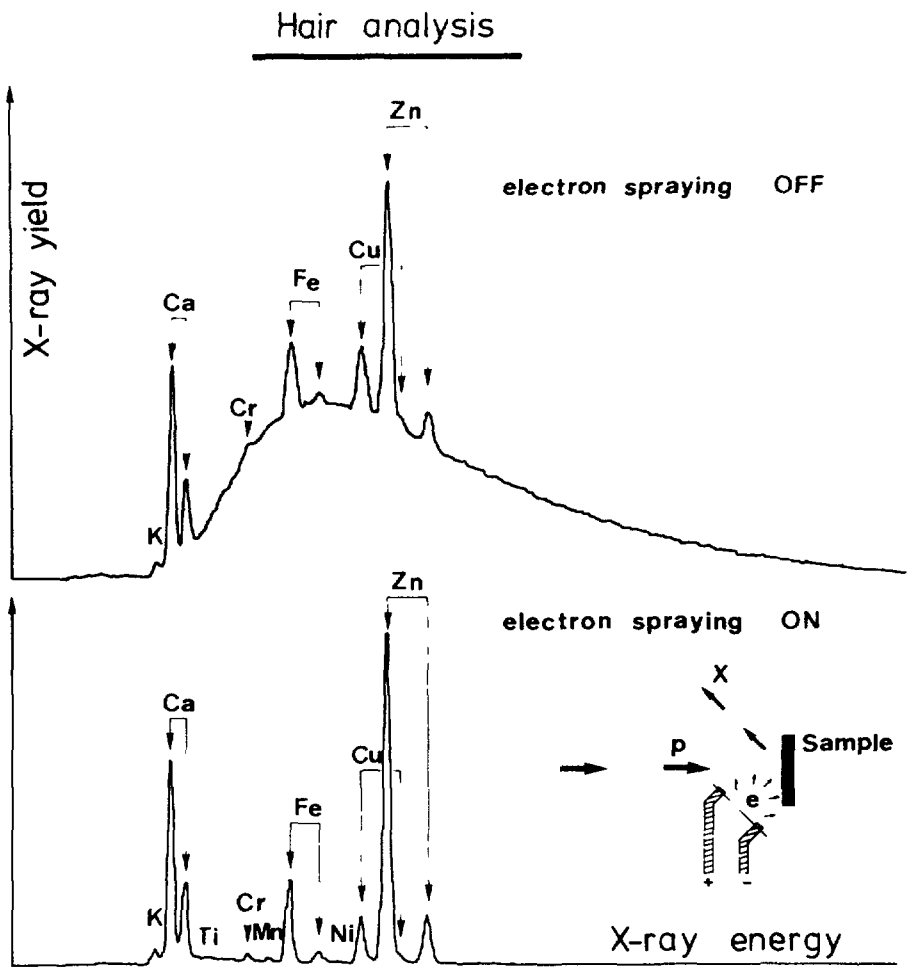

Fig.1 : Typical spectra of X-rays following hair bombardment. (a) : without and (b) with electron spraying.

Let us come back to the analysis of chromium; after washing, rincing and drying, the samples were analysed for chromium; a serie of 99 samples was measured. In a first run, 46 samples (blank) were analysed and the chromium content was found to be less than 9 ppm, this value being in good agreement with the content of chromium in human hair. The second serie, 53 samples showed a large spread in the chromium content : from 10 to 970 ppm. A statistical study of these results indicates that there is no correlation between Zn and Cr or Fe and Cr. These results indicate that the people corresponding to the second serie of samples have been over-exposed to chromium pollution. These results have been sent to the Health Department of Mexico.

Another work consisted in the analysis of powdered hair supplied by I.A.E.A. in the scheme of an intercomparison round; since the results have not been sent in time, they have not been reproduced in the I.A.E.A. report. We give here the value obtained in our laboratory (values in ppm):

Pb	:	7.7 ± 1.1
Zn	:	206.3 ± 8
Mn	:	2.8 ± 0.14
Fe	:	27.4 ± 0.9
Cu	:	10.1 ± 0.2
Br	:	3.4 ± 0.8

Let us recall that these measurements were obtained by the PIXE technique.

2. ANALYSIS OF LIQUIDS.

In medical applications ion beam analysis is used for the detection of trace elements in liquids (blood, serum, etc...) and in tissues (muscles, fibres, bones, teeth, etc...). Liquids can be deposited on porous backing like nucleopore, carbon, kapton or polystyrene foils; they can also be dried and readily pelletized. These processes result in a large increase in the sensitivity, but sometimes with loss of some elements.

Another technique was developped at L.A.R.N.. It consists of bombarding the liquid drop hanging from a pipette or a little trickle of flowing liquid. This technique has proven to be excellent for biological liquid investigations (Fig.2) and is usually called non vacuum analysis. Of course, here there is no preconcentration or chemical separation and the sensitivity is lower than for dried samples, but it has the advantage that only one drop of liquid is used and that the analysis is very fast. This could even be done on-line on a liquid flowing down from the body or from an organ of the patient. The monitoring can be carried out by adding a heavy metal (As) to the solution, but this technique of internal moni-

Experimental device for liquid analysis

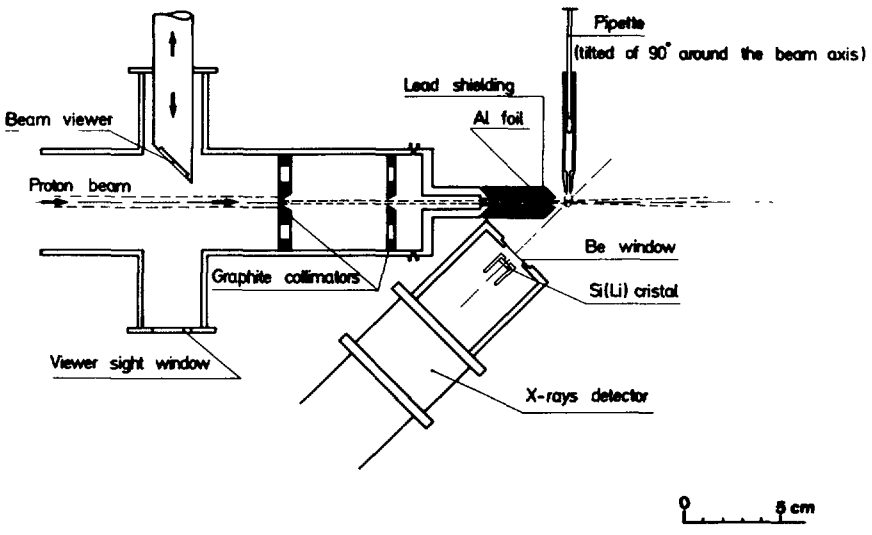

Fig.2a : Internal standard technique. The detector is placed at 135° and shielded against X-rays from the Al foil.

Experimental device for non vacuum analysis

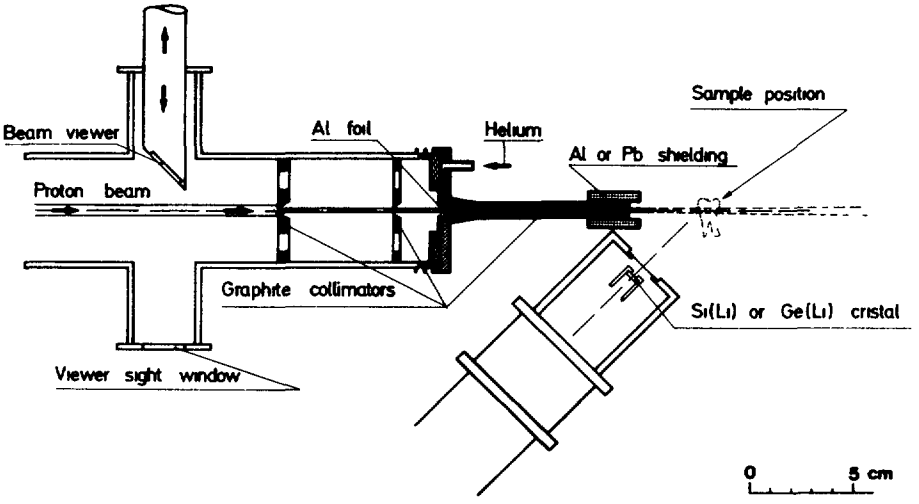

Fig.2b : External standard technique. Measurements are normalized on the radiation emitted by Argon of the air.

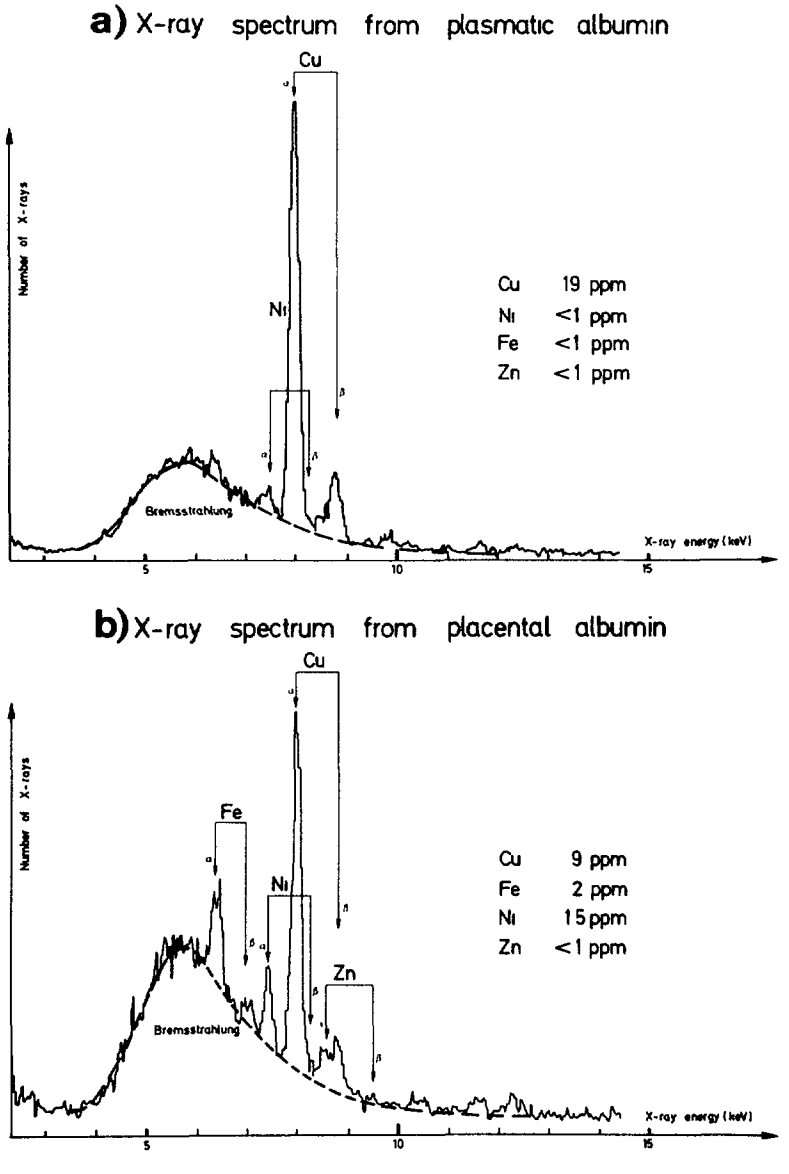

Fig.3 : Single drop spectra of two different albumins. The quantitative determinations were made by the addition of a small quantity of As solution. The bremsstrahlung amplitude also provides a good reference.

toring can be replaced by a simpler one which consists in counting X-rays from the beam exit window (a melt foil) or sometimes X-rays from the Argon present in air between the window and the sample. This technique has been widely used at L.A.R.N. for the analysis of a number of liquids.

Measurements are rapid and can be repeated on a large number of samples. 150 albumins from placental and plasmatic origins were analysed in this way (Fig.3). This work was undertaken since these albumins are used in the treatment of cancer; albumin is a protein component of human serum playing the role of keeping the blood volume constant and maintaining the osmotic pressure in the blood vessels. This is why heavy elements present in albumin are of great importance; as seen above, they can modify the osmotic capability of the membranes. The results obtained at L.A.R.N. have been compared with the results from Atomic Absorption measurements and the technique is found to be extremely reliable.

CONCLUSIONS.

In conclusion, the programme initiated by I.A.E.A. on Nuclear Methods for Health-Related Monitoring of Trace Element Pollutants has stimulated the activity in this field and has allowed our laboratory to develop some aspects of this technique.

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CONCENTRATIONS OF HEAVY METALS IN HUMAN BLOOD IN RELATION TO THEIR RESPECTIVE ATMOSPHERIC LEVELS

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Abstract

Air samples from five different monitoring stations around the city of Teheran were collected at different seasons, time (day and night) and under different weather conditions (clear or rainy days). The main elements measured in this work were Pb, Cr, Se, As, Mn and Sb.

Air and blood samples from the non-polluted city of Manjil were compared with those of Teheran. 300 blood samples from Teheran and 30 samples from Manjil were studied.

1. INTRODUCTION

If heavy metals such as Pb, Cd, Hg and As enter into the environment, severe health effects can occur when the concentrations are more than the permitted levels advised by pathologists (1). In general, every poisonous material entering the body is taken up by tissues which have similar chemical properties.

The following steps are of interest with respect to poison entering the body.

1. Exposure and penetration.
2. Distribution and translocation.
3. Biotransformation and metabolism.
4. Deposition and metabolism.
5. Excretion and elimination.

The absorbed foreign material is transported to different tissues, mainly bones, lipids and brain, and then deposited there (2).

Lead is one of the main toxic elements which enters into the environment by means of combustion of fuel from motor vehicles. By inhalation, consumption of food or drinking water, or even in some cases by absorption through the skin, it finally finds its way into the blood.

About 95% of the absorbed lead is bound to haemoglobin, a small part is bound to plasma proteins, and the rest is thought to be deposited in other parts of the body (3).

There have been many investigations concerning lead and the relationship between its levels in blood and the environment. In 1976, Goldsmith and Hexter (4) established a relationship between lead in air and blood samples collected in some parts of the United States. However, in 1969, Stopps (5) made a large survey of blood samples from inhabitants of remote villages in Brazil and factory workers in big cities in the

Table 1- Mean concentration of elements in several sampling stations in Tehran during Spring and Summer.

Location	St_1	St_2	St_3	St_4	St_5
Element	Concentration ngr/m^3				
Pb	480±50	500±66	670±80	630±90	850±100
Zn	380±18	580±20	400±100	580±50	1090±200
Sb	30±6	30±4	90±16	70±12	90±10
Mn	100±11	110±8	140±10	230±15	160±10
Se	60±4	70±6	100±9	120±8	80±5
Cr	40±3	50±5	90±8	200±10	150±13
As	50±7	60±2	100±9	90±9	70±4

Location	
St_1	The North of Tehran
St_2	The East of Tehran
St_3	The West of Tehran
St_4	The Centre of Tehran
St_5	The South of Tehran

Table 2- Mean concentration of elements in several sampling stations in Tehran during Autumn and winter.

Location	St_1	St_2	St_3	St_4	St_5
Element	Concentration ngr/m^3				
Pb	360±40	550±53	420±38	580±29	700±90
Zn	230±25	510±30	200±14	330±18	700±70
Sb	10±1	20±3	10±2	50±7	80±6
Mn	80±7	100±7	180±12	130±9	120±4
Se	40±3	60±5	70±2	40±4	50±5
Cr	50±8	20±1	80±11	28±3	60±7
As	40±5	40±8	70±3	10±2	90±8

Table 3- Mean concentration of elements in Manjil during Spring and Summer.

Element	Concentration ngr/m^3
Pb	40±3
Zn	43±2
Sb	9±1
Mn	11±2
Se	7±0.9
Cr	8±1.5
As	11±1

United States; the concentrations of lead were found to be very similar in each group. His results were attributed to some factors (contamination) existing in remote villages of Brazil. In our work, the results were very similar to those of Goldsmith and Hexter (4) and Stopps (5), i.e. regarding air and water. At this point we were encouraged to investigate another factor, i.e. water contamination. This was one of the most important factors in this study.

2. EXPERIMENTAL PROCEDURE

2.1. Air sampling

Air samples were collected by means of suction pumps with a maximum flow-rate of 100 liters per minute. Various types of filters have been recommended for this purpose; in our work millipore EHMP 04700 filters (6) were used. All samplings were at a height of 2 m above ground level (the maximum height of a person) using an air volume of 72 m^3. Monitoring station were installed at the Nuclear Research Centre and four other locations in Teheran.

2.2. Method of measurement

Materials collected on the filters was dissolved in super-pure nitric acid and analysed by electrothermal atomic absorption spectrometry (AAS). High precision was obtained down to the µg/kg range. With this method Pb, Zn, Mn, Cr, Se, As and Sb were quantitatively measured. The results are given in tables 1, 2 and 3.

2.3. Preparation of blood for analysis

Elements in human blood were studied after extraction with a suitable complexing agent. For the best yield, various complexing agents and solvents were investigated with the help of neutron activation analysis (NAA).

An investigation of different complexing agents, i.e. EDTA, oxine, dithizone and ammonium pyrolidine dithiocarbamide (APDC) showed that ADPC is the most suitable one for this purpose (Table 5). To 5 ml of blood, 5 ml of N-butylacetate treated with a 3 % solution of each complexing agent were added prior to measurement by AAS.

Different concentrations of ADPC i.e. 0.5, 1, 2, 3, 4 and 5 %, were investigated in this work. The most suitable concentration of ADPC was found to be 3% (Table 6).

Different solvents such as $CHCl_3$, CCl_4, C_6H_6, $(C_2H_5)_2O$, and $C_6H_2O_2$ were used with ADPC as a complexing agent and the amount of lead in each sample was measured. The most suitable solvent for this work was found to be N-butylacetate (NBA) (see table 4).

The yield of vanadium was measured as follows. 5 ml of blood were treated with 1 ml of a 10 ppm vanadium solution and mixed with a 3% APDC solution and 5 ml of NBA. After a complete extraction, vanadium was measured by NAA. The same procedure was carried out with vanadium concentrations of 20 and 30 ppm. The average yield was found to be 84%.

Table 4- A suitable solvent for extraction

Solvent	Used lead conc. µgr/gr	Isolated lead conc. µgr/gr
Diethylether	0.1	0.09 ± 0.01
N-Butylacetate	0.1	0.1 ± 0.03
Carbon-tetrachloride	0.1	———
Benzene	0.1	0.08 ± 0.02
Chloroform	0.1	———

Table 5- A suitable complexing agent for extraction

Complexing Agent	Used lead conc.	Isolated lead conc.
ETDA	0.1	———
Oxine	0.1	———
Dithizone	0.1	0.09±0.01
APDC	0.1	0.1 ±0.05

Table 6- Determination for the most suitable concentration of APDC

Blood Sample	Vol.APDC (ml)	Conc. APDC (%)	Isolated lead Conc. (µgr/gr)
EXP. 1	0	0	0.10
EXP. 2	2	0.5	0.38
EXP. 3	2	2	0.40
EXP. 4	2	3	0.45
EXP.5	2	4	0.45
EXP.6	2	5	0.45

2.4. Determination of lead in blood samples collected in Teheran & Manjil

Blood samples were collected from the following hospitals: Shohada, the Heart Clinic, Fatemeh, Firouzghar, Aburyhan, Pars, and the French Polyclinic where air samples were previously collected. Blood samples from residences in Manjil were also collected and the measurements were carried out for comparison. In this work a total of 300 blood samples from Teheran and 30 blood samples from Manjil were studied.

The average concentrations of lead found in blood samples in different locations in Tehran and Manjil are shown in table 7.

2.5. Water analysis

Water samples from the cities of Teheran and Manjil were collected and the concentrations of lead in the samples were measured. The results are shown in table 8. As shown in the table the average concentration of lead in Manjil water was 84.9% higher than that in Teheran water. This agrees well with the observation of a higher lead content in blood samples from Manjil citizens.

Table 7 - Lead concentration in Tehran and Manjil .

Location	Lead concentration in air* $\mu gr/_{m}3$	Lead concentration in blood $\mu gr/\frac{cc}{100}$
St_1	0.48±0.05	19±2.12
St_2	0.50±0.06	26±3
St_3	0.67±0.08	28±1.8
St_4	0.63±0.09	26±2.20
St_5	0.85±0.10	32±3.90
Manjil	0.04±0.005	19±3

* - Samples in Spring and Summer

Table 8- Amount of lead in water samples in Tehran and Manjil.

Location	Concentration µgr/1oo mil	percent in diff. *
Tehran	0.61±0.01	0
Manjil $site_1$	1.40±0.30	130.30%
Manjil $site_2$	1.49±0.35	145.08%
Manjil $site_3$	0.97±0.08	59.83%
Manjil $site_4$	0.82±0.04	34.90%
Manjil $site_5$	0.94±0.10	54.09%

* The percentage difference with result to values found for Tehran.

3. RESULTS AND DISCUSSION

From this survey it was found that the concentrations of elements in the air varies in different locations of Teheran. The concentrations were somewhat lower in the fall and winter due to the local winds and air in these seasons. The results are shown in tables 1, 2 and 3 and a gamma-ray spectrum of an air filter sample is shown in Figure 1. It was also found that the concentrations of elements increased during the day due to traffic in the city. Lead in air was always present at a higher concentration than that of any other heavy metal. This is mainly due to combustion of tetraethylene lead added to gasoline.

The recommended maximum permissible concentration of lead in the air is taken to be 1.5 $\mu g/m^3$, though in the Soviet Union the allowance is only 0.7 $\mu g/m^3$ while the WHO acceptance value is 2 $\mu g/m^3$ (7).

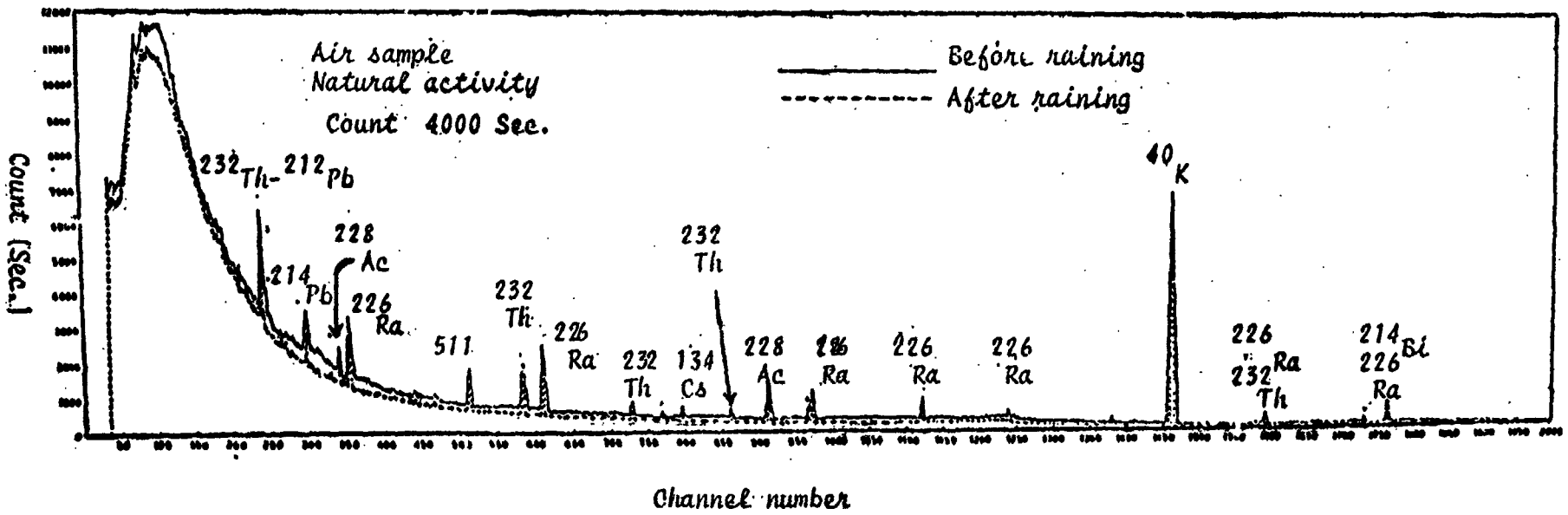

Figure 1. Gamma-ray spectrum of a Millipore filter sample observed with the 60-cm^3 Ge(Li) detector.

Table 7 shows that the concentration of lead in the air is related to that found in blood samples. The average concentration of lead found in blood samples in Teheran was 26±4.7 µg/100 ml, which is similar to that in Manjil, 19±3 µg/100 ml. The concentrations of lead in the air in Teheran (0.62±0.14 $\mu g/m^3$) and in Manjil (0.04±0,005 $\mu g/m^3$) show a big difference. No relationship can be observed between the lead concentrations of blood and air in both cities. This suggests that another factor such as water should be considered.

Table 8 shows that the average concentration of lead in Manjil water was obviously higher than that in Teheran. This may explain why the average amount of lead in blood from Manjil is not lower than that for Teheran.

4. NEEDS FOR FUTURE RESEARCH

To obtain better results the following points should be considered. More samples of both blood and air are necessary for the determination of lead and other heavy elements in order to know the relationship between their concentrations in these samples. Other factors such as age, sex, smoking habit, weight etc., also need to be considered.

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HEALTH RELATED MONITORING OF TRACE ELEMENTS BY PIXE

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Abstract

Trace element concentrations were studied in human blood serum, hair and skin by PIXE analysis. Variations in the concentrations of some elements were observed in cases of health disorders, and hair appeared to be the best easily accessible monitor for trace elements.

1. INTRODUCTION

The subject of this project was the analysis of trace elements in human tissues and fluids by PIXE in order to:

- establish fast and reliable analysis procedures for the various types of human tissues and fluids, with external beam PIXE,
- establish the "normal" levels of trace elements for the Greek population,
- investigate any possible correlations between changes in elemental concentrations and health disorders, and
- search and examine meaningful trace element monitoring procedures for health related problems.

2. EXPERIMENTAL PROCEDURE AND RESULTS

2.1. The PIXE analysis

The Proton Induced X-ray Emission (PIXE) method with external beam[1,2] was used for the elemental analysis of the samples. The analysis was performed at the Tandem Accelerator Laboratory of the NRC DEMOKRITOS. The PIXE set-up with the external beam which was first successfully developed in this laboratory is described in refs 3-5. A thin kapton foil (1.2 mg/cm^2) was used as an exit window for the 2.5 MeV protons. The external beam technique is most suitable for the analysis of thick uniform samples in the form of pellets. The pellets were placed at 45 degrees relative to the incoming beam. Each sample was irradiated for about 5 min, and the total proton current (of the order of 50 nA) was integrated at the target and window together, as described in ref 5. A Ge(in) detector with working resolution of about 180 eV was used, together with the associated standard electronics for amplification, pile-up rejection and pulse-height analysis.

The elements that could usually be detected were K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr and Pb. The detection limit for each of them was of the order of 0.1 ppm for serum, 1 ppm for hair and about 0.3 ppm for skin.

2.2. Analysis of human blood serum

Blood serum samples from more than 100 persons belonging to different groups were collected and analysed. Each sample of about 1 ml was freeze-dried, powdered, and about 30 mg of the powder was pressed into a pellet of 7 mm diameter for irradiation with protons.

The observed concentration values of the various elements for healthy people were all within the limits reported in the literature for people in other countries. We have observed, however, certain variations in the elemental concentrations between the different groups, such as higher values for the Pb and Br content in the samples collected from people living in Athens relative to the ones from the rural areas, or differences in the K content between the male and the female subjects.

Blood serum samples were also analysed for three groups of people with skin diseases (two types of skin tumors and psoriasis) as well as for a group of welders suspected to have lead poisoning. There was no indication of any systematic differences in the blood of these groups from "normal", although distinct abnormalities have been observed in the trace elements of other tissues of these people, as will be discussed below.

2.3 Analysis of skin samples

The skin samples were freeze-dried, powdered and pressed into pellets for the PIXE irradiations. Affected and healthy skin samples (along with blood serum samples) were analysed from 41 patients suffering from epitheliomas and from 6 psoriatic patients.

For the healthy skin one could make the following comments on the results:

- people from rural areas appear to have drier skin,
- the contents of Cu, Pb and especially of Br is higher in Athens than in rural areas.

Significant differences were found in the comparison between the concentrations in the epitheliomas and the healthy samples. The concentrations of K, Fe, Cu, Zn and Rb appear to be much higher in the epitheliomas, while the Br concentration is lower and shows marked variations. The elements Ca and Pb show no variations. No significant differences were observed, on the other hand, in a similar comparison for the psoriatic patients.

The concentrations of all elements measured in the blood serum for these people were found to be normal, as mentioned before.

2.4 Analysis of hair samples

Emphasis was given to the analysis of human hair samples, as they were expected to be good and easily accessible specimens for trace element monitoring. Nails were also considered for this purpose, but it was concluded they are more susceptible to contamination, and therefore a less valuable organ for monitoring.

Considerable difficulties were encountered in the process of transforming the hair samples into powder form. Partial burning could give results only at high temperatures (above 400 degrees) at which high losses of trace elements are expected. An attempt was made to use mortars from porcelain or agate to grind the hair samples to powder in the presence of liquid nitrogen. The results of this attempt were encouraging, but the powder was not homogeneous, and the analysis showed the presence of some contamination. The use of a commercial freezer/mill gave good results in transforming the samples into powder, but heavy contamination was introduced by the metallic parts of the grinding vials and the magnetic impactors. This problem was solved by constructing plastic vials, and replacing the impactors with others covered with teflon.

After the establishment and thorough testing of the procedure, hair and serum samples from 45 persons were analysed. The results justified our efforts for the cases of suspected lead contamination. Practically all samples of 16 people working in cable welding showed high lead levels, varying between 14 and 136 ppm with an average of 62 ppm, compared to the "normal" population average of 9 ppm. The lead level in the blood serum was normal for all of them.

Suspecting possible external contamination of the hair samples mentioned above, due to the nature of the work of these people, we called back six of the welders and collected head and public hair from each of them this time, and analysed them again. The lead content was high for both types of samples, although not the same in the two samples, probably due to the different growth rates.

For this group of 6 people the blood was tested for increased strippled cells, which is the characteristic finding in the case of lead excess. The results were negative for all of them.

3. CONCLUSIONS

The trace elements of the various tissues and fluids are characteristic, and in most cases of health disorders they appear to change their concentrations. Even if the cause of these changes is not yet understood in most cases, it is an indication which can be used for monitoring the health condition of the living beings.

Blood serum does not appear to be a good monitor, perhaps because of the fast changes that it undergoes. Of the other easily accessible organs, hair appears to be a good tissue to analyse for trace elements, but a more extended study is probably needed of the significance of high and low levels, and for understanding their changes connected to specific health disorders.

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SIGNIFICANCE OF ELEMENTAL DEPOSITION IN HAIR TO INTERNAL CONTAMINATION

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Abstract

In standardized animal experiments the deposition of Cd, Hg and As in anaphase hair was studied. Due to rates of endogenous transfer observed hair analysis is considered less suitable as an indicator of endogenous "contamination" in the case of Cd than in Hg and As. Studies of the influence of a mild washing procedure recommended by IAEA/RL/41H on anaphase hair loaded with Cd or Hg demonstrated a heavy impact of washing on Cd but no influence on Hg.

1. OBJECTIVES, MATERIAL AND METHOD

In the programme of 1981-1983 the findings of our previous contract where we had used single injections of radioactive Cd-109 were supplemented by animal experiments using chronic feeding at different levels for prolonged periods of time. This resembles more closely the situation of a chronic exposure in man. The animal species, the method of inducing new hair growth and the sampling was the same as before. A detailed description is given in (1) and (2). In the same animal modell experiments were done with radioactive Hg-203 (3) which was administered as a single dose by stomach tube in order to study the endogenous deposition only.

A further series of experiments was started on As in hair. These were done with single i.m. injections of stable As_2O_3 and with single doses of As_2O_3 administered by stomach tube. The analysis was by NAA including a step of chemical separation. Furthermore the impact of a mild washing procedure recommended in IAEA/RL/41H was studied on Cd (4)and on Hg. Whereas in the Cd study the impact on the endogenous and the exogenous component were considered by using radioactive Cd-109 as a single dose as well as stable $CdCl_2$ in the drinking water and by the use of animals housed in conventional cages and in metabolic cages , in the Hg experiment only the impact on the endogenous component was studied following a single dose of Hg-203 (as $HgCl_2$) administered by stomach tube.

2. DETAILED DESCRIPTION OF THE STUDIES

This is given in the publications (1-5) as far as the studies on Cd and Hg are concerned. The main experiments on As are not yet finished. Therefore only preliminary information on some parameters is given in the following paragraph.

3. COMPREHENSIVE REPORT AND CONCLUSIONS

3.1 Endogenous Transfer to Hair

The chronic studies on Cd generally confirm our findings obtained with the acute exposure (6,7). Cd was deposited in hair relative to the level (dose) supplied. Accordingly the deposition in newly growing hair (anaphase) ceased when the supply of Cd in the food was interrupted. Our finding that Cd in hair did not increase in parallel to the accumulation in the total body or in the organs, especially in the critical organs (2,5), is also in accordance with what we had found in the acute experiments. With contrast to the experiments where Cd-109 was injected in those where it was administered per os a rather large exogenous component could be distinguished if the animals were kept in conventional rat cages. This component was absent if the animals were kept in metabolic cages.

In control animals kept in metabolic cages and fed without Cd in the drinking water the concentration of Cd in 1g newly grown hair was between 0.1 and 0,7 ppm in different experiments. In animals supplied with 300 ppm Cd in the drinking water, a dose level which eventually leads to kidney damage, it was approximately 2 ppm Cd (2,5). Since the treated animals ingested $\sim$1900 times more Cd than the controls an increase of Cd in food of a factor $>$1900 was reflected in the hair of the rats by a mean increase of between 1 and 2 ppm i.e. (5) a factor of 16-20 relative to the controls (Table 1). An increase of Cd in food above normal by a factor 10 could therefore not have been distinguished from the unexposed controls by hair analysis. - Note: In the renal cortex of not occupationally exposed modern man between 2 and 120 ppm Cd have recently been reported (8). This is only by a factor between $<$2 and 10 below the level of fatal kidney damage (200 ppm). It might therefore be suspected that a chronic ingestion 10 times higher than normal would be fatal in man. Therefore an indicator which cannot differentiate between a normal intake and an intake of 10 times normal would not be useful in man.

Table 1

Comparison in Food and Hair of the Relation between Unexposed Rats and Rats Exposed to 300 mgCd/l

Cd ingested		Cd in hair*	
µg/d	relative to "unexposed"	µg/g	relative to "unexposed"
$\sim$ 4500	x1900	$\sim$2	x16 to 20

*induced hair 10d after eruption through the skin

The endogenous deposition of As in hair was studied using the same procedure of hair induction as in the studies with Cd and Hg. Stable As was administered as a solution of As_2O_3 by stomach tube. Depending on the amount administered (50µg and 500µg) the amount of As in hair grown within

10d after the administration was 0,14 ± 0,07 or 0,18 ± 0,04 % * (mean ± standard error for n=5). With this method the intestinal absorption could not be determined. According to the literature (9) maximum absorption may be 80%, however, in the experiment it might have been less due to the use of As_2O_3. The possibly lowest absorption was arbitrarily assumed at 30%. Assuming 80% absorption the deposition observed in 1g hair corresponds roughly to 0,2% of the absorbed amount. Assuming 30% absorption it was 0,5% of the absorbed amount. - In another experiment the deposition in growing hair (anaphase) and in resting hair (telophase) was studied after intramuscular injection of a rather high dose (5mg) of As_2O_3. In 1g of hair grown within 10 days after injection 0,38% of the dose was found. This corresponds well with the findings in the per os study. - Note: With Cd and Hg we had found different rates of deposition after per os and parenteral administration. - If As_2O_3 was injected during the telophase there was practically no deposition (i.e. it was the same as in controls which had received an injection of saline). A transfer of As by sebum or by external sources was therefore absent.

In the experiments with Hg and As where the elements were administered as a single dose by stomach tube the deposition in hair relative to the amount absorbed in the intestine was much higher than with Cd (Table 2). This indicates a higher potency of hair to reflect an increased ingestion (more precisely resorption) of these elements compared to Cd. It is likely that such a difference in the rate of deposition in hair between Cd on the one hand and Hg and As on the other is also the case in man.

Table 2

	Accumulation in Hair* after a Single Peroral dose	
	% of intest. absorption	relative to Cd
Cd	~ 0,05	1
Hg	~ 0,5	x10
As	~0,2 - 0,5	x4 to 10

*induced hair 10d after eruption through the skin

3.2 Influence of Washing

The influence of the washing procedure recommended with IAEA/RL/41H was also studied in rat hair loaded with the elements. A rather extensive study was undertaken with Cd (4). With Hg an experiment using radioactive Hg-203 provided sufficient information. With Cd the procedure was found to remove amounts of > 60% of the endogenous component. Surprisingly the loss was higher with the chronically supplied stable Cd than with radioactive Cd administered as a single dose (Table 3 and 4). This may be due to a different distribution along the length of hair.

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* of the administered dose

Table 3:

Loss of Stable Cd in Hair Subjected to Washing
(% Loss per g)*

	In Metabolic Cages	In Conventional Cages	Significance (2P)
mechanical agitation	97±1 (1%) n = 10	88±2 (2%) n = 8	<0.001
by ultrasound	99±1 (1%) n = 10	77± (8%) n = 7	<0.001

* mean ± standard error (relative standard error)
n = pairs of subsamples

Table 4 :

Loss of Radioactivity in Hair Subjected to Washing Using Ultrasound as a Means of Agitation

In Metabolic Cages (% loss per g Hair)		In Conventional Cages (% loss per g Hair)	
$\bar{x}$	64	$\bar{x}$	70
$s_{\bar{x}}$	6	$s_{\bar{x}}$	2
$s_{\bar{x}}$ (%)	9	$s_{\bar{x}}$ (%)	3
n	10	n	8

With Hg a washing experiment was only done using hair which contained radioactive Hg-203 from a single dose administered by stomach tube. In this case the washing procedure had no influence on the Hg-203 in the hair. This is in accordance with the findings of Das et al. (8) in human hair. It is noteworthy that in our experiment the Hg-203 was of endogenous origin, whereas in the human hair analysed by Das et al. the origin may have been endogenous and/or exogenous. The different impact of washing on Cd and Hg is not only of importance with respect to analytical practice but may also indicate a differencein the chemical binding.

4. APPLICABILITY OF THE FINDINGS

Based on these findings it may be recommended in applications of hair analysis not to take low levels of Cd in hair as necessarily indicating a low (or no) internal exposure, especially if the hair sample was washed (by a method similar or more aggressive than the one recommended by IAEA).

At the other hand based on our findings it seems very unlikely that the resorption of a substantial amount of (inorganic) Hg is not reflected by an elevated deposition of Hg in hair growing at the time of resorption.

5. RELEVANCE OF THE WORK TO THE NEEDS OF THE PARTICIPANTS COUNTRY

The results are relevant with respect to the application of hair analysis as a tool for assessing the exposure of man (and animals) to Cd, Hg and As irrespective of the area or the country. Such assessment of exposure is of special interest to countries where these elements are mined, milled, refined or technically used to a large extent or where contamination of food may occur.

6. NEEDS FOR FURTHER RESEARCH

6.1 The same experimental procedure which has been used to compare Cd,Hg and As should be employed to evaluate and compare the relative significance of hair analysis for the assessment of internal exposure (deficiency, adequacy or excess) of the most important toxic and essential elements and their different forms of chemical binding .

6.2 Our findings on the impact of washing on Cd in hair are partially contradictory to some other investigators using human hair of unexposed individuals and other washing methods. A study on the influence of the IAEA recommended procedure on human hair, possibly taken from a person who had been internally contaminated could close the gap between experiment and practice. This should be done by an investigator with practice in work with human hair.

6.3 Further studies on the influence of this washing procedure on other elements under the same experimental standards (induced hair from rats) might be very useful to evaluate the influence of mild washing on the endogenous component of other elements in hair.This ultimately may lead to recommendations concerning the use of preanalytical washing with analysis of specific elements. Studies with some elements are already under way in our laboratory.

6.4 Rat hair is morphologically and chemically very similar to human hair but the rates of transfer of elements into or onto the matrix may possibly be different in some cases. Therefore the very detailed and statistically well based data obtained from the well controlled experiments with rats should somehow be linked to the situation in humans. A first approximation may be obtained by studies in monkeys. One such study was originally part of our program 1982. It had to be postponed due to cuttings in technical personal.

6.5 In the further future it may be an interesting subject of animal experiments to find out if there is a change in the rate of element deposition in hair under pathological conditions due to toxicity or deficiency of the respective elements. Another similar question which might be resolved by animal experiments is: Do changes in supply of other elements interfere (+or-) with the deposition of an element in hair?

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EMPLOI DE L'ANALYSE PAR ACTIVATION INSTRUMENTALE A L'ETUDE DE LA CONTAMINATION DE L'HOMME ET DE SON MILIEU ENVIRONNNANT PAR LES ELEMENTS TOXIQUES A L'ETAT DE TRACE

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Abstract

Trace element contents are determined in human hair and in some environmentals samples such as vegetables and river waters pathways through which these elements are incomporated in human body, and in atmospheric dust, probable source of external contamination. 26 elements are determined in hairs, 11 in foodstuffs, 16 in river waters and 19 in atmospheric dust, using instrumental neutron activation analysis. The Hg and I contents in hairs are too higher due to the use of antiseptic soaps containing 3 % of mercur iodide.

Résumé

Les teneurs des traces métalliques sont déterminées dans les cheveux et dans quelques composants de l'environnement tels que : les légumes et les eaux des rivières voies d'accès de ces éléments dans l'organisme humain, ainsi que dans les poussières atmosphériques source de contamination externe. 26 éléments sont déterminés dans les cheveux, 11 dans les légumes 16 dans les eaux des rivières, et 19 dans les poussières atmosphériques, par analyse par activation instrumentale ; les teneurs en Hg et I sont très élevées dans les cheveux, à cause de l'emploi des savons antiseptiques contenant 3 % d'iodure de mercure.

1.- INTRODUCTION

Les sciences de l'environnement connaissent à l'heure actuelle un regain d'intérêt. Cet intérêt est justifié en partie par l'inquiétude survenant de la pollution et la dégradation de la nature par l'activité humaine.

En effet, les déchets domestiques et industriels sont déversés dans la nature et vont perturber l'équilibre naturel existant.

Certains de ces déchets peuvent être toxiques et atteindre l'homme à travers la chaîne alimentaire. D'où la nécessité de les dépister et de prévenir toute perturbation de l'équilibre naturel.

Un des aspects les plus importants de la pollution de la nature concerne les constituants minéraux dans les systèmes biologiques car ils interviennent dans divers processus physiologiques tels que les réactions enzymatiques, le métabolisme, la catalyse, etc ...(1,2). Il devient donc évident que la qualité de l'alimentation de l'homme doit être évaluée entre autres en termes de sa richesse en éléments essentiels ou toxiques présents.

Cette étude présente les résultats d'analyse des échantillons de cheveux humains, des légumes zaïrois, de la jacinthe d'eau et des eaux des rivières FUNA, LUBUDI et N'DJILI principaux cours d'eau qui charient les déchets des activités de l'homme dans la ville de Kïnshasa. Ces eaux sont utilisées soit à des fins sanitaires et publiques soit pour l'irrigation.

L'analyse par activation neutronique qui convient à la détermination des éléments à l'état de trace a été utilisée. Son choix a été dicté à la fois par ses performances et aussi parce qu'elle peut convenir pour un travail de routine de dosage simultané des éléments dans une série d'échantillons.

2.- MATERIELS ET METHODES

2.1.- Echantillonnage et conditionnement

2.1.1.- Les cheveux

Les échantillons des cheveux ont été collecté au sein de la population de Kinshasa et Mbandaka principalement au sein de la population estudiantine. L'âge des sujets varie entre 18 et 32 ans.

Les échantillons sont lavés avec l'acétone et l'eau suivant le procédé proposé par l'A.I.E.A. (3). Le séchage s'effectue à la température ambiante, dans une boîte à gants ventillée, pendant une nuit. Les prises d'essai varient entre 20 et 300 mg de cheveux.

2.1.2.- Les légumes et jacinthes d'eau

Les légumes analysés sont achetés sur le marché de Kinshasa. Après avoir écarté les parties non comestibles, les échantillons sont lavés à l'eau distillée plusieurs fois. Ils sont séchés à l'étuve à 85° C jusqu'à poids constant, et sont ensuite moulus au moulinex électrique. La poudre obtenue est passée au tamis de 0,16 mm de diamètre.
Avant chaque analyse, la poudre est laissée à l'étuve à 85° C pendant 24 heures (4). Les prises d'essai sont d'environ 500 mg de matières sèches. Les prélèvements de la jacinthe d'eau ont lieu à trois endroits différents du fleuve Zaïre (MALUKU, NDOLO et GOMBE) à Kinshasa.

2.1.3.- Les eaux des rivières

Les échantillons d'eau analysés sont prélevés à 50 cm de profondeur dans les rivières LUBUDI, FUNA et N'DJILI. L'échantillonnage est effectué dans les flacons en polyéthylène nettoyés au préalable avec l'acide nitrique concentré et l'eau de robinet et rincés avec l'eau distillée et l'eau à analyser.

Les formes insolubles sont éliminées par filtration sur verre fritté JENA n° 2. Le filtrat est acidifié avec l'acide nitrique purifié pour éviter d'éventuelles modifications physico-chimiques (5-7). Une partie de l'échantillon est évaporée à l'étuve à 85°C pour des longues durées d'irradiation.

2.1.4.- Les poussières atmosphériques

Les poussières atmosphériques sont recueillies sur les filtres des climatiseurs de 0,5 mm de diamètre. Les points de prélèvements d'échantillons choisis sont les suivants :

A.- KINGABWA, Zone industrielle, à l'Est de la ville ;
B.- La Cité de la Radio et de la Télévision, au Centre de la ville ;
C.- Le Centre Météorologique de Binza, à l'Ouest de la ville ;
D.- Le Campus Universitaire de Kinshasa, au Sud de la ville.

Pour disposer d'échantillons homogènes, les poussières recueillies sont traitées mécaniquement à l'aide d'un tamis en nylon dont les pores ont 250 microns de diamètre. Des prises d'essai sont d'environ 100 mg de poussière.

2.2.- Etalons et standards de référence

Les étalons utilisés sont soit des solutions préparées à partir des réactifs chimiques de pureté analytique, soit des standards ALFA Products pour la spectrophotométrie d'absorption atomique, ou encore les standars de référence G2, AGV1, BCR1, DTS1 (8) SRM 1571 et SRM 1633 (4).

Pour les éléments de longues périodes, les étalons liquides sont soit évaporés à sec directement dans la gellule (cas des eaux) soit sur des supports non activables (amidon ou filtre millipore).

2.3.- Méthodes d'analyse

2.3.1.- Analyse par activation instrumentale

Les échantillons et étalons sont enfermés dans des gellules en polyéthylène. Les irradiations ont lieu dans le réacteur Triga Mark II du Centre Régional d'Etudes Nucléaires de Kinshasa, ayant un flux neutronique de 2.10^{12} n Cm^{-2} sec^{-1}. Les durées d'irradiation varient d'une minute à 30 heures en discontinue. Pour la mesure des activités, les détecteurs Ge (Li) et Ge ayant respectivement 3,1 keV et 2 keV de résolution sur le 2e pic de ^{60}Co ont été utilisés. Ces détecteurs sont connectés aux spectromètres gamma équipés de microprocesseurs Multi-20 de marque Intertechnique.

2.3.2.- Spectrophotométrie d'absorption atomique

Le plomb et le Zinc ont été dosés par absorption atomique à l'aide d'un spectromètre VARIAN TECHTRON modèle AA_6.

3.- RESULTATS ET DISCUSSION

3.1.- Cheveux

Le tableau 1 résume les résultats obtenus pour l'ensemble des échantillons analysés. Les détails tenant compte de l'âge, sexe, traitement des cheveux, etc... sont donnés ailleurs (9). Les valeurs moyennes et leurs déviations standards sont évaluées pour les teneurs au-dessus de la limite de détection. Ce tableau est scindé en deux parties différenciant les échantillons suivant leurs origines. Dans la première partie sont donnés les résultats des échantillons de la population de Kinshasa et

dans la deuxième, les résultats des échantillons de la population de Mbandaka. Les nombres entre parenthèses repris aux colonnes 2 et 3 donnent les nombres de détermination. Les observations suivantes peuvent être tirées :

- Les valeurs observées sur les sujets de Kinshasa sont plus élevées par rapport à celles de la population de Mbandaka ;
- les teneurs des éléments analysés sont semblables à celles observées ailleurs (3,10,11)sauf pour Hg et I. Les teneurs élevées de ces deux éléments sont attribuables à l'emploi des comestiques (12 - 14) en particulier des savons antiseptiques contenant 3 % d'iodure de mercure.

Le tableau 2 regroupe les concentrations des éléments déterminés par groupe d'âge. Il faut noter, en passant, que ces résultats ont été obtenus et traités au LOS ALAMOS NATIONAL LABORATORY, New Mexico (U.S.A.) (9).

TABLEAU 1 : CONCENTRATION DES ELEMENTS DETERMINES DANS LES CHEVEUX DES ZAIROIS (*en ppm*)
CAS DE LA VILLE DE KINSHASA ET DE LA VILLE DE MBANDAKA

ELEMENTS	VILLE DE KINSHASA		VILLE DE MBANDAKA	
	Moyenne arithmétique avec déviation standard	Intervalle de variation des valeurs	Moyenne Arithmétique avec déviation standard	Intervalle de variation des valeurs
Au	0,15 ± 0,11 (11)	0,02 - 0,33	0,04 ± 0,003 (16)	0,02 - 0,1
Br	10,32 ± 7,58 (14)	2,1 - 26,09	-	-
Cl	198,87 ± 197,53 (29)	29,3 - 822,24	-	-
Co	1,7 ± 1,68 (32)	0,19 - 6,1	0,57 ± 0,12 (4)	0,45 - 0,73
Cr	7,48 ± 7,23 (34)	0,4 - 37,7	14,52 ± 6,11 (16)	5,71 - 27,88
Cu	9,54 ± 3,78 (17)	3,21 - 20,13	12,97 ± 4,11 (8)	7,8 - 19,85
Hg	115,08 ± 144,2 (39)	1,63 - 543,4	108,48 ± 117,92 (14)	4,86 - 388,92
I	63,84 ± 50,80 (35)	0,3 - 169,8	-	-
Mn	4,59 ± 3,61 (49)	0,49 - 18,9	-	-
Na	298,88 ± 466,08 (17)	9 - 1730	-	-
Sb	6,31 ± 5,32 (37)	0,27 - 19,8	1,02 ± 0,82 (12)	0,44 - 3,35
Se	-	-	0,035 ± 0,01 (5)	0,025 - 0,49
Sc	-	-	2,64 (1)	-
Zn	206,25 ± 295,86 (42	63,99 - 397,1	102,87 ± 37,37 (16)	34,83 - 187,09

Tableau 2 Concentration des éléments déterminés dans les cheveux par groupes d'âges (en ppm). Cas de la ville de Kinshasa.

ELEMENT	19A (7)	20A (11)	22A (4)	23A (4)	24A (4)
Na	8.21-311	3.2-500	18.3-93.8	12.3-520	5.30-44
Mg	2.8-160	63-600	75-156	80-410	67-180
Al	49.2-630	27.0-600	142-480	120-320	69-106
Cl	39-150	21-1220	64-720	87-270	19-650
K	440	190-320	120	268	112
Ca	12-1630	280-3640	393-1100	274-2970	334-1870
Ti	0.041-43	9.2-44	9.4-51	36.6-54	8.0
V	0.09-1.1	0.083-0.86	0.22-80	0.20-0.76	0.11-0.25
Mn	4.7-8.5	1.4-8.7	1.4-6.8	3.0-19	1.6-5.8
Cu	.017-15	7.6-20	13-16	10-18	6.0-16
Br	.33-44	0.71-80	1.6-6.6	0.6-2.2	0.98-16
Sr	7.1	8.0-41.0	7.0	12	5
I	9-150	2-95	4-310	130-480	3-110
Ba	7-85	13-20	6-310	20-380	9-62
Dy	0.40-0.80	0.027	1.3	1.1-7.0	0.41-2.8
Sc	0.0062-0.024	0.0015-0.060	0.010-0.050	0.0086-0.044	0.0040-0.025
Cr	0.33-1.4	0.32-1.3	0.38-1.8	0.22-1.3	0.52-4.0
Fe	45-380	32-250	71-320	70-250	33-100
Co	0.072-0.22	0.11-0.21	0.11-0.25	0.17-0.32	0.090-0.38
Zn	130-220	91-250	97-170	86-160	120-150
Se	0.53-31	0.26-130	0.27-25	26-61	0.44-110
Ag	< 1.0	2.3	< 0.9	< 1.0	< 1.0
Sb	0.21	0.14	0.26	0.23-0.38	0.29
Cs	0.051-0.13	.04-0.08	0.092	0.034	0.036
Ce	1.9	< 0.39	< 0.30	0.54	0.46
Hg	0.79-340	8.0-1120	1.2-600	260-540	4.3-1050
Th	0.051-0.11	0.084-0.09	0.037-0.08	0.055-0.09	0.050

TABLEAU 3 : TENEURS MINIMALE, MAXIMALE ET MOYENNE DES ELEMENTS DETERMINES DANS LES EAUX DES RIVIERES FUNA, LUBUDI ET NDJILI (en mg/l)

ELEMENTS	RIVIERE FUNA			RIVIERE LUBUDI			RIVIERE NDJILI		
	Minimum	Maximum	Moyenne	Minimum	Maximum	Moyenne	Minimum	Maximum	Moyenne
Al	0,23	5,26	2,56	5,96	14,36	12,46	0,24	6,70	3,07
Au	0,002	0,02	0,014	0,002	0,01	0,017	0,001	0,07	0,019
Br(ug/l)	0,10	76,00	22,56	0,22	4,83	2,12	0,25	1,89	1,06
Cl	12,30	69,98	37,87	29,62	56,04	41,12	4,30	49,12	18,94
Fe	0,74	5,73	2,45	1,04	12,89	8,21	2,10	5,66	3,07
I	0,02	0,16	0,07	0,17	0,35	0,26	0,06	0,62	0,24
K	3,32	8,60	4,09	4,48	8,18	6,39	2,51	7,21	4,58
Mn	0,01	0,08	0,04	0,03	0,08	0,05	0,01	0,04	0,03
Na	8,30	26,39	14,36	17,65	23,08	20,37	3,10	8,65	5,62
Sb(ug/l)	0,09	0,79	0,24	0,24	2,08	1,16	0,05	45,97	12,12
Sc(ug/l)	0,30	0,51	0,42	0,73	2,68	1,76	0,19	0,87	0,46
V (ug/l)	-	-	5,92	1,41	4,43	2,94	1,08	2,91	1,76
Cr	0,02	0,08	0,05	-	-	-	0,01	0,04	0,02
Cu	0,05	0,12	0,08	-	-	-	-	-	-
Zn	0,24	0,25	0,25	-	-	-	0,82	1,26	1,04
Co(ug/l)	-	-	-	0,09	0,34	0,18	-	-	-

3.2.- Eaux des rivières

Le tableau 3 donne les valeurs minimales, maximales et moyennes des concentrations des éléments déterminés dans les eaux des rivières. Les eaux de la rivière N'DJILI contiennent de faibles quantités d'éléments à l'état de trace et sont donc moins minéralisées que celles des deux autres rivières. Les eaux de la LUBUDI paraissent les plus minéralisées. Les concentrations des éléments observées dans les trois cours d'eau sont en général conforme aux normes de potabilité et sont d'ailleurs du même ordre de grandeur que celles observées dans les eaux naturelles (15-18) sauf pour Al et Fe (tableau 4). Les valeurs élevées de Al proviennent des terrains traversés par les eaux. Le Fe n'est pas toxique mais à des teneurs élevées, il peut dénaturer le goût de l'eau et colorer les vêtements au lessivage (18).

Le niveau du Cr paraît supérieur à la limite de tolérance permise. Il est cependant bien connu que cet élément existe normalement dans l'eau sous forme de Cr^{+3}, ayant une très faible toxicité. Les limites données au tableau 7 se réfèrent à sa forme hexavalente qui est fort toxique. Comme conséquence, des valeurs relativement élevées du Cr stable dans l'eau ne provoquent pas nécessairement des effets nuisibles à l'homme (18).

TABLEAU 4 : VALEURS MAXIMALES DES ELEMENTS DOSES DANS LES EAUX DES RIVIERES FUMA, LUBUDI ET NDJILI, LES VALEURS OBSERVEES DANS LES EAUX DES U.S.A. ET LES NORMES DE POTABILITE DE : O.M.S. , U.S.A. , U.R.S.S. ET CANADA (en mg/l)

Eléments	Valeurs maximales observées	VALEURS OBSERVEES AUX U.S.A.			NORMES DE POTABILITE			
		Minimum	Maximum	Moyenne	O.M.S.	U.S.A.	U.R.S.S.	CANADA
Al	14,30	0,001	2,76	0,074	-	-	-	-
Au	0,07	-	-	-	-	-	-	-
Cl	69,98	-	-	-	200-6000	250	-	250
Fe	12,89	0,001	4,6	0,052	0,03	0,3	0,5	0,3
I	0,62	-	-	-	-	-	-	-
K	8,5	-	-	-	-	-	-	-
Mn	0,08	0,0003	3,23	0,058	0,1	0,05	0,05	0,05
Na	26,39	-	-	-	-	-	-	-
Sb	0,046	-	-	-	-	0,1	0,05	-
Sc	0,0027	-	-	-	0,01	-	-	0,01
Co	0,00034	0,001	0,048	0,017	-	1	1	-
V	0,0059	0,002	0,3	0,04	0,1	-	-	-
Cr^{+6}	0,075*	0,001	0,112	0,0097	0,05	0,05	0,1	0,05
Cu	0,12	0,001	0,048	0,015	1	1	0,1	1
Zn	1,26	0,002	1,183	0,864	45	45	-	-

* Cr total

3.3.- Légumes et jacinthe d'eau

Onze éléments de longue période ont été déterminés quantitativement dans les légumes. Les résultats d'analyse sont donnés au tableau 5. Le tableau 6 donne les résultats de trois plantes également consommées par les populations autochtones. Il s'agit de P. Tetragonolobus, P. Palustris et S.Stenocarpa.

TABLEAU 5 : TENEURS DES ELEMENTS MINERAUX DANS LES LEGUMES (en ppm)

ELEMENTS	Colocassia	Amarantus	Solanum sp.	Brassicia Oleracea	Ipomea batatas	Gnetum Africanum	Hibiscus Acetosela (Vert)	Hibiscus Acetosela (Rouge)
Hg	0,314 ± 0,016	0,228 ± 0,011	0,240 ± 0,012	0,298 ± 0,014	0,231 ± 0,015	0,225 ± 0,022	0,128 ± 0,006	0,274 ± 0,014
Th	-	0,642 ± 0,031	1,778 ± 0,85	0,833 ± 0,039	0,460 ± 0,02	-	-	-
Ba	-	79,84 ± 5,509	21,66 ± 1,495	34,608 ± 2,381	-	23,33 ± 1,609	-	39,51 ± 2,723
Sr	-	189,42 ± 16,67	61,82 ± 5,44	100,31 ± 8,63	48,2 ± 3,241	-	-	112,51 ± 2,726
Cs	0,78 ± 0,07	1,16 ± 0,09	0,42 ± 0,08	0,57 ± 0,04	1,56 ± 0,15	0,92 ± 0,08	0,61 ± 0,04	3,50 ± 0,03
Sc (10^{-3})	16 ± 0,95	24,90 ± 1,53	13,70 ± 0,69	4,50 ± 0,20	9,50 ± 0,60	6,90 ± 0,44	4,90 ± 0,31	9,96 ± 0,36
Rb	139,44 ± 10,18	13947,09 ± 8,13	31,60 ± 2,31	50,82 ± 2,71	192,11 ± 12,02	42,12 ± 3,07	22,69 ± 1,65	50,34 ± 3,78
Fe	165,85 ± 5,88	194,09 ± 12,8	843,92 ± 50,95	184,25 ± 6,54	199,63 ± 7,09	466,69 ± 28,57	324,71 ± 22,53	370,60 ± 11,24
Zn	125,08 ± 6,57	268,31 ± 16,08	246,79 ± 10,96	251,64 ± 12,35	58,25 ± 5,38	97,89 ± 5,14	65,94 ± 3,45	77,80 ± 4,38
Co (10^{-3})	13,7 ± 0,87	10,5 ± 0,66	4,43 ± 0,35	9,40 ± 0,22	6,10 ± 0,38	15,10 ± 0,96	25,40 ± 1,75	19,10 ± 0,691
Cr	1,51 ± 0,03	1,71 ± 0,03	1,92 ± 0,04	1,16 ± 0,03	1,13 ± 0,04	1,58 ± 0,06	1,058 ± 0,01	1,30 ± 0,03

TABLEAU 6 : TENEURS DES ELEMENTS MINERAUX DANS P. PALUSTRIS, P. TETRAGONOLABUS ET S. STENOCARPA

ELEMENTS	P. TETRAGONOLABUS			P. PALUSTRS		S. STENOCARPA	
	Graines	Feuilles	Gousses	Graines	Feuilles	Graines	Tubercules
Fe	243,28	123,17	212,17	381,31	342,28	125,85	65,07
Zn	68,83	68,62	117,91	93,78	124,16	46,62	66,02
Cr	1,32	1,48	1,67	1,26	2,04	1,03	1,02
Sc	0,03	0,03	0,05	0,05	0,05	0,01	0,03
Rb	15,58	3,93	24,35	25,20	15,40	38,59	39,26
Co	0,38	0,15	0,31	0,17	0,13	0,05	0,02
Cs	0,12	0,27	13,34	0,14	0,45	0,30	0,24

Les parties comestibles de ces plantes ont été analysées. Sept éléments traces ont été déterminés quantitativement : Fe, Zn, Cr, Sc, Rb, Co et Cs. Il ressort des résultats que le Fer s'accumule le plus dans les feuilles pour le P. Palustris et les tubercules pour le S. Stenocarpa (19). Le P. Tetragonolobus contient assez de Co, un des composants de la vitamine C. Quant à la jacinthe d'eau, plusieurs utilisations de cette plante, entre autres comme légumes, aliment pour bétail, engrais, etc... ont été proposées.

Le dosage des éléments minéraux susceptibles de toxicité a été entrepris en vue de déterminer l'utilisation de cette plante dans l'alimentation de l'homme ou de bétail. Des essais ont portés sur la détermination des éléments suivants : Mo, Cd, Ni, Ba, Sb, Al, Cu, Co, Zn, I. Seuls Cu, Co, Zn, Ba et Sb ont pu être détectés et déterminés quantitativement de manière non destructive. Le tableau 7 donne les résultats déterminés dans les feuilles, tiges et racines des jacinthes d'eau récoltées à différents endroits du fleuve Zaïre. D'une manière générale, les éléments métalliques s'accumulent le plus dans les racines que dans les autres parties de la plante.

Les niveaux des éléments dosés dans la jacinthe sont supérieurs aux quantités déterminées dans les légumes locaux (tableau 3).
Ils restent néanmoins inférieurs aux niveaux estimés toxiques pour l'alimentation animale (20 - 22).

TABLEAU 7 : TENEURS DES ELEMENTS DETERMINEES DANS LES CENDRES DE JACINTHES (en ppm)

ELEMENTS	H A L U K U			N D O L O			G O M B È		
	Feuilles	Tige	Racine	Feuilles	Tige	Racine	Feuilles	Tige	Racine
Ba	221,86	475,72	293,50	346,81	524,51	495,45	614,63	661,29	269,31
Co	0,66	1,73	13,09	3,45	3,47	63,39	4,05	4,40	47,51
Cr	27,32	75,61	47,21	21,25	29,63	60,10	16,16	89,39	25,91
Sb	0,38	8,25	8,31	1,41	2,28	5,47	0,02	5,65	10,30
Zn	63,07	178,11	346,83	421,68	233,10	657,46	349,53	186,77	589,71

3.4.- Les poussières atmosphériques

Le tableau 8 donne les résultats des teneurs obtenues pour 19 éléments métalliques dosés dans des échantillons de poussières atmosphériques. Les valeurs plus élevées en Ca, Hg, Ga, Sb, Cl, Au, Co et Cr sont observées au site A et peuvent provenir du milieu ambiant (laboratoires, sol). Br, Sm, Mn, V, Al et Pb sont plus abondants dans les échantillons B, prélevés en pleine cité résidentielle. Pb et Br proviendraient des gaz d'échappement des véhicules.

TABLEAU N° 8 : TENEURS DES ELEMENTS METALLIQUES DANS LES POUSSIERES ATMOSPHERIQUES DE KINSHASA

ELEMENTS	S I T E A				S I T E B			SITE C	SITE D
	A - 1	A - 2	A - 3	A - 4	B - 1	B - 2	B - 3	C_1	D_1
Ag	6,95± 0,42	5,31+ 0,47	-	-	4,23 ± 0,08	-	-	-	-
Al	35,5 ± 0,71	25,1 ± 2,17	14,8 ± 2,06	25,9 ± 1,24	56,5 ± 1,2	57,3 ± 0,86	48,9 ± 2,89	44,1 ± 1,30	35,4 ± 1,40
Au	1,84± 0,03	0,67± 0,02	0,18 ± 0,06	7,58 ± 0,28	0,52 ± 0,03	0,56± 0,04	0,74 ± 0,03	0,67± 0,03	0,28 ± 0,02
Br	194± 17	44,5 ± 1,2	293 ± 16	260 ± 18	433 ± 9,21	404± 36	110 ± 3,01	362± 7,80	243 ± 31
Ca	234± 9,8	97,3 ± 2,49	54,2 ± 3,01	55,6 ± 4,3	47,8 ± 2,01	49± 1,90	45,8 ± 1,79	52,4 ± 3,62	42,6 ± 2,30
Cl	16,2 ± 0,42	9,97± 0,37	7,91 ± 0,5	39,1 ± 1,17	9,54 ± 0,24	7,79± 0,62	5,52 ± 0,08	3,26± 0,10	2,72 ± 0,24
Co	19,6 ± 0,65	27,4 ± 1,01	-	97,2 ± 7,2	15,3 ± 0,90	16,6 ± 0,74	16,4 ± 0,64	56,7 ± 2,10	65,70 ± 6,80
Cr	96,8 ± 1,2	140 ± 4,1	63 ± 5,6	196 ± 21	38,20 ± 0,9	29,4 ± 2,80	41,30 ± 3,20	87 ±10,50	153 ±10,00
Eu	1,41± 0,04	0,39± 0,02	0,64 ± 0,05	1,05 ± 0,12	1,18 ± 0,06	1,76± 0,09	1,23 ± 0,08	2,29± 0,19	1,88 ± 0,13
Fe	22,6 ± 0,44	8,69± 0,24	17,9 ± 0,97	19,3 ± 0,87	21,7 ± 0,60	18,80± 0,30	27,7 ± 1,40	33,90± 2,30	13,50 ± 0,71
Ga	1,61± 0,16	4,85± 0,33	-	1,26 ± 0,09	-	-	-	2,12± 0,16	3,05 ± 0,12
Hg	0,97± 0,17	0,06± 0,007	-	0,22 ± 0,01	-	-	-	0,03± 0,002	-
Mn	379± 0,17	359± 1,20	367 ± 16	178 ± 6,02	372 ± 10	393± 3,7	478 ± 2,9	406± 12	264 ± 10
Sb	63,1 ± 3,6	9,37± 0,34	3,04 ± 0,06	21,2 ± 1,67	0,5 ± 0,05	0,72± 0,01	0,51 ± 0,3	1,04± 0,04	5,62 ± 0,37
Se	9,75± 0,38	3,5 ± 0,27	-	-	-	-	-	16,70± 0,15	-
Sm	1,2 ± 0,16	2,28± 0,12	3,04 ± 0,06	2,86 ± 0,27	10,4 ± 0,58	2,95± 0,23	2,61 ± 0,17	1,46± 0,12	2,07 ± 0,29
Pb	947	476	1860	850	1250	1300	2220	670	280
Zn	1130± 103	2480 ± 231	1270 ± 91	1730 ± 123	742 ± 33	953± 43	854 ± 62	2500± 127	898 ± 850
V	45,1 ± 4,92	35± 4,5	23,3 ± 1,93	50,2 ± 3,17	117 ± 2,01	126± 2,30	55,4 ± 2,14	18,40± 1,10	28,50 ± 1,70

Le site D, situé presqu'à la périphérie contient des teneurs très faibles en éléments métalliques.
Les valeurs observées dans nos échantillons sont voisines de celles observées dans l'échantillon de poussière atmosphérique de Milan (23) sauf pour le Hg (23, 2 ppm), Zn (7434 ppm), V (1990 ppm), Pb (5540), Mn (1274).
Eu paraît plus élevé dans nos échantillons (0,5 ppm dans l'échantillons de Milan).

4.- CONCLUSIONS ET PERSPECTIVES

L'analyse par activation instrumentale montre qu'il est possible de déterminer simultanément un grand nombre d'éléments métalliques, dans un délai relativement raisonable, dans une variété de substances. Les éléments déterminés en routine dans les substances biologiques, comprennent Al, Au, Ba, Br, Ca, Cl, Co, Cr, Cu, Fe, Hg, I, K, La, Mg, Na, Rb, Sb, Se, V et Zn. Des procédés de séparation radiochimiques doivent être développés pour le dosage d'autres éléments intéressants tels que As, Cd, Ni, etc...
D'autres méthodes d'analyses telles que la spectrophotométrie d'absorption atomique, la fluorescence-X, etc... doivent également être développées.

Les résultats obtenus pour les légumes sont exploités dans une étude beaucoup plus approfondie qui a pour objectif l'étude de la valeur nutritive des graines et tubercules, la détermination des substances antinutritionnelles et la promotion de l'utilisation de ces graines et tubercules dans les habitudes alimentaires de la population en vue de combattre la malnutrition protéino-calorique (19).

Quant à la jacinthe d'eau (Eichornia crassipes) les résultats obtenus sont exploités dans la fabrication des aliments pour bétail en particulier les porcs et la volaille (21).

Les teneurs élevées en Hg et I ne reflètent pas les teneurs naturelles de ces éléments dans les cheveux des sujets Zaïrois normaux.

Il faudra dans l'avenir étudier le mode d'absorption de ces éléments sur les cheveux et le procédé adéquat pour l'élimination des contaminations externes dues à l'emploi des comestiques. La

collecte d'un grand nombre d'échantillons représentatifs de toutes les couches, l'échantillonnage des cheveux à différents endroits de la tête d'un même sujet, l'analyse des étalons standards de référence, la poursuite du contrôle de la qualité des eaux et des aliments et l'étude de la pollution atmosphérique, conduiront à des conclusions plus adéquates.

L'analyse des sérums sanguins permettra d'élucider les effets d'absorption par l'organisme humain de Hg et I dus aux comestiques.

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METAL ANALYSES OF HAIR AND URINE AND THEIR USE AS EPIDEMIOLOGICAL INDICES OF ENVIRONMENTAL POLLUTION

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(I) The Significance of Elemental Analysis of Hair as Means of Detection of Environmental Pollution

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Abstract

Correlation of metal concentration in hair with those in the critical organs was investigated by tracer studies using ^{203}Hg, ^{51}Cr, ^{75}Se, ^{109}Cd and ^{65}Zn in mice. The accumulation of these elements in organs of the mouse including hair during acute contamination was confirmed. While reported results of metal concentrations in critical organs and hair were compiled and compared, these studies led to the following conclusions.

Hair was found to be a reasonable indicator to verify the contamination by mercury and chromium as these elements are readily deposited into hair and stay comparatively long time. The time dependent shifts of zinc and selenium in hair reflected their kinetics in the whole body, though their concentrations in hair were not higher than those in other organs. Hair was found to be a poor indicator in case of cadmium, as the concentration of cadmium in hair was not parallel to that in the critical organs of the same mouse.

(II) Effect of Millimolar Level of Calcium Intake on Calcium, Phosphorus and Cadmium Content in Rats

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Abstract

The effect of millimolar level of Ca administration through drinking water that is 1/75 of the Ca requirement on rats of SPF Fisher strain chronically fed with low calcium diet was demonstrated by the aleration of organ distribution of Ca, P and Cd. Livers, kidneys, femurs, hairs and feces were collected from each animal with or without Cd administration about 600 days after the initiation of the experiment. Calcium, phosphorus and cadmium in each sample were analyzed by inductively coupled plasma spectroscopy and flameless atomic absorption spectrophotometry. The administration of millimolar level of Ca led to increase of Ca accumulation in liver and bone, and decrease of Ca in kidney, serum and hair among females. It seems to indicate a stimulative role of small amount of Ca to prevent the loss of Ca from the skeletons to outside the body among females irrespective of Cd administration.

(Nutrition Reports International to be published in 1984)

NEUTRON ACTIVATION ANALYSIS OF HAIR ELEMENTS. INFLUENCE OF RESIDENCE, OCCUPATION AND HEALTH STATUS

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Abstract

26 trace elements are determined in human head hair by n.a.a. in combination with a.a.s. and a.e.s. Mean values obtained are compared with literature data. For selected elements the influence of age in the first years of life, of residence, professional burden, hormons, and diseases was studied.

1. INTRODUCTION

The investigation of the concentration of essential and toxic trace elements in human head hair was focussed on normal values, professional burden with toxic elements and influence on health.

The determination of normal values demonstrates the possibilities of the methods and allows the comparison with data found in the literature. If the values determined are higher or lower than the mean values of the literature, we can look for regionally extended sources of food contamination or a deficiency of essential elements. The need of high quality normal values has been formulated by the Advisory Group Meeting "Applications of nuclear methods in environmental research"[1].

The investigation into the influence of professional burden by toxic elements allows us to develop methods for monitoring individual burden.

According to a proposal by MOEPERT and BALDAUF [2] we had started our investigations with a study about the influence of mammary carcinoma on the trace element content of human head hair. Our work was done in co-operation with physicians who

know very well the state of health of the people from whom they collect the samples.

2. METHODS

2.1. Neutron activation analysis

The samples were collected and cleaned according to the IAEA-recommendation [3], irradiated in the core of the Rossendorf Research Reactor and measured with the help of a Ge(Li)-spectrometer. For the activation of short-lived nuclides ^{20}F, ^{77m}Se, ^{110}Ag, ^{28}Al, ^{128}I, ^{38}Cl the samples are irradiated within foils and containers of polyethylene in the pneumatic tube system. Experimental details of the analysis are published [4].

Our results of the analysis of the standard reference material HH-1/IAEA are shown in table 1.

Table 1: Analysis of SRM HH-1/IAEA, (ppm)

Element	N	A.M.	S.D.	Element	N	A.M.	S.D.
F	3	1270	70	Zn	6	174.8	6.5
Mn	3	0.80	0.12	Se	5	0.37	0.02
Cr	4	0.27	0.06	I	4	28.3	1.4
Co	5	6.74	0.22	Au	2	0.0164	0.0013
Cu	3	9.61	0.26				

2.2 Comparison between n.a.a., a.a.s., and a.e.s.

For a.a.s. samples (100-1000 mg) are ashed in open air at 820°K, dissolved in 0.1 N HCl, diluted, and measured with an atomic absorption spectrometer type AAS 1N (Carl Zeiss, Jena) using an acetylene-air flame.

For a.e.s. the samples (50 mg) are dry ashed on carbon powder and the measurements are performed with a carbon arc using a quartz crystal spectrometer type Q 24 (Carl Zeiss, Jena) with registration on photoplates.

Table 2: Determination of Mn, Cu, and Zn by a.a.s. and n.a.a.

	Mn	Cu	Zn
N	10	10	10
A.M./ppm	3.8	18.8	176
A.M. (n.a.a.)/ppm	3.7	18.5	180
A.M. (a.a.s.)/ppm	3.9	19.0	172

Table 2 shows a comparison between n.a.a. and a.a.s. for Mn, Cu, and Zn. We see, that we can use both methods for these elements [5]. Table 3 shows values only determined by a.a.s. A number of elements were determined in five subsamples of the hair of two persons. Table 4 gives the list of elements determined and of methods used. For six elements the relative standard deviation R.S.D. is listened in table 5.

Table 3: Elements determined by a.a.s.

Element	sex	N	A.M./ppm	S.D./ppm	Element	sex	N	A.M./ppm	S.D./ppm
Cu		23	16.7	9.2	Pb		15	7.7	3.7
Zn		24	163	38	Ca	m	8	712	546
Fe		22	24.4	8.7	Ca	f	14	4670	4560
Mn		22	1.85	1.6	Mg	m	9	52	47
Ni		16	2.1	1.5	Mg	f	14	360	330

The R.S.D. is smaller by use of a.a.s. than for a.e.s. and n.a.a., but the weights of the subsamples were higher by a factor 10.

Table 4: Two samples analysed by different methods (n.a.a. = 1, a.a.s. = 2, a.e.s. = 3)

Element	Ag	Al	Au	B	Ba	Br	Ca	Cd	Cl
c_1/ppm	0.86	14.6	0.014	3.35	2.05	0.42	9800	0.23	64
c_2/ppm	0.41	23.5	0.015	1.35	0.2	9.1	186	0.26	1370
Method	1	1,3	1	3	3	1	2	2,3	1

Element	Co	Cr	Cu	F	Fe	I	K	Li	Mg
c_1/ppm	0.10	0.28	11.2	76	18.1	0.65	28.6	4.8	960
c_2/ppm	0.1	0.54	10.4	43	21.3	1.04	11.9	0.24	23
Method	1	1	1,2,3	1	1,2,3	1	1,2	2	2,3

Element	Mn	Na	Ni	Pb	Se	Si	Sn	Zn
c_1/ppm	10.4	21.9	3.6	4.7	0.32	9.4	1	233
c_2/ppm	0.39	14.1	0.3	11.3	0.35	34	1	148
Method	1,2,3	1,2	2	2,3	1	3	3	1,2

Table 5: R.S.D./% for n.a.a., a.a.s., and a.e.s.

Method	Sample	Cu	Fe	Mg	Mn	Pb	Zn
n.a.a.	1	9.0	15		4.2		4.6
	2	5.8	30		11		5.2
a.a.s.	1	6.9	4.9	4.2	3.3	9.8	4.7
	2	13	5.1	5.2	4.5	7.8	5.4
a.e.s.	1	9.6	2.1	8.3	15	5.0	
	2	8.1	15	13	21	31	

Until now we are not sure, that the determined Fe content is true. Table 6 shows 5 samples where Fe is determined by photometry, a.a.s., instrumental and radiochemical n.a.a. The values obtained by different methods show roughly the same deviations like values obtained for different persons.

Table 6: Determination of iron in the hair of five persons by different methods (ppm)

Sample	photom-etry	a.a.s.	instru-mental n.a.a.	radio-chemical n.a.a.	A.M.
1	18.6	15.5	18.8	11.6	16.1
2	22.7	15.8	26.1	26.7	23.9
3	16.4	11.2	14.8	7.9	12.6
4	11.2	19.7	27.0	19.2	19.3
5	38.6	25.4	25.4	19.7	27.3
A.M.	21.5	17.5	22.4	17.0	19.7

3. RESULTS AND DISCUSSIONS

3.1 Normal values

Values obtained by n.a.a. for normal persons were summarized in [4] and compared with the median M of the mean values from the literature [6] and with the geometric mean G.M. of the values determined by TAKEUCHI et al. [7]. Until 1980 most of the selenium values found in the literature were higher than our values. We found a remarkably low-standard deviation, therefore we assume that our values reflect the minimum for good health. PARTSCHEFELD (cit. by ANKE and RISCH [8]) detected some locations in the G.D.R. with a deficiency of Se in the hair of cows.Low selenium concentrations in human head hair were also found by CIGNA ROSSI et al. [9] in an area of Amiata mountains in Italy and by OBRUSNIK and BENCKO [10].

3.2 Hair of children

The concentrations of Cu, Zn and Au in the hair of new-born children are shown in table 8. The content of Cu and its standard deviation is lower than the corresponding values for adults.

Table 7: Comparison of determined contents with data from the literature, G.M./ppm, M/ppm [6]

Element	n.a.a. G.D.R. [4]	n.a.a. Japan [7]	n.a.a. [6]	a.a.s. a.e.s. [6]
F	54			
Al	17.7	10	4.5	16.8
Cl	890	300	1775	
Cr	0.54	0.56	3.15	0.77
Mn	1.34	0.48	1.47	1.07
Fe	20	28	33	22
Co	0.38	0.041	0.45	0.21
Cu	11.7	11.1	17.8	14.4
Zn	151	176	166	164
Se	0.31	0.7	1.95	
Ag	0.24	0.28	2.28	1.0
I	0.94	0.43	1.02	
Au	0.019	0.011	0.071	

Table 8: Concentration of Cu (ppm), Zn (ppm), and Au (ppb) in the head hair of 20 male and 21 female new-born children from Jena [11]

Element	Sex	A.M.	S.D.	G.M.	A.S.D.	M.	Range
Cu	m	8.55	3.08	8.25	1.16	7.78	6.7.-21.3
	f	7.69	1.11	7.62	1.11	7.40	6.1.-10.9
Zn	m	204	42	201	1.15	192	144-338
	f	220	80	210	1.26	193	151-456
Au	m	8.55	6.2	6.6	2.00	6	2-21
	f	8.57	6.0	6.8	1.97	8	2-25

In the hair of these children the contents of Mn, Cu, Zn, and Au were determined until an age of about two years [12]. The values are listed in table 9. It is surprising that the contents of Cu, Zn, and Au are going through a maximum nearby eighty days, where the values are enhanced for these elements by factors of 4, 5, 15, and 2.4, respectively. A maximum of the manganese content appears some month later.

In the first month an exchange of trace elements takes place between different compartments in the human body, e.g. of Cu from the liver into the serum. A high production rate of hormons was found also in this time.

Table 9: Medians of the concentrations (ppm) of Mn, Cu, Zn, and Au in the hair of children of different age

Age group (days)	1	83	224	402	778
Mn	0.095	0.27	0.29	0.23	0.40
Cu	7.6	14.9	8.8	8.6	8.8
Zn	193	880	221	137	93
Au	0.007	0.081	0.068	0.035	0.029

We have measured the content of Cu and Zn in the hair of persons in dependence upon age. We have found the same dependence like TAKEUCHI [7]. But for females between 12 and 18 years Cu concentrations between 20 and 100 ppm are observed frequently, while most of the other values are close to the mean value of 11 ppm.

3.3 Influence of residence

With an increased number of determinations the differences of the Mn and Zn concentrations in the hair of women from Berlin, Dresden, and Jena (limestone region) have been established (table 10).

Table 10: Regional influence on the Mn and Zn concentration (ppm) in the hair of women, taking no contraceptiva

	Berlin	Jena	Dresden
Mn	1.34	0.39	2.00
Zn	130	197	157

3.4 Medical application of trace elements

The gold content of serum, liver and hair of persons being treated with Sanocrysin (sodium gold thiosulfate) for rheumatoid arthritis was determined [13,14]. One week after the application of 35 mg Au the gold concentration in serum amounts to about 5 ppm. In liver samples up to 300 ppm were determined. In the hair 0.44 $\tilde{x}$ 1.74 ppm (range 0.21 - 1.3 ppm,

Table 11: Se content (ppm) in the hair of normal and diseased persons

Group(Sex)	N	A.M.	S.D.	G.M.	S.D.	number of cases in stated range 0.1 - 0.21	0.22 - 0.46	0.47-1.00
Normal (m)	30	0.36	0.08	0.35	1.24	2	25	3
Euthr. goitre (m)	4	0.40	0.09	0.39	1.23	0	3	1
Normal (f)	26	0.30	0.07	0.29	1.31	3	23	0
Euthr. goitre (f)	28	0.42	0.07	0.42	1.20	0	21	7
Hyper-thyroidism (f)	6	0.40	0.09	0.39	1.26	0	5	1
Mammary carcinoma	17	0.30	0.09	0.26	1.74	5	11	1
Cervix carcinoma	8	0.36	0.14	0.34	1.44	0	6	2

median 0.5 ppm, N = 10) was found. This relatively low increase may have been caused also by external contamination during sampling.

3.5 Influence of diseases

The content of Se was determined in the hair of normal and diseases persons (Table 11 [14]). The influence of some types of carcinoma on the copper and zinc content is shown in table 12 [15,16,17]. Depending on the type of carcinoma an enhanced content of Cu or Zn or both elements was observed.

Whereas the iodine content in the hair of patients suffering from thyroidic disfunctions decreases, goitre carcinoma is indicated by a high value (table 13 [12]).
After surgical resection of parts of the thyroidic gland the iodine content in the hair increases [19]. For folicular-papillar, papillar, folicular and oncocytar carcinoma 1.8, 28, 36, and 245 ppm, respectively, of I were found in the hair. These high values don't correlate with the application of iodine compounds but with the content of Mn and Au.

Table 12: Content of Cu and Zn in the head hair of female adults with tumours (Berlin)

Group		Zn		Cu	
	N	A.M.	S.D.	A.M.	S.D.
Normal	19	129.5	35.8	12.2	4.0
Mammary carcinoma	52	181.9	36.8	16.7	12.9
Cervix carcinoma	10	186.4	57.4	16.9	8.4
Stomach carcinoma	10	148.0	57.8	20.4	8.2
Colon carcinoma	10	144.1	69.9	23.3	18.2
Rectum carcinoma	27	178.9	67.1	14.3	8.4
Skin melanom	26	192.4	56.4	12.2	3.6
Goitre carcinoma	37	181.1	19.4	19.4	8.8

Tabelle 13: Concentration of iodine (ppm) in the hair of patients from Dresden with different thyroidic disfunctions

Group (Sex)	N	A.M.	S.D.	G.M.	A.S.D.
Normal (m)	76	1.22	0.69	1.04	1.80
Normal (f) without contraceptiv.	15	0.50	0.42	0.40	1.89
Normal (f) with contraceptiv.	7	3.09	2.01	2.47	2.14
Euthyreosis (m)	4	0.16	0.10	0.14	1.71
Euthyreosis (f)	8	0.48	0.35	0.39	1.93
Enhanced iodine avidy	29	0.29	0,14	0.28	1.68
Hyperthyreosis (m)	3	0.32	0.19	0.27	2.08
Hyperthyreosis (f)	34	0.46	0.45	0.37	1.89
Thyroid. carcinoma without prev.treatm.(m)	12	9.88	21.0	2.13	5.13
" " " (f)	16	9.13	18.6	1.83	6.61

3.6 Influence of hormons

Women who are taking contraceptiva [20] show a significant enhancement of the content of zinc (table 14) and iodine

Table 14: Influence of hormonal contraceptives on trace element concentration (ppm) in the head hair of female adults from Jena

Element	N	Before application		One month after application		9 month after application	
		A.M.	S.D.	A.M.	S.D.	A.M.	S.D.
Cr	10	1.22	1.0	1.32	1.1	0.58	0.31
Mn	8	0.38	0.29	0.32	0.17	0.35	0.30
Co	10	0.062	0.02	0.075	0.02	0.066	0.02
Cu	10	13.5	3.8	14.8	6.5	12.9	2.1
Zn	10	192	47	211	74	246	48
Se	10	0.67	0.16	0.67	0.25	0.44	0.11

(table 13) in hair, demonstrating the mobilisation of trace elements by hormon activity. This was observed also in other examples. Enhancement of trace element concentrations three month after birth and after resection of the thyroidic gland and the appearance of extremely high Cu contents in the hair of females between 12 and 18 years.

3.7 Professional burden with toxic elements

In table 15 we see a significant enhancement of Mn and Cr in the hair of welders [4,21] and of F in the hair of workers in a fluorine factory.

Table 15: Professional burden with toxic elements

Element	Control group			Burdened persons			Occupation
	N	G.M.	A.S.D.	N	G.M.	A.S.D.	
F	16	54	1.9	18	900	2.3	workers in a fluorine factory
Cr	56	0.54	1.85	52	2.27	2.3	welders
Mn	450	1.4	2.1	460	7.0	2.3	welders

4. CONCLUSIONS

Hair reflects the status of most of the trace elements. Professional burden significantly influences the values and after elemental burden other influences are not detectable.

Hormonal activity has a large influence on trace element content in hair, the influence of residence was also observed, but the effect of diseases observed until now are small.

The small differences between the mean values of Cu, Zn, Se and other elements between a number of countries allow us to define median values for comparison. The small regional differences of mean values and the small influence of diseases investigated until now are in contrast with large individual deviations.

5. NEEDS FOR FURTHER RESEARCH

The reasons for the large individual deviations are unknown until now. We propose to check the healthy people which show extreme contents of trace elements and to publish case reports for this persons. The investigation of drinking water and of feed especially for these persons should be included in the programme.

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PIXE ELEMENTAL ANALYSIS OF ENVIRONMENTAL AND BIOLOGICAL SAMPLES *

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Abstract

A PIXE (Particle Induced X-ray Emission) analytical system was implemented at the Physics Department of the Pontifícia Universidade Católica do Rio de Janeiro (PUC/RJ) and used in projects involving the analyses of environmental and biological samples. This report describes the PIXE analytical system at PUC/RJ and summarizes the work done under IAEA Research Contract #2553/R2/RB.

1. INTRODUCTION

A PIXE (Particle Induced X-ray Emission) system for elemental analysis, based on the method suggested by Johansson et al. [1], was developed at (PUC/RJ), Depto. de Fisica, in 1976 [2-4]. The PIXE system was implemented by taking advantage of an extant 4.5 MV Van de Graaff accelerator and a home-built scattering chamber initially designed to measure L x-ray cross sections of heavy elements such as Au, Tl, Pb, Bi, Th, and U [5].

Following the calibration of the PIXE system implanted at PUC/RJ, a theoretical discussion of the uncertainties associated with the non-uniformity of the particle beam and the non-homogeneity of the target sample was undertaken, and a proton beam diffusing system was inserted in the beam path to improve the beam profile for PIXE analysis [6,7]. A number of elemental analyses of environmental and biological samples from several origins have been made since the inception of the PIXE system at PUC/RJ [4,8-11]. The experimental arrangement for PIXE analysis at PUC/RJ has been described in detailed elsewhere with schematic views of the accelerator and peripheral equipment [4,8,12].

2. APPLICATIONS OF PIXE AT PUC/RJ

2.1 Elemental concentrations in aerosols

The first application of the PIXE system implemented at PUC/RJ was made by analyzing aerosol samples collected daily at approximately 7 PM for a 21-day period in a highly popu-

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* This report summarizes the work done at PUC/RJ under the IAEA Research Contract # 2553/R2/RB.

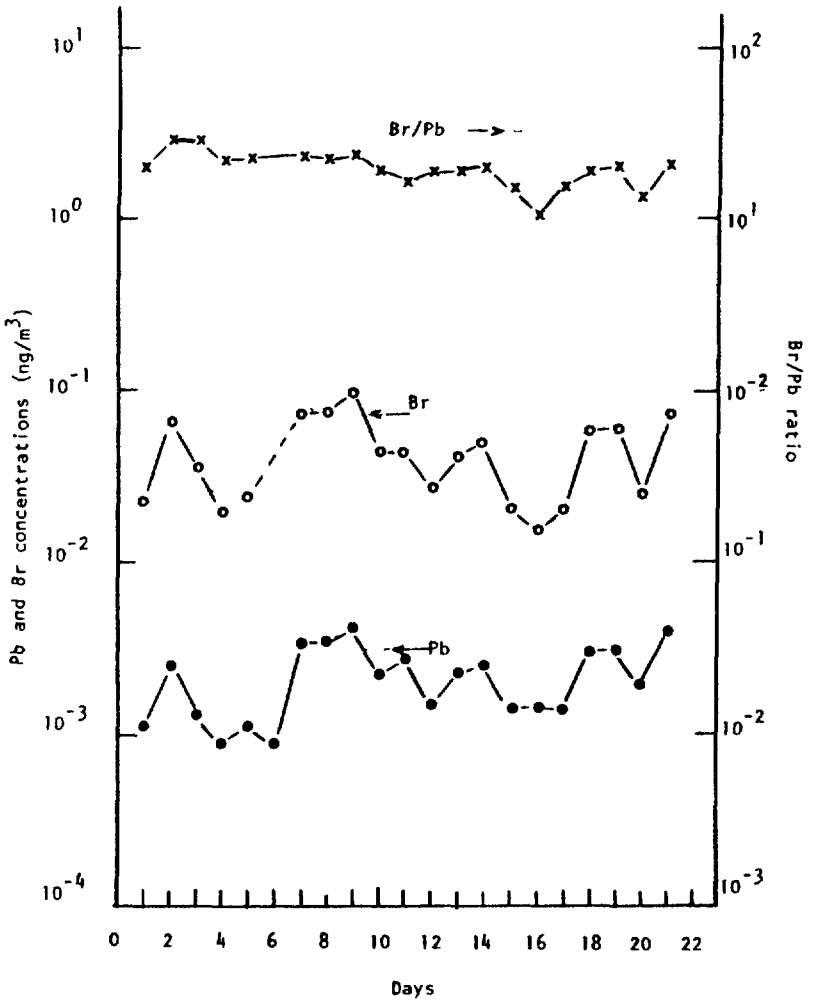
lated residential and commercial area (≈4 x 10^4 persons/km^2) of Rio de Janeiro, located along the sea coast. The air particulate samples were collected with a cascade impactor (Casella type). The Casella type cascade impactor, which is not the most adequate for PIXE analysis, was the only cascade impactor available at PUC/RJ for aerosol sampling at that time.

Taking into account that at least 90% of the particles smaller than 2.5 μm in diameter pass the second stage of Casella type cascade impactors, and 90% of particles larger than 5.4 μm in diameter are retained in the first two stages of the cascade impactor and do not reach the filter, only two stages of the cascade impactor were used for collecting aerosols. Air particulates were collected on nuclepore filters 10 μm thick with 0.4 μm pore size, after passing through the cascade impactor. The air flux through the filter was about 17.5 l/min. The filters were then mounted on Al rings and placed in the disc holder to be analyzed by PIXE in the scattering chamber. The aerosol target samples were irradiated with 2 MeV proton beam with a current range from 24 to 109 nA.

Daily as well as average week-day values of the concentrations of Ca, Fe, Cu, Zn, Br and Pb for the period covered by sampling have been reported elsewhere [4]. The daily concentrations of Br and Pb as well as the daily Br/Pb ratio in the aerosol samples are presented in Figure 1 to illustrate how PIXE analysis can be used to identify the origin of air pollutants. The approximately constant Br/Pb ratio indicates a possible common origin for Br and Pb in the aerosols, which is likely to be automobile exhausts.

Aerosol samples were collected also in an industrial area of Rio de Janeiro and analyzed by PIXE for elemental concentrations. The results showed a higher Pb concentration in air, but no constant Br/Pb ratio [13]. The excess Pb concentration in the air of this industrial area of Rio de Janeiro can be traced back to releases from metallurgical industries located in the area. These releases contain Pb associated with particles of typical size around 30 μm , which are not likely to be inhaled under normal respiratory conditions.

Further research in industrial hygiene and air pollution will be helpful in answering some germane questions concerning the respirable fraction and the regional deposition of particles in the human respiratory system. The use of PIXE as an analytical tool, in association with techniques already in use in aerosol studies, can contribute toward a better understanding of the particle deposition and retention in the human respiratory track, despite progress experienced by the field of inhalation of particles in the last decade by using more conventional techniques [14-22].



Daily concentrations of Br and Pb in aerosol samples and the corresponding Br/Pb ratios.

Figure 1.

2.2 Environmental samples of the Brazilian cerrado

A vast region in the Brazilian central plateau is characterized by a flora called cerrado and by a somewhat peculiar fauna. An area of about 13 km^2 in this region is maintained as an ecological reserve (RER) used for inter-disciplinary study involving biologists, chemists, geologists, botanists, and physicists. This area is regarded as a relatively non-polluted area, at least as far as most industrial pollutants are concerned. The Fundacão Instituto Brasileiro de Geografia e Estatística (IBGE) owns the RER area, which is located 50 km south of Brasilia, and about 2400 km northwest of Rio de Janeiro.

The PIXE technique was used as an analytical tool to determine the metal concentrations in samples of soils and particulate matter suspended in natural springs and rainwater collected in the RER area. The relative concentrations of K, Ca, Zn, Cr, Cu, Ni and Ti to Fe were determined in these environmental samples as well as the time variations of those relative concentrations occurring in suspended matter found in rainwater collected in the RER area.

The results of the determinations of the concentrations of each of the above mentioned elements relative to Fe in the environmental samples of the Brazilian cerrado were presented and discussed elsewhere [9]. The most interesting results from the PIXE analysis of environmental samples collected in the RER area were the following:

(i) confirmation of the well known property that low calcium soils tend to have relatively high concentrations of heavy metals;
(ii) observation of the high relative concentration (7.5 - 22%) of the Ti/Fe ratio in the soils of the area; and
(iii) observation of seasonal variations in the Zn/Fe, Cr/Fe, and Cu/Fe ratios found in suspended matter in rainwater collected in the RER area.

2.3 PIXE analysis of human hair and nails

Human hair was chosen for the first attempt to make a quantitative PIXE elemental analysis of a biological sample in Brazil. The choice was made under the belief that hair could play an important role in monitoring the contamination of human beings exposed to environmental pollutants.

Two independent approaches were used for sample target preparation for PIXE analysis of scalp hair. First, eight hair strands of nearly circular cross section were mounted on an aluminum frame without any previous treatment other than the standard cleaning procedures for conventional hair analysis. Since hair is a poor electrical conductor, an accumulation of positive charges from absorbed protons occurs during irradiation. The resulting discharge produces a white background radiation which interferes with the detection of characteristic x-rays emitted from the target sample made of hair strands. This interference was avoided by spraying the target sample, while being irradiated, with electrons released from a thin aluminum film placed on the collimator near the target. Figure 2 shows two spectra which illustrate the effect of spraying electrons on a target sample made of hair strands while being irradiated by 2 MeV protons.

A second method of hair target preparation consists in labelling the samples internally with strontium, as suggested by Whitehead [23]. Hair samples were prepared by dissolving 60

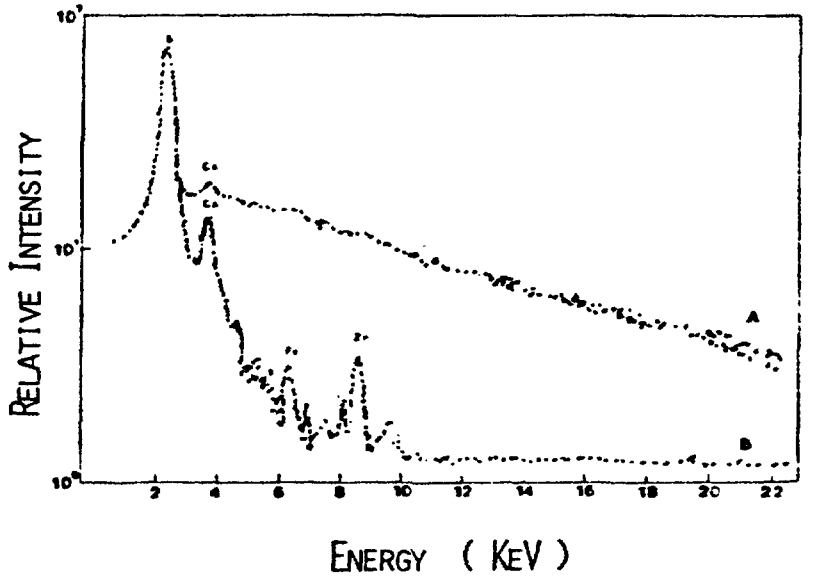


Figure 2. Spectrum A corresponds to hair irradiated by 2 MeV protons without electrons being sprayed on the target sample. Spectrum B corresponds to hair irradiated by 2 MeV protons while electrons are being sprayed on the target sample. Adapted from reference [8].

mg hair in 1 ml HNO_3 to which 20 µl of a solution containing strontium was added. The strontium solution was prepared by adding 150 mg $Sr(NO_3)_2$ to 1 ml of doubly distilled water. The target itself was prepared by dripping 5.0 µl of the final solution onto a Nuclepore filter 0.4 µm pore size mounted on an aluminum ring appropriate to fit the target holder disc. The nitric acid and the strontium solution were tested for purity by dripping aliquots of each onto Nuclepore filters which were irradiated under the same conditions as those used for irradiating the hair target samples [10].

Table I shows a comparison between averages and ranges obtained with PIXE analysis of hair samples by using the two different methods for target sample preparation described above. As shown in Table I, although the ranges and the average concentrations obtained by using method II appear to be consistently higher than the results obtained by using method I (with the exception of the chromium results), the detailed results of individual samples reported by Baptista et al. do not necessarily show the same trend [10]. This apparent paradox is caused by the fact that the same elements were not always detected by both methods; and Table I includes only detected results.

Table I. Comparison between averages and ranges of PIXE analysis of hair samples using two different techniques of target preparation (mg/g). Adapted from Baptista et al. [10]

ELEMENT	TECHNIQUE	AVERAGE	RANGE
Ca	I*	1.5 (8)†	0.35 - 2.7
	II**	1.6 (8)	0.46 - 3.4
Cr	I	1.9×10^{-2} (3)	$9.0 \times 10^{-3} - 2.9 \times 10^{-2}$
	II	n.d.	------
Mn	I	6.0×10^{-3} (2)	6.0×10^{-3}
	II	8.7×10^{-3} (3)	$7.4 \times 10^{-3} - 9.3 \times 10^{-3}$
Fe	I	4.8×10^{-2} (8)	$1.3 \times 10^{-2} - 9.5 \times 10^{-2}$
	II	8.1×10^{-2} (8)	$2.9 \times 10^{-2} - 0.18$
Ni	I	4.3×10^{-3} (4)	$1.9 \times 10^{-3} - 1.1 \times 10^{-2}$
	II	7.3×10^{-3} (8)	$3.7 \times 10^{-3} - 1.3 \times 10^{-2}$
Zn	I	0.27	0.14 - 0.51
	II	0.31	0.16 - 0.58

* Using hair strands mounted on aluminum rings.

** Hair dissolved in HNO_3 and labelled with $Sr(NO_3)_2$.

† Numbers within parentheses indicate number of hair samples where the elements were detected.

From time to time during 1980 and 1981, samples of hair and nails have been collected in Rio de Janeiro from two subjects. Hair and nails are still being collected from one of these subjects.

Sample preparation for PIXE analysis of nails was quite similar to that used for hair, by means of labelling the sample internally with $Sr(NO_3)_2$. A detailed description of the sample preparation for PIXE analyses of nails as well as the results of the analyses of hair and nails up to 1981 were reported previously [13]. The elemental concentrations in human nails seem to follow a pattern similar to that found in hair of the same subject, based on the limited data available thus far. The pattern of elemental concentrations in human hair and nails of the same individual seems to be Ca > Zn > Fe > Cu >, with Fe and Cu transposed in some nail samples [8,11,24]. A more detailed discussion of the work carried out in Brazil on the PIXE analysis of elemental concentrations in human hair and nails has been published elsewhere [11].

2.4 Particle size distribution of uranium in suspended dust

The excess of lung cancer among uranium miners from several parts of the world is well documented and is traditionally attributed to the exposure to short-lived ^{222}Rn daughters which irradiates the tracheobronchial epithelium with alpha particles. Singh et al., however, reports an average uranium concentration in uranium miners' lungs of 89 pCi ^{238}U/kg wet weight in 13 samples, with a range from 6.1 to 311 pCi ^{238}U/kg wet weight [25]. These authors and other investigators suspect that the uranium concentrations in uranium miners' lungs might be associated with inhaled particles which do not clear the lungs at the same rates that the submicron particles usually do.

Local uranium concentrations in particles of the order of 10 μm in diameter may be 10^4 times higher than the average uranium concentration reported in uranium miners' lungs by Singh et al. [25]. This means that local uranium concentrations in particles 10 μm in diameter may be higher than 10^3 ppm vis-a-vis the 0.3 ppm* average found in uranium miner's lungs. In addition, studies reported by Chan et al. suggest the possibility that there is significant tracheobronchial deposition of particles around 10 μm diameter [14].

Taking into account the above reasoning, localization of such uranium-bearing particles in lung tissues may be possible by scanning such tissues with a PIXE microprobe. One of us, ASP, is presently engaged in a research effort at University of Utah/Brookhaven National Laboratory to detect such particles [26].

Other potential hazards associated with significant uranium inhalation can be found in certain occupational areas of U_3O_8 production plants.Figure 3 shows the relative uranium content in suspended dust as a function of particle size. The samples of suspended dust were collected by means of a home-built cascade impactor (Battelle type) in the precipitation-filtration area of the U_3O_8 production plant in Pocos de Caldas, Minas Gerais, Brazil. It appears from Figure 3 that the uranium content in suspended dust is higher in the larger particles than in the smaller ones collected in that occupational area of the Brazilian uranium mill. These results may be characteristic only locally or may be common to uranium mills throughout the world. Further research is necessary to reach secure conclusions about the particle size

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* 89 pCi $^{238}U/kg = \frac{89 \times 10^{-12}}{3.33 \times 10^{-7}} \left[\frac{Ci\ ^{238}U}{kg} \times \frac{g}{Ci} \right]$

$\simeq 2.7 \times 10^{-4}$ g $^{238}U/kg$

$\simeq 0.3$ ppm

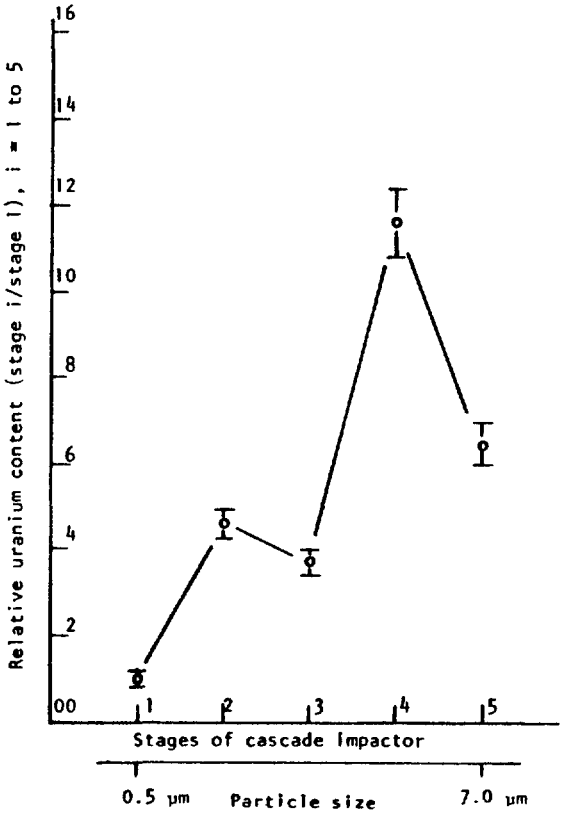

Figure 3. Relative uranium contents in suspended dust as a function of particle size.

distribution of uranium in critical occupational areas of uranium mills. However, the most important aspect of this research thus far has been to demonstrate the feasibility of using PIXE analysis as a tool to study particle size distribution of uranium in suspended dust.

2.5 External beam experiment

Beam extraction for PIXE analysis has long been recognized as a necessary step in eliminating some difficulties associated with the preparation of many environmental and biological samples. Several aspects of sample preparation of environmental and biological materials have been discussed in a previous progress report [27].

External beams for PIXE analysis have been chosen to be used with liquid samples which would evaporate under low pressure and with those biological samples which have low thermal conductivity. There are a number of ingenious techniques for bringing the proton beam from line vacuum conditions into atmospheric pressure. Seaman and Shane brought the beam into the atmosphere through thin foils made of mylar, aluminized mylar, aluminum, and nickel [28]. Modjtahed-Zadeh et al. used a helium chamber separated from vacuum by a beryllium window [29]. Katsanos et al. irradiated

liquid samples in air by bringing the beam to non-vacuum conditions through a 7.6 μm beryllium foil [30]. Deconninck extracted a beam 1 mm in diameter and 50 nA of current intensity through a 2.3 mg/cm^2 aluminum window to irradiate liquid samples [31]. Shroy et al. used a windowless exit port to bring the beam to atmospheric conditions by using pinholes with apertures from 100 down to 12.5 μm in diameter, and differential pumping [32].

Some very interesting papers dealing with applications of external beams have been presented in the second PIXE conference held in Lund, although the advantages and disadvantages of using an external beam vis-a-vis the irradiation of samples in vacuum were not discussed at that Conference. There is an obvious simplification in sample preparation procedures by extracting the beam for PIXE analysis. However, inherent problems associated with beam extraction techniques remain to be solved. The accurate measurement of beam intensity in air is one of these problems. An effort was initiated at PUC/RJ to detect and measure the beam intensity of a proton beam extracted to the air.

A detailed description of the experimental arrangement mounted at PUC/RJ to extract and detect the proton beam in the air was presented in the last progress report, which included a schematic view of the sliding current integrator used to determine the external beam current at the target sample site [33]. A 2 MeV proton beam was extracted through an aluminum window 12.5 μm thick. The beam current in the air was detected by an electronically insulated metallic disk acting as a Faraday cup. The electrical pulses generated by the protons striking the aluminum disk were digitized and integrated. According to a number of measurements made of the external to internal integrated proton beam current, 27 ± 8% of the beam crosses the aluminum window placed at the end of the beam line and reaches a target sample placed in the air 8.0 cm away. This method of detecting and measuring the intensity of the internal beam current has the advantage of indicating with a certain degree of accuracy the proton beam current actually reaching the target sample.

The external beam can also be easily monitored by the detection of either the characteristic x-ray peak of argon present in the air irradiated by the external beam before reaching the target sample, or of one or more gamma rays produced by nuclear reactions which occur in the aluminum window and surrounding materials likely to be reached by the beam. However, the addition of a gamma ray detector near the end of the beam line is necessary in the latter case, as shown by Deconninck [34]. The detection of argon characteristic x-rays to monitor the external beam may be made in some cases with the same Si(Li) detector used to obtain x-ray spectra from irradiated target samples. However, the low energy (2.96 KeV) of the argon K_α x-ray peak associated with the time variations of the argon concentration in air make the use of this technique to monitor the external beam difficult under the usually uncontrolled atmospheres found in accelerator laboratories which are involved in PIXE analysis only part-time.

External irradiation with currents up to 100 nA were performed in the preliminary experiments. Several environmental and biological samples were irradiated by the external proton beam implemented at PUC/RJ. However, the calibration procedures were interrupted because modifications had to be made in the accelerator for other experiments. The experiments necessary to calibrate the external beam of the PIXE system at PUC/RJ are relatively simple compared to those already undertaken, and it is expected they can be reinitiated in the near future. When the external beam is finally operational for quantitative PIXE analyses, the results then obtained by irradiating IAEA standards and reference materials such as human hair (HH-1), animal bone ashes (H-5), dried plankton (MA-A1), and dried fish (MA-A2) will be used to compare results obtained under vacuum and non-vacuum conditions. Analytical results of the IAEA reference materials HH-1, MA-A1, and MA-A2 obtained under vacuum conditions have been reported earlier [12,27]. A series of analyses of HH-1 was included in an IAEA intercomparison exercise. Participation in future IAEA intercomparison exercises using H-5 and other reference materials is expected to include results to be obtained with the external beam.

3. CONCLUSIONS

The main conclusions to be drafted from this report can be listed as follows:

(i) PIXE analysis of environmental samples have been successfully undertaken in a series of projects.

(ii) Sample preparation procedures have been improved to allow PIXE elemental analysis of biological samples such as hair and nails.

(iii) A proton beam was extracted to the air, and a device to detect and integrate the external current reaching the target sample was developed to facilitate PIXE analysis of liquids and biological materials with low thermal conductivity.

(iv) A project is underway to establish, via PIXE analysis, the particle size distribution of uranium in suspended dust in critical occupational areas of a uranium mill.

(v) The IAEA Research Contract No. 2553/R2/RB has helped to establish a reliable system for PIXE analysis of environmental and biological samples at PUC/RJ, but future support from IAEA will be welcome to maintain the feasibility of this PIXE system.

4. ACKNOWLEDGEMENT

The authors wish to register that they are indebted to many individuals who helped in diverse phases of this project. Special credits are due to the staff and graduate students at the Laboratorio F. X. Roser, Depto. de Física, PUC/RJ for their aid throughout the years.

The Brazilian agencies Comissão Nacional de Energia Nuclear (CNEN), Conselho de Desenvolvimento Científico e Tecnológico (CNPq), and Financiadora de Estudos e Projetos (FINEP) sponsored this work in conjunction with the IAEA.

One of us, ASP, is particularly grateful to the director and administrative staff of the University of Utah, Division of Radiobiology, where this report was typed and printed.

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ELEMENTAL ANALYSIS OF HAIR SAMPLES USING ENERGY DISPERSIVE X-RAY FLUORESCENCE AND ATOMIC ABSORPTION SPECTROSCOPY

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Abstract

Elemental analysis of hair samples was performed using energy dispersive X-ray fluorescence. The ion exchange preconcentration technique was employed. The capacity of the exchanger used-cellulose hyphan at different pH was investigated to determine the optimum pH for the resin. The capacity of the resin to take up elements of interest from mixed solutions was also analysed using atomic absorption spectroscopy.

1. INTRODUCTION

The radioisotope energy dispersive X-ray fluorscence (EDXRF) is anuseful technique for multi-element analysis of samples. The sensitivity of the method for the different elements of the periodic table depends on the excitation source used. This technique is widely used for the analysis of solid samples.

An attempt to analyse hair samples quantitatively using bulk material was not successful due to the difficulty in incorporating standards in the solid form. Quantitative analysis of liquid samples also proved to be not successful due to lack of sensitivity.

Different preconcentration techniques to present the liquid sample in a more dense form and hence improve the sensitivity are applied to energy dispersive X-ray fluorscence when liquid samples are to be analysed(1). The ion exchanger preconcentration technique was chosen here and was found to be strongly pH dependnt

Lieser et at (2) have used the EDXRF method for the analysis of water. They used cellulose hyphan ion exchanger for the preconcentration of the water samples. The water passed through a small column filled with 1-2 g of cellulose substituted with hyphan as a group of high selectivity, eluted afterwards with a small amount of hydrochloric acid, shaken with 0.1 g of cellulose hyphan for 30 minutes while the pH was slowly adjusted to 7 with soduim hydroxide and filtered in a spectrocup to form a thin layer sample.

In this study we have used a modified Lieser method. The procedure has been simplified and an infinitly thick sample was used for EDXRF analysis. Sodium hydroxide and buffer solutions (acitic acid sodium acetate) were both used for the adjustment of the pH.

Atomic absorption spectroscopy was used here to establish the capacity of the resin and for the analysis of hair samples from normal and polluted groups.

2- EXPERIMENTAL

The atomic absorption spectrometer (aus JENA AAS IN) was used to measure the capacity of the resin for iron, copper, zinc and lead. 0.5 mmole of iron, copper, zinc and lead were added to 50 ml of sodium chloride solution and completed to 100 ml with distilled deionised water. The pH of the final solution was adjusted with NaoH and buffer solution. The mixture was then shaken with 1 g of cellulose hyphan for 48 hours. The solution was then filtered and the concentration of each element in the filterate was measured for pH ranging from pH=3 to pH=7.

Solutions of iron, copper, zinc and lead in different concentrations were prepared to check the ability of the resin to take up elements from a multielemental solution. The solutions were neutralized and passed through a column of proclain crucible (diameter 25 mm) containing 0.5 g of cellulose hyphan. The concentrations of the different elements in the effluent were measured using the AAS.

Human hair samples were also analysed using AAS. Scalp hair samples were collected at random from voluntary military students who were assumed to be healthy and also from a lead battery factory workers who present a suspected exposed group. Sample collection was convied according to the IAEA procedure (3). A pair of stainless steel scissors was used to cut 1-2 cm of hair close to the sclap from the nape of the neck.

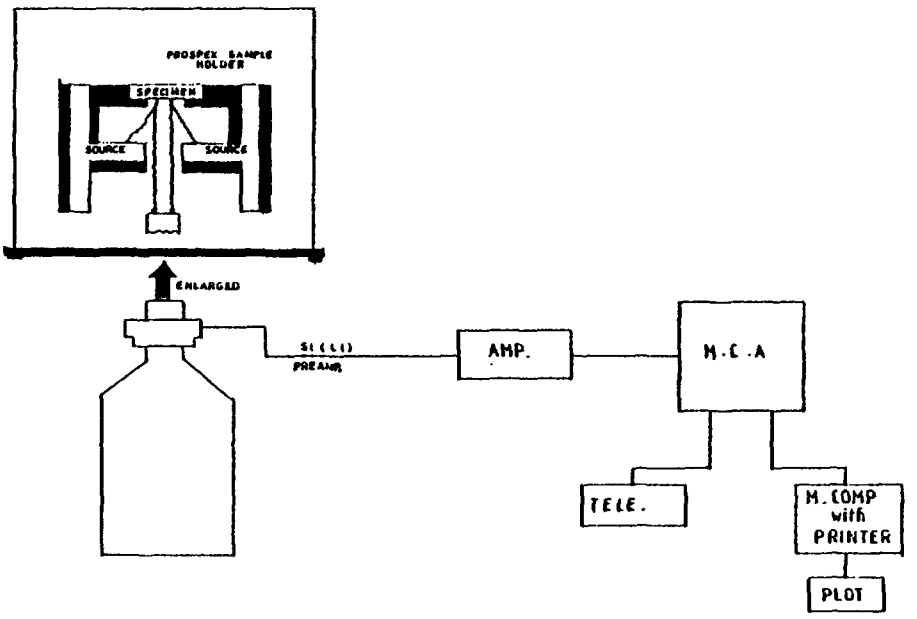
The samples were washed prior to analysis to remove exogenous contamination as recommended by the IAEA advisory group (4). A sample approximately weighing 300 mg of scalp hair was placed in a beaker and stirred for 10 mins periods succesively with acetone three portions of water and again with acetone. The hair sample was dried at room temperature in a clean dust-free room for twenty four hours and then weighed to a tenth of miligram. The cleanded weighed sample was digested with nitric acid and the excess acid was evaporate to near dryness. The solution was carefully maintained below boiling point to permit the loss of vapour but to prevent metal losses due to aerosol formation. The residue was diluted to a volume of 25 ml with distilled deionised water and stored in a polyethlene container ready for AAS measurements.

Stock standard solution of 1000 ppm of iron, copper, zinc and lead were prepared by dissolving the appropriate amounts of the nitrate salts of these elements in distilled deionised water. Different concentrations of these standard solutions were prepared by diluting the stock solution with distilled deionised water.

The EDXRF measurement was performed on trial hair samples, which was dissolved and then preconcentrated in cellulose hyphan ion exchanger. The dissolution was done using nitric acid as described above, neutralizing the solution to a pH of 7 and passing to it through a column packed with 0.5 g of cellulose hyphan. The packing material with the bound trace element was oven dried to a constant weight at 105°C, mixed thoroughly and powdered. An aliquot of 0.65 g was then pressed giving a disc under 10 tons of pressure using a hydraulic press giving a disc of 1 mm thickness and 20 mm diameter. Discs were also formed using standard solutions containing iron, copper and zinc.

The energy dispersive X-ray fluorescence apparatus used is shown in figure (1) with the source, sample and detector arranged in the backscatter geometry. A 30 mm^2 Si (Li) detector with energy resolution of about 180 KeV for Mn K X-ray and the appropriate electronics was used. The radioisotopes available for excitation are ^{109}Cd, ^{57}Co and ^{241}Am.

X-ray spectra were recorded for bulk hair, a disc containing preconcentrated hair solution and also for a blanck disc of cellulose hyphan for comparison and to check the purity of the cellulose hyphan. Measurements were also performed on the discs made from the standard solutions and the intensity ratios were calculated.



Fig(1): EDXRF Apparatus

3- RESULT AND DISCUSSION

The distribution coefficient (kd) for copper, iron, zinc and lead ions as a function of pH were calculated as given bleow

$$kd = \frac{CE}{CS} \quad \frac{(mmole/g)}{mmole/ml} \qquad (1)$$

where CE and CS are the capacities of the exchanger and the solution respectively. Fig (2) shows a graphical representation of Kd vs pH. The capacity of the cellulose hyphan is found to increase with the pH reaching a maximum at pH = 7 and the selectivity is found to be in the following order Cu Fe Zn Pb.

It was also noticed that the capacity of the resin decreases when neutralising with NaOH only. This is because the pH of the solution is lowered due to the fact that when the resing exchange cation with the solution, it releases hydrogen ions (H^+) to the solution. Thus lowering of the pH will result in the decrease of the capacity of the resin.

Buffer solution was used instead of NaOH alone. The hydrogen ion concentration is kept constant which is seen from the buffer action relationship below:

$$CH_3COOH \rightleftarrows H^+ + CH_3COO^- \qquad (2)$$

$$CH_3COONa \rightleftarrows Na^+ + CH_3COO^- \qquad (3)$$

Any hydrogen ion released from the exchanger will be taken up by the acetate ion (CHCOO) to from acetic acid which dessociates at once and so equilibrium is maintained leaving the pH constant.

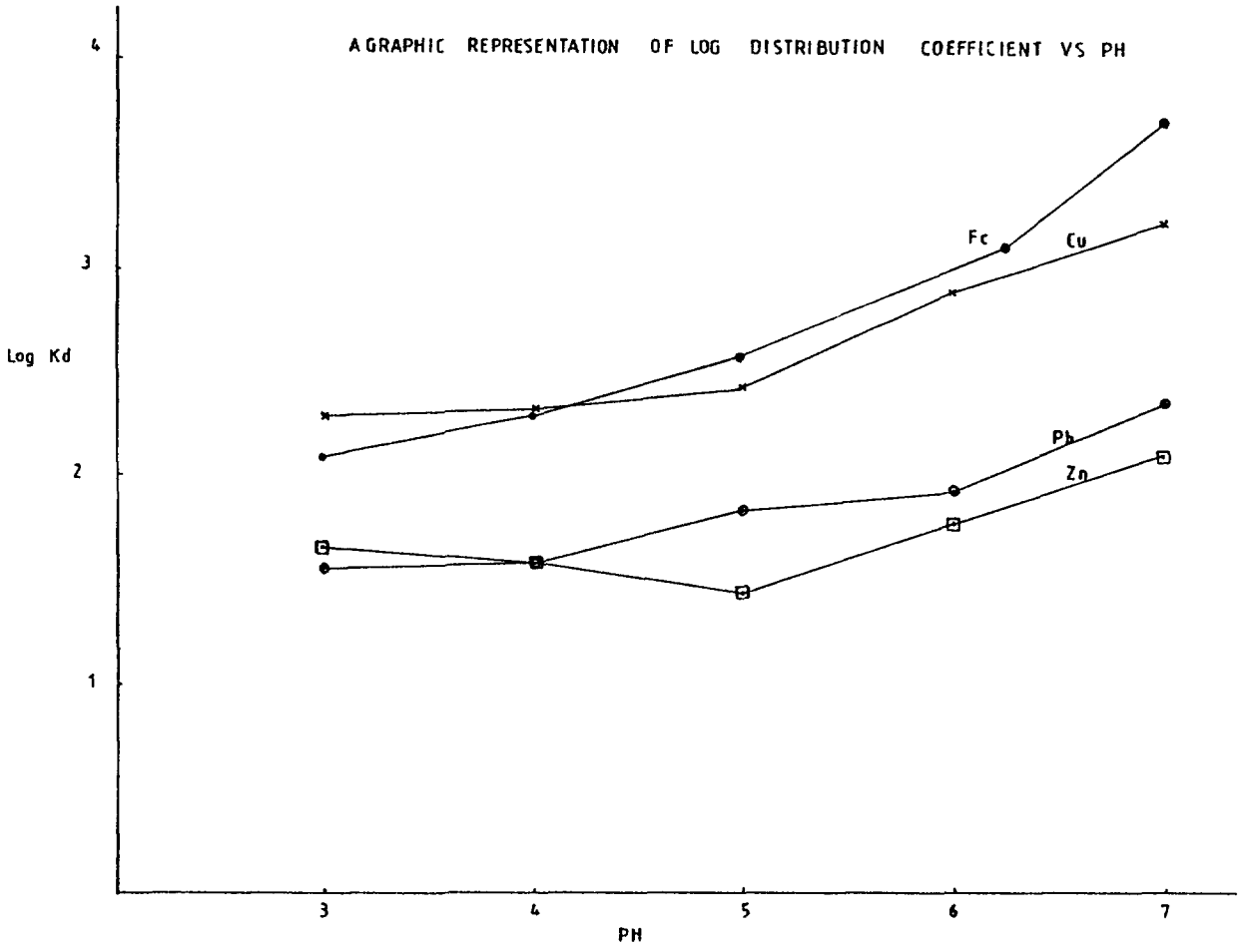


Fig (2): Graphic representation of distribution coefficient VS pH

Good binding capacities have been reported for CA-hyphan for some elements (5), however, the binding capacities for copper, iron, zinc and lead were checked. Table (1) shows the atomic absorption studies for the different elements and the figures in brackets are the maximum concentrations of the elements taken completely by the resin.

The result of the elemental analysis of 20 hair samples analysed by AAS is presented in table (2). The range of elemental content in the control group were found to be (in ppm): Zn (18-218), Fe (21-198), Cu (4-23) and lead (25-65). On the other hand, the range of values for the suspected exposed group was found to be Zn (23-144), Fe (23-288), Cu (10-26) and lead (320-2505).

While there is clear overlap in the concentration of Zn, Fe and Cu in the control and the exposed group, there is marked increase in the concentration of lead in the exposed group.

Only a qualitative EDXRF study was done. The blank disc from the CA-hyphan was used for the background subtraction using the intensity ratio method to correct for matrix effects. The cellulose is quoted (5) to have Br, Cu, Cr, Fe and Zn as incepient impurities. Fig (3) the X-ray spectra for the clean dried material compared with the preconcentrated sample disc to check qualitatively the binding capability of the CA-hyphan and the blank disc using ^{109}Cd as the excitation source and a recording time of 5000 seconds. It shows that the trace analysis of several elements is feasible. From the results of measurements of standard solutions, the slope for the caliration curve for Fe, Cu and Zn are shown in Fig (4).

TABLE I

Binding Capacity Measurement

Element	Initial solution concentration μg/g	Effluent concentration μg/g	Binding capacity %
Cu	(72)	-	100
Fe	288 (192)	68	76
Zn	144 (64)	32	78
Pb	1800 (800)	590	57

Table (2)

Atomic Absorption Studies of Hair Samples

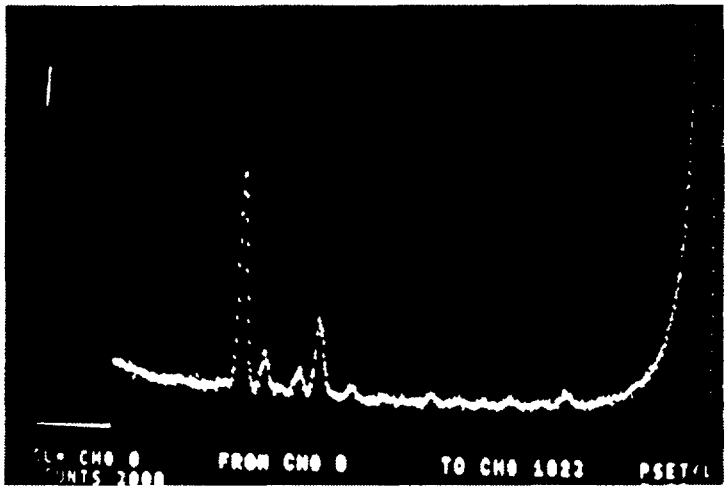
(a) Control group

Sample No	Zn	Fe	Cu	Pb
1	78.5	41.6	12.1	25.0
2	218.3	135.4	23.4	29.5
3	72.2	59.6	13.6	38.3
4	131.3	41.6	3.8	64.7
5	143.4	177.0	15.1	51.4
6	81.2	20.8	9.8	64.7
7	18.4	197.9	6.0	45.0
8	156.7	-	21.5	63.0
9	92.0	72.9	7.0	61.0
10	64.8	250.0	6.3	58.0

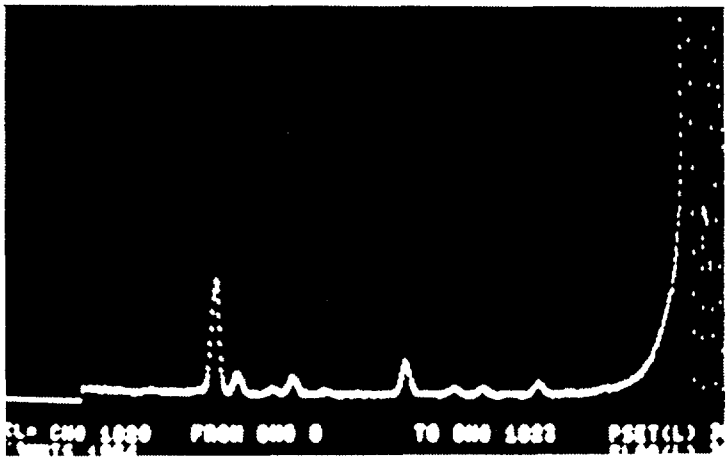
(b) Exposed group

Sample No	Zn	Fe	Cu	Pb
1	118.5	114.5	14.5	712
2	78.9	186.5	21.3	755
3	109.0	85.9	26.1	1091
4	76.3	83.3	24.9	1123
5	23.0	23.3	-	2505
6	144.0	288.0	11.0	590
7	112.0	160.0	24.0	460
8	90.0	81.0	10.0	320
9	64.0	45.0	-	-
10	-	115.0	-	-

a)



b)



c)

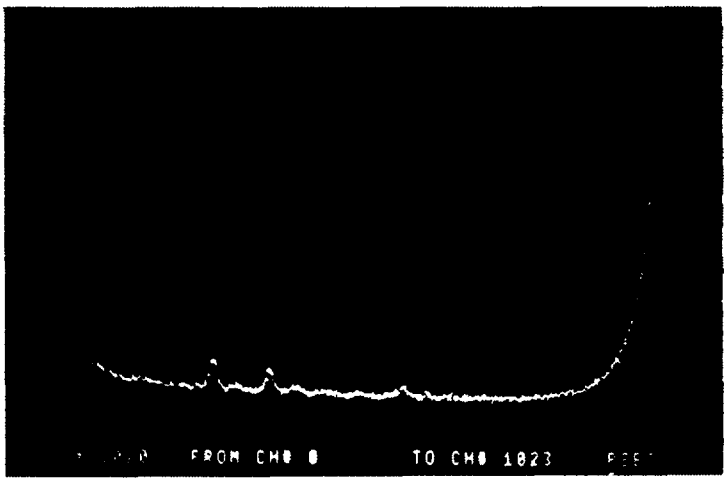


Fig (3): X-ray spectra of

a) preconcentrated hair extra t
b) bulk hair
c) blanck disc of CA-hyphan

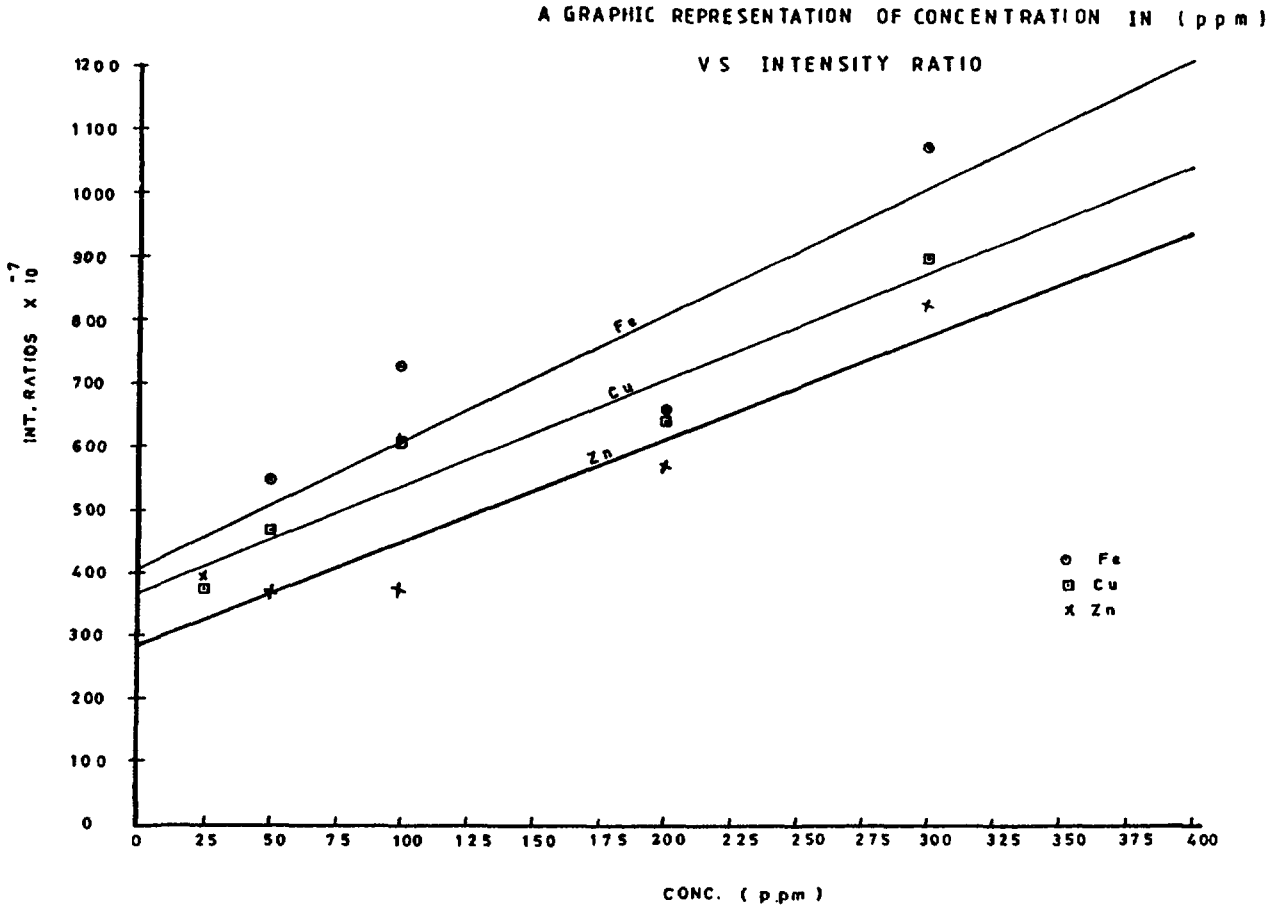


Fig (4): Graphic representation of concentration (ppm) VS intensity ratio

CONCLUSION

The cellulose hyphan may be conveniently used for preconcentration of hair solution since most of elemental content of hair samples could easily be retained in the resin. The preliminary results of EDXRF studies suggest that the method could be implemented in the quantitative analysis of trace elements in hair and may further be used for the determination of the elemental content in other biological samples.

The atomic absorption study of hair samples showed that there is marked increase in the lead content in the hair samples from the group of workers in a the lead battery factory which indicates that hair may be used as an environmental exposure monitor.

ACKNOWLEDGEMENTS:

This work was performed in the Applied Nuclear Science Laboratory Physics Department, University of Khartoum. We are thankful to the head of the department for providing all the necessary facilities.

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Summary Report (1)

CO-ORDINATED RESEARCH PROGRAMME ON NUCLEAR METHODS FOR HEALTH-RELATED MONITORING OF TRACE ELEMENT POLLUTANTS

INTRODUCTION

This Co-ordinated Research Programme (CRP) was initiated in 1979 as an extension of an earlier CRP on Nuclear-Based Methods for the Analysis of Pollutants in Human Hair.

The primary aims of this CRP were to develop and test nuclear techniques for a health-related monitoring system which would work as a sequence of the following operations:

1) Analysis of scalp hair for primary screening-out of groups and individuals with increased levels of trace elements;

2) Elucidation of the nature of contamination (internal, external, etc.) in these groups or individuals by analysing;

   a) their hair and nails as well as single hairs along their length and cross section

   b) their blood and its components

   c) their excreta

   d) any other tissues which can be analysed in vivo

3) Search for sources of the contamination by analyzing inhaled air, drinking water and food, and by performing tracer experiments if necessary.

During the lifetime of this programme, 19 different institutes from 17 countries participated in it, 11 with research contracts and 8 with research agreements. Total Agency support for the programme in the form of research contracts amounted to about US$ 110,000. The total costs, including those covered by the institutes themselves, are estimated to be of the order of US$ 800,000.

The first meeting of the contract and agreement holders in this CRP was held in Namur, Belgium, in September 1981, and the second and final meeting took place in Petten, The Netherlands, in May 1983.

RESULTS AND CONCLUSIONS

The main analytical methods used in this CRP were instrumental neutron activation analysis and radiochemical neutron activation analysis. Together with instrumental methods, neutron activation analysis now covers some 30 elements in most environmental samples. For the determination of many trace elements of biological interest by neutron activation analysis, radiochemical separations are necessary in order to achieve the sensitivity required (more correctly, to reduce the activity of other interfering activation products). However, particularly in such applications, neutron activation analysis now has to compete with

a number of conventional analytical techniques (e.g. atomic absorption spectroscopy and polarography) which not only have sufficient sensitivity and specificity but can also deal with a large throughput of samples. For these reasons, radiochemical neutron activation analysis is economically competitive only if it can be used routinely on a relatively large scale. Single element separation techniques are at a disadvantage unless they are very simple and can be applied quickly. Mutlielement separation techniques are generally to be preferred provided that the elements of interest can be resolved satisfactorily by means of gamma-ray spectrometry.

The other analytical techniques such as proton-induced X-ray emission spectrometry, X-ray fluorescence spectrometry and graphite furnace atomic absorption spectrometry were also used in this programme. Also included were radiotracer experiments with laboratory animals. This study brought more insight into the mechanisms of trace element deposition in hair and internal organs. The analytical methods developed by the participants were found to be very useful for single and multielement determination of trace concentrations in hair and other matrices. The precision and sensitivity of the measurements were found to be generally satisfactory. However, there is still concern about the accuracy. The destruction technique influences AAS. For INAA this could be a matter of the standards used while in the case of PIXE there are the matrix effects to be considered. For PIXE methods there are also the problems associated with infinitely thin and infinitely thick targets. The participants agreed therefore that the accuracy of the methods used should be routinely checked by analysing various suitable certified and other standard reference materials.

In connection with this CRP and another related environmental health research project, a powdered hair reference material (HH-1) was prepared and issued in 1980 for an intercomparison study of trace and other elements. All the participants in the present CRP and several other interested laboratories (totalling altogether over 100 institutes) were sent this intercomparison sample. Results were received from 70 laboratories altogether for more than 40 elements. Details were published by M'Baku and Parr (J. Radioanalytical Chemistry 69 (1982) 171). It was noted that the results of the intercomparison were sufficiently consistent and that certified concentration values could be derived for about 20 elements, including most of the important toxic and essential trace elements, although the 95% confidence intervals of the overall mean values were somewhat wide with the exception of a few elements (Co, Cu, Hg, Se and Zn). This clearly indicates that there is a need for more research.

The participants regretted that the HH-1 reference material was no longer available after completion of the intercomparison. Therefore, they strongly felt that another hair reference material should be made available in larger bulk for an eventual certification of a few elements. The participants unanimously agreed that there is a justified need for such a reference material based on hair. This is because (1) hair mineral analysis is increasingly proposed as a method for the assessment of human contamination with environmental mineral pollutants and as a diagnostic tool for uncovering mineral deficiencies and related health disturbances, and (2) a reference material based on hair would help those laboratories involved in this field of research with analytical quality control aimed at improving reliability (accuracy and precision) of their methods.

The washing method used prior to analysis is a critical step in hair trace mineral analysis. The participants mainly used the IAEA recommended method. In addition to this, other washing procedures were also tested. A very detailed study on this point was carried out in Canada using human scalp hair. Important factors investigated included, among other things, pre-versus post-irradiation washings, efficiency of a single reagent in removing exogenously deposited contaminants, comparison of various washing procedures which use a combination of different reagents in sequence, etc. The IAEA and other hair washing methods that utilise mild treatments with organic solvents, water and detergents were found to be effective for removing exogenous contaminants such as oils, lacquers and loose dust particles. More severe treatments with sodium hydroxide, chlorhydric acid and strong chelating agents such as EDTA, were found to leach significant amounts of trace elements from hair with increasing time and number of washings. The effect of usage of certain medicated shampoos containing large quantities of certain trace elements such as selenium and zinc was also investigated. Most of the elements externally deposited by shampoos can be removed by the washing method recommended by IAEA with the exception of selenium. It was also observed that externally deposited mercury could not be removed by any of the hair washing methods presently available. A radiotracer study conducted in the Federal Republic of Germany with laboratory rats gave somewhat different results. The mild washing procedure recommended by IAEA was shown to leach significant amounts of internally deposited arsenic and cadmium from growing hair of laboratory rats, whereas no loss was observed for mercury as reported by the Canadian study.

The suitability of hair trace mineral analysis as a means for epidemiological monitoring of environmental exposure was evaluated. Overall, results obtained during this programme lend further support to the body of evidence that hair elemental analysis is a suitable method for screening population groups for community exposure to environmental inorganic pollutants. Nails were found to be less reliable. However, uncertainty still remains as to the meaningful interpretation of hair elemental analysis data in cases involving environmental exposure of individual subjects. This is mainly due to a lack of knowledge about the quantitative relationships, if any, between hair mineral contents and internal concentrations.

A study was carried out in the Federal Republic of Germany to investigate the practical question as to whether hair trace mineral content reflects the body intake and the internal body mineral status. Radiotracer techniques were used to study the distribution in laboratory animals of arsenic, cadmium and inorganic mercury. Results obtained indicated that hair is not, at least for laboratory rats, a good indicator of internal arsenic, cadmium and inorganic mercury. It was concluded that more research was needed on the relationships between hair mineral content and the internal body mineral status.

In order to study the above-mentioned problem, a new Co-ordinated Research Programme was initiated by the Agency in 1983. This new programme is restricted to the topics of (1) analysis of hair and internal organs (autopsy samples), (2) studies in experimental animals of mineral distribution in the body, and (3) development of metabolic models to describe the relationship between mineral levels in hair and internal body burdens.

A body of data was generated during this programme on several toxic and potentially toxic trace elements in human specimens, some environ-

mental media (air and water) and a number of diet items. Overall, the results indicated that the contamination with elements surveyed was low, although a few cases of relatively high levels were observed for lead and mercury.

It was also agreed by the participants that the development in the countries concerned, of analytical capability for assessing toxic substances of environmental and occupational significance, is of significant value to the countries concerned. Moreover, the verification that the pollution is absent (or below levels that give rise to concern) is worthy of support by the Agency.

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Part II

RCA REGIONAL CO-ORDINATED RESEARCH PROGRAMME ON HEALTH-RELATED ENVIRONMENTAL RESEARCH USING NUCLEAR TECHNIQUES

DETERMINATION OF MERCURY AND OTHER TOXIC ELEMENTS IN FISH AND FOODSTUFFS USING DESTRUCTIVE NEUTRON ACTIVATION ANALYSIS

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Abstract

Concentrations of mercury in fish, serum, rice and tobacco collected from Iran were measured by radiochemical neutron activation analysis (RNAA). The average mercury contents in white Caspian fish were 21.6 ppb for male and 8.9 ppb for female, respectively. No significant mercury contamination was found in the biological samples analysed in this study.

1. INTRODUCTION

In recent years, the toxicity of mercury compounds in general and methyl mercury in particular has become quite well known. Methyl mercury has a great tendency to deposit in fat tissues of man and animals including fish. Mercury can cause paralysis at high doses. This compound also causes nerve damage and distortion of chromosomes and may act as a carcinogen. Therefore, a regular checking of mercury compounds in waste material from indstrial processes is of considerable importance for public health.

A considerable amount of work has been devoted to the development of analytical methods for mercury including activation analysis and atomic absorption spectrometry (1-3). The extremely high toxicity of mercurial compounds makes it necessary to use very sensitive methods of analysis. For the analysis of fish samples from the Caspian Sea from northern parts of Iran, where in many cases the mercury content is at the ppb level, activation analysis provides a suitable method due to its high sensitivity and relative freedom from contamination problems.

Several non-destructive methods of activation analysis for the determination of trace elements in foodstuffs have been published. Foodstuffs and other biological samples usually contain much sodium, potassium, phosphorus and bromine, and the activation products of these elements generally dominate the gamma spectrum to such an extent that the determination of most other elements is impossible by purely instrumental means. One great advantage of the destructive method used in this work is the separation of interfering radionuclides such as ^{24}Na, ^{42}K, ^{82}Br, ^{32}P and ^{75}Se applied after irradiation of the samples. The gamma spectra of ^{197}Hg and ^{203}Hg are otherwise obscured by the Compton background resulting from the high activity of ^{24}Na. Furthermore, ^{75}Se is known as a strongly interfering element having a gamma-ray energy around 0.28 Mev, close to that of the only gamma-ray of ^{203}Hg (1).

In this work, thermal neutron activation analysis with radiochemical processing has been applied for the determination of Hg in fish and caviar from the Caspian Sea coast of northern Iran. A part of this work has been allocated to investigate mercury in some oriental tobaccos from northern regions of Iran. The main purpose of this study was to examine

whether pesticides and environmental conditions influence the mercury content of tobacco. Details of this investigation relating to the determination of bromine have been published elsewhere.

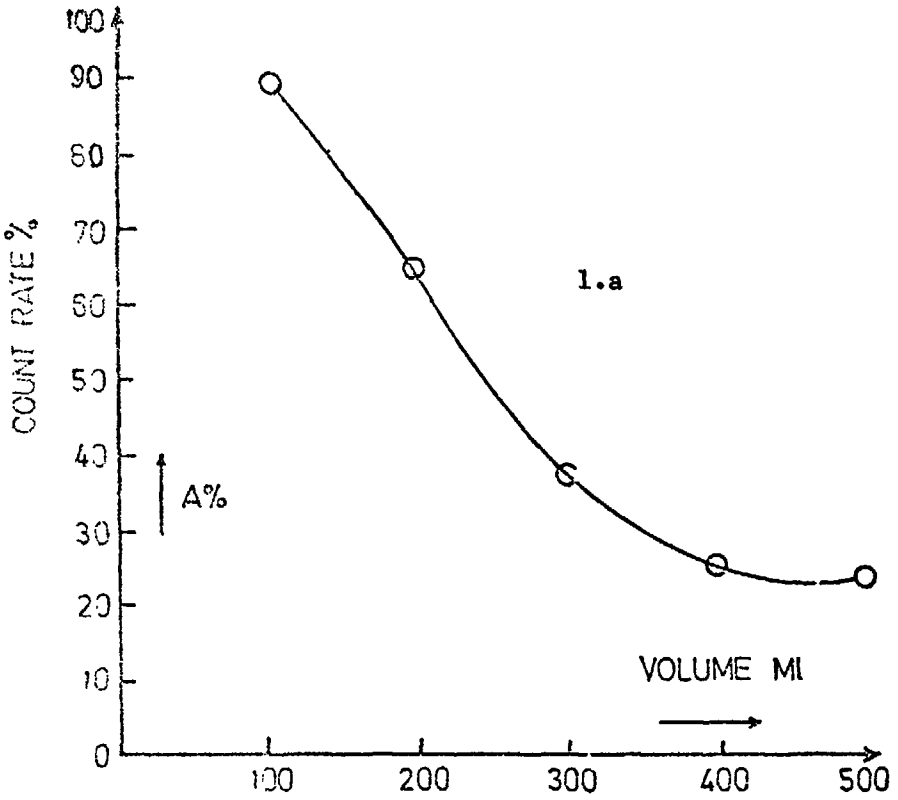
2. EXPERIMENTAL

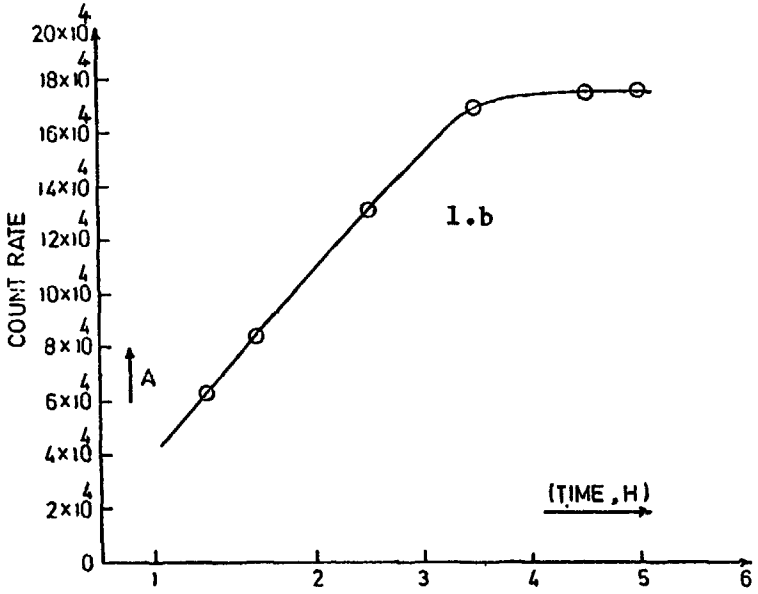
Homogenized samples (150–200 mg), together with standard samples of orchard leaves or bovine liver from the US National Bureau of Standards, were sealed in quartz ampoules and irradiated for 30 hours at a thermal neutron flux density of $6 \times 10^{12} n.cm^{-2}s^{-1}$ in the nuclear reactor of the Nuclear Research Centre, Teheran. After a decay period of two days the separation of mercury was performed. The ampoules were dipped into liquid nitrogen to reduce the pressure of gas formed during irradiation of the samples and broken inside a piece of polyethylene tubing containing a mixture of concentrated HNO_3/H_2SO_4 (9:1). The contents of the tubing were transferred to a siliconized apparatus described by Bethge (4) and rinsed twice with 5 ml of concentrated HNO_3/H_2SO_4. At this point the solution was refluxed twice at 300^oC with a trap containing 2N NaOH mounted at the top of the condenser to avoid the escape of any volatiles, i.e. ^{82}Br. To the cold refluxed solution a mixture of 5 ml 70% $HClO_4$ and 0.5 g glycine in 5 ml H_2O was added. At about 120^oC, due to the reducing action of the glycine and the HCl produced from $HClO_4$, $HgCl_2$ is formed in this solution. By distillation of the mixture at 250^oC, chloride and bromide of mercury and gold are quantitatively separated. Water is added to the distillate to obtain a volume of 200 ml.

Isotopic exchange is used to remove some elements in both distillate and residue fractions. Clean copper foil placed in the distillate will take up mercury and gold thus leaving bromine in the distillate solution. The foils were then sealed individually in very thin polyethylene sheets and were used for counting. Generally, the recovery of mercury was about 93 ± 1 %. A number of factors determine the optimum conditions for the isotopic exchange reaction (5). Fig. 1 shows the effect of altering the volume of solution, pH and time of isotopic exchange. The optimum conditions were applied for all mercury separations.

The samples and standards were counted in fixed geometries with a trapezoidal Ge(Li) detector coupled to a multi-channel analyzer. The detector has an active volume of 40 cm^3 and a resolution of 2.98 keV for the 1.33 MeV photopeak of ^{60}Co.

The overall detection limit of the method is 10^{-9}g mercury in 100–150 mg of sample.





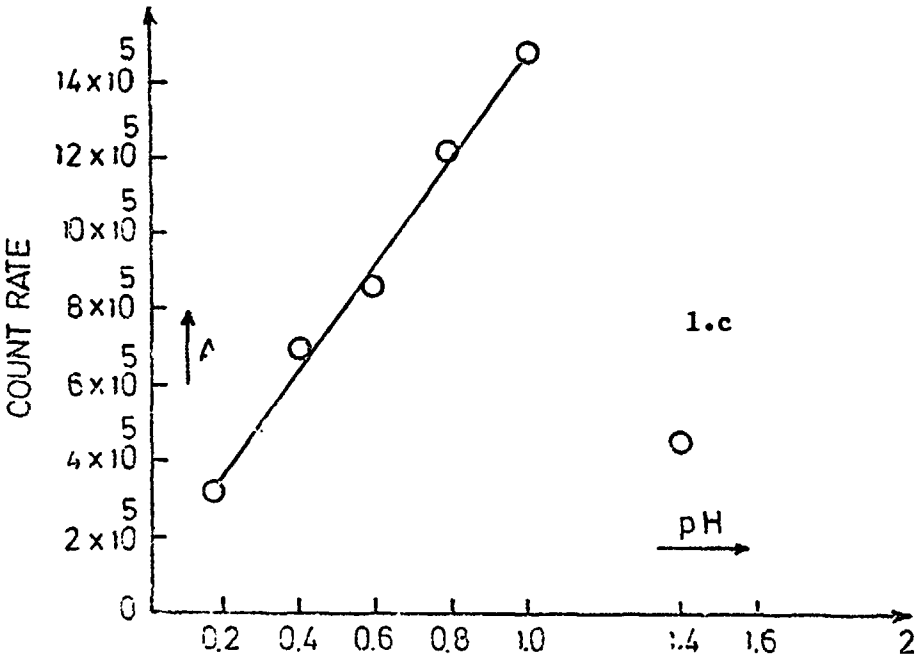


Fig. 1 Parameters affecting the speed of isotopic exchange

1.a The relation of the volume of solution to the deposited mercury

1.b The relation of the time to the deposited mercury

1.c The relation of the pH to the deposited mercury

3. RESULTS AND DISCUSSION

Fig. 2 shows the spectrum of mercury after irradiation of a fish sample for 30 hours and a decay time of 24 hrs and separation of interfering radionuclides. Photopeaks of ^{197}Hg and ^{203}Hg were recorded and were utilized in calculating the results. In this spectrum, two radionuclides, ^{226}Ra and ^{198}Au, appear as very minor components which do not interfere at all.

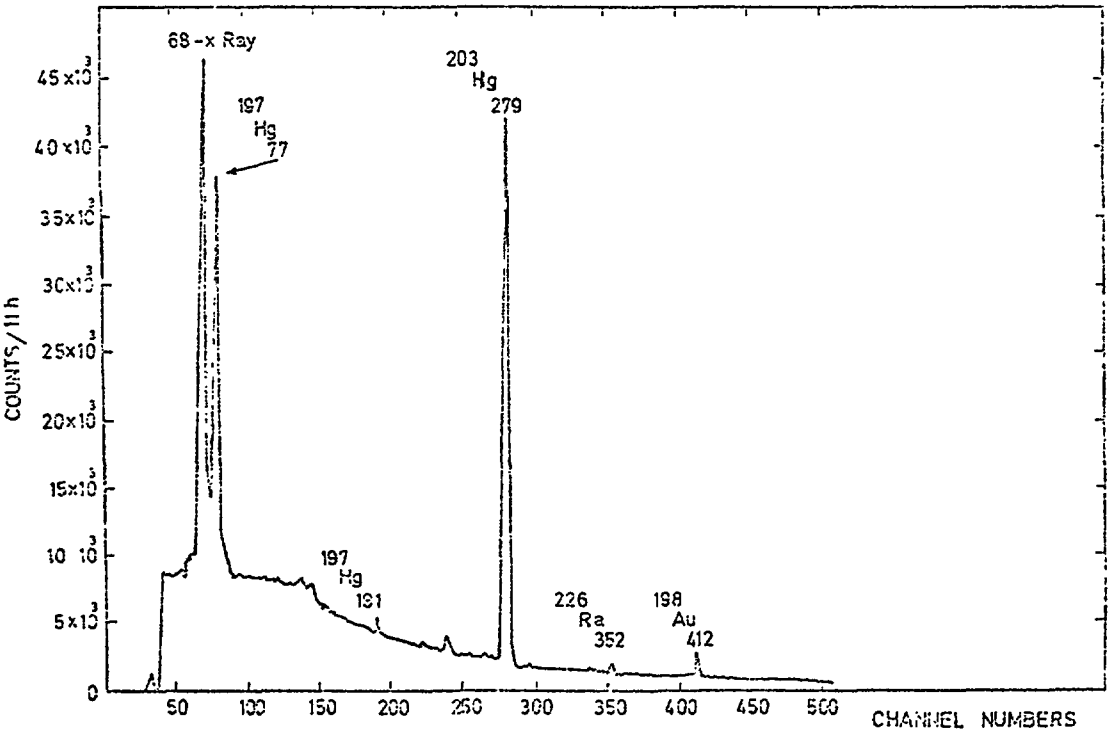


Figure 2 Gamma spectrum obtained for a Caspian white fish sample with a Ge (Li) detector
Irradiation time : 30hr, decay time 24 hr.

The results for mercury in white fish and caviar from the Caspian Sea coast are given in Table 1.

Table 1 Average Mercury Content of White Fish and Caviar From Caspian Sea

	Location	No. of Experiment	µg/kg
Female white fish	Anzali	3	8.9 ± 0.5
" " "	Ghazian	3	2.9 ± 0.4
Male white fish	Anzali	3	19.5 ± 3
" " "	Ghazian	3	21.6 ± 0.7
Caviar*	Golshan	3	3.4 ± 0.1
Caviar	Golshan	3	4.4 ± 0.3
Caviar	Pole-Rood	3	1.5 ± 0.4
Caviar**	Babolsar	3	13 ± 5
Caviar	Laysar	3	2.8 ± 0.7

* - Unsalted
** - Big river

From a survey of over 40 samples of white Caspian fish studied in this work the average mercury content was found to be 21.6 ppb for male and 8.9 ppb for female white fish; results for caviar were variable. The amount of mercury in male fish was much higher than in female fish. This is due to the living habits of male white fish which usually swim in upper reaches of the river where industrial wastes are more frequent. However, a comparison between the results obtained in this work and those obtained by others in Europe (5,6,7,8) shows much lower concentrations of mercury in Caspian fish. Population density and industrial activities are known to be the main factors affecting contamination of rivers, and hence leading to higher concentrations of mercury in related samples. For Iranian caviar, this is the first such report on mercury analysis which showed that the levels are far below those permitted by the World Health Organization (9).

The mercury contents of some other biological specimens have been measured by the same procedure. The results are shown in Table 2. Table 3 shows the results for mercury in various types of tobacco from the northern region of Iran. All results for either sprayed (methylbromide) or non-sprayed tobacco indicate that the mercury contents are below the permissible value (about 0.5 μg/g).

Table 2 Mercury Content of Some Biological Materials

Biological Material	No. of determinations	Average μg/kg
Serum of cancerous blood No. 1	3	9.3 ± 2.2
No. 2	3	2.48 ± 1.32
No. 3	3	141.25 ± 11.25
No. 4	3	20.97 ± 2.78
Rice before being cooked (10)	3	14.7 ± 0.7
Rice after being cooked	3	12.15 ± 2.2

Table 3 Concentrations of Mercury in Different Grades of Iranian Tobaccos

Growing Place	Brand	Concentration μg/kg
Gilan	Virginia	15.3 ± 5
Gilan	Virginia*	14.5 ± 2
Masendaran	Tikolak	52.9 ± 9
Masendaran	Trabusan	8.3 ± 0.1
Masendaran	Basma	14.8 ± 2
Gorgan	Trabusan	16.0 ± 3
Gorgan	Basma	10.2 ± 1
Khoi	Tikolak*	19.9 ± 5
Khoi	Basma	20.1 ± 9
Khoi	Basma*	15.5 ± 5
Uromieh	Basma	15.8 ± 5
Uromieh	Basma*	11.5 ± 4

Note: All samples were sprayed with methylbromide except those indicated by *

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NEUTRON ACTIVATION ANALYSIS IN THE MONITORING OF HEALTH-RELATED TRACE ELEMENT POLLUTANTS

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Abstract

The development and validation of methodology to determine trace elements in hair is described. The potential role of hair as a first level monitor in a multilevel scheme of monitoring exposure to inorganic pollutants is demonstrated. The application of mathematical methods in enhancing the information content of analytical data is illustrated through the pattern recognition approach.

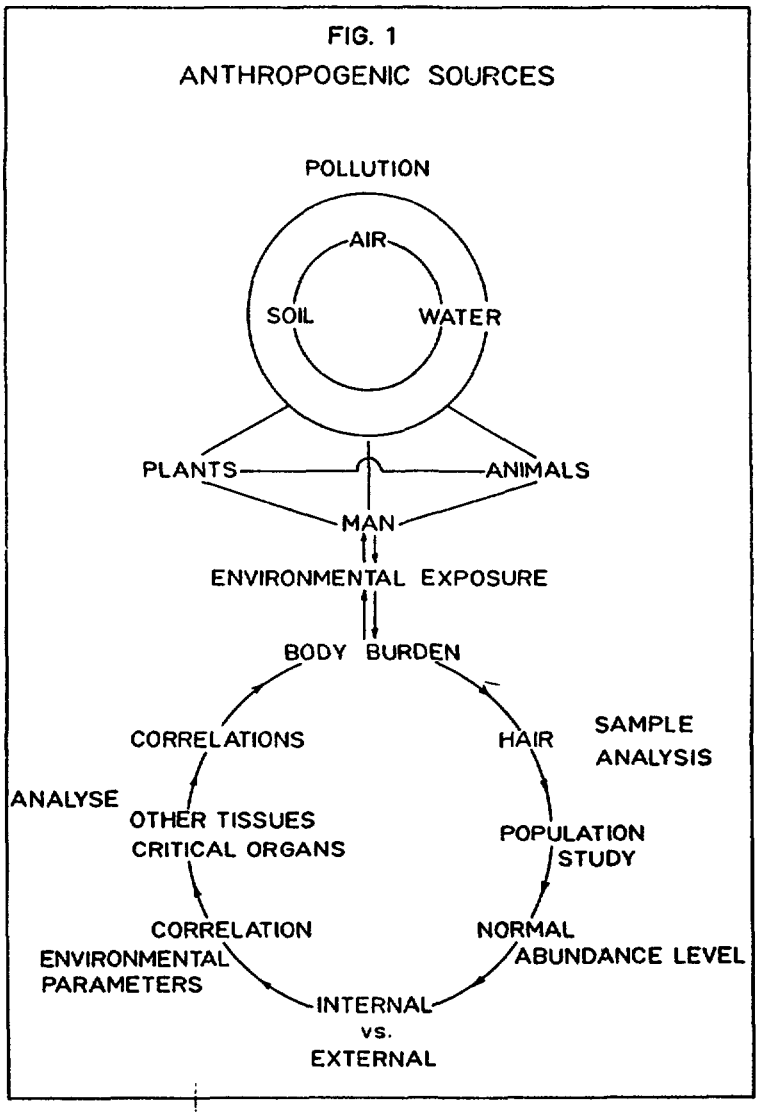
1. INTRODUCTION

The rapid developments in industrialisation and the increasing awareness for the need to preserve the quality of the environment have created an apparent dichotomy. Analytical chemistry bridges those two seemingly opposing streams and nuclear methods have made significant contributions in analytical chemistry. The expanding knowledge of the role of the elements (metals) in living systems has increased the need for the detection and monitoring of their concentration levels in and around man to establish "normal" levels and to evolve standards and regulations.

The work described here summarises the results of a program to help establish the usefulness of hair as an indicator of environmental exposure; the program spanned two research contracts (1810/RB and 2606/RB) lasting six years during 1976-1984.

2. HUMAN HEAD HAIR

Our view of the role of hair as an indicator of environmental exposure is depicted in Fig. 1. In connection with our earlier work[1] on hair for forensic purposes, washing with ether was standardised. However, since the washing procedure recommended[2] was different, detailed investigations were carried out on the effect of different washing procedures, in particular comparing the effect of washing with ether and with acetone, water (3 times), acetone. The analytical methodology followed[3] was validated through the analysis of certified materials and participation in intercomparison exercises.



2.1 Student Population

Scalp hair samples from nationwide student population were collected, washed and analysed by INAA for 21 elements (Na, Cl, K, Sc, Cr, Mn, Fe, Co, Cu, Zn, As, Se, Br, Rb, Ag, Cd, Sb, I, La, Ce, Au). A secondary standard of hair was developed and characterised during the course of this program for use as a multielement comparator. Analysis of the results using pattern recognition (PR) techniques showed statistically significant separations between male and female, vegetarian (a group, rather unique to this region) and non-vegetarian besides different geographical locations. These findings were presented at the IAEA symposium on Nuclear Activation Techniques in Life Sciences[4].

2.2 Bombay General Population

Following the countrywide population study, albeit on a small scale, scalp hair samples were collected from the general population in metropolitan Bombay area and were analysed by INAA. The differentiation by age group was clear.

PR analysis of the results gave an excellent example of the role of feature selection; principal component analysis (PCA) using data on ten of the elements did not show any separation of samples belonging to an industrial area from those belonging to normal residential areas. A Fisher discriminant analysis (FDA) of the data showed only four elements (Cr, Mn, As, Cd) to have good discriminatory power and a PCA using these four elements produced a very effective separation of the industrial area from rest of the metropolis. These results have been published[5].

3. ANALYSIS OF HAIR AND BLOOD SAMPLES FROM PERSONS SUFFERING FROM CARDIOVASCULAR DISORDER

Samples of blood and hair from thirteen subjects with known cardiovascular disorder and from ten 'normal' subjects were collected under the guidance of medical personnel. The hair samples were collected from five or six different positions of the head and washed before irradiation. The blood samples were collected using fresh disposable plastic syringes and were lyophilised prior to irradiation.

The mean values for the elements determined are summarised in Tables I and II. The pairwise correlations among trace elements in blood and hair are given in

Table I
Mean values of Trace Elements in Hair (ppm)

Element	Normal	Pathological
Br	6.1	1.9
Co	0.03	0.08
Cr	-	1.1
Cu	12.3	16.0
Fe	65	-
K	13	17.0
Mn	1.2	2.0
Sb	0.20	0.27
Se	0.82	0.34
Zn	127	129

Table 2
Mean values of Trace Elements in (Whole) Blood (ppm, ug/g of lyophylised blood)

Element	Normal	Pathological
Co	0.10	0.06
Cr	1.36	0.49
Fe	2420	2085
Sb	0.11	0.10
Se	0.67	0.85
Zn	24	25

Table 3
Significant Correlations among Trace Elements in Blood

	Normal	Pathological
Sb-Se	-0.78	0.68
Cr-Zn	-0.77	
Se-Zn	-0.88	0.72
Fe-Se		0.72
Sb-Zn		0.92
Cr-Co		0.70

Table 4
Significant Correlations among Trace Elements in Hair

	Normal	Pathological
Sb-Co	0.77	0.98
Sb-Zn		-0.65
Sb-Fe	0.94	
Co-Fe	0.90	
Co-Zn		-0.63

Table 5
Significant Correlations among Trace Elements in Hair and Blood

Normal	Pathological
Sb(B)-Co(H)=0.88;	Sb(B)-Co(H)=-0.65
Sb(B)-Zn(H)=0.78;	Zn(B)-Sb(H)=-0.60
Co(B)-Co(H)=-.66;	Zn(B)-Co(H)=-0.68
Se(B)-Co(H)=-.74	
Co(B)-Fe(H)=-.88	
Co(B)-Se(H)=-.68	
Fe(B)-Se(H)=-.69	

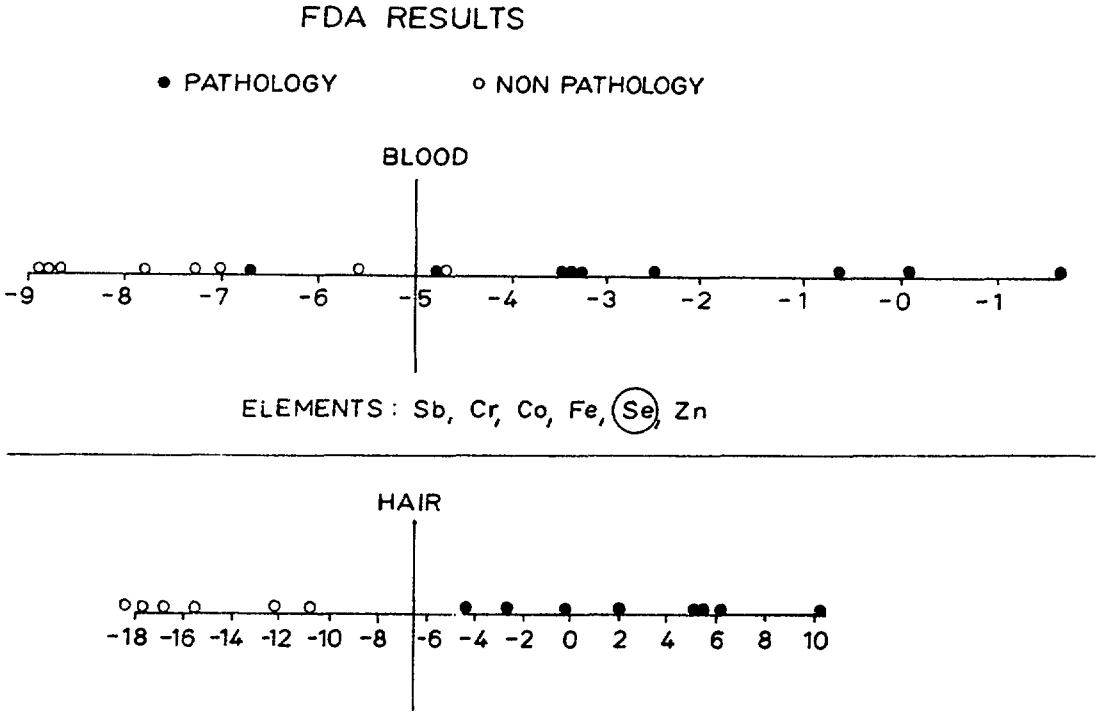


FIG. 2

Tables III and IV, while the correlation of elements in blood with those in hair are given in Table V. The correlation coefficients are significant at 5%. FDA of the trace element data for blood and hair for the two groups of subjects is given in Fig.2. While the two groups are well differentiated, a few features are noteworthy: (i) the discriminant coefficients indicate that only Se provides the discrimination between the two groups based on results for blood, (ii) hair seems to provide better discrimination between the two groups, with all the elements considered, except Mn and Zn, having significant values for discriminant coefficients, (iii) pooling of blood and hair data does not discriminate the two groups.

4. ANALYSIS OF HAIR SAMPLES FROM WOMEN USING COPPER IUD'S

Hair and blood samples from women using copper IUD contraceptives and also from women not using the device were analysed for copper. The results from the analysis of blood have been published[6]. Hair samples from some of the subjects using IUDs were sectioned to correspond to the time of insertion of the device so that the section of hair present at the time of insertion will serve as additional control. The mean value for the controls is 12.4 ± 5.2 ppm ($n = 28$) and that for the persons using IUDs is 11.2 ± 3.8 ppm ($n = 29$). The inference that there is no significantly higher values of copper in subjects using the device is in agreement with that drawn from the results on the analysis of blood. In view of the advantage of having the built-in control and the 'cumulative nature' of the concentration in hair as compared to the 'temporal nature' in blood, the hair data would be expected to be very useful.

5. INTERPRETATION OF DATA

The primary objectives of the analysis of the data for studies in environmental exposure should be (i) to classify the population into groups based on the attributes studied on them, (ii) to establish causative features that are responsible for the grouping/discrimination observed, and (iii) to extract the sources in the environment and pathways to the system.

Pattern recognition[7,8] offers a powerful tool in the processing of the data for these objectives. The PR methods developed and applied in this laboratory are discussed elsewhere[9,10] in which both spectral and non-spectral data have been processed to extract significant (chemical) information. Suffice it to say that this PR approach provides an insight into the processes and steps that are otherwise not discernible. Using a combination of the different PR techniques and applying the spirit of chemical mass balance, so successfully applied[11] to the analysis of data on air filters, it is expected[12] that it would be possible to identify the sources and apportion their contributions to the total exposure. With regard to hair, in particular, sectional analysis and analysis of other body hair can help establish[13] the internal or

external nature of the 'source'; in addition, representation of the elemental abundances in hair needs further examination[14].

6. CONCLUSION

A major finding of this program has been that hair can be an effective first level monitor in a multi-level scheme of monitoring the exposure to inorganic pollutants and assessing the burden, as depicted in Fig. 1.

7. OTHER ACTIVITIES

7.1 Intercomparison exercise

The following intercomparison samples were analysed as part of the analytical quality control: Animal Muscle H-4, Soil S-5, Sea plant SP-M-1, Ge(Li) data G-1, synthetic resin SNR-1, Human hair HH-1, Dried animal blood A-13 and Animal bone H-5. Dried animal blood and animal bone showed the limitations of INAA, with the animal bone sample posing problems of homogeneity. The participation in G-1 brought out the effectiveness of good 'manual' observations. The results for H-4, S-5, SPM-1, SNR-1 and HH-1 are summarised in Table VI.

Table 6
Results for some of the Intercomparison Excercises participated
(Concentrations in microgram/gm dry weight)

Element	H-4		S-5		SP-M-1		SNR-1			HH-1	
	This work	IAEA[1]	This work	IAEA[2]	This work	IAEA[3]	This work	IAEA[4] Mean	True[4] value	This work	IAEA[5]
As	< 0.04	0.007	96.2	93.9	6.8	4.5	0.09	0.109	0.110	0.041	0.05
Au							0.005	0.0059	0.0089	0.021	0.03
Ba			610	562	46						
Br	5.3	4.07	1.8	5.4[a]	670		2.6	2.437	2.11	3.5	4.16
Ce			65.5	59.7							
Co	0.0093	0.008	14	14.8	2.04	2.8				7.13	5.97
Cr	0.08	0.08	37	28.9[a]	4.2	4.3	0.62	0.75	0.65	0.32	0.27
Cs			54.5	56.7[a]	0.27		0.33	0.318	0.33		
Cu	4.35	3.96	55	77.1		13	2.5	2.382		11.8	10.23
Fe	47	49.1	48500	44500[a]	2080	1790	3.02	8.225		118	23.7
Ga			21.5	18.4							
Hg			0.013	0.79[b]	0.56	0.5	0.11	0.114	0.250	1.54	1.70
K	14900	15800	17750	18600	6000		2.6	2.43		6.85	9.21
La			30.5	28.1	6.0		0.12	0.107	0.110		
Mn	0.70	0.52	875	852[a]	58.5	61	0.72	0.723	0.65	1.3	0.85
Na	2120	2060	19050	19200	80400					15.8	12.6
Rb	16.4	18.7	125	138	4.2		12	11.4	13.1		
Sb	0.006		15	14.3[a]	0.86	0.65	<0.05	0.065	0.07	0.037	0.03
Se	0.40	0.28	2.8	1.3[b]	0.14	0.18	0.45	0.374	0.44	0.37	0.35
Sr			400	330[b]	330		24	27.04	27		
Th			12.5	11.3							
Zn	86	86.3	360	368	90	66				185	174.08

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a. Recommended value with reasonable degree of confidence. b. Information value.

7.2 Project Newsletter

Several issues of Project Newsletter were brought out during the course of the programme which served as an effective channel of communication.

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TRACE METAL POLLUTANTS IN FILIPINO HUMAN HEAD HAIR

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The full length report is available directly from Dr. P.A. Kapauan.

Abstract

Hair samples from residents of different geographical locations in the Philippines were analyzed for lead and cadmium by differential pulse anodic stripping voltammetry and for mercury by cold vapour atomic abosorption spectrophotometry. Baseline values of these elements in hair were obtained for the different regions and for the total population sampled.

(The Philippine Journal of Science Vol.III, (1982), 145)

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STUDIES OF TRACE ELEMENT POLLUTANTS IN BIOLOGICAL AND ENVIRONMENTAL MATERIALS

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Abstract

The analytical capabilities based on the principles of particle-induced X-ray emission (PIXE) and atomic absorption spectroscopy (AAS), so far developed to study the trace element composition of different biological and environmental specimens, are reported here. Using these methods, some baseline studies have been performed on human blood, hair, nail, water, air particulates, etc. In this report, a brief account of this research is presented and the need for future research in the related area is discussed.

1. INTRODUCTION

The pollution of the biosphere by heavy metals is a global concern of the present time. Realizing the untoward effects of heavy metal contamination on human life, the International Atomic Energy Agency (IAEA) started the programme on Health-related Environmental Research using Nuclear Techniques, for the purpose of establishing the analytical competence more of general kinds for environmental research in each of the laboratories concerned and to demonstrate its applicability in baseline studies.

The Bangladesh Atomic Energy Commission (BAEC) participated in the above programme within the framework of the Regional Cooperation Agreement (RCA) for South East Asia, under the research contract 2536/RB (Dec., 1979 to July, 1983). The present report contains the account of the work carried out under the programme along with a discussion on the need for further research in the field of trace element analysis of environmental materials including food items. Appendix I contains the list of publications from the work completed under the programme.

2. EXPERIMENTAL WORK

The basic object of the experimental work carried out under the programme was to establish the PIXE method and to develop one of its variants for trace element analysis in biological and environmental materials and to validate it by analysing standard reference materials. The other aspect of the experimental work was to establish AAS method for trace analysis in all areas of interest including the validation of the PIXE methods developed for the same purpose. The following is a summary of these investigations.

2.1 Development of the PIXE method

Elemental analysis in biological materials is performed in this laboratory mainly using the external beam technique of the PIXE method. The geometry of the external beam setup is illustrated in Fig.1. In this arrangement, 2.5 MeV proton beams are extracted through 1.12 mg/cm^2 Kapton windows. Samples are irradiated in the form of pellets, 1-mm thick and 7-mm diameter, weighing about 50 mg. In all measurements, characteristic X-rays are detected with an Ortec Si(Li) detector having the resolution of about 170 eV at 5.9 keV. Data acquisition and processing are performed with standard Canberra/Ortec electronics.

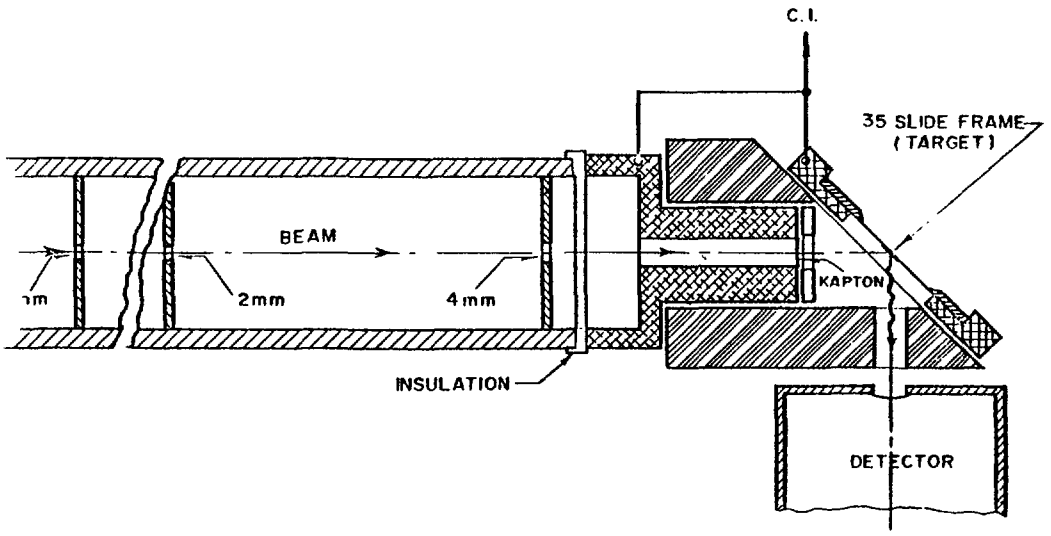

FIG. 1. The geometry of the external beam PIXE setup.

The concentration calibration in PIXE analysis is defined as the number of X-rays per ppm per μC of charge from an element of interest and it is an uniformly varying function of nuclear charge (Z). In view of the fact that biological materials have the light element matrix predominantly consisting of H, C, N, O, S, etc., we used the NBS orchard leaf standard (SRM 1571) for concentration calibration in all our analyses of biological materials. The details of these experimental and theoretical studies have been reported earlier[1,2]. Fig.2 illustrates an X-ray spectrum of the NBS orchard leaf standard. A typical calibration curve obtained for a 20 μ C irradiation of the orchard leaf standard using 44 mg/cm^2 plastic absorber and a detector solid angle of 0.018 sr is shown in Fig.3.

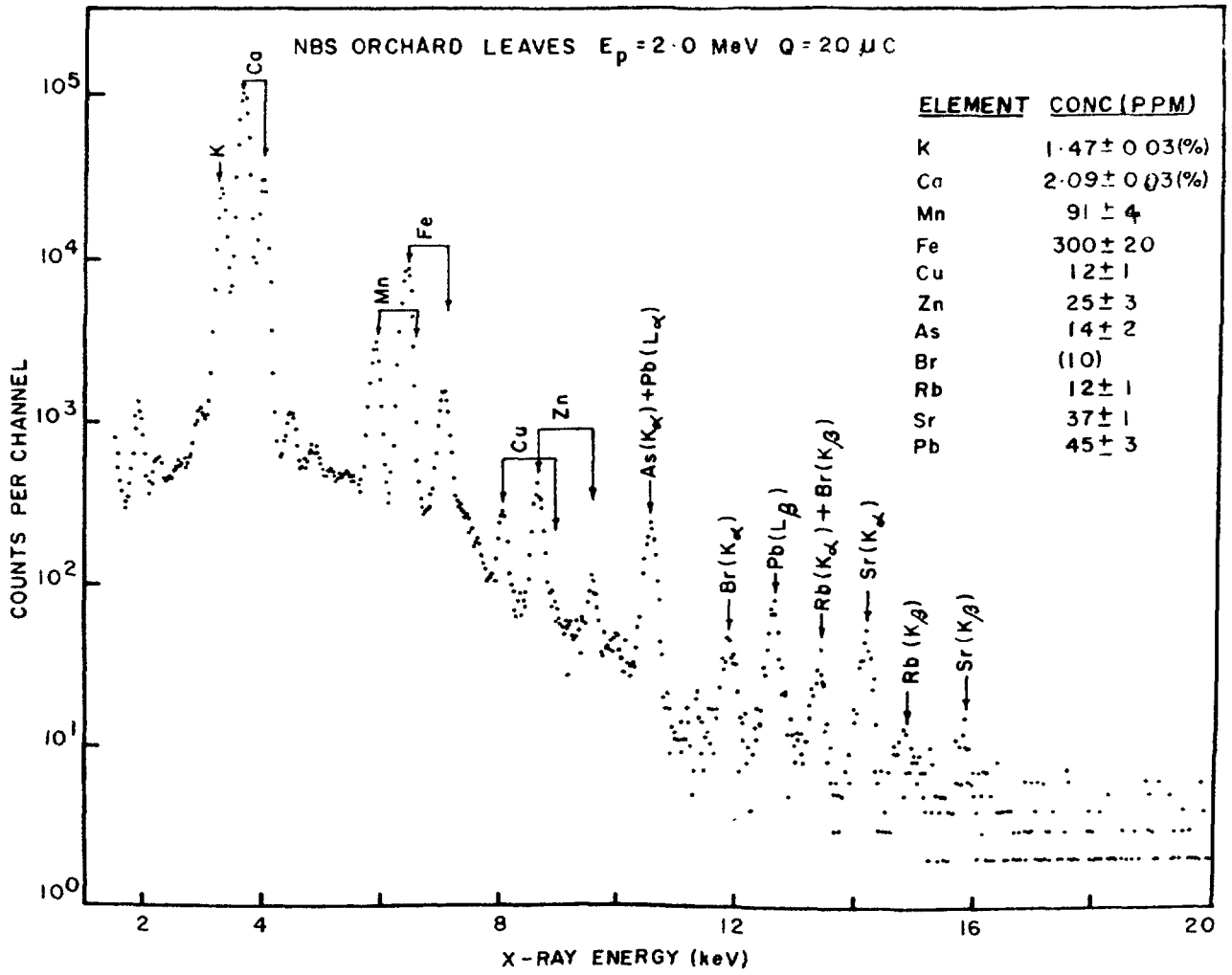

FIG. 2. A PIXE spectrum of the NBS orchard leaf standard (SRM 1571).

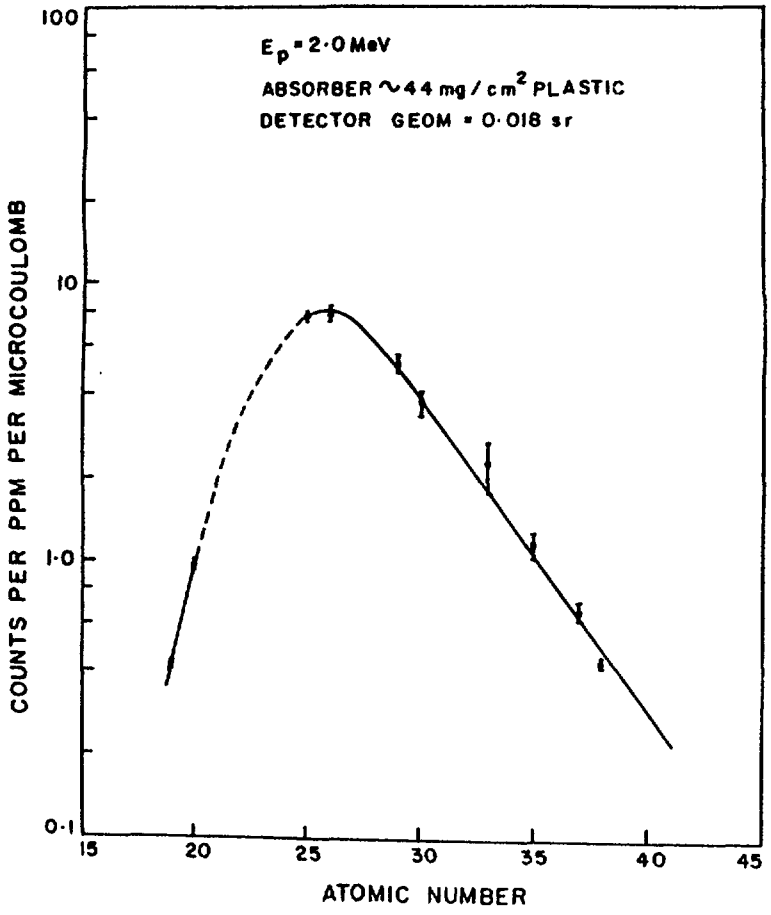

FIG. 3. X-ray yield curve for concentration calibration using the NBS orchard leaf standard.

Using the above calibration procedure, several NBS standards of biological origin were analyzed. The results from the present study were found in good agreement in many cases with certified values, barring the errors associated with the manual area integration of some complex X-ray peaks. These results were reported[3] in the third International Conference on PIXE. As an illustration, the results of the bovine liver (SRM 1577) analysis are shown in Table 1 along with some literature values[4,5] for this standard.

2.2 Trace element composition of human whole blood and head hair in Bangladesh

The level of trace elements in a particular population depends on local factors such as geochemical variability and dietary habits. It is, therefore, necessary to have baseline data information before the level of contamination can be assessed. With this end in view and in the absence of such data in Bangladesh, two baseline studies were performed, one on human whole blood (HWB) and the other on head hair (HH). In each case, 100 adult subjects were selected from a group of 500 population.

Blood samples, 2 ml each, were drawn with a stainless steel needle in a glass syringe and transferred to a previously weighed 5 ml glass vials, warmed for 10-15 min in a water bath to break the cells and finally freeze dried for 72 h to constant weight. The dried mass was ground to powder in an aluminum carbide mortar, to make pellets of standard size.

Table 1 : Trace element concentration in Bovine Liver (SRM 1577) in ppm (μg/g)

Element	This work	Ref (4)		Ref (5)	Certified value
		PIXE	INAA		
K	0.99± 0.03(%)	0.05± 0.07(%)	0.94± 0.05(%)	-	0.97± 0.06(%)
Ca	140 ± 7	90 ± 30	300	-	124 ± 1
Mn	9.3± 0.5	8.0± 1.0	10.7± 0.3	9.2± 1.8	10.3 ± 1.0
Fe	270± 18	248± 16	273 ± 5	273± 8.5	268 ± 8
Cu	180± 15	197±16	199 ± 6	186± 5.5	191 ± 10
Zn	144± 17	116± 2	126± 2	132± 3.3	130 ± 13
Br	9.7± 0.5	10.0± 1.0	9.3± 0.8	9.5± 1.0	(10)
Rb	18.8± 1.9	9.2± 1.6	19.2± 1.4	16.8±	18.3± 1.0

Hair samples, about 5 g each, were randomly cut from different areas of the head with stainless steel scissors, washed with water and acetone in turn as recommended by the IAEA , air dried in a clean room and finally charred at 180°C for about 1 hr to make them brittle so that they can be easily ground to powder. From the powdered mass, standard pellets were prepared for proton irradiation. In all cases, the NBS orchard leaf was used as such for concentration calibration. The findings from both the HWB and HH studies are available in literature[6,7] and they are reproduced in Tables 2 and 3 along with some other results[8,9].

2.3 Analysis of human finger nails

A PIXE method has been developed to study the trace element composition of human finger nails. In this method, nail samples, about 150 mg each, were collected from ten fingers with stainless steel blade. They were soaked in water to remove any loose dirt, then washed with deionized water and acetone in turn. The clean samples were oven dried at 110°C for 1.5 h to constant weight. The dried nail samples were heated at 200±5°C for 2 h in order to easily powder the materials. From the powdered mass, 50-mg pellets were prepared with a hand-press pellet maker for irradiation. The details of this investigation has been reported[10].

Using the present method, the trace element composition (K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr and Pb) of 51 nail samples collected from adults were determined by comparison with a calibration obtained from the NBS orchard leaf standard as mentioned before. Table 4 contains these results along with some literature values[9].

Table 2: Trace element concentrations in human whole blood, in ppm (μg/ml)

Element	No. of samples	This work				Ref. 9	
		Range	A.M.*	G.M.†	Median**	Range	Weighted mean
K	100	800-1250	1076± 96	1047×÷ 1.3	1077 ± 54	1450-1920	1622
Ca	100	30-80	52.9± 7.4	52.3×÷ 1.15	52.7 ± 7.9	57.5-78	60.5
Fe	100	280-410	339± 23	330×÷ 1.3	336 ± 6.4	301-530	447
Cu	100	0.4-2.76	0.98± 0.40	0.91×÷ 1.47	0.92 ± 0.08	0.64-1.28	1.01
Zn	99	3.0-10.8	4.39± 0.96	4.36×÷ 1.14	4.36 ± 0.39	4.8-9.3	7.0
Br	100	0.2-2.0	1.10± 0.35	1.04×÷ 1.42	1.05 ± 0.14	103-8.1	4.7
Rb	100	2.5-6.0	4.18± 0.71	4.12×÷ 1.18	4.10 ± 0.29	1.17-5.98	2.94
Pb	93	0.2-1.0	0.53± 0.17	0.50×÷ 1.47	0.55 ± 0.18	0.88-0.40	0.214

A.M. Arithmetic mean, G.M. Geometric mean.

† Uncertainties are the antilog of standard deviation of the log of concentration.

* Uncertainties are the standard deviations.

** Uncertainties due to counting statistics.

Table 3: Trace element concentration (μg/g) in hair of normal population

Element	No. of samples with detectable conc.	No. of samples in the close distribution.	This work				Ref. 8	
			Range	A.M.*	G.M.†	Median**	A.M. (Range)	G.M. (Range)
K	77	74	10.3-149.9	48.4± 30.1	40.1×÷ 1.88	41.0±12.3	16.8-95	14.2-42
Ca	102	100	217.7-1423	652± 255	605×÷ 1.48	609± 36.5	510-2650	386-3000
Ti	17	17	1.5-6.1	3.20± 1.43	2.91×÷ 1.55	2.57±0.52	-	2.4-3.6
Cr	40	36	0.6-5.8	2.45± 1.43	2.1×÷ 1.85	2.04± 0.32	0.46-4.1	0.34-2.6
Mn	92	82	0.53-6.05	2.33± 1.35	1.96×÷ 1.81	1.90 ± 0.23	1.1-23	0.49-8.8
Fe	102	101	6.25-106.8	29.7± 17.3	25.76×÷ 1.70	25.5±0.34	60-122	27-106
Ni	30	28	0.37-3.25	1.25±0.72	1.07×÷ 1.75	1.16± 0.23	1.01-18	2.8-14
Cu	102	101	3.7-13.9	6.78±1.60	6.60×÷ 1.25	6.79± 0.32	11-25.4	9.6-20.6
Zn	102	101	75.6-277	141± 34	137×÷ 1.25	134± 1.10	138-308	128-261
Br	100	98	0.69-5.44	2.15± 0.83	2.0×÷ 1.48	2.06± 0.37	2.3-39	1.92-27
Sr	49	40	0.85-5.32	2.55±1.14	2.30×÷1.58	2.14± 0.60	-	-
Pb	96	85	0.91-11.2	4.18±2.37	3.56×÷1.78	3.53±0.56	-	-

A.M. Arithmetic mean. G.M. Geometric mean.

* Uncertainties are the standard deviations

† Uncertainties are the antilog of the standard deviation of the log of concentrations.

** Uncertainties are due to counting statistics.

For some of the studies, A.M.'s are not available.

Table 4: Trace element concentration (μg/g) in Human Nails in Bangladesh adult population

Element	No. of samples	Range	Arithmetic mean(AM)*	Geometric mean(GM)**	Median***	Ref. 10 Range	Ref. 10 Weighted mean
K	51	25 - 241	91.1 ± 41.0	82.4 ×÷ 1.56	84.8 ± 72	357 - 2800	-
Ca	51	385 - 2,522	926 ± 383	862 ×÷ 1.45	855 ± 10.7	368 - 3400	-
Ti	48	3.50 - 36.8	11.6 ± 7.9	11.1 ×÷ 1.76	9,25 ± 1.07	0.28 (one value only)	-
Mn	50	0.30 - 5.05	1.69 ± 1.06	1.38 ×÷ 1.97	1.41 ± 0.27	0.04 - 2.1	-
Fe	51	15.6 - 360	77.8 ± 67.2	64.4 ×÷ 1.89	57.3 ± 3.8	27 - 347	-
Ni	48	0.38 - 9.81	2.34 ± 1.77	1.79 ×÷ 2.23	1.83 ± 0.20	0.033, 11.9 (only two values)	-
Cu	49	1.67 - 27.2	6.85 ± 4.40	5.26 ×÷ 1.65	5.65 ± 0.56	11.2 - 53.0	23.4
Zn	50	72.0 - 171	113 ± 20	112 ×÷ 1.19	112 ± 12	73 - 304	-
As	16	0.31 - 1.26	0.61 ± 0.21	0.67 ×÷ 1.53	0.53 ± 0.29	0.2 - 3.3	-
Se	51	0.41 - 2.00	1.28 ± 0.34	1.24 ×÷ 1.36	1.21 ± 0.26	1.14, 8 (only two data)	-
Br	50	0.68 - 4.03	1.65 ± 0.71	1.52 ×÷ 1.50	1.51 ± 0.33	9, 10 (only two values)	-
Rb	46	0.54 - 2.68	1.41 ± 0.54	1.29 ×÷ 1.54	1.35 ± 0.35	3.1 (one value only)	-
Sr	50	0.60 - 5.60	2.00 ± 0.98	1.78 ×÷ 1.65	1.83 ± 0.64	0.017, 0.65 (only two values)	-
Pb	48	0.59 - 10.3	4.39 ± 7.03	3.80 ×÷ 1.70	4.04 ± 0.88	13.8 - 39	-

* Uncertainties are the standard deviations.
** Uncertainties are the antilog of standard deviation of the log of concentration.
*** Uncertainties are due to counting statistics.

2.4 PIXE analysis of water residues

The analysis of drinking water for essential and toxic elements is an important consideration related to public health. Such a study of the municipal water supplies in Bangladesh has not yet been performed. Moreover, these elements, either toxic, essential or indifferent, are found in drinking waters at such a concentration level that they often become difficult to measure directly without any preconcentration step. In view of this situation, a PIXE method using a preconcentration technique has been developed to study heavy element status in drinking waters.

The preconcentration step consists of evaporation of 250 ml of water sample with 200 mg of arshless cellulose powder in a platinum dish. From the residue, pellets are prepared in the same way for proton irradiation. The concentration calibration was constructed using the same cellulose powder as the matrix doped with known amounts of different elements from atomic absorption standards. The mix was homogeneously dispersed with methanol and dried under infrared lamp. From the dried residues, standard pellets were prepared for concentration calibration. A typical X-ray spectrum from a drinking water residue obtained from a Dhaka City Supply is shown in Fig.4.

2.5 Heavy element composition of Bangladeshi tobacco

In order to find the possibility of accumulation of heavy toxic elements in human body through tobacco smoking, a study to investigate the trace and minor elements in 10 different brands of cigarette tobacco commercially made in Bangladesh, has been completed and the results reported [11]. In this study, the external beam PIXE method was used where samples were irradiated as pellets. The results are summarised in Table 5 along with some data from other studies [12,13].

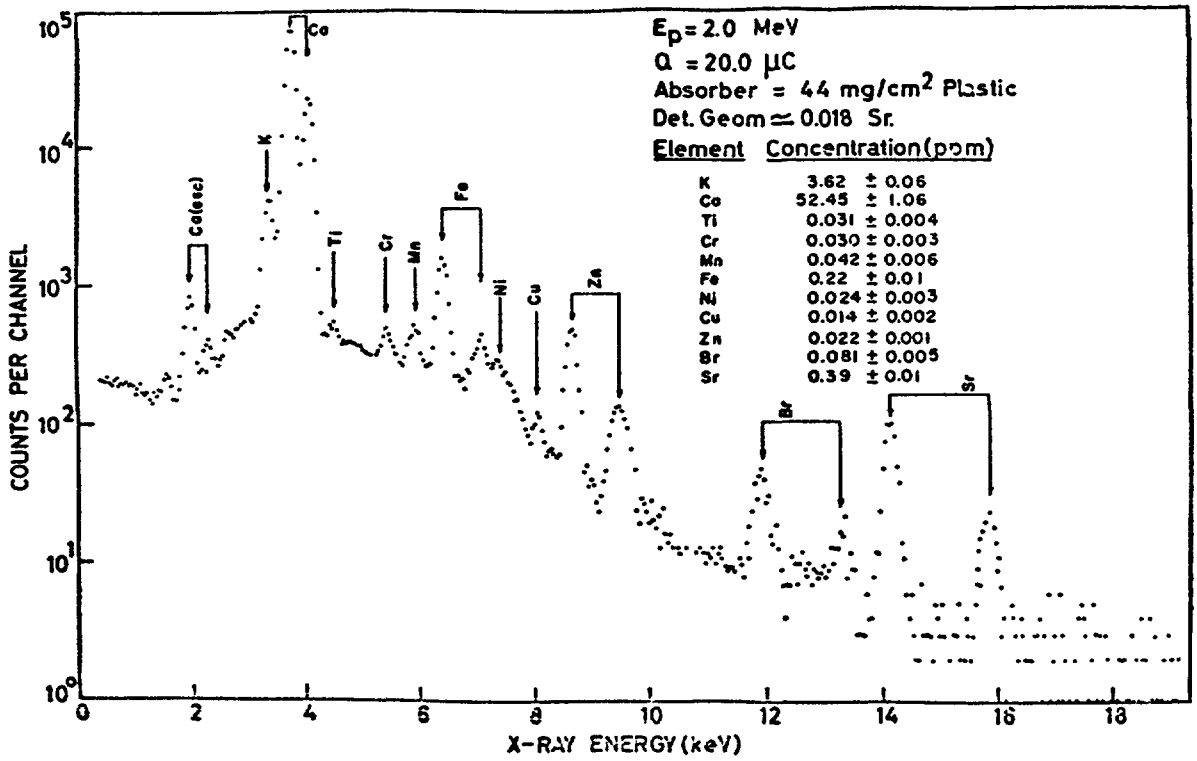

FIG. 4. A typical PIXE spectrum from a drinking water residue obtained from a Dhaka City water supply.

TABLE 5: Trace element concentrations in Bangladeshi Tobacco (in ppm).

Elements	No. of Samples.	This work		Ref. 12 (non-Japanese Brand)		Ref. 12 (Japanese Brand)		Ref. 13 IPI Tobacco
		Range	A.M.*	Range	A.M.*	Range	A.M.*	
K	10	27,200-50,300	37,500± 10,100	28,700-49,200	41,600±8,258	32,500-40,400	35,691±2,982	39,600
Ca	10	293-9300	6,680 ± 2,900	24,100-36,000	28,350±4,667	19,600-27,900	24,775±2,775	25,300
Ti	10	87-350	190 ± 80	-	-	-	-	-
Cr	4	61-100	85 ± 17	-	-	-	-	-
Mn	10	60-180	130 ± 39	134-287	206±57	144-227	189±24	213
Fe	10	1,400-4,100	2,600±800	446-851	653±142	330-610	483±89	489
Ni	10	15-47	30±13	-	-	-	-	-
Cu	10	16-30	24±6	-	-	-	-	70.1±1.6
Zn	10	33-85	59±20	23-42	32±7	16-130	48±32	30.2
Br	10	9-23	17±5	-	-	-	-	-
Rb	10	54-79	65±8	14-22	16±3	17-30	23±4	15.5
Sr	10	24-118	96±34	52-81	67±11	66-106	88±11	25.6

A.M. = Arithmetic mean,

* Uncertainties are the standard deviations.

Table 6 : heavy element composition of the Dhaka City air (August-October, 1982)

Sampling Point	Elements determined ($\mu g/m^3$)							
	K	Cu	Cu	Fe	Zn	Ni	Pb	Mn
Shahbag Market	15.4	1.8	1.0	1.2	-	-	-	-
Gausia Market	4.8	1.5	0.8	0.5	0.1	0.2	0.3	-
Farmview Super Market	0.8	2.2	0.1	1.4	-	-	0.3	-
Nabisco Biscuit Factory	1.9	1.6	0.1	1.0	-	0.1	0.1	-
Beg Rubber Industry	5.2	9.6	1.5	4.2	1.0	0.7	1.4	-
Albert David	1.0	0.4	-	0.3	-	0.2	0.2	-
Jamila Tannery	1.5	0.5	-	0.3	-	0.1	0.2	0.03
Motijheel C/A.	-	2.3	0.06	0.2	0.1	0.03	0.3	0.03
Fulbaria Bus Station	0.7	1.7	-	1.0	0.1	0.03	0.23	0.03
IWTA Terminal Sadarghat	9.3	0.6	0.2	0.4	0.09	-	-	0.04

2.5 Development of atomic absorption spectrophotometric methods

During the project period, IAEA provided us an atomic absorption spectrophotometer. It had been in regular use to provide analytical service required by different institutions in the country, including the BAEC.

In the context of the present study, methods have been developed to analyze air particulates for heavy elements. The results for 10 sampling stations throughout the Dhaka City for the period August-October, 1982, are given in Table 6. This investigation is planned to continue for a couple of years more.

In view of the demands for analytical services, received from the medical hospitals in the Dhaka City, an atomic absorption spectrophotometric method has been developed to analyse Cu, Zn and Mg in urines from patients suspected to be suffering from Wilson's disease. The analytical data thus provided were found very helpful for confirmation of diagnosis. It may be noted here that children suffering from Wilson's disease in Bangladesh were found to have 0.1 - 0.6 ppm of Cu against the normal value of about 0.04 ppm in urine.

2.6 Intercomparison programme of the IAEA

During the lifetime of the project, two intercomparison studies were conducted by the Agency; one on human head hair (HH-1) and the other on a set of five IAEA and NBS reference materials (IAEA/RCA/RUN-1). This laboratory participated in both the studies and performed the analysis using PIXE and AAS methods. These studies in fact have been very helpful in assessing our analytical competence in trace analysis. The experience gained through this study would be of immense benefit in planning future measurements more cautiously where necessary.

3. FUTURE WORK PLAN

The future work plan of this laboratory in heavy trace metal analysis is to generally improve the accuracy and the precision of the methods already developed, by analyzing more reference materials expected through the Agency and to develop more analytical competence in the following areas of interest :

- Study of the levels of nutritional and toxic elements in commonly consumed food items in Bangladesh, particularly fish.
- Systematic analysis of aerosols collected from work environments as well as open atmosphere.
- Study of the level of Cd and Se in surface waters in Bangladesh.
- Metabolic aspects of trace elements in humans and animals.

ACKNOWLEDGEMENTS

We are very much thankful to the IAEA for providing us technical assistance in support of the work reported here and also for helping us in procuring valuable items required by this research. The authors record with gratitude the cooperation received during the course of this work from the members of the Chemistry, Experimental Physics, Technical Physics, Electronics and the General Services and Engg. Divisions of the AECD. The continued interest of Dr. Anwar Hossain, Chairman, BAEC and Dr. M.A. Rab Molla, Director, AECD, in this research has always been very inspiring.

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TRACE ELEMENT ANALYSIS OF HUMAN HEAD HAIR BY NEUTRON ACTIVATION TECHNIQUE

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Abstract

28 elements in reference hair sample (HH-1) and 44 hair samples of Seoul, Korea have been analyzed by instrumental neutron activation analysis. The analytical results of reference sample are good agreed with those of IAEA report within 10% deviation except those of some elements. For the 44 hair samples of Seoul, the range of content of each element is fallen in $\pm 3\sigma$ from his mean value if rejecting one or two of the highest data.

1. INTRODUCTION

In the problem of pollution of the biosphere, man himself undoubtedly occupies the central position as a target. However, it would be a real disaster if man himself became contaminated to levels giving rise to harmful somatic or genetic effects. It is therefore an urgent problem to determine the initial levels of trace elements in man and the extent of his contamination in areas where these elements are expected to show anormalous concentrations. As it is impossible to determine the trace elements composition of the whole body, human head hair is regarded as an indicator of the degree of contamination of man by pollutants.

For national scale survey of the degree of contamination of man, it would be ideal to have a random sampling of the entire population with all possible epidemiological characteristics such as age, sex, place, socio-economic status, cultural background and etc. But it is very difficult and tremendous work to cover entire population with all epidemiological characteristics. Furthermore, our traditional old custom makes it more difficult to persuade rural peoples to obtain hair samples from them.

Fortunately, we take advantage of our unique recruiting system which all recruits from all over the country must have their hair cut in the recruit training center. The recruit population covers all provinces of our country. But due to their uniform sex and age, it covers only limited epidemiological characteristics. On the other hand, the fact that all recruits are healthy enough to be recruited and have same sex of male and age of 22 years old is very advantageous to compare geographical differences.

2. EXPERIMENTAL

2.1. Collection and pretreatment of sample : 44 hair samples were collected from the recruits of Seoul, Korea together with the answers to questionaire.

In order to remove most of the adhering dust and oily materials and any other loosely-bound contaminants from perspiration and external source, each hair sample was given a pre-irradiation washing treatment[1]. The procedure consists of washing each sample of hair in clean Pylex beaker with 10 minute manual shaking with 25ml portions of Reagent Grade acetone and successively, distilled-deionized water, distilled-deionized water, distilled-deionized and Reagent Grade acetone, decanting off the washing liquid after each 10 minute washing. After washing, hair samples were airdried at room temperature in a dust-free area.

A 50mg of each hair sample was accurately weighed and put into the polyethylene vial of ca. 1.5ml capacity and sealed for determination of some trace elements which produce short-lived radioisotopes. Another 50mg of each hair sample was also put into the quartz tube and sealed for determination of some trace elements which produce medium-lived radioisotopes. A weighed iron wire was attached to the outside of the vial as a neutron flux monitor. It was previously reported that the iron wire which contains manganese as impurities was used as the flux monitor[2] or a single comparator[3]. The other 50mg of each sample was put into quartz tube and sealed for the determination of long-lived activities. Before used for hair sample container, quartz tube, of which diameter is 10m/m and length is 3cm and one side was sealed, was boiled with 50ml 6N HCl solution in beaker for one hour, washed with distilled-deionized water three times and acetone and then dried in oven. A 100μg of cobalt was attached to the outside of the quartz tube for neutron flux monitor. The cobalt monitor was prepared as follows; 50mg of high purity cobalt metal powder was accurately weighed and dissolved in 2ml of 6N HNO_3 solution and diluted to 50ml in volumetric flask. From the flask, 100 lambda was pipetted onto small piece of polyethylene sheet and dried with infra-red lamp. The polyethylene sheet was wrapped and inserted into a small polyethylene bag. The bag was wrapped again with aluminum foil.

2.2. Irradiation and Activity Measurement : All the samples were irradiated with the neutron flux monitors in the neutron flux of 1×10^{13} neutrons·cm^{-2}·sec^{-1} using TRIGA Mark III reactor. The sample in the polyethylene vial was irradiated using pneumatic transfer system for 5 minutes for the determination of short-lived elements. The samples in the quartz tube were irradiated at rotary speciman rack for 1 day for the determination of medium-lived elements and 5 days for the determination of long-lived elements.

The irradiated samples were counted by Ge(Li) detector (ORTEC, FWHM = 1.9keV at 1.33MeV of Co-60) connected with 4000 channel analyzer (ORTEC, Model 7044). The counting time was 200sec after 3 minute cooling for the 5-minute irradiated sample, 1000sec after 1 day cooling for the 1-day irradiated sample and 4000sec after 24 day cooling for the 5 day irradiated sample.

The combination of irradiation, cooling and counting time for three groups of nuclides is summerized in Table 1.

2.3. Standardization : The each standard solution of the elements determined in this experiment was prepared from respective high purity metals or reagent grade chemicals by dissolving in HNO_3 and/or HF solution. From the standard solution of Ti, I, Mn, Mg, Cu, V, Cl, Al, Ca and S, 1-5ml portion of each solution was pipetted into a volumetric flask, respectively and mixed together for the mixed standard solution of short-lived elements. The other two mixed standard solutions were prepared similarly as mentioned above for the medium-lived elements such as Au, As, Cd, Br, Na, K, La and W and for the long-lived elements such as In, Cr, Hg, Th, Sb, Cs, Fe, Zn and Co, respectively.

Table 1. Combination of irradiation, cooling and counting times for the three groups of nuclides analyzed at present work.

Group of nuclide	Irradiation time	Cooling time	Counting time
Short-lived; ^{51}Ti, ^{128}I, ^{56}Mn, ^{27}Mg, ^{66}Cu, ^{52}V, ^{38}Cl, ^{28}Al, ^{49}Ca, ^{37}S.	5 min	3 min	200sec
Medium-lived; ^{198}Au, ^{76}As, $^{115m}In(Cd)$, ^{82}Br, ^{24}Na, ^{42}K, ^{140}La, ^{187}W.	10h/d X 1	1 day	1,000sec
Long-lived; ^{114m}In, ^{51}Cr, ^{203}Hg, $^{233}Pa(Th)$, ^{124}Sb, ^{134}Cs, ^{59}Fe, ^{65}Zn, ^{60}Co	10h/d X 5	3 week	4,000sec

For short-lived nuclides, about 2ml of the mixed solution was pipetted into the polyethylene vial of 3ml capacity and Fe wire was attached on the outside of the vial. The vial was irradiated for 5 minutes and cooled for 3 minutes. Then, the vial was opened and 1ml of the solution was pipetted into a new vial. The γ-ray spectrum was applied for the activity of each nuclide. The irradiated iron-wire was measured with the analyzer under the 0.847 MeV peak of ^{56}Mn which is originated from the manganese impurity. The activity of each standard element was normalized with the activity of manganese monitor. From each mixed standard solution of the medium-lived elements and the long-lived elements, 2ml was pipetted into quartz tube and irradiated with Co monitor for 1 day and 5 days, respectively. After cooling the samples for appropriate times, each gamma-ray spectrum was applied for the activities of nuclides. The activity of each standard elements was also normalized with the activity of Co monitor.

2.4. Analysis of Hair Samples : The reference hair sample(HH-1) was analyzed 7 times as mentioned above and the analytical result is shown in Table 2. Among the collected hair samples in Korea, 44 samples in Seoul were analyzed for short-lived, medium-lived and long-lived elements and the results are shown in Table 3.

Table 2. Analytical result of reference hair sample, HH-1, (ppm)

Element	Analytical Results							Average(±1σ)	Data from IAEA
Ti	3.81	3.28	2.57	2.91	3.58	3.32	4.40	3.41 ± 0.55	
I	62.0	59.8	63.4	51.9	52.8	52.7	58.7	57.3 ± 4.4	20.25 ± 8.91
Mn	1.21	0.832	1.17	1.13	0.973	0.980	1.01	1.04 ± 0.12	0.85 ± 0.25
Mg	102	101	132	92.7	108	104	79.6	103 ± 15	62.01 ± 0.58
Cu	22.0	15.5	14.2	18.6	17.9	16.0	19.1	17.6 ± 2.4	10.23 ± 3.17
V	0.129	0.161	0.179	0.105	0.104	0.119	0.0990	0.128 ± 0.028	0.14 ± 0.15
Al	7.10	6.16	5.98	4.45	6.55	4.67	5.13	5.72 ± 0.92	5.50 ± 2.58
Cl	2530	2220	2800	2650	2400	2490	2570	2520 ± 170	2265.29 ± 478.28
Ca	735	730	839	815	607	698	706	733 ± 72	522.03 ± 160.22
S	48100	61900	64400	68700	56900	48900	61300	58600 ± 7200	48707 ± 150
Au	0.0210	0.0350	0.0284	0.0303	0.0332	0.0240	0.0273	0.0285 ± 0.0046	0.03 ± 0.01
As	0.0513	0.0630	0.0521	0.0438	0.0473	0.0557	0.0479	0.0516 ± 0.0059	0.05 ± 0.02
Cd	0.310	328	247	236	268	231	257	0.268 ± 0.034	0.26 ± 0.13
Br	4.07	3.19	3.67	4.53	4.88	3.80	3.67	3.97 ± 0.53	4.16 ± 2.09
W	0.0373	0.0146	0.0216	0.0117	0.0438	0.0270	0.0211	0.0253 ± 0.0108	
Na	10.8	10.3	12.9	12.8	13.2	11.8	12.6	12.1 ± 1.0	12.64 ± 4.77
K	8.41	7.31	9.10	8.37	6.93	7.43	8.87	8.06 ± 0.77	9.21 ± 5.15
La	0.0121	0.0144	0.0110	0.00903	0.00869	0.0130	0.0144	0.0118 ± 0.0022	0.01 ± 0.0
In	0.36	0.61	0.54	0.42	0.39	0.47	0.47	0.466 ± 0.0805	
Cr	0.247	0.231	0.208	0.284	0.231	0.287	0.264	0.250 ± 0.027	0.27 ± 0.16
Hg	0.990	1.47	2.84	2.21	1.36	1.73	1.20	1.69 ± 0.60	1.7 ± 0.24
Th	0.11	0.079	0.081	0.10	0.14	0.10	0.10	0.101 ± 0.019	
Sb	0.0215	0.0228	0.0271	0.0364	0.0338	0.0372	0.0368	0.0308 ± 0.0063	0.03 ± 0.01
Cs	0.51	0.78	0.94	0.67	0.55	0.77	0.84	0.723 ± 0.144	
Sn	190	250	240	180	180	210	210	209 ± 26	
Fe	28.8	20.7	25.6	27.3	21.4	28.1	27.6	25.6 ± 3.0	23.7 ± 9.7
Zn	142	153	143	174	183	167	156	158 ± 14	174.09 ± 31.58
Co	6.03	6.12	5.74	5.43	6.41	6.37	5.94	6.01 ± 0.32	5.97 ± 1.21

Table 3. The summary of analytical result and comparison with others (ppm)

Element	This work			Others			
				Japan[5]		India[6]	
	No. of sample	Arithmatic mean (±1 σ)	Ragne	Mean (±1σ)	Range	Mean (±1σ)	Range
Ti	44	6.30 ± 5.07	0.40-18	4.0 ± 2.1	0.70-34		
I	"	1.03 ± 0.47	0.37-2.3	0.43 ± 0.45	0.049-3.29	2.2 ± 2.5	0.3-13
Mn	"	3.54 ± 2.04	1.0-8.7	1.27 ± 2.46	0.12-21.9	4.21 ± 3.66	0.2-19.8
Mg	"	374 ± 147	130-670	83 ± 64	9.8-405		
Cu	"	31.2 ± 9.8	13-53	18.0 ± 25.4	5.37-184	21 ± 9.1	7-53
V	"	0.223 ± 0.121	0.045-0.46	0.086 ± 0.88			
Al	"	7.49 ± 2.79	2.5-14	13.7 ± 11.5	0.24-65		
Cl	"	1,800 ± 780	640-3,200	1,174 ± 831	50.6-4.178	532 ± 454	52-2,180
Ca	"	1,630 ± 650	570-3,400	946 ± 571	157-3,184		
S	"	130,000 ± 30,800	75,000-210,000	60,000 ± 109,000	32,400-85,900		
Cd	"	0.343 ± 0.440	0.050-2.0	0.82 ± 2.1	0.25-7.42		
Au	"	0.0406 ± 0.0397	0.0010-0.17	0.013 ± 0.026	0.0006-0.21	0.080 ± 0.12	0.01 ± 0.78
W	"	0.0113 ± 0.0164	0.0010-0.075	0.037 ± 2.2	0.01-0.47		
As	"	0.275 ± 0.206	0.015-0.74	0.22 ± 2.2	0.046-1.45	0.10 ± 0.15	0.01 ± 0.89
Br	"	3.45 ± 2.49	0.26-10	5.38 ± 6.43	0.43-49	2.1 ± 1.8	0.05 ± 9.0
K	"	35.7 ± 21.3	2.4-93	42.1 ± 38.8	2.7-280	42 ± 32	3.8 ± 165
La	"	0.0246 ± 0.0259	0.0050-0.092	0.023 ± 2.7	0.0029-0.59	0.050 ± 0.05	0.003 ± 0.22
Na	"	64.5 ± 44.6	5.1-210	48.7 ± 60.7	6.74-547	96 ± 75	24 ± 530
In	"	1.75 ± 1.86	0.039-9.3				
Cr	"	2.33 ± 2.48	0.10-10	1.4 ± 3.0	0.1-14	0.46 ± 0.39	0.05 ± 2.63
Th	"	0.545 ± 0.547	0.032-2.7				
Hg	"	1.88 ± 1.65	0.37-9.4	4.2 ± 1.95	0.99-13.2		
Sb	"	1.60 ± 1.68	0.070-6.6	0.2 ± 0.66	0.009-4.3	0.12 ± 0.15	0.003 ± 1.53
Cs	"	0.620 ± 0.675	0.061-2.4				
Fe	"	152 ± 162	32-760	183 ± 59	76-550	60 ± 38	8.4 ± 334
Zn	"	215 ± 160	32-700	183 ± 59	76-550	138 ± 44	62 ± 430
Co	"	0.481 ± 0.522	0.042-2.7	0.048 ± 0.22	0.0081-2.2	0.07 ± 0.10	0.01 ± 1.18

3. RESULTS AND DISCUSSION

The hair sample analyzed in this work were collected from young men lived in Seoul and 10cm long from scalp. It is also well known that the growth rate of adult hair is 1cm per month or 12cm per year.[4] The analytical results of this work, therefore, should reflect the normal values of trace element concentration in hairs of Seoulite at present.

When the present method was applied to the reference hair sample(HH-1) as shown in Table 2, the analytical results of 28 elements were good agreed with the those of IAEA report[7] within 10% deviation except I, Mg, Cu, Ca and S, while the contents of these elements are higher than those of IAEA report. The deviation between the two results were 20% for S, 40% for Ca, 60% for Cu and 300% for I.

As shown in Table 3, most of the ranges of the trace element concentrations in hair of Seoulite are fallen in $\pm 3\sigma$ from their arithmatic means except S, Cd, Au, W, In, Th, Hg, Fe and Co. The range of these elements are also fallen in $\pm 3\sigma$ from their means, if one or two of the highest raw data are rejected for the calculation of their means and ranges.

Sulfur is the richest one among trace elements in hair and it's concentration is known to be 4.1% or 41000ppm by a IAEA publication . But it's concentration in our data is 131000ppm and about three times higher than the value by the IAEA publication. The reason of such a high concentration of sulfur is not explained at present.

It is noted that the analytical results of hair samples of Seoul obtained in this work are comparable with the corresponding values of other countries given by others as shown in Table 3. Comparing with the results of Japan, these two data are similar about the elements of Ti, Cl, As, Br, K, La, Na, Cr, Fe and Zn, while our data are higher 2 or 3 times than the data of Japan about the elements of I, Mn, Mg, Cu, V, Ca and S and our data are lower than the data of Japan about other elements. But, in case of the elements of Sb and Co, our data are much higher by factor of 8-10 than the data of Japan. Otherwise, comparing with data of India, our data are much similar with the data of India than those of Japan.

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BASELINE STUDY OF PESTICIDE RESIDUES AND TOXIC CONTAMINANTS IN ENVIRONMENTAL SAMPLES IN THAILAND BY NEUTRON ACTIVATION TECHNIQUE

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Abstract

The technique of neutron activation, both instrumental and radiochemical, is used for the investigation of pesticide residues and contaminants, viz. Hg, Se, As, Cd, Cu, Br, Co and Zn in rice and marine fish in Thailand. More than 500 samples of 6 species including squid of fish caught from polluted and non (less)-polluted areas in Thai waters, and of 17 varieties of non-glutinous rice and 6 varieties of glutinous rice of both brown and milled collected from 21 different rice experiment stations throughout the Kingdom are analyzed. The results of this study positively indicate that there are no contamination in fish and rice in Thailand. Additionally, the baseline concentration of studies trace toxic elements is established.

1. INTRODUCTION

The research on the investigation of trace toxic elements both from the residues of (inorganic) pesticides and contaminants in various environmental matrices in Thailand using nuclear based techniques, mostly neutron activation analysis (NAA) has been carried out at the Office of Atomic Energy for Peace (OAEP) since 1972. The elements under the investigation were As, Br, Cd, Co, Hg and Zn in numerous varieties of samples, e.g. Bowen's kale (1), indigenous vegetables and fruits (2), brown and milled glutinous and non-glutinous rice around Thailand (3), marine fish from polluted and non-polluted areas in the Gulf of Thailand (4). Unfortunately, no conclusions could be drawn since the baseline levels of such elements were not known in Thailand.

As generally recognized that the baseline concentration is extremely essential for indicating of pollution problems. Additionally, Thailand is also wellknown as one among the agricultural countries and exporters of the numbers of agricultural products. It is, therefore, the purpose of this study to apply the technique of NAA to the establishment of the baseline levels of trace toxic elements from both residues of pesticides and contaminants by multi-elements determination of As, Br, Cd, Co, Cu, Hg, Se and Zn both instrumentally and radiochemically in marine fish and rice which are the staple food of Thai's people. It is strongly believed that this study will consequently be a great help for Thailand's economic in view of quality assurance of our trade as well as the health and welfare of her people.

The work had been performed during April 1977 - October 1981 with collaboration with Department of Agriculture and Fishery Department, Thailand.

2. EXPERIMENTAL

2.1 Collection and preparation of samples

2.1.1 Fish Six varieties of common marine fish, selected in accordance with their public flavour for Thais in both taste and cost, namely squid (Loligo spp.), scad (Caranx spp.), chub mackeral (Rastrelliger spp.), thread fin bream (Nemipterus spp.), pony fish (Leiognathus Equlu spp.) and bigeye fish (Priacanthus Payenus spp.) caught from both polluted and non (less)-polluted areas in Thai waters, as shown in Fig.1, four times every year up to 3 years in relation to the peak period of monsoon season (Jan., April, July, Oct./Nov.) were supplied by Fishery Department. The total number of 564 fish was used throughout this study.

The muscle tissue of individual fish, except squid, about the same length and weight was sectioned, weighed and freeze-dried. The dry samples were again re-weighed and kept in a separate clean polyethylene container and stored in a desiccator for the investigation.

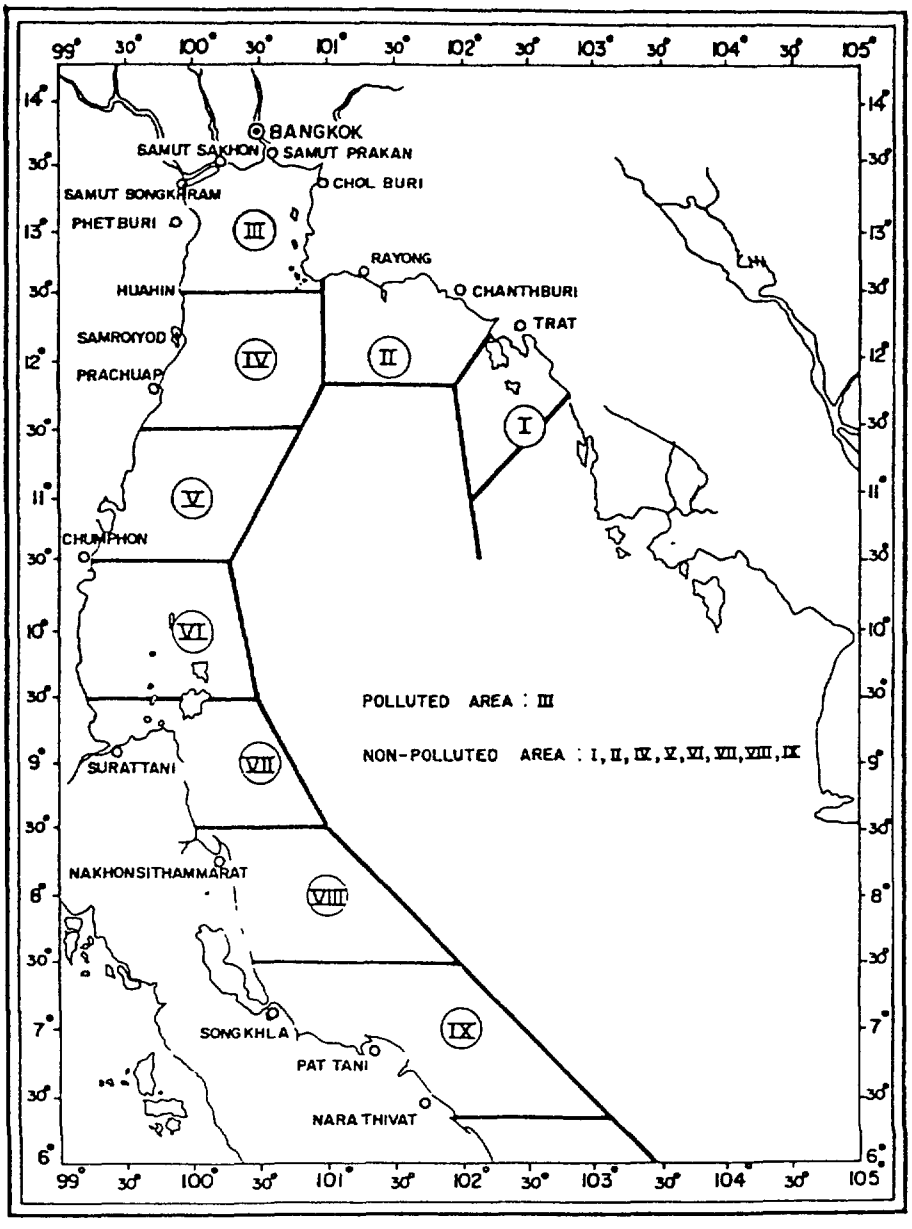

Figure 1 : Fish collection area in the Gulf of Thailand

2.1.2 Rice Seventeen varieties of non-glutinous rice and six varieties of glutinous rice collected from 21 different rice experiment station through out the Kingdom were kindly provided by the Department of Agriculture. The paddy about 1 kg in weight, was previously husked and divided into two portions. The first portion was the brown rice. The second portion was milled and polished and named the milled rice. Individual brown and milled rice was separately kept in a clean polyethylene container for further analyses.

2.2 Neutron irradiation

Samples and standards were irradiated simultaneously in a selected facility, either in a rotary speciman rack "Lazy Susan" or special design wet tube in the Thai Research Reactor-1/ Modification 1 (TRR-1/M-1) which has Triga Mark III core, mormally operating at 1 MW and has been routinely operated for 5-6 hours a day, five days a week. The isotopes ^{76}As, ^{82}Br, ^{115}Cd (^{115m}In), ^{60}Co, ^{64}Cu, ^{203}Hg, ^{75}Se and ^{65}Zn were chosen for this investigation. The detail of this irradiation was also described in Table 1.

TABLE 1. SURVEY OF IRRADIATION DETAIL IN THE TRR-1/M-1 (THAI RESEARCH REACTOR-1 /MODIFICATION 1)

Element	Facility	Thermal neutron flux n/cm^2-sec	Time of irradiation	Container	Remark
Hg, Se	Wet tube	10^{11}	2 months	quartz capsules (1.9 cm i.dx8.5 cm) in aluminium container (5.0 cm i.d.x19.5 cm)	10 samples and 2 mixed standards in one container
As, Cd, Cu,Zn	Lazy Susan	$3x10^{12}$	5 days (~25 hrs)	sample in aluminium foil, standard in quartz ampoule (0.9 cm i.dx7 cm) both packed in aluminium container (2.5 cm i.dx10.5 cm)	4 samples and one mixed standard in one container
Br, Co, Zn	Lazy Susan	$3x10^{12}$	5 days (~25 hrs)	polyethylene capsules (1.0 cm i.dx1.5 cm) in aluminium container (2.5 cm i.dx10.5 cm)	

2.2.1 Instrumental analysis After neutron irradiation, the samples and standards were then measured after a cooling time of 5-7 days for ^{82}Br and 1-2 month for ^{60}Co and ^{65}Zn respectively with using a 26 cm^3 Ge(Li) detector with a energy resolution of 2.2 keV for the 1333 keV gamma rays of ^{60}Co connected to either a 4096 channel analyzer with mini computer (ORTEC Model 7032) or a 1024 channel analyzer (Tracor Northern TN-1706). The areas under the photopeaks corresponding to the γ-ray of ^{82}Br at 777 keV, ^{60}Co at 1333 keV and ^{65}Zn at 1116 keV of samples and standards were compared.

2.2.2 Radiochemical analysis With the limitation of the present available facility, As, Cd, Cu, Hg and Se could not be determined instrumentally. Additionally, the determination procedures for As, Cd, Cu and Hg which were previously developed and employed in our laboratory and was described elsewhere (1-4) were quite satisfactory but it was time consuming. It was not quite the proper technique to handle the large number of samples. Consequently, the direct combustion technique described by Rook (5) and the ion-exchange technique described by Morrison and Potter (6) were modified and employed for the investigation of Hg, Se; As, Cu, Cd, Zn respectively.

3. RESULTS AND DISCUSSION

The reliability test with using Bowen's Kale and Bovine liver (SRM 1577) of NBS as indicated in Table 2 was shown quite satisfactory. The limit of detection for Br, Co, Zn (INAA); As, Cu, Cd, Hg and Se (RNAA) as obtained was 10^{-3}, 10^{-3}, 10^{-3}; 10^{-6}, 10^{-5}, 4×10^{-5}, 10^{-5}, 9×10^{-5} mg/kg respectively. Additionally, numerous standard reference materials and dummy samples were frequently used for quality control of the analytical results.

TABLE 2. THE RELIABILITY TEST OF THE ELEMENT DETERMINED WITH USING STANDARD REFERENCE MATERIAL

Element	Bowen's Kale		Bovine Liver (SRM 1577)	
	Certified value	result of this investigation*	Certified value	result of this investigation*
As	0.129 ± 0.023	0.1128 ± 0.0107	0.055**	0.0760 ± 0.0080
Cd	0.746 ± 0.237	0.7355 ± 0.0807	0.27 ± 0.04	0.2722 ± 0.0166
Hg	0.1663±0.0235	0.1850 ± 0.0103	0.016±0.002	0.0167 ± 0.001
Se	0.120 ± 0.0207	-	1.1 ± 0.1	1.0103 ± 0.0347
Br	25.62 ± 1.50	24.50 ± 2.0	-	-
Co	0.0585± 0.008	0.056 ± 0.007	-	-
Zn	32.74 ± 2.66	31.83 ± 0.51	-	-

* at least three sets of the investigation

** not yet certified

In order to correct for flux gradients in the irradiation position, a flux monitor, normally, a copper disc was used throughout the study.

The chemical yield of used separation procedures, which was previously tested with using the appropriate radiotracers, for Cd, Cu, Hg, Se was about 100% and for As was 65%.

3.1 Fish

The total number of 147, 81, 208 and 120 samples of six varieties of common marine fish caught from both polluted and non-polluted areas was investigated for Hg, Se; As, Cd; Br; Co and Zn respectively and the summary in concentration ranges, averages and (proposed) baseline of elements determined was presented in Table 3. The results up to present, as indicated in Table 4, showed no significant difference in concentration of elements in fish caught from both polluted and non-polluted areas. Additionally, in comparison with values reported by FAD/WHO in 1972 (7) and others as cited in Table 5, the result of this study indicated much lower in concentration. Consequently, it could be stated that there is no identification of pollution of the elements surveyed in Thai waters.

Since area III is the estuary of the main rivers of Thailand, it is considered the only polluted area in the Gulf of Thailand. In accordance with Holden (8), only muscle tissue was used to represent the edible part.

Apart from this work, the research on the investigation of trace toxic elements with particular attention to As, Cd, Cr, Hg, Pb, Se etc. in surface water, sediment, plankton, shellfish etc, is planned to be carried out at this office. The main objective is to study the uptake and the correlation of thus trace toxic elements in environmental matrices.

3.2 Rice

Large number of samples of non-glutinous and glutinous rice was investigated for As, Cd, Cu; Hg, Se; Br, Co and Zn and the summary in concentration ranges, averages and (proposed) baseline of elements determined was presented in Table 6. In comparison with the results of the other investigators, as indicated in Table 7, the result of this study was within that range. Consequently it can be concluded that there is no contamination in Thai rice.

Since brown rice is still favourably consumed by some countrymen in various parts of the country, and a rice bran which is left over from milling brown rice is also used for chicken, duck and pig feeding in Thailand, the investigation for such elements is essential.

It is our intention to study the in put of elements determined. The correlating samples, viz. planted soil, before and after harvesting, every batches of used fertilizers and pesticides were collected for investigation. It is expected that the results could be published in internation journal in a very near future.

TABLE 3. CONCENTRATION RANGES, AVERAGES AND BASELINE OF ELEMENTS DETERMINED IN MARINE FISH IN THAI WATERS (mg/kg WET WEIGHT)

Type of sample	Parameter	N	Hg $\times 10^{-4}$	Se $\times 10^{-4}$	N	As $\times 10^{-4}$	Cd $\times 10^{-4}$	N	Br $\times 10^{-3}$	N	Co $\times 10^{-3}$	Zn $\times 10^{-3}$
Thread fin bream	Range	43	50-588	1403-12453	20	<0.1-6969	30-1509	60	712-11593	34	7-85	1401-11804
	Average (± 6)		235(19)	4820(471)		1119(437)	514(108)		4110(2530)		28(22)	5182(2358)
	Baseline		218	3936		817	514		3863		27	4975
Bigeye	Range	21	124-367	5402-7892	14	7-5180	<4-1031	36	1053-16245	19	5-149	1626-6478
	Average (± 6)		246(16)	6989(162)		149(36)	335(91)		6134(3606)		33(34)	4371(1631)
	Baseline		246	6989		120	335		5844		26	4371
Scad	Range	16	13 - 179	2086-6537	15	24-175	<4-1826	15	3634-11549	6	15-47	4750-10467
	Average (± 6)		56(11)	3781(311)		65(8)	513(136)		5799(2169)		32(13)	7470(1658)
	Baseline		48	3598		65	419		5389		32	7470
Chub Mackeral	Range	3	75-262	2991-7408	-	-	-	2	4541-4742	2	14-32	6149-11143
	Average (± 6)		157(55)	5509(1312)					4642(81)		23(9)	8646(2497)
	Baseline		157	5509					4642		23	8646
Pony	Range	4	41 - 89	3318-8874	-	-	-	10	3866-15739	6	15-93	5453-13335
	Average (± 6)		60(10)	6197(1247)					7599(3601)		45(29)	9423(2536)
	Baseline		60	6197					6694		45	9423
Squid (Mollusk)	Range	60	10-273	1045-8529	32	11-2242	49-7792	85	994-25476	53	6-141	2254-17722
	Average (± 6)		94(8)	3552(200)		389(85)	1912(325)		8778(5252)		33(26)	7560(3341)
	Baseline		91	3468		330	1722		8379		31	7365
Fish (Overall)	Range	87	13-588	1403-12453	49	<0.1-6969	<4-1826	123	712-16245	67	5 - 149	1401-23174
	Average (± 6)		194(17)	5230(204)		521(63)	462(28)		5261(3189)		31(26)	5932(3382)
	Baseline		143	4835		384	434		4995		31	5667

N = number of sample analyzed

TABLE 4. RANGES AND AVERAGES OF ELEMENTAL CONCENTRATION OF FISH IN ACCORDANCE WITH LOCATION

Type of fish	Location	Concentration in mg/kg (wet weight) $\times 10^{-4}$					
		N	As	Cd	N	Hg	Se
Thread fin bream	P	10	<0.1 - 6969 (2358)	47 - 1509 (677)	14	107 - 588 (288)	2366 - 12453 (6386)
	N.P.	10	19 - 334 (116)	30 - 892 (350)	29	50 - 418 (210)	1403 - 10488 (4036)
Bigeye	P	3	7 - 117 (53)	<4 - 54 (31)	5	124 - 204 (164)	5402 - 7669 (6109)
	N.P.	11	48 - 518 (175)	<4 - 1031 (470)	16	144 - 367 (266)	6355 - 7892 (7265)
Scad	P	7	40 - 175 (82)	237 - 1826 (671)	5	33 - 179 (67)	3208 - 5398 (3396)
	N.P.	8	24 - 114 (59)	<4 - 1568 (513)	11	13 - 94 (36)	2086 - 6537 (3616)
Chub Mackeral	P	--	--	--	2	133 - 262 (198)	6120 - 7408 (6764)
	N.P.	--	--	--	1	75	2991
Pony	P	--	--	--	--	--	--
	N.P.	--	--	--	4	41 - 89 (60)	3318 - 8874 (6197)
Squid	P	5	29 - 2242 (878)	187 - 5544 (1491)	9	16 - 273 (93)	1321 - 8527 (3742)
	N.P.	27	11 - 1217 (299)	49 - 7792 (2021)	51	10 - 258 (84)	1045 - 7592 (3310)

N = Number of sample analyzed
(--) = Average concentration
P = Polluted area
N.P. = Non-polluted area

TABLE 5 MERCURY, SELEMIUM, ARSENIC AND CADMIUM IN FISH AND FOOD ACCORDING TO OTHER REPORTS

Type of food	Unit in wet weight	Hg		Se		As		Cd	
		Conc.^{n}	Ref.	Conc.^{n}	Ref.	Conc.^{n}	Ref.	Conc.^{n}	Ref.
Normal Diet									
UK	mg/day	-	-	0.2	10	-	-	-	-
USA	"	0.043-0.107	9	-	-	0.4-0.9	19	0.016-0.5	21-23
West Europe	"	0.007-0.01	10-11	-	-	0.1	10	0.048-0.064	10,24-25
Japan	"	-	-	-	-	0.07-0.17	20	0.059	26
Toxic Diet	"	0.3 - 0.5	9	5	12	5-50	12	3	27
Maximum legal limit	mg/kg	0.5	9	3	12	2.3	19	0.4	28
Acute lethal dose	mg	150-300	12	70-500	12	100-300	12	4000	27
Fish	mg/kg	Table 18	-	0.1-16	14-18	0.5-16	19	0.03- 1.7	25, 27
	"	0.0070-15	13	-	-	2.0-44	13	-	-
Shellfish	"	-	-	-	-	0.5-80	19	0.1 - 118	25, 27

TABLE 6. CONCENTRATION RANGES, AVERAGES AND BASELINE OF ELEMENTS DETERMINED IN RICE (mg/kg)

Type of Rice	Parameter	N	Hg $\times 10^{-4}$	Se $\times 10^{-4}$	N	As $\times 10^{-3}$	Cd $\times 10^{-3}$	Cu $\times 10^{-3}$	N	Br $\times 10^{-3}$	Co $\times 10^{-3}$	Zn $\times 10^{-3}$
Non-glutinous												
Brown	Range	46	14-225	119-982	54	10-2542	0.4-2055	399-7311	58	109-2073	16-582	8173-83558
	Average (± 6)		72(44)	394(195)		599(623)	506(519)	2385(1558)		510(326)	102(86)	26176(12971)
	Baseline		68	381		563	420	2292		465	93	25169
Milled	Range	46	11-137	110-670	90	0.1-2358	0.4-2761	403-5438	69	4-1927	5-315	1783-50103
	Average (± 6)		49(34)	297(159)		565(519)	361(383)	2172(1147)		354(291)	50(49)	18833(7567)
	Baseline		43	297		545	334	2135		316	46	18374
Glutinous												
Brown	Range	15	42-151	155-904	11	18-958	0.4-1411	993-2714	21	297-2877	12-207	13975-70993
	Average (± 6)		88(32)	421(296)		199(268)	364(384)	1812(864)		755(577)	72(54)	26651(13845)
	Baseline		88	421		123	259	1620		649	65	24434
Milled	Range	15	24-104	104-776	24	25-1385	0.4-990	584-4822	22	86-842	2 - 194	8096-31336
	Average (± 6)		66(24)	310(225)		313(357)	270(261)	1991(1132)		367(186)	54(45)	18068(6385)
	Baseline		66	310		266	204	1741		344	47	18068

N = number of sample analyzed

TABLE 7 ARSENIC, CADMIUM, MERCURY, AND BROMINE IN RICE ACCORDING TO OTHTER REPORTS

Type of food	Unit in wet wt.	As		Cd		Hg		Br	
		Conc.[n]	Ref.	Conc.[n]	Ref.	Conc.[n]	Ref.	Conc.[n]	Ref.
Rice									
General	mg/kg	0.1-0.5	19	0.04	27	0.004-0.015	30	-	-
Korea/Japan	"	0.04-1.2	13	0.008-0.37	13,27	0.004-1.00	13,31-32	0.026-1	13,33
USA	"	< 0.1	29	-	-	-	-	-	-

4. ACKNOWLEDGEMENTS

The authors are indebted to the IAEA for its partial support of this work through Research Contract No.2224/RB (1978-1981) and Technical Assistance Project No. THA/5/021. They are also grateful for their counterparts from Marine Fisheries Division, Department of Fisheries and Rice Division, Department of Agriculture, of Ministry of Agriculture and Co-operative of Thailand for providing fish and rice. They also wish to express their special sincere appreciation to Mr.S.P.Kasemsanta, the former Secretary General of OAEP and currently a Project Co-ordinator, UNDP/IAEA Regional Industrial Project, Dr. S.B. M Baku, the former IAEA project Officer of this contract, Dr. H.A. Das, the Agency's expert under THA/5/021, for their valuable suggestions, comments and strongly support regarding this work.

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TRACE ELEMENTS IN ANIMALS AND FOODSTUFFS

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Abstract

In order to obtain information on pollution levels in the environment, some trace elements in biological materials were determined by neutron activation analysis, flameless atomic absorption spectrometry and inductively-coupled plasma atomic emission spectrometry.

For estimating the radiation dose to the thyroid in man, and in order to study the relationship between radioiodine and stable iodine, measurements were made of iodine in cow's milk from Japan by neutron activation analysis (NAA).

In this paper, data for iodine in cow's milk, as well as some other trace elements such as aluminium, cobalt, copper, iron, manganese, zinc and mercury are presented.

1. INTRODUCTION

Trace substances, including harmful ones such as mercury, lead, arsenic and organo-halogens, are continuously taken up by the human body through foodstuffs, drinks and ambient air. It is important to be aware of the levels of trace and toxicological elements in animals and foodstuffs because, from such data, one can predict the levels of these pollutants in man and his environment. Therefore, much data concerned with pollutants in many environmental and biological samples have, up to the present, been reported by many investigators in the field of environmental research.

The present authors also feel that it is of paramount importance to investigate the relationship between radioactive and non-radioactive elements in foodstuffs and environmental and biological samples. In this connection, iodine, bromine and chlorine in cow's milk from Japan were simultaneously determined by radiochemical NAA.

Several other trace and toxicological elements were determined in animals and human bones and dairy products by flameless atomic absorption spectrometry (AAS) and inductively-coupled plasma atomic emission spectrometry (ICP-AES).

In addition, in order to find out whether there are any correlations between trace elements in human organs and hair, an analysis of some trace elements in human liver, brain and hair was carried out by means of flameless AAS and ICP-AES.

In this report, the analytical results for trace elements are summarized. Simultaneously, the necessity of checking the analytical performance of each laboratory is more and more widely recognized; therefore a large volume of powdered reference hair was prepared and was checked for homogeneity by the three analytical methods mentioned above.

2. EXPERIMENTAL

2.1. Determination of iodine, bromine and chlorine in cow's milk

2.1.1. Collection of cow's milk samples: samples were collected from commercial stores near Chiba, eastern area of Japan and Hokkaido.

2.1.2. Irradiation: irradiation was carried out with a Van de Graaff accelerator for one hour, as already reported in ref. 1.

2.1.3. Radiochemical procedure: radiochemical separation for the determination of iodine, bromine and chlorine was carried out as reported in ref. 1. The separation of ^{80}Br, ^{82}Br and ^{38}Cl from the irradiated samples was mainly performed by an anion exchange method.

2.1.4. Activity measurement: the radiochemical purity of the separated ^{128}I, ^{80}Br, ^{82}Br and ^{38}Cl was checked by gamma-ray spectrometry and by following the decay curves by beta counting with a GM counter.

2.1.5. Results and discussion: the amounts of iodine, bromine and chlorine in cow's milk samples were simultaneously determined by RNAA and the results are given in Table 1. The accuracy of the procedure was checked by the standard additions method. For example, it can be seen that the average precision is about $\pm$ 5% for an iodine concentration of 0.045 ppm and the limits of detection for iodine with the proposed method by gamma-ray spectrometry and beta-counting are 10 and 15 μg, respectively.

It seems that the proposed method is simple and rapid for the determination of halogens in a large volume of liquid sample. By this method, the determination of sub-micro amounts of halogens in the samples can easily be achieved without any other chemical procedure.

From the data in Table 1, it can be seen that the seasonal variation in the amounts of iodine in cow's milk from Japan is correlated with that of bromine and, at the same time, that of chlorine tends to increase from month to month. The biological half-life of iodine can be estimated from the equation.

$$Y = 110.5 - 13.2\ X$$

where Y = amount of iodine in milk (μg/L) and X = month. The baseline level of iodine in cow's milk can also be determined as about 60 ppm.

2.2. Determination of trace elements in Japanese dairy products and in bovine and human bone

2.2.1. Analytical technique: instrumental neutron activation analysis (INAA).

2.2.2. Sample collection: samples were collected from several areas of Japan as shown in Table II.

Table I. Iodine, bromine and chlorine content in cow's milk (in ppm)

Location	Month	Iodine	Bromine	Chlorine
Iwate	Jan.	0.117	20.7	256.1
"	Feb.	0.126	25.6	254.6
"	Mar.	0.146	27.8	287.0
"	Apr.	0.089	10.1	190.8
"	May	0.089	8.9	348.4
"	Jun.	0.078	9.1	384.2
"	Jul.	0.058	10.1	224.0
"	Aug.	0.069	6.3	359.8
"	Sept.	0.074	9.5	266.7
"	Oct.	0.049	24.1	629.4
"	Nov.	0.047	21.8	627.2
"	Dec.	0.088	16.4	662.7
Nagano	Jan.	0.118	8.71	281.6
Shimodate	"	0.100	9.11	298.3
Shizuoka	"	0.117	8.70	298.3
Sayama	"	0.128	9.10	487.0
Choshi	"	0.069	9.10	356.1
Kushiro	"	0.107	14.40	286.9
Asahikawa	"	0.136	15.00	346.2
Obihiro	"	0.093	14.80	296.1
Nagano	Apr.	0.088	7.84	255.8
Shimodate	"	0.114	11.80	119.1
Shizuoka	"	0.093	5.60	259.7
Sayama	"	0.093	14.80	301.6
Choshi	"	0.109	11.80	315.2
Kushiro	"	0.054	21.60	410.4
Asahikawa	"	0.041	13.30	297.2
Obihiro	"	0.056	17.60	317.4
Kyoto	Jun.	0.175	5.749	139.1
Kanagawa	"	0.160	6.458	156.3
Kobe	"	0.316	5.667	137.1
Nagano	Oct.	0.113	7.97	298.5
Nagano	"	0.099	8.31	266.8
Shimodate	"	0.080	16.80	273.0
Shimodate	"	0.075	16.90	308.6
Shizuoka	"	0.072	9.09	312.4
Shizuoka	"	0.058	8.66	285.8
Sayama	"	0.093	18.50	321.2
Sayama	"	0.103	16.10	317.8
Choshi	"	0.117	10.90	524.0
Choshi	"	0.087	9.72	321.7
Kushiro	"	0.070	18.80	357.1
Kushiro	"	0.068	19.90	299.3
Asahikasa	"	0.066	17.60	820.8
Asahikawa	"	0.074	20.60	527.4
Obihiro	"	0.070	20.70	319.5
Obihiro	"	0.099	17.60	623.2
Nagano	Nov.	0.100	9.96	300.7
Shimodate	"	0.088	15.10	299.1
Shizuoka	"	0.094	10.50	288.1
Sayama	"	0.128	17.70	310.7
Choshi	"	0.119	13.80	341.6
Kushiro	"	0.084	11.40	411.2
Asahikawa	"	0.078	15.90	366.8
Obihiro	"	0.089	27.60	311.9

Table II. Trace elements in biological materials (ppm)

	Bovine bone*1			Human bone*2			Dairy products*3			Rice*2
	FAAS	ICP	NAA	FAAS	ICP	NAA	FAAS	ICP	NAA	FAAS
Al	16.99,	17.50,	---	12.52,	10.00,	---	457.12,	427.22	---	---
Cd	4.15,	----,	---,	2.05,	---,	---,	---,	---,	---,	---
Co	0.24,	0.20,	0.18,	0.36,	0.35,	0.31,	0.13,	0.15,	0.12,	0.211
Cr	2.12,	2.51,	1.88,	2.55,	2.69,	2.22,	31.80,	27.33,	24.13,	---
Fe	12.25,	14.65,	14.00,	71.55,	74.21,	70.88,	(1.47,	1.66,	1.39)*4	0.012
Hg	---,	---,	---,	---,	---,	---,	---,	---,	---,	0.099
Mg	(5.68,	5.48,	---,	5.21,	5.55,	---,	8.71,	9.92,	---,)*4	---
Mn	9.51,	10.33,	---	4.11,	4.56,	---	311.30,	354.22,	---,	---
Mo	---,	8.14,	---,	---,	1.31,	---,	---,	0.99,	---,	---
Ni	---,	9.00,	---,	---,	12.21,	---,	---,	18.22,	---,	---
Si	323.40,	356.41	---,	612.5,	670.0,	---,	1224.0,	1277.4,	---,	---
Sr	352.81,	378.52	---,	125.4,	137.5,	---,	76.19,	98.08,	---,	---
Zn	144.21,,	151.90,	158.8,	210.4,	267.5,	233.5	505.11,	522.8,	511.0,	24.55

*FAAS : by flameless atomic absorption spectrometry
*ICP : by inductively-coupled plasma atomic emission spectroscopy
*NAA : by neutron activation analysis
*1 : sample collected from Kobe
*2 : sample collected from Kyoto
*3 : sample collected from Osaka
*4 : ( )*4:X1000

2.2.3. Sample irradiation: after ashing at 450°C, the samples (weight 0.1 - 0.2 g) were irradiated at a thermal neutron flux density of 2.3 - 5.4 x 10^{13} n.$cm^{-2}s^{-1}$ for one hour, together with cobalt (10 μg) as a comparator standard, in the KUR reactor of Kyoto University or in JRR-2.3.4 at the Japan Atomic Energy Research Institute. The samples irradiated in polyethylene vials were stored for about a month to allow radionuclides of shorter half-lives to decay.

2.2.4. Activity measurement: the irradiated samples and standards were transferred into new polyethylene containers and measured with a Canberra 70 cm^3 coaxial Ge(Li) detector connected to a 4000 channel pulse height analyser. The counting time was generally 80,000 s. The results obtained are given in Table II.

2.3. Flameless atomic absorption spectrometry

2.3.1. Sample digestion: some ashed samples (0.2 - 0.5 g) were directly dissolved in 3 ml of concentrated nitric acid; the dairy products and the dried rice (0.2 - 0.3 g) were digested in 3 ml of concentrated nitric acid in teflon digestion vessels at 110°C for 14-16 hr. The digested samples were then diluted to 50 or 100 ml.

2.3.2. Measurement of trace elements: a Hitachi 170-70 flameless atomic absorption spectrometer was used; the measurements were carried out by the standard additions method. The results obtained are given in Table II.

2.4. Inductively-coupled plasma atomic emission spectroscopy

2.4.1. Instrumentation: a Hitachi super scan 306 (electroatomizer, power supply/controller etc.) was used.

2.4.2. Elements determined: the elements for which the original multielement cassette was aligned, and the current list of elements and wavelength are: Al (309.27 nm), Co (228.80 nm), Cr (205.55 nm), Cu (324.75 nm), Fe (238.20 nm), Mg (279.55 nm), Mn (257.61 nm), Si (251.61 nm), Sr (407.77 nm) and Zn (213.85 nm). High purity stock solutions of standards were prepared in the laboratory. The determinations were made by the standard additions method. The details will be published elsewhere. The results obtained are given in Table II.

2.5. Preparation of reference powdered hair

2.5.1. Sample collection: scalp hair samples (about 3 cm from the end of scalp hair) were collected from about 400 healthy Japanese students with similar dietary habits.

2.5.2. Preparation method for powdered hair samples: powdered hair samples were made by two methods. After washing by the IAEA's recommended method [2], (1) an agate ball mill (250 ml volume) with electrically controlled rotating speed and time was used to prepare large volume samples, and (2) a self-made machine constructed from an old fashioned loud-speaker, as vibrator, combined with a teflon container (100 ml) and a teflon coated steel ball was used to prepare small volume samples (less than 100 mg).

2.5.3. Homogeneity test for the prepared powdered hair samples: homogeneity testing was carried out by NAA, flameless AAS and ICP-AES for Co, Zn, Hg, Fe, Pb, Cd etc. The results obtained are given in Table III. A test for statistical outliers was applied using the Dixon method.

2.6. Trace elements in human tissues

2.6.1. Sample collection: samples were obtained from subjects with diseases such as stomach and liver cancer.

2.6.2. Elements determined: elements such as Cu, Mn, Al, Zn, etc. were determined by AAS and ICP-AES. The results obtained are given in Table IV.

Table III. The check of homogeneity for the powdered hair samples

Total counts/g of sample (80000 sec)

Statistical data of each elements measured

Elements	average	variance	std/dev	max.value	min.value
Iron-1	8631.0	1.18E+06	1088.6	10494.3	7741.6
Iron-2	5063.5	180764	425.2	5770.7	4693.7
Cobalt-1	12957.0	7.98E+06	2825.2	17240.6	9942.1
Cobalt-2	11790.3	3.84E+06	1960.8	14711.8	9495.0
Zinc	291691	1.58E+08	12581.2	303939	272387
Mercury	136070	3.11E+07	5585.1	139039	126107

Rejection test for the obtained data in the samples

Element	Fe-1	Fe-2	Co-1	Co-2	Zn	Hg
R1(min)	0.366	0.265	0.273	0.449	0.557	0.930
R2(max)	0.640	0.610	0.492	0.421	0.068	0.018
S(0.05)	0.642	0.642	0.642	0.642	0.642	0.642
R1<>S:min	R1<S	R1<S	R1<S	R1<S	R1<S	R1>S
R2<>S:max	R2<S	R2<S	R2<S	R2<S	R2<S	R2<S

Absorbance/g of sample

Statistical data	Mn	Pb	Fe	Cu	Zn	Cd
Number of data	20	20	20	20	20	20
Average	123.15	117.55	29.057	76.30	90.56	156.94
Variance	66.73	171.93	4.61	80.22	12.22	89.21
std/deviation	8.17	13.11	2.15	8.95	3.49	9.44
Maximum value	135.47	144.44	32.25	93.31	96.99	181.74
Minimum value	110.68	101.77	24.07	61.60	83.87	145.90

Rejection test of data	Mn	Pb	Fe	Cu	Zn	Cd
R1(min.)	0.061	0.057	0.282	0.170	0.266	0.080
R2(max.)	0.118	0.237	0.185	0.117	0.270	0.335
S(0.05)	0.45	0.45	0.45	0.45	0.45	0.45
min. value	R1<S	R1<S	R1<S	R1<S	R1<S	R1<S
max. value	R2<S	R2<S	R2<S	R2<S	R2<S	R2<S

*R1<S or R2<S datum not Reject,R1>S or R2>S datum Reject.

Table IV. Some elements in brain tissues

Copper content in brain tissues

Sample No.	SA-569	KA-455	RN-565	KA-445	KA-444	SA-5949
			ug/gram sample			
26	3.321	3.655	0.849	27.432	5.954	36.809
No.of data	20	20	21	21	21	21
Average	3.006	2.567	1.474	3.658	2.003	4.114
Variance	2.509	1.603	0.998	2.028	0.655	5.704
std/dev	1.584	1.266	0.999	1.424	0.809	2.388
Max.value	5.904	5.351	3.452	7.294	4.049	13.719
Min.value	0.3459	0.345	0.3458	1.717	0.819	2.111

Aluminum concentration in brain tissues (ppm)

Sample No.	SA-569	KA-455	RN-565	KA-445	KA-444	SA-5949
26	1.240	1.563	1.270	1.017	1.236	1.312
27	11.031	1.620	—	4.195	3.558	2.961
No.of data	21	21	21	21	21	21
average	1.510	1.043	1.083	1.447	1.693	1.615
variance	0.038	2E-03	8E-03	0.629	0.218	0.266
std/dev.	0.194	0.047	0.090	0.793	0.467	0.516
max.value	2.004	1.207	1.303	4.593	2.524	3.175
min.value	1.318	0.980	0.935	0.981	0.324	1.096

Manganese concentration in brain tissues (ppm)

sample No.	SA-569	KA-455	RN-565	KA-444	KA-445	SA-5949
26	3.0418	4.4590	1.4924	3.4226	3.9959	1.136
27	1.3282	4.4264	—	0.6748	0.1377	8.849
No.of data	21	21	20	21	21	21
average	1.2970	0.5731	0.5622	0.4781	0.6126	0.5447
variance	0.8036	0.1879	0.0334	0.0648	0.1149	0.0594
std.dev	0.8964	0.4335	0.1830	0.2546	0.3391	0.2438
max.value	3.7411	1.7282	1.0060	1.3158	1.4327	1.1430
min.value	0.4755	0.1264	0.3269	0.1869	0.2357	0.2470

Iron concentration in brain tissue (ppm)

Sample No.	SA-569	KA-455	RN-565	KA-445	KA-444	SA-5949
26	246.564	47.786	132.175	143.804	57.321	40.672
27	193.632	1389.640	230.893	82.793	213.929	321.276
No.of data	21	21	20	21	21	21
average	206.558	88.730	132.487	97.110	99.865	58.039
variance	13341.3	3258.72	10056.7	7301.49	6858.05	1183.18
std/dev	115.504	57.085	100.283	85.448	82.813	34.397
max.value	544.868	212.996	499.786	387.807	338.114	175.766
min.value	90.835	18.811	33.423	9.039	20.039	22.511

Zinc concentration in brain tissue (ppm)

Sample No.	SA-569	KA-455	RN-565	KA-445	KA-444	SA-5949
26	11.185	13.347	8.754	12.123	6.996	3.681
27	3.962	17.101	—	59.639	13.447	501.100
No.of data	21	21	20	21	21	21
Average	10.444	10.309	11.385	9.742	8.117	10.509
Variance	28.204	23.305	30.936	29.211	10.638	14.984
Std/dev.	5.311	4.828	5.562	5.405	3.262	3.871
Max.value	24.404	21.525	21.102	21.347	13.433	24.009
Min.value	4.012	4.422	3.016	3.494	2.694	5.125

*26:liver sample
*27:hair sample

3. DISCUSSION

This work has shown that, despite such analytical problems as matrix effects, interferences, etc., flameless AAS and ICP-AES, like NAA, are extremely suitable tools for the precise and rapid determination of trace elements in biological materials. New information on the occurrence of trace elements in biological materials can be obtained by these analytical methods.

Baseline data on trace elements, as exemplified by the data in Tables II and III, is essential for environmental pollution studies in Japan. From Table III it can be concluded that the powdered hair samples described in this report are suitable for analytical quality control, and also that human hair may be used to test for diseases such as Minamata or Wilson's disease in human health-related environmental research.

From the data reported in section 2.6 it appears that trace elements are not homogeneously distributed within a single organ. The trace elements concentrations in single samples were normalized to the respective mean concentration value for the whole organ. One brain sample of 0.25 - 2 g wet weight is not representative of the mean value of the whole organ. From these data, the relationships between trace element concentrations in individual organs and disease cannot yet be explained.

ACKNOWLEDGEMENTS

The authors thank Mr. S. Shibata of the National Institute of Radiological Sciences and Mr. K. Sasajima of the Research Reactor Institute of Kyoto University for their assistance in the experimental work, and Mr. S. Ikeda of the Scientific Instrument Centre of the Nissei Sangyo Co. Ltd. for providing the Hitachi Inductively Coupled Plasma Emission Spectrometer used in this investigation.

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MEASUREMENT OF TRACE ELEMENTS IN HUMAN HEAD HAIR, TOBACCO, COAL AND FOOD ARTICLES OF PAKISTAN

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Abstract

Increasing contamination of biosphere with toxic elements may affect human health as these elements can enter human body through food chain. Therefore the levels of these elements should be monitored in the atmosphere, food articles, body tissues and fluids. In Pakistan studies were carried out on the measurement of certain toxic and other elements in human head hair, cigarette tobacco, tea leave, coal and food articles to establish base line levels.

1. INTRODUCTION

Ever increasing release of foreign chemicals into the environment from various activities of man is polluting the biosphere with toxic elements. These pollutants find their way to human body through food chain, water and atmosphere and may accumulate in the vital organs. The exposure of human body to abnormal concentrations of toxic elements may adversly affect human health as these can interfere in the normal biochemical functions. Therefore it is important to monitor the levels of toxic elements in human tissues and body fluids as well as in food articles and other environmental samples of interest. Such studies will help in establishing the base line levels of toxic elements in various body organs and food articles.

In view of the effect of environmental pollution on human helath, IAEA in 1978 initiated an RCA project on "Health related environmental research using nuclear techniques", Pakistan, alongwith other countries of the region, is participating in this project under a Research Agreement No.2370/CF. During the last four years we have pursued studies on the measurement of certain essential and toxic trace elements in human head hair, cigaratte tobacco, tea leaves, coal, and certain vegetables.

2. EXPERIMENTAL PROCEDURE

Instrumental Neutron activation analysis technique was employed for the analysis of these materials. Optimum conditions for obtaining interference free photopeaks of the desired elements were determined by variation of irradiation and cooling times followed by high resolution gamma-ray spectrometry of the irradiated sample. The elements were usually divided into three groups. The first group containing Na, K and Mn was

irradiated for one minute and radioassayed after two hours cooling time. The second group containing As, Br, Au and Cu was irradiated for one hour and measured after 2-3 days cooling. The third group containing rest of the elements was irradiated for 48 hours and measured after 2-4 weeks. Radiochemical separations were also employed in certain cases.

A 30 Cm^3 Ge(Li) detector and a computerized multichannel analyzer were used for measuring gamma-ray spectra. This system has an energy resolution of 2.1 KeV for 1332.5 KeV gamma-rays of CO-60 and a peak to compton ratio of 40:1.

Appropriate photopeaks of the desired elements were selected and their purity was checked. The accuracy of the procedures was checked by analysing appropriate NBS and IAEA Standard Reference Materials.

3. SUMMARY OF THE RESULTS

3.1 Human Head Hair

The prevailing concentration levels of 12 trace elements were measured in human head hair samples collected from 45 female and 60 male donors living in various areas of Rawalpindi and Islamabad. In order to define base line levels, the arithmetic mean, the geometric mean, the median and the range of concentration of all the elements were computed (Table 1). The population distributions of these elements were plotted as histograms of concentration in linear co-ordinates.

TABLE-1 TRACE ELEMENT CONCENTRATION IN HUMAN HEAD HAIR

ELEMENT	RANGE	A.M. $\pm$ S.D.	G.M. $\times$ G.S.D.	MEDIAN
Cu	2.1 - 24.6	9.6 $\pm$ 4.82	8.6 $\times$ 1.62	8.4
Mn	0.49- 16.15	4.27 $\pm$ 3.60	2.92 $\times$ 2.50	3.13
Zn	128.5 -480.0	255.1 $\pm$76.5	244.9 $\times$ 1.33	245.8
Fe	11.3 -156.4	51.1 $\pm$33.2	41.4 $\times$ 1.94	44.8
Co	0.04- 1.70	0.33 $\pm$ 0.40	0.18 $\times$ 2.96	0.17
Cr	0.19- 6.34	1.42 $\pm$ 1.29	1.01 $\times$ 2.24	0.89
Au	0.01- 3.01	0.31 $\pm$ 0.52	0.13 $\times$ 3.63	0.11
Ag	0.01- 3.93	0.47 $\pm$ 0.68	0.23 $\times$ 3.30	0.18
Sb	0.03- 0.70	0.15 $\pm$ 0.13	0.12 $\times$ 1.94	0.11
As	0.04- 1.41	0.26 $\pm$ 0.28	0.17 $\times$ 2.5	0.14
Se	0.42- 1.91	1.03 $\pm$ 0.29	0.99 $\times$ 1.32	0.97
Hg	0.17- 8.80	1.73 $\pm$ 1.68	1.23 $\times$ 2.27	1.21

A.M. - Arithmetic mean. G.M. - Geometric mean. S.D. - Standard deviation
G.S.D. - Geometric standard deviation. All values are in ppm.

Screening of the data showed that four persons were exposed to higher levels of Se and two to Hg. The higher levels of Se were found to be due to the use of anti-dandruff shampoos. The cause of the elevated levels of Hg could not be explained with the available information. However, the time of maximum exposure of the person to Hg was estimated by measuring the concentration of Hg along the length of the hair strands from the root to the distal end (Fig 1). It was estimated to be approximately 18 months from the date of collection of the sample. The comparison of the data for male and female groups does not show any significant difference except for Mn, Co, Ag and Au. The concentration of these elements are higher in the female group as compared to the male group. It is rather difficult to find a possible explanation for higher concentrations of Mn and Co in the female group. However, the higher concentration of Ag and Au in the female group may possibly be due to the extensive use of Ag and Au jewelry in our society.

The comparison of our data with those of other countries in Table 2 shows that our values of Fe, Mn, Se and Sb are similar to those of India. The values of Zn, Cr, Co and As are higher and that of Au, Ag and Cu are lower than that of India. Our values of Hg are comparable with that of Iraq but lower than those from many other countries. The details of this work were published[1].

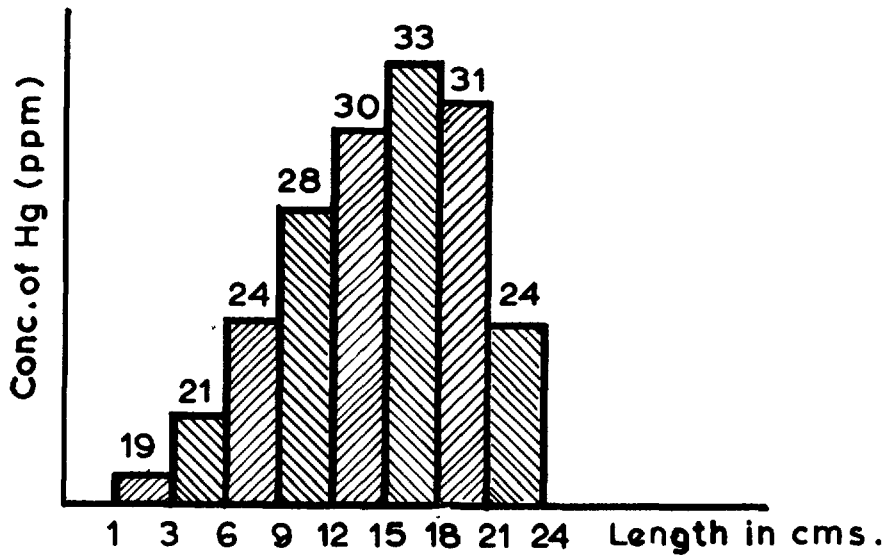

Fig.1 · Conc. of Hg along the length of the hair sample.

TABLE - 2 INTERCOMPARISON OF TRACE ELEMENTS DATA OF HUMAN HEAD HAIR

ELEMENTS	COUNTRIES					
	PAKISTAN	INDIA	IRAQ	JAPAN	U.S.A.	ENGLAND
Cu	8.6 x 1.62	15.3x1.56	N.A.	11.4x1.6	15 x 1.4	20.6 x 1.61
Mn	2.92x 2.50	2.5lx2.66	N.A.	0.49x2.6	0.14x 1.7	1.33x2.6
Zn	244.9 x 1.33	128x1.5	165x1.6	179 x1.30	164 x 1.4	261x1.4
Fe	41.4 x 1.94	50x1.72	106x2.5	N.A.	30 x 1.7	N.A.
Co	0.18x 2.96	0.05x2.16	0.22x2.2	0.041x2.5	0.03x 1.6	N.A.
Cr	1.01x 2.24	0.34x2.34	2.6 x3.0	N.A.	1.5 x 2.7	N.A.
Au	0.13x 3.63	N.A.	0.029x3.4	0.01 x3.7	N.A.	0.047x2.8
Ag	0.23x 3.30	0.39x2.58	0.35x2.5	0.28 x2.1	N.A.	N.A.
Sb	0.12x 1.94	0.09x2.16	1.2 x3.8	N.A.	0.166x 2.1	0.41 x2.59
As	0.17x 2.51	0.07x5.31	0.26x2.0	N.A.	0.13 x 4.6	0.46 x2.28
Se	0.99x 1.32	1.32x2.46	0.92x2.6	0.70 x1.89	1.15 x 4.7	N.A.
Hg	1.23x 2.27	N.A.	0.73x3.0	3.8 x1.59	1.8 x 1.5	3.51 x3.03

3.2 Cigarette

The concentration of 15 elements were measured in cigarette tobacco and cigarette wrapping paper of 11 brands of local and foreign made cigarettes commonly used in Pakistan. It was observed that in relatively cheaper brands the concentration of Sb Co, As and Hg were higher in the wrapping paper as compared to their respective tobaccos, which indicates the need for improving the quality of the wrapping paper. For inter-comparison of the brands, the concentration of each toxic element namely Co, Sb, Se, Br, As and Hg in the tobacco and the wrapping paper are plotted in Fig.2 which indicates the relative toxicity of a brand. These elements are partialy or completely volatilized in the smoke and are inhaled or adsorbed through tongue and mouth. The transference of these elements in the smoke was estimated indirectly by analyzing the cigarette ash. Their adsorption on the cigarette filter was also studied by analyzing the filter before and after smoking the cigarette. The data show that almost all of As, Br, Hg and 80% of Sb and 55% of Se are volatalised into smoke. The cigarette filter does not adsorb these element except 10% of Hg. The details of these studies were published[2].

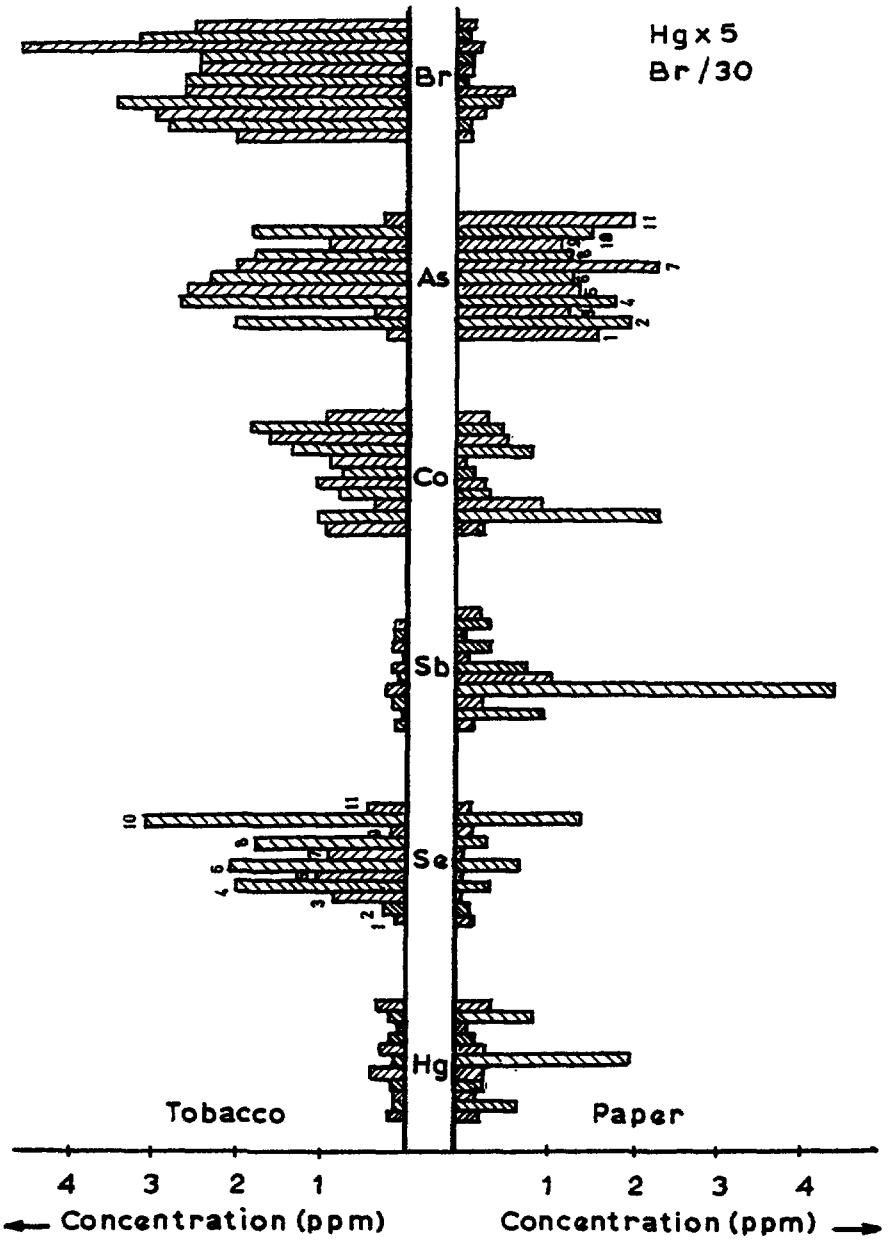

Fig. 2. Distribution of toxic elements in various brands of cigarette (1-11)

3.3 Tea

The concentration of 19 trace elements in tea leaves of three commonly used brands were measured and the data were compared with the reported values of some of these elements in tea from Iran and Japan. The transference of certain toxic and other elements into the drinkable liquid portion was also studied by brewing or boiling 2g of tea leaves in 100 ml of water for 2 min. The transference of As, Hg, Se, Sb and Br into the consumable portion was found to be 80%, 19%, 17%, 35% and 75% respectively in the brewing process and 100%, 34%, 56%, 29% and 93% respectively in the boiling process. These studies indicate that transference of most of the toxic elements studied are greater in boiling process as compared to brewing of tea. The daily intake of these elements through tea was calculated assum-

ing an average daily consumption of 3 cups (300 ml) of tea. The daily intake was estimated to be 1.3ug, 0.04 ug, 24ng, 0.6ug and 27ug of As, Hg, Se, Sb and Br respectivley. The details of this work were published[3].

3.4 Determination of Hg in water

A radiochemical method for the separation and determination of mercury in portable water was developed. A known amount of the sample was irradiated in a silica capsule for 48 hours. The irradiated sample after appropriate cooling was transfered to a beaker containing mercury carrier and the capsule was rinsed with dilute HNO_3. The volume of the solution was reduced by heating on a steam bath and then transferred to a separatory funnel.2 ml of a mixture of PAN and TBA was added to complex mercury which was extracted in 5ml of chloroform. The organic phase containing radioactive mercury was assayed by gamma-ray spectrometry. This procedure was used for the determination of ionic Hg concentration in drinking water samples collected from 5 cities of Pakistan. The concentration of Hg in water samples of Karachi, Lahore, Islamabad, Peshawar and Swat was found to be 2.9 ug/1, 3 ug/1, 1.7 ug/1, 1.2 ug/1 and 1.1 ug/1 respectively. These data indicate an increasing trend of Hg concentration from less industrialized to more industrialized areas. Although the levels of Hg are relatively higher in Karachi and Lahore yet these are below the maximum permissible limit of 5 ug/1 set out by U.S public health services. The detials of this work were published[4].

3.5 Coal

One of the major sources of environmental pollution is the combustion of fossil fuel specially coal as it contains a number of toxic elements which are released to the atmosphere during the burning process. In Pakistan the annual consumption of coal (in 1982-83) is estimated to be 2.4 million metric tons. About 96% of the coal is used in brick kilns and most of these kilns are located in and around the major cities. Therefore it is important to measure the concentration of toxic elements in coal and their transference into the atmosphere. For this study the lignite coal samples were collected from a brick kiln operating near Islamabad.

The concentration of 25 elements were determined in local coal as well as in US-NBS Eastern Coal SRM-1632a. The coal ash was also analysed to indirectly estimate the transference of these elements into the smoke. The ash was produced by gradually burning the coal sample in a clean muffled furnace at 110°C, 300°C, 400°C, 500°C and 750°C for 4,2,1 and 1 hour respectively. The concentration of these elements in coal, coal ash and their transference in smoke is presented in table 3. The data indicates that 70-90% of As, Se, Hg and Br are volatilzied on combustion whereas Lu, Tb, Yb, Rb, Ta and Ba are partially volatilized (25 to 45%). The remaining elements are mostly retained in the ash. The comparison of Pakistani Coal with the Canadian Coal in Table 4 shows similar volatilization behaviour of toxic elements. The ash residue of our coal was found to be about 22% while that of various Canadian Coal ranged from 7 to 33%. This work has been submitted for publication[5].

TABLE - 3 TRACE ELEMENT CONCENTRATION* (ppm) IN LOCAL COAL AND ITS ASH

ELEMENTS	LOCAL COAL	LOCAL COAL ASH	TRANSFERENCE (%)
Br	4.0 ± 0.1	1.4 ± 0.1	92
Hg	0.47 ± 0.07	0.23 ± 0.08	89
Se	1.51 ± 0.15	1.33 ± 0.14	80
As	18.5 ± 3.2	21.9 ± 2.9	73
Sb	1.93 ± 0.06	7.13 ± 0.8	18
Lu	0.36 ± 0.03	0.914 ± 0.061	45
Tb	0.59 ± 0.07	1.74 ± 0.28	35
Yb	1.71 ± 0.41	5.06 ± 0.59	34
Rb	28.6 ± 2.0	89.2 ± 8.9	31
Ta	0.29 ± 0.02	1.00 ± 0.09	25
Ba	532 ± 76	1808 ± 255	25
Co	12.42 ± 0.98	46.3 ± 1.97	17
Cs	1.32 ± 0.08	4.95 ± 0.71	17
Sc	4.60 ± 0.27	17.30 ± 0.98	17
Cr	51.6 ± 1.29	195.6 ± 7.2	16
U	1.99 ± 0.10	7.55 ± 0.60	16
Eu	0.46 ± 0.05	1.76 ± 0.16	16
Mn	438 ± 12	1695 ± 72	14
Fe(%)	4.38 ± 0.19	17.10 ± 0.89	14
Na(%)	0.190 ± 0.009	0.745 ± 0.091	13
In(ppb)	127 ± 3	504 ± 20	12
Th	3.60 ± 0.18	14.61 ± 0.88	10
La	9.69 ± 0.87	40.85 ± 4.85	7
K(%)	0.36 ± 0.03	1.60 ± 0.17	2
Zn	13.6 ± 0.74	60.7 ± 0.42	1
Si(%)	4.95 ± 0.24	22.1 ± 1.10	1

*Average of at least 8 independent determinations.

TABLE - 4 VOLATILITY OF VARIOUS ELEMENTS ON STATIC COAL ASHING.

VOLATILITY	CANDIAN COAL (JERVIS 6)	PAKISTANI COAL
Mostly Volatilized (75-100%)	Cl,Br,I,Se,Hg.	Br,Hg,Se.
Partially Volatilized (25-75%)	Na,K,Sb,Sc,Sr.	As,Sb,Lu,Tb,Yb, Rb,Ta.
Mostly retained in ash (10-25% volatilized)	Ba,Sn,Hf,Eu,U.	Ba,Co,Cs,Sc,Cr,U, Eu,Mn,Fe,Na,In,Th.
Retained in ash (10% volatilzied)	Al,Ca,Ce,Co,Cr,Cs,Dy, Fe,Mg,Mn,Ta,Ti,Th,V,Zr.	La,K,Zn,Si.

4. FUTURE PLAN OF WORK

Studies are being pursued on the measurement of certain toxic trace elements in few brands of coffee and the intake of these elements through drinking of coffee. It is planned to carry out studies on the determination of trace elements in egg yolk and egg white, chicken meat and in certain vegetables used in Islamabad. Some studies have already been initiated and preliminary results of a few vegetables are listed in Table 5.

TABLE - 5 CONCENTRATION OF TOXIC & OTHER ELEMENTS IN VEGETABLES (ppm)

ELEMENTS	POTATO	SPINACH	PEAS	TOMATO	TINDA	GARLIC	GINGER	ONION
Na(%)	0.057	3.74	0.006	0.037	0.018	0.082	0.016	0.098
K(%)	1.75	4.06	0.46	3.68	0.74	1.73	3.30	1.43
Cu	11.1	48.9	3.5	12.3	9.2	9.1	42.7	48.9
Mn	10.2	213	9.8	9.6	20.4	19.7	9.6	10.1
Fe	51	651	75	121	178	276	162	419
Zn	29	41	21	31	56	41	77	22
Co	0.06	0.15	0.05	0.11	0.08	0.18	0.07	0.22
Cr	1.4	6.6	-	-	2.8	5.2	0.8	19.1
Br	0.13	-	0.13	0.19	0.21	0.45	0.31	0.17
Hg(ppb)	26	89	-	-	42	35	12	42
Se	0.04	0.12	-	-	0.06	0.71	-	0.04
Sb	0.03	0.11	-	-	0.13	-	0.11	0.14

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SCALP HAIR AS AN INDICATOR OF ENVIRONMENTAL POLLUTION IN MALAYSIA

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Abstract

The concentration of trace elements such as As, Br, Co, Cr, Fe, Hg, Sb, Se and Zn in the hair of the two population groups living in different regions of Malaysia were analysed by Instrumental Neutron Activation Analysis. The results for all elements analysed, except mercury, do not differ significantly from reported values for other region of the world. Mercury from the urban sample is about twice the concentration of the rural sample.

1. INTRODUCTION

In recent years, the determination of trace element levels in human scalp hair has become popular for monitoring environmental exposures,evaluating heavy metal poisoning, assessing nutritional status, and diagnosing diseases [1-10]. Hair of normal, healthy individuals generally contain each trace element within a well-defined range of concentration. Marked deviations from the values indicate physiological or environmental disorder. Unlike other tissues, hair is a metabolic end product that incorporates trace elements into its structure during its growth.

During the growth phase of a hair, matrix cells of the hair follicle show intense metabolic activity and produce hair at a rate of approximately 0.4 mm per day. Developing hair is exposed to the metabolic environment for a relatively short period of time. As a growing hair approaches the skin surface, its outer layers become hardened and relatively impermeable, thereby sealing in metabolic products accumulated during its formation. The trace element composition of the hair reflects the composition of the medium from which it was formed. In this way, hair provides a historical record of trace elements assimilated from the environment.

There is still a lack of information on the variability of trace element concentrations in hair as a function of various local factors in population groups not exposed to abnormal environmental pollution. A knowledge of the natural levels of trace elements in hair and other tissues is very important for assesing the degree of human contamination in areas where these elements are expected to show anomalous concentrations.

With these considerations in mind a study on selected population groups within Malaysia was started to assess the variability of the concentrations of trace elements in the hair of a normal population as a function of geographical and

economic factors. Trace elements such as As, Br, Co, Cr, Fe, Hg, Sb, Se and Zn were analysed in the hair samples of two population groups living in different regions of Malaysia. All analyses were carried out using instrumental neutron activation analysis.

2. MATERIALS AND METHODS

2.1. Sample Collection

Hair sampels were obtained from donors residing in Kuala Lumpur, Petaling Jaya and Sepang districts. Kuala Lumpur, the capital city of Malaysia has a population of more than one million whilst Petaling Jaya has a population of approximately 100,000. Both cities are situated in the Kelang Valley, the largest industrial, business and commercial centre in Malaysia. Sepang is an agricultural area on the west coast of Selangor.

A total of 35 hair samples were collected. Each sample approximately 1000 mg was clipped from 10 places from the head scalp with a pair of stainless steel scissors. Each sample is given a code number and particulars of the donor such as place of residence, ethnic group, age and sex were recorded.

2.2. Sample Preparation

About 400 mg aliquot of each hair sample was cut to a length of 2mm to 5mm and washed in a conical flask with distilled water (50 ml), acetone (50 ml) followed by distilled water (2 x 50 ml) and acetone (2 x 50 ml). The samples were later dried in an oven at 30°C for 20 hours.

About 100 mg of hair sample together with standard reference materials and blanks were irradiated in the PUSPATI TRIGA MARK II reactor for 8 hours at a flux of 2.5×10^{12} n cm^{-2} s^{-1}.

2.3 Measurement of Activities

The gamma-ray acitivities of the samples were measured by a high resolution spectrometer consisting of ORTEC Hyperpure Germanium detector with a sensitive volume of 78 cm^3, FHHM 1.80 keV at 1322.4 keV. The multi-channel analyser used was CANBERRA model series 85 with 4096 channels. The activation spectrum of each sample was plotted by HP-7470A graphic plotter, Gamma-ray peak intensities were printed out by TELETYPE 43 line printer.

3. RESULTS AND DISCUSSION

Results of the analyses are presented in Table 1 and Table 2. To ascertain the analytical procedure used, standard reference materials such as SOIL-5, SL-1, NBS/SRM-1633 were analysed and the precision for all elements of interest are in the region of 87 - 95%.

The arithmetic mean values for the concentration of all the elements studied, except Hg, do not differ significantly from reported values for other regions of the world [10]. The Hg level is quite high compared to 1.4 ± 2.1 in Iraq [11] or 4.2 ± 1.95 in Japan [12]. The mercury contamination source is not yet established.

TABLE 1: Trace Element Hair Concentration in 35 Samples Collected from Selangor

Element	Mean	Median
As	0.64 ± 0.54	0.52
Br	8.9 ± 6.6	6.22
Co	0.08 ± 0.04	0.07
Cr	1.34 ± 0.94	0.95
Fe	65 ± 31	57
Hg	7.43 ± 4.45	7.25
Sb	0.31 ± 0.21	0.21
Se	0.57 ± 0.16	0.54
Zn	189 ± 88	166

TABLE 2: Trace Element Contents of the Two Population Groups

Element	RURAL		URBAN	
	Mean	Median	Mean	Median
As	0.27 ± 0.23	0.15	0.83 ± 0.56	0.70
Br	8.3 ± 5.6	6.03	9.1 ± 7.0	6.22
Co	0.13 ± 0.04	0.12	0.06 ± 0.02	0.07
Cr	0.78 ± 0.30	0.74	1.63 ± 1.03	1.36
Fe	84 ± 31	84	52 ± 23	47
Hg	4.34 ± 2.34	4.24	8.98 ± 4.51	8.36
Sb	0.37 ± 0.19	0.34	0.27 ± 0.21	0.19
Se	0.5 ± 0.12	0.55	0.58 ± 0.18	0.53
Zn	192 ± 105	168	187 ± 83	166

4. CONCLUSION

It was found that samples from rural areas contain a higher concentration of Co and Fe, whereas samples from urban areas contain a higher concentration of As, Cr and Hg. The concentrations for other elements analysed are more or less the same. As (0.70 ppm) in the urban sample is about 5 times the value of those found in other countries. Hg from the urban sample is about twice the concentration of the rural sample. The Hg concentration from the two samples is higher compared to those reported by other countries.

During the contract period competence in analytical technique based on INAA has been developed. Trace element analysis in hair can be carried out on a routine basis and we are quite confident of the results. The INAA technique can be applied to other kinds of environmental samples and it is complementary to Atomic Absorption Spectrometry currently used widely by analytical laboratories in the country. We are now planning to use the neutron activation analysis technique for analysis of trace elements in foodstuffs such as rice, fish, meat and vegetables, as past of the Food Contamination Analysis Programme organised by the Health Authority of Malaysia. This particular programme will be supported by our institute, PUSPATI and hopefully financial grant will be obtained from the IAEA.

The contract on the research coordinated project will come to an end on 31st March 1984. However, this project will be extended in our institute and future work will include study of the variability of trace elements in hair samples from Malay, Chinese and Indian communities.

ACKNOWLEDGEMENT

This project was supported by IAEA under contract No. 2713/R1/RB and Universiti Kebangsaan Malaysia. The services provided by Tun Ismail Atomic Research Centre (PUSPATI) is greatly appreciated.

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SAMPLE PREPARATION TECHNIQUES FOR (p, X) SPECTROMETRY

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Abstract

Samples are ashed at low temperature, using oxygen plasma; a rotary evaporator, and freeze drying speeded up the ashing. The new design of apparatus manufactured was only 10 watt but was as efficient as a 200 watt commercial machine; a circuit diagram is included. Samples of hair and biopsy samples of skin were analysed by the technique.

A wool standard was prepared for interlaboratory comparison exercises. It was based on New Zealand merino sheep wool and was 2.9 kg in weight. A washing protocol was developed, which preserves most of the trace element content. The wool was ground in liquid nitrogen using a plastic pestle and beaker, driven by a rotary drill press.

1. INTRODUCTION

Although (p,X) analysis using thick targets, is quite possible, analysis using thin targets avoids the problems of calculating cross sections for proton absorption, and absorption of the resultant x-rays before they reach the detector. It may be possible also to prepare the target so that most of the matrix is removed, and concentrate elements of interest.

2. METHODS OF REDUCING ORGANIC CONTENT & SOLUBILISING

2.1 Solution by alkali

This is not useful since the sample weight increases (1).

2.2 Dry oxidation

This type of ashing is usually done at temperatures of 500-600°C and often leads to the volatilisation and loss of elements such as halogens, lead, cadmium, and mercury, (2).

2.3 Wet oxidation

For the (p,X) technique a major difficulty is that few thin backings will maintain their integrity with the strong acids used. Even Kapton, a tough polyimide cannot withstand either perchloric or sulphuric acids.

Attempts to use nitric acid/hydrogen peroxide to wet-ash hair added many trace elements to the sample from the glass by leaching, and in addition the weight of the ashed hair was equivalent to about 25% of the fresh weight. This was shown to be due to oxidation of the sulphur in the hair, to sulphate, rather than being lost as sulphur dioxide. This meant that little was gained by the oxidation for the purposes of (p,X) spectrometry which is improved in sensitivity most when the ash percentage is least.

2.4 Plasma ashing

In this method, oxygen is ionised by a radiofrequency source, and passed at low pressure over the sample to be ashed. Even at low temperatures (generally less than 100°C) the sample is oxidised, but a method to trap volatiles must still be included (3,4).

A commercial LFE-301 asher loaned us by the D.S.I.R. Soil Bureau was 200 watt. Ashing to constant weight usually took 24-36 hours for most samples. Following that, the samples were dissolved in concentrated cold nitric acid. Reproducibility was as bad as ±100% for the subsequent analysis for samples dried on Kapton. This was due to microscopic insoluble residues.

Mr J. Patterson of Chemistry Division constructed an improved plasma asher. This asher puts the sample in a tube right inside the radio-frequency coils, so that the oxygen ions are created almost in the sample itself. In the top of the tube is a cold finger, cooled by water, on which some products of the ashing collect. After ashing, some concentrated nitric acid is added and the ash and acid refluxed for one minute.

For replicate hair specimens the reproducibility was equal to the best recorded in the literature (±10%). Interestingly the ash percentage was much higher - 3% compared with 0.5% for the LFE asher. Reproducibility with the new asher was better for other samples also.

The equipment was reconfigured so that the ashing chamber was a glass test tube with ground glass joint to fit on a Buchi rotary evaporator. The angle was kept very shallow, so that the sample tumbled readily. Some tubes were also made with internal ridges to aid in mixing the samples. LFE asher, rotary evaporator and manual vibrator gave half value times for weight decrease of IAEA animal blood of 27,7 and 1.8 hours. Manual vibration was best.

The ashing of Bowen's Kale was partially improved by freeze-drying it which perhaps burst open cells and exposed more surfaces for oxidation.

An asher along the lines of Mr Patterson's was made with improved circuitry. A circuit diagram is attached (see appendix). This was designed and made by Mr P.Pohl of this institute.

It is obvious that the plasma ashing system needs a lot more investigation. At the moment the speed of ashing is very sample dependent, and some samples yield high ash percentages, and take much time to ash, and give analyses very erratic in their reproducibility.

The original work of Gleit and Holland (5) gave ash was in all cases soluble in acid without residue, but they do not report on reproducibility of ashing.

2.5 Oxygen flask ashing

This good method burns the sample in an enclosed quartz flash with oxygen, and a cold finger to trap volatiles, (6).

3. ANALYSIS OF SAMPLES

3.1 Intercomparison samples

To the ash 0.25 ml of Aristar nitric acid was added and a small coverglass with water placed over the top. The vial was gently heated until the nitric acid just boiled and reflux was continued for about one minute. Each vial solution was analysed in duplicate. 5-microlitre was taken and dried on Kapton and irradiated with 2.5 MeV protons from a Van de Graaff accelerator. Uniformity of beam was ensured by using a proton microprobe and scanning the spot over the sample. Scanning of the beam was such that the dried sample spot was eventually completely covered by the microprobe beam to avoid problems due to inhomogeneity in the dried sample spot. X-ray spectra were taken with a Si(Li) detector.

One plant material ash contained significant calcuium sulphate and required dilution to dissolve it.

Another type of sample would not completely dissolve in the nitric acid until some HCl was also added. Microprobe analysis showed this to have been due to formation of ferric phosphate which is not soluble in nitric acid alone.

For many of the samples the $\pm$10% reproducibility criteria arbitrarily set was not met for many of the analyses meaning that further work on sample prepartion is required.

3.2 Biopsy samples of skin

These were taken from edges of wounds resulting from surgery. The collaborator in this programme was Dr Andre van Rij of Otago Medical School Dunedin, and it was an attempt to examine whether the zinc levels in healing tissues varied and whether other trace elements also varied.

Sample weights varied from 1 mg to 300 mg with a mean of 75 mg and standard deviation of 86 mg.

The results showed great variations in trace elements content between samples meaning other studies are needed, with many samples from the same piece of tissue to establish natural variations with location. The method is well suited to analysis of these very small tissue fragments.

3.3 Comparison of (p,X) analysis of thin & thick targets

The main advantage of using thin targets for analysis is the lack of corrections required. However it is obvious that the method has ironically, limitations which are still matrix dependent! It is much harder to prepare a concentrated homogeneous solution than one would imagine, and this may explain some of the rather erratic results obtained via the atomic absorption spectroscopy technique in the experience of the Agency when interlaboratory comparison exercises are organised.

The thick target analysis technique, suffers from problems of corrections, inhomogeneity, and changing geometry. The first is already mentioned - some of the parameters used have several percent error on them, which limits accuracy.

The second is a property of the sample, and may be quite severe for biological samples. The actual weight of sample analysed cannot be more than about 1 mg at the usual energies of a small Van de Graaff accelerator. This limitation is quite severe. One is asking that the homogeneity of an environmental solid sample be guaranteed to better than ±10% on a scale of 1 mg. This is probably impossible without sample pretreatment and very difficult even with it.

The third problem may arise if the analysis is done in a vacuum. Volatilisation of elements is quite possible and will change the geometry of analysis and introduce further imprecision. This can be avoided if the analysis is performed in air, using an external proton beam.

All in all, for bulk analysis, (p,X) spectrometry is not optimum as a technique, but still has a strong potential for spatial analysis on a small scale, and for microanalysis.

4. PREPARATION OF WOOL STANDARD

I have attempted to prepare a trace element standard based on New Zealand sheep wool.

I used merino wool, which is fine in texture. A merino fleece still attached to the hide was obtained by courtesy of the Ministry of Agriculture and Fisheries from their research station at Tara Hills near Omarama in the South Island.

4.1 Cleaning

In this case the wool was cut off the hide with a serrated glass knife and before cleaning weighed 4.8 kg.

I attempted merely to degrease wool to a standard similar to that of the commercial scourers. That is remove 20% of the starting weight, of which 16% is grease and 5% suint. It was not possible to follow the standard I.A.E.A. protocol for hair (Ryabukhin (7)) since the grease is not very soluble in the solvents suggested.

The wool was lightly pummelled for 15 seconds with minimum volume of Stoddart's solvent in borosilicate beakers using a large polyethylene piston, shown to be free of significant trace elements by (X,X') spectrometry and then for a similar time with distilled water (for each of two rinses). This gave a dry yield of about 70% of the initial weight.

4.2 Carding

Commercial wool, is already cleaned and carded. However analysis showed a large proportion of the trace elements was removed and in addition although the homogeneity was excellent for copper and zinc, it was ±38% for iron. It seems that such wool is dangerous to use for a standard for trace elements. Carding of the merino fleece was still needed.

X-ray fluorescence analysis of a number of polypropylene combs of clear or tortoiseshell appearance showed that some were very low in trace elements and very suitable for carding wool.

4.3 Pulverisation

The traditional way of doing this is percussion under liquid nitrogen. A number of systems were tried; Waring Blendor, ultrasonication, manual grinding, electromagnetic vibration using a loudspeaker coil, pneumatic vibration, and mechanical vibration, but all gave very low yields.

By far the best solution proved to be a semi-manual one. A low-trace-element polyethylene pestle was used in a rotary drill press as a source of rotary power, and the wool sample was frozen in a Nalgene (polymethylpentene) beaker (also very low in trace elements). The beaker was well insulated with polystyrene foam in a rigid enclosure, and manually moved against the ridged pestle to grind the wool, 75 g an hour of a ground wool could be routinely produced.

It appears that a better solution than any of the above may exist (pers. comm. R. Parr, IEAE). A teflon analogue of the commercial equipment for grinding rocks between cylindrical steel concentric rings which is rotated eccentrically has been made by the NBS in the USA. Its output is apparently an order of magnitude greater than the best mentioned above.

4.4 Homogeneity testing

Homogeneity testing via (X,X') spectrometry, and neutron activation analysis showed reproducibility at the 150 mg level for Fe was $\pm$8.6% and for Zn was $\pm$2.4%. For Cobalt and silver the figure was $\pm$10%.

4.5 Adequacy of sheep wool as a trace element standard

The three kilo sample, may be adequate for use as such a standard, as shown by the analyses so far. However future changes would be necessary, since microscopic examination showed the presence of residual dirt. The only solution, more rigorous cleaning, will also remove trace elements.

What are the relative advantages and disadvantages of sheep wool and hair for trace elements?

I think the wool, being a commercial product is probably available much easier in very large quantities. However the well known heterogeneity of human head hair is probably also found for sheep wool. In addition the initial dirtiness of sheep wool can only be described as high, It is thoroughly cleaned commercially, but sheep are in a much less controlled environment than humans and it is possible that heterogeneity will be greater. More research is needed to settle this point. It has already been shown that a standard of sufficient homogeneity can be produced from hair (standard HH-1) but that is not yet clear for wool. This means that there is slightly more risk involved in attempts to work with wool.

Either type of standard sample is a good one for analysis because both have potentially a low ash weight, and this is useful for those analysts who are using destructive techniques.

A final advantage of either type of material which has not been exploited yet, is that both materials are weak ion exchangers. It is therefore possible to adsorb trace elements onto them from solution. If there is some specific element which is difficult to analyse a semi-artificial standard could be made up, rather like the ion-exchange beads already used by the agency.

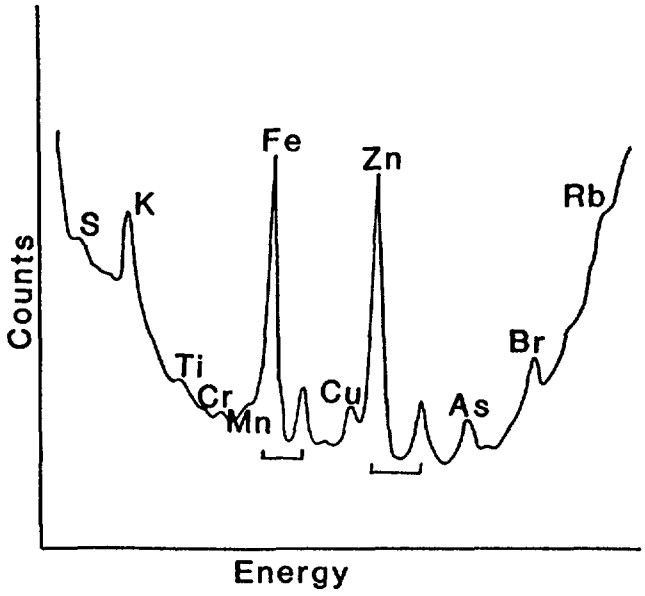

FIGURE 1 - (XX') SPECTRUM OF WOOL.
Mo ANODE USED.

5. RECOMMENDATIONS

5.1 Low temperature ashing be used for sample preparation in (p,X) spectrometry, but more research be devoted to best means of doing this for vegetable tissues.

5.2 Sheep wool be further investigated for preparation of a trace element standard, with special attention to heterogeneity problems.

5.3 Consideration be given to the preparation of a trace element standard based either on wool or hair, but containing trace elements adsorbed from solution.

5.4 Further research be done on using (p,X) spectrometry for analysis of very small samples, such as biopsy tissues.

6. ACKNOWLEDGEMENTS

I have been helped substantially by many members of the Electronics section of this institute, by Mr Ken Marment, and Mr Matthew Connor besides those mentioned in the text.

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APPENDIX - P. Pohl

27 MHz Power Source -

The circuit presented produces some 10 watts of 27 MHz power into a 50 Ω load.

TR1 operates as an oscillator whose frequency is determined by a 3rd overtone 27 MHz crystal.

TR2 amplifies the 27 MHz to a power level of about 1 watt.

TR3 further amplifies this to the required level of about 10 watts.

Load impedance mismatch is sensed and displayed on "Forward Power' and 'Reflected Power' meters. Excessive load mismatches (resulting in high reflected power readings) are used to decrease the gain of TR3 by changing its bias condition - Note (1): this is to prevent destruction of TR3 by accidental shorting/disconnection of the load.

Components -

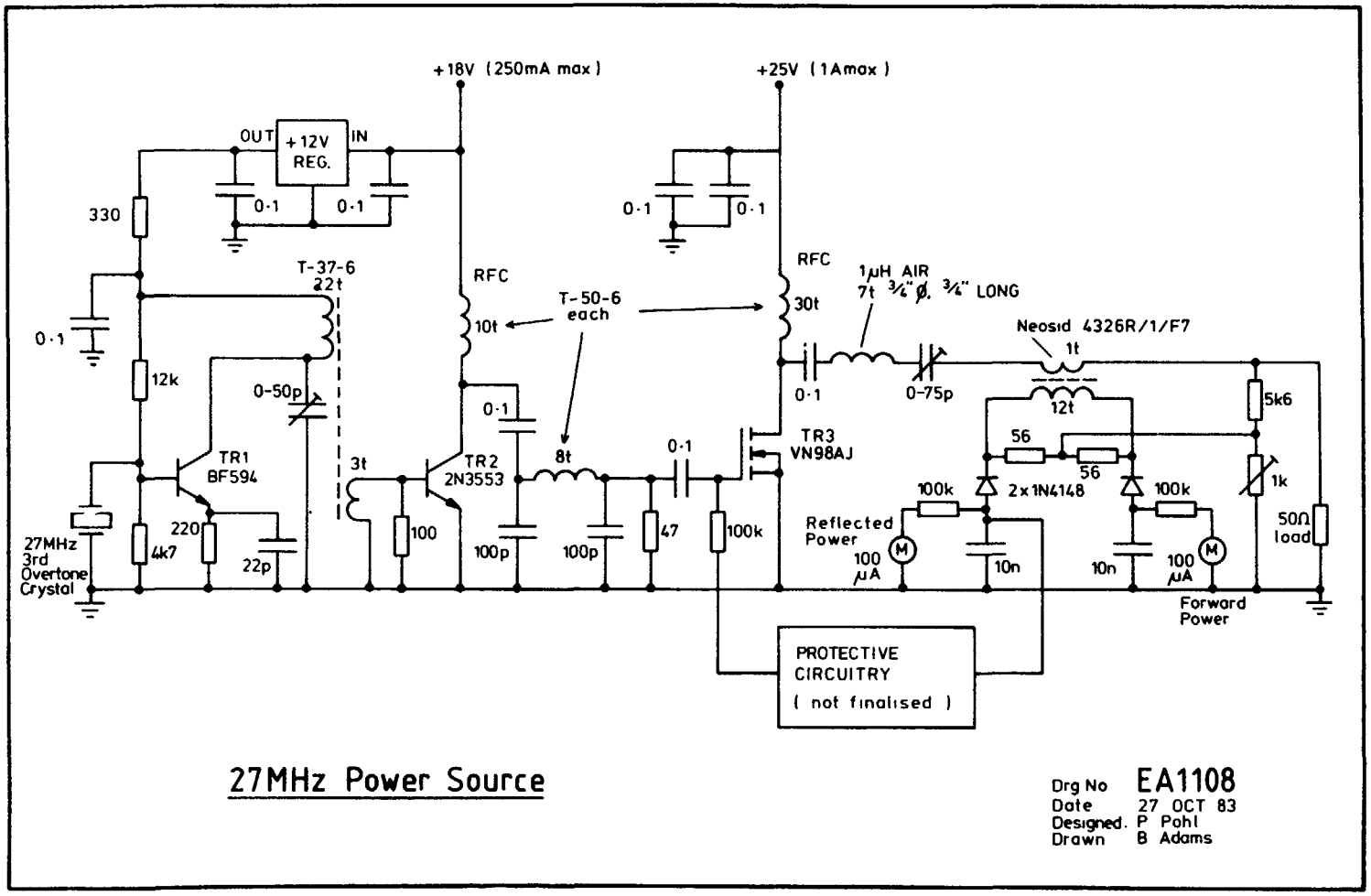
Conventional except for:

TR3 : Power MOSFET : Siliconix VN98AJ or similar.

Coils :Amidon Associates.

Crystal:
27 MHz 3rd overtone : exact frequency depending on local authorized frequency.

Note (1): Siliconix application note AN80-6.


+18V (250mA max)
+25V (1Amax)
OUT
+12V REG.
IN
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0·1
0·1
0·1
330
T-37-6
22t
RFC
10t
T-50-6 each
RFC
30t
1μH AIR
7t ¾" ø, ¾" LONG
Neosid 4326R/1/F7
1t
12t
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0-75p
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12k
0-50p
TR1
BF594
3t
TR2
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8t
0·1
TR3
VN98AJ
56
56
100k
2x1N4148
100k
1k
0·1
27MHz
3rd
Overtone
Crystal
4k7
220
22p
100
100p
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CIRCUITRY
(not finalised)
27MHz Power Source
Drg No EA1108
Date 27 OCT 83
Designed. P Pohl
Drawn B Adams

A STUDY OF TRACE ELEMENT CONCENTRATIONS IN HUMAN HAIR OF THE INHABITANTS OF THE JAKARTA CITY

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Abstract

A STUDY OF TRACE ELEMENT CONCENTRATIONS IN HUMAN HAIR OF THE INHABITANTS OF THE JAKARTA CITY. By applying instrumental neutron activation analysis, a study was carried out to investigate the concentration of the elements : Au, Br, Co, Cr, Fe, Hg, Sb, Se and Zn in human hair samples of the inhabitants of the Jakarta City. A total of 263 samples, consisting of 177 males and 86 females of the age between 10 and 60 years, have been collected from the donors in various residential district. The concentration ranges, the median, the average concentration and the frequency distribution of each element found in the samples are reported in discussed. The results showed that except for Co, Se and Zn, the concentration of the other elements were comparable to the reported values from other regions of the world. Co and Se were found to be higher and Zn was lower. The study of Hg in hair samples of the dentist and in hair of the population suspected to be contaminated with Hg from industrial effluents were also done. The results showed that Hg in hair of dentist was 4-5 times higher than in the population suspected to be contaminated with Hg. The arithmetic mean for Hg in this population was 4.68 ± 4.66 for males and 5.03 ± 4.51 for females.

1. INTRODUCTION

In the last ten years there has been an increasing growth of industrial activity and more extensive use of chemicals in the jakarta area. These activities indicate an ever increasing quatities of toxic element released into the environment. In the long term period the quantity of these elements can reach a concentration level that can create a problem to the population.

To be able to judge whether the population has been exposed to the abnormal quantities of environmental pollutants it is essential to establish the normal concentration of trace elements in the population. Hair,as a minor organ by which many metals are excreated, can be used as an indicator of toxic elements in the body. In 1976, the IAEA Advisory Group suggested that one of the first step in approaching the problem of man's contamination to the environmental pollutants is by analysing the content of trace elements in hair samples, collected in a statistical random fashion througout the population of each country (1). Many authors have determined the trace element content in hair samples from different region world to find out the normal level of the element in the population studied or the extend of his contamination in areas where the population is exposed to contaminated food, water, or occupational and other causes of exposure. The compilation of the concentration of the elements reported by the authors from different regions of the world has been prepared by the IAEA (2) and U.S. EPA (3).

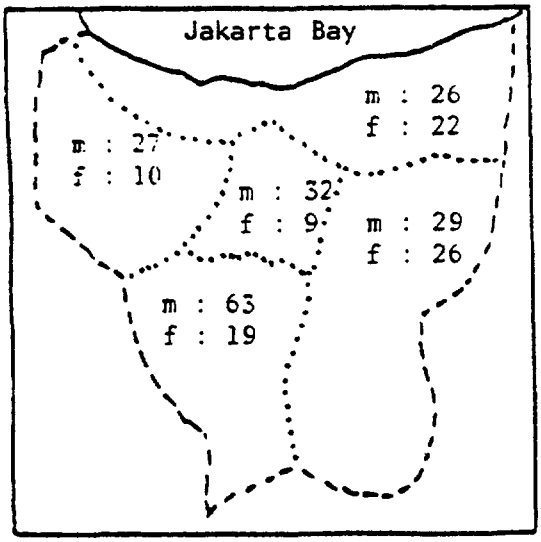
In participating the IAEA programme on Health Related Environmental Research Using Nuclear Techniques, a study was carried out to find the concentration of several trace elements in hair samples of the inhabitants of the jakarta city, using instrumental neutron activation analysis. The purpo-

se of this study was to find the present level of the elements : Au, Br, Co, Cr, Fe, Hg, Sb, Se and Zn in the population of the jakarta city. Instrumental neutron activation analysis was also used to determine the concentration of Hg in hair of the dentist and in hair samples of the population living in northern part of the jakarta, along the region of jakarta bay. The jakarta bay is polluted with industrial effluents and most of the population living in this area are local fishermen and they are suspected to be exposed with Hg through consumption of fish and seafood contaminated with Hg. The purpose of this work was to find the extent of Hg contamination in the two exposure groups.

2. EXPERIMENTAL

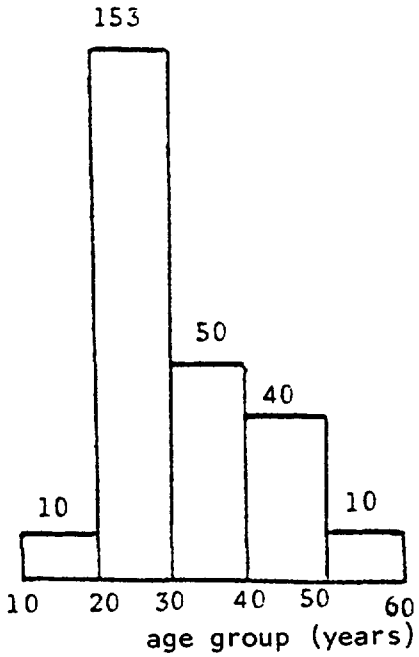
2.1 Samples

Sampling of hair from the population of the jakarta city was carried out within 3 months in September - November 1980. During this sampling period, a total of 263 samples, consisting of 177 males and 86 females of the age between 10 and 60 years, were collected from donors in various residential district of jakarta. The number of donors obtained from various residential district and the age distribution of the samples are given in Figure 1 and 2.



Number of male and female donors obtained in each administrative regions of jakarta

FIGURE 1.



The age groups distribution of the samples

FIGURE 2.

Samples of hair from the population living in the contaminated area of jakarta bay was done by Centre for Ecological Study, National Institute for Health Research and Development from the total about 200 samples collected, 78 of them consisting of 26 males and 52 females were selected so as to represent the population in the viewpoints of the resident time and the quantity of seafood consumed.

The hair samples of the dentist were collected during sampling period in October 1982. During this sampling period, a total of 62 samples, consisting 34 males and 28 females of different age, were collected from the den-

tist working in dental hospital of jakarta. Each hair sample obtained was then selected and only the first 10 cm from the scalp was taken for analysis. The hair samples were then washed with 25 ml of ether, acetone, water, water and ether respectively. After washing the samples were dried in a glove box.

Sampling and washing procedures recommended by the IAEA (2) were followed.

2.2 Neutron Activation Analysis.

About 100 - 200 mg of each sample was weighted and put into a polyethylene capsule. The capsule was then heat sealed. The standard of the elements were prepared by placing a drop of standard solution of the element on a whatman No. 42 filter paper. The blank was the same filter paper as used for the standard. In several cases, the NBS reference standard material No. 1571, ordward leaves was also used to check the precision of the analytical procedures. The intercomparison study for trace elements analysis of human hair samples organized by the IAEA was also followed during this study.

Irradiation of the samples was carried out in Triga Mark-II Reactor in Bandung at a neutron flux of about 10^{12}n. cm^{-2}. sec^{-1}. In each irradiation 30 capsules, consisting of samples, standard and blank were irradiated together for about 40 hours. After a cooling period of 5-7 days, they were counted for 3600 s in a 51 cc Ge(Li) detector. The detector was coupled to a programmable - 4096 channels analyser IN-90, INTERTECHNIQUE. The system was adjusted at 1 KeV per channel and the system resolution was 2 KeV for the 1332 KeV Co-60. The gamma spectrum of the samples , standards and blank were stored in a magnetic disk and then analyse by MULTI-4 microcomputer. The computer was programmed to identify the peaks in the spectrum, checks its shape, calculate the net peak area and then compared it to the net peak area of the standard at a corrected time. In analysis of Hg the photopeak of Hg-203 at 279 KeV was used after correction for the contribution from Se-75. The gamma lines and the relevant nuclear reaction used in the analysis are given in Table 1.

TABLE 1. ELEMENT DETERMINER, THE RELEVANT NUCLEAR REACTION AND GAMMA LINES USED.

Element	Nuclear Reaction	Energy of-γ lines (KeV)
Au	$^{197}Au(n,\gamma)^{198}Au$	412
Br	$^{81}Br(n,\gamma)^{82}Br$	554
Co	$^{59}Co(n,\gamma)^{60}Co$	1172
Cr	$^{50}Cr(n,\gamma)^{51}Cr$	320
Fe	$^{58}Fe(n,\gamma)^{59}Fe$	1098
Hg	$^{202}Hg(n,\gamma)^{203}Hg$	279
Sb	$^{121}Sb(n,\gamma)^{122}Sb$	564
Se	$^{74}Se(n,\gamma)^{75}Se$	264
Zn	$^{64}Zn(n,\ )^{65}Zn$	1115

TABLE 2. THE RANGE, MEDIAN AND AVERAGE CONCENTRATION OF THE ELEMENTS (PPM) IN HAIR OF THE JAKARTA METROPOLITAN

Element		No. of detected samples	Range	Arithmetic mean ± s.d		Geometric mean × s.d		Median *	Median **
Au	M	107	0.01 - 4.28	0.81	142	0.43 - 2.63		1.05	0.01
	F	71	0.16 - 4.54	1.04	1.92	1.34	1.87	1.18	0.07
Br	M	160	0.49 -28.90	8.60	7.38	5.80	2.48	8.05	5.05
	F	72	2.10 -18.60	6.65	4.95	5.31	3.42	6.13	4.41
Co	M	109	0.01 -12.60	3.87	4.72	2.11	2.13	1.97	0.68
	F	75	0.09 -14.10	5.20	5.36	1.89	2.54	2.09	1.70
Cr	M	148	0.07 -26.12	5.92	7.19	2.20	2.62	1.62	0.90
	F	64	0.33 -18.60	5.83	5.88	3.14	2.72	3.77	2.70
Fe	M	174	5.20 -65.00	27.0	17.9	21.96	1.25	19.20	18.60
	F	77	9.60 -99.30	38.8	13.3	23.33	1.34	33.40	29.30
Hg	M	173	0.07-106.20	6.94	5.59	3.24	3.12	4.90	4.30
	F	75	0.17- 35.15	7.45	5.36	4.34	3.25	5.86	5.40
Sb	M	96	0.02- 18.32	3.26	4.89	1.83	2.05	0.86	0.30
	F	33	1.02- 14.60	5.27	4.77	4.63	2.74	3.79	-
Se	M	108	0.10- 61.35	6.80	15.90	4.54	3.59	7.60	6.78
	F	75	2.49- 27.61	9.70	8.60	7.79	3.12	6.98	5.08
Zn	M	177	10.3 -388.8	130.0	68.7	103.4	1.50	104.3	98.4
	F	86	18.9 -182.4	90.4	50.6	54.7	1.36	70.4	60.2

* median of the detected samples
** median of the analysed samples.

3. RESULTS AND DISCUSSION

The concentration range, the median and the average concentration of each element analysed in male and female samples of the population of the jakarta city are shown in Table 2 and their frequency distribution are given in Figure 3 and 4. The concentration of Hg in hair samples of the dentist and in hair samples of the population suspected to be contamined with Hg from industrial effluents are shown in Table 3.

The concentration range, the arithmetic and geometric means of each element showed in Table 2 and 3 were calculated from the sample which has the concentration equal or larger than the detection limit of each element. The median was obtained in two-ways, one from the number of the samples which showed a detacteble content of the element equal or larger than the detection and the other was from the number of the samples analysed. The median, the arithmetic and geometric means obtained from the first method tend to overestimate the true values, however the median obtained by the second method may give a better values, because they are not influenced by the number of determined values and detection limits.

TABLE 3. COMPARISON OF MERCURY CONCENTRATION IN HAIR SAMPLES OF THE DENTIST AND PEOPLE LIVING IN THE SUSPECTED CONTAMINATION AREA

	Dentist occupational exposed		Population living in a suspected contamination area	
	male	female	male	female
No. of samples	34	28	26	52
Range	1.67-156.71	2.16-126.14	1.25-24.70	1.20-24.70
Arithmetic mean $\pm$ s.d	29.04$\pm$ 30.61	26.19$\pm$ 31.24	4.68$\pm$ 4.66	5.03$\pm$ 4.51
Geometric mean $\overset{\times}{:}$	18.60 $\overset{\times}{:}$ 3.24	14.83 $\overset{\times}{:}$ 2.48	3.71$\overset{\times}{:}$ 1.83	4.15 $\overset{\times}{:}$1.37
Median	17.92	14.92	3.38	3.45

As it is shown in Table 2, the concentration of the elements Cr, Co, Hg, Sb and Se had a relatively large standard deviation compare to the other elements studied and their frequency distribution tend to be normal form in function of the logarithmic concentration. The median and the geometric mean of those element were about the same value but the arithmetic mean has higher. For the other elements, the median, the arithmetic and geometric means were about the same values. Those two types of the element may correspond to the non-essential or toxic element and essential element.

The concentration valuesof the element studied in the population, except for Co, Se and Zn, were comparately to the concentration values reported from other regions of the world (2).

Se was found in about 73 % of all the samples and the mean value for Se was found higher than the value reported in population from other country (2, 3). The relatively high concentrationsof Se in human hair samples are generally due to the contamination of hair from some kind of shampoo which contain Se coumpounds. It was also found that male hair samples had a relatively higher concentration of Se than in females.

The concentrationsof Co in males and females of the jakarta's population were about the same values and these values were higher than the reported values from other countries (2, 3). However, no explanation have been found for this.

The mean concentration value for Zn found in male hair samples was close to the value reported by SAKURAI (4). However, in female hair the value for Zn was lower. It is not known whether this low concentration for Zn found in the population studied has lead to Zn deficiency.

Mercury was found in almost all of the hair samples of the population of jakarta city. The mean concentration for Hg found in this population were comparable to the reported values other country (2, 3). The concentration range of Hg in males was wider than females, however, most of the female hair contain Hg in a higher concentration than in males as it is shown in Figure 3. The mean concentration for Hg in females hair of this

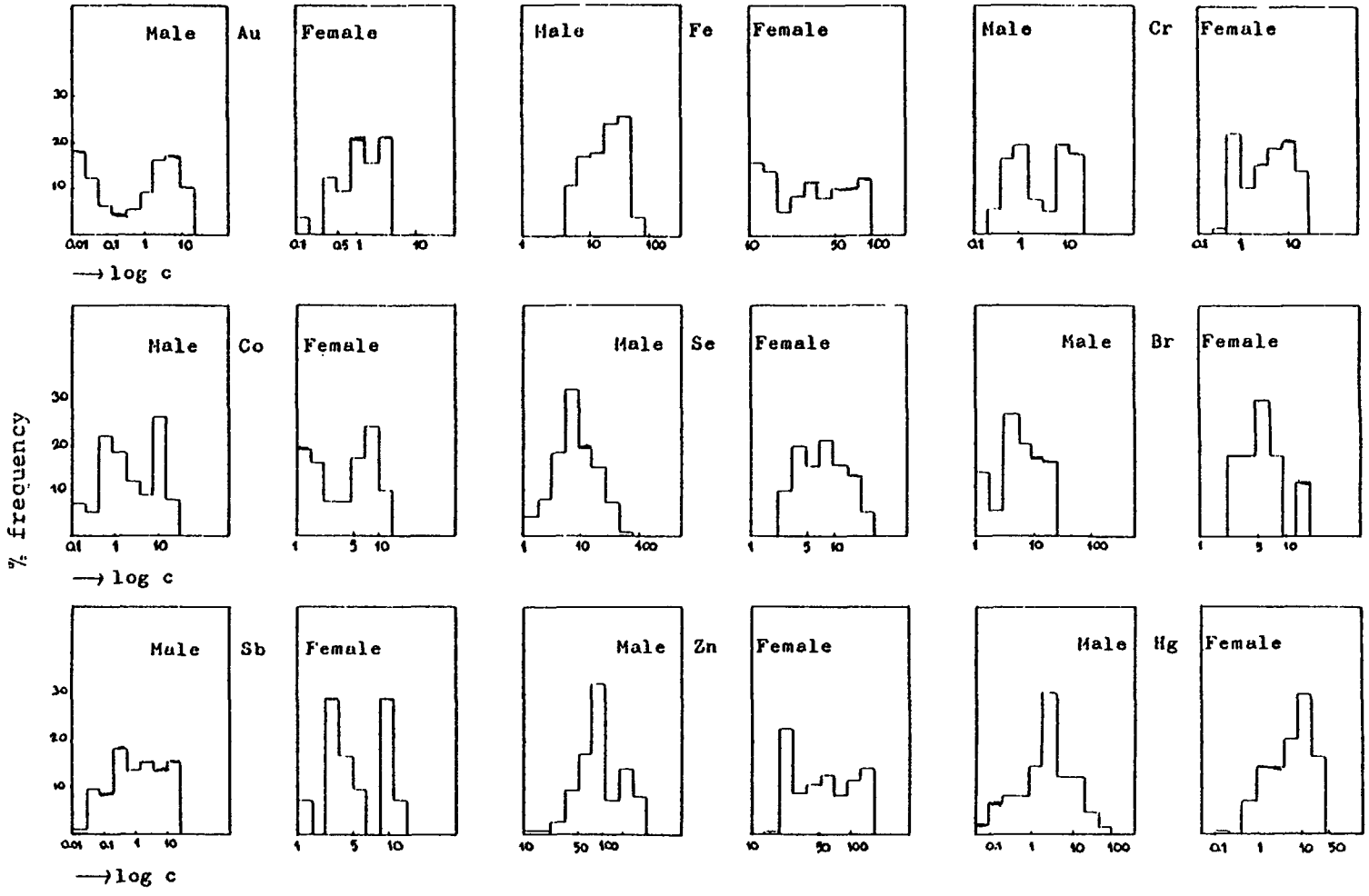


Figure 3. Frequency distribution of the elements as a function of log-concentration in the samples.

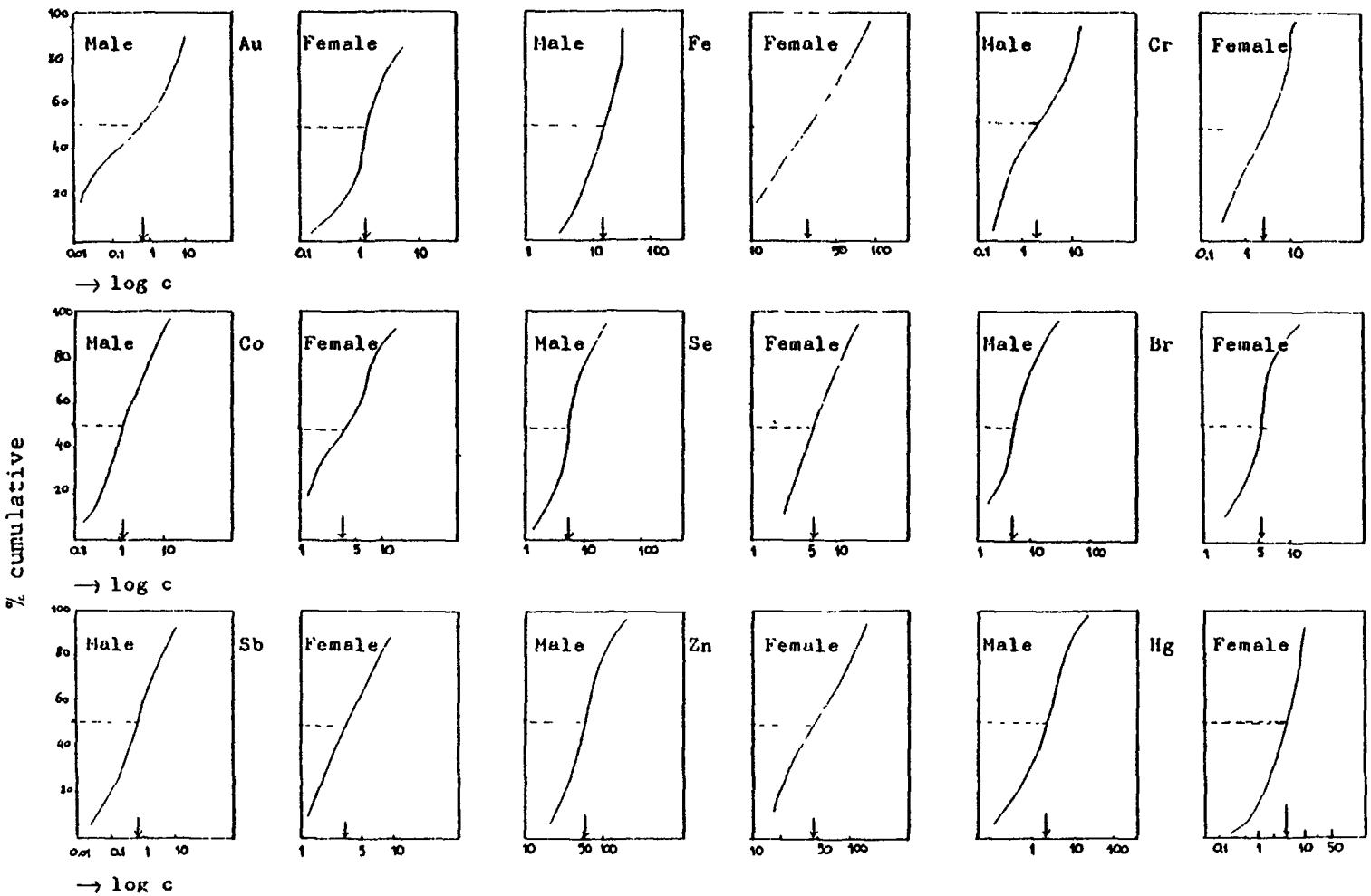


Figure 4. Cumulative frequency distribution as a function of logarithmic concentration. expected median.

population was higher than that for males. It is suspected that the relatively high concentration of Hg found in females may be due to contamination of Hg from some kind of cosmetic (bleaching cream) which contain Hg. The effect of bleaching cream on the concentration of Hg in hair samples is now under investigated under the cooperation with Pharmaceutical Research Centre, National Institute for Health Research and Development.

All of the hair samples obtained from the dentist and the population living in the suspected contamination area contain Hg. The concentrations of Hg found in these samples are shown in Table 3. The mean concentration for Hg in hair of the dentist were found 4-5 times higher than in hair samples of the population suspected to be contamined with Hg. LENIHAN (5) found that the concentrations of Hg in hair of the dentist and his assistants were higher than the control. The relatively high concentration of Hg found in hair samples should be due to occupational exposure.

The concentration of Hg in hair samples of the population suspected to be contaminated with Hg from industrial effluent as it is shown in Table 3 was about the same value to the population of the jakarta (as it is given in Table 2). This mercury concentration level was comparable to the normal level usually found in human hair and for below the threshold toxic level of 50 - 200 ppm (3). This result gives an indication that the population living in the Jakarta Bay area was not contaminated with Hg as it was suspected.

Many factors such as dietary habits, mode of hair treatment, disease, dental treatment, etc., have some influences on the trace element content in human hair, such factors were not mentioned in this study.

4. CONCLUSION.

By applying instrumental neutron activation analysis technique the concentrations of the elements : Au, Br, Co, Cr, Fe, Hg, Sb, Se and Zn have been determined in human hair of the inhabitants of the jakarta city. The samples comprised 177 males and 86 females between the ages of 10 and 60 years. The concentrations of the elements studied, except for Co, Se and Zn, were comparable to the values reported from other region of the world. The concentrations of Co and Se were found at the high concentration level, while Zn was lower. The values of the elements found in this study could be regarded as the present level of the elements in the inhabitants of the Jakarta City. The concentration of Hg in hair of the dentist was 4-5 times higher than the population of the Jakarta City. The concentration of Hg in the population living in the area suspected to be contaminated with Hg from industrial effluent was the same value to the population of the jakarta City and this value was still in the normal level and no indication of Hg contamination to the population.

ACKNOWLEDGEMENTS

This study was carried out under the Research Contract of the IAEA Programme on Health Related Environmental Research Using Nuclear Techniques. The financial support of the IAEA is gratefully acknowledged.

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Summary Report (II)

RCA REGIONAL CO-ORDINATED RESEARCH PROGRAMME ON HEALTH RELATED ENVIRONMENTAL RESEARCH USING NUCLEAR TECHNIQUES

INTRODUCTION

This programme was started by the Agency in 1978 for the purpose of promoting applications of nuclear-based analytical techniques in health-related environmental research. The original work-scope foresaw the establishment of a monitoring system for screening population groups by means of hair analysis, with emphasis on the toxic heavy metals As, Cd, Hg, Pb and Se. Subsequently, in 1980, the work-scope was revised to emphasize the establishment of analytical competence for more general kinds of environmental research (not only hair analysis) in each of the laboratories concerned and its demonstration by application in pilot studies, including the measurement of baseline values (e.g. in hair, tissues and food).

The programme was organized by the Agency within the framework of the Regional Co-operation Agreement for South East Asia (RCA). New Zealand was included in the programme at a time when that country was expected to join RCA. Iran was also included, though not an RCA country, because of the similarity of the work being carried out by the participant from that country.

During the lifetime of this programme, 12 different institutes from 12 countries have participated in it, 8 with research contracts and 4 with research agreements. Total Agency support for the programme to-date in the form of research contracts has amounted to about US$ 100,000. The total costs, including those covered by the institutes themselves, are estimated to be of the order of US$ 600,000.

The first meeting of the programme was held in Bangkok, Thailand, in 1978, the second meeting was held in Bombay, India, in 1981, while the third and final meeting took place in Bangi/Kuala Lumpur, Malaysia, in November 1983.

RESULTS AND CONCLUSIONS

All participants agreed that the research programme as a whole can, with some qualifications, be regarded as a success. They felt that it had given a strong impetus to areas of research that otherwise might have not been supported in their countries; many of these areas are now regarded to be of great potential importance. In all countries of the region there has in recent years been a considerable growth of interest in problems of environmental contamination with heavy metals such as Hg, Cd, As and Pb, and in many of these countries public interest groups and environmental lobbies are now very active. Many of the present participants in the programme can quote examples where their work has enabled the authorities to disprove claims about possibly injurious levels of toxic substances in the environment, e.g. of mercury in fish.

In all such cases it was shown that environmental contamination was, if anything, lower than in many industrialized countries, and was in any case below levels that might be a cause for concern. The main benefits of the programme, however, are not so tangible but are long-term in

nature, and are expected to develop on the foundation of analytical competence that this programme has sought to establish.

The main applications of nuclear techniques in such work are (1) in carrying out small-scale pilot investigations, particularly baseline measurements, and (2) in providing validation support for larger routine investigations in which conventional non-nuclear techniques (e.g. atomic absorption spectroscopy) are being used. The applicability of nuclear-based techniques such as instrumental neutron activation analysis (INAA), radiochemical neutron activation analysis (RNAA), X-ray fluorescence (XRF) and particle induced X-ray emission analysis (PIXE) was discussed in detail. INAA is a method of good general applicability provided that the sensitivity requirements are met, which is often the case for measurements of trace elements in such materials as hair, sediments and air filters. Its special advantage is that it is a multielement method. RNAA is the method of most general applicability and has been found to be particularly useful in this programme for measurements of As, Hg and Se. XRF and PIXE are both microanalytical methods which are useful for spatial localization studies, e.g. measurements of the distribution of an element along the length of a hair or in a single cell. They are applicable to bulk analysis only in special cases, e.g. the analysis of air filters. Further details are given Table 1.

Table 1 Applicability of nuclear-based techniques[1] in health-related environmental research. The table identifies which nuclear-based techniques are generally applicable for the analysis of the specified heavy metals in different kinds of matrix (note: this is only a general indication since there may be differences depending on the details of the specimen and of the technique used).

	Matrix			
Element	Hair	Food	Fish	Other[2]
As	I R X_1	(I) R	R	R X_1
Cd	(I) R	R	R	I R
Hg	I R	(I) R	R	(I) R X_1
Pb	X	-	-	-
Se	I R	(I) R	R	I R

1. I = instrumental neutron activation analysis
R = radiochemical neutron activation analysis
X = XRF or PIXE [X_1 = PIXE with external beam]
If enclosed in brackets, technique is applicable only if elemental concentration is relatively high.

2. Other = e.g. soil, air particulates, water

The analysis of hair has featured prominently in this programme to-date, and has generally been found to be useful as a "first level" monitor of environmental contamination. For example, if the concentration of a trace element in a specimen of human hair is within the normal range, then this is a reliable indication that contamination is absent. If, on the other hand, the concentration is elevated, then this is not necessarily a proof of significant contamination but rather an indication that other kinds of detailed investigation (generally much more difficult) should be carried out, e.g. of levels in blood and urine. Concentrations of trace elements in hair are known to be affected by external factors such as shampoo use (containing Se) or local medicines (containing Hg).

The results of the intercomparison organized by the Agency in 1982/83 indicate that most of the participating laboratories still need to do additional work for at least some of the elements of interest in order to achieve satisfactory accuracy and precision. However, some of their difficulties certainly stem from the fact that the choice of intercomparison materials was not ideal. Some of the elements of interest were present only at a very low concentrations in the materials provided, and some were not even certified. Although the coordinated research programme is now officially at an end, all participants agreed to do further work to improve their analytical capabilities. To this end a new quality control exercise is being organized by the Agency, using as intercomparison materials (1) human hair (from S. Ohno), (2) wool (from N.E. Whitehead), (3) a geological material, and (4) a biological material.

With reference to the human hair reference material prepared by S. Ohno and the wool reference material prepared by N.E. Whitehead, it was agreed that these are insufficient in quantity to justify the further work that would be necessary before they could be issued as primary reference standards. However, they will certainly be useful for the purposes mentioned in the preceding paragraph, as well as for use by individual laboratories as internal quality control standards. The originators of these materials agreed to make them available for these purposes.

The need was also confirmed by the participants for a new primary hair standard to replace the human hair reference material HH-1 that is no longer available. This should be prepared in sufficient amount (>20kg) to guarantee its availability over a period of several years to the many laboratories (>100) on a worldwide basis that are known to be engaged in work on trace elements in hair. The Agency was strongly recommended to make arrangements for the preparation of such a material.

As for the future, all the participants intend to carry on with various kinds of health-related environmental research, and would be grateful for further support from the Agency under its research contract programme, either within the RCA framework, or as part of a global coordinated research programme. The main topic of current interest to most of them concerns toxic heavy elements in food. A proposal was developed for a new programme on this subject having to do with the monitoring of compliance with national and international regulations on the maximum permissible concentrations of toxic elements in human foodstuffs. The main purpose of this programme would be to develop nuclear analytical techniques that could be used to provide validation support for routine monitoring programmes, or directly in small-scale pilot investigations. The participants requested the Agency to develop a

more detailed proposal along these lines, possibly with the help of consultants, with a view to implementing it in the form of a new coordinated research programme as soon as possible.

The participants also identified a need on the part of the RCA countries for more training in nuclear analytical techniques as applied in health-related environmental research. The Agency was requested to include a proposal for such a course in its plans for 1985.

A further topic of interest to many of the participants concerns simple methods for database management and mathematical methods for the interpretation of analytical data obtained from monitoring programmes (e.g. in the present case, of data obtained from the monitoring of toxic heavy elements in foodstuffs and human tissues). Questions arise as to how such data should be evaluated and reported (e.g. the use of means, medians, ranges, and percentiles, and the application of tests for the significance of differences between several data sets). The Agency was requested to explore to what extent it can develop specific programmes in these areas with a view to including this topic in future training courses and offering advice to participants in coordinated research programmes.

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