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Determination of arsenic and mercury level in scalp hair from a selected population in Penang, Malaysia using XRF technique

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HIGHLIGHTS

- XRF technique of measurement trace elements (As and Hg) in human hair for people in Penang, Malaysia.
- The results are measured for samples in black ashed form.
- The higher concentrations of As and Hg in the hair of town population suggests the presence of external sources of contamination in Penang environment.
- This study will be a reference for future studies to compare the ratios of As and Hg in the human hair for people in Penang.

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ABSTRACT

As with many cities all over the world with active industrial developments, the city of Penang in Malaysia has also the potential of being exposed to industrial pollution. Such exposure would certainly have a detrimental impact on the environment and the people. The determination of trace elemental levels in hair which is well known as a method for environmental exposure monitoring, evaluation of heavy metal poisoning, assessment of nutrient levels and disease diagnoses. In this study, it is selected as the method to determine the possible exposure to pollutants in the form of unwanted trace elements. The natural levels of trace elements in hair are hence monitored first as reference values for the assessment of the possible human contamination levels. In this work the concentrations of As and Hg in the human scalp hair of 100 residents of Penang were determined using XRF. The results of this study are compared with the results obtained in other cities where such measurements have also been carried out.

1. Introduction

In recent years, the determination of levels of trace elements in hair has developed into a technique of option for monitoring environmental exposure, estimating heavy-metal poisoning, reviewing nutritional status, and diagnosing diseases (Bencko, 1995; Moo and Pillay, 1983; Tavakkoli et al., 2000). The selection of hair as the major bioptate in multi-element analysis is defensible as follows:

Hair is a protein tissue with a very low metabolic activity and contains a 'record' of metabolic processes in the organism over a long period of time (Vazina et al., 1998). At the same instance, hair is simply collected and does not need any particular storage space. Hair has been reported to be stable for long periods of time (Foo and Tan, 1998). In general, hair also contains a higher concentration of metals than blood or urine, which makes analysis easier (Airey, 1983; Foo and Tan, 1998; Maugh, 1978). In general the concentration of elements in hair is many times higher than in other biological preparations. The elemental content in hair mirrors individual peculiarities of a human being such as sex, age, dietary and pharmacological effects, environmental conditions, etc (Vazina et al., 1998).

Hair samples can be easily obtained in a non-invasive way. They can be stored for an unlimited time, can be frequently used for repeated analyses without damage, are easy to transport and can be sent by mail (Vazina et al., 1998). Laker explained the advantages of hair analyses for the investigation of trace element levels over other materials such as blood and urine because it is easier to collect, and stored and the trace elements are present in higher concentrations, especially in comparison to those in blood samples (Laker, 1982). Hair of regular, healthy individuals in general contains all trace element within a well defined

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concentration range. Therefore knowledge of the natural levels of trace elements in hair is very important for assessing the degree of human contamination in areas where these elements are expected to show anomalous concentrations (Tavakkoli et al., 2000).

Human hair grows at a rate of approximately from 1 to 1.5 cm per month. The elemental level in hair reflects its level in the body medium from which it was formed and provides a historical record of elements assimilated from the environment (Foo and Tan, 1998). Finally the World Health Organization (WHO), Environmental Protection Agency (EPA) and International Atomic Energy Agency (IAEA) recommended the use of hair as a significant biological material for universal environmental screening (Sthiannopkao et al., 2010). In this work, trace element levels in hair is monitored for environmental exposure.

Recently, for a common of toxic trace metals this method has proved to be a well-suited biological marker of work-related and environmental exposure of man (Bencko, 1995). Hair samples are good pointers for exact toxic elements to which subjects have been exposed throughout the previous 2–18 months (Samanta et al., 2004).

Arsenic is the worst cancer-causing element circulated commonly in the environment from equally natural and anthropogenic resources. In soil it can provide risk to human health either with ingestion via the food chain or through secondary pollution of air and water because of dust and leaching loss (Wu and Chen, 2010).

Arsenic causes an especially high risk of cancer in skin, bladder, liver, lung, and kidney as well as other health effects and toxicity to humans (Samanta et al., 2004). While there are metabolically toxic materials in the epidermis, the roots are influenced by the physical condition status of the living beings and their analyses are used as a tool to screen work-related and environmental exposure to toxic elements (Mandal et al., 2003). Scalp hair has therefore been constantly proposed as a potentially useful tissue in that it can document the extent of and changes in the level of many trace elements in the body over a long period of time. The amount of As in hair shaft segments reflects the As burden at the time during hair was formed (Chappell et al., 1999; Saad and Hassanien, 2001). Arsenic concentrations in hair can be used as biomarkers for arsenic exposure in humans (Gault et al., 2008b). Hair concentrations of As reflect the quantity of As absorbed into the human body during the a number of months previous hair sampling (Wu and Chen, 2010).

Mercury and its compounds arise in nature in the environment, but their utilization in manufacturing and their discharge into the atmosphere by the burning of fossil fuels and the processing of ores has increased environmental levels (Airey, 1983). Mercury is certainly a toxic element and its neurotoxic results is well known in that there are many cases of Hg exposure in humans (Agusa et al., 2005). Mercury has been measured in human hair in studies of environmental concentrations in polluted and unpolluted area. The quantity of mercury previously emitted and being recycled in the environment and latest releases from natural and anthropogenic sources is considerable (Airey, 1983). Hajeb et al. (2008) studied the relationship between mercury concentration and fish consumption in several states in Malaysia.

Within several developing Asian countries in which industrial development and population increase are noticeable, environmental pollution has also become a significant issue. There have been many studies of trace elements in hair using XRF for cities, for example, Khartoum by Eltayeb and Van Grieken (1989), Damascus, Syria by Khuder et al. (2008), and Penang, Malaysia by Aldroobi et al. (2012). Regarding Penang, elements Cu, Zn and Pb were studied. The present study focused on the analysis of As and Hg levels in human hair samples collected from the Penang city in Malaysia.

2. Experimental

2.1. Instrumentation

The detector utilized was a Low Energy Germanium Detector, LEGe (CANBERRA), Model Number: GL0210R with an area of 200 mm^2, and thickness 10 mm, and resolution (FWHM) 5.9 keV at 122 keV. Source: Am-241 ring source (100 μCi) was used, which provides photon

Table 1
Results of mercury and arsenic determination in Penang (mg/kg).

Element	As (mg/kg)	Hg (mg/kg)
Average	1.16	4.88
Median	1.04	4.92
Range	0.10–4.57	2.2–17.5

Table 2
Hair mercury concentration in populations from selected states in Malaysia (mg/kg).

State	Range	Average	Year	Reference study
Johor	0.60–19.76	9.94	2008	Hajeb et al. (2008)
Kedah	0.05–21.00	13.69	2008	Hajeb et al. (2008)
Kuala Lumpur	0.20–16.40	6.62	1987	Sarmani (1987)
Kuala Lumpur	0.59–18.37	3.38	2004	Sarmani and Alakili (2004)
Penang(Kuala Juru)	0.45–16.87	3.61	1994	Sarmani et al. (1994)
Penang (island)	2.2–17.5	4.88	2012	Current study
Selangor	0.66–6.90	3.01	1994	Sarmani et al. (1994)
Selangor	0.02–19.74	6.78	2008	Hajeb et al. (2008)
Terengganu	6.79–18.31	12.08	1994	Sarmani et al. (1994)
Terengganu	0.10–19.90	10.85	2008	Hajeb et al. (2008)

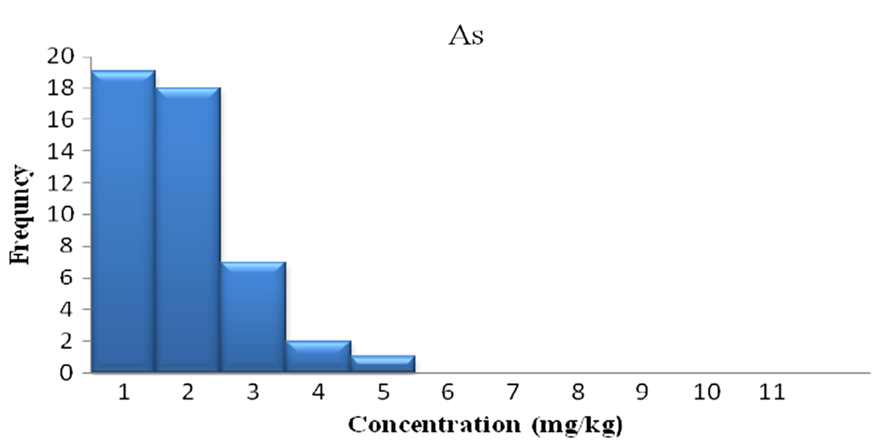

Fig. 1. Frequency distribution of hair arsenic concentrations for Penang.

Table 3
Comparison of hair mercury level (mg/kg) of Malaysian with other countries, adapted from Airey (1983).

Country	Mean hair mercury concentrations (mg/kg)	Total number of sample	Country	Mean hair mercury concentrations(mg/kg)	Total number of sample
America South	1.3	4	**Spain**	2.7	3
Australia	1.7	1518	**Sweden**	7.9	1
Bolivia	1.3	1	**Switzerland**	0.8	2
Brazil	5.7	1	**Thailand**	2.1	2
Burma	3.5	30	**U.K.**	5	1223
Canada	1.8	827	**U.S.A**	2.9	444
China	2.8	99	**Venezuela**	1	24
Finland	1.4	200	**Pakistan**	3.5	25
France	1.3	226	**Papua, New Guinea**	2.8	133
W. Germany	0.5	30	**Poland**	0.3	1
Hong Kong	3	26	**South Africa**	1.9	32
India	1.6	46	**Pribilof Is**	4.6	49
Iraq	1	100	**Monaco**	1.7	33
Italy	1.6	361	**Nepal**	0.3	45
Japan	5	1916	**New Zealand**	1.8	100
Kenya	7.9	71	**Norway**	2.7	1
S. Korea	2.3	420	**Penang, Malaysia**	4.8	50
Mexico	1.5	10	**Cambodia**(Agusa et al., 2005)	3.1	40
Tokyo, Japan(Nakagawa, 1995)	2.98	–	**Bangladesh**(Holsbeek et al., 1996)	0.44	219
Medan, Indonesia(Feng et al., 1998)	3.13	–	**Seoul, Korea**(Lee et al., 2000)	1.7	211
Doha, Kuwait(Al-Majed and Preston, 2000)	4.181	100	**Mansoura, Egypt**(Mortada et al., 2002)	0.23	93

Table 4
Comparison of hair arsenic level (mg/kg) of Malaysian cities.

Cities	As in human hair (mg/kg)	References
Penang	1.16	Present work 2012
Kuala Lumpur	0.83	Sarmani (1987)
Sepang	0.27	Sarmani (1987)
Alor Star	0.29	Sarmani (1987)

Table 5
Comparison of hair arsenic level (mg/kg) of Malaysian with other countries.

Countries	As in human hair (mg/kg)	References
West Bengal, India	3.43	Samanta et al. (2004)
Southern China	2.95	Wu and Chen (2010)
India	0.61	Takagi et al. (1986)
Japan	0.05	Takagi et al. (1986)
Canada	0.016	Takagi et al. (1986)
Brazil	0.2	de Figueiredo et al. (2007)
China	0.73	Jun-fa (2004)
Egypt	0.30	Saad and Hassanien (2001)
Pakistan	0.43	Kazi et al. (2009)
Sweden	0.085	Rodushkin and Axelsson (2000)
USA	0.01	DiPietro et al. (1989)
Poland	0.02	Takagi et al. (1986)
Italy	0.09	Caroli et al. (1992)
United Kingdom	0.81	Smith (1964)
Nigeria	0.09	Oluwole et al. (1994)
Cambodia: Kien Svay, district	1.41	Gault et al. (2008a)
Cambodia:Preak Russey, village	5.64	Sampson et al. (2008)
Cambodia: Kandal	3.03	Sthiannopkao et al. (2010)
Penang, Malaysia	1.16	Present work 2012

emissions of 14.0 keV, 17.8 keV, 26.34 keV, 33.2 keV and 59.53 keV (Beckhoff et al., 2006). The standard sample utilized is a standard reference material, IAEA-086, date/btl. No. 1995/178.

2.2. Hair collection

As hair grows, it is capable of accumulating mercury from blood, scalp sweat, sweat and dirt wiped onto the hair from hands, dust, air, dyes, shampoos and bleaches. It is important to note that mercury levels in the armpit hair, pubic hair, chest hair, and beards are not compared with mercury levels of head hair. Such hairs have different growth rates, are exposed to different amounts of sweat, and are usually covered by clothing and have different concentrations of mercury. Mercury is deposited in hair as it grows, and the amount deposited reflects the body burden of mercury (Airey, 1983). The human scalp hair samples were collected from 50 persons. Hair samples ranging in weight from 1.5 g to 2.5 g were collected from the donors at a barber shop in Penang using stainless steel scissors (Eltayeb and Van Grieken, 1989). The age range of individuals extended from 14 to 67 years (mean: 35.2). No specific area or distance from the scalp was sampled but most of the hair samples consisted of hair strands of 1–5 cm in length (Eltayeb and Van Grieken, 1989).

2.3. Sample preparation

Samples were prepared in line with the procedure recommended by the IAEA (Ryabukhin, 1978). The hair samples were washed in acetone, three portions of water and again with acetone (Ryabukhin, 1978). The IAEA method was applied in the present study for hair washing. Actually the washing process is very important for removing external contamination. Moreover, arsenic adsorbed to the hair sample makes it impossible to differentiate between exogenously and endogenously bound As (Mandal et al., 2003). Each stage of the washing process took 10 min with continuous stirring. The samples were dried afterwards for 24 h at room temperature and stored in sealed labeled plastic bags. Thereafter, 1 g of the hair sample was placed in a small dish and ashed in an oven at 200 °C for about 1 h.

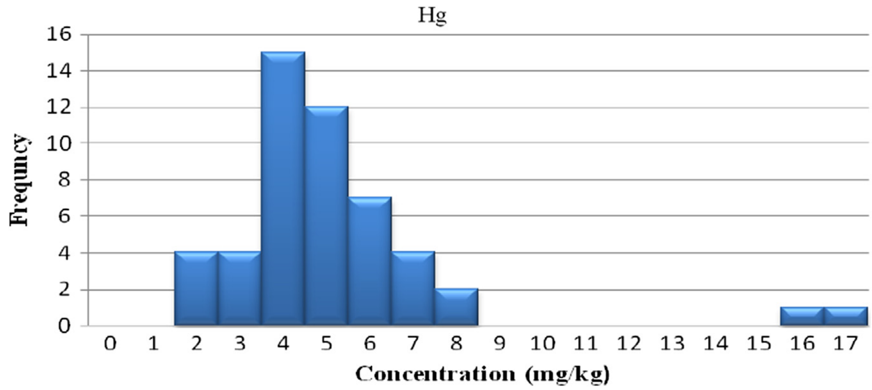

Fig. 2. Frequency distribution of hair mercury concentrations for Penang.

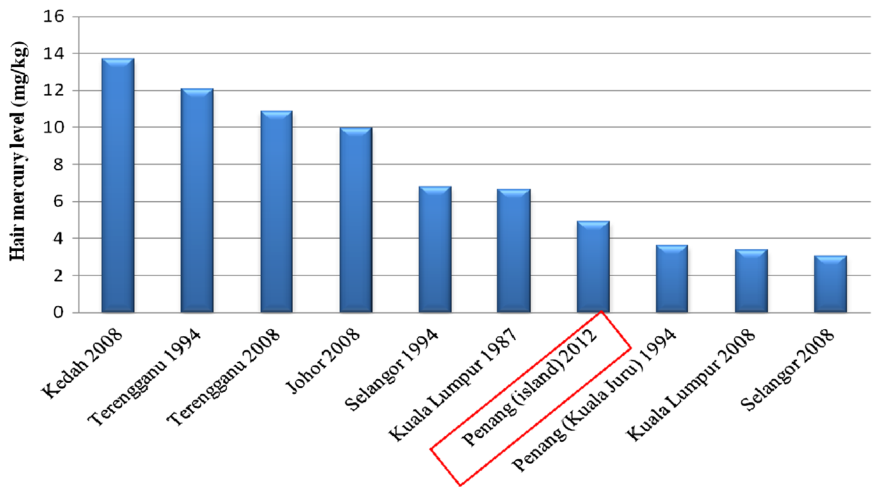

Fig. 3. Hair mercury concentration in populations from four states in Malaysia.

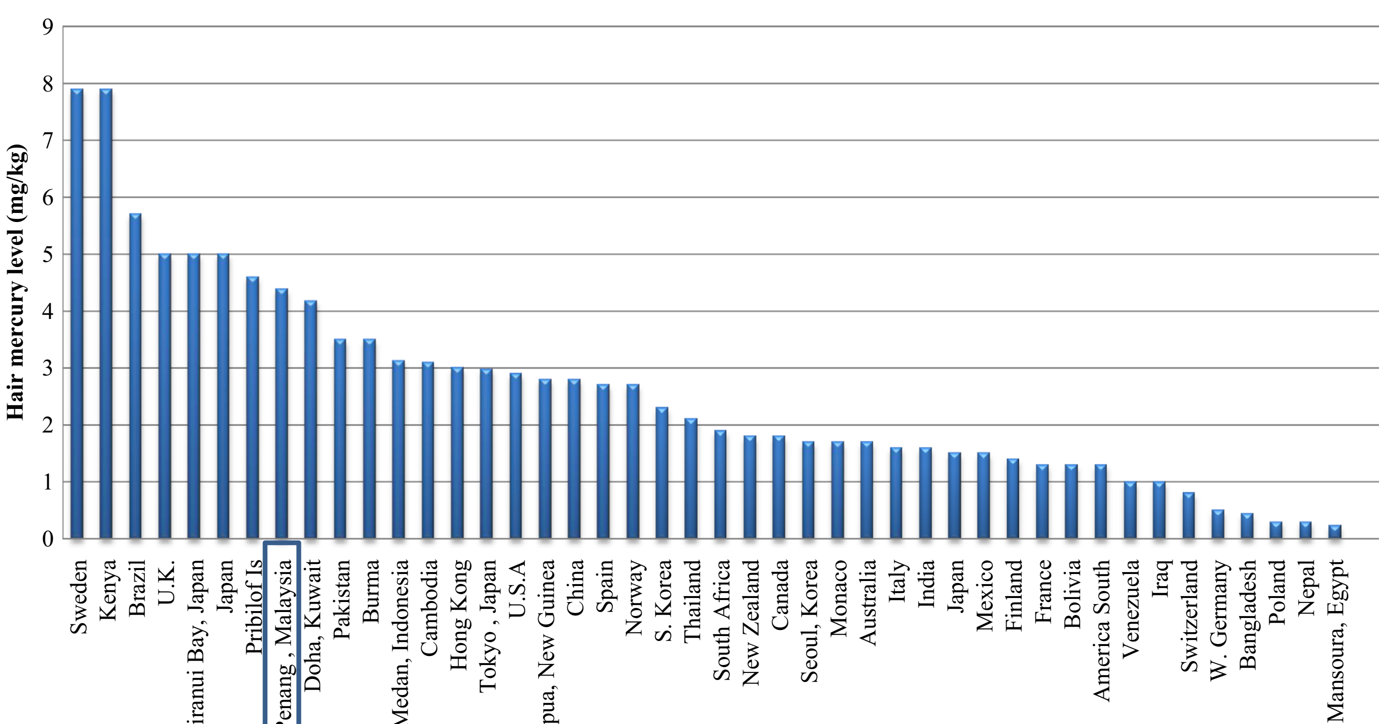

Fig. 4. Comparison of hair mercury level (mg/kg) in different countries.

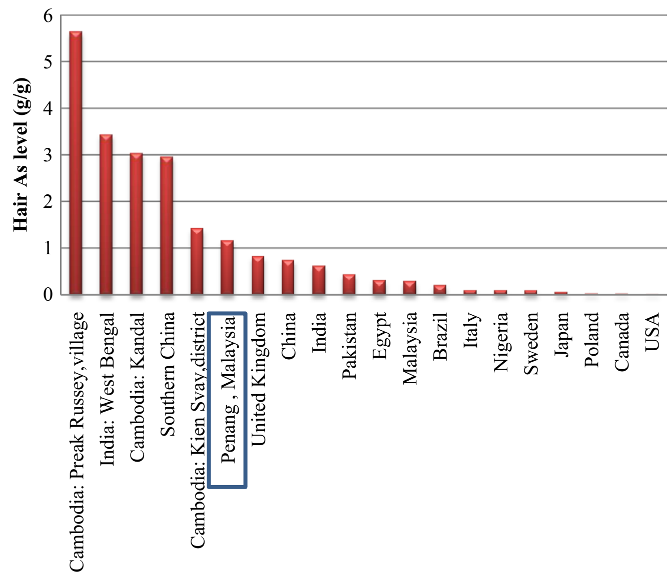

Fig. 5. Comparison of hair arsenic level (mg/kg) of Malaysian with in other countries.

The obtained ash was cooled, homogenized in a mechanical agate mortar with a pestle, then pressed by a hydraulic press 20 kPa in the form of a pellet of 2.2 cm in diameter with mass of about 0.8 g (Havranek et al., 1989).

2.4. Energy calibration and standardization

At the beginning of the analysis, energy calibration on the measuring system must be performed, i.e. for each element one energy region must be selected thereby determining the lines to be used for measurements. For this reason, the method based on the measurements of known artificial standards for individual elements for the selected energy region. Comparing the spectra of standards with those of measured samples, the elements present in the analyzed hair were identified. This procedure is based on the fact that the detected count rate is proportional to the weight fraction of elements in the sample, the amount of element to be determined is then obtained by estimating the peak area in comparison with those in the spectrum of the standard sample (Havranek et al., 1989).

2.5. Irradiation measurements

The samples and standards were irradiated with γ-rays from an Am-241 (100 μCi) source and data collected using the LEGe detector.

3. Results and discussion

The sensitivity of the analysis of trace elements in biological samples is based on several factors, which include: mass density of the fluorescent element in the sample, matrix composition, fluorescent X-ray lines, geometry and design of the detection system, and excitation energy. For estimation of sensitivity and accuracy of a broad range of trace elements, detection limits are calculated in similar matrices (Dede et al., 2001). The results are measured for samples in black ashed form. Ashing caused a mass loss of about 30% experimentally. Table 1 and Fig. 1 show the results which was found for people in Penang. Tables 2–5 and Figs. 2–5 provide a comparison of results obtained from Penang in this study with other studies. Table 3 and Fig. 3 show the comparative results of the mercury in hair for the study area against worldwide values. Table 4 and Fig. 4 show the comparative results of arsenic in hair for several locations in Malaysia including Penang.

Concentrations of toxic metals in hair (arsenic and mercury) depend on the environmental exposure. While the elemental concentrations in hair samples vary considerably with geographical location, nutritional status, and environmental features, the results from the experiments were also compared with results reported by related studies and the ranges of universal mean values. Fig. 3 shows the comparative results of the arsenic in hair for the study area against worldwide values. Fig. 4 shows the comparative results of arsenic in hair for several locations in Malaysia including Penang.

Evaluation of our data with other studies indicates that the levels of Hg and As in hair among individuals vary with environment in different countries. Concentration of As in hair was evaluated against values from other countries except Cambodia and India where As concentration was reported very high. Arsenic in healthy adults was found to be in the range of 0.13–0.71 mg/kg (Chappell et al., 1999; Sarmani, 1987) and Hg was found in range 1.25–7.6 mg/kg (Sarmani, 1987). Concentration of Hg in hair was compared against values from other states in Malaysia was reported in Table 2. The concentration of Hg in Penang is lower than five states in Malaysia. However, in Fig. 3 concentration of Hg in Penang is comparably higher than countries with the exception of Japan, Sweden, Kenya, Brazil and UK.

Arsenic concentrations in hair of residents in Penang (average 1.16 mg/kg) were lower than those in other As-contaminated areas of the world, but were higher than those of people in non-contaminated areas. Cumulative As exposure was evaluated to be lower than the threshold levels, which might explain the absence of symptoms of chronic As poisoning and arsenicosis in the people of Penang. The high hair concentrations of As and Hg is possibly related to the various sources of pollution typically present in urbanized centers.

The higher concentrations of As and Hg in the hair of town population suggests the presence of external sources of contamination in Penang environment which will be studied in future work.

4. Conclusions

For this study, hair samples from 50 individuals in Penang were analyzed for As and Hg concentrations using XRF analysis, presented and compared with similar results from other countries. The hair mercury levels found in the Malaysian people in Penang is 4.8 mg/kg while arsenic level is 1.16 mg/kg. This level of As and Hg in Penang is close to the worldwide range when compared with another countries. The results for both elements investigated do not differ considerably from reported values for other regions of the world. This study will be a reference for the next studies in future to compare the ratios. XRF was used for the first time to measure the material which irradiated As and Hg for Penang. This study will be a reference for future studies to compare the ratios of As and Hg in the human hair for people in Penang.

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