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Biological reference materials and analysis of toxic elements

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Biologische Referenzmaterialien und Analyse toxischer Elemente

Summary. Biological monitoring of toxic metal pollution in the environment requires quality control analysis with use of standard reference materials. A variety of biological tissues are increasingly used for analysis of element bioaccumulation, but the available Certified Reference Materials (CRMs) are insufficient. An attempt is made to review the studies made using biological reference materials for animal and human tissues. The need to have inter-laboratory studies and CRM in the field of biological monitoring of toxic metals is also discussed.

Introduction

Pollution is a growing hazard to human health. In developing countries, the chemical industries are proliferating and their harmful effects on the environment are different and higher [37]. The harmful environmental pollutants as heavy metals are the second most important toxicants causing adverse effects on organisms. The metal levels in biological tissues in polluted and unpolluted environments provide an insight into potential bioaccumulation, mobility within the ecosystem and response relationship. Monitoring the metal bioaccumulation in organisms needs a strict analysis of quality control samples for which purpose suitable Certified Reference Materials (CRMs) are of prime importance for accuracy and precision [10, 14].

The use of animal and human tissues for monitoring metal pollution in environment is reviewed. The extent to which the quality of element analysis and its improvement are discussed.

Biological monitoring

Jenkins [19] reported that there are two fundamental biomonitoring methods for environmental elements. The first method is to measure the bioaccumulation, while the second is the measurement of toxic effects of elements on organisms. Analysis of animal tissues for element levels provides the data regarding the baselinelevels, fate and bioavailability of contaminants within the ecosystem [38]. A large number of animal and human tissues were analysed to investigate the suitability of such tissues as biological indicators of body burden of metal pollution (Table 1).

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Animal tissues

Butler et al. [4] reported that the required criteria for being a useful indicator organism are the ability of the animal to accumulate metals in the body, availability for adequate sampling without killing the animal, sedentary nature and long survival to reflect the level in the environment. Shellfish fits many of these requirements [4] and may be the best indicator of Pb in estuarine and marine environment [39]. The fishery products such as sole, cod, herring, shrimp, mussel, pike-perch and eel can be used to analyse metal levels for monitoring human potential risk of toxic elements [13]. Certain tissues such as liver and kidney represent target organs for metals such as Pb, Cd and Hg. Krishnasamy and Ayyadurai [22] analysed Zn, Cu and Hg in random samples of liver and kidney collected from beef stalls of Madras to report a possible source of metal contaminated food for human consumption. Honda et al. [16] reported that feather is the best indicator of about 70% levels of Hg in birds.

Human tissues

Element analysis in human tissues is the most common application of biological monitoring for screening, diagnosis and assessment of exposure to elements in occupational and environmental health. Hair analysis is widely used as a biological sample [2, 34] and particularly, it accumulates high concentration of Hg and As [17]. The advantages and disadvantages in using hair were discussed [20]. Metal level in blood provides reliable indices for the present state of exposures to metals. Fergusson and Purchase [8] have stated that human teeth provide an integrated historical record of lead exposure, and that no international quality control or reference tooth material is available commercially.

Standard reference material

Analytical data without precision and accuracy are not useful in environmental health, because many decisions that influence the quality of life are based on such analytical data [22]. Besides the significant development in analysis, an improved quality assurance for analysis is essential. Proper application of quality assurance requires a CRM that matches as closely possible (e.g. with respect to matrix type and element levels of interest) the ‘real’ sample [28].

Table 1. Biological tissues and BRMs used in biological monitoring of toxic elements

No.	Animal	Biological tissue	Element	BRM used	Observation	Refer-ence
1	Shellfish	Soft tissue and shell	Pb	Internal quality control and dentine samples used	Best indicator of Pb	[30]
2	Shrews and voles	Whole body, liver, kidney, teeth and bone	Cd	Not used	Liver and kidney are the target organs for Cd toxicity and accumulation	[1]
3	Cow	Blood	Pb	Not used	Blood of cow could be indicator of Pb	[21]
4	Terrestrial mammal and aquatic birds	Liver and kidney	Cd	Not used	Cd level is best monitored in kidney and liver	[9]
5	Bovine ruminant, Japanese serows	Brain, liver, kidney, spleen, stomach, in-testine, heart, lung, skin, fleece, bone, gonad	Fe, Mn, Zn, Cu, Co, Ni, Pb, Cd and Hg	Bone and other tissue of dolphine	Heavy metal distribution in different tissues	[15]
6	Polar bear	Liver	22 elements	NBS bovine liver and oyster tissue, tuna	Poor accuracy and precision for certain elements. Good for certain elements and comparable analytical procedures	[26]
7	Human	Lungs	15 elements	Not used	Lung is a useful indicator of exposure to metallic particulate	[11]
8	Human	Liver and kidney	About 20 elements	NBS bovine liver and oyster tissue	Results were in good agreement with the reported value and no element interference	[33]
9	Alopecia patients	Serum, erythrocyte, hair and urine	12 elements	NBS bovine liver	Element by element analysis is better for accurate data	[25]
10	Human	Hair	10 elements	NBS bovine liver	The unified results of 93%	[35]
11	Human	Scalp hair	10 elements	NBS bovine liver	Liver Hg, Se, Cu and Mn reported	[39]
12	Human	Scalp hair	Pb	NBS orchard leaves	Hair SRM was not available, so an alternate SRM was used	[6]
13	Patients	Serum, hair, sweat	Zn	Not mentioned	Sweat Zn measurements may be more sensitive than serum or hair	[7]
14	Woman	Scalp and pubic hair, blood, milk	Fe, Cu, Zn and Pb	Not used		[32]
15	Autopsied human	Cortex and medulla of kidney	Cd	NBS bovine liver and horse kidney powder	As NBS liver had a low level of Cd, horse-kidney powder was used	[31]
16	Human	Scalp hair	About 22 elements	9 NBS and 6 IAEA SRMs used	Many SRMs used for valid results	[5]

A National Bureau of Standard (NBS) program for biological and environmental Standard Reference Materials (SRM) with the certification of orchard leaves marked the beginning of a period of rapid improvement in analytical techniques. The total number of SRMs from NBS was enhanced to 19 [12] and 21 CRMs were available commercially from six agencies [24]. Parr et al. [29] reported that 60 CRMs have been made available from nine agencies and that certain CRMs are lacking for Al, F, I, Mo, Si, Sn and V.

Evaluation of quality control studies

Recently, a number of CRMs has been increased, but, when the appropriate CRMs with wide range of element concentration are not available, a non-relevant CRM is often used (Table 1). When Scott et al. [31] observed higher level of Cd in the cortex and medulla of autopsied kidneys in comparison to the first SRM of NBS (bovine liver with a concentration of 0.27 ± 0.04 μg Cd/g), they used a second CRM from Ms. Birger Lind, Sweden (dried horse kidney with a value of 224 μg Cd/g), as higher concentration. Iyengar et al. [18] suggested that CRMs are needed at the lowest possible concentration of elements. In our studies, certified reference material of human hair powder was analysed and found to be in agreement with the reported values (Table 2). Considering all, the CRMs are required at the lowest and highest concentrations of elements.

Need for CRM

Certified reference materials should be as identical as possible to the actual monitoring samples and should contain

Table 2. Comparison of estimated values of elements with certified values of human hair (NIES, Japan)

No.	Elements	Value (μg/g ± SD) certified	Value (μg/g ± SD) estimated	Percentage difference
1	Cadmium	0.2 ± 0.03	0.15 ± 0.04	25
2	Chromium	1.4 ± 0.2	1.67 ± 0.5	19.3
3	Copper	16.3 ± 1.2	16.86 ± 0.4	3.3
4	Manganese	5.2 ± 0.3	4.8 ± 0.3	7.6
5	Nickel	1.8 ± 0.1	1.71 ± 0.1	5
6	Lead	6.0[a]	6.2 ± 0.4	3.3
7	Zinc	169.0 ± 10	156.73 ± 6.1	7.3

[a] Not certified
Courtesy to Prof. K. Okamoto, NIES, Japan

comparable concentration of elements being analysed. When there is a lack of appropriate CRM commercially available for the desired biological tissues, the available CRMs are used for the quality control studies. Chattopadhyaya et al. [6] reported that when hair SRM was not available, an alternate NBS orchard leaves was used. IAEA provided human hair (HH-1) reference material [24] but, its stock was exhausted. Then, the need of application and availability of appropriate CRM of this kind was perceived and subsequently a supply of human hair CRM is being undertaken at NIES, Japan [27].

A number of studies were carried out to monitor the human body burden of heavy metals by analysing biological tissues such as hair, nails, teeth, blood and autopsied tissues viz., kidney, liver, muscle, brain and bone but the use of CRM of human tissue is meagre (Table 1). Table 3 shows the critical organs of human beings for the bioaccumulation of elements. Human CRM for hair and serum are available but many CRMs are lacking for important tissues namely, kidney, liver, bone and teeth which are critical tissues for many elements. As Wren [38] suggested the criteria for the selection of tissues for monitoring of proposed studies, the selection of biological tissues for the preparation of CRMs must be based upon the objectives, priority, species availability and the specific accumulation properties of tissues.

Interlaboratory studies

Inter-laboratory studies among 43 laboratories from 12 countries were arranged to determine the effect of using a common set of blood standards of Se in reducing the interlaboratory coefficient of variation (CV) for the assay of blood Se [36]. From these studies, it is suggested that a common set of standards preferably those of similar matrix and Se concentration to the samples may be used in reducing interlaboratory CVs.

M'Baku and Parr [24] conducted interlaboratory studies among 100 laboratories for the analysis of trace and other elements of 40 with IAEA powdered human hair reference materials (human hair HH-1) and concluded that this type of interlaboratory study and a certified reference material of this kind are essential for the valid data. Moreover, those laboratories which produce precise, accurate and reliable data during the participation may come forward for the preparation of new and appropriate CRMs for the widely used biological materials.

Table 3. Percentage of bioaccumulation of elements in target organs in total body burden

No.	Tissue	Element (percentage to total body burden)
1	Bone	F (95), Mn (43.4), Pb (91.6), Ba (91), Au (52), Sb (25), Be (34.5), Al (34.5)
2	Bone marrow	Co (18.6)
3	Fat	V (90), Sn (25), Hg (69.2)
4	Hair	Methyl mercury – best indicator
5	Hemoglobin	Fe (70)
6	Kidney	Cd (27)
7	Liver	Cd (27), Mo (193)
8	Lung	Al (19.7), Ti (49)
9	Lymph	Ti (49.7)
10	Muscle	Zn (65.2), Cu (34.7), Se (38.3), Br (60), Hg (69.2), Li (50)
11	Skin	Cr (37), Ni (18)
12	Teeth	Pb (best indicator)

Data from [3, 7, 16]

Conclusion

The analysis of toxic elements in biological tissues for monitoring of environmental pollution needs usage of biological reference material for accuracy and validity of data. Production of varied reference materials of biological tissues and interlaboratory analysis are essential for reliable analysis in environmental monitoring of toxic elements.

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