ANALYTICAL REFERENCE MATERIALS. VIII.
DEVELOPMENT AND CERTIFICATION OF A
NEW GREAT LAKES SEDIMENT REFERENCE MATERIAL
FOR EIGHT TRACE METALS
by
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Research and Applications Branch
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867 Lakeshore Road, P.O. Box 5050
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MANAGEMENT PERSPECTIVE

Any data-generating process requires the use of Certified Reference Materials (CRMs) to ensure some degree of accuracy. Proper matrix and concentration matching between CRMs and environmental samples enhances accuracy. Diversified environmental samples require diversified CRM matrices, analytes and concentration levels.

This newly developed Great Lakes sediment CRM provides different matrix, analytes and concentration levels to complement those we have developed previously. Certified values for total Mn, Fe, Co, Ni, Zn, As, Se and Hg are given.

Dr. J. Lawrence
Director
Research and Applications Branch

PERSPECTIVES-GESTION

Tout procédé de génération de données nécessite l'utilisation de matériels de référence homologués (MRH) pour assurer une certaine précision. Une correspondance appropriée des matrices et des concentrations entre les MRH et les échantillons prélevés dans l'environnement favorise cette précision. Le prélèvement d'échantillons diversifiés requiert des matrices, des mélanges à analyser et des concentrations diversifiés dans les MRH.

Le nouveau MRH pour les sédiments des Grands Lacs fournit des matrices, des concentrations et des mélanges différents qui complètent ceux qui existent déjà. Les valeurs homologuées pour Mn, Fe, Co, Ni, Zn, As, Se et Hg totaux sont indiquées.

Dr. J. Lawrence
Directeur
Direction de la recherche et des applications

ABSTRACT

The development and certification of a new Great Lakes sediment reference material is described. The new matrix, analytes and concentration levels differ from but complement those previously reported, thus enhancing diversity of our quality control samples and effectiveness of the overall Quality Assurance program at NWRI. Using multi-laboratory and multi-methodology approach, the certified values for total metals, in $\mu g/g$ except Fe in %, were derived to be 1264 ± 91 Mn, 6.0 ± 0.4 Fe, 15.3 ± 1.7 Co, 52.0 ± 6.1 Ni, 1396 ± 107 Zn, 18.8 ± 1.5 As, 1.15 ± 0.19 Se, and 2.75 ± 0.28 Hg.

RÉSUMÉ

La mise et point et l'homologuation d'un nouveau matériel de
référence pour les sédiments des Grands Lacs sont décrites. Les
nouveaux mélanges, matrices et concentrations diffèrent, tout en les
complétant, de ceux existants, ce qui assure la diversité des
échantillons de contrôle de la qualité et l'efficacité du programme
de contrôle de la qualité mis en place à l'Institut national de
recherche sur les eaux. Les analyses effectuées dans plusieurs
laboratoires et l'utilisation de plusieurs méthodes ont permis d'obtenir
les valeurs homologuées suivantes pour les métaux totaux, exprimées en
ug/g, sauf en % pour Fe: 1264 $\pm$ 91 pour Mn, 6,01 $\pm$ 0,39 pour Fe,
15,31 $\pm$ 1,65 pour Co, 51,95 $\pm$ 6,13 pour Ni, 1396 $\pm$ 107 pour Zn,
18,77 $\pm$ 1,50 pour As, 1,15 $\pm$ 0,19 pour Se, et 2,75 $\pm$ 0,28 pour Hg.

INTRODUCTION

Certified Reference Materials (CRMs) are used to help ensure accuracy in many applications such as methods validation, intra- and interlaboratory quality control, surveillance and monitoring, and trend analysis. The development of CRMs has been a key activity in our Quality Assurance (QA) program for several years. Although CRMs are available through some other agencies, the research and development of new ones is actively thriving everywhere. The driving forces are many, but the main one is possibly the need to achieve the ideal state of matrix and concentration matching with environmental samples, thereby maximizing accuracy.

The lack of matrix matching can seriously cause biased data and erroneous conclusions, one recent example of which being the production of biased high SO_4 data in coloured waters [1,2]. A large variety of CRM matrices, analytes and concentration levels are required for the many different research areas. Great Lakes research demands Great Lakes CRMs. We have developed a few such materials for As, Se, and Hg [3], chlorobenzenes and hexachlorobutadiene [4], PAHs [5], and PCBs [6].

To fulfill our QA requirements, we continue development of more pertinent CRMs. In this paper, a new sediment CRM (made up of sediments from two different Great Lakes locations) for total Co, Mn, Fe, Ni, Zn, As, Se and Hg is described.

EXPERIMENTAL

Preparation of sediment reference material

Due to intense industrial activities in this region, sediments from both Lake Ontario and Hamilton Harbour were selected. Five hundred

kilograms of wet surface sediment from each location were collected using a double Shipek sampler. Drying, freeze-drying, and screening through a 74 μm vibrating screen of each sediment were done separately. Then 160 kg of Lake Ontario sediment was mixed with 53 kg of Hamilton Harbour sediment and the mixture blended in a 570-litre blender. This mixed-sediment CRM was identified as WQB-3, the matrix of which may be described by the geochemical composition shown in Table 1.

After 12-hour blending, six samples were taken from the blended sediment (two from the top: T-1 and T-2, two from the middle: M-1 and M-2, and two from the bottom: B-1 and B-2) for homogeneity test by the 2-way analysis of variance (ANOVA). The latter was earlier described in detail [3] and applied here to arsenic data. Table 2 shows the ANOVA results, giving both F_{column} and F_{row} smaller than $F_{critical}$, which indicates bulk homogeneity. Subsampling was then made into 100-ml amber bottles. For this study, 2800 subsamples of 40 g were selected.

Methodologies

Four independent methodologies were used, namely atomic absorption spectrometry (AA), inductively coupled plasma (ICP) and Direct Current Plasma (DCP) atomic emission spectrometry, and neutron activation analysis (NA). The AA, ICP and DCP methodologies involve wet chemical digestions. For AA analysis of Mn, Fe, Co, Ni and Zn, 1 g sediment was digested in a hot mixture of $HF-HNO_3-HClO_4$ acids (10 ml-15 ml-10 ml) until complete dissolution and the final solution made up to 100 ml with 5% HCl. The analysis was made by air-acetylene flame AA spectrometry with automated background correction. Atomic absorption determinations of Hg were made using the cold-vapor technique, whereas those of As and Se were by hydride-generation techniques [7].

In ICP analyses, 0.25 g sediment was digested in $HF-HNO_3-HClO_4$ hot acid mixture until complete destruction and the final solution made

up to 25 ml with 10% HCl. The digest was injected as aerosol into the argon plasma generated by 1500 watt radio frequency power, and the analysis of Co, Ni, Zn, Fe and Mn made with an Applied Research Laboratories ICP spectrometer. The ICP analyses of As and Se are previously described in detail [3]. For DCP analyses, 0.25 g sample was digested via lithium metaborate fusion at 950°C [8] and the final solution made up to 50 ml with 5% HNO_3. The digest was aspirated at 2 ml/min and sprayed into the argon plasma and the analysis made with Beckman Spectraspan V DCP spectrometer equipped with background correction.

Neutron activation analysis does not involve any wet chemical digestion. Sediment sub-samples, ranging from 0.6 g to 3 g were encapsulated in polyethylene vials and irradiated in neutron flux of SLOWPOKE reactor [9]. The irradiation time was two minutes for Mn, one hour for As, five hours for Co, Fe and Zn, and six hours for Hg and Se. The flux was 10^{11} neutrons $cm^{-2}s^{-1}$ for Mn and 10^{12} for the other elements. The gamma-ray spectrum was accumulated on a Ge detector and analyzed with a multichannel analyzer.

RESULTS AND DISCUSSIONS

Homogeneity test on subsamples

During bottling process, one sample out of about 100 samples was selected for further homogeneity testing of subsamples. The homogeneity criterion was set at ±5% coefficient of variation by a single method - single parameter testing on 30 samples. Table 3 presents the test results for the eight elements studied with the coefficients of variation ranging from 1.1% for Co to 3.7% for Mn, which confirms homogeneity of subsamples.

Certification process

Detailed procedures are cited elsewhere [3], but the process comprises the following criteria. The desirable number of acceptable determinations, n, for each element is 120. In our case, n ranges from 190 for Hg to 290 for Mn. A minimum of two independent methods are required for each element. In this work, three independent methodologies were used for all elements (except Mn with four and Hg with two methodologies).

A minimum of three independent laboratories is recommended for each element. This work involved six proven laboratories, selected on the basis of known performances. Usually each laboratory analyzed two different sets of samples at two different times without prior knowledge of sample type. A data set was selected on the grounds of acceptable precision and accuracy with respect to one or more known values. Some suspect results determined to be outliers [10,11] were discarded; the percentage of outlying results for each selected data set is generally less than 5%. The recommended values for each element would be given at 95% tolerance limit [12, 13].

Method compatibility

For each of the four methodologies used, at least two sets of data were generated, selected, combined and the mean calculated. Before pooling all data from the methodologies, the individual means were shown to be compatible.

The method compatibility is defined for each metal as the percent difference between the highest and the lowest of the individual means. Taking Mn as an example, the highest mean is 1284 μg/g by NA and the lowest mean is 1234 μg/g by AA, giving a percent difference of 4% as the index of method compatibility. Table 4 lists all the calculated indexes and shows that they are below 10%, the desirable upper limit, for all metals except Se. Selenium in sediment, as previously

emphasized [3], is a very difficult element to analyze. The index of 25% is admittedly high but not unreasonable considering the analytical difficulties and the very low-level of 1-1.3 ppm Se. Nevertheless, it is recognized that the Se recommended grand mean to be derived below may need revision if future research findings warrant it.

Grand mean

We have been calculating grand means, $\bar{X}$, by using the pooled total number of observations, N, as follows

$$\bar{X}_N = \sum n_i \bar{x}_i / N$$

where n_i and $\bar{x}_i$ refer to the number of observations and mean value of data set i. Recently, ISO [14] (International Organization of Standardization) recommends $\bar{X}$ calculation using the number of participating laboratories, L, instead of N as follows

$$\bar{X}_L = \sum \bar{x}_1 / L$$

where $\bar{x}_1$ is the mean from each laboratory or each independent set of data. Comparing the two grand means, Table 5 shows that for all practical purposes, they are identical. We also included in the Table a third kind of grand mean derived from total number of methodologies used, M, as follows

$$\bar{X}_M = \sum \bar{x}_m / M$$

where $\bar{x}_m$ is the mean from each methodology. As can be seen, there is no significant difference between the three grand means, and therefore we shall continue using $\bar{X}_N$ along with pooled standard deviation [15].

Recommended values

Table 6 summarizes the recommended values with 95% tolerance limit and coefficient of variation (% CV).

CONCLUSION

In conclusion, we have developed and certified a new Great Lakes sediment reference material for total Mn, Fe, Co, Ni, Zn, As, Se and Hg using a multi-laboratory multi-methodology approach. The material provides new and different matrix, analytes and concentration levels, which enhances diversity of quality control samples, and increases the effectiveness of the overall quality assurance program at NWRI.

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TABLE 1

Geochemical Compositon of WQB-3*

Constituent (total element a_s)	Concentration % m/m
SiO_2	52.9
Al_2O_3	11.5
Fe_2O_3	8.1
MgO	2.8
CaO	6.6
Na_2O	1.0
K_2O	2.7
TiO_2	0.7
MnO	0.2
P_2O_5	0.3
C (total organic carbon)	3.0
N (total organic nitrogen)	0.2
Loss on ignition (1040°C)	13.5

* The compositon of the 10 major elements were determined by XRF analysis (one time analysis of 10 replicates, uncertified).

TABLE 2

Analysis of Variance Results on Arsenic Data (μg/g) determined by NA

Replicate	Sample						Mean	Standard Deviation	% CV
	B-1	B-2	M-1	M-2	T-1	T-2			
1	19	20	19	19	19	18	19.0	0.63	3.3
2	20	19	20	19	19	18	19.2	0.75	3.9
3	21	18	19	19	18	19	19.0	1.10	5.8
4	20	20	20	19	18	19	19.3	0.82	4.2
5	19	20	19	18	18	20	19.0	0.89	4.7
Mean	19.8	19.4	19.4	18.8	18.4	18.8			
Std. Dev.	0.84	0.89	0.55	0.45	0.55	0.84			
% CV	4.2	4.6	2.8	2.4	3.0	4.5			

Overall mean = 19.1

Overall Std. Dev. = 0.80

Overall % CV = 4.2

F_{column} = 2.34   versus $F_{critical}$ = 2.71

F_{row} = 0.23   versus $F_{critical}$ = 2.87

TABLE 3
Homogeneity Test on 30 WQB-3 Subsamples for
Total Mn, Fe, Co, Ni, Zn, As, Se and Hg
(μg/g, except Fe %)

	Mn	Fe	Co	Ni	Zn	As	Se	Hg
	1300	5.8	14.9	55.0	1399	18.3	1.24	2.93
	1300	6.1	14.8	55.0	1398	18.2	1.17	2.97
	1300	6.2	14.9	54.0	1418	18.5	1.23	3.02
	1400	6.3	14.6	54.0	1369	18.4	1.28	3.01
	1300	5.9	14.7	54.0	1365	18.2	1.26	3.01
	1300	6.1	14.8	56.0	1392	18.1	1.23	2.79
	1300	5.4	14.8	54.0	1389	18.0	1.37	2.97
	1400	6.0	14.7	53.0	1370	18.0	1.28	3.02
	1300	6.3	14.9	55.0	1394	17.5	1.27	3.22
	1400	6.1	14.6	57.0	1374	18.6	1.33	2.90
	1300	6.1	14.7	54.0	1394	18.1	1.24	2.96
	1300	6.1	14.7	54.0	1380	18.5	1.20	3.06
	1300	6.3	14.7	56.0	1395	18.1	1.24	2.83
	1400	6.2	14.8	52.0	1396	18.6	1.21	2.87
	1300	6.2	14.9	56.0	1403	18.3	1.18	2.86
	1300	6.3	14.9	53.0	1405	18.8	1.19	2.98
	1300	6.1	14.7	54.0	1374	18.6	1.27	2.85
	1400	6.2	14.9	54.0	1408	18.0	1.25	2.82
	1300	6.0	15.2	53.0	1391	17.7	1.31	2.91
	1400	5.9	14.8	56.0	1399	18.1	1.24	2.88
	1400	6.1	15.3	57.0	1445	18.1	1.20	2.99
	1400	6.1	14.7	51.0 ·	1382	18.0	1.25	2.90
	1300	6.1	14.8	53.0	1382	18.5	1.28	2.87
	1400	6.0	14.9	53.0	1401	18.4	1.23	2.78
	1400	5.9	14.8	51.0	1390	17.9	1.27	2.90
	1300	5.9	14.9	52.0	1403	17.8	1.27	2.90
	1300	5.8	15.0	52.0	1423	18.4	1.19	2.91
	1400	5.9	15.0	51.0	1416	17.6	1.25	3.18
	1400	6.0	14.7	59.0	1394	16.9	1.27	2.95
	1300	5.9	14.6	54.0	1366	17.8	1.26	3.12
$\bar{x}$	1340	6.0	14.8	54.1	1394	18.1	1.25	2.95
s.d.	50	0.2	0.2	1.9	18	0.4	0.04	0.11
% CV	3.7	3.2	1.1	3.5	1.3	2.2	3.5	3.6

TABLE 4
Method Compatibility for WQB-3
all concentrations in μg/g, except Fe in %

Metal	Methodology	No. Data Sets Selected	Mean per Methodology	Method Compatibility %
Mn	AA	3	1234	
	ICP	2	1259	4.0
	DCP	1	1245	
	NA	5	1284	
Fe	AA	2	5.8	
	ICP	3	6.2	7.0
	NA	6	6.0	
Co	AA	2	15.3	
	ICP	2	15.3	0.2
	NA	5	15.3	
Ni	AA	5	51.8	
	ICP	4	51.3	3.6
	DCP	1	53.1	
Zn	AA	4	1401	
	ICP	4	1391	0.7
	NA	2	1399	
As	AA	2	19.0	
	ICP	3	18.4	3.2
	NA	9	18.7	
Se	AA	5	1.11	
	ICP	2	1.02	25.0
	NA	3	1.31	
Hg	AA	5	2.78	
	NA	3	2.66	4.7

TABLE 5

Comparison of Grand Means

(μg/g, except % Fe)

Metal	$\bar{X}_L$	$\bar{X}_N$	$\bar{X}_M$
Mn	1262	1264	1256
Fe	6.0	6.0	6.0
Co	15.5	15.3	15.3
Ni	51.9	52.0	52.1
Zn	1397	1396	1396
As	18.7	18.8	18.7
Se	1.14	1.15	1.15
Hg	2.71	2.75	2.72

TABLE 6
Recommended Values of Heavy Metals
(μg/g, except % Fe)

Metal	$\bar{X}$	Tol. Limit	% CV	No. of Analyses
Mn	1264	91	3.4	292
Fe	6.0	0.4	3.1	273
Co	15.3	1.7	5.1	246
Ni	52.0	6.1	5.5	231
Zn	1396	107	3.6	249
As	18.8	1.5	3.8	253
Se	1.15	0.19	7.7	216
Hg	2.75	0.28	4.8	191