NEW REFERENCE MATERIALS

Continuing list of available, new and announced reference materials

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Preparation and certification of JAC river water reference material for trace element analysis

Abstract The Japan Society for Analytical Chemistry has recently issued a river water-certified reference material (CRM) for use in the ultratrace analysis of elements in fresh water. The river water CRM consists of a set of two (natural and spiked) 500-ml samples. The natural water is certified for Pb, Cr, As, Cu, Fe, Mn, Zn, B and Al at their sub-μg/l levels, while the spiked water is intended for use in the regulatory analysis of tap water and fresh water.

Key words River water · Trace element analysis · Regulatory analysis · Reference materials

Introduction

The Japan Society for Analytical Chemistry (JAC), an academic body, has recently initiated the production of a variety of certified reference materials to serve the needs of JAC members for analytical quality assurance. Advantages of this certification system are that collaborative analysis involving qualified laboratories can be efficiently organized, bearing in mind the analytical techniques available, the matrix of the sample to be analyzed, substances and their concentrations to be determined, and so on. Furthermore, appropriate advice and suggestions on sample preparation procedures can be obtained from the members working in the various scientific fields. Since the preparation and certification of reference materials (RMs) are undoubtedly in need of developments in separation and detection techniques, clean technology, and contamination-free sample preparation, this type of CRM programme is expected to make a large contribution to the progress of the analytical community. Table 1 shows the certified values for two JAC CRMs, i.e. High-purity Silicon Dioxide (JAC 0011–0013) [1] and High-purity Aluminum (JAC 0021–0023) [2], each for the determination of three different levels of trace U and Th in the LSI = large scale integrated circuit materials.

In Japan, the water quality standard has recently been revised, resulting in new regulatory limits for trace elements down to μg/l (ppb) levels. Analytical problems associated with ultratrace analysis have been reported, e.g. sensitivity, selectivity, and contamination, and therefore there is a great demand from a number of water quality laboratories for a water RM certified for regulatory elements at their μg/l levels. The JAC has recently undertaken the preparation and certification of a river water RM for ultratrace element analysis.

Preparation

River water used for this reference material was obtained at a water filtration plant in Yokohama, where river water was being supplied through a pipeline from the Doushi River (Yamanashi Prefecture). The river water was filtered through 0.45-μm porosity filters, pooled to five polyethylene drums of 200-l capacity and acidified immediately with high-purity nitric acid to pH approximately 1.3. The polyethylene drums were transported to a clean laboratory and allowed to stand for a few weeks. The acidified river water was refiltered through 0.2-μm porosity filters. Out of the five drums, two were used for "natural level" samples and the other three were prepared as "spiked" samples. The unspiked river water was blended and packed into 700 acid-washed Teflon PFA bottles, each containing 500 ml of the water. To prepare the spiked river water, each of the following elements was added as a solution prepared from a high-purity metal or its salt to give a final concentration corresponding to 1/10–1/2 of the regulatory limit: Pb, Cr, Cd, As, Se, Cu, Fe, Mn, Zn, Ni, B and Al. After blending, the spiked river water was packaged into 900 acid-washed Teflon PFA bottles, each containing

Table 1 Certified values for JAC High-purity Silicon Dioxide and High-purity Aluminum CRMs

High-purity Silicon Dioxide		
	U (ng/g)	Th (ng/g)
JAC 0011	9.4 ±0.4	8.7 ±0.9
JAC 0012	1.0 ±0.1	0.85±0.14
JAC 0013	0.12±0.02	0.21±0.02
High-purity Aluminum		
	U (ng/g)	Th (ng/g)
JAC 0021	5.5 ±0.8	9.8 ±1.7
JAC 0022	1.0 ±0.1	1.7 ±0.4
JAC 0023	0.10±0.01	0.086±0.037

500 ml of the water. The JAC River Water RM consists of a set of two bottles: the natural (JAC 0031) and the spiked (JAC 0032) waters.

Certification

A homogeneity test was performed on both natural and spiked waters, using graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS). Triplicate analyses of six randomly selected bottles showed good homogeneity of the prepared materials. Storage tests carried out by determining trace levels of Zn, Cu and Pb by isotope dilution (ID)-ICP-MS showed no significant changes of the element concentrations over several months.

At this stage, a Technical Committee in charge of the certification of the river water RM was organized within the JAC. Collaborative analysis of the river water RM was designed by the committee and then carried out by 35 participating laboratories to determine Pb, Cr, Cd, As, Se, Cu, Zn, Mn, Fe, Al and B, for which the regulation limit had been set, and to determine Ca, Mg, K and Na. Analytical techniques used include ICP-MS, ID-ICP-MS, ICP atomic emission spectrometry (ICP-AES), GFAAS, hydride generation AAS, flame photometry, neutron activation analysis, and spectrofluorimetry.

Certification of the river water RM was conducted according to the ISO Guide 35 [3]. Technical consideration was first given by the committee to each of the reported values with respect to suitability, detection limit, and selectivity of the methods employed for the elements. Analytical values judged not appropriate were eliminated from further statistical treatment. Secondly, two statistical outlier tests, Cochran's test followed by Grubbs's test [4], were applied to reject outliers if present. Finally, certified value was computed as an average value of all the acceptable values. The uncertainty of the certified value was estimated as the 95% confidence limits of the mean, according to the ISO Guide 35, based on a full-nested design of ANOVA = analysis of variance.

Table 2 Certified and reference values for JAC River Water CRM (*a,* ICP mass spectrometry; *b,* isotope dilution ICP mass spectrometry; *c,* ICP emission spectrometry; *d,* graphite furnace atomic absorption spectrometry (GFAAS); *e,* hydride generation AAS; *f,* flame AAS; *g,* flame photometry; *h,* neutron activation analysis; *i,* spectrofluorimetry)

	JAC 0031 (natural level)			JAC 0032 (spiked)	
	Certified value	Method		Certified value	Method
	(μg/l)			(μg/l)	
Pb	0.026 ± 0.003	a, b	Pb	9.9 ± 0.2	a, b, c, d
Cr	0.14 ± 0.02	a, d	Cr	10.1 ± 0.2	a, c, d
Cd	(0.003)[a]	a	Cd	1.00 ± 0.02	a, c, d
Se	(0.1)[a]	a, e, h	Se	5.2 ± 0.3	a, d, e, h
As	0.28 ± 0.04	a, d, e, h	As	5.5 ± 0.3	a, d, e
Cu	0.88 ± 0.03	a, b, c, d	Cu	10.5 ± 0.2	a, c, d
Fe	6.9 ± 0.5	a, c, d	Fe	57 ± 2	a, c, d
Mn	0.46 ± 0.02	a, c, d	Mn	5.4 ± 0.1	a, c, d
Zn	0.79 ± 0.05	a, b, c, d, e	Zn	11.3 ± 0.4	a, c, d
B	9.1 ± 0.5	a, c	B	59 ± 2	a, c
Al	13.4 ± 0.7	a, c, d, i	Al	61 ± 2	a, c, d, i
Ni	–		Ni	10.2 ± 0.3	a, c, d
	(mg/l)			(mg/l)	
K	0.68 ± 0.02	a, c, f, g, h	K	0.67 ± 0.01	a, c, f
Na	4.2 ± 0.1	a, c, f, g	Na	4.5 ± 0.1	a, c, f, g
Mg	2.83 ± 0.06	a, c, f, h	Mg	2.86 ± 0.04	a, c, f
Ca	12.5 ± 0.2	a, c, f, h	Ca	12.5 ± 0.2	a, c, f

[a] Values in parentheses are reference values

Table 2 lists the certified and reference values for JAC River Water CRM [5]. For the background level "natural" sample, the certified values are given for Pb, Cr, As, Cu, Mn and Zn at their sub-μg/l levels, for Fe, B and Al at μg/l levels, and for K, Na, Mg and Ca at mg/l levels. The concentrations of the heavy metals are extremely low, even at the 1/10–1/2 concentrations of those in NRCC = National Research Council Canada (SLRS-3 is identifier) SLRS-3 Riverine Water CRM. For Cd and Se, however, only reference values are given for information. For the high level "spiked" sample, the certified values are provided for Pb, Cr, Cd, Se, As, Cu, Fe, Mn, Zn, B, Al, Ni, K, Na, Mg and Ca. For the elements being regulated, the intended concentrations corresponding to 1/10–1/2 of the water quality standards were achieved. The spiked river water will be of great use to laboratories engaged in regulatory analysis of tap water and fresh water.

References

1. Certificate for High-purity Silicon Dioxide reference material (1993) Japan Society for Analytical Chemistry, Tokyo
2. Certificate for High-purity Aluminum reference material (1995) Japan Society for Analytical Chemistry, Tokyo
3. Certification of reference materials – general and statistical principles (1989) ISO Guide 35, 2nd edn, Geneva
4. General rules for permissible tolerance of chemical analyses and physical tests (1991) Japanese Industrial Standard Z 8402
5. Certificate for River Water reference material (1996) Japan Society for Analytical Chemistry, Tokyo

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