Letters to the Editor

A New Certified Reference Material, Vehicle Exhaust Particulates

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The National Institute for Environmental Studies (NIES) has issued a variety of biological and environmental certified reference materials (CRMs) for use primarily in the validation of analytical methods and in the calibration of analytical instruments. Table 1 shows the present status of the NIES CRM program. The currently available CRMs from NIES are Pepperbush[1], Pond Sediment[2], Chlorella, Human Hair[3], Mussel[4] and Tea Leaves[5], the elemental composition of which has been certified. Sargasso (No. 9) and Rice Flour—Unpolished (No. 10) reference materials have been prepared for trace element analysis and are in the process of certification.

In spite of the greatly increasing demand for reference materials of air particulate matter, the availability of CRMs of such materials has been limited, probably due to difficulty in collection of sufficient quantities. The "Urban Particulate Matter" Standard Reference Material (SRM) issued by the US National Bureau of Standards (NBS) is the only currently available reference material certified for elemental composition. Recently, "Urban Dust/Organics" and "Diesel Particulate Matter" SRMs certified for organic compounds have been issued by NBS for use in analysis of polyaromatic hydrocarbons. Therefore, the development of a new type of air particulate matter reference material "Vehicle Exhaust Particulates", which is closely related to automobile transportation problems, has been undertaken at NIES.

The material used for this reference material was collected from electrostatic precipitators in huge ventilators connected to a highway tunnel. The electrostatic precipitators were situated between moving cloth filters. Preliminary analysis demonstrated that the contribution from pavement material was small. About 7 kg of the material was used for the preparation of this reference material. Because the material readily produced a dust cloud and had an irritating smell of gasoline, it was treated under wet conditions, whenever possible, for safe operation with respect to occupational health and danger of explosion.

About 300 g of the material and 1 l of 35% ethanol were mixed well in a 10 l polyethylene container. After repeating this mixing procedure for the remaining samples, all mixtures were combined together in a large polyethylene tray, mixed again and air-dried for 2 weeks. The material was transferred to aluminum trays, dried in an air-oven at 60°C for 5 days and crushed into a fine powder in polyethylene bags with a wooden hammer. After being passed through a 2-mm nylon screen, the powder was packaged into about 1000 bottles. At this stage a homogeneity test using

Table 1 Present status of NIES certified reference material program

Material	Content	Status
No. 1 Pepperbush	14 g/bottle	certified for 16 elements
No. 2 Pond Sediment	20 g/bottle	certified for 13 elements
No. 3 Chlorella	36 g/bottle	certified for 9 elements
No. 4 Freeze-dried Human Serum	10 vials/package	analysis in progress
No. 5 Human Hair	2 g/vial	certified for 13 elements
No. 6 Mussel	10 g/bottle	certified for 14 elements
No. 7 Tea Leaves	22 g/bottle	certified for 11 elements
No. 8 Vehicle Exhaust Particulates	7 g/bottle	certified for 16 elements
No. 9 Sargasso	10 g/bottle	analysis in progress
No. 10 Rice Flour—Unpolished	set of 3 bottles (60 g each)	analysis in progress

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Table 2 Analytical values for NIES certified reference material No. 8 "Vehicle Exhaust Particulates"

Certified values			
Minor constituents	Content (wt., %)*	Trace constituents	Content (μg/g)*
Ca[a,c,e]	0.53±0.02	Pb[a,c,d]	219±9
Al[a,c,e,g]	0.33±0.02	Sr[a,c,e]	89±3
Na[a,b,c,e]	0.192±0.008	Cu[a,c,d,e]	67±3
K[a,b,c,e]	0.115±0.008	Cr[a,c,e]	25.5±1.5
Zn[a,c,d,e]	0.104±0.005	Ni[a,c,d,e]	18.5±1.5
Mg[a,c,e]	0.101±0.005	V[a,c,e,f]	17±2
		Sb[a,c,e]	6.0±0.4
		Co[a,c,e,f]	3.3±0.3
		As[a,c,e]	2.6±0.2
		Cd[a,c,d,e]	1.1±0.1

Analytical techniques used: a, atomic absorption spectrometry; b, flame emission spectrometry; c, inductively coupled plasma emission spectrometry; d, isotope dilution mass spectrometry; e, neutron activation analysis[6]; f, spectrophotometry; g, spectrofluorimetry.

Reference values (μg/g)*					
P	510	Se	1.3	Ag	0.20
Br	56	La	1.2	Sm	0.20
Mo	6.4	Sc	0.55	Eu	0.05
Rb	4.6	Th	0.35	Lu	0.02
Ce	3.1	Cs	0.24		

* On an "as received" basis.

several bottles indicated that the prepared material was not sufficiently homogeneous for certain elements, due mainly to deposition of water-soluble inorganic constituents onto the surface during the drying process. Therefore, re-mixing of the material was carried out: all samples were combined together into a 30 l polyethylene bottle and mixed by rolling the bottle on a ball-mill apparatus for 2 h. The mixed powder was packaged again into about 1000 glass bottles (7 g each).

A homogeneity test of the final product was performed by inductively coupled plasma emission and atomic absorption analyses for the acid-solutions of the samples. Six bottles were randomly selected from the lot of 1000 bottles and 5 aliquots (about 300 mg) were taken from each bottle. The homogeneity of the Vehicle Exhaust Particulates was determined using one-way analysis of variance. For the elements, Al, Ca, Cd, Co, Cr, Cu, K, Mg, Na, Ni, P, Pb, Sr, V and Zn, variations between bottles were estimated to be less than 1% as relative standard deviation. However, for Fe, Mn and Ti, between-bottle variations were significant, though the reason for this has not been identified.

Collaborative studies on the elemental analysis of the Vehicle Exhaust Particulates sample have been performed by 20 participating laboratories using various analytical techniques. Table 2 shows the certified and reference values for NIES Vehicle Exhaust Particulates reference material. The certified values are based on results of determinations by at least three independent analytical techniques. Technical considerations and statistical outlier tests were first applied and the certified value is the mean of the acceptable values. Certified values are provided for Al, As, Ca, Cd, Co, Cr, Cu, K, Mg, Na, Ni, Pb, Sb, Sr, V and Zn, while reference values are reported for Ag, Br, Ce, Cs, Eu, La, Lu, Mo, P, Rb, Sc, Se, Sm and Th. The elemental composition of NIES Vehicle Exhaust Particulates CRM is considered typical of automobile emission particulates. Further details of preparation, analysis and certification of this reference material will be described elsewhere. The NIES Vehicle Exhaust Particulates CRM is available in bottles containing 7 g on request from NIES.

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