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NIES Certified Reference Material "Vehicle Exhaust Particulates"

The National Institute for Environmental Studies (NIES) announces the availability of NIES Certified Reference Material No.8 "Vehicle Exhaust Particulates"

In spite of the greatly increasing demand for reference materials of air particulate matter, the availability of reference materials of such materials has been limited, probably due to difficulty in collection of sufficient quantities. The "Urban Particulate Matter" Standard Reference Material 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 has been issued by NBS for use in analysis of polyaromatic hydrocarbons (PAHs). 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 NIES Vehicle Exhaust Particulates reference material was prepared from particulate matter collected from electrostatic precipitators in huge ventilators connected to a highway tunnel. The particulate matter was mixed making a paste with 35 % ethanol, air-dried, oven-dried, made into fine powder, sieved and finally homogenised in a polyethylene container on an ball-mill apparatus. The bottles contain about 7 grams of material. The prepared material contains about 80% of carbon, together with relatively low levels of Al, Ca and heavy metals.

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 is considered typical of automobile emission particulates.

Preparation of Material

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 fliters and preliminary analysis demonstrated that the contribution from pavement material was small. About 7 kg of the material were used for the preparation of this reference material. During preparation, special care was taken when handling such a large amount of potentially hazardous 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.

We examined the following three methods to produce homogeneous and easy-to-handle material. First, we examined a "tablet" method to bind the material under pressure, but there were difficulties in producing identical tablets and there was a contamination problem due to the binders. Next, we examined a "sedimentation granules" method by suspending the material in a 35 % ethanol solution but in this case leaching of inorganic constituents from the material was significant. Finally, we adopted a "paste-granules" method by making a paste with 35% ethanol. About 300 g of the material and 1 litre 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 ℃ for about 5 days and crushed into a fine powder in polyethylene bags with a wooden hammer. After passing through a 2-mm nylon screen, the powder was packaged into about 1000 glass bottles.

At this stage, a homogeneity test using 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 hr. The mixed powder was packaged again into about 1000 glass bottles (7 g, each).

Homogeneity Assessment

A homogeneity test of the final product was performed by inductively coupled plasma emission and atomic absorption analyses following acid-dissolution 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 (total 30 samples).

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 and V, variations between bottles were not significant. However, for Fe, Mn and Ti, between-bottle variations were significant, though the reason for this has not been identified.

Certified Values

The certified values are based on results of determinations by at least three independent analytical techniques. The uncertainties of the certified values were estimated based on consideration of 2 times the standard deviation of the mean of the acceptable values, and of the 95 % confidence intervals for the mean of individual methods.

Instructions for Use

(a) Sampling

Before sampling, mix the material well by vigorously shaking the bottle for about 1 min. Use a minimum sample weight of 300 mg for a single analysis. When a finer powder is required for analysis, transfer the content to an agate mortar and grind.

The material readily adheres to the wall of glass and Teflon vessels by electrostatic attraction and care should be taken in transfer operations.

(b) Basis of analytical data

Analytical results should be based on an "as received" basis without drying the sample. After usage, close the inner cap of the bottle tightly and keep the bottle in a silica-gel desiccator.

(c) Sample dissolution

This reference material contains siliceous material. The certified and reference values are based on analyses performed on the entire sample. Therefore, decomposition procedures should be designed to achieve complete dissolution of the material such as by the use a mixture of nitric/perchloric/hydrofluoric acids.

In our experience it was necessary to heat the sample at around 200 ℃ in the presence of perchloric acid to dissolve the material completely. Hydrofluoric acid was also added after the digestate became a clear yellow colour.

Analytical Values for NIES Certified Reference Material
No. 8 "Vehicle Exhaust Particulates"

Certified Values

Element	Content*	Elements	Content*
Minor Constituents	Wt. Percent	Trace Constituents	μg/g
		Lead[a,c,d]	219±9
Calcium [a,c,e]	0.53±0.02	Strontium [a,c,e]	89±3
Aluminum[a,c,e,g]	0.33±0.02	Copper[a,c,d,e]	67±3
Sodium[a,b,c,e]	0.192±0.008	Chromium[a,c,e]	25.5±1.5
Potassium [a,b,c,e]	0.115±0.008	Nickel[a,c,d,e]	18.5±1.5
Zinc[a,c,d,e]	0.104±0.005	Vanadium[a,c,e,f]	17±2
Magnesium [a,c,e]	0.101±0.005	Antimony[a,c,e]	6.0±0.4
		Cobalt[a,c,e,f]	3.3±0.3
		Arsenic [a,c,e]	2.6±0.2
		Cadmium [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, thermal inonization, [e] instrumental neutron activation analysis, [f] spectrophotometry, [g] spectrofluorimetry

Reference Values

	μg/g		μg/g
Phosphorus	510	Scandium	0.55
Bromine	56	Thorium	0.35
Molybdenum	6.4	Cesium	0.24
Rubidium	4.6	Silver	0.20
Cerium	3.1	Samarium	0.20
Selenium	1.3	Europium	0.05
Lanthanum	1.2	Lutetium	0.02

* On an "as received" basis (see "Instructions for Use").

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