Preparation of the particulate sample for calibration
of inter-laboratory analysis

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Abstract : A procedure for preparing the particulate sample for calibration of the results of inter-laboratory analysis has been proposed.

A large amount of the dust, that was collected from the filter attached to the air conditioning unit fixed on the roof of an office building, was mixed and riffled to obtain the homogeneous dust mixture. Homogeneity of the mixture was statistically examined by treating the analytical data of the aliquots. Evaluation was made by comparison of the variance due to analytical error and inhomogeneity to that of analytical error ; the prepared sample was distributed to six laboratories and analyzed by neutron activation analysis, atomic absorption spectrometry, and X-ray fluorescence analysis, and the results are shown for 35 elements.

Standard reference samples are useful to compare analytical procedure and analytical results of inner- and inter-laboratory study. There are many kinds of the standard reference samples of high quality, i.e., G-2 and W-1 of the U.S. Geological Survey. These standard samples are widely distributed over the world and their analytical data are collected and systematically examined. These samples include various materials : rocks and minerals, soils, foodstuffs and even biological substances in their stable forms. However, atmospheric samples, which are recently required to have been assayed, are not contained in these series of standards, probably because of the wide variety of the sample quality.

There was a requirement to prepare a common sample for analytical study of airborne particulate matters, and an investigation was made on the method of preparation of the common sample.

Particulate matters existing in the atmosphere of urban districts are mostly less than 100 $\mu g/m^3$, and we only get milligrams of samples by filtration of $100 m^3$ of air even in the heavily polluted areas. This amount is not sufficient to prepare samples to suit our purpose of preparing a large amount of uniform sample. Therefore, we decided to use the dust collected from a filter at an air inlet of a large office building.

The dust collected was dried and mixed well, and the degree of mixing was examined by statistical techniques. An estimate of the uniformity of the sample was made by a comparison of the variance of analytical and mixing errors, $V_{anal+mix}$, and the variance of analytical errors, V_{anal} of the analytical data of the sample. The sample is regarded as statistically uniform when the value defined by the next formula becomes unity, so there is no significant difference between two variances questioned, which also means no increase of analytical errors due to inhomogeneity of the samples.

$$F = V_{anal+mix} / V_{anal} \qquad (1)$$

Experimental

About 6 kg of the dust precipitated on a

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cloth filter attached to an air inlet of an air conditioning unit, which was placed on the roof of an office building of some 50 m high, was collected by a vacuum cleaner for home use. The collected dust was carried to our laboratory in a polyethylene bag. 2 kg of the dust was dried in an oven of $105 \pm 5°C$ for one hour and sieved through the standard sieves of 50, 100, and 200-mesh sieves, and it was again dried in an oven under the same conditions for about one hour, by levelling the dust powder in a vat to about 1 cm thickness.

The dried powder was put into a 5-litre polyethylene bottle with a large mouth, and mixed by rotating the bottle enclosing the stirring bodies in it : one hundred of 25 mmϕ balls of 34 g each, and twenty of 25 mm$\phi \times$ 25 mm cylinders of 22.5 g each, both covered with polyurethane film.

The degree of mixing was examined by chemical analysis of the six aliquots of each sample taken from the mother body before mixing, 3 hrs and 6 hrs after the start of mixing. The coefficients of variations of the analytical data for zinc in the samples were 4, 3, and 1 to 2%, respectively, and no improvement was seen for the samples longer than 6 hrs mixing. The stirring time, therefore, was decided as 10 hrs for the sample preparation.

For further mixing, the following procedures were repeated four times, i.e., the powder was divided into two equal parts by a riffle, and half of each part was spread one over the other in a large vat to form four layers from the bottom to the top, and th surface of the layer was divided into 16 equal parts for the repeated riffling procedures. By four repeated cycles of this procedure, the sample powder is to be divided into 1.7×10^7 parts theoretically, hence if the original dust powder was 1 kg in weight, one single division by this riffling is to be some 60 μg.

The prepared sample was named for convenience as AS-1, and was statistically examined for homogeneity by the data obtained by chemical analysis of the sample.

100 mg of AS-1 was first extracted, in a 250 ml Erlenmeyer flask with a reflux con-

densor, with nitric acid (1+1) by direct heating for 30 min. Add 3 ml of hydrogen peroxide and heat another 30 min. The residue was filtered off from the extract through a filter paper (No. 5c, Toyo Roshi Co.) and filled up with water to a mark in a 100 ml volumetric flask. The solution was then analyzed by atomic absorption spectrometry employing the Varian-Techtron AA-5 instrument.

Two series, A and B, of samplings of the aliquots were made for statistical evaluation of AS-1. In series A, the 100 mg aliquots were taken randomly from the whole sample, while series B consisted of the pairs of 100 mg aliquots taken from 0.3 g of the 'very carefully mixed' samples ; the 0.3 g part of AS-1 was taken by the same procedure as in series A, and mixed again for three minutes 'thoroughly' by a vibrational mixer (Spex Mixer-Mill, No. 5100).

Results and discussion

If we assume the aliquots of series B are mixed 'throughly', and if, also, errors of analysis are the same for both series, the difference of the errors of A and B series

Table 1 Analytical results of the aliquots of series A by atomic absorption spectrophotometry (μg/g)

No. of aliquot	Element	Zinc ($\times 10^3$)	Copper ($\times 10^2$)	Lead ($\times 10^3$)	Manganese ($\times 10^3$)
X_1		3.13	3.5	2.6	1.07
X_2		3.11	3.4	2.6	1.06
X_3		3.10	3.3	2.7	1.09
X_4		3.05	3.4	2.6	1.08
X_5		3.09	3.6	2.6	1.10
X_6		3.03	3.4	2.6	1.08
X_7		2.96	3.3	2.6	1.08
X_8		2.97	3.5	2.8	1.06
X_9		2.98	3.5	2.6	1.10
X_{10}		3.00	3.4	2.7	1.09
$\bar{x}$		3.04	3.4	2.7	1.08
V*		3970	99	4900	210
c.v. (%)		2.1	2.8	2.6	1.3

$$* \ V = \sum_{i=1}^{n} (x_i - \bar{x}^2)/(n-1)$$

will show the degree of uniformity of the mother body. For this comparison, the principle of analysis of variance (equation 1) was applied, in which F values of the analytical data were compared with $F_{\phi_2}^{\phi_i}(\alpha)$ from the F distribution table at significance

Table 2　Analytical results of the aliquots of series B by atomic absorption spectrophotometry $(\mu g/g)$

No. of aliquot	Zinc $(\times 10^3)$	Copper $(\times 10^3)$	Lead $(\times 10^3)$	Manganese $(\times 10^3)$
X_{11}	3.06	3.7$_6$	2.5$_6$	1.11
X_{12}	3.10	3.7$_6$	2.6$_6$	1.10
X_{21}	3.05	3.7$_9$	2.6$_6$	1.10
X_{22}	3.15	3.6$_2$	2.5$_8$	1.09
X_{31}	3.11	3.5$_5$	2.5$_6$	1.09
X_{32}	3.02	3.4$_8$	2.5$_8$	1.10
X_{41}	3.01	3.4$_4$	2.7$_1$	1.10
X_{42}	2.96	3.6$_1$	2.6$_4$	1.10
X_{51}	3.02	3.4$_7$	2.5$_9$	1.11
X_{52}	2.97	3.3$_4$	2.6$_2$	1.10
X_{61}	2.99	3.3$_4$	2.5$_8$	1.08
X_{62}	3.01	3.3$_9$	2.6$_2$	1.08
X_{71}	3.01	3.5$_5$	2.5$_7$	1.11
X_{72}	2.97	3.4$_8$	2.5$_9$	1.10
X_{81}	3.07	3.4$_8$	2.6$_2$	1.10
X_{82}	2.94	3.4$_8$	2.6$_2$	1.08
X_{81}	2.94	3.5$_9$	2.5$_9$	1.09
X_{82}	2.99	3.3$_5$	2.5$_8$	1.10
$X_{10\ 1}$	3.04	3.4$_6$	2.1$_1$	1.06
$X_{10\ 2}$	3.01	3.4$_7$	2.5$_0$	1.0$_7$
$\bar{R}*$	0.06	0.08	0.05	0.09
$V**$	2680	48	1800	60
c.v.(%)	1.7	2.0	1.6	0.7

$* \ \bar{R} = \sum_{i=1}^{n} |x_{11} \quad _{12}|/n$

$** \ \sqrt{V} = \bar{R}/c$, where $c = 1.16$

Table 3　Analysis of variances for the atomic absorption data

Element	$V_{anal+mix}$	V_{anal}	Variance ratio(F)*
Zinc	3970	2680	1.48
Copper	90	48	1.9
Lead	4900	1800	2.7
Manganese	210	60	3.5

$* \ F_9^9(0.05) = 3.18, \quad F_9^9(0.01) = 5.35$

Table 4　Analytical results of AS-1 (individual aliquot) by instrumental neutron activation analysis* $(\mu g/g)$

No. of aliquot	Aluminum $(\times 10^4)$	Chlorine $(\times 10^4)$	Vanadium $(\times 10^2)$
X_1	5.14	3.56	2.9
X_2	5.58	3.34	2.9
X_3	5.45	3.15	2.9
X_4	5.48	3.21	3.0
X_5	5.60	3.31	2.7
X_6	5.73	3.31	3.0
X_7	5.66	3.42	3.0
X_8	5.67	3.26	2.8
X_9	5.79	3.32	3.1
X_{10}	5.56	3.12	3.0
$\bar{x}$	5.57	3.31	2.9
$V**$	3.34×10^6	1.79×10^6	134
c.v.(%)	2.3	4.0	4.0

* T. Mamuro (Radiation Center of Osaka Prefecture)

$** \ V = \sum_{i=1}^{n}(x_i - \bar{x}^2)/n-1$

Table 5　Analytical results of AS-1 (repeated analysis) by instrumental neutron activation analysis* $(\mu g/g)$

No. of analysis	Aluminum $(\times 10^4)$	Chlorine $(\times 10^4)$	Vanadium $(\times 10^4)$
X_1	5.74	3.34	2.8
X_2	5.49	3.29	2.8
X_3	5.36	3.40	2.8
X_4	5.39	3.35	3.0
X_5	5.44	3.37	3.0
$\bar{x}$	5.48	3.37	2.9
$V**$	2.29×10^6	5.73×10^5	120
c.v.(%)	2.8	2.4	3.8

* T. Mamuro (Radiation Center of Osaka Prefecture)

$**V = \sum_{i=1}^{n}(x_i - \bar{x})^2/n-1$

Table 6　Analysis of variances for the data of neutron activation analysis*

Element	$V_{anal+mix}$	V_{anal}	Variance ratio(F)**
Aluminum	3.34×10^6	2.29×10^6	1.46
Chlorine	1.79×10^6	5.73×10^5	3.12
Vanadium	134	120	1.12

* T. Mamuro (Radiation Center of Osaka Prefecture):

$** \ F_4^9 \ (0.05) = 6.00$

Table 7　Results of inter-laboratory analysis of AS-1 (μg/g)

analytical method	INAA[a]	INAA[b]	NAA[c]	INAA[d]	XF[e]	AAS[d]	ASS[f]
element							
Ag	3	3.7					
Al	38000	56000	56000	53000			
As	60	43					
Au	0.09		0.42	0.4			
Ba		680		150			
Br	350	350		350			
Ca		65000	56000	59000			
Cd						19	19
Ce		33		28			
Cl		33000	34000				
Co	23	30	30	17			
Cr	370	360	330	340	300		
Cs	3.8	4.1					
Cu		600		370	2100	340	320
Eu		0.8		0.9			
Fe	47000	48000	39000	42000	47000	43500	44400
Ga				14			
Hf	3.3	3.4					
Hg	9			4			
K		9700		9300			
La	21	17		13			
Lu		0.3					
Mg		20000	16000	23000			
Mn	1200	1900	1300	1300	900	1080	
Na	12000	15000	13000	15000			
Ni		250		160	200	175	164
Pb					1800	2640	2030
Rb		45					
Sb	39	44	29	43			
Sc	12	8.6	12	9.5			
Se	2		16	10			
Sm	3.2	3.6					
Ta		1.2					
Th	3.9	6.2					
Ti		5600	4500	4300	2900		
V	200	290	240	270	100	300	
W	3.2	28		34			
Zn	2800	3800	4100	3300		3040	

INAA: Instrumental neutron activation analysis, NAA: Neutron activation analysis,
XF: X-ray fluorescence analysis, AAS: Atomic absorption spectrophotometry,
a) Japan Atomic Energy Research Institute, b) Radiation Center of Osaka Prefecture, c) Atomic Energy Research Institute, Rikkyo University, d) Faculty of Engineering, Keio University, e) Keihin Branch, Kanagawa Prefectural Environmental Center, f) Japan Environmental Sanitation Center.

level, α, and degrees of freedom of ϕ_1 and ϕ_2. Hypothesis H_0 which predicts no significant difference presents between $V_{anal+mix}$ and V_{anal} is evaluated in the following criteria ;

(1) Hypothesis H_0 is rejected if $F \leq F_{\phi_2}^{\phi_1}(\alpha)$

(2) Hypothesis H_0 is rejected if $F > F_{\phi_2}^{\phi_1}(\alpha)$

The analytical data of series A aliquots are shown in Table 1. The coefficient of variations of the analytical results of zinc, copper, lead, and manganese are 2.1, 2.8, 2.6 and 1.3 %, respectively, and variance $V_{anal+mix}$, is shown at the second line from the bottom. Analytical results, coefficients of variations, and variances of the aliquots of series B are shown in Table 2.

The F values of each element calculated from the analytical data are shown in Table 3 ; those of zinc, copper, lead, and manganese are 1.5, 1.9, 2.7, and 3.5, respectively. $F_9^9(0.05)$ cited from the F distribution table is 3.18 for 5 % significance level, so the hypothesis H_0 is accepted for zinc, copper, and lead. The F value of 3.5 for manganese is rejected as it exceeds 3.18 slightly, but it is accepted for 1 % significance level $F_9^9(0.01) = 5.35$.

Therefore, the homogeneity of the AS-1 sample has been proved by statistical treatment of the analytical results atomic absorption spectrophotometry.

Homogeneity of the AS-1 sample was also examined by instrumental neutron activation analysis at Radiation Center of Osaka Prefecture (Mamuro, 1975). The analytical data for ten individual aliquots and those of five repeated determinations of one aliquot are shown in Table 4 and 5, respectively. With these data, F values of aluminum, chlorine, and vanadium are 1.46, 3.12, and 1.12, respectively, all of which are smaller than 6.00 for $F_4^9(0.05)$, concluding the acceptance of the hypothesis H_0, i.e., statistical homogeneity (Table 6).

The AS-1 sample thus prepared was distributed to several laboratories for levelling reliability of the analytical data. The results are shown in Table 7.

Due to the hygroscopic property of the AS-1, it must be kept in a controlled atmosphere of 50 % humidity at 25°C, at least for 24 hrs before weighing. This can be done in a desicator whose atmosphere is equilibrated with 43.2 wt % of sulfuric acid at 25°C. The AS-1 equilibrated in the atmosphere of 50 % humidity increases its weight by 0.15 % in 30 min. To minimize the effect of inhomogeneity, the AS-1 has to be sampled at least 100 mg or more as an aliquot.

Conclusion

An atmospheric sample for calibration of analytical procedures and tools was tentatively prepared, and it was shown that the proposed procedure for preparation of the homogeneous sample is usable for evaluation of the analytical results of the environmental samples.

Acknowledgement

Literature cited

T. Mamuro et al.: Radioisotopes 24, 47 (1975).

大気中の金属分析のクロスチェック
用共通試料作成について

及川紀久雄（日本環境衛生センター技監室）
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大気浮遊粒子状物質中の金属成分の分析に関して，分析方法のチェックおよび分析所間の分析値のクロスチェックのための標準試料作成方法の検討を行った．

すなわち，著者らは大型ビルディングの屋上の空調装置のエアフィルターから大量の粒子状物質を採取し，これから標準試料を作成することとした．得られた粒子状

物質を乾燥後，縮分器を用いて分割混合したのち，原子吸光分析法によって分析し，その分析値について検定を行ったところ，1％の有意水準において均一性が認められた．

　また，6か所の分析機関において放射化分析，けい光X線分析および原子吸光分析などにより，クロスチェックを行ったところ，分析値の比較を行うための標準試料として十分であることがわかった．ことに放射化分析による35種類の元素の分析値は，この標準試料の均質性のみならず放射化分析の精度のよさを示す結果となった．