

〈Technical Report〉

**Determination of Trace Elements in Airborne Particulates by  
Instrumental Neutron Activation Analysis**

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**중성자 방사화분석법을 이용한 대기분진시료의 정량**

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**Abstract**

Trace elements in airborne particulates were analyzed by instrumental neutron activation analysis (INAA) under the optimum analytical condition. Neutron irradiation for sample was done at the irradiation hole (neutron flux,  $1 \times 10^{13}$  n/cm<sup>2</sup> · s) of TRIGA MARK-III research reactor in the Korea Atomic Energy Research Institute.

For the verification of the analytical method, NIST SRM-1648 and NIES CRM No.8 were chosen and analyzed. The accuracy and precision of the analysis of 40 and 24 trace elements in the samples were compared with the certified and reported values, respectively.

The analytical method was found to be reliable enough when the analytical data of NIES sample were compared with those of different countries. In the analytical result of two or both of standard reference materials, relative standard deviation was within the 15% except a few elements and the relative error was within the 10%. We used this method to analyze 30 trace elements in airborne particulates collected with the high volume air sampler (PM-10) at two different locations and also confirmed the possibility to use this method as a routine monitoring tool to find out environmental pollution sources.

## 1. Introduction

Global environmental conditions changing rapidly and the international concern about environmental pollution is very high because of industrialization and urbanization to improve human life recently. Accordingly, a lot of effort to make comfortable living environment is required. The analyses of environmental samples have been done with some methods necessitates wet chemical treatments and instrumental analytical methods such as Atomic Absorption Spectrometry(AAS), Particle Induced X-ray Emission Spectrometry(PIXE), Inductively Coupled Plasma Spectrometry(ICP), X-ray Fluorescence Spectrometry (XRF), etc. Even though highly sensitive analytical techniques for the analysis of trace components of samples are developed recently, most methods need chemical preparation, decomposition and preconcentration. Furthermore, the quantitative analyzable elements are limited. However, these problems can be easily solved by Instrumental Neutron Activation Analysis(INAA) and the fast and accurate results can be obtained nondestructively[1–3]. INAA for the airborne particulates was first developed by Dams et al [4] and Zoller et al[5] in 1970 and recently recognized as a proper method to analyze many environmental samples rapidly and accurately. It is one of a national cooperative research project of International Atomic Energy Agency(IAEA). Analysis of environmental samples have been actively promote to standardize the analytical method and analytical quality assurance[6].

Due to the differences in nuclear properties of the stable isotopes, sensitivities and detection limits are vary from a kind of element. For instance, elements such as Al, As, Ca, Sc, Sb, In, Mn, Se, Na, V, Zn, halides and many rare-earths were easily detected by neutron activation methods with good precision. On the other hand non-destructive analysis of elements such as Cd, S, and Pb were difficult or impossible. Typically 30–40 trace elements in airborne particulates can be determined in ppm level. When specific

elements are abnormally high, air pollution sources [7] could be identify by enrichment factor[8] and receptor model[9], and this results can be used to establish a more effective plan to air pollution. For this emission source studies, a continuous collection of comprehensive analytical data should be required. The qualification program is proved as a useful tool to the reasonable result and improve the accuracy and precision of analytical method with standard reference materials[10].

In this study, investigated element components in environmental samples by non-destructive thermal neutron activation analysis. The analytical methods of airborne particulates can be established from the National Institute of Standards and Technology, U.S.A. (NIST) standard reference material(SRM 1648) and National Institute for Environmental Studies, Japan (NIES) certified reference material(CRM No.8) with the precision and accuracy.

## 2. Experimental

### 2.1. Sampling and Sample Preparation

Standard reference materials : To identify the analytical process and comparative analysis, standard sample(NIST SRM 1648, urban particulate matter and NIES CRM No.8, urban dust) were chosen. Standard samples were pretreated according to NIST recommendation. The samples were dried at 105°C for 8 hours before use and cooled at room temperature in the desiccator. 10–100mg of samples were weighed and removed in polyethylene vial and heat sealed. The high pure polyethylene vial was pre-washed with spectro grade dilute nitric acid and acetone and performed the blank test to identify the impurity concentrations.

**Collection of airborne particulates :** For the collection of airborne particulates, we selected two sites, the outer region of Seoul and Wonju and installed the PM 10 sampler(high volume air sampler, KIM-OTO, Japan, Model 121) according to the recom-

mended method. Atmospheric conditions such as temperature, humidity, wind direction, wind velocity and the change of weather condition were recorded regularly during the sample collection for calibration. The flow rate of sampler was adjusted to  $1500 \pm 50$  l/min and collected for 24 hours. The total volume of air sampled through the filter was calculated as following.

$$V = 1/2(F_i + F_f) \times 0.001T \quad (1)$$

where,  $V$  = Total volume of air sampled through the filter ( $m^3$ )

$F_i$  = Initial air flow rate(l/min),

$F_f$  = Final air flow rate(l/min)

$T$  = Sampling period(min)

The filter used high purity silica fiber(ADVANTEC, Toyo, QR100,  $8'' \times 10''$  size) and has low pressure drop before and after filtering and have a high collection efficiency. The impurity concentration of the filter was determined for subtract blank value from total value. To find out the periodic change of the concentration, sample was collected day and night at every week. Collected samples were stored 24 hours in a controlled atmosphere( $25^\circ C$ , 50% relative humidity) and removed polyethylene vial after weighed at the same condition and cutted regular size( $25 \times 100$  mm).

## 2.2. Sample Irradiation

Samples were irradiated with thermal neutrons from TRIGA MARK-III research reactor in the Korea Atomic Energy Research Institute. Pneumatic Transfer System( $PTS \phi = 1.2 \times 10^{13} n/cm^2 \cdot s$ ) was used for short time irradiation and Rotary Specimen Rack ( $RSR \phi = 3.0 \times 10^{12} n/cm^2 \cdot s$ ) for medium and long time irradiation. Samples were irradiated at the same geometric position to minimize the geometry error. Commercial activation wires(Au, Cu, Mn, R/X activation wire, 99.99% purity, Reactor Exp. Inc.) used to monitor the thermal and epithermal neutron flux.

The analytical condition was optimized considering the preliminary results.

## 2.3. Radioactivity Measurement

Gamma-ray spectrum and the activity of samples irradiated with neutrons were obtained with the following equipments. The head part of the high pure germanium semi-conductor detector(EG&G ORTEC, GMX-25190P) was surrounded with 10cm thick lead shielding box( $75 \times 90 \times 90$  cm) lined inner wall with 0.1cm Cd and Cu plate to minimize influence of external radiation, interaction with surrounding material and  $\gamma$ -radiation. Detector is coaxial type with 25% relative efficiency and 1.9 keV resolution(FWHM) at 1332 keV of  $^{60}Co$  and peak to Compton ratio is 45 : 1. Detector was connected with the personal computer and 8K-multichannel analyzer(EG&G ORTEC, 919A MCB, Maestro-II) for activity measurement and data analysis. Energy and efficiency calibration were done with the radioactive multi nuclide reference source(NEN Products Inc., NES-602, 1" diameter disc type) certified by NIST. Dead time of detector was maintained below 5%. Decay and pile up correction were done automatically[11].

## 2.4. Data Treatment

—Calculation of elemental concentration : Concentration of elements were calculated with the new fortran code for rapid and simple data treatment after obtained the  $\gamma$ -ray spectrum under the presetting analytical condition. Peak area obtained via Covell method[12] from  $\gamma$ -ray activity and the following equations (2) and (3) applied the nuclear data[13, 14].

$$W = A \cdot M / \phi \cdot \sigma \cdot N_A \cdot a \cdot \epsilon \cdot b \cdot (1 - e^{-\lambda}) e^{-\lambda t_d} \quad (2)$$

where,  $W$  : weight of interest element, g

$N_A$  : Avogadro's Number,  $6.025 \times 10^{23}/mol$

$A$  : Induced radioactivity of sample

irradiated, cps  
 $M$  : Atomic weight of interest element, g/mol  
 $a$  : Isotopic abundance  
 $b$  : Specific  $\gamma$ -ray emission probability  
 $\Phi$  : Thermal neutron flux, n/cm<sup>2</sup>s  
 $\sigma$  : Thermal neutron cross section,  
 barn =  $10^{-24}$  cm<sup>2</sup>  
 $\varepsilon$  : Relative counting efficiency of the detector, cps/dps  
 $\lambda$  : Decay constant,  $\ln 2/T_{1/2}$   
 $T_i$  : Irradiation time  
 $T_d$  : Cooling time

Because, the same irradiation and counting conditions of standard materials are applied the comparative method,  $\Phi$ ,  $\sigma$ ,  $N_A$ ,  $a$ ,  $M$  are constant in the equation (2). Therefore, errors from the uncertainties of nuclear data, neutron flux, etc. can be minimized after just compared the activity of the sample and the standard material via equation (3).

$$W_x = W_{STD} \{A_x/A_{STD} (f e^{-\lambda T_d} e^{-\lambda \Delta T_d})\} \quad (3)$$

where, subscript  $STD$  and  $x$  stand for the standard reference material and the sample, respectively, and a terms in parenthesis is the correction factor for short half-life nuclide (cooling and counting time correction).

— **Detection limit** : Detection limit largely affected by the interaction between nuclides and composition, concentration of elements [15]. The detection limits were calculated with the following Currie's definition [16].

$$\text{Detection Limit} = (K_Q^2/2)[1 + \{1 + (4B/K_Q^2)\}^{1/2}] \quad (4)$$

where,  $B$  is the total count of natural background which include the natural activity, scattering, and electronic noise, etc. and  $K_Q$  is the value of 100 divided by allowable uncertainty in %.

### 3. Results and Discussion

#### 3.1. Estimation of the Analytical Conditions and Detection Limits

The analytical conditions such as neutron flux, irradiation facilities, irradiation time, cooling time and counting time are important factors to determine detection limits, analytical accuracy and precision because the elemental composition in samples are diverse in simultaneous multi-elemental analysis at trace level. Instrumental and analytical condition must be set with the extra efforts in case of the analysis of airborne particulates where many elements are coexisting at trace level. The analytical conditions for the elements are presented in Table 1. The detection limits and Signal to Noise ratio in which obtained under established analytical conditions are presented in Table 2.

The detection limits are greatly influenced by the interference between the nuclides and elemental composition. The detection limits were calculated by Currie's definition allowable 10% uncertainty which included the systematic errors and statistic error. The

Table 1. The Optimum Condition for the Analysis of Environmental Samples.

Irradiation facility	neutron flux (n/cm <sup>2</sup> . sec)	Sample weight	Irradiation Time	Cooling Time	Counting Time	Element detected
PTS	$1 \times 10^{13}$	5–10 mg	2 m	10 m	300 s	Al, Ba, Br, Ca, Cl, Cu, Dy, I, In, Mn, Na, Ti, V
RSR	$3 \times 10^{12}$	50–100 mg	10 h	5–7 d	2000 s	As, Au, Ba, Br, Cd, K, La, Lu, Mo, Na, Sb, Sm, U, W, Zn
"	"	"	10 h	15–30 d	4000 s	Ag, Ce, Cr, Cs, Co, Eu, Fe, Hf, Hg, Lu, Nd, Rb, Sb, Sc, Se, Ta, Tb, Th, Tm, Yb, Zn

Table 2. Nuclear Properties and Detection Limits of Radioisotopes Used.

Element	Isotopes	Half-life	Gamma energies used, (keV)	Detection limit (ppm)	S/N ratio
<b>Short-lived isotopes</b>					
Al	Al-28	2.24 m	1778.9	5.6E + 02	52.45
Ba	Ba-139	83.3 m	165.9	2.1E + 03	0.08
Br	Br-80	17.7 m	616.2	1.9E + 02	0.72
Ca	Ca-49	8.72 m	3084.4	1.8E + 04	—
Cl	Cl-38	37.3 m	1642.4, 2167.8	1.2E + 03	11.62
Cu	Cu-66	5.1 m	1039	1.6E + 03	0.22
Dy	Dy-165	2.33 h	94.7	9.6E + 00	0.07
I	I-128	25.0 m	442.3	1.1E + 02	0.11
In	In-116m	54.2 m	416.9, 1097.3	3.6E + 00	0.10
Mn	Mn-56	2.58 h	846.7, 1810.7	8.8E + 01	10.23
Na	Na-24	15.02 h	1368.4, 2754.1	1.4E + 03	12.32
Ti	Ti-51	5.76 m	320.1	2.4E + 03	0.49
V	V-52	3.76 m	1434.2	2.3E + 01	2.57
<b>Medium-lived isotope</b>					
As	As-76	26.3 h	559.1	9.5E + 01	1.54
Au	Au-198	2.7 d	411.8	4.3E - 02	0.03
Ba	Ba-131	11.7 d	123.8, 496.3	1.2E + 03	0.18
Br	Br-82	35.3 h	554.3, 776.5	9.7E + 01	2.82
Cd	In-115m	53.5 h	336.3	4.5E + 02	0.05
K	K-42	12.38 h	1524.7	1.3E + 04	1.20
La	La-140	40.23 h	487.0, 1596.2	4.6E + 01	12.28
Lu	Lu-177	6.7 d	208.4	1.5E + 00	0.08
Mo	Mo-99	66.9 h	140.5	4.5E + 01	0.03
Na	Na-24	15.02 h	1368.4, 2754.1	4.0E + 03	21.80
Sb	Sb-122	2.72 d	564.1	7.2E + 00	3.76
Sm	Sm-153	46.7 h	103.2	6.0E + 00	0.92
U	Np-239	2.35 d	277.5	2.6E + 00	0.04
W	W-187	23.9 h	685.8	4.9E + 00	0.09
Zn	Zn-69m	13.9 h	438.6	5.6E + 03	0.08
<b>Long-lived isotopes</b>					
Ag	Ag-110m	252 d	657.7, 884.4	5.7E + 00	0.44
Ce	Ce-141	32.5 d	145.5	1.6E + 01	0.59
Co	Co-60	5.26 y	1173.2, 1332.5	3.4E + 00	6.13
Cr	Cr-51	27.72 d	320.1	3.0E + 01	4.26
Cs	Cs-134	2.06 y	795.6	6.3E + 00	0.16
Eu	Eu-152	12.3 y	121.8, 1407.9	6.5E - 01	5.47
Fe	Fe-59	44.6 d	1099.3, 1291.6	2.4E + 03	26.85
Hf	Hf-181	42.4 d	482.2	2.8E + 00	0.55
Hg	Hg-203	46.6 d	279.2	6.1E + 00	0.18
Lu	Lu-177m	161 d	378.5	1.5E + 00	0.08
Nd	Nd-147	10.99 d	91.4	6.8E + 01	0.08
Rb	Rb-86	18.7 d	1076.6	1.8E + 02	0.28
Sb	Sb-124	60.1 d	1691.0	1.8E + 01	25.95
Sc	Sc-46	83.8 d	889.4, 1178.0	4.9E - 01	5.29
Se	Se-75	118.5 d	264.6	2.9E + 01	0.34
Ta	Ta-182	115 d	1221.4	3.5E + 01	5.10
Tb	Tb-160	72.4 d	879.4	1.6E + 00	0.09
Th	Pa-233	27.0 d	311.9	2.9E + 00	0.71
Tm	Tm-170	129 d	84.3	4.4E + 00	0.07
Yb	Yb-169	31 d	177.0	4.7E + 00	0.09
	Yb-175	19 d	396.3	7.0E + 00	0.16
Zn	Zn-65	265 d	1115.4	1.4E + 02	16.70

S/N : Signal to Noise

detection limits of trace components were in the range of 10–0.01 ppm which were from 1/2 to 1/100 of the measured concentrations according to nuclides.

### 3.2. Blank Test of the Filter

The analytical results of the blank filters are

presented in Table 3 together with those of the other filters. The blank values of impurities are used for a correction of individual concentration.

Silica fiber filter used for the high volume sampling has lower impurities than the others as As, Cr, Mn, Zn, Fe and etc. that are important elements in the environmental pollution research using NAA method. It is prove that the silica fiber filter is appropriate for the analysis of airborne particulates.

Table 3. Elemental Composition(Blank Value, ng/cm<sup>2</sup>) of Various Filter Materials.

Element	Polystyrene (Deibag)	Cellulose ester (Millipore, 0.45 $\mu$ m)	Cellulose paper (Whatman No.41)	Glass fiber	Quartz fiber	Silica Fiber (This work)
As	—	—	—	80	1.4	0.39
Au	—	—	—	—	—	0.008
Ba	500	100	100	—	20	79.1
Br	—	—	—	—	10	3.72
Ca	300	250	140	—	3880	1270
Ce	—	—	—	—	20	3.18
Co	0.2	1	0.1	—	1.5	0.58
Cr	2	14	3	80	6	33.1
Dy	—	—	—	—	—	1.14
Eu	—	—	—	—	—	0.005
Fe	85	300	40	4000	1550	210
Hf	—	—	—	—	4	1.79
Hg	1	1	0.5	—	—	0.6
Ho	—	—	—	—	—	0.24
I	—	—	—	—	—	1.79
K	—	—	—	—	600	588
La	—	—	—	—	14	1.36
Lu	—	—	—	—	0.06	0.006
Mn	2	2	0.5	400	40	10.5
Mo	—	—	—	—	—	415
Na	—	—	—	—	12000	1346
Nd	—	—	—	—	—	0.17
Sb	1	3	0.15	30	60	0.33
Sc	—	—	—	—	0.8	0.006
Sm	—	—	—	—	1.8	1.19
Tb	—	—	—	—	—	0.15
Th	—	—	—	—	2	1.41
U	—	—	—	—	—	1.0
W	—	—	—	—	0.8	0.87
Yb	—	—	—	—	—	0.48
Zn	515	20	25	160000	10	30.1
Zr	—	—	—	—	—	60.7

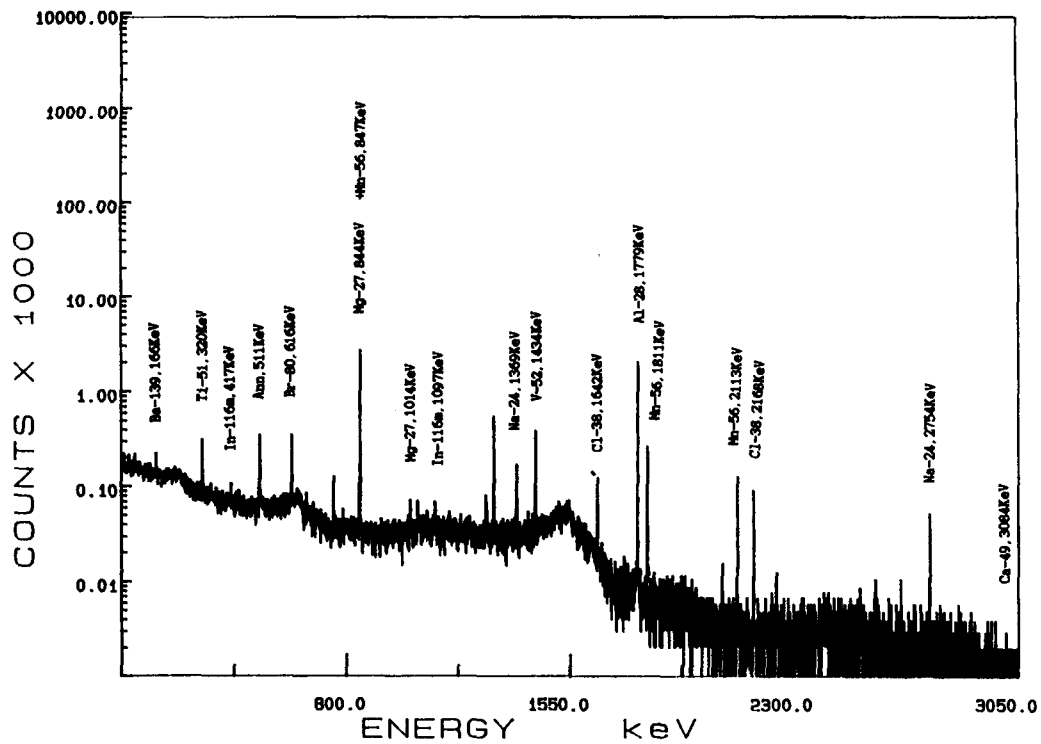


Fig. 1. Gamma-ray Spectrum of Short-Lived Nuclide for NIST SRM 1648.

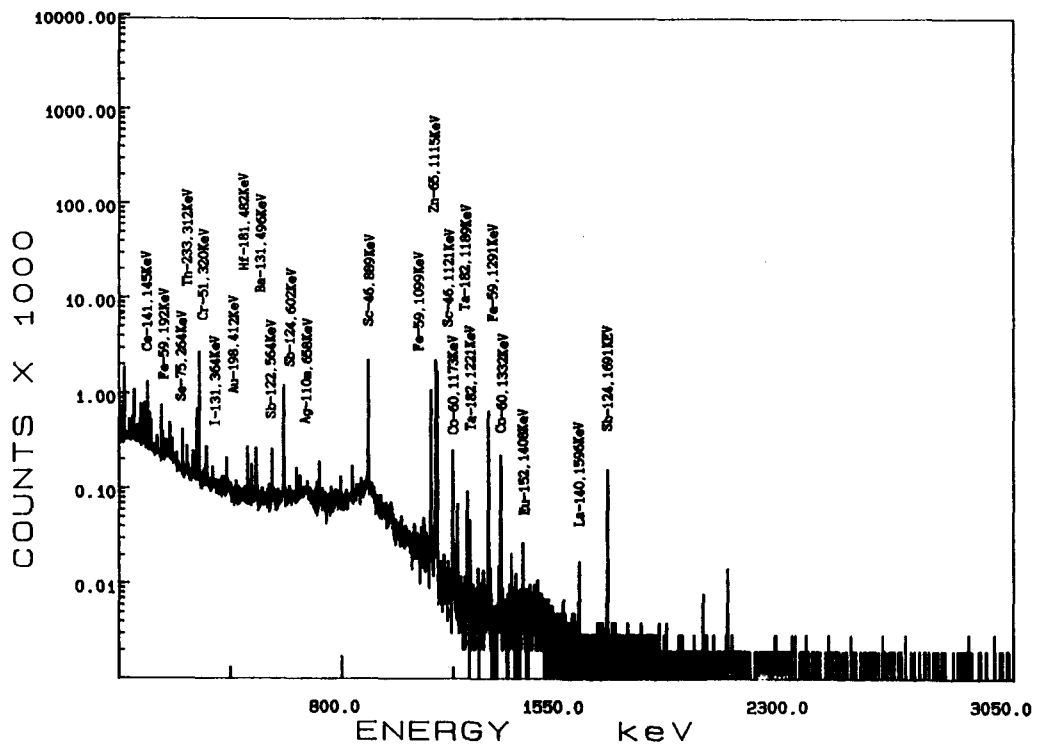


Fig. 2. Gamma-ray Spectrum of Medium and Long-Lived Nuclide for NIST SRM 1648.

Table 4. Analytical Results of Airborne Particulate Matter, NIST SRM 1648 by INAA.

Element	Nuclide	This Value, ppm		Certified Value (ppm)	Relative Error (%)
		Range	Mean (rsd, %)		
Al, %	<sup>28</sup> Al	2.42 – 3.99	3.47 (15.4)	3.42 ± 0.11	1.5
As	<sup>76</sup> As	89.7 – 146	103 (17.5)	115 ± 10	10.5
Au	<sup>198</sup> Au	0.036 – 0.069	0.05 (23)		
Ba	<sup>131</sup> Ba	610 – 894	729 (15.9)	(737)	1.0
Br	<sup>82</sup> Br	441 – 580	524 (8.5)	(500)	4.7
Ca, %	<sup>49</sup> Ca	0.588 – 0.845	0.71 (12)		
Cd	<sup>115</sup> Cd	67 – 86.1	76.6 (12.5)	75 ± 7	2.1
Ce	<sup>141</sup> Ce	41.4 – 48.6	44.9 (1.94)	(55)	18.4
Cl, %	<sup>38</sup> Cl	0.399 – 0.605	0.48 (16.6)	(0.45)	6.4
Co	<sup>60</sup> Co	16.8 – 20.5	7.62 (5.7)	(18)	
Cr	<sup>51</sup> Cr	382 – 412	397 (2.9)	403 ± 12	1.5
Cs	<sup>134</sup> Cs	2.6 – 3.6	3.1 (11.9)	(3)	3.7
Cu	<sup>66</sup> Cu	459 – 933	706 (29.8)	609 ± 27	16.4
Dy	<sup>165</sup> Dy	2.4 – 4.2	3.25 (16.8)		
Eu	<sup>152</sup> Eu	0.45 – 0.57	0.49 (10.2)	(0.8)	62
Fe, %	<sup>59</sup> Fe	3.38 – 3.82	3.60 (4.0)	3.91 ± 0.1	7.9
Hf	<sup>181</sup> Hf	4.03 – 4.83	4.34 (5.9)	(4.4)	15.5
Hg	<sup>203</sup> Hg	2.72 – 4.85	3.67 (17.2)		
I	<sup>128</sup> I	20.1 – 27.6	23.2 (12.2)	(20)	16.4
In	<sup>116m</sup> In	0.92 – 1.43	1.12 (17.9)	(1.0)	12
K, %	<sup>42</sup> K	0.96 – 1.22	1.05 (9.2)	1.05 ± 0.01	0.2
La	<sup>140</sup> La	32.4 – 36.1	34.8 (3.7)	(42)	17.2
Lu	<sup>177</sup> Lu	0.44 – 0.62	0.51 (10.5)		
Mn	<sup>56</sup> Mn	618 – 1060	845 (15.7)	(860)	1.7
Mo	<sup>99</sup> Mo	31.3 – 49.6	37.5 (17.6)		
Na, %	<sup>24</sup> Na	0.34 – 0.52	0.406 (15.2)	0.425 ± 0.002	4.5
Nd	<sup>147</sup> Nd	24.8 – 31.9	27.9 (9.4)		
Rb	<sup>86</sup> Rb	47.0 – 66.1	53.7 (13.9)	(52)	3.3
Sb	<sup>124</sup> Sb	47.5 – 58.6	53.1 (9.0)	(45)	18.1
Sc	<sup>46</sup> Sc	5.5 – 6.1	5.83 (3.3)	(7)	16.7
Se	<sup>75</sup> Se	28.5 – 44.6	36.9 (15.3)	27 ± 1	35.9
Sm	<sup>153</sup> Sm	4.8 – 5.2	5.09 (4.1)	(4.4)	15.5
Ta	<sup>182</sup> Ta	5.4 – 10.2	8.44 (17.3)		
Th	<sup>233</sup> Pa	6.6 – 8.7	7.73 (7.8)	(7.4)	4.4
Ti, %	<sup>51</sup> Ti	0.24 – 0.58	0.41 (29.3)	(0.40)	2.5
U	<sup>239</sup> Np	2.9 – 3.6	3.05 (12)	5.5 ± 0.1	44.5
V	<sup>52</sup> V	104 – 173	139 (15.9)	140 ± 3	0.7
W	<sup>187</sup> W	3.8 – 6.4	5.3 (19.6)	(4.8)	10.4
Yb	<sup>175</sup> Yb	2.21 – 3.38	3.09 (14)		
Zn, %	<sup>65</sup> Zn	0.39 – 0.63	0.433 (6.9)	0.476 ± 0.014	9.0



### 3.3. Analysis of Standard Reference Materials

**NIST SRM 1648 reference material:** The analytical procedure was identified after 42 elements were quantitatively analyzed and compared with the certified values establish a routine analytical method of the airborne particulates. Figures 1 and 2 show the  $\gamma$ -ray spectrums of the short lived, the medium and long lived nuclides, respectively.

The elemental concentrations, relative standard deviations and relative errors against certified values were calculated by the relevant equations and presented in Table 4.

After the repetitive analysis at least 5 times, the

relative standard deviations were within 15% except Au, As, Hg, In, Mo, Ta, Cu, Ti and W and these results are reasonable to the reported values[17]. The precision of analysis was reliable considering 10% statistic uncertainty of radioactivity counting. The relative errors against the certified values of the standard materials[10] were within 15% except Ce, Cu, Eu, Hf, La, Sb, Sc and U. Otherwise, Al, Ba, Cr, Cs, K, Mn, Na, Rb, Th, Ti and V are agreed within 5% and Ag, As, Cl, Fe, W and Zn within 10%.

**NIES CRM No. 8 reference material:** The analytical results of the another reference materials are presented in Table 5.

Both the absolute and comparative methods are

**Table 5. Analytical Results of Airborne Particulate Matter, NIES CRM-8 by INAA.**

Nuclide	This Value, ppm							Certified value, ppm	
	Absolute Method			Relative Method			R.E %	Mean	rsd, %
	Range	Mean(rsd, %)	R.E %	Range	Mean (rsd, %)	R.E %			
Al	Al-28	2940-3740	3380(18.5)	2.4	2140-4870	3332(28.9)	1.0	3300	6.1
As	As-76	1.96-2.62	2.36(10.7)	9.2	2.0-3.6	2.86(16.8)	10	2.6	7.7
Ba	Ba-131	49.9-217.5	129.8(44.3)		191-296	244(21.5)		-	
Br	Br-82	38.4-73.5	60.5(21)	7.9	40.7-67.5	55.8(15.7)	0.4	(56)	
Ca	Ca-49	5710-8080	6827(12.8)	29.4				5300	3.8
Ce	Ce-141	2.5-3.7	3.1(11.5)	3.1	2.7-3.6	3.17(10.3)	2.2	(3.1)	
Cl	Cl-38	1008-1290	1150(11.1)		500-1200	860(29)		-	
Co	Co-60	3.0-3.5	3.37(4.6)	3.3	2.9-3.7	3.24(16.1)	1.8	3.3	9.1
Cr	Cr-51	35.6-47.7	41.8(10.5)	25.5	30.9-38.2	34.4(7.9)	35	25.5	5.9
Fe	Fe-59	3670-5840	4656(13.2)		3700-6500	4800(17.3)		-	
Hf	Hf-181	0.17-0.21	0.19(8.7)					-	
I	I-128	1.0-1.32	1.18(10.5)		16.2-24.8	19.04(15)		-	
La	La-140	1.13-1.34	1.25(5.7)	4.2	1.1-1.5	1.37(11.3)	14	(1.2)	
Mn	Mn-56	65.3-81.3	73.8(7.1)		61.1-74.7	74.03(31)		-	
Na	Na-24	1600-2500	1917(16.4)	0.2	1500-2700	1910(19.4)		1920	4.2
Sb	Sb-124	5.2-7.8	6.81(12.4)	13.5	5.4-6.5	6.17(6.5)	28	6.0	6.7
Sc	Sc-46	0.47-0.64	0.54(8.6)	1.4	0.43-0.69	0.56(16.5)	1.8	(0.55)	
Se	Se-75	1.3-1.6	1.51(8.6)	16				(1.3)	
Sm	Sm-153	0.22-0.27	0.25(6.0)	23	0.18-0.27	0.22(13.6)	10	(0.2)	
Th	Pa-233	0.29-0.54	0.42(19)	20	0.22-0.54	0.39(26)	11.4	(0.35)	
Ti	Ti-51	294-592	411(24)		300-600	430(4.3)			
V	V-52	14-18	16.2(10.6)	4.7	11.6-24.3	17.46(76)	2.7	17	11
W	W-187	6.2-8.3	7.25(10.3)		5-9.9	7.32(33)		-	
Zn	Zn-65	834-1140	1005(11)	3.4	960-1260	1103(9.5)	6.1	1040	4.8

\* r.s.d. : relative standard deviation

R.E : relative error

Table 6. Intercomparison of Analytical Results of NIES CRM No.8 Sample by INAA.

	China	Indonesia	Japan	Malaysia	Thailand	Korea		Certified value(ppm)
						Range	Mean	
Ag	0.168–0.239	–	–	–	–	–	–	(0.20)
Al	3580–4420	4000	3600	3270	3328–3384	2940–3740	3380	3300
As	2.08–2.73	3.03–5.0	–	5.61	2.53–2.74	1.96–2.62	2.36	2.6
Au	–	–	4.5(ppb)	–	–	–	–	–
Ba	88.4–93.3	–	119	–	–	49.9–217.5	129.8	–
Br	53.2–56.4	–	58	37.25	–	38.4–73.5	60.5	56
Ca	4690–5340	–	3700	5452	–	5710–8080	6827	5300
Ce	3.23–3.61	3.4–4.6	4.9	–	–	2.5–3.7	3.1	(3.1)
Cl	362–508	–	793	1081	–	1008–1290	1150	–
Co	3.01–3.68	2.8–3.3	3.1	4.6	–	3.0–3.5	3.37	3.3
Cr	27.2–31.4	23–44	31.7	36.8	24.26–26.17	35.6–47.7	41.8	25.5
Cs	0.202–0.244	0.49	–	1.2	–	–	–	(0.24)
Cu	–	–	57	–	–	–	195.3	67
Eu	0.163–0.196	0.2–0.4	0.081	0.27	–	0.012–0.033	0.02	0.05
Fe	4650–4870	4700–6100	5364	6110	–	3670–5840	4656	–
Hf	0.148–0.167	–	0.138	–	–	0.17–0.21	0.188	–
I	–	–	3.2	–	–	1.0–1.32	1.18	–
K	1170–1400	–	–	1200	1212–1294	–	–	1150
La	1.09–1.30	1.21–2.1	–	1.32	–	1.13–1.34	1.25	(1.2)
Lu	0.0131–0.0173	–	–	–	–	–	–	(0.02)
Mg	594–1120	2000	–	972	–	–	–	1010
Mn	61.6–82.4	67–101	108	71	59–63	65.3–81.3	73.8	–
Mo	6.05–6.85	–	4.1	–	–	8.3–11.2	9.8	(6.4)
Na	1830–2070	1800–2200	1700	1912	–	1600–2500	1917	1920
Nd	0.97–1.21	–	–	–	–	–	–	–
Ni	–	–	17.6	–	–	–	–	18.5
Rb	3.48–3.72	4.5	5.5	–	–	–	–	(4.6)
S	–	–	2.1	–	–	–	–	–
Sb	5.46–5.63	5.8–8.8	7.1	6.2	5.73–6.03	5.2–7.8	6.81	6.0
Sc	0.555–0.575	0.6	0.9	0.6	–	0.47–0.64	0.54	(0.55)
Se	–	–	1.4	–	–	1.3–1.6	1.51	(1.3)
Si	–	–	–	–	18076–18542	–	–	–
Sm	0.169–0.196	0.2–0.4	–	0.27	–	0.22–0.27	0.25	(0.2)
Sr	–	–	–	–	84.04–93.88	–	–	89
Ta	–	–	1.26	–	–	–	–	–
Tb	–	–	–	2.50	–	–	–	–
Th	0.321–0.375	–	0.38	–	–	0.29–0.54	0.42	(0.35)
Ti	262–419	–	296	272	–	294–592	411	–
V	16.4–18.9	19	14	17.0	16.64–18.69	14–18	16.2	17
W	5.47–5.77	–	5.9	6.17	–	6.2–8.3	7.25	–
Yb	0.0641–0.0860	–	–	–	–	–	–	–
Zn	970–1120	930–1900	970	1348	–	834–1140	1005	1040

used and compared each other. The comparative method produces more accurate results as expected because reduced the uncertainty caused by nuclear data itself, and neutron flux changes. The relative errors to the certified values and the present values [10] are well agreed in a range of 3–11%.

### 3.4. Comparison of Results of Analysis with Other Countries

The analytical results, average and range, of the

same sample from the different countries are presented in Table 6.

The our results are better than those of the other countries in comparison with the certified values.

### 3.5. Application on the Samples Collected in Suburban and Rural Area

–. The analysis of the samples collected in suburban area: The analysis of 30 elements in samples collected from May of 1993 to February of

Table 7. Analytical Results of Airborne Particulate Matter Sampled Monthly at Suburban Area (ng/m<sup>3</sup>).

Element	May	Jun.	Jul.	Aug.	Nov.	Jan.	Feb.	Average
TSPM	71500	59600	11000	53400	43300	21650	63550	
Al	2045	2795	2290	2310	2790	2370	2250	2407
As	9.99	3.79	13.9	5.33	5.43	6.50	3.04	6.85
Au	0.018	0.005	0.001	0.005	0.006	—	0.008	0.007
Br	19.9	7.18	2.49	1.58	16.9	4.19	32.3	12.1
Ca	180	120	130	105	140	360	90	161
Cd	6.95	6.56	5.16	—	—	—	9.17	6.96
Ce	0.46	1.08	0.36	0.09	0.35	0.25	0.52	0.44
Cl	1150	890	40.5	630	590	710	460	639
Co	0.82	0.64	0.46	1.40	0.82	0.73	0.77	0.81
Cr	0.14	0.30	0.01	0.32	1.62	10.2	0.43	1.86
Cs	0.50	—	—	0.37	—	—	—	0.44
Fe	250	110	110	160	90.3	180	220	160
Hf	0.24	0.16	0.33	0.14	0.18	0.07	0.18	0.19
Hg	0.79	0.20	—	0.30	0.40	0.14	0.42	0.38
K	880	330	100	400	290	280	400	383
I	8.71	2.39	0.09	5.61	1.99	1.34	13.4	4.79
In	0.05	0.04	—	0.06	0.08	0.09	0.16	0.08
La	0.20	0.17	0.12	0.10	0.12	0.11	0.15	0.14
Lu	0.34	0.03	0.02	—	0.05	—	—	0.11
Mn	26.2	12.9	1.64	15.3	8.06	13.8	18.0	13.7
Na	240	180	60	160	160	120	210	168
Sb	11.8	8.01	2.83	8.86	8.01	2.95	17.2	8.52
Sc	0.04	0.02	0.01	0.03	0.02	0.02	0.04	0.03
Se	5.59	1.29	—	2.86	4.43	2.29	10.8	4.53
Sm	0.03	0.11	0.04	0.04	0.09	0.05	0.07	0.06
Th	0.15	0.38	0.15	0.27	0.08	0.22	0.18	0.20
U	—	0.29	—	—	—	—	—	—
V	20.5	17.0	3.14	7.09	9.52	—	29.8	14.5
Yb	—	0.06	0.01	0.13	0.23	—	0.17	0.12
Zn	190	125	45	160	145	105	265	148

\* TSPM : Total Suspended Particulate Matter

1994 were carried out and investigated the elemental distribution and variation in time. The results are summarized in Table 7.

Elemental concentrations were high in May and February generally. It is explain that caused by the phenomena of yellow sand storm and the increase of fossile fuel's consumption, respectively. Some elements emitted mainly from soil such as Al, Au, Eu, In, La and Sc showed the same concentrations in time.

— . **The analysis of the samples collected in rural area :** The samples collected from July to

November of 1993 were analyzed by the method mentioned above and the results are summarized in Table 8.

Most of elemental concentration were generally constant in time but showed a little high values in september and october particularly.

— . **Comparison for difference of suburban and rural area :** The concentrations of heavy metals such as As, Cd, Cr, Hg, Zn were higher than the samples collected in suburban area. The differences were specially large in winter time. Change of the concentrations of elements mainly depends on

**Table 8. Analytical Results of Airborne Particulate Matter Sampled Monthly at Rural Area (ng/m<sup>3</sup>).**

Element	Jul.	Aug.	Sep.	Oct.	Nov.	Average
TSPM	7600	42720	49990	35500	9350	
Al	1820	2270	3320	3160	1660	2446
Ba	—	—	19.7	—	22.6	21.2
Ca	55.4	125	63.2	65.5	—	77.3
Fe	—	—	—	94.2	93.6	93.9
K	118	134	278	300	60.8	178
Na	20	21	70	70	79.8	52.2
As	1.04	1.85	5.08	17.5	0.75	5.24
Au	0.0007	0.0003	0.0002	0.0002	0.0003	0.0003
Br	1.80	4.41	8.36	4.58	1.68	4.16
Cd	—	—	2.45	—	—	—
Ce	0.19	0.13	0.19	0.26	0.51	0.26
Cl	98.4	—	107	133	30	92.1
Co	0.51	0.46	0.91	0.64	0.77	0.66
Cr	—	—	0.38	—	0.02	0.20
Dy	0.09	0.06	0.11	0.06	0.07	0.08
Eu	0.007	0.009	0.02	0.03	0.01	0.02
Hf	0.09	0.13	0.13	0.23	0.10	0.14
Hg	—	—	0.11	0.11	0.04	0.09
I	0.16	0.28	0.39	0.23	0.55	0.32
Mn	1.24	4.86	9.62	16.14	4.13	7.20
Sb	0.64	2.65	4.29	8.01	0.27	3.17
Sc	0.015	—	0.021	0.025	0.014	0.02
Se	—	—	2.02	1.30	—	1.66
Sm	0.051	0.047	0.038	0.034	0.045	0.04
Th	0.01	0.062	0.002	0.01	0.01	0.02
U	0.01	0.067	0.051	0.018	0.075	0.04
V	2.15	2.84	3.85	4.96	15.86	5.93
Zn	11.5	36.6	73.1	92.1	45.5	53.3

\* TSPM : Total Suspended Particulate Matter

meteorological conditions such as wind direction, wind velocity, humidity, rainfall and snowfall. The analytical procedures will be further modified and standardized to make NAA as a firm tool for the rapid and accurate analysis of airborne particulates as a part of environmental monitoring.

### 3.6. Investigation of Source Apportionment of Element

— **Calculation of enrichment factor:** The first step of find out the pollution source is calculation of enrichment factor(EF)[7]. An enrichment factor of an element is defined as the double ratio of the element of interest in the sample to a reference element in the sample divided by the ratio of the same elements found in a reference material(e.g. rock, soil, seawater, etc). This expression can be written as follows :

$$\text{Enrichment Factor, EF} = (X_i/C_i)_{\text{APM}} / (X_i/C_i)_{\text{REF}} \quad (5)$$

where X=the concentration of the element of interest and

C=the concentration of the reference element and subscript <sub>APM</sub> and <sub>REF</sub> mean airborne particulates and reference material. In general EF calculations in air dust, Al or Sc is taken as the reference element both in the sample and reference material(rock or soil) because those are supposed to be a unique element in soil and rock. An enrichment factor of 10 or greater is indicate that the source of the trace elements are crustal origin. Figure 3 shows enrichment factors calculated using Taylor's crustal concentration data.[18]. And average value of elemental concentrations in two areas using Sc as a reference element which is known to be existing in soil uniformly.

Elements in the right side of the figure are showed high EF and their emission sources are assumed probably anthropogenic. EF values of Zn, As, Hg, Br, Cd, Sb and Se were very high( $10^4$ – $10^5$ ) but the values of Fe, Ca, Cr and rare earth elements were low. Rural area showed generally lower EF values than suburban's. Distribution of EF values are well

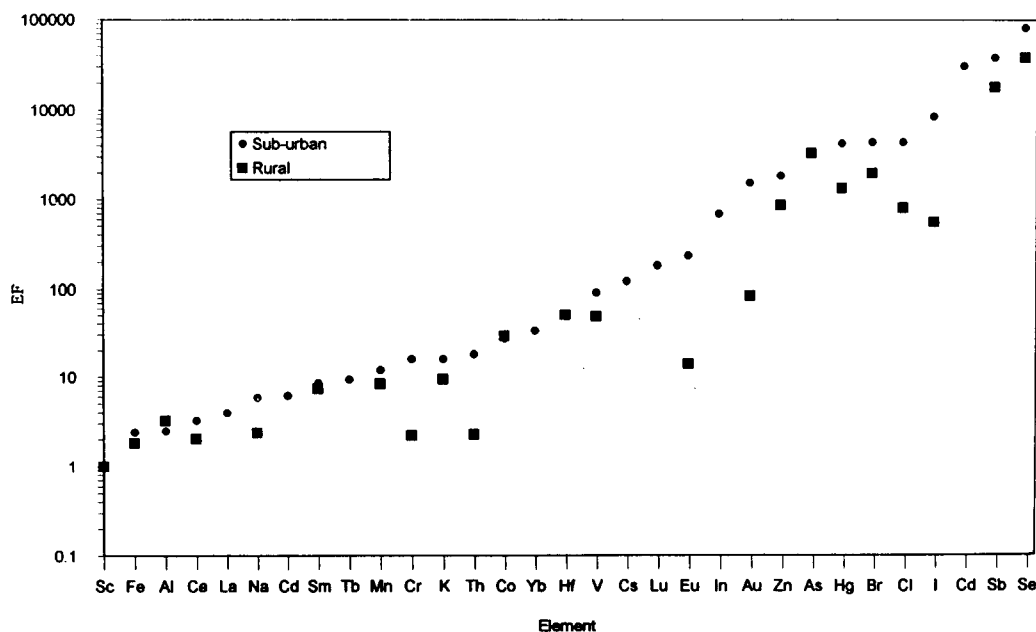


Fig. 3. Comparison of Enrichment Factor, Relative to Crustal Composition of Taylor and Normalized by Sc, Between Sub-Urban and Rural.

agreed with those of IAEA's reports[19]. It is illustrated that analytical methods and results of this works are reliable.

#### 4. Conclusion

NIST SRM-1648 and NIES CRM No. 8 are chosen to be analyzed by NAA among the environmental standard reference materials to establish a routine NAA method for airborne particulates among environmental samples. The analytical method was confirmed to be reliable after the accuracy and precision of the analysis of 40 and 24 trace elements in the samples were compared with the certified and reported values, respectively.

We applied this method to analyze 30 trace elements in airborne particulates collected at two different locations. The results of NAA were used to investigate the emission sources of environmental pollution. Neutron activation analytical method with research reactor is proved to be a useful tool for environmental monitoring.

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