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Precision and Accuracy in Elemental Determination in Environmental Samples Using Instrumental Neutron Activation Analysis

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Abstract. Thirty elements were determined in different environmental certified reference materials (CRMs) with high accuracy and precision using instrumental neutron activation analysis (INAA). The relative error of most of the elements was found to be within 10% and the standard deviation was less than 15%. The Z-score, as an analytical performance indicator, was also less than ±2. The accourate determination of various trace and major elements, at extremely low concentrations, usually present in very small amounts of airborne particulate matter on filter media was performed satisfactorily by INAA, which is otherwise regarded as a problem in such determinations. On the other hand, nevertheless, INAA appeared to be an inadequate method for the analysis of Ca because of the low count rate.

Keywords: elemental analysis, environmental elements, precision analysis, environmental contamination, instrumental neutron activation analysis, INAA

Introduction

Trace metals play an important role in biological processes, both as essential components and toxins (Ward *et al.,* 1979). Their determination in environmental samples is, therefore, a subject of considerable interest. An excess or absence of some essential trace elements causes serious problems to the physiology of the body. It is thus very important to check the levels of such trace elements precisely and accurately. Therefore, sensitive analytical methods and equipment are required to measure trace elements, since the quantities of biological samples available for analysis are usually very small. The importance of a sensitive analytical method for trace elements investigations is widely recognized not only for the determination of these elements in biological samples, but also for the important work of evaluation and solution of environmental pollution problems (Chung *et al.,* 2002; Kyotani and Iwatsuki, 2002; Sandroni and Smith, 2002; Marco *et al.,* 1999; Rizzio *et al.,* 1999). Instrumental neutron activation analysis (INAA) is generally recognized as a reference method of choice due to its accuracy and precision. This method has high sensitivity, multielement analysis capability, and nondestructive application. The desirble simple sample treatment, preceding analysis, makes the procedure fast with the added advantage of less reagent consumption and low possibilities of sample contamination.

The objectives of the present work were to check the accuracy and precision of INAA for elemental analysis to determine methodological problems of this analytical technique, if any, and to obtain an insight on its suitability for the analysis of different elements in enviromental samples of different origins.

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Materials and Methods

Instrumentation and the facilities used. Sample irradiation was carried out at HANARO (24 MW research reactor) in Korea Atomic Energy Research Institute (KAERI). Gamma-ray counting was performed using a high purity Ge-detector of 25% relative efficiency and energy resolution of 1.9 keV at 1332 keV of ^{60}Co, coupled with 8K-multichannel analyzer (EG&G Ortec, MCB) and a personal computer. GammaVision software was used for the acquisition of gamma-ray spectra and for the evaluation of spectra. Elemental concentration was calculated using Windows PC-code, Labview software, developed at the NAA Laboratory, Korea Atomic Energy Research Institute, with the nuclear data library. For medium and long counting, automatic sample-changer was coupled to the counting system.

Irradiation and gamma-ray counting. Samples were packed in clean polyethylene containers and irradiated using pneumatic transfer system (PTS) with thermal neutrons at the HANARO Research Reactor in Korea Atomic Energy Research Institute. After irradiation, the samples were repacked in pre-weighed polyethylene vials, the weight was recorded, and gamma-ray was counted. Samples were typically irradiated for 1-3 min for short half-lived nuclides and 1-4 h for medium and long half-lived nuclides.

Results and Discussion

Sourcing and nomenlature of the environmental samples. Five certified reference materials (CRMs) were selected for the present study to cover various types of samples related to enviromental elements. These were soil SRM 2709, coal-fly ash SRM 1633a, urban dust SRM 1649a, and air particulates on filter media SRM 2783, all prepared and certified by the National Institute of Standards and Technology (NIST), and human hair GBW 09101, prepared and certified by Shanghai Institute of Nuclear Science, China. Three replicates of each CRM were analyzed using absolute method.

Analysis of air particulates on filter media. For elemental determination of the air particulates on filter media SRM 2783, the filter was cut into three pieces: half of the filter was irradiated for the activation of medium and long half-lived nuclides, a quarter of the filter was irradiated for short half-lived nuclides, and the remaining quarter of the filter was kept for other possible measurements or replicates. For the determination of elements by INAA, the filter pieces were pressed into polyethylene containers and irradiated using PTS with thermal neutron. After irradiation, the filter pieces were wrapped in aluminium foils for counting to avoid contamination from the containers.

Twenty five elements, Al, Ca, Cl, Cu, Mg, Ti, V, Ba, Dy, K, Mn, Na, As, Br, La, Sm, Ce, Zn, Co, Cr, Fe, Hf, Sb, Sc and Th were analyzed. Two critical quality control issues are taken into consideration in any multielement analysis, which are the accuracy and precision of measurement. Therefore, the relative error (RE) and coefficient of variation (CV) were calculated, which are shown in Table 1. The perecntage RE and CV, in other terms the accuracy and precision, were calculated using the following equations:

$$RE = \frac{\text{certified value - mean value}}{\text{certified value}} \times 100 \quad (1)$$

$$CV = \frac{\text{standard deviation (sd)}}{\text{mean value}} \times 100 \quad (2)$$

As is evident from Fig. 1, the CV for most of the elements was less then 10%. The accuracy of analysis was thus very good for all the elements, except for As. The RE for As was likewise camparatively higher (13%). The precision of measurement for other elements, nevertheless, was quite high as evident from their low RE (< 5%). The Z-score values for all elements were calculated using the following equation, which are presented in Table 1.

$$\text{Z-score} = \frac{\text{mean of measured value - certified value}}{\sigma_H} \quad (3)$$

where:

$$\sigma_H \text{ (Horwitz function)} = 0.02 \times \left[\frac{(\text{certified value} \times 10^{-6})^{0.8495}}{10^6} \right]$$

The data presentad in Table 1 indicate these measurements to be reasonable. The Z-score values for all elements were generally within the acceptable range (±2). Accurate determination of very low levels of trace elements has been reported as the main analytical problem in the analysis of airborne particulate matter collected on the filter media (Rizzio *et al.,* 1999; Gallorini, 1995; Ondov *et al.,* 1995). From the present study, however, it can be concluded that the determination of a large number of elements, including trace and major elements, present in extremely low concentrations in very small quantities of the airborne particulate matter on filter media, can be performed satisfactorily by INAA.

Analysis of the soil sample. Twenty seven elements were determined in San Joaquin soil, NIST SRM 2709, using INAA. The results obtained, together with calculated RE and the Z-score, are given in Table 1. The Z-score values for all the elements were noted to be acceptable, except for Ca and Al. The calculated RE and CV values are shown in Fig. 2. The RE values were found to be below 10% for all elements, except Ca and Hg. The relatively higher RE value for the volatile element Hg may be due to losses during the irradiation process. Higher RE (14%) in Ca is not understandable due to uncertainty of efficiency in the 3084 keV region. However, the calculation of CV, across the replicates was less than 10% except Zn, which showed excellent reproducibility. It can thus be concluded that INAA is a suitable method for the determination of 27 elements in the studied San Joaquin soil, NIST SRM 2709, with high degree of precision and accuracy.

Analysis of hair sample. Using INAA, the measurement of twenty elements, Al, Ca, Cl, Cu, Mg, S, V, Ba, I, Mn, Na, As, Br, Zn, Co, Cr, Fe, Hg, Sb and Se in the human hair standard reference material, GBW 09101, was found to be possible. The RE and CV values of different elements are presented in Fig. 3, which shows that the RE and CV values for most of the elements were below 10%. Though RE values in the case of Mn, Ca, As and Hg were comparatively larger than other elements, the precision of measurement for all the four elements was quite good. The higher RE may be attributed to the loss of volatile elements (As, Hg) due to irradiation. It may also be noted from Table 1 that the Z-score values for all the elements were acceptable, except for S and Ca. On the basis of this study it may be concluded that INAA, besides its multielement capability, is an effective method for the determination of elements in biological samples in terms of accuracy and precision.

Table 1. Relative error (RE) and Z-score of elemental analysis of standard reference materials (SRMs) using instrumental neutron activation analysis (INAA)

Element	Standard reference materials (SRMs)														
	NIST 2783 (air particulates)			NIST 1633a (coal-fly ash)			NIST 2709 (soil)			NIST 1649a (urban dust)			SINSC GBW 09101 (human hair)		
	Certified value	Relative error (%)	Z-score value	Certified value	Relative error (%)	Z-score value	Certified value	Relative error (%)	Z-score value	Certified value	Relative error (%)	Z-score value	Certified value	Relative error (%)	Z-score
Al	23210	6.1	-1.73	143000	5.9	-2.21	75000	7.66	2.6				13.3	-5.7	0.53
Cl										0.28%	-3.6	0.74	152	4.1	-0.55
Ca	13200	0.2	-0.1	11100	18.8	-4.7	18900	14.0	-3.9				1090	15.8	-2.84
Mg	8620	0.3	-0.1	4550	-2.6	0.6	15100	-4.1	1.1	0.92%	0.36	-0.09	105	1.6	-0.2
Ti	1490	1.8	-0.3	8000	-0.6	0.2	3420	-1.26	0.3						
S										3.27%			46900	7.0	-2.22
V	48.5	-1.8	0.2	297	7.3	-1.1	112	-0.3	0.03	345	1.54	-0.23	0.069	10.2	-0.43
I													0.875	0	0
Ba	335	-8.2	1.2	1500	1.9	-0.4	968	-1.8	0.3	569	-5.33	0.87	5.41	-1	0.08
Dy							3.5	-8.2	0.6						
K	5280	1.3	-0.3	18800	5.1	-1.4	20300	5.4	-1.5						
Mn	320	-2.8	0.4	179	15.3	-2.1	538	6.62	-1.1	237	-22.7	3.23	2.94	18.1	-1.33
Na	1860	1.1	-0.2	1700	8.7	-1.7	11600	-1.73	0.44				266	8.6	-1.25
Sr				830	-2.0	0.3									
As	11.8	14.1	-1.28	145	9.0	-1.2	17.7	6.59	-0.6	67	7.82	-0.92	0.59	14.4	-0.83
Br										0.12%	-9.72	1.76	0.602	-1.7	0.1
La							23	-4.82	0.5	33	7.02	-0.74			
Sm	2.04	4.4	-0.3				3.8	-5.20	0.4	4.7	5.11	-0.46			
Ce	23.4	5.8	-0.59	180	4.7	-0.65	42	-3.1	0.34	52	9.72	-1.1			
Co	7.7	2.5	-0.21	46	-0.6	0.07	13.4	1.54	-0.14	16.4	-2.66	0.3	0.135	-1	0.04
Cr	135	-9.8	1.28	196	-1.1	0.16	130	-10.1	1.31	211	-1.30	0.2	4.77	2.8	-0.22
Cs				11	-1.1	0.1	5.3	-6.96	0.56	2.84	4.17	-0.3			
Fe	26500	-8.9	2.59	94000	-2.3	0.81	35000	1.29	-0.37	2.98%	-0.76	0.2	71.2	8.3	-0.99
Hf				8	7.3	-0.62	3.7	-1.82	0.14	4.4	0.02	0.0			
Hg				0.16			1.4	14.48	-0.95				2.16	25	-1.75
Rb	24			131	-7.5	0.98	96	-6.49	0.81	48	-0.81	0.1			
Sb	71.8	-4.1	0.49	6.8	9.9	-0.82	7.9	-0.96	0.08	29.9	5.91	-0.6	0.21	-0.3	0.02
Sc	3.54	-10.9	0.83	40	-4.1	0.45	12	-0.19	0.02	8.7	-5.96	0.5			
Se				10.3			1.57			25.6	-9.05	0.9	0.58	0.3	-0.02
Th	3.23	-6.8	0.51	24.7	3.9	-0.4	11	-7.24	0.65	6.6	-7.23	0.6			
Yb							1.6	-6.63	0.44						
Zn	1790	3.3	-0.64	220	-5.7	0.8	106	6.25	-0.79	0.17%	10.40	-2.0	189	5.8	-0.8

Analysis of coal-fly ash. Coal-fired power stations are a big source of atmospheric pollution. Therefore, interest is growing in recent years in the accurate determination of elemental composition of coal-fly ash. The results of analyses of the coal-fly ash, NIST SRM 1633a, by INAA are given in Table 1 together with the calculated RE and the Z-score values. Twenty seven elements, namely, Al, Ca, Mg, Ti, V, Ba, Dy, K, Mn, Na, Sr, As, K, La, Sm, Ce, Co, Cr, Cs, Fe, Hf, Rb, Sb, Sc, Th, Yb and Zn were determined with acceptable accuracy and precision. Fig. 4 shows a comparison of the RE and CV values of different elements. It is evident that the RE values were less than 10%, except for Ca and Mn, and the CV values were less than

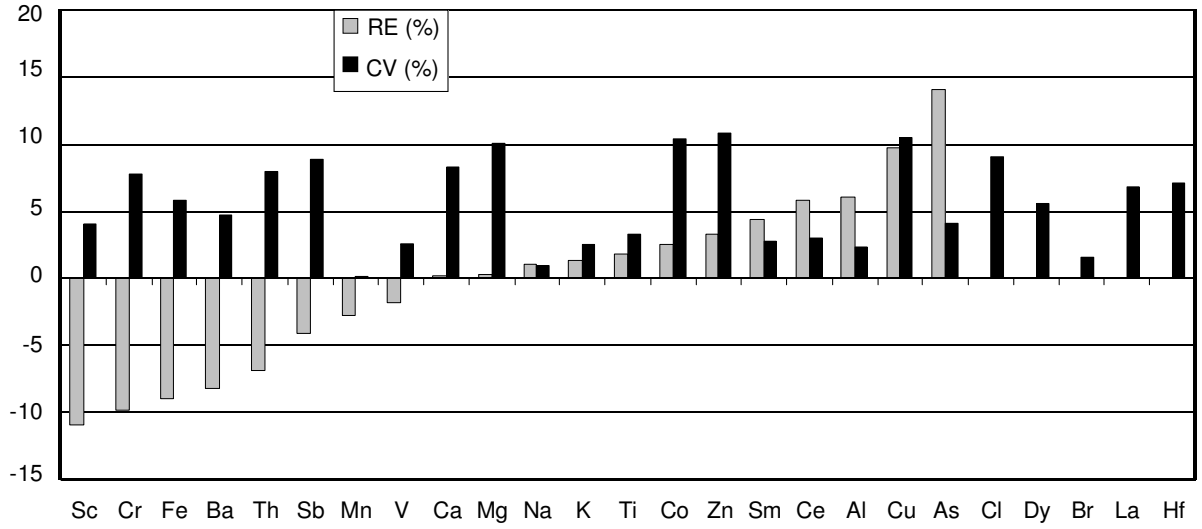

Fig. 1. Relative error (RE) and coefficient of variation (CV) of elemental determination by instrumental neutron activation analysis (INAA) of the National Institute of Science and Technology standard reference material, SRM 2783, for air particulates on the filter medium.

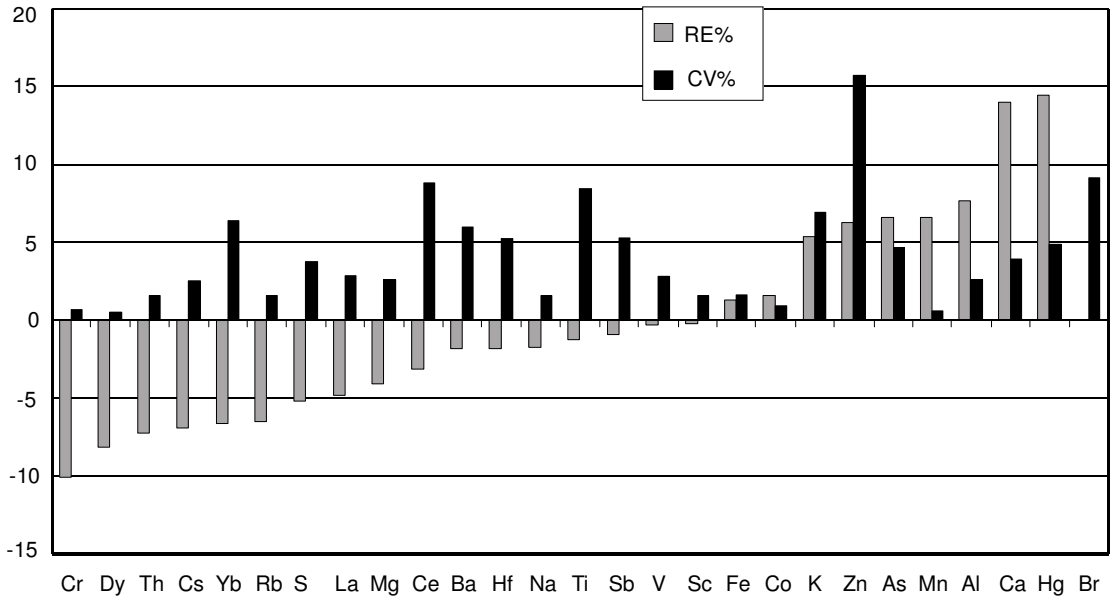

Fig. 2. Relative error (RE) and coefficient of variation (CV) of elemental determination by instrumental neutron activation analysis (INAA) of the National Institute of Science and Technology standard reference material, SRM 2709, for soil.

5%, except for Mg and Zn. Though RE for Ca and Mn was relatively larger, the precision was very good (within 5%). The Z-score values for these two elements were not within the acceptable range, while for other elements the Z-score values fell within the acceptable range. The reason for deviation of Ca is not clear and cannot be explained due to unknown uncertainty of efficiency at the 3084 keV region. From the abovementioned discussion it is concluded that INAA can be considered as an appropriate analytical method for elemental determination of atmospheric samples containg coal-fly ash.

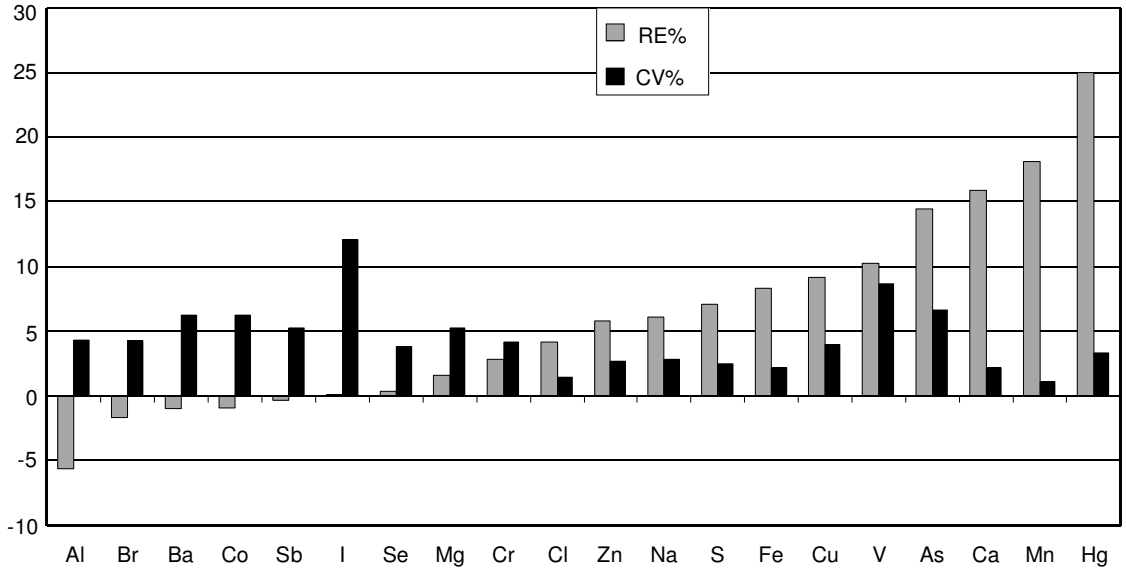

Fig. 3. Relative error (RE) and coefficient of variation (CV) of elemental determination by instrumental neutron activation analysis (INAA) of the Shanghai Institute of Nuclear Science standard reference material, GBW 09101, for human hair.

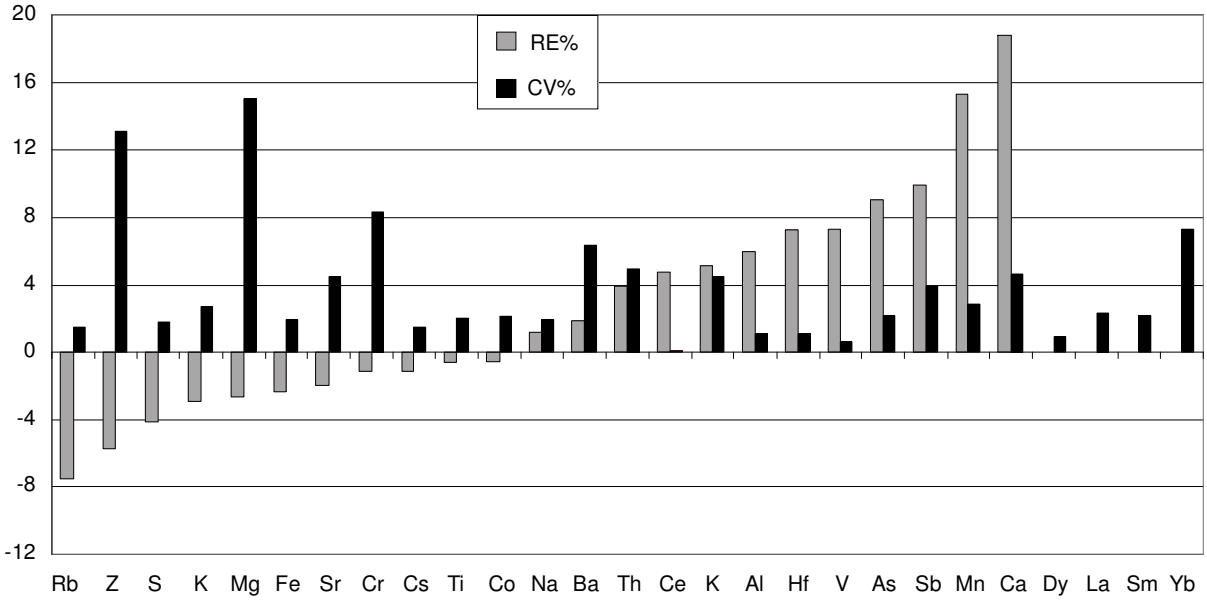

Fig. 4. Relative error (RE) and coefficient of variation (CV) of elemental determination by instrumental neutron activation analysis (INAA) of the National Institute of Science and Technology standard reference material, SRM 1633a, for coal-fly ash.

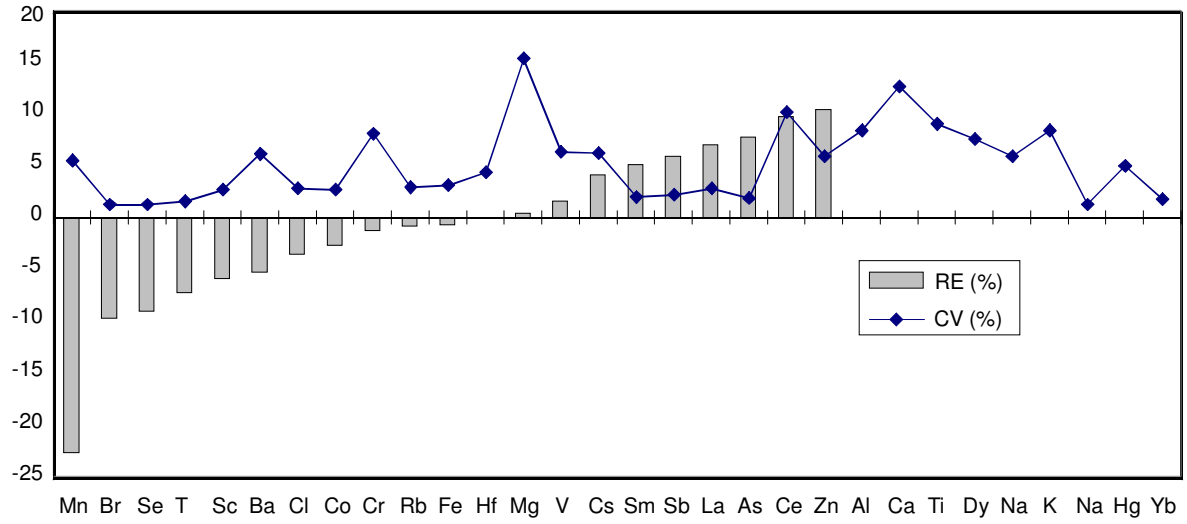

Fig. 5. Relative error (RE) and coefficient of variation (CV) of elemental determination by instrumental neutron activation analysis (INAA) of the National Institute of Science and Technology standard reference material, SRM 1649a, for urban dust.

Analysis of urban dust. Trace metals are found in atmospheric aerosol particles, originating from the wind blown dust, fossil-fuel combustion, and refuse incineration. Their accurate measurement is an important aspect of environmental monitoring and research. The analysis of urban dust, of the environmental sample NIST SRM 1649a, was thus carried out for precise determination of elements by INAA. Thirty elements were determined in the urban dust, on the environmental sample using INAA. The observations so obtained are given in Table 1. To check accuracy and precision of analysis, the RE and CV values were calculated. Fig. 5 shows that RE for all the elements was less than 10%, except Mn, whereas the CV values for most elements was less than 10%, except for Ca and Al. Table 1 further shows that the Z-score values for all the elements was acceptable, except for Mn. The measured concentration of Mn was significantly higher than the certified value. Though samples were irradiated with thermal neutron (R_d ~205), this higher value may be attributed to the production of Mn nuclide from (n, p) reaction of Fe, which was present in significant amounts in the sample. The results show that high precision multielement determination in the urban dust CRM, NIST SRM 1649a, by INAA was definitely possible.

Conclusion

Determination of about thirty elements, in five certified environmental reference materials, using INAA was achieved with high accuracy and precision. However, some ambiguity was found in the analysis of Ca using this procedure, which may be attributed to the detection limit being high and the gamma-energy line to be large (3084 KeV).

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