



## Proficiency Testing for the Evaluation of the Quality of Analytical Results in the Nuclear Industry†

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To evaluate the quality of analytical results in the nuclear industry, we participated in proficiency testing, called EQRAIN trace elements No. 17, which was held under the auspices of the commission for the establishment of analysis methods. The concentrations of 15 elements (Cd, Ni, Eu, As, Fe, U, Sm, Li, Nd, Zr, Pb, Cr, Al, B and Ca) were determined by ICP-AES. Although standard solutions on a volume basis were prepared for a calibration curve, the density of the mother standard solution was not used to calculate the concentration of the standard diluted solution. Based on preliminary tests, the analytical results with a background correction were more accurate than those without background correction. To obtain accurate and reproducible analytical results, an analysis was performed in triplicate using a two-point calibration on five different dates. The relative variations of all elements except Zr were within less than  $\pm 2\%$ . However, as the relative variation of Zr was incompatible at 3.6%, the content of Zr will be measured using a high-performance ICP-AES.

**Key Words:** Proficiency test, Evaluation, Analytical, ICP-AES, Background correction.

### INTRODUCTION

After Greenfield and Fassel reported the use of plasma as a spectrometric excitation source<sup>1,2</sup> at the end of the 1960's, inductively coupled plasma-atomic emission spectrometry (ICP-AES) was developed for commercialization in 1974. The increase in the demand of ICP-AES for environmental analysis, such as the analysis of drinking water, sediment, sludge, soil and fly ash samples, led to its widespread use in routine analysis due to such advantages as its wide dynamic range, high sensitivity, freedom from matrix interference and multielemental analysis capability. The elemental analysis of a solution can be performed by ICP-AES<sup>3</sup>, inductively coupled plasma mass spectrometry (ICP-MS)<sup>4</sup> and flame-atomic absorption spectrometry (FAAS)<sup>5</sup>. Because the element concentration in the sample was in the range of 0.20 to 8.1 mg L<sup>-1</sup> in preliminary tests, ICP-AES was selected to measure its concentration.

To improve the quality of the analytical and measurement results with the maximum possible accuracy in the nuclear field, the commission for the establishment of analysis methods (CETAMA) has organized interlaboratory measurements, such as round robin tests, for many years. In particular, the weight measurement of uranium or plutonium is referred to as the quality evaluation of analytical results in nuclear industry (EQRAIN). To evaluate the quality of the analytical results of Korea Atomic Energy Research Institute (KAERI) laboratory,

we participated in the EQRAIN trace elements No. 17 proficiency training, held under the auspices of CETAMA.

The purpose of this study is to obtain accurate analytical results by ICP-AES in spite of its disadvantage including a poor reproducibility. In general, internal standardization (IS) in ICP-AES has been used to normalize any drift and instability of the instrument response<sup>6-8</sup>. In addition, a high-performance (HP) ICP-AES (HP-ICP-AES)<sup>9</sup> was recently developed to obtain high precision and high accuracy analytical results comparable to classical methods such as titration and gravimetric analysis. Although internal standardization in ICP-AES and HP-ICP-AES are useful techniques to obtain the high precision analytical results, these techniques were not applied. To correct for instrumental drift in this study, the measurements of a standard and a sample were alternatively carried out by ICP-AES.

### EXPERIMENTAL

A sequential ICP-AES (Activa M; Horiba Jobin Yvon SAS, Longjumeau, France) was used to measure Cd, Ni, Eu, Fe, U, Sm, Li, Nd, Zr, Pb, Cr, Al, B and Ca in the sample due to the advantages of a charge-coupled device detector over a photomultiplier tube (PMT), including better productivity and reproducibility. The concentration of arsenic was also determined using a sequential ICP-AES (Ultima 2C; Horiba Jobin

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Yvon SAS) due to its higher sensitivity than the Activa M instrument. The operating conditions for the determination of 15 elements were the same as those cited in a previously except for the nebulizer<sup>10</sup>; a cross-flow Teflon Mira Mist nebulizer was used. Distilled and demineralized water (DDW), with a specific resistance of 18.5 M $\Omega$ -cm, was prepared using a Milli-Q plus Ultra Pure Water System (Millipore, Billerica, MA, USA).

The HNO<sub>3</sub> used (Merck, Darmstadt, Germany) was of analytical grade. The concentration of the stock solution of the 15 elements (Spex CertiPrep, Metuchen, NJ, USA) was 1,000 mg L<sup>-1</sup>. A 100-fold diluted standard solution containing 15 elements in 5 % HNO<sub>3</sub> was prepared to produce a calibration curve and yield rough analytical results. The mixed standard solution in 5 % HNO<sub>3</sub> for calibration was prepared as shown in Table-1. A mixed standard solution based on the concentration of the sample was also prepared to correct the drift of the instrument as shown in Table-1. Although standard solutions based on a volume basis were prepared to generate a calibration curve, the density of the mother standard solution was not used to calculate the concentration of the diluted standard solution. The analysis was performed in triplicate using a two-point calibration.

TABLE-1  
PREPARATION OF THE STANDARD SOLUTION

Element	Concentration (mg L <sup>-1</sup> )	
	Correction of drift	Calibration curve
Cd, Ni, Eu, As, Fe, U	0.5	1.0
Sm, Li, Nd, Zr	1.0	5.0
Pb	2.0	5.0
Cr	2.0	10.0
Al, B	4.0	10.0
Ca	8.0	10.0

## RESULTS AND DISCUSSION

**Investigation of analysis lines for 15 elements:** As the concentrations of the 15 elements in the sample were unknown, the most sensitive wavelengths for all elements were selected. To choose an analytical line, the spectral interferences of each wavelength on the most sensitive wavelength for all elements were investigated. If spectral interference was found in the most sensitive wavelength, the next most sensitive wavelength was examined. The selected analytical wavelength including a background position was shown in Table-2. Because of the different peak heights in the background of Pb 220.353 nm, the background position was set symmetrically on both positions at  $\pm 0.1337$  nm. Negative signs in Table-2 indicate a position to the left of the analytical wavelength.

As shown in Table-3, in preliminary tests, although the analytical results of only 7 elements with and without background correction were provided, the analytical results with a background correction were clearly more accurate than those without a background correction. In particular, the analytical results obtained without background correction were severely affected by low-concentration and low-sensitivity elements, such as Ni and Pb, respectively. However, the accuracy of the high-concentration and high-sensitivity elements, such as Ca, was not influenced by the background correction as shown in Table-3. Although the analytical results of 5 replicates measu-

TABLE-2  
SELECTED ANALYTICAL WAVELENGTH  
AND BACKGROUND POSITION

Element	Wavelength (nm)	Background position (nm)	Instrument
Cd	226.502	-0.1223	Activa M
Ni	221.650	-0.1130	Activa M
Eu	412.970	-0.0802	Activa M
As	188.983	0.0285	Ultima 2C
Fe	259.940	0.1359	Activa M
U	385.958	-0.0545	Activa M
Sm	359.260	-0.1155	Activa M
Li	670.792	-0.1004	Activa M
Nd	401.225	-0.0904	Activa M
Zr	343.823	0.0950	Activa M
Pb	220.353	$\pm 0.1337$	Activa M
Cr	205.571	-0.1096	Activa M
Al	396.152	-0.0901	Activa M
B	249.773	-0.0626	Activa M
Ca	317.933	-0.0705	Activa M

rements a date were not provided, preliminary tests showed that the analytical results with five different dates measurements were more accurate than those with 5 replicates measurements of one date.

TABLE-3  
COMPARISON OF ANALYTICAL RESULTS WITH AND  
WITHOUT BACKGROUND CORRECTION

Element	Concentration (mg L <sup>-1</sup> )		
	Reference	With BG	Without BG
Cd	0.202	0.199	0.209
Ni	0.350	0.352	0.367
Eu	0.496	0.510	0.520
Sm	0.808	0.834	0.840
Pb	1.500	1.510	1.617
B	4.220	4.221	4.289
Ca	8.060	8.243	8.172

BG = Background

**Analysis of 15 elements:** Although ICP-AES has merits such as its ability to perform multielement analysis, its drawback is instrumental drift. In addition, even though reproducibility, meaning short-term stability, is a component of the precision of a test method, it has a significant effect on the reliability of the result. Because of the poor reproducibility of ICP-AES, the measurements of a standard and a sample were carried out alternatively to correct for instrumental drift. To obtain accurate and reproducible analytical results, the analysis was performed in triplicate using a two-point calibration on five different dates.

As shown in Table-4, the analytical results of 11 elements were in a good agreement with the reference values (less than  $\pm 1$  % relative variation). In addition, the analytical results of Ni, Pb and B elements agreed well with the reference values (less than  $\pm 2$  % relative variation), as shown in Table-4. However, the relative variation of Zr was 3.58 %, which is incompatible because it exceeds the cutoff of 2 %. On the other hand, excellent elemental analysis with a relative expanded uncertainty on the order of 0.1 % was reported by Salit *et al.*<sup>9</sup> using a HP-ICP-AES. Therefore, the Zr content will be measured using a HP-ICP-AES and the cause of high error for Zr will also be examined.

TABLE-4  
ANALYTICAL RESULTS OF PROFICIENCY TESTING

Element	Reference value (mg L <sup>-1</sup> )	Measured value (mg L <sup>-1</sup> )		Relative variation (%)	Compatibility
		X	SD		
Cd	0.202	0.200	0.001	-0.99	Compatible
Ni	0.350	0.356	0.002	1.71	Compatible
Eu	0.496	0.495	0.003	-0.20	Compatible
As	0.55	0.545	0.004	-0.91	Compatible
Fe	0.646	0.649	0.006	0.46	Compatible
U	0.702	0.708	0.005	0.85	Compatible
Sm	0.808	0.813	0.006	0.62	Compatible
Li	0.903	0.902	0.008	-0.11	Compatible
Nd	1.05	1.055	0.010	0.48	Compatible
Zr	1.2	1.243	0.014	3.58	Not compatible
Pb	1.5	1.486	0.010	-1.07	Compatible
Cr	2.2	2.198	0.021	-0.09	Compatible
Al	3.01	3.006	0.024	-0.13	Compatible
B	4.22	4.270	0.024	1.18	Compatible
Ca	8.06	8.065	0.054	0.06	Compatible

### Conclusion

The analytical results of all elements except Zr agreed well with the reference values, with a relative variation of less than  $\pm 2\%$ . Consequently, the Zr content will be measured

using a HP-ICP-AES. As accuracy assessment is a very important component in analytical measurements, we will continually participate in this type of round robin test to improve the quality of our analytical results.

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