Uncertainty Estimation for the Determination of Ni, Pb and Al in Natural Water Samples by SPE-ICP-OES

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In this paper we propose uncertainty estimation for the analytical results we obtained from determination of Ni, Pb and Al by solid-phase extraction and inductively coupled plasma optical emission spectrometry (SPE-ICP-OES). The procedure is based on the retention of analytes in the form of 8-hydroxyquinoline (8-HQ) complexes on a mini column of XAD-4 resin and subsequent elution with nitric acid. The influence of various analytical parameters including the amount of solid phase, pH, elution factors (concentration and volume of eluting solution), volume of sample solution, and amount of ligand on the extraction efficiency of analytes was investigated. To estimate the uncertainty of analytical result obtained, we propose assessing trueness by employing spiked sample. Two types of bias are calculated in the assessment of trueness: a proportional bias and a constant bias. We applied Nested design for calculating proportional bias and Youden method to calculate the constant bias. The results we obtained for proportional bias are calculated from spiked samples. In this case, the concentration found is plotted against the concentration added and the slop of standard addition curve is an estimate of the method recovery. Estimated method of average recovery in Karaj river water is: (1.004±0.0085) for Ni, (0.999±0.010) for Pb and (0.987±0.008) for Al.

Keywords: Solid phase extraction; Amberlite XAD-4; inductively coupled plasma-optical emission spectroscopy (ICP-OES); Uncertainty

1. INTRODUCTION

DETERMINATION OF trace metal ions in natural waters is becoming increasingly important because of the increase interest in monitoring environmental pollution. For preconcentration, different procedures such as liquid-liquid extraction, co-precipitation, electro-deposition and solid phase extraction mainly using ionic exchange resins have been developed [1]. Among all these procedure solid phase extraction techniques are quite popular since they offer a number of important advantages over other preconcentration methods. One of these benefits is that sorbent material can be packed into mini-columns or cartridges which provide sufficient adsorption capacity for many applications. In solid phase extraction, various sorbents such as activated carbon, octadecyl bonded silica membrane disk, silica-gel, polyurethane foam, chelex 100 and Amberlite XAD resin family have been used for the peconcentration of trace metal ions from various media such as natural water samples, urine, geological samples [2-7]. Amberlite XAD-4 is a polymeric adsorbent with excellent physical, chemical and thermal stability and it is also stable at all pH range in aqueous solutions [8-12]. Analytical result must be validating because they are used as a peace of valuable information for a certain aim. Therefore, analysts are increasingly impelled to validate analytical procedures and to estimate the uncertainty associated to the results these procedures provide. Uncertainty can be obtained either by calculating all the sources of uncertainty individually (bottom-up approach) or by grouping all sources of uncertainty. However, the last one is not straightforward; other approaches based on calculating uncertainty using information

from the validation process have been proposed [13-15]. The approach proposed in [14,16,17] can be used when routine samples have similar level of concentration because the bias of analytical procedure is assumed to be constant throughout the concentration range and when the routine samples vary within a range of concentration, trueness should be verified using samples that cover the whole concentration range [14,16]. Another protocol proposed by Ellison [15], verify trueness in the terms of method recovery. Therefore, the bias of analytical results is only assumed to be proportional. However, there may be two types of bias (proportional and constant bias). So, another approach proposed by Morato that calculate uncertainty in wide range of concentration and assume both types of bias may be present. In this approach recovery is estimated with the method of averaged recovery and constant bias with the Youden method [17, 18]. The aim of this study was to develop a Morato method in uncertainty estimation of analytical results obtained by assessing trueness and employing spiked samples in determination of Ni, Pb and Al in river water samples by SPE-ICP-OES.

2. EXPERIMENTAL SECTION

2.1. Instrumentation

An Optima 2100 DV inductively coupled plasma optical emission spectrometer (Perkin Elmer Instruments, Shelton, CT, USA) was used for metal determination. The operation conditions and the analytical wavelengths are summarized in Tab.1 Sample solution was driven through the columns with a

multi-channel Heidolph PD 5001 peristaltic pump. The pH values were controlled with a Mettler Toledo MA235 pH meter (Mettler Toledo Instruments CO. LTD, Shanghai, China) supplied with a combined electrode. A self-made polytetrafluoroethylene (PTFE) mini-column (50×5 mm i.d.), packed with XAD-4, was used for separation/preconcentration.

Parameters	
RF power (watts)	1300
Nebulizer gas flow rate (L min^{-1})	0.8
Auxiliary gas flow rate (L min^{-1})	0.2
Plasma gas flow rate (L min^{-1})	15
Sample flow Rate (ml min^{-1})	1.5
Wavelength (nm)	Ni 231.640, Pb 220.353
	Al 396.153

Tab. 1 Instrumental and operating conditions for ICP-OES measurements

2.2. Chemicals and solutions

All chemicals used were of analytical-reagent grade. Deionised water was used throughout. Multi-element standard (various concentrations) and model solution were prepared by dilution of single element 1000 mg l^{-1} stock solutions. Nitric acid, hydrochloric acid, methanol, sodium acetate, acetic acid ammonia solutions were purchased from Merck. Amberlite XAD-4 (surface area, 750 m^2 g^{-1} and bead size, 20 – 50 mesh) were obtained from Fluka. Column experiments were performed with micro-particles prepared by crushing XAD-4 resins in a mortar, subsequently sieving into fractions. Fractions were cleaned thoroughly washed in the sequence of 1.0 mol l^{-1} NaOH, DI water, 2.0 mol l^{-1} HNO$_3$ and DI water. It was finally washed with methanol and dried in the air. 8-HQ (from Fluka) solution (0.5 mol l^{-1}) was prepared in 2.0 mol l^{-1} hydrochloric acid.

3.2. General procedure

The performance of proposed column was tested with model solution prior to its application to real water samples. 100 ml of the model solution containing 10 µg each of Ni, Pb and Al prepared and 100 µl of 8-HQ solution was added to form the metal-complexes. The pH was adjusted to desired value with addition appropriate volume of nitric acid and ammonia solution. The sample solution was passed through a cleaned and conditioned column at a flow rate of 6.0 ml min^{-1} by using a peristaltic pump. After loading further washing with buffer solution served to remove any sample still present in the column. Finally, the metal-complexes retained on the mini-column were eluted with 2.0 mol l^{-1} nitric acid solution. The eluted trace elements were measured by ICP-OES. The column could be used repeatedly after regeneration with 2.0 mol l^{-1} nitric acid solution, DI water, and methanol and DI water, respectively.

4.2. Sample collection

Samples used for the developing of the analytical procedure were collected from Karaj River in the city of Karaj – Iran.

All samples were collected in pre-cleaned high density polyethylene bottles. Collected samples acidified at pH lower than 2.0 by adding concentrated nitric acid in order to avoid metal adsorption on to the inner bottles walls, then samples were filtered through a 0.45 µm polycarbonate membranes nucleopore filter.

5.2. Influence of analytical parameter

The influence of various analytical parameters including the amount of solid phase, pH, elution factors (concentration and volume of eluting solution), volume of sample solution, and amount of ligand on the extraction efficiency of analytes was investigated and after finding the optimum situation of analyse, all experiments runs and the uncertainty of analytical result estimated.

Effect of pH: The pH value plays an important role in the complexation of 8-HQ with metals which form uncharged chelate complexes. The influence of pH on the solid phase extraction of trace metal ions was studied in the range of 2-12 using acetic acid (2M)/ sodium acetate (2M) and ammonia (1M)/ Nitric acid (1M) for pH adjustment respectively. Each pH value was tested more than three times. The results has shown the most of the studied metals are largely formed/retained at pH=8. Quantitative recoveries were obtained in the pH range of (6-12) for Ni and Pb and 7.5 for Al. Therefore, the optimum pH was 8 for studied metals.

Effect of volume and concentration of nitric acid for elution: In order to study the influence of eluent in solid phase extraction of metal ions, two nitric acid solutions, 2.0 and 4.0 mol l^{-1}, were simultaneously studied for eluting volumes between 2.5-10 ml. Result has shown those efficient metals elutions are reached under 5-10 ml nitric acid volume when using 2.0 mol l^{-1} nitric acid as eluting solution. Similar results have been obtained by using 4.0 mol l^{-1} nitric acid. Therefore, the lowest nitric acid concentration (2.0 mol l^{-1}) and the lowest nitric acid volume (2.5) were chosen for most of the studied elements.

Effect of resin amount: To test the resin amount for quantitative retention of analytes, the column was filled with different amounts of Amberlite XAD-4 (200- 700 mg). The procedure was applied to the model solutions given above by use of these columns. The quantitative recoveries for all the examined analytes were obtained in range of 300-600 mg of resin. As a result in all experiments 300 mg of XAD-4 was used.

Effect of sample volume: In order to explore the possibility of enriching low concentration of the metal ions from large volumes, the influences of the sample volume on the recoveries of the investigated metal ions were examined and maximum applicable sample volume was determined. The recoveries of the metal ions from different volumes of aqueous model solution containing the same amounts of the metal ions were tested in the range of 50-800 ml. The recoveries were found to be stable up to 400 ml of sample volume. The highest preconcentration factor was found to be 40 according to 2.5 ml of the final solution.

Effect of ligand concentration: The influence of the 8-HQ concentration on the recovery of the metals was investigated in the range of 10-400 μl, 0.5 mol l^{-1} 8-HQ solution using the aforementioned model solution. . The quantitative values were obtained after 5×10^{-5} mol l^{-1} of 8-HQ. After this point the recoveries were quantitative in all working range of 8-HQ.

3. STATISTICAL METHOD

3.1. Uncertainty and validation of analytical procedures

Analytical procedures should be validated before they are used to analyse routine samples. In this process, the systematic errors are estimated in the assessment of trueness. Uncertainty and trueness are much related concepts. This is because we can not guarantee the correctness of all the systematic errors if we have not previously assessed the trueness of the analytical method and, consequently, it is impossible to ensure that the true value is included within the interval "estimated value ±U (where U is the uncertainty of the estimated result). Therefore every analyst should verify the trueness of the method before calculating uncertainty. Uncertainty can then be calculated using the information generated in the assessment of trueness. When dealing with spiked samples and recovery estimation, analytical results maybe corrected for these errors so that the final results are traceable. Moreover the uncertainty of these results should also be calculated as a measure of their reliability. Some component of this uncertainty can be obtained using information generated when the analytical procedure is validated within the laboratory. Uncertainty should then consider all the sources of error of the analytical results can calculated in a general way by grouping all these sources in four terms:

$$U = \sqrt{u^2_{precision} + u^2_{Trueness} + u^2_{pretreatments} + u^2_{Otherterms}} \; .$$

The first component of uncertainty $u^2_{precision}$ depends on the intermediate precision of the procedure and also takes into account the fact that results depend on the matrix of the routine samples. The second term, $u^2_{Trueness}$, consider the uncertainty caused by systematic errors. i.e. constant and proportional bias in the assessment of trueness. The third term, $u^2_{pretreatment}$, considers the uncertainty caused by the lack of homogeneity of the sample and pretreatment not carried out in the assessment of trueness. Finally, the forth component, $u^2_{Otherterms}$, contains all the sources of uncertainty not considered in the former terms [13,19,20]. In this study we calculate two terms ($u^2_{precision}$ and $u^2_{Trueness}$) and also consider two situation (with a spike uncertainty and without it) to estimate the final uncertainty in precision study.

3.1.1. Precision study

Precision is assumed to be approximately the same across the concentration range in which the analytical procedure is validated. Therefore, the precision can be estimated simply by test sample that lies within the concentration range studied. The within-laboratory precision of an analytical method should be characterized by the repeatability and the run-different intermediate precision. The experimental design we have proposed is a two-factor fully-nested design [21]. Here the factors studied are the p-run and n-replicate, one of which is inside the other. For consistency, we shall always consider the case where factor B (replicate) is nested within factor A (each run). The use of the analysis of the variance (ANOVA) provides the information about intermediate and the repeatability precisions.

3.1.2. Assessment of trueness

Trueness is defined as the closeness of agreement between the average values obtained from a large set of test results and accepted reference value. Trueness should be evaluated, in terms of bias, through the analysis of reference samples. However, not all the references have the same level of traceability. Therefore, the reference selected should be the one that has the suitable level of traceability for our purpose. The references commonly used in chemical analysis are certified reference materials (CRM), Reference materials/in house materials, Reference methods, Proficiency testing and spiked samples. The last once have the lowest of traceability. However, the analyst usually has to resort to spiked samples when the other references are not available. In the assessment of trueness, proportional and constant bias is calculated from spiked samples. Constant bias (when samples free from the analyte are available) must be calculated using the Youden method. The proportional bias can be expressed either as instrumental response or if a standard curve is used, as concentration [22-24]. We use the standard curve and concentration to express our results.

3.2. Standard addition method (SAM): calculation of proportional bias and related uncertainty

100 ml of each river water (four samples) are spiked with analyte quantities of 10, 20, 40 μg for Ni, Pb and Al each spiked sample analysed twice so that the precision of the analytical procedure and the variability of results with the matrix can be obtained. Fig.1 shows the proposed experimental design for obtaining information of the between-matrix variance, S^2_{matrix} and the variance associated to precision, $S^2_{precision}$. Table 2 shows ANOVA table for Nested-two factor design with random effect and expected mean square. From this table we can calculate the expected mean square for spike, σ^2_α, matrix σ^2_β and precision σ^2. If estimation of matrix variance and spike variance is negative we assume 0 for results [21,23]. SAM results expressed as a concentration when we use standard curve. Therefore, SAM curve performed by plotting concentration found versus concentration added. The slop of the SAM curve is an estimate of the method recovery (R). When we have obtained the R, and its uncertainty

$$u(R) = \sqrt{s(b_{SAM(conc)})^2 + \left(\frac{R}{b_{SC}}\right) s(b_{SC})^2}$$

(These expression are shown in Appendix A) we can evaluate whether the proportional bias is significant or not by t-test.

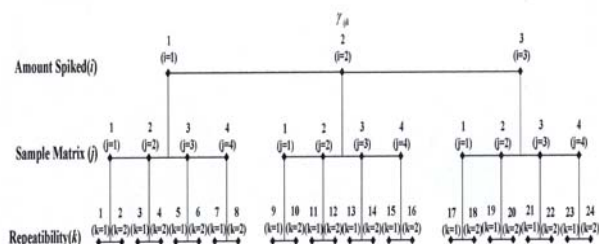$$\left| \overline{R} - 1 \right| \le t_\alpha / 2.eff \times u(R), \quad [21].$$

Fig.1 Experimental design for obtaining information about matrix variability and precision from the results obtained with spiked samples. Each measurements of metal concentration is denoted by γ_{ijk}, where i the number of the treatment, runs from 1 to a (a=3) represented the amount of analyte added; j, denoted the number of different samples used for i treatment, runs from 1 to b (b=4); and k the observation number from the jth samples on the i treatment, runs from 1 to n(n=2), so γ_{ijk}, represent the result for the kth analysis of the jth samples spiked an amount of analyte i.

Source of Variation	SS	df	MS	Expected mean square
Spike	1.974	2	0.987	$\sigma^2 + 8\sigma_\alpha^2 + 2\sigma_\beta^2$
Analyst + Matrix	15.172	9	1.686	$\sigma^2 + 2\sigma_\beta^2$
Intermediate precision	7.944	12	0.662	σ^2
Total	25.09	23		

Tab.2 ANOVA table for Nested two-factor design with Random factor effects for Ni in Karaj River

3.3. Youden method: calculation of constant bias and related uncertainty

The Youden method consists of analysing two or more different amounts (weight or volumes) of a test sample under condition of repeatability or intermediate precision. Youden plot can be defined as a sample concentration curve plotted against sample amounts and the intercept of it shows the constant bias (δ_{ct}). The uncertainty associated to

$$\delta_{ct}, u(\delta_{ct}) = \sqrt{s(a_{YOU(conc)})^2 + u^2_{condition} + u(sc)^2},$$

where $s(a_{You(conc)})$ represents the standard deviation of the intercept of the Youden curve obtained when concentration is

plotted against the amount of sample. $u_{condition}$, denote the uncertainty associated with how the amounts of sample and standards of the standard curve are analysed. If they are analysed under intermediate conditions, $u_{condition}$ = 0. If they are analysed under repeatability conditions, $u_{condition} = s_{run}$. Finally, $u(sc)$ is the uncertainty associated with converting the instrumental response of the amount of analysed into the concentration found, using the standard curve. It is calculated as

$$u(sc) = \sqrt{\frac{s(a_{sc})^2}{b^2 sc} + \frac{s(b_{sc})^2 \times a^2_{You}}{b^2_{sc}} - 2\frac{a_{You}}{b^2_{sc}} \text{cov}(a_{sc}, b_{sc})}$$

where $s(a_{sc})$ represent the standard deviation of the intercept of the standard curve, $s(b_{sc})$ denotes the uncertainty of the slope of the standard curve, $\text{cov}(a_{sc}, b_{sc})$ denotes the covariance of the intercept and the slop of the standard curve and a_{You} represents the intercept of the Youden concentration curve [14,18,25]. These expressions are shown in Appendix A. The Youden method provides a good estimate of constant bias whenever the matrix effect is the same for all amounts of sample. This can be assumed if the variance of the residuals of the Youden plot does not differ significantly from the repeatability or intermediate variance.

3.4. The results of routine samples are expressed as concentration

The concentration of the routine samples, conc, is obtained by using a standard calibration curve. This concentration is calculated as $conc = \dfrac{c_{found} - \delta_{ct}}{R}$ where c_{found} is the concentration found with the analytical procedure after having converted the instrumental response into concentration with a standard curve, R the method recovery and δ_{ct} denotes the constant bias. The concentration of future samples is obtained by correcting results by both biases. The standard uncertainty of the concentration, u, is obtained by applying propagation low to conc equation,

$$u = \frac{1}{R}\sqrt{(conc \times u(R))^2 + u(\delta_{ct})^2 + u(c_{found})^2}.$$

The first two terms of this equation consider the uncertainty associated with the assessment of trueness, $u_{trueness}$: $u(R)$ represents the uncertainty of the method recovery and $u(\delta_{ct})$ denotes the uncertainty of constant bias. The third term, $u(c_{found})$, is the uncertainty of the concentration found for the routine sample with the standard curve and considers the uncertainty associated with precision $u_{precision}$. The practical

estimation of the components of uncertainty and expression are referred to [14].

4. RESULTS AND DISCUSSION

The analysis of the spiked samples provides information about proportional bias and precision. Table 3 shows the estimated of variance component of variable in Nested – design, S^2_{matrix}, S^2_{Spike} , precision and calculated result obtained for Ni in Karaj river water. The results of other metals are represented in Tab.4. Each result was calculated as the difference between the result after analyzing the spiked sample once and the average result after analysing the sample containing the native elements three times. The results were expressed as concentration found after using a calibration curve.

Variation Source	Variance Component	Estimated Variance Component	Calculated
Matrix	S^2_{Matrix}	$\dfrac{MS_{Analyst+Matrix} - MS_{Intermediate\ precision}}{n}$	0.512
Spike	S^2_{Spike}	$\dfrac{MS_{Spike} - MS_{Analyst+Matrix}}{bn}$	0.00
precision	$S^2_{precision}$	$MS_{precision}$	0.662

Tab.3 Estimated of Variance component of variable in Nested – design for Ni in Karaj river

Metals	S^2_{Matrix}	S^2_{Spike}	$S^2_{precision}$
Ni	0.512	0.00	0.662
Pb	2.271	0.00	0.835
Al	0.071	0.00	0.666

Tab.4 Estimated of Variance component of variablein Nested – design for Ni, Pb and Al in Karaj river water

Tab.5 shows the recovery, *R* and its uncertainty *U(R)*, obtained when analytical results are expressed as concentration found. To compare the results of this method, recovery was calculated using the method of averaged recovery as others do [15-17]. Recovery was calculated for each spiked sample and the overall recovery was the estimated as the mean of the n recoveries calculated. The uncertainty of this average recovery was calculated using the precision information from the results of the spiked samples:

$$U(R) = \frac{1}{n} \sqrt{\frac{S^2_I + S^2_{Matrix}}{b^2_{SC} \sum_{i=1}^{n} C^2_{ad.i}}} .$$

The metals of five different amounts w_i (100, 200, 300, 400 and 500 ml) of Karaj River were analysed under intermediate precision conditions. The analytical results were expressed as concentration found. Tab.5 also shows the constant bias and its uncertainty when results are expressed as concentration found. The variance of the residuals of the Youden plot was compared with the variance associated with the intermediate precision of the method. Since the difference between the variances was not statistically significant for the metals determined, we assume that the matrix effect was the same for all the amounts of sample and, therefore, that a correct estimation of the constant bias was obtained from the Youden plot. The uncertainty related to real samples was calculated in two ways: (a) when results are expressed as a concentration found and (b) when recovery was estimated with the method of average recovery. Tab.6 shows the concentration, together with its uncertainty, for all the metals and for two procedures. As we can see in Tab.6, results of two procedure are likely to be similar Estimating recovery with the method of average recovery in Ni produces slight higher uncertainty values than the uncertainty of concentration found but in Pb and Al which have low concentration in samples, method of average recovery provides lower uncertainties than estimating it with regression procedure. Moreover, it is obviously recognized that in metals with lower concentration the differences between two results is higher. As we can see in Tab.6 constant bias which is not usually considered in the uncertainty budget is not negligible for Ni and Al and should taken into account.

Metals	Standard addition		Average recovery		Youden curve	
	R	*u(R)*	*R*	*u(R)*	δ_{ct}	$u\delta_{ct}$
Ni	0.985	0.021	1.004	0.008	0.095	0.298
Pb	1.012	0.028	0.999	0.01	-0.804	0.421
Al	1.010	0.014	0.986	0.008	0.386	0.390

Tab.5 Recovery, R, and its uncertainty, $u(R)$, obtained with the standard addition curve (section 3.2). Constant bias, δ_{ct} and its uncertainty, $u\delta_{ct}$, obtained with Youden curve (section 3.3)

Metal	Concentration Found		Method of average recovery
	With spike	**Without spike**	
Ni	3.90 ± 1.160	3.90 ± 1.160	4.093 ± 1.197
Pb	8.742 ± 1.528	8.742 ± 1.528	8.039 ± 0.408
Al	1.311 ± 0.311	1.311 ± 0.311	1.711 ± 0.180

Tab.6 Concentration together with its uncertainty, obtained with the procedures for the metals analysed
*Results are expressed in parts per million

5. CONCLUSIONS

The aim of this study was to estimate the uncertainty of result obtained in determination of trace elements in natural water sample by SPE-ICP-OES method. In this study used XAD-4 resin as a sorbent material for separation and preconcentration of trace metals Ni, Pb and Al (8-HQ complexes) from aqueous solution. The procedure is simple but requires very clean instrument and high purity reagents. In this method, the sample volume required is low when comparing to other methods and XAD-4 columns can be reused for several times without losing of analytical performances. Then we describe an estimation of measurement uncertainty for the analytical result, using the information generated when the trueness of analytical procedure is assessed using spiked samples. For this, we have developed Marota procedure which involves estimating the constant and proportional biases of the analytical procedure, produces lower uncertainties than other methods.

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APPENDIX

Standard deviation of the slope of the standard addition curve of section 3.2 :

$$s(b_{SAM(conc)}) = \sqrt{\frac{s^2_{e.SAM(conc)}}{\sum(c_{ad,i} - \overline{c}_{ad})^2}}$$

Standard deviation of the slope of the standard addition curve section 3.2 :

$$s(b_{sc}) = \frac{s_{e,}s_c}{\sqrt{\sum(c_i - \overline{c})^2}}$$

Standard deviation of the intercept of the Youden curve of section 3.3 :

$$s(a_{You(conc)}) = s_{e,You(conc)}\sqrt{\frac{\sum w_i^2}{n_{You}\sum(wi - \overline{w})^2}}$$

Standard deviation of the intercept of the intercept of the standard curve section 3.3 :

$$s(a_{sc}) = s_{e,,sc)}\sqrt{\frac{\sum c_i^2}{n_{sc}\sum(c_i - \overline{c}_i)^2}}$$

Covariance between the slop and the intercept of the standard curve section 3.3 :

$$\text{cov}(a_{sc}, b_{sc} = \frac{\overline{c} \times s^2_{e.sc}}{\sum(c_i - \overline{c})^2}$$