



Uncertainty estimation for the determination of Fe, Pb and Zn in natural water samples by SPE-ICP-OES

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ABSTRACT

In this paper we estimate measurement of uncertainty for determination of Fe, Pb and Zn in natural water samples 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 kinds of bias (proportional bias and constant bias) estimated. 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. Estimated uncertainty in Karaj water is: (1.0198 ± 0.0075) for Fe, (0.999 ± 0.010) for Pb and (1.0321 ± 0.0137) for Zn.

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

1. Introduction

Direct determination of trace elements in extremely low concentration by atomic absorption and inductively coupled plasma emission in many cases is difficult. This is not only due to the insufficient sensitivity of the methods, but also to the matrix effect [1]. One of the methods to accomplish in this task is solid-phase extraction which can be used with different sorbents such as activated carbon, octadecyl bonded silica membrane disk, silica-gel, polyurethane foam, chelex 100 and Amberlite XAD resin [2–7]. Amberlite XAD-4 is a non-ionic cross-linked

polymeric adsorbent which use for preconcentration of trace elements from different matrix [8–12]. Analytical result must be validating because they are used as a piece of valuable information for a certain aim. Method validation consists of deriving experimental values for the selected performance criteria. There are several types of performance criteria. The basic parameters usually refer to reliability of the method and are commonly derived by using statistical procedures [13]. Trueness and precision are the commonest which used individually in this study. Among different validation processes we consider uncertainty, important quality parameters. It is widely recognized that the evaluation of the uncertainty associated with a result is an essential part of any quantitative analysis. Uncertainty can be obtained either by calculating

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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 [14,15]. 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 calculates uncertainty in wide range of concentration and assumes 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]. This paper follows the last approach, we proposed assessing trueness by employing spiked samples and using regression techniques to estimate recovery and constant bias in a situation that calibration curve is used and results express as a concentration. (Moreover, in both situations results can be analyzed under repeatability or intermediate precision). 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 Fe, Pb and Zn 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 Table 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.

2.2. Chemicals and solutions

All chemicals used were of analytical-reagent grade. Deionized water was used throughout. Multi-element

Table 1
Instrumental and operating conditions for ICP-OES measurements

Parameters	
RF power (W)	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)	Fe 238.204, Pb 220.353 Zn 235.485

standard (various concentrations) and model solution were prepared by dilution of single element 1000 mg l⁻¹ stock solutions. Nitric acid, hydrochloric acid, methanol and ammonia solutions were purchased from Merck. Amberlite XAD-4 (surface area, 750 m² 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 HNO₃ 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.

2.3. General procedure

The performance of proposed column was tested with model solution prior to its application to real water samples. One hundred ml of the model solution containing 2 µg each of Fe, Pb and Zn prepared and 100 µl of 8-HQ solution was added to form the metal complexes. The pH was adjusted to desired value with the addition of 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.

2.4. 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.

2.5. 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 analyte, all experiments runs and the uncertainty of analytical result estimated.

2.5.1. Effect of pH

The pH value plays an important role in the complexation of 8-HQ with metals which form uncharged chelate complexes. In order to evaluate the effect of pH, the pH values of the sample solutions were adjusted in the range of 2–12 before the proposed method was applied. Each pH value was tested more than three times. The results have 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 Fe, Pb and Zn is efficiency complexed and retained at pH values within 2–12. Therefore, the optimum pH was 8 for most of the studied metals.

2.5.2. Effect of volume and concentration of nitric acid for elution

Different nitric acid solutions were tested in order to obtain optimum volume and concentration of eluent. Two nitric acid solutions, 2.0 and 4.0 $\text{mol}\cdot\text{l}^{-1}$, were simultaneously studied for eluting volumes between 2.5–10 ml. Result has shown those efficient metals elutions are reached under 2.5–10 ml nitric acid volume when using 2.0 $\text{mol}\cdot\text{l}^{-1}$ nitric acid as eluting solution. Similar results have been obtained by using 4.0 $\text{mol}\cdot\text{l}^{-1}$ nitric acid. Therefore, the lowest nitric acid concentration (2.0 $\text{mol}\cdot\text{l}^{-1}$) and the lowest nitric acid volume (2.5 ml) were chosen for most of the studied elements.

2.5.3. 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 resin. As a result in all experiments 300 mg of XAD-4 was used.

2.5.4. 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.

2.5.5. 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 $\text{mol}\cdot\text{l}^{-1}$ 8-HQ solution using the aforementioned model solution. The quantitative values were obtained after using 5×10^{-5} $\text{mol}\cdot\text{l}^{-1}$ values 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 cannot 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 $\pm U$ (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 may be 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 components 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 and analytical results can be calculated in a general way by grouping all these sources in four terms:

$$U = \sqrt{u_{\text{precision}}^2 + u_{\text{Trueness}}^2 + u_{\text{pretreatments}}^2 + u_{\text{Other terms}}^2}$$

The first component of uncertainty, $u_{\text{precision}}$, 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, $u^2_{\text{Pretreatment}}$, 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, $u^2_{\text{Otherterms}}$ contains all the sources of uncertainty not considered in the former terms [13,19–21]. In this study we calculate two terms ($u^2_{\text{precision}}$ and u^2_{Trueness}) and also consider two situations (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]. Fig. 1 shows the proposed experimental design. 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 ones 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. We use the standard curve and concentration to express our results [22–24].

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

One hundred ml of each river water (four samples) are spiked with analyte quantities of 2, 4, 6 µg for under study elements and spiked 0 used as a standard for analytical comparison, each spiked sample analyzed 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, $S^2_{\text{matrix}} = \left(\frac{SSB(A) / df_{SSB(A)} - SSE / df_{SSE}}{n} \right)$, and the variance associated to precision, $S^2_I = SSE/df_{SSE} + SSA/df_{SSA}$. The slope of the SAM curve is an estimate of the method recovery (R). When we have obtained the R, and its

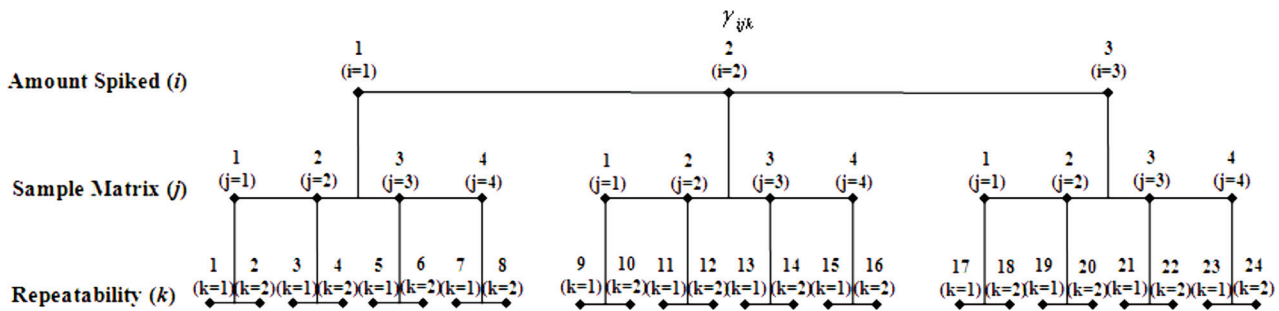


Fig. 1. Experimental design for obtaining information about matrix variability and precision from the results obtained with spiked samples. Each measurements of metal concentration is denoted by γ_{ijk} , where i the number of the treatment, runs from 1 to a represented the amount of analyte added; j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

uncertainty $u(R) = \sqrt{s(b_{Sam(conc)})^2 + \left(\frac{R}{b_{SC}}\right)^2 s(b_{SC})^2}$ (these expressions are shown in Appendix A) we can evaluate whether the proportional bias is significant or not by t -test. $|\bar{R} - 1| \leq t_{\alpha}/2\text{eff} \times u(R)$ [21].

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

This method is based on the analyses of different amounts (w_i) 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 shows the constant bias (δ_{ct}). The uncertainty associated to δ_{ct} , $u(\delta_{ct}) = \sqrt{s(a_{YOU(conc)})^2 + u_{condition}^2 + u(SC)^2}$, 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 analyzed. If they are analyzed under intermediate conditions, $u_{condition} = 0$. If they are analyzed under repeatability conditions, $u_{condition} = s_{run}$. Finally, $u(sc)$ is the uncertainty associated with converting the instrumental response of the amount of analyzed into the concentration found, using the standard curve. It is calculated

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

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 slope of the standard curve and a_{You} represents the intercept of the Youden concentration curve [18,25,26]. These expressions are shown in Appendix A.

Once constant and proportional biases of the analytical procedure have been evaluated, this information can calculate the uncertainty of all the future routine samples determined with this procedure [14].

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 $\text{conc} = \frac{c_{\text{found}} - \delta_{ct}}{R}$ 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 law to conc equation, $u = \frac{1}{R} \sqrt{(\text{conc} \times u(R))^2 + u(\delta_{ct})^2 + u(c_{\text{found}})^2}$. 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, $u(c_{\text{found}})$, is the uncertainty of the concentration found for the routine sample with the standard curve and considers the uncertainty associated with precision $u_{\text{precision}}$. 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 2 shows the Anova table for nested two-factor design with random effect for Fe in Karaj River as an example. Table 3 shows estimated variance component of variable in nested-design and calculated result obtained for metals. Table 4 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 [17,21].

Table 2
Anova table for nested two-factor design with random effect for Fe in Karaj River

Source of variation	SS	df	MS	Expected mean square
Spike	2.098	2	1.049	$\sigma^2 + 8\sigma_{\alpha}^2 + 2\sigma_{\beta}^2$
Analyst + Matrix	6.006	9	0.667	$\sigma^2 + 2\sigma_{\beta}^2$
Intermediate precision	6.645	12	0.554	σ^2
Total	14.749	23		

Table 3
Estimation of variance component of variable in Nested design for Fe, Pb and Zn in Karaj river water

Metals	S^2_{Matrix}	S^2_{Spike}	$S^2_{\text{precision}}$
Fe	0.056	0.048	0.554
Pb	2.271	0.000	0.835
Zn	0.000	0.000	0.138
$\frac{MS_{\text{Analyst+Matrix}} - MS_{\text{Intermediate precision}}}{n}$			
$\frac{MS_{\text{Spike}} - MS_{\text{Analyst+Matrix}}}{bn}, MS_{\text{precision}}$			

Table 4

Recovery, R , and its uncertainty, $u(R)$, obtained with the standard addition curve (constant bias, δ_{ct} and its uncertainty, $u\delta_{ct}$, obtained with Youden curve)

Metals	Standard addition		Average recovery		Youden curve	
	R	$u(R)$	R	$u(R)$	δ_{ct}	$u\delta_{ct}$
Fe	1.129	0.101	1.0198	0.0075	-0.349	0.409
Pb	1.012	0.028	0.999	0.010	-0.804	0.421
Zn	1.005	0.046	1.0321	0.0137	0.011	0.048

Table 5

Concentration together with its uncertainty, obtained with the procedures for all the metals analyzed

Metal	Concentration found		Method of average recovery
	With spike	Without spike	
Fe	17.464 ± 0.2397	17.464 ± 0.3247	17.8245 ± 0.2999
Pb	8.742 ± 1.528	8.742 ± 1.528	8.039 ± 0.408
Zn	1.887 ± 0.0459	1.8870 ± 0.0456	2.0514 ± 0.0960

*Results are expressed in parts per million.

The metals of five different amounts w_i (100, 200, 300, 400 and 500 ml) of Karaj River were analyzed under intermediate precision conditions. The analytical results were expressed as concentration found.

Table 4 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. Table 5 shows the concentration, together with its uncertainty, for all the metals and for two procedures. As we can see, results of two procedures are likely to be similar and the proposed method provides good result.

5. Conclusions

The aim of this study was to estimate the uncertainty of result obtained in determination of trace elements in water sample by SPE-ICP-OES method. XAD-4 resin as a sorbent material for separation and preconcentration of Fe, Pb and Zn (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.

Appendix A

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

$$s(b_{SAM(\text{conc})}) = \sqrt{\frac{s^2_{e,SAM(\text{conc})}}{\sum (C_{ad,i} - \bar{c}_{ad})^2}}$$

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

$$s(b_{sc}) = \frac{s_e s_c}{\sqrt{\sum (c_i - \bar{c})^2}}$$

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

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

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

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

Covariance between the slope and the intercept of the standard curve Section 3.3:

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

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