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

AZAM GHORBANI*, MOHAMMAD RABBANI†, SYED WAQIF HUSAIN,
MAHMOOD MAHMOODI‡ and MOHAMMAD SABERR-TEHRANI
Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran
Fax: (98)(21)44865182; Tel: (98)(21)44865179; E-mail: ghorbani.azam@gmail.com

This work describes measurement uncertainty estimation for determination of Fe, Co and Ni 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. 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: (i) a proportional bias and (ii) a constant bias. We applied Nested design for calculating proportional bias and Youden method to calculate the constant bias. The results 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: (1.0198 ± 0.0075) for Fe, (1.0215 ± 0.0133) for Co and (1.004 ± 0.0085) for Ni.

Key Words: Uncertainty estimation, Solid phase extraction, Inductively coupled plasma-optical emission spectroscopy (ICP-OES).

INTRODUCTION

In general, environmental waters can not be analyzed without sample pretreatment in order of determination of trace amount of elements[1]. A simple preparation step is necessary to extract traces of elements from the aqueous medium. Several sample preparation methods have been developed for extraction of elements from water, mainly liquid-liquid extraction (LLE) and solid-phase extraction (SPE). Solid phase extraction techniques are quite popular since they offer a number of important advantages over other preconcentration methods. 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].

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†Department of Chemistry, Islamic Azad University, North Tehran Branch, Tehran, Iran.
‡Department of biostatistics, Tehran Medical Sciences, Tehran, Iran.

The polymers most commonly used are styrene-divinyl benzene copolymers such as XAD-4 and acrylate polymers (Amberlite XAD-7). XAD-4 is a polymeric adsorbent with excellent physical, chemical and thermal stability and is stable at all pH range in aqueous solution[8-13]. 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[14-16]. The proposed approach[15,17,18] 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[15,17]. Another protocol proposed by Ellison[16], verify trueness in terms of recovery method. Therefore, the bias of analytical results is only assumed to be proportional. However, there may be two types of bias (proportional bias 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[18,19]. The aim of this study is to develop a Morato method in uncertainty estimation of analytical results obtained by assessing trueness and employing spiked samples in determination of Fe, Co and Ni in river water samples by SPE-ICP-OES.

EXPERIMENTAL

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 mm × 5 mm i.d.), packed with XAD-4, was used for separation/preconcentration.

All chemicals used were of analytical-reagent grade. Deionized 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 and liquid ammonia 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, deionized water, 2.0 mol L^{-1} HNO_3 and deionized 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.

TABLE-1
INSTRUMENTAL AND OPERATING CONDITIONS FOR ICP-OES MEASUREMENTS

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})	15.0
Sample flow rate (mL min^{-1})	1.5
Wavelength (nm)	Fe 238.204, Co 238.892, Ni 231.640

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 2 μg each of Fe, Co and Ni prepared and 100 μL of 8-HQ solution was added to form the metal-complexes. The pH was adjusted to desired value with appropriate buffer 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, deionized water and methanol and deionized water, respectively.

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 by adding concentrated nitric acid in order to avoid metal adsorption to the inner bottles walls. Then samples were filtered through a 0.45 μm polycarbonate membranes nucleopore filter.

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 similarly to previous report[13] and after finding the optimum situation, all the experiments run and the uncertainty of analytical result estimated.

Effect of pH: 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 showed the studied metals are largely formed/retained at pH = 8. Quantitative recoveries were obtained in the pH range of (6-12) for Fe, Co and Ni.

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 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 mol L^{-1}) and the lowest nitric acid volume (2.5) were chosen for most of the studies.

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.

Effect of ligand concentration: The influence of the 8-hydroxyquinoline (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.

Statistical method

Uncertainty and validation of analytical procedures: Analytical procedures should be validated before they are used to analyze 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 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 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 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 result scan calculated in a general way by grouping all these sources in four terms:

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

The first component of uncertainty, $u^2_{\text{precision}}$, 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, $u^2_{\text{pretreatments}}$, 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, $u^2_{\text{Other terms}}$, contains all the sources of uncertainty not considered in the former terms[13,19,20]. In this study we calculate two terms ($u^2_{\text{precision}}$ and u^2_{Trueness}) and also consider two situation (with a spike uncertainty and without it) to estimate the final uncertainty in precision study.

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 proposed experimental design 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, the case is also considered 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.

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, all the references have not the same level of traceability. Therefore, the reference selected should be the one that has the suitable level of traceability for this studies. 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 present results.

Standard addition method (SAM): The calculation of proportional bias and related uncertainty: 100 mL of each river water (four samples) are spiked with analyte quantities of 2, 4 and 6 μg for Fe, Co and Ni 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, $S^2_{\text{precision}}$. 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[22,24]. 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. $|\overline{R} - 1| \leq t_\alpha/2.\text{eff} \times u(R)$ [22].

TABLE-2
ANOVA TABLE FOR NESTED TWO-FACTOR DESIGN WITH
RANDOM FACTOR 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	–	–

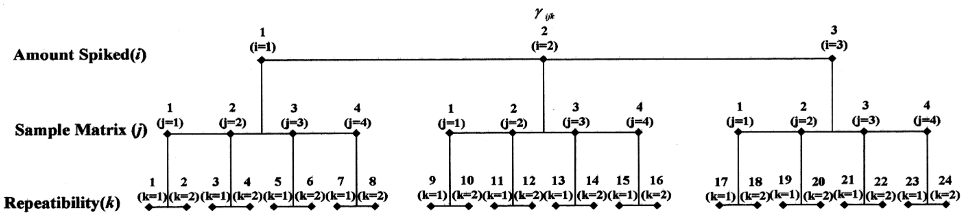

Fig 1. Experimental design for obtaining information about matrix variability and precision from the results obtained with spiked samples. Each measurements of metal concentration is denoted by γ_{ijk}, where i the number of the treatment, runs from 1 to a (a = 3) represented the amount of analyte added; 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

Youden method: calculation of constant bias and related uncertainty: The Youden method consists of analyzing 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 δ_{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 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 as:

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

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, $\mathrm{cov}(a_{sc}, b_{sc})$ denotes the covariance of the intercept and the slop of the standard curve and a_{You} represents the intercept of the Youden concentration curve[15,19,25]. 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.

The results of routine samples are expressed as concentration: The concentration of the routine samples, concentration is obtained by using a standard calibration curve. This concentration is calculated as:

$$\mathrm{conc.} = \frac{c_{found} - \delta_{ct}}{R}$$

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 concentration equation,

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

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 the work of Maroto *et al.*[15].

RESULTS AND DISCUSSION

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

TABLE-3
ESTIMATED OF VARIANCE COMPONENT OF VARIABLE IN NESTED DESIGN FOR Fe, Co AND Ni IN KARAJ RIVER

Metals	S^2_{Matrix}	S^2_{Spike}	$S^2_{precision}$
Fe	0.0560	0.048	0.554
Co	0.1905	0.000	0.538
Ni	0.5120	0.000	0.662

$\frac{MS_{Analyst+Matrix} - MS_{Intermediate\,precision}}{n}$, $\frac{MS_{Spike} - MS_{Analyst+Matrix}}{bn}$, $MS_{precision}$.

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[16-18]. 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 analyzed under intermediate precision conditions. The analytical results were expressed as concentration found. Table-4 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, it is assumed 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. Table-5 shows the results of two procedure are likely to be similar and the shows the accuracy of applied method.

TABLE-4
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

Metals	Standard addition		Average recovery		Youden curve	
	R	u(R)	R	u(R)	δ_{ct}	$u\delta_{ct}$
Fe	0.101	1.129	0.0075	1.0198	0.409	-0.349
Co	0.116	0.925	0.0133	1.0215	0.004	-0.009
Ni	0.985	0.021	1.0040	0.0080	0.095	0.298

TABLE-5
CONCENTRATION TOGETHER WITH ITS UNCERTAINTY, OBTAINED WITH THE PROCEDURES FOR THE METAL ANALYSED

Metal	Concentration Found		Method of average recovery
	With spike	Without spike	
Fe	17.464 ± 0.2397	17.4640 ± 0.3247	17.8245 ± 0.2999
Co	11.5713 ± 0.4503	3.86782 ± 0.1123	12.0969 ± 0.3045
Ni	3.9000 ± 1.1600	3.90000 ± 1.1600	4.0930 ± 1.1970

*Results are expressed in parts/million.

Conclusion

The aim of this study is 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 Fe, Co and Ni (8-HQ complexes) from aqueous solution. 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:

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

Standard deviation of the slope of the standard addition curve:

$$s(b_{sc}) = \frac{s_{e},s_{c}}{\sqrt{\Sigma(c_{i} - \bar{c})^{2}}}$$

Standard deviation of the intercept of the Youden curve:

$$s(a_{You(conc)}) = s_{e,You(conc)}\sqrt{\frac{\Sigma w_{i}^{2}}{n_{You}\Sigma(wi - \bar{w})^{2}}}$$

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

$$s(a_{sc}) = s_{e,.sc)}\sqrt{\frac{\Sigma c_{i}^{2}}{n_{sc}\Sigma(c_{i} - \bar{c}_{i})^{2}}}$$

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

$$\mathrm{cov}(a_{sc}, b_{sc} = \frac{\bar{c} \times s^{2}{}_{e.sc}}{\Sigma(c_{i} - \bar{c})^{2}}$$

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