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RESEARCH ARTICLE

Experimental estimation of the systematic errors due to matrix interferences in trace analyses

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Abstract

In analytical chemistry, several types of errors are usually encountered when determinations of trace elements are carried out. The assessment of systematic error is of crucial importance, especially when complex samples have to be analyzed (Miller et al., 2010; Massart et al., 1988). This paper deals with the application of a simple method for the assessment of the constant and proportional systematic error on the determination of Li in a very complex sample, such as water oilfield brine, with a salinity several times higher than sea water, as well as on the determination of nitrates in a river water sample. Both types of systematic errors were found in oilfield water, while no systematic error affected the results of river water. The application of the standard addition method (SAM) might be a useful tool in overcoming the proportional systematic error, only in cases when the constant systematic error is not present.

INTRODUCTION

When trace levels of any element are analyzed in the presence of very high concentrations of a matrix constituent, the results are subject to systematic errors. The overall systematic error is often considered to be a bias between test procedures, which implies that one method runs higher or lower than the other. In contrast to random errors, systematic errors cannot be revealed merely by making repeated measurements. If the true result of the analysis is not known in advance, very large systematic errors might occur, which could go undetected.

"A formidable protection against systematic errors" is the use of standard reference materials (Miller et al., 2010). However, the reference materials are not always available in the laboratories. In addition, the use of reference materials has shown to give accurate results only for the particular analyzed material. Real samples change widely in their composition depending mainly on their nature, (sediments, waters and biota for example). It means that matrix composition and effect on the response signal of the solute could be quite different, depending on the individual sample.

Comparison of the results obtained with two physically and chemically unrelated procedures can also be applied for the analysis of the same sample. Regression analysis or statistical tests can be applied to treat the results obtained by both techniques (Massart et al., 1988). The standard addition method (SAM), has been recommended in many publications as a successful tool for checking the accuracy of a determination, carried out in the presence of matrix interferences (Reynolds et al., 1970), but some erroneous conclusions have been made concerning what this technique can and cannot achieve. However, latter, it was pointed out that SAM cannot be used to overcome all interferences (Klein, 1977). Most particularly, nonspecific background is not corrected by this approach. It has been shown that SAM avoids only proportional systematic errors, which modifies the slope of calibration curve and not those interferences which affect the absorbance at zero concentration, known as systematic constant error (Price, 1985; Baraj et al., 1994; Taylor, 1981).

From the above mentioned procedures the conclusion drawn is that the options used are no helpful for the assessment of systematic errors (proportional or constant). In this paper, a simple procedure is described on the estimation of the systematic error types and its application on AAS determination of Li in oilfield brines. The evaluation of systematic errors on the determination of nitrate by UV-VIS technique in river water sample was also carried out. Particularly, this approach is valuable on trace metal analysis of very complex samples, in which limited dilution is carried out. The matrix effect causes severe interferences, resulting in both types of systematic error, proportional and constant, especially when dealing with geological, brines or sea water samples (Baraj et al., 1999).

Estimation of constant and proportional systematic errors

For the analyses of an unknown sample, a series of solutions were prepared, each containing a constant volume of the unknown solution. If we consider the true value as “μ”, than the mean concentration found was C_{mean}, which is an estimation of “μ” (the true value). A linear model could be developed, according to which the mean of the experimental series, C_{mean}, is the sum of the true value, “μ” and the free term, “a”, as follow, (Carjekov, 1983);

$$C_{mean} = a + b\mu \tag{1}$$

The result can differ from the true value and statistically this difference is referred to as the systematic error, “ε”. It is assumed that random errors are not significant (systematic errors can be determined only when random errors are small), (Miller et al., 2010). Thus, the systematic error is the difference between the mean measured value, $C_{mean,}$ and the true value, μ;

$$\varepsilon = a + b\mu - \mu = a + (b-1)\ \mu \tag{2}$$

where “a” is a measure of the constant error and “(b-1)” a measure of the proportional error. The object of the following procedure is to verify whether a=0 and b=1, which is in fact the null hypothesis. By accepting (verifying) the null hypothesis (when it is true), one concludes with a certain probability (usually 95%) that neither constant systematic error, nor proportional systematic error is present. For the estimation of both components of systematic error (in a statistical way), in an unknown sample, three sets of analysis of the sample on identical conditions were performed. The sample solution was divided into a number of aliquots and put into volumetric flasks. The first series contains a constant volume, V_x, of unknown solution, C_x. In the second series, the volume of the unknown solution added is twice higher than in the previous one. However, it might be 2, 3...,5 times higher than the added volume, but should take care on the calculation of the propagated errors, because these coefficients must be taken into account when the S_a and S_b are estimated. The propagation error law should be applied (Miller et al., 2010). The third series was prepared like the first one, but in each flask, a known amount of the analyte was spiked. All solutions were then diluted to the same volume.

n_1 (usually n=5) replicates were carried out in order to determine the concentration of the analyte. According to eq. (1), for the mean value found, it can be written:

$$C_{mean1} = a + b\mu \tag{3}$$

A set (n_2) of measurement of the above sample, twice in concentration is carried out:

$$C_{mean2} = a + 2b\mu \tag{4}$$

The third series (n_3) was prepared as in the first series, spiking a certain known amount of the analyte, ΔC, in each replicate. Thus:

$$C_{mean3} = a + b\ (\mu + \Delta C) \tag{5}$$

For the three series, the standard deviations of the results, S_{C1}, S_{C2} and S_{C3} were respectively calculated. The term "a" is calculated by difference of equation 3 with equation 4:

$$a = 2C_{mean1} - C_{mean2} \tag{6}$$

and "b" by the difference between equations 5 and 3:

$$b = (C_{mean3} - C_{mean1})\Delta C^{-1} \tag{7}$$

For Sa and Sb estimation, the formula of the propagation of random errors, applied for simple linear equations 6 and 7, should be taken into account, (Miller et al., 2010).
It should remember as well that standard deviations of the respective means should be used, as ($S^2C_{mean1} = S^2_1 \backslash n_1$ and $S^2C_{mean2} = S^2_2 \backslash n_2$). Consequently, the following formulas are obtained:

$$S_a = (4S_1^2 / n_1 + S_2^2 / n_2)^{0.5} \tag{8}$$

$$S_b = \Delta C^{-1}(S_1^2 / n_1 + S_3^2 / n_3)^{0.5} \tag{9}$$

The null hypothesis of constant systematic error is rejected when:

$$|a| > t_{0.95,(n_1+n_2-2)} S_a \tag{10}$$

Where "t" is the student test value, at 95% confidence level, with n_1+ n_2-2 degrees of freedom. The null hypothesis to proportional systematic error is rejected when:

$$|b-1| > t_{0.95,(n_1+n_3-2)} S_b \tag{11}$$

Experimental

Instrumentation and reagents.

A UV2100 Shimadzu UV/VIS spectrophotometer and a Varian AA10+ model spectrometer were used to determine nitrates and Li concentration in samples, respectively. In order to have the best sensitivity the instrumental parameters were optimized prior to measurements. All chemicals used were of analytical reagent grade, purchased from Merck.

Results and discussion

Estimation of systematic error on Lithium determination in oilfield brines by AAS technique

Lithium is one of the important microelements in underground waters, used by geochemists to determine the origin of waters in oil wells (Collins, 1975). Lithium has also been used as a trace metal that meets all criteria to be used as a normalizing element, for identification of what proportion of the sedimentary metal load is natural and what proportion is anthropogenic (Loring & Rantala, 1995).
Although, flame emission or absorption spectrometry, have been the most popular methods for its determination (due to low detection limit obtained and relatively instrumental simplicity), they are subject to several types of interferences (Kirkbright, 1974).

Particularly, the determination of lithium in brines and geological samples (rocks and sediments), in which the concentration of other constituents accompanying the analyte is very high, should lead to severe interferences in both emission and absorption modes.

In a previous work (Baraj et al., 1994) we observed scattering, ionisation and spectral interferences during lithium determination in brines in emission mode. The spectral interferences occurred due to calcium and strontium presence in the sample.

Table 1. Lithium concentration in oilfield brine (µg/mL)

No/µg/L	***1***	***2***	***3***	***4***	***5***	***Mean***	***S 10^3***
C_1	0.0865	0.0904	0.0943	0.0910	0.0885	0.09014	0.00292
C_2	0.149	0.1450	0.153	0.147	0.151	0.149	0.00316
C_3	0.477	0.4690	0.473	0.481	0.465	0.473	0.00632

Adopting the null hypothesis that there is no a systematic error present, i.e. a=0; b=1 and using equations 6, 7, 8 and 9 give:

$$a = 0.0313 \qquad t_{(0.95,n_1+n_2-2)} \times S_a = 2.31 \times 0.00297 = 0.00686$$

$$b = |b-1| = 0.0428 \qquad t_{(0.95,n_1+n_3-2)} \times S_b = 2.31 \times 0.00492 = 0.0114$$

Following the procedure was found that:

$$a = 0.0313 > t_{(0.95,n_1+n_2-2)} \times S_a = 0.00686$$

$$|b-1| = 0.0428 > t_{(0.95,n_1+n_3-2)} \times S_b = 0.018$$

From t-distribution, the critical value of "t", for 8 degrees of freedom, is 2.31 (significance level of 0.05) (Miller et al., 2010). It means that both proportional and constant systematic errors are present in the determination of Li in brines of oilfield sample. The null hypothesis should be rejected. It means that if a calibration curve is taken by variable amounts of analyte, but identical concentrations of the same interfering matrix elements, the slope and the intercept will be different from the calibration curve obtained without having interfering elements. The significance of constant systematic error makes ineffective the use of SAM. In a previous work (Baraj et al., 1999) we tried to assess the matrix interferences on Li determination in brines, by applying factorial design. Factorial design might evaluate the interfering elements and their contribution on the signal, but is not effective on distinguishing the systematic errors types. However, we tried to eliminate matrix interference by SAM, which appeared ineffective (Baraj et al., 1999; Mirlean et al., 2003). This is in good agreement with conclusions drown in actual work.

Estimation of systematic error in spectrophotometric determination of nitrates in river water

There are several spectrophotometric methods for the determination of nitrate ions in water samples. One of the most sensitive is an indirect method based on Griess reaction after reduction of NO_3^- to NO_2^- (APHA, 1995). It was applied for systematic error assessment on the determination of nitrates content in Tirana River water. The sampling site is located in the upper stream, within a mountainous uncontaminated area, which normally have been used as a reference sampling point. The measurements were carried out at pH=0.8 and at λ= 530 nm. The results obtained for the three series of the unknown sample are shown in table 2. The filtered river sample was pipetted into a 50mL volumetric flask (the volume taken depend on nitrates concentration). The dilution to the mark was made with NH_4Cl-EDTA solution (APHA, 1995). After the reduction of nitrates to nitrites in a Cd-column, the first 15 mL were discarded. From the rest, V mL was placed (10 mL in our case) into a 25 mL flask and 0.5 mL sulphanilamide reagent was added and left to react for 5 min.

Finally, 0.5 mL of NED-dihydrochloride was added for coupling reaction and bi-distilled water was used for dilution to the mark. For the second series the same procedure as on (1) was followed, but 2V mL was pipetted and the third is prepared like first one, but 0.04 µg/mL NO_3^-N in the final volume was spiked.

To find out if systematic error is present during Li determination in oilfield brines by AAS technique, in absorption mode, the above described procedure was applied. On table 1 the data obtained to a brine sample are shown. The concentrations of Ca, K and Na were respectively 4000, 2000 and 30000 mg\L. The C_1 series was prepared in 25 ml flask, containing 5 ml of the unknown sample solution. C_2 series contain 10 ml of the unknown sample, while the third series was prepared as the first one, but 10 µg Li was spiked into 25 mL flask. Deionised water was used to bring the volume to the mark.

Table 2. Nitrates concentration in River (µg/mL)

No	***1***	***2***	***3***	***4***	***5***	***Mean***	***S 10^3***
C_1	0.0474	0.0483	0.05	0.0519	0.0486	0.0492	0.00176
C_2	0.093	0.092	0.098	0.1	0.094	0.0954	0.00344
C_3	0.0907	0.094	0.0867	0.0904	0.0915	0.0907	0.00263

Adopting the null hypothesis that there is no a systematic error present, i.e. a=0; b=1 and using equations 6, 7, 8 and 9 give:

$$a = 0.00308 \qquad t_{0.95,n_1+n_2-2} \times S_a = 2.31 \times 0.0022 = 0.0051$$

$$b = 1.036 \qquad |b-1| = 0.036 \quad t_{0.95,n_1+n_3-2} \times S_b = 2.31 \times 0.035 = 0.082$$

Following the procedure was found that:

$$a = 0.00308 < t_{0.95,n_1+n_2-2} \times S_a = 0.051 \;; \qquad |b-1| = 0.036 < t_{0.95,n_1+n_3-2} \times S_b = 0.082$$

From t-distribution the critical value of t for 8 degrees of freedom is 2.31 (significance level of 0.05) (Miller et al., 2010) It means that both proportional and constant systematic errors are not present in the determination of NO_3^- in river water determined by this method.

Conclusions

When complex samples have to be analyzed, estimation of the systematic errors is well recommended. In this paper, the application of a simple statistical method was found to give relevant results in assessment of the constant and proportional systematic error in samples of different matrixes. Both types of systematic errors were present in the determination of Li in an oilfield water sample by means of the AAS technique, while no systematic error affected the results of nitrates determination in a river water sample, by SF UV-VIS.

Application of the standard addition method (SAM) can be a useful tool in overcoming the proportional systematic error, but only in cases when the constant systematic error is not present. Conclusively, in order to overcome severe interferences in such complex samples, other alternatives should be taken into account. Processes such as ion exchange as well as liquid extraction, etc., are good alternatives of samples treatment before the analyses of the interest analyte.

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