Validation and Optimization of a Method for Sb Determination from Bottled Natural Mineral Waters by ICP-OES

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In the present work, it was developed a simple, cheap and quick method for Sb determination from mineral water, using ICP-OES, using two different calibration proceedings: calibration curve method (CCM) and standard additions method (SAM). On the studied concentration range, the parameters such as the calibration curve slope, linearity expressed through correlation coefficient r = 0.9992, limits of detection LoD = 0.67 μg L^{-1} and quantification LoQ = 2.01 μg L^{-1}, the standard deviation of repeatability of 0.25 μg L^{-1}, the accuracy of 0.16 μg L^{-1} satisfy the performance criteria. The value of extended uncertainty with a confidence level of 95 % (k = 2), is 1.0 μg L^{-1} obtained for Sb content of 4.10 μg L^{-1}. The mineral waters were analyzed also by the addition standard method. One of the advantages of this method is to eliminate interference from the matrix. By the method of standard additions, the detection limit decreased from LoD=0.67 μg L^{-1} to 0.16 μgL^{-1}.

Keywords: *ICP-OES, mineral water, Sb, validation*

In the latest decades, consumption of bottled water has risen with 125 %, as compared to 1990 [1]. Bottled mineral water gained popularity, based on its purity and well-balanced chemical composition [2, 3]. According to European Directive 2009/54/CE [4] and Government Decision no. 1020/2005 [5] , the term *mineral water* refers to microbiologically pure water that comes from ground water or underground aqueous reservoirs. It differs from common drinking water by its nature, characterized by mineral composition, original purity and certain effects of its elements and constituents. Opposed to this opinion, mineral water can be contaminated by storage, because of the release of Sb by degradation of polyethylene terephthalate (PET) used for packaging. Migration of Sb from PET bottles into mineral water could pose a risk to human health, with certain effects on the organism such as: respiratory, cardiovascular, gastrointestinal, dermal, and reproductive effects [6, 7]. Due to high amount of Sb in PET, Sb_2O_3 is listed as a main pollutant by European Union (EU) and United States Environmental Protection Agency (US EPA). The maximum admissible concentration of antimony in drinking water, according to European Directive EC 98/83/EC, 1998 is 5 μg L^{-1} [8] and US EPA is 6 μg L^{-1} [9]. In Romania, Law No. 458 (2002) [10] for drinking water and Government Decision No. 1020/2005 for natural mineral water limit the maximum admissible concentration to 5 μg L^{-1}. Many research studies have been made on Sb migration, used in industrial synthesis of PET [11,12] in various foods and beverages, including drinking water [13]. Several studies are present in the literature in which Sb content in mineral waters is determined by different analytical techniques: HG -AFS [14, 15], ICP-SF-MS [16], ICP-MS [17].

The objective of the present study is to develop and validate a method for Sb determination, by ICP-OES, in a laboratory that fulfils the requirements of quality management system and to demonstrate its suitability for water quality control according to EU Directive 2009/54/EC and Government Decision no. 1020/2005. These documents state the acceptance criterion of the method without stating the type of equipment, the laboratories having the possibility to use their own equipment and proper method, too.

Experimental part

Equipment

For the determination of Sb content the Optima 2100 DV ICP-OES System (Perkin Elmer) was used, with dual view optical system that combines the radial and axial view of the plasma in a single sequence which functions as a transistor based radiofrequency generator with 40 MHz frequency. The system comprises of a nebulizer PEEK Mira Mist® coupled with a Baffled Cyclonic spraying chamber. The spectrometer consists of an optical module which includes an Echelle monochromator with bidimensional, charged coupled device, detector. The spectral domain is between 165 and 800 nm.

Reagents

All the reagents used for antimony determination were analytical grade. A Quality Control Standard 21 stock solution of 100 mg L^{-1} Sb concentration, from Perkin Elmer and HNO_3 ≥ 69.0 % Trace SELECT , Sigma-Aldrich were used. For the preparation of working solutions ultrapure water with a resistivity of 18.2 M Ωcm^{-1} was used, produced by EASY pure Ro Di, Barnstead, USA. For ICP-OES purging gas Argon 5.0 of > 99.999 % purity (Linde Gas Romania) was used.

Mineral water samples

The three carbonated mineral water samples, showed in table 1, were purchased from local market, with different compositions and origins. There were bottled in PET-bottles, in batches of four samples each, of 1.5 L. The chemical composition of the natural mineral waters were determined in our laboratories by using methods described in [18-20].

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Table 1
PRESENTATION OF MINERAL BOTTLE SAMPLES

No.	Mineral water samples	Chemical composition
1	Carbonated mineral water	pH = 6.10; HCO_3^- = 1281 mg L^{-1}; CO_2 > 2500 mg L^{-1};
2	Carbonated mineral water	pH = 5.52; HCO_3^- = 1895 mg L^{-1}; CO_2 min. 2500 mg L^{-1};
3	Carbonated mineral water forte	pH = 6.89; HCO_3^- = 1281 mg L^{-1}; CO_2 min. 4000 mg L^{-1};

Working mode

Measurement method for Sb using ICP-OES

The selected and optimized operation parameters of the method are presented in [21]. The standard solutions of 2; 5; 10; 15 and 20 µg L^{-1}, used for the development of calibration curve, were obtained by diluting the 100 mg L^{-1} Quality Control Standard 21 stock solution.

Sample preparation

Samples of mineral water from PET bottles were acidified with 1 % HNO_3 69.0 % and CO_2 was removed by stirring for 1 hour, on the magnetic plate.

Sample analysis

Sample analysis using the calibration curve method (CCM) was performed in duplicate, keeping the same conditions as used for generating the calibration curve. Each result represents the average of two independent measurements. Sample of mineral water were fortified with 100 mg L^{-1} Quality Control Standard 21 stock solution, at different concentrations in the domain: 2-10 µg L^{-1} and analysis by standard additiond method (SAM).

Results and discussions

The performance parameters of the developed method were: linearity, precision (repeatability), accuracy, measurement uncertainty, limits of detection (*LoD*) and quantification (*LoQ*). The performance parameters of the atomic spectrometry techniques, namely graphite furnace atomic absorption spectrometry (GF-AAS), sector field inductively coupled plasma mass spectrometry (ICP-SF-MS), hydride generation atomic fluorescence spectrometry (HG-AFS) respectively, reported by other authors are presented in table 2.

Validation of the method for Sb determination from natural mineral water by CCM

Linearity

Linearity was evaluated based on the regression function of calibration by using five standard solutions prepared in a range of concentrations between 2 - 20 µg L^{-1}. The equation of the calibration curve is presented below. (fig. 1). The linearity, fulfills the acceptance criterion (table 5), based on a correlation coefficient, r=0.9992.

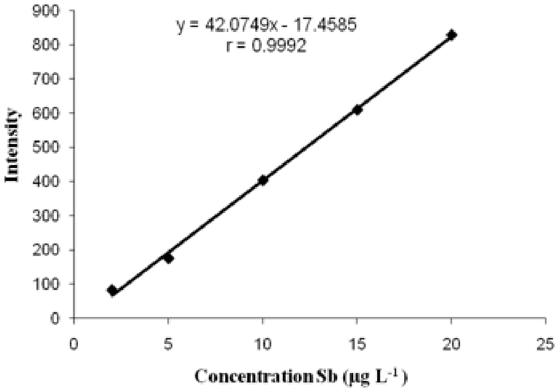

Fig. 1. Calibration curve for the concentration range 2 µg L^{-1} to 20µg L^{-1} Sb

Limits of Detection ***(LoD)*** *and Quantification* ***(LoQ)***

For determination of the limit of detection (*LoD*) and limit of quantification (*LoQ*), ten standard solutions were measured with the smallest concentration on the calibration curve, i.e. 2 µg L^{-1}. The standard deviation of the determinations set with an average content of 2.04 µg L^{-1} was 0.22 µg L^{-1}. The limits of detection (*LoD)* and quantification (*LoQ*) were calculated using formula (eqs.1, 2) obtaining the following results: 0.67µg L^{-1} and respectively 2.01µg L^{-1}.

$$LoD = 3 \times s \quad (1)$$

$$\mathrm{LoQ} = 3 \times \mathrm{LoD} \quad (2)$$

The results for *LoD* and *LoQ* fulfill the acceptance criteria presented in table 5.

Table 2
COMPARATIVE DATA OF THE PERFORMANCE PARAMETERS IN LITERATURE

Literature method	Performance parameter	Reported value in literature	Reference
GF-AAS	correlation coefficient, r *LoD/LoQ*, (µg L^{-1})	0.999 1.0 /3.7	[22]
ICP-SF-MS	*LoD* (ng L^{-1})	0.7	[16]
ICP-MS	*LoD /LoQ*, (µg L^{-1})	0.02 /0.07	[17]
HG-AFS	*LoD /LoQ*, (µg L^{-1}) Accuracy, δ (µg L^{-1}) RSD % Measurement uncertainty, (µg L^{-1})	0.112 /0.375 0 8 0.8 obtained for Sb content of 13.8 µg L^{-1}	[15]
ICP-MS	*LoD/LoQ*, (µg L^{-1}) Accuracy, δ (µg L^{-1}) RSD % Measurement uncertainty, (µg L^{-1})	0.003 /0.010 0.2 2 0.4 obtained for Sb content of 14.0 µg L^{-1}	

Precision (Repeatability)

The repeatability of the method has been determined by measuring ten samples of the same concentration, closed to the maximum admissible one in repeatability conditions. The value of the standard deviation (s_r) was obtained at an average content of 4.10 µg L^{-1} is 0.25 µg L^{-1}, thus acceptance criteria being fulfilled. The obtained RSD was 6.21 %.

Accuracy

The accuracy of the method was determined in two different ways presented below:

-based on the difference (δ) between the average content of ten measurements of 10 µg L^{-1} standard solutions and theoretical antimony content of reference material (10 µg L^{-1} Sb); the obtained result, δ = 0.16 µg L^{-1}, fulfills the acceptance criterion presented in table 5.

-based on the method of standard additions, applied to three types of mineral water consisting in adding different volumes of 100 mg L^{-1} Quality Control Standard 21 standard solution (Perkin Elmer, USA), in the analyzed samples; thus the mineral water samples were fortified with a standard solution at three levels of concentration (table 3) and analyzed in triplicate.

Accuracy (% the recovery degree) was measured as the difference between the concentration of the spiked and unspiked sample, compared to the concentration of the analyte added to the spiked sample. The accepted values for the recovery degree depending on the analyte concentration must be within the domain 40 % ≤ R % ≤ 120 % [23]. The results of the study are presented in table 3. The obtained recovery degree values stand in the 95 % - 109 %, and fulfilled the required criteria for all levels of the tested concentrations.

Average recovery degree of the method was R = 102 %.

The statistical test:

$$t = (100 - \bar{R}) / s_{\bar{R}} \le t_c \qquad (3)$$

where: $\bar{R}$ - average recovery, %; $s_{\bar{R}}$ - standard deviation of recovery; t_c - critical *t* value; *t* - calculated *t* value, applied to the recovery degrees does not emphasize the existence of any systematic errors due to matrix or method. The values obtained by using the calculated *t*-test (eq. 3) are between 0.275 and 3.500 and do not exceed the critical value, t_c = 4.303, n = 2 and a confidence level of 95 % [24].

Quantification of uncertainty

Uncertainty sources that significantly affect the concentration are presented in table 4.

The uncertainty of determination of concentration based on calibration curve, *u(c)* presented in figure 2 is determined using formulae (eqs. 4-6), [25].

$$u(c) = \frac{S}{B_1}\sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(c_o - c_{med})^2}{S_{xx}}} \qquad (4)$$

where:

$$S_{XX} = \sum_{j=1}^{n} (c_j - c_{med})^2 \qquad (5)$$

and

$$S = \sqrt{\frac{\sum_{j=1}^{n} \left[A_j - (B_0 + B_1 \times c_j)\right]^2}{n-2}} \qquad (6)$$

where S is residual standard deviation; B_1 - slope of the calibration curve; B_0 - intercept; p - number of measurements made to determine c_0; n- number of standard solutions used for calibration; c_0 - antimony content in sample solutions; c_{med} - average value of antimony content in standard solutions used in calibration curve; *j* - index for number of standard solutions used in calibration curve; *Aj* = *j*th measurement of the intensity of the *j*th calibration standard solution; *cj* -concentration of the *j*th calibration standard solution.

The combined uncertainty u_c, according to the rule of propagation of uncertainty [25] is:

$$u_c = c \times \sqrt{\left(\frac{u(\delta)}{\delta}\right)^2 + \left(\frac{u(\mathrm{Re}\,p)}{\mathrm{Re}\,p}\right)^2 + \left(\frac{u(P)}{P}\right)^2 + \left(\frac{u(c)}{c}\right)^2} \qquad (7)$$

The composed uncertainty based on (eq. 7) for the determination method of Sb with a content level of 4.10 µg L^{-1}, expressed as standards deviation, is u_c = 0.5 µg L^{-1}.

Table 3
THE OBTAINED RESULTS OF RECOVERY DEGREE

Sample	Sb			R (%)
	$C_{measured}$ (µg L^{-1})	$C_{calculated}$ (µg L^{-1})	R (%)	Average recovery degree on sample
Sample 1	0.344	-	-	-
Sample 1 + 2 µg L^{-1}	2.39	2.05	102	**106**
Sample 1+ 5 µg L^{-1}	5.67	5.33	107	
Sample 1+ 10 µg L^{-1}	11.2	10.9	109	
Sample 2	0.475	-	-	-
Sample 2 + 2 µg L^{-1}	2.35	1.95	97.5	**97.1**
Sample 2+ 5 µg L^{-1}	5.24	4.77	95.4	
Sample 2 + 10 µg L^{-1}	10.3	9.83	98.3	
Sample 3	0.613	-	-	-
Sample 3 + 2 µg L^{-1}	2.73	2.12	106	**101**
Sample 3+ 4 µg L^{-1}	4.48	3.87	96.8	
Sample 3+ 6 µg L^{-1}	6.66	6.05	101	

Table 4
THE BUDGET OF UNCERTAINTY

Component u(x)	Source	Value	Unit	Standard uncertainty	RSD
u (δ)	Accuracy	10.16	µg L^{-1}	0.11	0.0109
u (Rep)	Repeatability	4.10	µg L^{-1}	0.25	0.0609
u (c)	Calibration curve fitting	4.10	µg L^{-1}	0.43	0.1048
u (*P*)	Standard purity	1	-	0.0029	0.0029

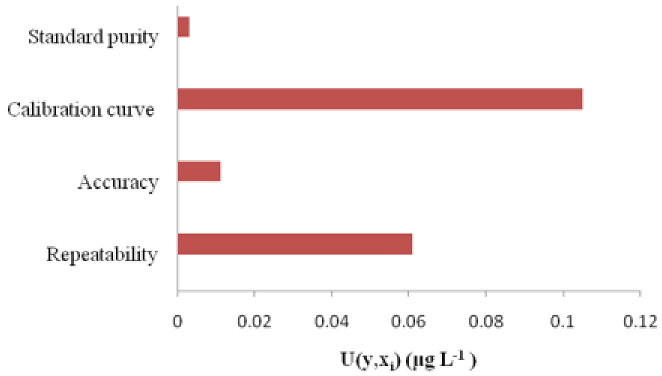

Fig. 2. Contribution of each component to the budget of uncertainties

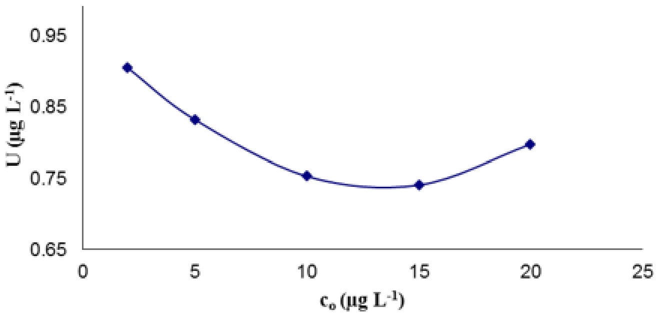

Fig. 3. The variation of U on Sb concentration (c_0)

Table 5
PERFORMANCE PARAMETERS OF THE METHOD FOR SB DETERMINATION FROM NATURAL MINERAL WATER BY CCM AND ACCEPTANCE CRITERIA

Parameter	Value	Unit	Acceptance criteria
Linearity, r	0.9992	-	≥ 0.997
LoD	0.67	µg L^{-1}	1.25
LoQ	2.01	µg L^{-1}	3.75
Repeatability, s_r	0.25	µg L^{-1}	1.25
Accuracy	0.16	µg L^{-1}	1.25
Extended uncertainty, (k = 2, P = 95 %)	1.0	µg L^{-1}	2

Table 6
COMPARATIVE RESULTS OF Sb DETERMINATION BY CCM AND SAM METHODS IN MINERAL WATERS FROM ROMANIA

Mineral water samples	Sb (µg L^{-1})		u_c (µg L^{-1})	Linearity, r		LoD (µg L^{-1})		LoQ (µg L^{-1})	
	CCM	SAM	SAM	CCM	SAM	CCM	SAM	CCM	SAM
Sample 1	< *LoQ* (0.344)	0.254	0.053	0.9992	0.9999	0.67	0.157	2.01	0.473
Sample 2	< *LoQ* (0.475)	0.422	0.065		0.9999		0.195		0.587
Sample 3	< *LoQ* (0.613)	0.641	0.125		0.9990		0.375		1.13

In the absence of an inter-laboratory study for determination of the performance of the method, the composed uncertainty gives a reasonable estimation of reproducibility.

As it can be noticed in figure 2, linear regression equation has the most important contribution on the measurement of uncertainty, followed by uncertainty of repeatability, uncertainty of accuracy and the purity of standard stock solutions.

The extended measurement uncertainty in the range of 2 -20mg L^{-1} depends on the level of concentration and this dependence is shown in figure 3.

For a 4.10 µg L^{-1} average concentration and a cover factor of k = 2, corresponding to a confidence level of 95 %, the extended uncertainty is 1.0 µg L^{-1}.

The results from the *in house* validation study (table 5) show that all the performance criteria are fulfilled.

The results obtained by CCM developed method for r, *LoD* and *LoQ* are comparable to those obtained by GF-AAS method (table 2). Instead of SAM method, the obtained value of *LoD* allows us to compare the results with those reported by HG-AFS method.

Analysis of mineral water samples by using the method of standard additions

In order to eliminate the interferences due to the matrix, the samples were analyzed by the method of standard additions. Comparative data are presented in table 6.

It is found that all analyzed waters comply with requirement EU Directive 2009/54/EC, presenting values of the concentration below the limit of detection of the method. The tested mineral waters fulfill the acceptability condition for the maximum admissible concentration of antimony of 5 µg L^{-1}, required by EU Directive 2009/54/EC and Government Decision no. 1020/2005, and it is smaller than the quantification limit of the method. Standard Additions Method (SAM) offers some great advantages: it overcomes matrix interferences [26] and it decreases the limit of detection from 0.67 to 0.16 µg L^{-1}. This decrease is due to the fact that standard additions are correlated with the measured Sb concentrations in the studied matrices, decreasing the component of the uncertainty through covariance.

Conclusions

An accurate analytical method for the determination of Sb in natural mineral water with direct analysis of mineral water samples was developed in this study. It represents a simple, cheap and fast measurement, characterized by high recovery at low concentration of Sb determined from carbonated mineral water, by ICP-OES technique. Over the studied concentration range, the calibration curve slope, expressed through correlation coefficient r = 0.9992, limits of detection *LoD* = 0.67µg L^{-1} and quantification *LoQ* = 2.01 µg L^{-1}, a value of 0.25µg L^{-1} for standard deviation of repeatability, accuracy of 0.16 µg L^{-1} satisfy the acceptance criteria. The value of extended uncertainty with a confidence level of 95 % (k = 2), is 1.0µg L^{-1} obtained for

Sb concentration of 4.10 μg L^{-1}. The calibration curve method was applied for Sb determination from three carbonated mineral waters, bottled in PET bottles, sold in supermarkets from Romania. The concentration of Sb in the analyzed mineral waters is below the *LoD* of the CCM developed method. Thus, Sb from the same mineral waters has been analyzed by standard additions method (SAM). The correlation coefficients of the calibration curves obtained by the method of standard additions ranged between r = 0.9990 and r = 0.9999, SAM offering some great advantages regarding the matrix interferences and decreasing the limit of detection from 0.67 to 0.16μg L^{-1}.

The developed method can be applied for Sb content in natural mineral waters according to Government Decision no. 1020/2005 and EU Directive 2009/54/EC, as well as in research studies for Sb migration from PET in various beverages.

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