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VALIDATION OF A METHOD FOR DETERMINATION OF ANTIMONY IN DRINKING WATER BY ICP-OES

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The method for the determination of Sb in drinking water, now recognized at European and international level is at the moment not validated, so there are no information about its performances. The purpose of this study is to characterize the proposed method for determining Sb, according to SR EN ISO 11885/2009 in a laboratory that meets quality management system, and to demonstrate its suitability for water quality control in accordance with EU Directive 1998/83/EC si law 311/2004. Relevant performance parameters were evaluated: linearity 0.9992, limit of detection 1.13 $\mu g\ L^{-1}$, limit of quantification 3.38 $\mu g\ L^{-1}$, precision (repeatability) 0.55 $\mu g\ L^{-1}$, accuracy 0.31 $\mu g\ L^{-1}$, recovery 103% and measurement uncertainty 1.7 $\mu g\ L^{-1}$. The studied method can be successfully applied for the quality control of drinking water.

Keywords: antimony, drinking water, validation, ICP-OES

1. Introduction

The toxicity of antimony and its compounds has been of increased concern worldwide [1]. Exposure to antimony and its compounds causes irritation of the respiratory tract, leading to pneumoconiosis, and can induce other health problems [2]. The International Agency for Research on Cancer has classified Sb_2O_3 as possibly carcinogenic to humans (Group 2B) [3]. Long exposures at concentrations higher than 9 mg/m^3 cause irritation of eyes, skin and lungs. Exposure at less higher concentrations of 2 mg/m^3 can cause problems of lungs, heart and stomach [3, 4].

Antimony is toxic even at low concentration levels. It comes from both natural processes and human activity. Its content in rivers is typically lower than 1 $\mu g\ L^{-1}$ and does not usually exceed 0.5 $\mu g\ L^{-1}$ in drinking water. Sb concentration has considerably increased in water systems over the last decades. It

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is mainly related to copper ore processing industry and coal and municipal waste combustion [5].

According to Law no. 311/2004, drinking water is defined as any water in its natural state, or after treatment, used for drinking, food preparation, or other domestic purposes, regardless of its origin and whether it is supplied through distribution networks, tanks or distributed in bottles or in other containers [6].

Bottled water is considered an important element in the human diet and plays a major role for the intake of a number of nutritional and toxic trace elements [7].

Therefore, regulations were developed by international, national and non-governmental organizations to define the quality of water that is safe and acceptable to consumers [8].

The World Health Organization (WHO) [9] establishes as maximum admissible concentration of antimony in drinking waters 20 µg L^{-1} and the United States Environmental Protection Agency (EPA) [10], 6 µg L^{-1}. Due to acute and chronic toxic effects, its concentration are regulated in drinking water in the United States, Canada, Europe and Japan in the range of values 2 - 6 µg L^{-1} [5]. EU Directive 2009/54/EC, Natural mineral water [11] and EU Directive 1998/83/EC, Drinking water [12] establishes as maximum admissible concentration of antimony in drinking waters a value of 5 µg L^{-1}.

In Romania, the legislation governing maximum permissible concentration of Sb in drinking and mineral water is limited at 5 µg L^{-1}, by Law No. 311/2004 Drinking water [6] and Government decision No. 532/2010, Natural mineral water [13].

Analytical methods capable to detect low concentrations are necessary for determining trace elements in drinking water (bottled mineral and tap water) [14].

Table 1

Methods of analysis of Sb in drinking water

No.	Matrix	Method	Limit of detection (µg L^{-1})	Reference
1.	Drinking water	ICP-QMS	0.01	[14]
2.	Drinking water	HG-ICP-OES	1.3	[15]
3.	Mineral water	ICP-QMS	0.002	[16]

The purpose of this study is to characterize the proposed method for determining Sb, according to SR EN ISO 11885/2009 [17] in a laboratory that meets quality management system and to demonstrate its suitability for water quality control according to EU Directive 1998/83 / EC and law 311/2004. The literature shows no interlaboratory collaborative study to determine the performance of this method.

2. Experimental

2.1. Equipment

An inductively coupled plasma optical emission spectrometer with axial and radial viewing plasma configuration (ICP-OES, Perkin Elmer, USA, Model Optima 2100 DV) operating at a 40 MHz free-running ratio-frequency was utilized. The nebulisation system was equipped with a PEEK Mira Mist® nebulizer coupled to a Baffled Cyclonic spray chamber.

The radiation separator, equipped with an Echelle grating, had a spectral range of 165–800 nm and a resolution of 0.009 nm at 200 nm.

2.2 Reagents

The reagents used were standard solution Quality Control Standard 21, of 100 mg/L concentration, by Perkin Elmer. Ultrapure water with a resistivity of 18.2 MΩ cm, produced by a EASY pure RoDi, Barnstead, USA, was employed for the preparation of all standard solutions.

2.3 Procedure

Plasma view mode is axial and spectral line was found at λ=206,836 nm. For the determination of Sb in drinking water the calibration curve was obtained by diluting the stock of 100 mg L^{-1}, Quality Control Standard 21, for preparing calibration standard solutions of: 2; 5; 10; 20; 30 µg L^{-1}. The solutions were analyzed automatically and the calibration curve was obtained. The drinking water samples were injected and analyzed in the same manner as the standard solutions, then there were processed the results. The operating conditions are shown in Table 2.

Table 2

Operating Conditions for Optima 2100 DV ICP-OES

No.	Parameter	Value
1.	Plasma viewing mode	*Axial*
2.	RF incident power	1.25 kW
3.	Nebulizer argon flow rate	0.75 mL/min
4.	Plasma argon flow rate	15 ml/min
5.	Auxiliary argon flow rate	1.5 ml/min
6.	The flow rate of the peristaltic pump	1.5 ml/min
7.	Total time for analysis	cca. 110 sec

The relevant performance parameters for this method were studied:

- linearity;
- limit of detection, limit of quantification;
- precision (repeatability);
- accuracy;
- recovery;

- measurement uncertainty.

3. Results and Discussion

3.1 *Linearity*

In this study, linearity was evaluated from the regression function of calibration using five standards in the 2 - 30 µg L^{-1}concentration range, using a stock standard solution Quality Control Standard 21, 100 mg L^{-1} (Perkin Elmer, USA).

The equation of the calibration curve is presented in Fig. 1. Linearity was assessed from the correlation coefficients of calibration curves and it was considered acceptable when $r \geq 0.997$. [18]

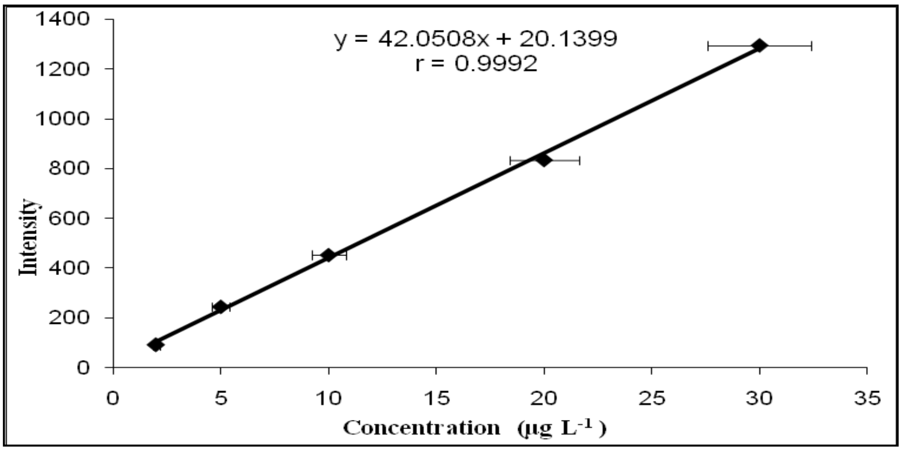

Fig. 1. Calibration curve in the concentration range of 2 µg L^{-1} to 30 µg L^{-1} Sb

3.2 *Limit of detection (LoD) and quantification (LoQ)*

Limit of detection *(LoD)* is the smallest amount of concentration of analyte in the sample that can be reliably distinguished from zero, while *LoQ* (limit of quantification) is the smallest amount and concentration of an analyte in the sample that can be determined with an established fidelity [17].

For determination of LoD and LoQ, ten measurements of a standard solution with the lowest concentration of the calibration curve, 2 µg L^{-1} were performed [6] and it was determined the standard deviation (s_r) of the set of measurements.

The method detection limit and quantification was determined with formulas [17]:

$$\left(LoD = 3 \times s_r\right) \quad (1)$$

$$\left(LoQ = 3 \times LoD\right) \quad (2)$$

The maximum admissible concentration (CMA) for Sb in drinking water according to Law 311 of 28 June 2004 [6] is 5 µg L^{-1} .

The results of LoD and LoQ are presented in Table 3 and meet the imposed acceptance criteria, according with the same law.

Table 3

Obtained values for detection and quantification limits in drinking water measurements and acceptance criteria

Average (µg L^{-1})	s_r (µg L^{-1})	LoD (µg L^{-1})		LoQ (µg L^{-1})	
		experi-mental	criterion LoD = 25% CMA	experi-mental	criterion LoQ = 75% CMA
2.16	0.38	1.14	**1.25**	3.42	**3.75**

3.3 *Precision (Repeatability)*

Experimental data for method repeatability was obtained by analyzing 10 samples of drinking water with concentrations closed to CMA in such conditions - same method, same analyst, same equipment, same day.

To demonstrate precision (repeatability), evaluation criteria are imposed by law 331 of 28 June 2004 [6]. The results and evaluation criteria are presented in Table 4, and meet the acceptance criteria.

Table 4

Repeatability Sb data for drinking water and acceptance criteria

Average value (µg L^{-1})	CMA (µg L^{-1})	Standard deviation (µg L^{-1})		Relative standard deviation, RSD (%)	
		measured	criterion of precision = 25%CMA	measured	criterion
11.1	5	0.55	**1.25**	4.98	**10**

3.4 *Accuracy*

In this paper accuracy was determined as difference (**δ**) between the average concentrations for the eight standard solutions of 10 µg L^{-1} concentration, closed to CMA, prepared by dilution from stock solutions, Quality Control Standard 21, 100 mg L^{-1}, (Perkin Elmer, USA), and the theoretical value of the Sb reference material (10 µg L^{-1}).

The results, $\delta = 0.31$ µg L^{-1} , meet the acceptance criteria according to Law 311 of 28 June 2004 [6], $\delta \leq 1.25$ µg L^{-1} : accuracy = 25% CMA.

The percentage recovery for drinking water, according to SR EN ISO 11885: 2009 [17] is in range between 92% ÷ 104%.

In our study, the percent recovery of 103 %, calculated as the ratio of the average of 8 measurements of the standards and their declared values meet the acceptance criteria.

3.5. *Uncertainty*

The significant uncertainty sources affecting the measured concentration identified are presented in Table 5.

Table 5

Uncertainty budget

Components u(x)	Sources	Value	U.M.	Standard uncertainty	Relativ standard deviation
u (c)	Calibration curve	11.09	µg L^{-1}	0.57	0.0515
u (Rep)	Repeatability	11.09	µg L^{-1}	0.55	0.0495
u (δ)	Accuracy	10.31	µg L^{-1}	0.31	0.0208
u (*P*)	Standard purity	1	-	0.0029	0.0029

The uncertainty of determining antimony concentration based on the calibration curve, u_c is determined by formula [19]:

$$u_{(c)} = \frac{S}{B_1}\sqrt{\frac{1}{p}+\frac{1}{n}+\frac{(c_o - c_{med})^2}{S_{XX}}} \tag{3}$$

where: $S_{xx} = \sum_{j=1}^{n}(c_j - c_{med})^2$ (4)

and $S = \sqrt{\left[\frac{\sum_{j=1}^{n}\left[A_j - \left(B_0 + B_1 \times c_j\right)\right]}{n-2}\right]^2}$ (5)

in which:

S= residual standard deviation

B_1 = slope calibration

Bo = intercept

p = number of measurements performed to determine c_0

n = number of standards used for calibration

c_0 = Sb concentration of standard solution j

c_{med} = the average value of standard solutions used for calibration

j = index for the number of standard solutions for calibration

Aj = j^{th} measurement of the intensity of the i^{th} calibration standard

cj =concentration of the j^{th} calibration standard

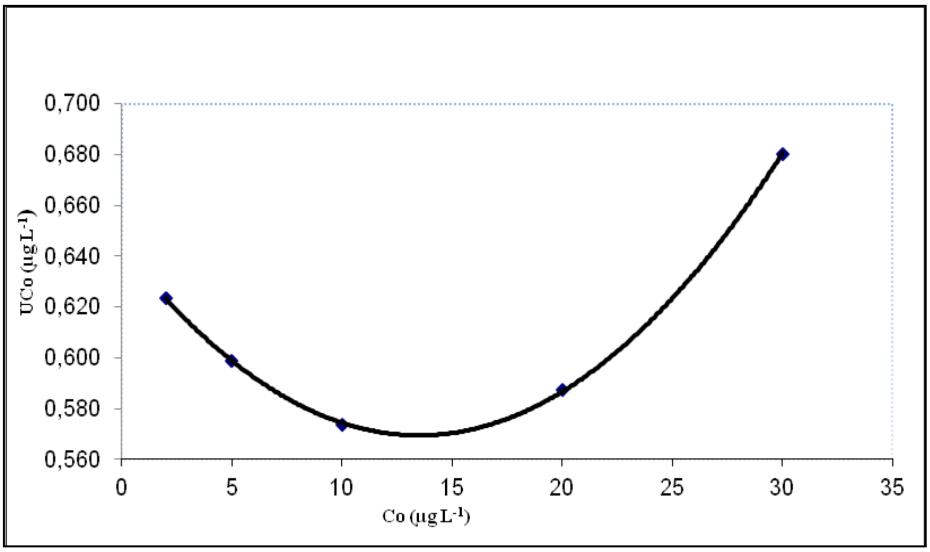

Fig. 2. Dependence u_c of concentration

Uncertainties associated to each component were calculated according to the uncertainty propagations rules [19] is:

$$u_c = c \times \sqrt{\left(\frac{u(c)}{c}\right)^2 + \left(\frac{u(\mathrm{Re}\,p)}{\mathrm{Re}\,p}\right)^2 + \left(\frac{u(\delta)}{\delta}\right)^2 + \left(\frac{u(P)}{P}\right)^2} \quad (6)$$

Composed uncertainty (u_c) of the method for antimony analysis at a concentration levels (c) of 11.1 µg L^{-1}, is expressed as a standard deviation having the value $u_c = 0.8$ µg L^{-1}.

As shown in Fig. 3 the largest contribution to the measurement uncertainty comes from the linear regression equation, followed by the uncertainty of repeatability and accuracy. Pure stock standard solutions used in preparing the standard have insignificant contribution.

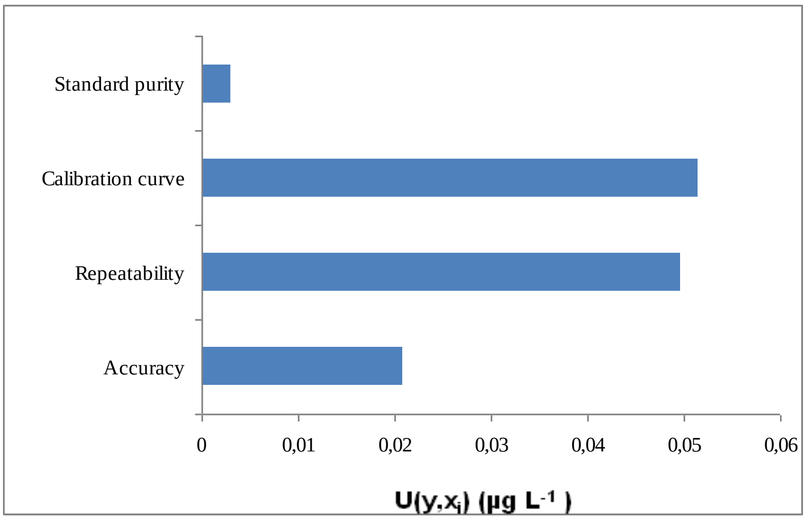

Fig. 3. The share of components on the budget uncertainties

For an average concentration of 11.1 µg L^{-1} and a coverage factor k = 2, corresponding to a confidence level of 95% the expanded uncertainty of the method is 1.7 µg L^{-1}.

Based on results obtained from ICP-OES method validation „in house'' (Table 6), it was observed that all acceptance criteria are meet.

Table 6

Results from validation of ICP-OES method to determine Sb in drinking water

Parameter	Value	Unit
Liniarity, r	0.9992	-
LoD	1.14	µg L^{-1}
LoQ	3.42	µg L^{-1}
Repetability	0.55	µg L^{-1}
RSD	4.98	%
Accuracy	0,31	µg L^{-1}
Recovery	103	%
Extended uncertainty, (k=2, P=95%), [19]	1.7	µg L^{-1}

4. Conclusions

The method has provided good validation parameters for linearity, the value of the correlation coefficient r ≥ 0.9992, the limit of detection 1.14 µg L^{-1} and the limit of quantification 3.42 µg L^{-1}. Repeatability value obtained was 0.55 µg L^{-1}, the accuracy value also was of + 0.31 µg L^{-1} and the recovery value obtain was 103%. The extended uncertainty value was 1.7 μg L^{-1} with a confidence level of 95% (k=2).

In the absence of interlaboratory collaborative results for determining method performance, the composed uncertainty provides a reasonable estimation of the reproducibility.

In conclusion, the method can be successfully applied for quality control of drinking water as regulated by law 311/2004 [6] si EU Directive 1998/83/EC [12].

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