The Optimization and Validation of a Method for Sb Determination from PET by ICP-OES

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In the present work it was developed a simple, cheap and quick method for Sb determination from PET in the 10 - 500 mg Kg^{-1} concentrations range, using an original digestion method coupled with the ICP-OES technique. The digestion method, developed and optimized for this study, uses a single digestion reagent (HNO_3), adequate the measurement equipment. It ensures a reduced digestion time (45 min.), thus having small energy consumption (0.15 KWh/sample) and uses standard digestion equipment. On the studied concentration range the method presents the following characteristics the calibration curve slope, expressed through correlation coefficient r = 0.9999, standard deviation of repeatability of 1.27 mg Kg^{-1}, RSD = 0.49 %, accuracy determined by recovery degree ranges between 85 % and 96 %, all being comparable with literature data. The value of extended uncertainty is 8.4 mg Kg^{-1} with a confidence level of 95 % (k=2), obtained for Sb content of 259.6 mg Kg^{-1}. The applicability of the method can be extended with the same digestion method and adequate modification of the concentration range for the calibration curve. The validated method for antimony content from PET cans can be applied in various research studies.

Keywords: ICP-OES; Sb; PET; digestion; drinking water; validation

Polyethylene terephthalate (PET) is a widely used material in the manufacture of packaging and films that come in contact with foodstuffs. Polyethylene terephthalate cans are more and more used for fresh drinks, mineral water, juices and beer [1]. Their use has increased over the last four decades due to the fact that are durable, hygienic and unbreakable. PET is a semi crystalline polymer in whose manufacture very few additives are used [2]. There is no need for plasticizers and antioxidants, while dyes are used in very limited amounts [3]. One of the additives used in the industrial synthesis of PET is antimony trioxide (Sb_2O_3). This is used as a catalyst, being preferred due to its catalytic activity, but also for colour and cost reasons [4]. Other catalysts which may be used are the ones based on titanium and germanium. The titanium catalyst requires high processing temperatures, while the latter is very expensive. Thus, the antimony trioxide (Sb_2O_3) is present in more than 90 % of the commercially available PET worldwide [5]. In the latest years, taking into consideration the antimony toxicity, a series of studies have been made on migration of this element from PET to food and beverages, including drinking water [6, 7]. Due to high amount of Sb in PET, Sb_2O_3 is listed as main pollutant by European Union (EU) and United States Environmental Protection Agency (USEPA), the maximum amount of antimony in drinking water, according to EU and USEPA being 5 μg L^{-1} and 6 μg L^{-1}, respectively [8, 9]. In Romania, Law No. 311/2004 for drinking water [10] Government Decision no. 532 of 2 June 2010 amending and supplementing the technical rules of exploitation and marketing of natural mineral waters approved by Government Decision no. 1020/2005 [11] limits the maximum allowable antimony amount in drinking and mineral water to 5 μg L^{-1}. Antimony content in PET has been determined through various analytical techniques, such as ICP-AES , ICP-MS , HG –AFS , GFAAS , XAFS, FAAS only for contents in range of 110 - 290 mg Kg^{-1} depending on PET type with measurement uncertainty was between 2.75 - 50 mg Kg^{-1} [12- 17].

There are several methods reported in literature as related to sample digestion. Ying-Ying Fan et al. [18] have mineralized PET foils from drinking water cans, using HNO_3 and H_2O_2, on a hotplate for 4 h at 250 °C. Carneado et al. [19] have developed a microwave based digestion method, on two stages: pre-digestion with H_2SO_4, then digestion with HNO_3. S. Keresztes et al. [20] digested PET samples in microwaves, in presence of HNO_3 and HCl. S. Rungchang et al [21] treated various commercially available PET types, using H_2SO_4, for 24 h at room temperature. The sample was then heated at 280°C for one hour for a complete digestion. With one exception, the digestion method for PET presented above requires at least two reagents. The digestion time needed for small pressures is between 20 min to 25 h.

The scope of the present work is to develop a simple, cheap and quick method for Sb determination from PET until 500 mg Kg^{-1} range, using an original digestion method which presents superior performances as compared to the methods specified in the literature, coupled with the ICP-OES technique.

Experimental part

Equipments

The Multiwave 3000 microwave digestor (Anton Parr GmbH, Austria) was used for PET digestion, the equipment having a combined pressure - temperature sensor and also an IR based temperature sensor.

For the determination of antimony content in PET the Optima 2100 DV ICP-OES System (Perkin Elmer) with dual view optical system was used. It combines the radial and axial view of the plasma in a single sequence and functions as a transistor based radiofrequency generator with 40 MHz frequency. The system comprises of a nebulizator PEEK Mira Mist coupled with Baffled Cyclonic spraying chamber.

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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 from PET were analytical purity types. There were used Quality Control Standard 21 solution of 100 mg L^{-1} concentration, from Perkin Elmer, nitric acid from Merck, with 65 % concentration, the sulfuric acid from Scharlau, 95 - 98 %, extra pure, and hydrogen peroxide 35%. For preparation of working solution and PET samples, ultrapure water with a resistivity of 18.2 MΩ cm^{-1} produced by EASY pure RoDi Barnstead USA was used. For ICP-OES Argon 5.0 of > 99,999 % purity (Linde Gas Romania) purging gas was used.

PET samples

Five PET samples from different drinks such as still (non-carbonated) water, sparkling (carbonated) water, carbonated beverages, beer from different brands, were purchased from a supermarket. Table 1 describes the PET bottle samples.

Table 1
PRESENTATION OF PET BOTTLE SAMPLES

PET bottle sample	Beverage	Colour of the PET
1	Sparkling water	Transparent
2	Carbonated beverages	Green
3	Still water	Light blue
4	Still water	Transparent
5	Beer	Brown

PET digestion method

The PET samples cans are cut in pieces of 1.0 x 1.0 mm, using a ceramic knife and washed with ultrapure water. The samples of 0.1 grams are weighed with analytical precision of 0.1 mg. The sample is then quantitatively transferred in the digestion vessel made of PTFE - TFM and 8 mL HNO_3 (65 %) are added. The two stages of the microwave digestion were: first stage performed at 160p C for 20 min, while the second stage at 190p C for 25 min, both at 800 W power. The digested samples are then diluted with ultrapure water to 100 mL in a flask, obtaining a clear solution.

Experimental method for Sb analysis using ICP-OES

The operation parameters for ICP-OES equipment are presented in table 2. The standard solutions of 10; 100; 200; 300; 400 and 500 μg L^{-1} used for development of the calibration curve, were obtained by diluting the stock solution of 100 mg L^{-1}, Quality Control Standard 21.

Table 2
EXPERIMENTAL OPERATIONS PARAMETERS

No.	Parameter	Value
1.	Plasma viewing mode	Axial
2.	Wavelength	λ=206.836 nm
3.	RF incident power	1.25 kW
4.	Nebulizer argon flow rate	0.75 mL min^{-1}
5.	Plasma argon flow rate	15 mL min^{-1}
6.	Auxiliary argon flow rate	1.5 mL min^{-1}
7.	The flow rate of the peristaltic pump	1.5 mL min^{-1}
8.	Total time for analysis	approx. 110 s

Results and discussions

Method optimization

Digestion of Sb from PET

The development and optimization of the method consisted of the variation of main working parameters, i.e. type and concentration of reagent (HNO_3, H_2O_2, H_2SO_4), temperature and digestion time. In the case of PET digestion with HNO_3 (65 %) and H_2O_2 (35 %), an opaque solution was obtained, fact reported also by Ying-Ying et al. [18]. In ICP-OES analysis, it is highly recommended a clear solution, ensuring thus a complete mineralization and not retaining the analyzed compound in solid particles. This inconvenient can be removed by adding sulfuric acid (98 %) while continuing the digestion on sand bath until clear solution. On the other hand the caveat is a larger time and increased number of necessary operations.

Digestion with HNO_3 (65 %) and H_2SO_4 (98 %) has many caveats: the reaction is highly exothermic with risk of damaging of reaction vessels by over-heating. The acid mixture is also foaming with the risk of losing parts of sample. The use of sulfuric acid reduces lifetime of vessels and gaskets because of its corrosive properties [22]. On the other hand, sulfuric acid can affect background emissions observed in ICP-OES, causing interferences in analysis. From this point of view, nitric acid (65 %) is recommended for sample preparation [23].

The performance parameters of the developed method were: linearity, precision (repeatability), accuracy, the recovery degree, uncertainty (U), limits of detection (LoD) and quantification (LoQ).

The acceptance precision criterion is calculated based on Horwitz equation [24]:

$$RSD < 0.6 \times 2^{(1-0.5 \lg C)} \quad (1)$$

where:

C is the sample concentration expressed as mass fraction

The acceptance criterion for measurement uncertainty U is:

$$U \leq 2 \times s_R \quad (2)$$

where s_R is standard deviation, and is calculated with formula (3):

$$s_R = \frac{RSD \times C}{100} \quad (3)$$

where, RSD is calculated using Horwitz equation (1).

Validation of the method for Sb determination from a commercially available PET type

Table 3
PERFORMANCE PARAMETERS OF THE METHOD FOR ANTIMONY DETERMINATION FROM A COMMERCIALLY AVAILABLE PET TYPE

Parameter	Value	Unit
Linearity, r	0.9999	-
LoD	10.2	mg Kg^{-1}
LoQ	20.4	mg Kg^{-1}
Repeatability, s_r	1.27	mg Kg^{-1}
RSD	0.49	%
Recovery	89.7	%
Extended uncertainty, (k = 2, P = 95 %)	8.4	mg Kg^{-1}

Linearity

Linearity was evaluated from regression function of calibration obtained using six standard solutions in domain 10 - 500 µg L^{-1}, prepared from standard stock solution Quality Control Standard 21 of 100 mg L^{-1} concentration(Perkin Elmer, USA). The equation of the calibration curve is presented in figure 1. The linearity, evaluated based on correlation coefficient r = 0.9999 fulfils the acceptance criterion of r ≥ 0.997 [25].

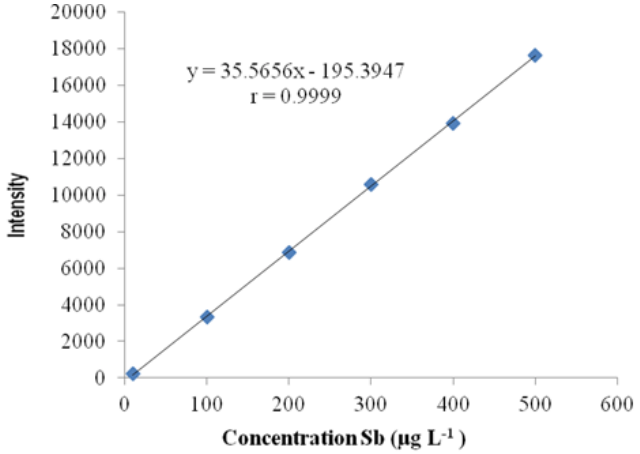

Fig.1. Calibration curve in the concentration range 10 µg L^{-1} to 500 µg L^{-1} Sb

The range of calibration between 10 - 500 µg L^{-1} corresponds to a range of concentrations of Sb in PET samples between 10 - 500 mg Kg^{-1}. Samples with higher concentrations of Sb in PET can be determined on the same calibration curve after appropriate digestion and dilution.

Precision (Repeatability)

Experimental data for Sb on repeatability were obtained analyzing 10 PET samples from a commercially available PET type, mineralized as per above described procedure. The value for relative standard deviation, at 259.6 mg Kg^{-1} average content was 0.49 %. This value is much smaller than the lower limit of 4.6 % calculated using Horwitz equation.

Accuracy

Taking into account the lack of a certified reference material for this matrix in this study the accuracy was determined as recovery degree, using standard addition method. The recovery tests were done using three PET samples from the commercially available PET type used, fortified with different volumes of standard solution, Quality Control Standard 21, concentration 100 mg L^{-1} (Perkin Elmer, USA). The concentrations of the fortified samples according to table 4 were obtained by adding the required volumes of standard solution before the digestion stage. The samples were processed according to method described at 3.1. The antimony amount was determined from each solution obtained, digested under same conditions.

The recovery degree (%) was calculated using the following formula [25]:

$$R\% = \frac{CF - CU}{CA} \times 100 \quad (4)$$

where:

CF – concentration of analyte (Sb) in fortified sample;

CU – concentration of analyte (Sb) in unfortified sample;

CA – concentration of analyte (Sb) added in fortified sample;

The results presented in table 4, show that determined values for recovery are between 85 and 96 %. Thus, the acceptance criterion 80 % ≤ R % ≤ 110 % is fulfilled for the entire concentration range tested [25].

Calculation of uncertainty

Uncertainty sources that significantly affect the concentration are presented in table 5.

The uncertainty of determination of concentration based on calibration curve, $u(c_0)$ is determined using formula [26]:

$$u(c_o) = \frac{S}{B_1}\sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(c_o - c_{med})^2}{S_{XX}}} \quad (5)$$

Sample	Sb		R %
	$C_{calculated}$ [mg Kg^{-1}]	R [%]	Average recovery degree on method
PET unfortified	303	-	89.7
PET+50 [µg L^{-1}]	347	88	
PET+100 [µg L^{-1}]	388	85	
PET+150 [µg L^{-1}]	447	96	

Table 4
EXPERIMENTAL RESULTS OBTAINED IN ACCURACY DETERMINATION AS DEGREE OF RECOVERY (%) FROM COMMERCIALLY AVAILABLE PET TYPE

Components u(x)	Sources	Value	Unit	Standard uncertainty	RSD
$u(R)$	Recovery	89.7	%	0.95	0.0106
$u(c_0)$	Calibration curve fitting	259.6	mg Kg^{-1}	3.11	0.0119
$u(P)$	Standard purity	1	-	0.0029	0.0029

Table 5
UNCERTAINTY BUDGET FOR THE STUDIED COMMERCIALLY AVAILABLE PET TYPE

where,

$$S_{XX} = \sum_{j=1}^{n} (c_j - c_{med})^2 \quad (6)$$

and

$$S = \sqrt{\frac{\sum_{j=1}^{n} \left[A_j - (B_0 + B_1 \times c_j)\right]^2}{n-2}} \quad (7)$$

where:

S = 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 solution;

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

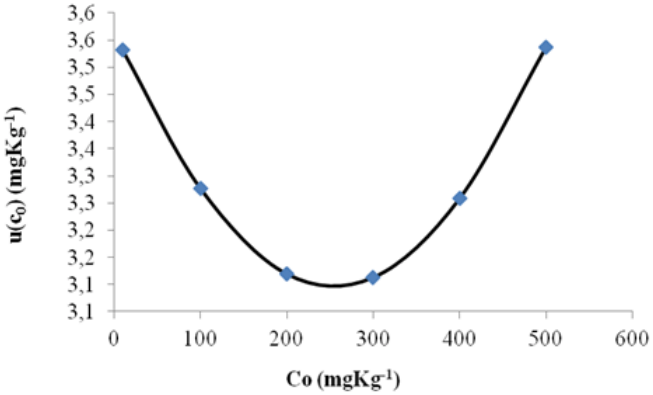

Fig. 2. The variation of $u(c_o)$ on Sb concentration (C_o)

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

The combined uncertainty u_c, according to the rule of propagation of uncertainty [26] is:

$$u_c = c \times \sqrt{\left(\frac{u(R)}{R}\right)^2 + \left(\frac{u(c)}{c}\right)^2 + \left(\frac{u(P)}{P}\right)^2} \quad (8)$$

u_c = 4.2 mgKg^{-1} mg Kg^{-1}, for an average concentration of antimony of 259.6 mg Kg^{-1} and a recovery degree of 89.7 mg Kg^{-1} .

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

As can be seen in figure 3, the greatest contribution to measurement uncertainty is given by linear regression equation, followed by uncertainty of recovery. The purity of

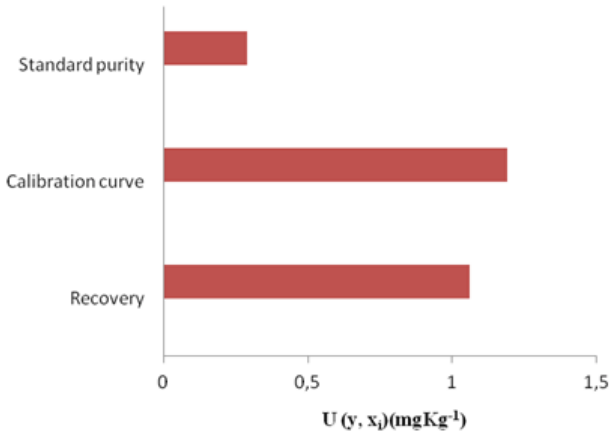

Fig. 3.Component contribution to the budget of uncertainties

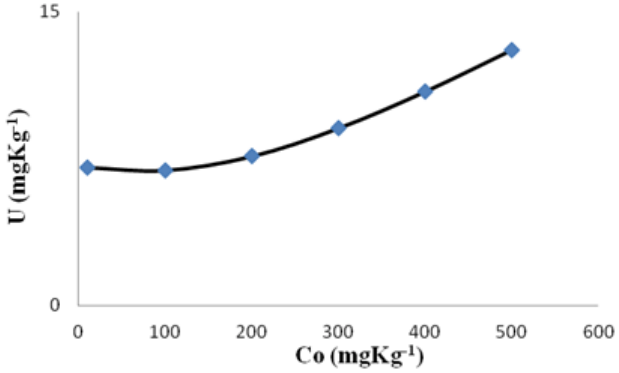

Fig. 4. The variation of U on Sb concentration (C_0)

Table 6

KEY PERFORMANCE PARAMETERS FOR OTHER METHODS IN THE LITERATURE IN COMPARISON WITH WORKING METHOD AND ACCEPTANCE CRITERIA

Performance parameter	Reported value	Reference	Performance parameters of our method	Acceptance criterion for proposed method	Reference
Linearity, r	R = 0.998	[27]	0.9999	r ≥0.997	[25]
Precision (repeatability)	RSD = 0.7 – 2 %;	[19]	0.49 %	RSD < 4.6 %	[24]
Accuracy (recovery degree)	97-98 % 102 %	[27] [19]	89.7 %	80 % ≤ R % ≤ 110 %	[25]
Measurement uncertainty	2.75 – 50 mg Kg $^{-1}$	[5],[13],[17], [18],[19],[20], [21]	8.4 mg Kg $^{-1}$	U ≤ 36 mg Kg $^{-1}$	[24]
Limit of Detection, LoD Limit of Quantification, LoQ	LoD: 0.3 µg L^{-1}; LoQ: 1.0 µg L^{-1}; LoD: 1.8 mg Kg $^{-1}$; LoQ: 6.0 mg Kg $^{-1}$;	[17] [27]	LoD:10.2 mg Kg $^{-1}$ LoQ: 20.4 mg Kg $^{-1}$	LoD ≤ 25 mg Kg^{-1} LoQ ≤ 50 mg Kg $^{-1}$	[25]

standard used for solution preparation has an insignificant contribution.

The concentration dependence in the range of 10 - 500 mg Kg^{-1} on extended measurement uncertainty is shown in figure 4.

For a 259.6 mg Kg^{-1} concentration and a cover factor of k = 2, corresponding to a trust level of 95 %, the extended uncertainty is 8.4 mg Kg^{-1}.

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

The limit of detection (LoD), of 10.2 mgKg^{-1} and limit of quantification (LoQ) of 20.4 mg Kg^{-1} calculated using formulas (9) and (10) fulfill the acceptance criteria imposed for the working range of 10 - 500 mg Kg^{-1} and are presented in table 6. u_c = 3.4 mg Kg^{-1} represents composed uncertainty for the standard solution of 10 mg Kg^{-1}.

$$LoD = 3 \times u_c \quad (9)$$

$$LoQ = 6 \times u_c \quad (10)$$

The key performance parameters for other methods in the literature and results from the i*n house* validation study and acceptance criteria for this method presented in table 6 show that all the performance criteria are fulfilled.

Analysis of PET samples

After the optimization of all conditions, the validated method was used to determine Sb in five types of PET packaging used for different beverages: natural carbonated mineral water, still mineral water and beer. The results are shown in table 7.

PET samples	Sb [mg Kg^{-1}]
1	259.6 ± 8.4
2	195.9 ± 7.6
3	171.1 ± 7.3
4	204.7 ± 7.7
5	229.6 ± 8.0

Table 7
THE CONCENTRATIONS OF SB IN DIFFERENT PET SAMPLES, AS PRESENTED IN TABLE 1

The averaged Sb contents determined in each analyzed PET are in the range 171.1- 259.6 mg Kg^{-1}, in accordance with other methods presented in the literature for Sb determination in PET [12-17].

Conclusions

The study presents a simple, cheap and quick way of antimony determination from PET in the range of 10 - 500 mg Kg^{-1}, based on an original digestion method coupled with ICP-OES measurement technique. The digestion method, developed and optimized for this study, uses only one digestion reagent (HNO_3), in comparison with other methods presented in the literature and shorter digestion time, too. The reagent is friendly to the measurement equipment, ensures a reduced digestion time (45 min.), thus having small energy consumption (0.15 KWh/sample) and requesting standard digestion equipment.

On the studied concentration range, the calibration curve slope, expressed through correlation coefficient r = 0.9999, standard deviation of repeatability of 1.27 mg Kg^{-1}, RSD = 0.49 %, accuracy determined by recovery degree ranges between 85 and 96 % satisfy the demands of chemists for these parameters, being comparable with literature data.

The value of extended uncertainty is 8.4 mg Kg^{-1} with a confidence level of 95 % (k=2), obtained for Sb content of 259.6 mg Kg^{-1}.

The value for acceptance criteria for detection and quantification limits is determined by the working range chosen, taking into account that most of PET samples in this study are in the selected concentration domain. The applicability domain of the method can be extended to higher contents with the same digestion method and corresponding modification of calibration curve.

In conclusion, the validated method can be applied for determination of antimony content from PET in various research studies.

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