

Determination of Inorganic Species of Sb and Te in Cereals by Hydride Generation Atomic Fluorescence Spectrometry

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Neste trabalho foi desenvolvido um sistema não cromatográfico rápido, sensível e simples para a determinação de Sb(III), Sb(V), Te(IV) e Te(VI) em amostras de cereais. O procedimento baseia-se na extração assistida por ultra-som e na determinação por espectrometria de fluorescência atômica acoplada com geração de hidretos (HG AFS). Foram realizados estudos preliminares com o intuito de avaliar a eficiência da extração usando 1 mol L⁻¹ ácido fosfórico, 1 mol L⁻¹ ácido nítrico, água régia, 1 mol L⁻¹ ácido sulfúrico e 6 mol L⁻¹ ácido clorídrico. A extração com água régia apresentou uma evidente interconversão das espécies durante o processo. No entanto, o H₂SO₄ apresentou-se como o melhor agente de extração com eficiências maiores do que 90% em relação ao conteúdo total de Sb e Te (ambos os elementos foram previamente quantificados), não apresentando interconversão nenhuma. Estudos de recuperação para diferentes níveis de adição das espécies comprovaram a não interconversão das espécies. O método forneceu limites de detecção na faixa de 0,1 a 1,0 ng g⁻¹ com desvios padrão relativos de 5,4-9,2% para 10 análises independentes de amostras que continham baixas concentrações de espécies de Sb e Te.

A non-chromatographic fast, sensitive and easy method has been developed for the determination of Sb(III), Sb(V), Te(IV) and Te(VI) in cereal samples. The procedure is based on ultrasound assisted extraction and determination by hydride generation atomic fluorescence spectrometry (HG AFS). Preliminary studies were made in order to get the best extraction efficiency using 1 mol L⁻¹ phosphoric acid, 1 mol L⁻¹ nitric acid, *aqua regia*, 1 mol L⁻¹ sulfuric acid and 6 mol L⁻¹ hydrochloric acid. The extraction with *aqua regia* showed a clear interconversion of the species during the process, being H₂SO₄ the best extractant with efficiencies greater than 90% from the total content of Sb and Te quantified previously and without species interconversion. This point was checked by recovery experiments at different spiked levels. The method provided limits of detection values from 0.1 to 0.5 ng g⁻¹ with relative standard deviation values from 5.4 to 9.2% of 10 independent analysis of samples containing few ng g⁻¹ of Sb and Te species.

Keywords: antimony, tellurium, cereals, speciation, hydride generation atomic fluorescence spectrometry

Introduction

Natural concentrations of Sb and Te in the environment are low. Their abundance in the earth's crust is of the order of 0.2-0.3 mg kg⁻¹.¹ In its metallic form, the major use of Sb is as hardener for Pb, *e.g.*, in lead-acid batteries, cable sheathings, ammunition, and as a component in

semiconductors. Important anthropogenic sources of Sb in the environment are emissions from vehicles (where it is used as a fire-retardant in brake linings), waste disposal and incineration, fuel combustion, metal smelters, and shooting activities.^{2,3} Antimony has no known essential biological function. Similar to other trace elements, it can be toxic at elevated concentrations, and some Sb compounds are even considered potentially carcinogenic. A potentially important Sb exposure pathway to humans

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and animals in areas with contaminated soils is through food and feed plants.⁴

On the other hand, pentavalent antimonials, such as, meglumine antimoniate and sodium stibogluconate are used for the treatment of leishmaniasis caused by protozoa.⁵ In addition, some Sb compounds show antitumor activity.⁶

Tellurium is a non-essential toxic element widely spread in nature, usually at low concentration levels which can affect various organs.⁷ Some studies indicated that tellurium's toxicity, bioavailability, and environmental transport mechanism highly depend on its chemical form and oxidation state; being tellurite 10 times more toxic than tellurate.⁸

The Food and Nutrition Board of the U. S. National Research Council recommends for a Sb intake of 50-200 $\mu\text{g day}^{-1}$, 10-40 $\mu\text{g day}^{-1}$ for infants and 20-120 $\mu\text{g day}^{-1}$ for children under the age of 6.⁹ The daily intake of tellurium for the average adult is judged to be around 0.6 mg and it is part of our diet.¹⁰

In comparison with extensive speciation studies carried out of other elements such as As and Se, only few works have dealt with the speciation of Sb and Te. Table 1 shows the data reported in the literature on the speciation analysis of Sb and Te in food samples. As it can be seen, some of the analysis has been carried out on certified reference materials. Major contributions on the Sb and Te speciation have been given by the authors in food samples such as garlic, mushrooms and milk.

Antimony(III) has been determined in meals and certified materials by voltammetry,¹¹⁻¹³ and by high performance liquid chromatography (HPLC) in environmental samples.¹⁴ In previous works, non-chromatographic determination of Sb(III) and Sb(V) was made in garlic, mushroom and milk samples by using hydride-generation-atomic-fluorescence spectrometry (HG AFS).¹⁵⁻¹⁷ The simultaneous speciation of As and Sb by (HPLC ICP MS) in fish sample was studied by Morita and co-workers.¹⁸

The methods proposed for Te speciation are complex and involve several sequential steps, thus making their use very difficult in routine analysis. In general these methods are based on chromatographic separations with element-specific detectors. A method for the determination of tellurite [Te(IV)] and tellurate [Te(VI)] by ion chromatography with inductively coupled plasma mass spectrometric detection (ICP MS) was developed by Kuo and Jiang,¹⁹ the analysis being carried out using dynamic reaction cell. A procedure for the fractionation and determination of Te(IV) and Te(VI) using a tungsten furnace was described by Narukawa.²⁰ The speciation analysis of tellurium by ICP MS using solid-phase extraction in the presence of ammonium pyrrolidine dithiocarbamate in water samples was studied by Yu and co-workers.²¹ A highly sensitive non-chromatographic procedure for the speciation of Te in milk samples by HG AFS was developed by Cava Montesinos and co-workers.²² It was used *aqua regia* as

Table 1. Contents of Sb and Te inorganic species in food samples

Specie	Sample	Technique	Concentration	Reference
Sb(III)	BCR-CRM 189	Voltammetry	$6.6 \pm 0.4 \mu\text{g g}^{-1}$	11
	NIST-SRM 1567a		$6.5 \pm 0.6 \mu\text{g g}^{-1}$	
	NIST-SRM 1568a		$7.3 \pm 0.5 \mu\text{g g}^{-1}$	
Sb(III)	BCR-CRM 189	Voltammetry	$7.2 \pm 0.4 \mu\text{g g}^{-1}$	12
	NIST-SRM 1567a		$6.6 \pm 0.4 \mu\text{g g}^{-1}$	
Sb(III)	Whole meal	Voltammetry	$0.94 \pm 0.06 \mu\text{g g}^{-1}$	13
	Wheat meal		$0.41 \pm 0.04 \mu\text{g g}^{-1}$	
	Maize meal		$0.171 \pm 0.008 \mu\text{g g}^{-1}$	
Sb(III) Sb(V)	Garlic	HG AFS	$7.2-17.1 \text{ ng g}^{-1}$	15
			$4.7-5.8 \text{ ng g}^{-1}$	
Sb(III) Sb(V)	Mushrooms	HG AFS	$4.6-11.4 \text{ ng g}^{-1}$	16
			$14.7-21.2 \text{ ng g}^{-1}$	
Te(IV) Te(VI)	Garlic	HG AFS	$5.4-9.4 \text{ ng g}^{-1}$	15
			$0.6-1.0 \text{ ng g}^{-1}$	
Sb(III) Sb(V)	Milk	HG AFS	$1.3-2.4 \text{ ng g}^{-1}$	17
			$2.3-8.3 \text{ ng g}^{-1}$	
Sb(III)	Fish	HPLC ICP MS	$0.010 \pm 0.004 \text{ mg kg}^{-1}$	18
Te(IV) Te(VI)	Milk	HG AFS	$0.7-6.3 \text{ ng g}^{-1}$	22
			$0.4-4.2 \text{ ng g}^{-1}$	

extractant with and without pre-reduction with potassium bromide at 75 ± 5 °C during 30 min inside a water bath.

Nowadays there is special attention in foods such as cereals, vegetables and pulses (dry bean seeds), because they are an important base of the diet around the world. On the other hand, from the methodological point of view it is clear that non-chromatographic methods of elemental speciation may offer cheaper, simpler, faster and more sensitive procedures than chromatographic ones,²³ and thus, they can offer a valuable alternative for routine speciation analysis. So, the aim of this work has been the development and application of a simple analytical procedure for the quantification of inorganic species of Sb and Te in cereal samples by HG AFS.

Experimental

Reagents, solutions and samples

All reagents used were of analytical grade and all solutions were prepared in ultrapure water with a minimum resistivity of 18 M Ω cm obtained from a Milli-Q Millipore system (Billerica, MA, USA). The 1000 mg L⁻¹ Sb(III) stock solution was from Scharlau Chemie (Barcelona, Spain) and Sb(V) stock standard was prepared by dissolving in water the adequate amount of H₆KO₆Sb from Fluka (Buchs, Switzerland). The stock solution of Te(IV) was prepared by dissolving in ultrapure water an appropriate amount of Na₂TeO₃ Sigma Aldrich (Steinheim, Germany) and Te(VI) standards were prepared by dissolving H₆O₆Te from Fluka. For sample preparation 37% v/v HCl from Merck and 65% v/v HNO₃ from J. T. Baker (Deventer, Holland) were used. A solution of 50% m/v KI Merck with 10% m/v ascorbic acid from Scharlau Chemie was employed to reduce Sb(V) to Sb(III), while KBr from Scharlau Chemie was employed to reduce Te(VI) to Te(IV). The ashing agent used for dry ashing of samples before the determination of the total trace element content was a mixture of 20% m/v Mg(NO₃)₂·6H₂O and 2% m/v MgO, both from Scharlau Chemie. Sodium tetrahydroborate from Fluka, dissolved in 0.1 mol L⁻¹ NaOH from Scharlau Chemie was used to generate the corresponding hydrides before the AFS determination of Sb and Te, this solution was prepared daily and filtered before use. For the extraction of inorganic species a 1 mol L⁻¹ H₂SO₄ from Scharlau Chemie and 0.1% m/v solution of the disodium salt of ethylenediaminetetraacetic acid from Panreac (Barcelona, Spain) were used. Argon C-45 with purity higher than 99.995% was employed as carrier gas and synthetic air was used in the Perma Pure drier system. Both gases were supplied by Carbueros Metálicos (Barcelona, Spain).

Instrumental

A continuous flow HG AFS model PSA Millennium Excalibur 10055 from PS Analytical (Kent, UK) was used for the analytical determinations. Boosted discharge hollow cathode lamps for Sb and Te, both from Photron (Victoria, Australia), were employed as excitation source. The instrumental parameters were adjusted according to the manufacturer recommendations, except the concentrations of HCl and sodium borohydride (NaBH₄), sample introduction system and the sample volume, which were implemented in previous studies.^{15,17,22} So, HCl concentration was fixed at 3.5 and 4 mol L⁻¹ for Sb and Te respectively, being the NaBH₄ concentration 0.7% m/v for Sb and 0.8% m/v for Te. In all experiments NaBH₄ and HCl flow rates employed were 4.5 and 9 mL min⁻¹ respectively. An ultrasound water bath from Branson (Danbury, CT, USA) for 10 tubes placed vertically inside it, 2.8 L of volume and operated at 130 W and 40 Hz was used for sample extraction. Other equipment included a sand bath Selecta (Model 600709, Abrera, Spain), and a Lenton ECF 12/45A muffle furnace equipped with a Eurotherm 2416 controller from Biometa (Lanera, Spain).

Certified reference materials and samples

Two certified reference materials were used, NIST 1573a (Tomato leaves) from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) and IAEA 140-TM (*Fucus* sp.) from International Atomic Energy Agency (IAEA, Viena, Austria). Samples of different cereals were purchased at the local market in Valencia (Spain). Rice, rice semolina, wheat semolina, wheat bran and rye flakes were ground in a domestic mill Taurus (Leida, Spain) and the powdered samples were stored in polyethylene bottles inside a dessicator until analysis together with wheat semolina and wheat corn that were stored directly.

Dry ashing mineralization for total element determination

Approximately 1 g of sample was accurately weighed and mixed with 2.5 mL of an ashing aid suspension containing 20% m/v Mg(NO₃)₂·6H₂O plus 2% m/v MgO, and 5 mL of 50% v/v HNO₃. The mixture was evaporated to dryness in a sand bath and mineralized in a muffle furnace at 450 °C with a gradual increase in temperature.²⁴ The white ashes were wetted with 1 mL water and dissolved with 9 mL of 10% v/v HCl. For Sb determination, 3 mL of this solution were transferred to a 50 mL polyethylene tube, as well as 8.75 mL of concentrated HCl and 600 μ L

of the 50% m/v KI plus 10% m/v ascorbic acid reducing solution. The final volume was made up to 30 mL with ultrapure water. For Te determination, 5 mL of the ashed sample solution were transferred to a 50 mL polyethylene tube, as well as 16.7 mL of concentrated HCl and 0.5 g of KBr. Then, this solution was diluted to 50 mL with ultrapure water. The final solution was warmed during 30 min at 75 ± 5 °C. Recovery studies previously made evidenced that for a spiked concentration of Sb and Te at 100 ng g⁻¹ level, the aforementioned elements were recovered at 91 and 98% respectively from vegetable, cereal and pulses samples.²⁴

Ultrasound-assisted extraction for inorganic trace element determination

Approximately 1 g of sample was accurately weighed inside a 50 mL polyethylene tube, and a volume of 10 mL of 1 mol L⁻¹ H₂SO₄ was added to the tube. The slurry was sonicated for 10 min, and the sulphuric extract separated by centrifugation at 3500 rpm for 10 min. The solid residue was washed with 10 mL of 0.1% m/v ethylenediaminetetraacetic acid (EDTA); this suspension was centrifuged for additional 10 min, and the supernatant was mixed with the previous extract. Two aliquots were taken from the final extract, for Sb(III) and Sb(V) determination. One of the aliquots was prepared in a medium containing 1% m/v KI and 0.2% m/v ascorbic acid and was left to react for 30 min for Sb(V) reduction; the another one was analyzed directly by HG AFS without pre-reduction; the final HCl medium in both cases, was adjusted to 3.5 mol L⁻¹. For Te speciation, two aliquots were taken also from the sonicated solutions. One aliquot was prepared in a medium containing 4 mol L⁻¹ HCl plus 1% m/v KBr and the solution was warmed for 30 min at 75 ± 5 °C before HG AFS determination of Te(IV) and Te(VI). The other one was analyzed directly after acidification for the determination of Te(IV).

Results and Discussion

Selection of the extraction conditions for inorganic antimony and tellurium determination

The selection of the extracting agents was based on previous works made for the determination of trace elements in garlic,¹⁵ and the speciation of As in cereals,²⁵ thus, the following extractants were investigated: 1 mol L⁻¹ HNO₃, 1 mol L⁻¹ H₃PO₄, 1 mol L⁻¹ H₂SO₄, 6 mol L⁻¹ HCl and *aqua regia*. Extractions carried out with 6 mol L⁻¹ HCl, 1 mol L⁻¹ HNO₃ and 1 mol L⁻¹ H₃PO₄ led to erroneous results of inorganic antimony [Sb(III) + Sb(V)] and tellurium [Te(IV) + Te(VI)] because the levels obtained were higher than the total concentration of these elements in the considered samples. These results may be explained by interference effects in the hydride generation process. Therefore, the aforementioned extractants were not taken into account for further studies. Sulphuric acid (1 mol L⁻¹) and *aqua regia* resulted the most efficient extractants of Te and Sb from cereals. However, for Sb, a separate extraction was carried out with *aqua regia* for the same sample of rice, giving different concentrations of Sb(III) and Sb(V), despite that the total content of inorganic Sb was quite reproducible. Additionally, the total content of Te species extracted was around 85% for the total content of Te, and data found for Te(IV) were quite higher than those expected (see Table 2). Consequently, 1 mol L⁻¹ H₂SO₄ was selected as the best extracting agent for speciation of Sb and Te in cereals. Results show a reproducible distribution of Sb and Te species in the studied sample, being Sb(V) and Te(VI) the main chemical forms in this sample.

Strategy for the speciation analysis of Sb(III), Sb(V), Te(IV) and Te(VI)

The speciation strategy was based on previous experience in non-chromatographic speciation by HG AFS which evidenced that Sb(V) reacts with NaBH₄ forming

Table 2. Selection of the best extractant for the Sb and Te determination in a rice sample

Extractant	Sb(III) (ng g ⁻¹)	Sb(V) (ng g ⁻¹)	Sb(III) + Sb(V) (ng g ⁻¹)	Te(IV) (ng g ⁻¹)	Te(VI) (ng g ⁻¹)	Te(IV) + Te(VI) (ng g ⁻¹)
H ₂ SO ₄ 1 mol L ⁻¹	0.15	0.47	0.63	0.28	0.87	1.15
	0.15	0.45	0.60	0.26	0.75	1.01
	0.16	0.49	0.64	0.27	0.73	1.00
<i>aqua regia</i>	0.13	0.36	0.50	0.58	0.19	0.77
	0.35	0.16	0.52	0.51	0.18	0.69
	0.26	0.25	0.51	0.53	0.36	0.90

Total Sb: 0.65 ± 0.03 ng g⁻¹; Total Te: 0.93 ± 0.04 ng g⁻¹.

stibine with a reaction kinetics slower than that of Sb(III).²³ So, the AFS signals produced by the pentavalent species of Sb depend on hydride generation conditions. In order to determine the total Sb content a pre-reduction is thus required to reduce quantitatively Sb(V) to Sb(III). Based on the different AFS sensitivity obtained from Sb(V) with and without pre-reduction, it could be possible to determine Sb(III) and Sb(V) concentrations on the same sample based on two independent measurements, one without a previous reduction and another after a quantitative transformation of Sb to Sb(III), and to establish a system of two equations with two unknowns related to the oxidation states of Sb.¹⁵ On the other hand, Te(VI) does not react with NaBH₄ to form the corresponding hydrides, being necessary to reduce it to the (IV) oxidation state with KBr or boiling using 2-6 mol L⁻¹ HCl before HG AFS measurements.²⁶ Therefore, speciation of Te(IV), Te(VI) can be easily carried out by HG AFS using a two step analysis. Samples must be analysed without pre-reduction, in order to determine Te(IV) concentrations; then, the sample must be treated with KBr in acidic medium at 75 ± 5 °C for 30 min in order to achieve a quantitative reduction of Te(VI) to Te(IV) present in the sample. The analysis of this last solution gives the total concentration of Te(IV) and Te(VI), and can be calculated by the difference between the two analysis performed.²²

Analytical figures of merit

The main analytical parameters of the developed procedure, such as sensitivity, limit of detection (LOD) and precision are summarized in Table 3, together with the slope of typical regression equations obtained before and after KI or KBr reduction. The LOD values were calculated by dividing three times the standard deviation of the fluorescence signal of 10 reagent blanks by the slope of the calibration curve, in the best experimental conditions, for each Sb and Te species. The LOD was also established for dried samples, taking into account the sample mass and dilution factor involved in the proposed method. The precision expressed as relative standard deviation (RSD%) for 10 replicate analysis of a sample is also reported. As it can be seen, concentrations from 0.1 to 0.5 ng g⁻¹ of Sb and Te species can be detected and concentrations of few ng g⁻¹ can be determined with relative standard deviations from 5.4 to 9.2%.

Accuracy studies

To evaluate the accuracy of the inorganic species determination in cereal samples, a series of recovery studies on a rice sample spiked with different concentrations of

Table 3. Analytical figures of merit obtained for non-chromatographic speciation of inorganic Sb and Te in cereal samples through HG AFS

Element	LOD (ng g ⁻¹)	RSD (%)	Regression equation
Sb(III) _{red}	0.1	7.6	y = 1280.9x + 8.8 R ² = 0.9974
Sb(III)			y = 1159.8x + 10.7 R ² = 0.9991
Sb(V) _{red}	0.2	5.4	y = 1167.8x + 4.6 R ² = 0.9995
Sb(V)			y = 544.9x + 12.4 R ² = 0.9961
Te(IV)	0.2	9.2	y = 315.8x + 4.2 R ² = 0.9922
Te(VI) _{red}	0.5	8.2	y = 426.6x + 11.8 R ² = 0.9991

Sb(III), Sb(V), Te(IV) and Te(VI) were made to verify the lack of interconversion of original species during the extraction and measurement steps. The sample was spiked with 10, 20 and 40 ng g⁻¹ of each specie before the extraction process. The recovery values were always higher than 95% for all the species considered at the spiked levels (see Table 4). These good recovery values evidence the stability of each species during the extraction process. In relation to organic species of Sb and Te, it was not possible to evaluate the possible presence of organic species because organic standards are not commercially available. However, the good correlation between the sum of inorganic species and the total concentration values seems to indicate the absence of organic species of the aforementioned elements in cereal samples.

It was also determined the concentration of Sb(III), Sb(V), Te(IV) and Te(VI) in two certified reference materials, NIST 1573a (tomato leaves) and IAEA 140-TM (*Fucus* sp). Results obtained (see Table 5) evidence that the sum of the analyzed species agree well with the total Sb certified value and in the case of Te, there is not available certified sample.

Analysis of commercial cereal samples

Samples of cereals, obtained from the local market of Valencia were analyzed by the proposed procedure and results found for Sb and Te species are summarized in Tables 6 and 7, together with data found for total Sb and Te determination based on dry-ashing mineralization and HG AFS. The *t*-test demonstrated that there are no significant differences between the results found for total Sb and total Te and those obtained from the sum of the species determined by the proposed method ($-0.49 < t_{\text{critical}} = 2.57$).

Table 4. Recovery percentages of inorganic Sb and Te species in cereal samples by HG AFS in three different addition levels, all results were the average and standard deviation of n = 3 determinations

Sb(III) (ng g ⁻¹)	Recovery (%)	Sb(V) (ng g ⁻¹)	Recovery (%)	Te(IV) (ng g ⁻¹)	Recovery (%)	Te(VI) (ng g ⁻¹)	Recovery (%)
10	99.4 ± 1.5	10	95.4 ± 1.4	10	99 ± 3	10	98.4 ± 0.9
20	97 ± 2	20	99 ± 3	20	94.6 ± 1.4	20	98 ± 2
40	101 ± 4	40	100.0 ± 0.7	40	98.9 ± 1.1	40	100.0 ± 0.8

Table 5. Antimony and Te species found in NIST 1573a (tomato leaves) and IAEA 140-TM (*Fucus* sp)

CRM	Sb(III) (ng g ⁻¹)	Sb(V) (ng g ⁻¹)	Sb(III) + Sb(V) (ng g ⁻¹)	Te(IV) (ng g ⁻¹)	Te(VI) (ng g ⁻¹)	Te(IV) + Te(VI) (ng g ⁻¹)
NIST 1573	14.4 ± 1.1	50.8 ± 1.7	64.8 ± 1.9	31 ± 2	11 ± 2	41 ± 3
IAEA 140-TM	50.0 ± 0.3	52.8 ± 0.4	103.5 ± 0.8	45.0 ± 0.15	20 ± 3	65 ± 3

Total certified value for NIST 1573a: Sb = 0.063 ± 0.006 µg g⁻¹; Recommended value for IAEA 140-TM: Sb = 0.103 µg g⁻¹.

Table 6. Determination of Sb(III) and Sb(V) in cereal samples by HG AFS, expressed as mean ± standard deviation for n = 3

Sample	Sb(III) (ng g ⁻¹)	Sb(V) (ng g ⁻¹)	Sb(III) + Sb(V) (ng g ⁻¹)	Total Sb ^a (ng g ⁻¹)
Rice	0.15 ± 0.01	0.47 ± 0.02	0.6 ± 0.2	0.65 ± 0.03
Wheat semolina	< LOD	< LOD	-	< LOD
Wheat flour	0.19 ± 0.03	0.22 ± 0.09	0.39 ± 0.03	0.34 ± 0.05
Corn flour	0.19 ± 0.07	0.33 ± 0.10	0.52 ± 0.09	0.5 ± 0.1
Rice semolina	0.17 ± 0.11	0.30 ± 0.09	0.38 ± 0.08	0.42 ± 0.06
Wheat bran	1.6 ± 0.4	1.2 ± 0.3	2.9 ± 0.5	2.9 ± 0.3
Rye flakes	1.5 ± 0.3	1.4 ± 0.3	2.9 ± 0.5	2.9 ± 0.1
Rye flour	< LOD	< LOD	-	< LOD

^aLOD for total Sb: 0.2 ng g⁻¹.

Table 7. Determination of Te(IV) and Te(VI) in cereal samples by HG AFS, expressed as mean ± standard deviation for n = 3

Sample	Te(IV) (ng g ⁻¹)	Te(VI) (ng g ⁻¹)	Te(IV) + Te(VI) (ng g ⁻¹)	Total Te ^a (ng g ⁻¹)
Rice	0.32 ± 0.07	0.70 ± 0.10	1.00 ± 0.14	0.93 ± 0.04
Wheat semolina	< LOD	< LOD	-	< LOD
Wheat flour	< LOD	< LOD	-	< LOD
Wheat corn	< LOD	< LOD	-	< LOD
Rice semolina	0.42 ± 0.06	0.97 ± 0.11	1.38 ± 0.16	1.41 ± 0.08
Wheat bran	4.2 ± 0.2	8.5 ± 0.3	12.7 ± 0.4	12.7 ± 0.5
Rye flakes	0.59 ± 0.08	0.72 ± 0.09	1.3 ± 0.2	1.3 ± 0.2
Rye flour	6.9 ± 0.3	12.9 ± 0.2	19.8 ± 0.3	20 ± 2

^aLOD for total Te: 0.8 ng g⁻¹.

From the different type of samples analyzed it can be concluded that Te(VI) is the main specie of Te in raw cereals and cereal based products. On considering Sb species it seems that Sb(V) is predominant in raw cereals

being modified the relationship between Sb(V) and Sb(III) from processed cereal based products. However, additional studies would be required to obtain a clear conclusion of this point.

Conclusions

The non-chromatographic strategy developed for Sb(III), Sb(V), Te(IV) and Te(VI) determination in cereals and cereal based products by HG AFS offers a simple and sensitive alternative to hyphenated techniques for speciation analysis. The speciation analysis of Sb and Te in cereal samples based on the sonication of samples for 10 min with 1 mol L⁻¹ H₂SO₄ at room temperature, followed by a washing step with EDTA provides quantitative recoveries of both considered elements and does not modify the original Sb and Te species present in cereals. The levels of Sb(III), Sb(V), Te(IV) and Te(VI) found, evidenced that the developed procedure is suitable to obtain quantitative data for cereal samples and that is a guarantee of the absence of risks in the consumption of the considered samples.

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