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Phosphate Interference in the Determination of Total Arsenic in Potatoes

Development of a Novel Method for Surveillance Analysis

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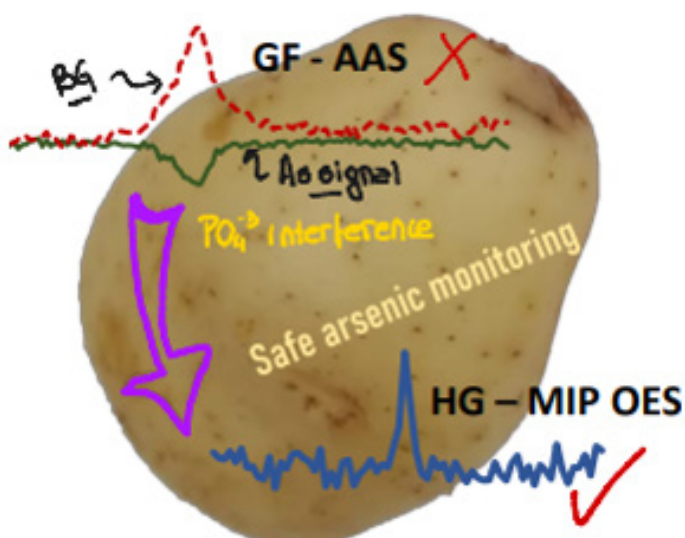
Given the high intake of potatoes by the world population, reliable methodologies with very low limits of detection are needed for the determination of highly toxic elements such as arsenic. For that purpose, graphite furnace atomic absorption spectrometry could be considered one of the techniques of choice; notwithstanding the matrix effect prevented its application in arsenic determination in potatoes as the analytical signal was absolutely depleted. The potential interferent was searched among the mineral content. As a result, it was found that the interference presumably could be attributed to phosphate. Attempts to overcome the matrix interference by different sample digestion methodologies, chemical modification and temperature variation in the graphite furnace ashing and ashing / atomization stage respectively, were unsuccessful. Consequently, an alternative methodology for determining arsenic in potatoes using hydride generation microwave induced plasma optical emission spectrometry was developed. Limit of detection was 0.0030 mg kg^{-1} in fresh potatoes. The developed method is a robust, simple and low cost alternative for total arsenic safe monitoring of this highly consumed worldwide vegetable.

Keywords: arsenic, phosphate interference in GF AAS, food safety, HG-MIP OES, potato

INTRODUCTION

The ability of potato plants (*Solanum tuberosum,* L.) to grow in soils exposed to different climate conditions spread its cultivation in many countries worldwide; per capita intake averages 33 kg per year.[1]

Potatoes have relatively fewer calories, comprehensive nutrition and high quality protein compared with rice and wheat. From the perspective of water conservation, potatoes can probably become a main food crop in the process of rain-fed agriculture promotion. Its consumption is nowadays promoted in countries where this food was not traditionally used.[2-4]

In developing countries potato crops offer a new world of possibilities for fighting poverty and malnutrition while securing food supply.[5-7] Particularly in South America, total demand for potatoes is projected to increase by over 4.6 million tons to 19.6 million tons in 2030. An increase in the average consumption per capita is also expected.[8]

Potatoes are a critical crop in terms of food security in the face of population growth and increased global demand for food. The environment where the plant grows, especially the soil and water, are sources of contamination.[9-11] In the particular case of arsenic, anthropogenic emissions are added to its normal presence in the earth's crust and once it enters the food chain it becomes a threat to human health.[12]

Being a massively consumed product, the evaluation of its innocuousness becomes more relevant. The Codex Alimentarius and other regional regulatory agencies have established maximum allowed levels for the peeled vegetable.[13-16]

Therefore, having reliable analytical methods with low detection limits to evaluate the presence of arsenic in potatoes is of the utmost importance, because achieving precision and accuracy at low levels is challenging in complex food matrices.[15]

Graphite furnace atomic absorption spectrometry (GF AAS),[17,18] microwave induced plasma spectrometry (MIP OES)[19,20] and ICP MS[21] have been used for the determination of inorganic compounds in potatoes.

In MIP OES the atomization takes place in low temperature nitrogen plasma and the atomic emission serves as the analytical signal for the elemental determination. Coupling hydride generation to microwave induced plasma optical emission spectrometry (HG-MIP OES) minimizes sample interaction with the matrix and enhances sensitivity, though it is a promissory technique for determining elements such as arsenic at low concentration levels.[22] One of its main advantages is being a cost-effective alternative for trace element analysis. Machado et al.[23] found it had a very good performance for the multielemental determination of several hydride forming elements in agricultural samples.

The aim of this work was to study and try to overcome the interferences present in the determination of total arsenic in potatoes by GF AAS and develop a novel method suitable for monitoring its content in surveillance programs. To the best of our knowledge, this is the first methodology available to determine total arsenic in potatoes by HG-MIP OES.

MATERIALS AND METHODS
Reagents
A commercial standard atomic stock solution of 1000 mg L^{-1} (Merck, Germany) of As was diluted with 4:21 $HNO_3{:}H_2O$ for preparing the working standard solutions. For the interference abatement, the chemical modifiers for graphite furnace tried were: Palladium (Merck, matrix modifier for graphite furnace, 10 g L^{-1}), ammonium dihydrogen phosphate (Merck, matrix modifier for graphite furnace, 99.99%), magnesium (Merck, matrix modifier for graphite furnace 10.0 g L^{-1}), iridium (Fluka, atomic absorption standard solution 1000 mg L^{-1}), cerium (III) (Sigma Aldrich, cerium (III) nitrate hexahydrate) and analytical grade $Ni(NO_3)_2$.

The reducing agent for hydride generation was 2.0% (w/v) sodium tetrahydroborate (Sigma Aldrich, ≥ 98.0%), prepared in 0.05 mol L^{-1} sodium hydroxide. For optimization of the sample digestion, analytical grade nitric acid, hydrogen peroxide and hydrofluoric acid were employed. The certified reference material (CRM) used was 1568 Rice flour from NIST. The deionized water used was ASTM type I (Millipore Direct-Q water purifier, Milestone, Sorisole, Italy). High purity Ar was employed.

Instrumentation

Before grinding (1 mm sieve, Model 4 Wiley mill, Thomas Scientific, NJ, USA), samples were dried by air circulation in an air-forced oven (Model DN93, Yamato, Tokyo, Japan). Subsequently, aliquots of dried and grinded samples were introduced in 100 mL high-pressure closed vessels (EasyPrep Plus), and digested in a microwave oven (Mars 6, CEM Corporation, Matthews, NC, USA).

The determination of arsenic by GF AAS was achieved in an electro-thermal atomic absorption spectrometer (Perkin Elmer HGA 900, Shelton, U.S.A.). Pyrocoated graphite tubes fitted with pyrolytic graphite L´vov platform were employed. Electrodeless discharge (400 mA, 193.7 nm, Perkin Elmer precisely, Shelton, CT U.S.A.) and deuterium (background correction) lamps were used.

In the interference studies, the determination of arsenic in samples and spiked samples was carried out in a sector field inductively coupled plasma mass spectrometer (Thermo Fisher Scientific Element 2, Bremen, Germany) and the determination of the inorganic content of the digested samples in an inductively coupled plasma atomic emission spectrometer (Thermo Fisher Scientifc ICAP Pro, Bermen, Germany).

The alternative method developed for arsenic determination employed a nitrogen microwave induced plasma atomic emission spectrometer 4210 (MIP OES, Agilent Technologies, Santa Clara, USA). The atomization was performed in a standard torch. Arsenic hydride was generated and separated from solution in a multimode spray chamber (MSIS, Agilent). Nitrogen (99.5%) was supplied by a nitrogen generator model 4107 (Agilent Technologies, Santa Clara, USA). Air was provided to the nitrogen generator by an air compressor model KK70 TA-200 K (DürrTechnik, Bietigheim-Bissingen, Germany).

Sample preparation

Potatoes were chopped with ceramic knives and dried at 70 °C, water content was determined after 96 hours. The analysis was performed in pools of whole potato, pools of peeled potato and pools of potato skin. Acid digestion was microwave assisted. Sample preparation procedure is summarized in Table I.

Table I. Sample preparation procedure

Amount of dried and grinded sample	0.5 g
HNO_3 1:1 (stand for 10 min after addition)	8 mL
Microwave oven heating program	Time
20 ºC to 120 ºC	20 min
120 ºC	20 min
120 ºC to 170 ºC	20 min
170 ºC	15 min

After digestion, the remaining solution was diluted with ultrapure water to 25 g. Samples and reagent blanks were determined by triplicate.

RESULTS AND DISCUSSION

Graphite furnace methodology

Chemical modifiers and ashing /atomization temperatures

In order to attempt arsenic determination by GF AAS on digested potatoes samples, several graphite furnace working conditions were studied by combining different chemical modifiers and ashing /atomization temperatures (Table II to VI).

Table II. Graphite furnace temperature program using no chemical modification. Temperatures in the pyrolysis stage / corresponding temperatures at the atomization stage.

Stage	Temperature (°C)	Hold time (s)	Ramp rate (°C s^{-1})	Internal Ar flow (mL min^{-1})
Drying (1)	110	30	1	250
Drying (2)	130	20	15	250
Pyrolysis	400 /500	30	10	250
Atomization	2000-2100/1000	5	0	0
Cleaning	2500	5	1	250

Table III. Graphite furnace temperature program using a mixture of Mg and Pd as chemical modifier (15 µg Pd – 1.6 µg Mg per firing) and (30 µg Pd – 3.2 µg Mg per firing). Temperatures in the pyrolysis stage / corresponding temperatures at the atomization stage.

Stage	Temperature (°C)	Hold time (s)	Ramp rate (°C s^{-1})	Internal Ar flow (mL min^{-1})
Drying (1)	110	30	1	250
Drying (2)	130	20	15	250
Pyrolysis	500/800-1200/1000	30	10	250
Atomization	1000-1500/2000/2000-2300	5	0	0
Cleaning	2500	5	1	250

Table IV. Graphite furnace temperature program using Pd as chemical modifier (5 µg and 10 µg Pd per firing). Temperatures in the pyrolysis stage / corresponding temperatures at the atomization stage.

Stage	Temperature (°C)	Hold time (s)	Ramp rate (°C s^{-1})	Internal Ar flow (mL min^{-1})
Drying (1)	110	30	1	250
Drying (2)	130	20	15	250
Pyrolysis	400/700/1000/1200	30	10	250
Atomization	1000-1500/2000/2000-2300/1500-1900-2300	5	0	0
Cleaning	2500	5	1	250

Table V. Graphite furnace temperature program using Ni as chemical modifier (20 µg Ni per firing) and (6 µg Ni per firing). Temperatures in the pyrolysis stage / corresponding temperatures at the atomization stage.

Stage	Temperature (°C)	Hold time (s)	Ramp rate (°C s^{-1})	Internal Ar flow (mL min^{-1})
Drying (1)	110	30	1	250
Drying (2)	130	20	15	250

Table V. Graphite furnace temperature program using Ni as chemical modifier (20 µg Ni per firing) and (6 µg Ni per firing). Temperatures in the pyrolysis stage / corresponding temperatures at the atomization stage. (continuation)

Stage	Temperature (°C)	Hold time (s)	Ramp rate (°C s^{-1})	Internal Ar flow (mL min^{-1})
Pyrolysis	800-1000-1200/1200	30	10	250
Atomization	2300/2500-2600	5	0	0
Cleaning	2600	5	1	250

Table VI. Graphite furnace temperature program using a mixture of Ce(IV) and Pd as chemical modifier (0.3 µg Ce(IV) and 30 µg Pd per firing). Temperatures in the pyrolysis stage / corresponding temperatures at the atomization stage.

Stage	Temperature (°C)	Hold time (s)	Ramp rate (°C s^{-1})	Internal Ar flow (mL min^{-1})
Drying (1)	110	30	1	250
Drying (2)	130	20	15	250
Pyrolysis	600-800-1200/800	30	10	250
Atomization	2400/2000-2600	5	0	0
Cleaning	2600	5	1	250

Each pool of digested samples (whole and peeled potato and potato skin) was run all together with a digestion blank, an arsenic standard solution (4 µg L^{-1} – As), a spiked digested sample (4 µg L^{-1} – As spike) and a CRM digest (5.8 µg L^{-1} – As in the test solution).

None of the chemical modifiers at any working conditions tried gave a signal, neither in the sample nor in the spiked one. Conversely, a pronounced negative signal was found (Figure 1). Both the standard and CRM digest solutions showed coherent signals.
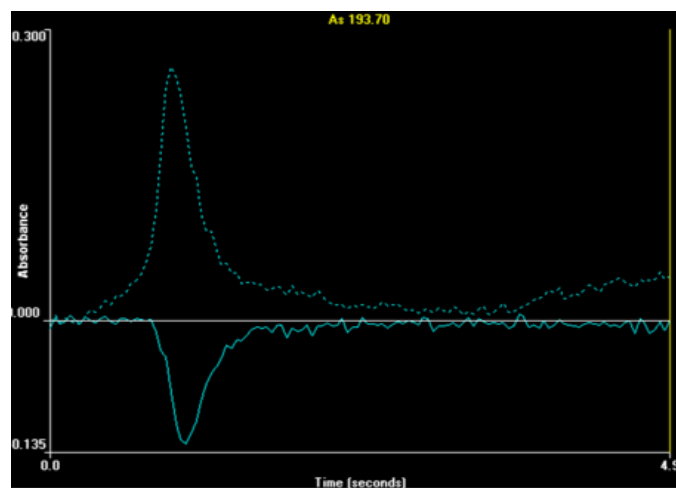

Figure1. Example of the negative signal found for As determination by ET AAS in the digested samples.

Therefore, to confirm that the interference was not caused by organic material remaining in solution that could not be eliminated during the furnace ashing stage, different mineralization strategies were assayed.

Sample digestion methodology

Table VII summarizes the additional digestions tried.

Table VII. Additional digestion mixtures assayed

Option	Reagents	Heating program
1	$(HNO_3:H_2O)(1:1)$	
2	$(HNO_3:H_2O_2:H_2O)(2:1:1)$	15 min ramp up to 220 °C, holding at that temperature along 20 min
3	$(HNO_3:H_2O_2:H_2O:HF)(2:1:1:0.25)$	

Option 1 used the same reagents at higher temperatures (220 °C instead of 170 °C). Option 2 incorporated H_2O_2 and option 3 incorporated H_2O_2 and HF. Both, option 1 and 2 remaining solutions were diluted with ultrapure water to 25 g. Option 3 was transferred to a PTFE vessel and heated at 200 °C almost to dryness. The residue was dissolved with 5% HNO_3, heated at 140 °C and diluted up to 25 g with ultrapure water.

When using 15 µg Pd and 1.6 µg Mg per firing at a pyrolysis temperature of 1000 °C and an atomization one of 2000 °C, the recovery for the certified reference material obtained for the three digestion reagent mixtures was between 97 and 104%; consequently, these conditions were chosen to perform arsenic determination on the sample digests.

Neither in the digested samples, nor in the spiked ones there was a signal, independently of the digestion method applied; a negative peak appeared instead. Spiked samples digest had a concentration of approximately 4 µg L^{-1} – As, hence a clearly detectable signal was expected. It was concluded that adding oxidizing reagents such as hydrogen peroxide and complexing reagents such as hydrofluoric acid to the digestion did not improve arsenic recoveries.

Curtis J. et al.[24] reported the use of a metallic coating on the graphite tube as an alternative to conventional matrix modifiers. The most commonly employed metals to form these coatings are the platinum group elements: ruthenium, rhodium, palladium, osmium, iridium, and platinum.

Ferreira de Oliveira et al.[17] reported the determination of arsenic by GF AAS in potato slurry using iridium as permanent chemical modifier finding suitable recoveries in spiked samples at 10, 20 and 50 µg L^{-1} concentration levels. According to their procedure, in the present work, the graphite tube was thus coated with a total of 500 ug of iridium. Using this permanent modifier, the recovery of the Certified Reference Material was found in the range 94 – 98% for the 3 digestions. However, the absorbance-time profile for both, the arsenic signal and the background signal for the samples were similar to the one found for the chemical modifiers previously studied. Unlike the results found by Ferreira de Oliveira et al.,[17] the recovery of arsenic found in the spiked samples was close to 25%. Despite this result being better, the interference in the sample has not yet completely abated. As the CRM employed to evaluate accuracy is similar but not exactly the same matrix, to rule out losses of arsenic during the digestion of the samples, the arsenic determination was carried out by Sector Field Inductively Coupled Plasma Mass Spectrometry (ICP-SFMS) in each digest.

The spectrometer was operated in high resolution mode (Resolution power ≈ 10000) to resolve polyatomic and isobaric interferences. The sample introduction system consisted of a combined Scott/cyclonic chamber and a 100 µL micro-flow nebulizer. The determination of arsenic was carried out by external calibration using germanium as internal standard, monitoring ions [72]Ge and [75]As. In the sample digests, the concentration of arsenic was lower than the detection limit (0.1 µg L^{-1}, determined as the concentration equivalent to 3 times the blank signal). On spiked samples, recovery was 95 – 102%. From

this experiment, it can be concluded that there is no arsenic loss during the digestion (for every mixture of reagents) and therefore the drawbacks found in the GF AAS determination are probably due to the presence of inorganic interferences.

Search of the inorganic matrix composition and interferent

In order to confirm the nature of the interference, the inorganic composition of the sample was determined after the wet digestion by ICP OES. The spectrometer was fitted with a cyclonic chamber and a 500 µL Meinhard nebulizer was used. The quantification was performed by means of an external calibration plot using yttrium as the internal standard. Results are presented in Table VIII.

Table VIII. Mineral composition of the digested samples determined by ICP OES. C: Concentrations of the different elements on the sample digest.

Concentration level	Inorganic composition
$C < 0,05$ mg L^{-1}	Ag, Cd, Co, Cr, Mo, Ni, Pb, Sb, Se, Tl, V
$0,05 \leq C < 1$ mg L^{-1}	B, Ba, Cu, Mn, Zn
$1 \leq C < 10$ mg L^{-1}	Al, Fe, Na
$10 \leq C < 100$ mg L^{-1}	Ca, Mg, P
$100 \leq C < 500$ mg L^{-1}	K

Solutions of 20 µg L^{-1} – As spiked in turn with Ag, B (as borate), Cd, Co, Cr, Mo, Ni, Sb (as antimonyl), Se (as selenite), V (0.050 mg L^{-1}), Al, Ba, Cu, Fe, Mn (1.0 mg L^{-1}), Ca, Fe, Na (10 mg L^{-1}), Mg, P (as phosphate) (100 mg L^{-1}) and K (500 mg L^{-1}) were run by GF AAS. The sole species causing a drop in arsenic signal with a similar profile as the one found for the samples was phosphate.

Arsenic solutions at 5 µg L^{-1} – As and 20 µg L^{-1} – As concentration levels were prepared in phosphate solutions containing 0 mg L^{-1} – P, 10 mg L^{-1} – P, 50 mg L^{-1} – P, 100 mg L^{-1} – P and 200 mg L^{-1} – P. The determination by GF AAS was performed using deuterium background corrector, nickel (6 µg per firing) as chemical modifier, two drying stages (110 °C and 130 °C respectively), pyrolysis at 1200 °C and atomization at 2500 °C. The analytical signal was integrated absorbance. Results found for these working conditions are presented in Figure 2 where the signal recovery is plotted against the phosphate concentration of the solution at each arsenic concentration level. The signal recovery was calculated as Equation 1:

$$Signal\ recovery\ (\%) = \frac{signal\ of\ the\ measured\ solution}{signal\ of\ the\ 0\ mg\ L^{-1} - P\ solution} \times 100 \qquad \text{Equation 1}$$
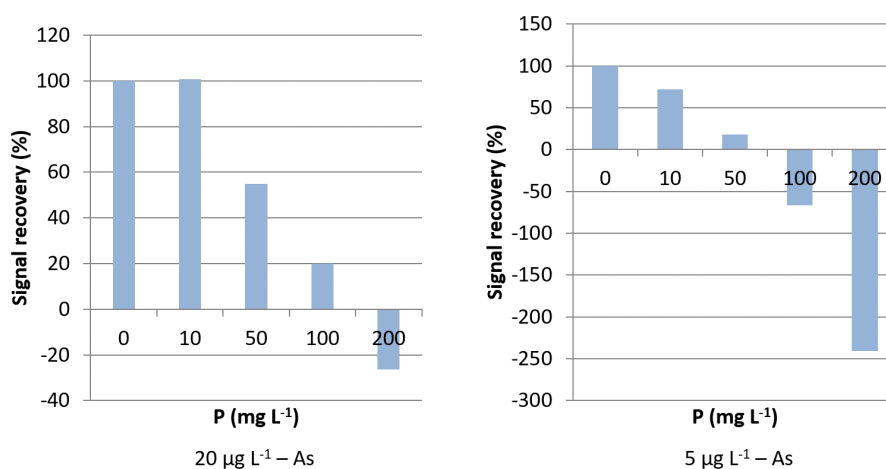
Figure 2. Arsenic signal recovery for each phosphate solution.

Chakraborti et al.[25] investigated the interference of phosphate in the determination of arsenic by GF AAS using nickel nitrate as matrix modifier in water samples, finding that the extent of the interference depended both on the concentration of phosphate and on the ratio of the concentration of As/PO_4 and could be overcome by careful optimization of the ashing conditions. Similar results were found in this work, but the interference could not be abated at lower pyrolysis temperatures as previously shown.

So far, arsenic determination by GF AAS in digested potato samples has been unsuccessful probably due to the non-specific absorption of the species formed in the thermal decomposition of phosphates.[26] Saeed and Thomassen[26] found that this spectral interference depends on the wavelength and the bandwidth and could not be suppressed in the assayed working conditions.

Pierce et al.[27] studied the interference of phosphate in arsenic determination by GF AAS and by hydride generation with argon-hydrogen flame and quartz tube flame atomization between 0.3 mg L^{-1} – P and 33.3 mg L^{-1} – P in 1.0 µg L^{-1} – As, 10 µg L^{-1} – As and 100 µg L^{-1} – As. They found a massive suppression of the signal for GF AAS, moderate signal suppression for hydride generation with argon-hydrogen flame and no signal suppression for hydride generation quartz tube flame atomization.

Hydride generation – microwave induced plasma spectrometry methodology
Development of an alternative MIP OES based method

Hydride generation (HG) is a well-established sample introduction technique for atomic spectrometry that separates the analyte from the matrix. Its hyphenation with microwave induced plasma emission atomic spectrometry (MIP OES) results in a powerful tool for trace level arsenic determination that has not been fully exploited so far.[22,28,29]

From the digest solution, arsenic was pre-reduced at room temperature to As(III) with 1 mL of 37% (w/v) HCl and 1 mL of 20% (w/v) KI per 10 mL of digested sample or standard solution. The arsine was generated by reduction with $NaBH_4$. (0.5 – 1.0 and 2.0)% (w/v) $NaBH_4$ in 0.5% (w/w) NaOH, finding higher analytical signals for the latter. Instrumental parameters such as pump speed, nitrogen flow-rate, viewing position, stabilization and reading time were also optimized. Table IX summarizes the working conditions assayed for each parameter and the optimum found.

Table IX. Optimization of the instrumental parameters of the HG-MIP OES

Parameters	Tested conditions	Optimum conditions
Pump speed	20 – 30 – 40 rpm	30 rpm (0.90 mL min^{-1})
Nebulizer N_2 flow	0.3 up to 1 L min^{-1} (every 0.05 L min^{-1})	0.7 L min^{-1}

(continues on the next page)

Table IX. Optimization of the instrumental parameters of the HG-MIP OES (continuation)

Parameters	Tested conditions	Optimum conditions
Viewing position	-120 up to + 120	+ 10
Read time	1, 2, 3, 5, 10, 20, 30 s	10 s
Stabilization time	5, 10, 20, 30, 40 s	20 s

The performance of the method (Table X) was assessed according to Eurachem Guide recommendations.[30] The figures of merit tested were linear range, limits of detection (3s) and of quantification (10s), precision (repeatability) and trueness. A six point external calibration curve was used for quantification. The linear range was evaluated up to 100 µg L^{-1}. Homoscedasticity of the variances was assessed by means of the Cochran´s C test (n = 4, k = 7, α = 0.05). As the Cochran test statistic calculated (C = 0.465) was lower than the tabulated one (C = 0.480), there was no statistical evidence to reject the null hypothesis and was though accepted.

For assessing the quality of the fit of the calibration curve an ANOVA test was performed; F(27, 0.05) = 3638 and F(27, 0.05) critical =1,8 E^{-29} thus the null hypothesis was rejected. The regression model does explain the variation between the independent and the dependent variable.

Limits of detection and quantification concentration were calculated from the standard deviation of the signal of ten blank digests. Precision under conditions of repeatability was calculated as the relative standard deviation of the concentration of 6 replicates of CRM. Trueness was assessed in 6 replicates of the CRM (5.8 µg L^{-1} – As in the test solution).

Table X. Performance of the determination of arsenic by HG-MIP OES in fresh potato

Figures of merit	
Linear range evaluated:	1.1 – 100 µg L^{-1}
Calibration function (R^2 = 0.9989)	I = 28.00C + 0.187
Limits of confidence:	I = 28,481C + 100,1 – I = 27,547C - 99,371
Limits of detection and quantification in the test solution, n = 10:	LOD: 0.30 µg L^{-1}
	LOQ: 1.0 µg L^{-1}
Limits of detection and quantification in potatoes (water content: 80%):	LOD: 0.0030 mg kg^{-1}
	LOQ: 0.010 mg kg^{-1}
Precision (repeatability, n = 6):	7.6%
Recovery (n = 6):	115%

The limit of detection of arsenic in fresh potato is sixty times better than the one found by Machado et al.[23] for solid samples, who developed a successful analytical method for the simultaneous determination of As, Bi, Ge, Sb and Sn also employing HG-MIP OES. As the authors explained, they worked in compromised conditions in order to fulfill their goal. In the present work, the methodology was optimized to ensure potatoes innocuousness related to their arsenic content, finding a performance as good as ICP MS for the same matrix.[21]

The interference of phosphate was also studied in the determination of arsenic by HG-MIP OES, finding as expected, no relevant differences for both arsenic concentration levels.

CONCLUSIONS

The determination of arsenic in potato samples could not be performed by GF AAS due to a suppressing interference produced presumably by phosphate that could not be overcome by chemical modification of the test solution and/or optimizing atomization and pyrolysis temperatures. Separation of the analyte from the matrix by hydride generation with MIP OES detection resulted in an interference free determination.

The novel approach presented in this work for total arsenic determination in potatoes is a suitable, reliable and economic tool for safe monitoring of this valued vegetable. Its performance is comparable to other cutting-edge techniques and enables the determination of arsenic at very low concentration levels with much lower operational costs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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