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Determination of total arsenic in soft drinks by hydride generation atomic fluorescence spectrometry

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Abstract

A highly sensitive and simple method has been developed for the determination of total arsenic, by continuous hydride generation and atomic fluorescence spectrometry (HGAFS), in refreshing drink samples as colas, teas and fruit juices. Samples were mixed with concentrated HCl and KI to obtain final concentrations of 2 mol l^{-1} and 1%, respectively. These solutions were aspirated and merged with a reducing $NaBH_4$ 3% (m/v) solution, with sample and $NaBH_4$ flow rates of 12.5 and 1.5 ml min^{-1}, respectively. The hydride generated in a 170 cm reaction coil was transported to the detector with an Ar flow of 400 ml min^{-1}. The recovery values of added concentrations, from 0.1 to 0.9 ng ml^{-1}, of arsenic in colas, teas and fruit juices were 94 ± 5, 101 ± 9 and 94 ± 6, respectively, achieving variation coefficients between 0.1% and 9%, confirming the accuracy of developed procedure. Detection limit, ranged from 0.01 to 0.03 ng ml^{-1}. On comparing the direct determination with a reference procedure made after dry ashing operation it can be noticed that the direct approach provides a simplification of the handling and time consuming, achieving statistically comparative results.

Keywords: Arsenic determination; Continuous hydride generation; Atomic fluorescence spectrometry; Refreshing drinks

1. Introduction

Arsenic is a covalent-hydride forming element which can be determined with a high degree of sensitivity and selectivity by atomic spectrometry after reaction with sodium borohydride. This strategy provides an excellent means for matrix isolation and increases the element intake inside the atomizer (Horlick, 1984).

Using hydride generation As has been determined by flame atomic absorption (Castillo, Mir, Martinez, & Gomez, 1986; Harriott, Burns, Chimpalee, & Donaghy, 1991) or inductively coupled plasma atomic emission (Pyen & Browner, 1988a, 1988b). Hydride generation coupled with atomic fluorescence spectrometry (HG-AFS) is one of the most powerful analytical tools for trace determinations. In recent years, the development of commercially available atomic fluorescence spectrometers has provided a suitable tool for As, Se, Sb and Te determination (Corns, Stockwell, Ebdon, & Hill, 1993).

The determination of As in waters by HG-AFS provides a limit of detection (LOD) of 100 ng l^{-1} (Corns et al., 1993), being found for the simultaneous determination of As, Se, Sn and Hg a LOD of 40 ng l^{-1} As (D'Ulivo, Fuoco, & Papoff, 1985), or for the determination of As and Sb a LOD between 5 and 20 ng l^{-1} As (El-Hadri, Morales-Rubio, & de la Guardia, 2000).

Atomic fluorescence spectrometry has been applied to the direct determination of As in degassed beer samples (Martinez, Morales-Rubio, Cervera, & de la Guardia, 2001) or sonicated milk (Cava-Montesinos, Cervera, Pastor, & de la Guardia, 2003) samples. However, till now there are no precedents on the determination of As in soft drinks.

It is well established that inorganic As presents risks for human health. It is a carcinogenic element, acts as endocrine disruptor and is linked to other human health abnormalities (Dudka & Miller, 1999; Mass et al., 2001; Mandal

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& Suzuki, 2002). So, the availability of analytical procedures for As determination is justified. Spanish regulation about arsenic content in soft drinks establish a maximum tolerable concentration level of 250 $\mu g\,l^{-1}$ for both, stored in metallic and non-metallic containers, samples (Real Decreto 15/1992 de 17 de enero: Reglamentación técnico sanitaria).

In general the metal concentration in foods is influenced by environmental and technical factors as soil, fertilizers, pesticides, herbicides, irrigation water, air contamination, food process, and it could be considered four potential sources for As contamination in soft drinks. Nowadays, residual waters is frequently employed to orchard trees irrigation and, sometimes these waters can contain appreciable levels of metal contamination that could be assimilated by the trees and the fruits.

Arsenic compounds are commonly used today as pesticides, wood preservatives or in alloys (Friberg, Nordberg, & Vook, 1986). A potential contamination source of foods by As could of the be the application of lead arsenate for pest control in orchards and nowadays it is still found elevated levels of arsenic in orchard soil caused by the common use of arsenate as pesticide for apples in the first half of the 20th century (Lisk, 1994; Murphy & Aucott, 1998; Wolz, Fenske, Simcox, Palcisco, & Kissel, 2003) in spite that it is not very probable that this kind of pesticides, employed 50 yr ago, could cause a serious soil contamination and should now the origin of presence of As in foods.

Water employed in the manufacturing process of soft drinks products could be one of the main sources of As found in this kind of samples. On comparing the results shown in this study with data reported for mineral and tap water (El-Hadri et al., 2000), it can be seen that As concentration in waters, colas and teas are of the same order. Nevertheless, the higher concentration of arsenic found in apple juice cannot be explained by this reason.

In soft drinks, the most important source of contamination should be the metallic material employed in the manufacturing of samples and the final storage recipients (cans, bottles or briks) and thus it is well known that acid drinks and foods, as juice fruits or cola beverages can cause metal leaching from storage recipients. On the other hand, metal containers employed nowadays for soft drinks are aluminium based, and As can be found as a common impurity from aluminium gray matter. So, it could be the most valid source of sample contamination by As.

The main purpose of the present paper has been to evaluate the conditions for the determination of total inorganic As in commercially available fruit juices, cola and tea drinks.

2. Experimental part

2.1. Apparatus

An atomic fluorescence detector excalibur PSA 10033 from PS Analytical (Kent, UK) equipped with an As boosted discharge hollow cathode lamp (BDHCL) Photron (Victoria, Australia) as excitation source, an hydrogen diffusion flame as the atom cell and a specific filter, to achieve isolation and reduction of flame emission, was used for As determination at the resonance wavelength of 193.7 nm.

A continuous flow vapour system Unicam VP-90 equipped with a B-type gas–liquid separator (Cambridge, UK) was employed for hydride generation. To retain the water vapor generated, a Perma pure drier tube PS Analytical, (Kent, UK) was placed before the detector.

Polytetrafluoroethylene (PTFE) tubes of 0.8 mm id were employed to construct the manifold. Flexible polyvinylchloride peristaltic pump tubes of 2.79 and 0.76 mm id were employed to transport the HCl carrier and the $NaBH_4$ reducing reagent, respectively.

2.2. Reagents, standards and samples

As^{III} stock standard solution of 1000 $mg\,l^{-1}$ was prepared by dissolving 1.320 g of As_2O_3 Riedel-de Haën (Hannover, Germany) in 25 ml of a 20% (m/v) KOH solution, neutralized with 20% (v/v) H_2SO_4 and diluted to 1 l with 1%(v/v) H_2SO_4.

Potassium iodide from Panreac (Barcelona, Spain) was added to samples and reagent blank solution for the reduction of As^V–As^{III} before the determination of total As. Sodium tetrahydroborate from Fluka (Buchs, Switzerland), was dissolved in 0.5% (m/v) NaOH Probus (Barcelona, Spain). Solutions were prepared daily and filtered before use through a nylon mesh of 0.45 μm pore-size from Lida (Kenosha, WI).

Hydrochloric acid solutions were prepared from 37% $d = 1.18\ g\,ml^{-1}$ HCl Fluka (Buchs, Switzerland). Argon C-45 (purity 99.995%), obtained from Carburos Metalicos (Barcelona, Spain), was employed as carrier gas for the atomizer. Synthetic air from Carburos Metalicos was used to dry the vapor phase in the Perma pure drier tube and to switch on-off the pneumatic Unicam UV-90 valve.

All solutions were prepared from analytical-reagent grade chemicals using ultrapure water, with a resistivity of 18 $M\Omega\,cm^{-1}$, which was obtained from a Milli-Q water purification system Millipore (Bedford, MA).

Apple juices and tea samples, obtained randomly from the local market in Spain, were used directly from their containers, 1 l briks, and were stored at 4 °C until their analysis. Cola samples, obtained from the local market in Spain, in 1.5 l bottles, were degassified by magnetic stirring and by sonication and stored at 4 °C before their analysis. For each individual sample two containers were purchased.

2.3. Fluorescence measurement

Using the manifold indicated in Fig. 1 and the instrumental and operational parameter shown in Table 1, $NaBH_4$ (3% m/v) and HCl (2.0 $mol\,l^{-1}$) solutions were continuously aspirated and merged in a reaction coil of 170 cm. The H_2 and hydrides generated were transported,

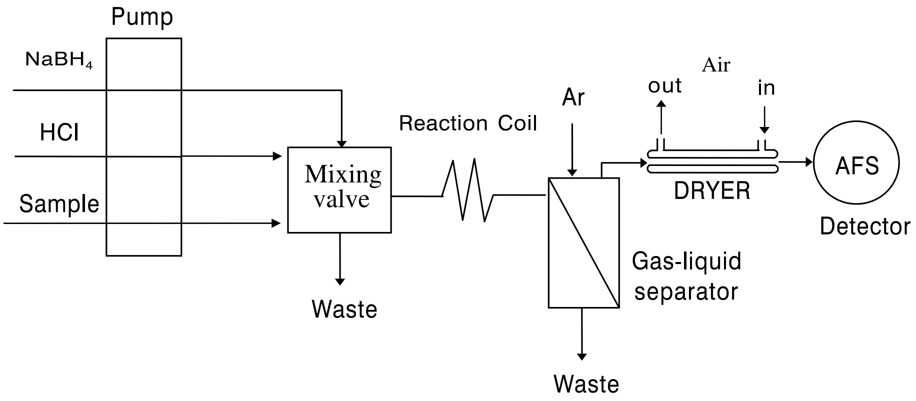

Fig. 1. Manifold employed for the HG-AFS determination of arsenic in refreshing soft drinks.

Table 1
Operating conditions for HG-AFS determination of As in soft drinks

Parameter	As
Spectrometer operating conditions	
Resonance wavelength (nm)	193.7
Bandpass (nm)	0.5
Primary current (mA)	27.0
Boost current (mA)	35.0
Gain	1.0
Potentiometer	5.5
Range	1000
Hydride generation conditions	
Reagent concentration	
HCl (mol l^{-1})	2.0
$NaBH_4$ (% m/v)	3.0
KI (% m/v)	1.0
Reagent flow rate	
Sample/HCl (ml min^{-1})	12.5
$NaBH_4$ (ml min^{-1})	1.5
Argon (l min^{-1})	0.4
Air (l min^{-1})	3.0
Reaction coil length (cm)	170
Atomic fluorescence measurement	
Delay time (s)	10.0
Rinse time (s)	30.0
measurement time (s)	20.0
Memory time (s)	30.0
Measurement mode	Peak height

by a 400 ml min^{-1} Ar flow, through a gas–liquid separator to the atomizer after being dried in a Permapure tube, using a dry synthetic air countercurrent at 3.0 l min^{-1}.

Samples and standards were aspirated through the carrier acid channel by using the directional valve. The fluorescence peak height measurements at 197.3 nm were taken using an acquisition time of 20 s. Calibration curves were prepared daily from As^{III} solution in 2.0 mol l^{-1} HCl at concentration levels ranged between 0.1 and 0.9 ng ml^{-1}.

2.4. Dry ashing reference method

The ashing procedure developed by Cervera, Navarro, Montoro, Catala, and Ybañez (1989) was employed to reduce samples to white ashes. Five milliliter of a solution containing the ashing agent, $Mg(NO_3)_2$ (10% m/v) and MgO (1% m/v), and 5 ml of HNO_3 40% (v/v) were added to 100 g of juice sample. The resulting solution was evaporated to dryness in a hot plate and put into a muffle furnace using the following heating program: (i) 150 °C for 60 min, (ii) 200 °C for 30 min, (iii) from 250 °C to 450 °C for 90 min and (iv) 450 °C for 12 h. The residue obtained was cooled to room temperature and wetted with 5–8 ml HNO_3 10% (v/v). Solution was dry again in the hot plate and put into the muffle oven using the heating program: (i) 150 °C for 60 min, (ii) 300 °C for 30 min and (iii) 450 °C for 12 h. This second step was repeated until white ashes were obtained. Finally, white ashes were wetted with 2 ml water, dissolved with 5 ml of 6 mol l^{-1} HCl and diluted to a final volume of 25 ml. From this mineralized juice solution, working sample solution was prepared by dilution to 50 ml taken from 0.5 to 2.0 ml and mixed with HCl and KI to a final concentration of 2.0 mol l^{-1} and 1% (m/v).

Six milliliter of a solution containing the ashing agent and 6 ml of HNO_3 40% (v/v) were added to 125 ml of degassified cola sample. The resulting solution was mineralized and diluted to a final volume of 25 ml as indicated before. From the mineralized cola solution, working sample solution was prepared by dilution to 50 ml taken from 4.0 ml and mixed with HCl and KI to a final concentration of 2.0 mol l^{-1} and 1% (m/v).

Five milliliter of a solution containing the ashing agent and 5 ml of HNO_3 40% (v/v) were added to 100 ml of tea sample. The resulting solution was mineralized and diluted to a final volume of 25 ml as indicated before. From the mineralized solution, working sample solution was prepared by dilution to 50 ml taken from 3.0 ml and mixed with HCl and KI to a final concentration of 2.0 mol l^{-1} and 1% (m/v).

2.5. Direct determination of total arsenic

From 2 to 5 ml of juice samples, as a function of the As content in samples, 20 ml of degassified cola samples or

10 ml of tea samples were mixed with 8.5 ml of concentrated HCl and 0.9 ml of concentrated KI before dilution to 50 ml with distilled water to obtain a final concentration of HCl and KI of 2.0 mol l^{-1} and 1% (m/v), respectively. These solutions were feed directly to the system and mixed to the $NaBH_4$ reductant solution to form the arsenic hydride, which further was detected by atomic fluorescence at 193.7 nm.

3. Results and discussion

3.1. Evaluation of hydride generation conditions

Employing the operational conditions indicated in Table 1 the analytical slopes of standard addition lines for each sample, analyzed directly or after a previous dry ashing treatment, were compared to that obtained by using an aqueous standard external calibration line.

Table 2 shows results obtained, and as can be seen for the main part of samples relative slopes, between 85% and 110%, were achieved using the standard addition method. In the case of apple juice and cola samples, standard addition slopes were statistically the same to those found using external standards, and for tea samples the standard addition calibration slopes were statistically comparable with that found by external calibration in all cases except for two samples. From data reported it can be concluded that no matrix effects could be noticed on measuring directly As from the HG-AFS of samples reduced with KI without any previous digestion.

Table 2
Ratio between standard addition line and external aqueous calibration slopes for both, direct and after a previous dry ashing sample treatment

Sample	Direct (R%)	Dry ashing (R%)
Apple juices		
Consumer	93 ± 4	87 ± 6
Dia	85 ± 9	80 ± 9
Hacendado	85 ± 9	88 ± 9
Don simon	99 ± 7	98 ± 6
Frusole	86 ± 5	90 ± 4
Hero	98 ± 3	89 ± 9
Colas		
Coca cola with cafeina	89 ± 7	98 ± 5
Pepsimax	92 ± 6	88 ± 4
Colaesky	85 ± 4	91 ± 7
Ultifress cola	85 ± 9	91 ± 7
Cola hacendado	98 ± 4	100 ± 4
Cola consumer	98 ± 5	93 ± 7
Teas		
San benedetto	116 ± 6	126 ± 8
Don simon	96 ± 9	107 ± 9
Nestea al limon	120 ± 10	130 ± 5
Te verde hacendado	104 ± 5	110 ± 3
Te al melocoton	102 ± 6	92 ± 8

Values indicated in % are the average of three independent calibration lines ± the corresponding standard deviations.

3.2. Study of interferences

According to the nature of samples analyzed, the effect of commons ions like Mg^{2+}, Ca^{2+}, K^{+}, NH_4^{+} and anionic species, such as phosphate or sulfate was evaluated on the HG-AFS determination of As^{III} and As^{V}. Additionally, other ions like Sb^{III}, Se^{IV} and Te^{IV}, which for volatile hydride; Cr^{III}, Cr^{VI}, Fe^{II}, Fe^{III} and Cu^{II} as commonly interferent transition elements and nitrate and bromide as common interferent anionic species in the hydride generation were evaluated.

Results obtained are summarized in Table 3, showing the tolerance limit concentration of interferent elements as those concentration giving a 10% signal difference and the critical limit concentration as those concentrations giving a 25% signal difference. As can be seen most of the species considered do not interfere at concentration levels commonly found in apple juice (Seow, Abdul Rahman, & Abdul Aziz, 1984;Alonso, Artigas, & Jimenez, 2003), colas Andruzzi, Trazza, and Marrosu (1983); Metrohm, and tea samples (Fernadez, Pablos, Martin, & Gonzalez, 2002).

3.3. Analytical figures of merit

The calibration graphs for HG-AFS was linear up to a concentration of 1.0 ng ml^{-1} As. The detection limit established as 3 s_b/slope, where s_b is the standard deviation of 10 blank measurements, varied between 5 and 20 ng l^{-1}, as a function of the experimental work session. Table 4 shows the repeatability and accuracy found for analyzed samples. The repeatability, evaluated from the relative standard deviation of three independent determinations of a same sample varied between 0.1% and 9% by using both, the direct determination and that after the dry ashing digestion. Ought to the lack of certified samples, the accuracy of the method was evaluated by recovery experiments carried out using samples spiked with known concentrations of arsenic at different levels, from 0.1 to 0.9 ng ml^{-1} and prepared and analyzed in the same way than commercial samples. For each group of processed samples, blanks (deionized water and reagents) and standards, were prepared following the same process than samples. As can be seen in Table 4, the analytical recovery values achieved in spiked samples were closed to 100% in all the cases.

3.4. Direct determination of arsenic content in market samples

As was determined by the direct procedure on seventeen soft drink samples obtained from the Spanish market and data found were compared with those obtained after dry ashing matrix decomposition. Data summarized in Table 5 shows a good agreement between all data found, thus evidencing the applicability of the method. Soft drink samples contain As at concentrations lower than 1 ng ml^{-1}. In the case of apple juice concentrations from 2 to 14 ng ml^{-1} were found and are of the same order than those found

Table 3
Study of interferences on the determination of 1.0 ng ml^{-1} Ar by HG-AFS

Interferent species	As(III)				As(V)			
	Tolerance limit (μg l^{-1})		Critical limit (μg l^{-1})		Tolerance limit (μg l^{-1})		Critical limit (μg l^{-1})	
Sb(III)	(+)	1–30	(+)	100	(o)	> 100	–	–
Se(IV)	(+)	1–1000	(+)	10 000	(−)	0.3	(−)	1–50
Te(IV)	(+)	>10	–	–	(+)	>10	–	–
Cr(III)	(−)	100	(−)	10 000	(+)	1000	(+)	3000
Cr(VI)	(+)	100–	(+)	100 000	(+)	1–10 000	(−)	100 000
Fe(II)	(−)	10 000	–	–	(−)	1–100 000	–	–
Fe(III)	(−)	1–100 000	(−)	1000	(−)	1–100	(−)	1000
Cu(II)	(−)	100	(−)	5000	(o)	>100 000	–	–
Mg^{2+}	(+)	1–1000	(+)	100 000	(o)	>100 000	–	–
Ca^{2+}	(o)	10 000	(−)	–	(−)	10 000	–	–
Sr^{2+}	(−)	>100 000	–	–	(o)	>100 000	–	–
K^{+}	(o)	100 000	–	–	(+)	10 000	(+)	100 000
NH_4^+	(−)	>100 000	–	–	(−)	300 –	–	–
PO_4^{3-}	(−)	1–30000	(+)	100 0000	(o)	30 000	–	–
NO_3^-	(−)	100–	(−)	100 000	(o)	>100 000	–	–
SO_4^{2-}	(o)	100 000	–	–	(o)	>100 000	–	–

(−), signal depression; (+), signal enhancement; (o), no interference.
Tolerance limit, interferent concentration giving 10% signal difference. Critical limit, interferent concentration giving 25% signal difference.

Table 4
Repeatability and accuracy of the As determination in soft drinks by HG-AFS analytical figures of merit

Sample	Direct		Dry ashing	
	CV (%)	R (%)	CV (%)	R (%)
Apple juice				
Consumer	0.2–3	95 ± 3	0.5–5	93 ± 3
Dia	1–3	89 ± 1	1–6	92 ± 5
Hacendado	0.2–5	88 ± 5	0.1–4	90 ± 3
Don simon	2–9	99 ± 2	0.6–3	96 ± 3
Frusole	2–9	87 ± 2	1–3	94 ± 2
Hero	0.1–9	99 ± 1	0.1–4	101 ± 1
Colas				
Coca cola with cafeina	0.4–9	98 ± 5	1–9	98 ± 2
Pepsimax	0.2–8	91 ± 2	0.3–9	90 ± 3
Colaesky	2–8	86 ± 5	2–3	98 ± 7
Ultifress cola	2–3	89 ± 3	1–8	91 ± 4
Cola hacendado	1–6	100 ± 3	2–6	101 ± 1
Cola consumer	0.2–6	95 ± 3	2–9	93 ± 2
Teas				
San benedetto	0.2–3	108 ± 5	0.1–0.7	119 ± 4
Don simon	0.7–6	92 ± 4	0.3–3	102 ± 6
Nestea al limon	0.5–5	101 ± 2	0.2–3	109 ± 1
Te verde hacendado	0.7–5	100 ± 6	0.2–1	95 ± 6
Te al melocoton	0.1–3	89 ± 7	0.2–8	112 ± 5

CV, coefficient of variation for three independent determinations.
R, recovery values for sample spiked with known concentrations of As^{III} from 0.1 to 0.9 ng ml^{-1}.
Values are the average of three independent analysis ± the standards deviation.

Table 5
Determination of As in refreshing drinks

Sample	Direct (ng ml^{-1})	Dry ashing (ng ml^{-1})
Apple juice		
Consumer	2.74 ± 0.03	2.56 ± 0.03
Dia	4.99 ± 0.08	4.7 ± 0.3
Hacendado	2.93 ± 0.14	2.54 ± 0.02
Don simon	2.2 ± 0.2	1.88 ± 0.05
Frusole	3.0 ± 0.2	2.55 ± 0.07
Hero	14.0 ± 0.2	13.6 ± 0.2
Colas		
Coca cola con cafeina	0.78 ± 0.01	0.84 ± 0.01
Pepsimax	0.23 ± 0.01	0.23 ± 0.01
Colaesky	0.24 ± 0.01	0.25 ± 0.01
Ultifress cola	0.21 ± 0.01	0.22 ± 0.04
Cola hacendado	0.33 ± 0.07	0.33 ± 0.02
Cola consumer	0.53 ± 0.08	0.52 ± 0.04
Teas		
San benedetto	0.64 ± 0.01	0.56 ± 0.02
Don simon	0.13 ± 0.01	0.13 ± 0.01
Nestea al limon	0.96 ± 0.01	0.90 ± 0.03
Te verde hacendado	0.60 ± 0.02	0.51 ± 0.04
Te al melocoton	0.58 ± 0.03	0.50 ± 0.06

Values are the average of three independent analysis ± the corresponding standard deviations.

in the literature (Schoof et al., 1999). The regression between both data population provided the equation $Y = (1.03 \pm 0.01)$, $X + (0.07 \pm 0.04)$ with a regression coefficient of $r^2 = 0.9993$. It evidences that the direct determination of arsenic in samples, reduced with KI, but without any previous digestion, provides accurate results, as well as does not requires any blank correction (the intercept is statistically equal to 0) and not presents constant relative errors (the slope is statistically comparable to 1).

4. Conclusion

Atomic fluorescence provides an extremely sensitive methodology for direct determination of As in soft drink samples as colas, teas and apple fruit juices, without requiring a previous digestion of the samples and is good enough for As concentration level in this kind of samples. On comparing the proposed procedure with a reference one based on a previous dry ashing digestion, it can be concluded that the direct approach is very fast and provides a sample handling simplification, achieving accurate results as has been demonstrated by recovery studies and by the analysis of real samples.

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