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Direct determination of arsenic in beer by electrothermal atomic absorption spectrometry with deuterium background correction (D_2-ET-AAS)

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Abstract

We describe here a method for the direct determination of As in beer by D_2-ET-AAS, using Pd modifier, the atomization from platform and insertion of a cooling step before atomization. This method results in a 40% increase of sensitivity in peak-height measurements. Pd was found to be the most advantageous chemical modifier for the elimination of phosphate interference compared to Ni or Pt + citric acid. In addition, Pd is able to stabilize As at charring temperatures of 1500 °C and further addition of V, Mg or Sr have no influence. Addition of the modifier to standards and samples made possible the use of matrix-free standard solutions for attaining accurate analysis of diluted samples. The accuracy was checked by the comparison of results of direct analysis of beer samples by the proposed method with those found for microwave-digested samples measured by an inductively coupled plasma orthogonal acceleration time-of-flight mass spectrometer (ICP-*oa*-TOFMS) method. The accuracy was also confirmed by the analysis of certified reference samples.

Keywords: Arsenic; ET-AAS; Beer; Background correction; Cool-down step

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1. Introduction

Arsenic is present in food and beverages because of its wide distribution in the environment from the sources being either natural or anthropogenic (Mandal & Suzuki, 2002). Uncontrolled intake of As into the organism could be potentially toxic, and although the European Union (European Commission, 1998) and the World Health Organization (WHO, 1993) established the permissible level 10 $\mu g\,l^{-1}$ only for As in drinking water, also the legislation concerning As contents in different kind of foods and beverages including beer as a widely consumed beverage exists in some countries. Whereas the maximum concentration of As in beer is fixed at 100 $\mu g\,l^{-1}$ by Spanish law, legislation in Czech Republic, Slovenia, Bulgaria and Hungary tolerates 200 $\mu g\,l^{-1}$, and in the United Kingdom and Ireland this level is established at 500 $\mu g\,l^{-1}$ (Martinez, Morales-Rubio, Cervera, & de la Guardia, 2001).

The most commonly applied method for determining As in wines and beer is hydride generation (HG) atomic absorption spectrometry (Baluja-Santos & Gonzalez-Portal, 1992; Cervera, Navarro, Montoro, Catala, & Ybañez, 1989; Herce-Pagliai, González, Camean, & Repetto, 1999). However, the HG technique normally requires the decomposition of the sample, which is time consuming. Therefore, there were some attempts for direct determination using atomic fluorescence spectrometry in conjunction with HG (Martinez et al., 2001; Segura, Madrid, & Cámara, 1999) or systems which couple HG system with graphite furnace with the role of *in situ* preconcentration (trapping) of the analyte (Matusiewicz & Mikołajczak, 2001).

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ET-AAS alone can be also an attractive alternative to HG techniques. Although its sensitivity is lower compared to techniques based on HG, it is still enough to perform rapid and accurate screening for As content in beer. Nevertheless, severe chemical and spectral interferences in the determination of As in food and vegetables and caused mainly by phosphates were frequently mentioned in the literature (Dupire & Hoenig, 1980; Hoenig & Van Hoeyweghen, 1982). The spectral interference caused by absorption of molecular species of P_2 and PO (Fernandez & Giddings, 1982; Saeed & Thomassen, 1981) cannot be, according to several authors, corrected by D_2 lamp and only the use of the stabilized temperature platform furnace concept including the use of Zeeman-effect background correction can overcome these problems (Fernandez & Giddings, 1982; Fernandez, Bohler, Beaty, & Barnett, 1981; Welz & Schlemmer, 1986). However, overcorrection at the PO bands has been observed even with an inverse Zeeman-effect graphite furnace, because the absorption profiles of certain PO bands are affected by the magnetic field (Ohlsson & Frech, 1989).

Chemical modifiers can also have an effect on this spectral interference (Tsalev, Slaveykova, & Mandjukov, 1990). It can be supposed from these studies that when appropriate electrothermal program and adequate modification are used, the direct determination of As using D_2 background correction can be successfully performed even in the presence of troublesome matrices such phosphate (Viñas, Pardo-Martínez, & Hernández-Córdoba, 1999).

Until now, to the best of our knowledge, only one method has been published describing the use of ET-AAS for As determination in beer, nevertheless the samples had to be ashed with magnesium salt which resulted in an increase of background absorbance and the use of Zeeman correction was then unavoidable (Cervera, Navarro, Montoro, de la Guardia, & Salvador, 1991). The primary aim of our work was to develop direct, quick and accurate method for determination of As in beer using ET-AAS instrumentation equipped with D_2 background correction system, which is still the most widely used in analytical laboratories.

2. Experimental

2.1. Instrumentation

Avanta P double beam atomic absorption spectrometer (GBC Scientific Equipment Pty Ltd., Australia) equipped with GF 3000 graphite furnace, autosampler PAL 3000 and deuterium arc background corrector was used. Super lamp (Photron Pty. Ltd., Australia) was the line source (lamp current 13 mA, wavelength 193.7 nm, spectral bandpass 2 nm). Both peak height and peak area absorbance values were measured. Pyrolytically coated graphite tubes (GBC, cat. no. 56GB715) with a preinstalled pyrolytic graphite L'vov platform were used. Argon was used as sheat gas; the internal gas flow in the graphite tube was interrupted during the atomization step.

Comparative study was performed using the Optimass 8000 ICP-*oa*-TOFMS instrument (GBC Scientific Equipment Pty Ltd., Australia). A detailed description of the instrument is given by Sturgeon, Lam, and Saint (2000). Concentric nebulizer Micro Mist (Glass Expansion Pty. Ltd., Camberwell, Victoria, Australia) coupled to a 70 ml thermostated (15 °C) cyclonic spray chamber (Glass Expansion) was used for sample introduction. Liquid uptake rate was controlled by selection of the instrument peristaltic (12 roller) pump speed and set for approximately 1 ml min^{-1}.

Microwave system Speedwave^{TM} MWS-3^{+} (Berghof, Germany) was used for digestion of reference samples as well as of beer samples for ICP-*oa*-TOFMS measurement. The maximum total output of the microwave generator is 1450 W. The calculations and statistical evaluation were carried out using commercial software ADSTAT 1.25 (Trilobyte Statistical Software Ltd., Pardubice, Czech Republic).

2.2. Reagents and standards

Reagents of analytical grade or higher quality were used. All solutions were prepared using deionized water. Water used in all experiments was purified using the Ultra-Clear (SG, Germany) pure water system to 0.05 $\mu S\ cm^{-1}$. All glass and plastic ware were immersed in 2 M nitric acid for 24 h followed by rinsing with deionized water.

Arsenic solution (As_2O_5 in 0.5 mol l^{-1} HNO_3) of 1 g l^{-1} As was obtained from Merck (Darmstadt, Germany). Nitric acid (65% m/v) was Suprapur® (Analytica Co. Ltd, Prague, Czech Republic). Palladium solution of 10 g l^{-1} Pd in 10% v/v HNO_3 was obtained from CPI International (USA). The solution of 1 g l^{-1} of Pd was prepared by diluting an appropriate amount of a 10 g l^{-1} with water. Platinum solution (H_2PtCl_6 in 2 mol l^{-1} HCl) of 1 g l^{-1} Pt was obtained from Fluka (Buchs, Switzerland). Phosphorus solution (1 g l^{-1}) was prepared by dissolving of ammonium dihydrogen phosphate (Analytica) in water. Magnesium nitrate of 10 g l^{-1} Mg and strontium nitrate and nickel nitrate solution of 1 g l^{-1} Sr and Ni, respectively, were prepared by dissolving of the appropriate amount of the salts (Lachema, Brno, Czech Republic) in water. Citric acid was purchased from Lachema and the working solution (50 g l^{-1}) was prepared by diluting of an appropriate amount of the component in water. Vanadium stock solution 5 g l^{-1} was prepared from ammonium metavanadate (Lachema) by dissolving of 1.147 g of the salt in 5 ml of 25% m/v ammonia solution (Lachema), than the mixture was transferred into a 100 ml volumetric flask containing approximately 50 ml of 50 °C water. The complete dissolution was obtained using ultrasounds. The final solution was diluted to 100 ml with water.

2.3. Procedure

2.3.1. Sample preparation

Beer samples were stored at 4 °C until they were analysed. Prior to the analysis, samples were degassed by means of ultrasound. Dilution in 1 + 1 ratio with water was used for ET-AAS procedure. For ICP-*oa*-TOFMS analyses, the samples were decomposed by microwave digestion. For this purpose 5 ml beer sample and 6 ml of nitric acid (65% m/v) were transferred into a 100 ml pressure resistant PTFE vessel. The samples were then digested following five-steps program: (i) 5 min at 150 °C and 50 % power; (ii) 5 min at 220 °C and 70 % power and (iii–iv) 5 min at 100 °C and 10% power. The resulting colourless solution was diluted to 25 ml with deionized water.

The commercially supplied quality control materials: Rice flour (SRM 1568a, National Institute of Science and Technology, NIST, USA) and Bush Branches and Leaves (GBW 07603, National Research Centre for Certified Reference Materials, NRCRM, China), were digested using the same digestion program as shown above. For this purpose 300–500 mg of the sample was digested in 6 ml HNO_3 and the final digest was diluted to 25 ml with deionized water.

2.3.2. Analytical procedure

For ET-AAS optimization studies, beer samples diluted to 1 + 1 with water and spiked with 50 $\mu g\,l^{-1}$ of As were used. A 10-μl aliquot of this solution and appropriate volumes of modifiers were injected together by means of autosampler on the platform. To achieve a total mass of the following investigated chemical modifiers: (i) 5 μg Pd, 5 μg Ni, 5 μg Pt + 100 μg citric acid; (ii) 10–40 μg Pd; (iii) 20 μg Pd + 10–20 μg Mg; (iv) 20 μg Pd + 1–5 μg Sr and (v) 20 μg Pd + 5–25 μg V, the following injection volumes were taken: (i) 5 μl of 1 $g\,l^{-1}$ Pd or Ni, 5 μl of 1 $g\,l^{-1}$ Pt + 2 μl of 50 $g\,l^{-1}$ citric acid; (ii) 1–4 μl of 10 $g\,l^{-1}$ Pd; (iii) 2 μl of 10 $g\,l^{-1}$ Pd + 1–2 μl of 10 $g\,l^{-1}$ Mg; (iv) 2 μl of 10 $g\,l^{-1}$ Pd + 1–5 μl of 1 $g\,l^{-1}$ Sr and (v) 2 μl of 10 $g\,l^{-1}$ Pd + 1–5 μl of 5 $g\,l^{-1}$ V. The temperature program used throughout this work is presented in Table 1.

Five aqueous standards were used to obtain the calibration curves and two standard additions were also made. The concentrations of solutions used in the calibration ranged from 5 $\mu g\,l^{-1}$ to 100 $\mu g\,l^{-1}$ of As. The calibration curves were linear in the concentration ranges of these standards. The direct calibration and standard addition method were controlled and compared by means of the instrument software. Correlation coefficients found were at least 0.999 for direct calibration and 0.99 for standard additions.

If operating conditions of ICP-*oa*-TOFMS procedure were adjusted according to the manufacturer's recommendations, the sensitivity of 101,000 counts s^{-1} per $\mu g\,l^{-1}$ (mass integrated peak) and resolution of 1400 was reached for ^{139}La. The same parameters for ^{238}U were 121,000 counts s^{-1} per $\mu g\,l^{-1}$ and 1700. Mass calibration was achieved using responses from ^{7}Li, ^{114}In and ^{238}U. Due to very good long-term stability of the instrument and no matrix influence under optimized conditions, no internal standardization was used. Direct aqueous calibration method was used for quantification. Peak area mode and five second data acquisition time and five replicates were used for measurement.

Table 1
Electrothermal program

Step	Temperature (°C)	Time (s)		Gas flow ($l\,min^{-1}$)
		Ramp	Hold	
Injection	20	–	–	–
Drying	75	15	10	3.0
	110	15	10	3.0
	250	20	10	3.0
Pyrolysis	1400	15	15	3.0
	1400[a]	0	1	0.0
Atomization	2600	0	2	0.0
Cleaning	2600	0.5	1	3.0
Cooling	40	25	5	3.0

[a] When cool-down step to 100 °C was applied, a 6 s ramp and 0 s hold times were added before the atomization step.

3. Results and discussion

3.1. Selection of the chemical modifier

3.1.1. Comparison of chemical modifiers for the elimination of phosphate interference

Many chemical modifiers, e.g. Pd, Pt, Ni and its mixtures have been reported to act as efficient thermal stabilizers of phosphorus, thus delaying and depressing the background signal and reducing the spectral interference effect of phosphates on the determination of various metals (Bauslaugh, Radziuk, Saeed, & Thomassen, 1984; Saeed & Thomassen, 1981; Tsalev et al., 1990).

Ni has been widely used as a chemical modifier during the analysis of As in foods (Cervera & Montoro, 1994). However, the necessity to use high amounts of modifier needful during the analysis of biological matrices and drinks (Cervera et al., 1991) will result in shortening the tube life, contamination the cones and windows of the graphite furnace and make the further analysis of nickel difficult. These problems are not observed with Pd modifier. Nevertheless, according to Welz, Schlemmer, and Mudakavi (1988), the influence of phosphate in the form of $CaHPO_4$, attributed to non-spectral effects, on As determination is troublesome even in the presence of Pd modifier. For this purpose the use of Rh will be more useful (Ni, Rao, & Li, 1996).

The effect of different modifiers: Pd (nitrate), Ni (nitrate) and Pt (hexachloroplatinic(IV) acid) + citric acid on the minimization of phosphate interference at arsenic determination was studied in the range of 1–5 μg of P, covering the

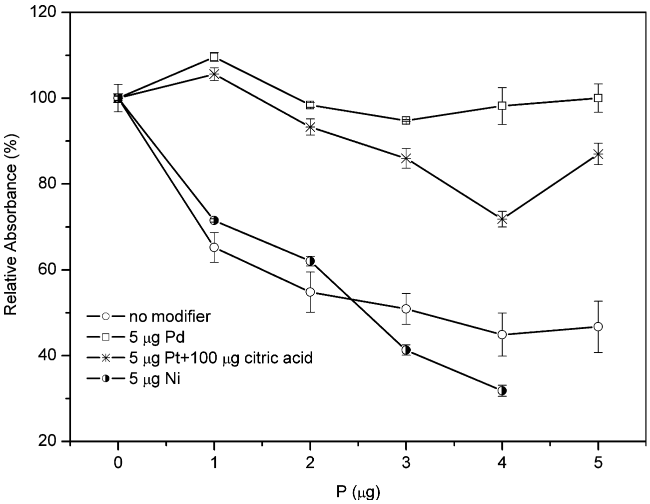

Fig. 1. Influence of P amount on the relative absorbance signal of As in the absence and presence of selected modifiers. The relative absorbance is defined as: Relative absorbance = integrated absorbance of 50 μg l^{-1} As in presence of P within the investigated range/integrated absorbance of 50 μg l^{-1} As. Bars indicate the range for each determination ($n = 3$).

amounts of P corresponding to the injection of 10 μl of non-diluted beer into the cuvette (Alcázar, Pablos, Martín, & González, 2002), using 5 μg of modifiers. Citric acid in the amount of 100 μg was used to remove chlorides in Pt compound and to increase the reduction conditions in the atomizer as well. With the addition of citric acid the chloride will be replaced by citrate and HCl which has a large dissociation energy and is stable in the high temperature environment, will be liberated (Ni et al., 1996). As shown in Fig. 1, of all tested modifiers Pd was found to be the most efficient in the elimination of phosphate interference. 5 μg of phosphorus in the form of ammonium phosphate can be tolerated without changes of sensitivity in presence of 5 μg of Pd.

3.1.2. Optimization of the amount of chemical modifiers and pyrolysis vs atomization curves

The influence of Pd concentration within the range of 5–40 μg onto background and specific absorbance value was studied. The use of Pd modifier in the amount lower than 10 μg for analysis of beer samples has resulted in overcorrection, thus 20 μg of Pd had to be applied for achieving the maximum background reduction and maximum absorbance. Further the mixtures of Pd with Sr or Mg and V were tested with the aim to increase the pyrolysis temperature and to decrease the background value. The concentration of Sr has varied in the range of 1–5 μg, 2 μg being considered as optimum since higher quantity did not produce additional delays of the atomization profiles but has increased background signals. The optimal amount of Mg and V was studied in the range of 10–20 μg and 5–25 μg, respectively. Mg (10 μg) was selected since the higher amount produced an increase of the background absorbance. No significant changes in the background or atomization signal were observed for V in the investigated range so 5 μg was selected.

The effect of pyrolysis and atomization temperature on specific and background absorption signal in the presence of all chemical modifiers studied is shown in Fig. 2. It can be seen that using Pd as the chemical modifier, the optimum ashing and atomization temperatures correspond to 1500 °C and 2600 °C, respectively, and the addition of further component did not have any influence on increasing of the pyrolysis temperature and sensitivity or reduction of background absorbance. A typical background absorbance of real samples in presence of Pd modifier was 0.15 and can be easily compensated using deuterium corrector. Therefore, Pd was finally adopted for the determination of As in beer.

3.2. Evaluation of matrix effects and study of introduction of a cooling-down step

As the sensitivity of As determination in the presence of matrix was significantly decreased when compared with results obtained for aqueous medium and the addition of further modifier did not have any influence, the introduction of a cooling-down step prior to the atomization of the analyte was studied. The insertion of a cooling step was earlier successfully applied to increase the sensitivity of some metals analysis in different matrix (Hinds, Katyal, & Jackson, 1988; Lynch & Littlejohn, 1990) and overcome interferences (Moreira, Curtius, & de Campos, 1995). Until now, to the best of our knowledge, this approach was not reported for As determination.

For this purpose, optimization of graphite furnace temperature program by the introduction of a cooling step was performed using Pd modifier. Insertion of a cooling-down step to 100 °C was chosen as the most adequate temperature resulted in the maximum increase of peak height by about 40% (Fig. 3). It may be supposed that this effect is due to a change in the response of the power supply controller that applies to the cuvette a different power from 100 and 2500 °C than between 1500 and 2500 °C. For a longitudinally heated graphite tube this results in a faster or slower heating rate, respectively. As a consequence, with using a cool-down step, also the atomization rate will be faster, resulting in an increased peak-height.

To check possible interferences of the whole matrix in the presence of Pd modifier, the slopes of the analytical curves found with matrix-free aqueous standards (direct aqueous calibration) and with that of standard addition were determined for both peak height and peak area measurements and for the program with a cool-down step (Table 2). Standard additions were applied to four beer samples (B1–B4). In addition, the values obtained for two samples and original program are shown. The pyrolysis and atomization temperatures used were 1400 and 2600 °C. The slope values are listed for direct calibration and slope differences are shown for the standard additions. It can be estimated from the data in Table 2 that, using a program with cool-down step, the deviations of slopes caused by the matrix effects are not significantly different for both peak height and peak area measurements. Not even differences of slopes of the calibration curves and standard additions graphs are significantly different (<15%), thus a direct aqueous calibration can be used for As measurement.

3.3. Analytical characteristics

Limits of detection (LOD) and limits of quantification (LOQ) based on repeated analysis of a sample with low As concentration were calculated as $3S_{\text{blk}}/m$ and/or $10S_{\text{blk}}/m$, where S_{blk} is the standard deviation of 10 blank measurements and m is the slope of the calibration graph. Characteristic masses were calculated from the slopes of the standard additions technique using the equation $m_0 = (0.0044 \times V)/m$, where V is the injection volume (10 μl) and m is the standard additions slope. LOD, LOQ and m_0 values calculated for conditions both with and without cool-down step are summarized in Table 2. Taking into account the sample dilution during the preparation step, LOD and LOQ values obtained for As in the original beer sample will be two times higher than those shown in Table 2. As the data demonstrate, when the cool-down step is employed, the peak height measurements result in higher analytical sensitivity (lower characteristic mass) and higher detection power (lower limit of detection).

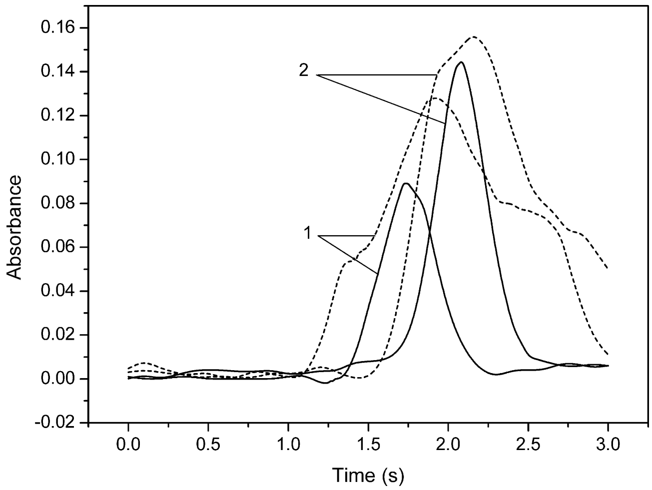

Fig. 3. Time-resolved traces for atomization of As from beer sample without (1) and with (2) 100 °C cool-down step.

The precision of the method was examined by five replicate measurements of 10 μg l^{-1} of As in beer. The relative standard deviation found out was 3.0%.

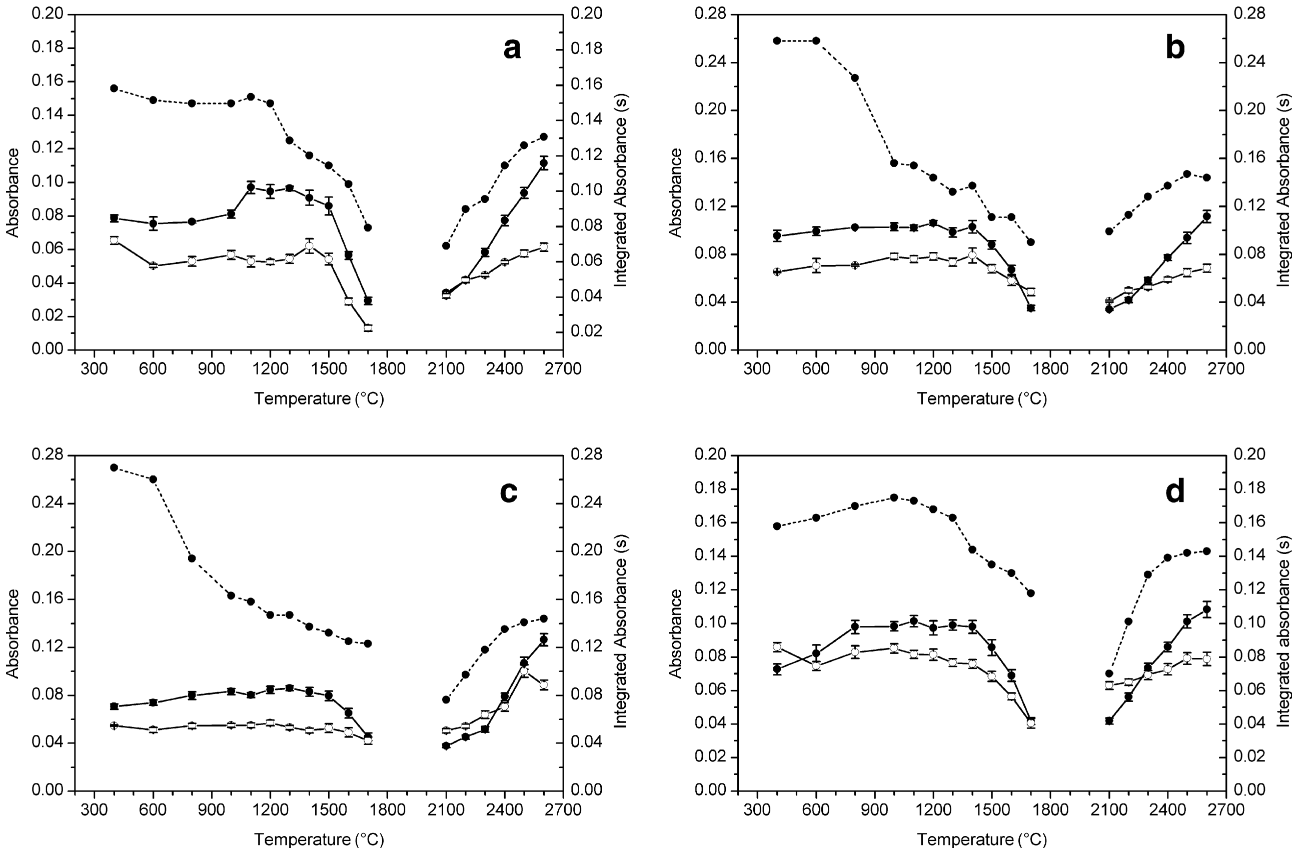

Fig. 2. Effect of pyrolysis and atomization temperature on As (solid lines) and background (dotted lines) absorption signals in beer in the presence of (a) 20 μg Pd; (b) 20 μg Pd + 10 μg Mg; (c) 20 μg Pd + 2 μg Sr and (d) 20 μg Pd + 5 μg V based on measurement of peak-area (○) and peak-height (●) absorbance. Bars indicate the range for each determination ($n = 3$).

Table 2
Comparison of analytical characteristics for the original program and the program with a cool-down step

	Measurement mode	Slope (1/μg l^{-1})	Differences (%)				m_0[c] (pg)	LOD (μg l^{-1})	LOQ (μg l^{-1})
		Aqueous	B1[a]	B2	B3	B4			
Conventional program	Peak height	0.00195	−35.6	−25.0	[b]	[b]	33 ± 4	1.6	5.2
	Peak area	0.00137	−8.9	−6.5	[b]	[b]	35 ± 1	2.2	7.4
Program with cool-down step	Peak height	0.00235	13.4	11.7	3.2	−2.1	18 ± 1	1.3	4.2
	Peak area	0.00130	8.2	6.9	6.8	4.6	32 ± 1	2.3	7.7

[a] B1, B2, B3, B4, beer samples.

[b] Not determined.

[c] Mean ± SD for results of independent measurements of two (conventional conditions) and/or four samples (program with cool-down step).

Typical number of firings was 500–550. After that, under the conditions described, only a small amount of carbon residues was observed on the platform. The presence of nitric acid in palladium modifier (10%) was found to be useful for elimination of carbon residues produced during the analysis, probably owing to support of ashing of the organic matrix.

3.4. Method validation and sample analysis

Because no reference sample of beer for the purpose of inorganic analysis exists, the adopted methodology, using Pd as chemical modifier and cool-down step, was validated by the analysis of six beer samples and comparing the results with those obtained using ICP-*oa*-TOFMS. Because the concentration of As in beer samples was below the LOQ for ET-AAS method, the samples both for ET-AAS and ICP-MS measurements were spiked with 30 μg l^{-1} of As. In all cases the calibration using aqueous standards was used. The results obtained using peak height measurements are shown in Table 3. For elucidation of any differences between the two methods, paired *t*-test was applied. The results were found to be the same ($p = 0.165$) at the significance level of 0.05.

The method was applied to the determination of low As concentration in certified GBW and NIST standards as well. The results found (mean of triplicate determinations ± SD) were 1.2 ± 0.1 μg g^{-1} and 0.31 ± 0.01 μg g^{-1} for GBW 07603 and NIST 1568a, respectively, and were in a good agreement with certified values (1.25 ± 0.10 μg g^{-1} and 0.29 ± 0.03 μg g^{-1} for GBW 07603 and NIST 1568a, respectively). The accurate result of low As concentrations determination in certified GBW and NIST standards confirms the reliability of the proposed method and demonstrates its applicability also for determination of As in vegetable and food samples.

Table 3
Determination of As in beer: comparison of methods

Sample	Concentration[a] (μg l^{-1})	
	ICP-*oa*-TOFMS	D_2-ET-AAS
1	34.4 ± 2.1	34.6 ± 1.7
2	37.6 ± 3.7	34.0 ± 0.4
3	34.6 ± 2.3	32.6 ± 1.6
4	39.2 ± 2.6	37.8 ± 0.5
5	30.2 ± 1.5	30.0 ± 1.1
6	35.5 ± 4.0	36.2 ± 0.9

[a] Each value is the mean ± SD ($n = 3$).

4. Conclusions

We can conclude from the presented results that the direct determination of As in beer using Pd as chemical modifier under optimized operating conditions, can be performed by ET-AAS even with instrumentation equipped with deuterium lamp background correction. The introduction of a cool-down step is recommended as it results in a significant increase of sensitivity by about 40% using peak-height measurement. As the effect of matrix was insignificant under the conditions described, direct aqueous calibration method could be used for a quantification of As in beer samples. Proposed simple method, in which the sample preparation consists in degassing and a simple dilution with water only, can be thus successfully applied for a rapid screening of As in beer for accurate determinations of As concentrations above 8.4 μg l^{-1}.

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