Talanta 84 (2011) 887–894

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Use of ion–molecule reactions and methanol addition to improve arsenic determination in high chlorine food samples by DRC-ICP-MS

Wei Guo[a,b,*], Shenghong Hu[a], Xiaofang Li[b], Jian Zhao[b], Shesheng Jin[b], Wenjuan Liu[b], Hongfei Zhang[a]

[a] Key Laboratory of Biogeology and Environmental Geology of Ministry of Education, Faculty of Earth Sciences, China University of Geosciences, Wuhan 430074, PR China
[b] Circulation Industry Promotion Center of the Ministry of Commerce, Beijing 100747, PR China

ARTICLE INFO

Article history:
Received 4 December 2010
Received in revised form 11 February 2011
Accepted 16 February 2011
Available online 23 February 2011

Keywords:
Ion–molecule reactions
Methanol addition
Arsenic
High chlorine food samples
DRC-ICP-MS

ABSTRACT

Direct determination of trace arsenic in high chlorine food samples by ICP-MS is complicated by the presence of $ArCl^+$ interferences, and the high first ionization energy of As (9.81 eV) also results in low analytical sensitivity in ICP-MS. In this work, two strategies based on ion–molecule reactions were successfully used to eliminate ArCl spectral interference in a dynamic reaction cell (DRC). The interference ion ($^{40}Ar^{35}Cl^+$) was directly removed by the reaction with methane gas, and the background signal was reduced by up to 100-fold at m/z 75. Alternatively, by using molecule oxygen as the reaction gas, $^{75}As^+$ was effectively converted to $^{75}As^{16}O^+$ that could be detected at m/z 91 where the background is low. The poor signal intensity of As or AsO was improved 3–4 times by addition of 4% methanol in the analyzed solutions. The limit of quantitation (LOQ) for ^{75}As (CH_4-DRC method) and $^{75}As^{16}O$ (O_2-DRC method) was 0.8 and 0.3 ng g^{-1} and the analytical results of seaweed and yellow croaker standard reference materials were in good agreement with the certified values. As the routine arsenic monitoring method in our laboratory, it was applied to the accuracy determination of 119 high chlorine food samples from eight different markets of Beijing.

1. Introduction

Arsenic (As) is one of the most frequently monitored toxic elements in food. The toxicity varies among chemical forms and human exposure to inorganic arsenic increases the risk of skin, bladder and kidney cancer [1]. The World Health Organization (WHO) has established a toxicological reference value of 0.015 mg kg^{-1} body weight per week for human intake of inorganic arsenic [2]. According to Chinese government recommended allowance, the total arsenic in some foods (i.e. salted duck egg and fermented bean curd) must be $\leq$0.5 mg kg^{-1} [3,4]. However, the difficulties on determining trace As in these food samples have been encountered by general food testing laboratories at present.

A variety of analytical methods, such as atomic absorption spectrometry (AAS) [5–8], atomic fluorescence spectrometry (AFS) [9,10], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [11–14] and inductively coupled plasma mass spectrometry (ICP-MS) [15–21], have been employed for the determination of trace As in food samples. Compared to AAS, AFS or ICP-AES, ICP-MS has emerged as a useful technique for trace As determination of food samples owing to excellent detection limit and multi-element capability with a large dynamic range over eight orders of magnitude. Unfortunately, there are still specific analytical difficulties from the interference of polyatomic ions originating from matrix elements and plasma gas in ICP-MS determination. Although arsenic is not subject to interference from isotopes of other elements, it is a problematical element when the presence of high chlorine matrix food samples for two reasons. Firstly, it is mono-isotopic at m/z 75, leaving no second-choice isotope, and at this mass there is a significant interference ($^{40}Ar^{35}Cl^+$) from matrix element and plasma gas; secondly, the high first ionization energy of As (9.81 eV) also results in relatively poor sensitivity in ICP-MS detection.

Attempting to eliminate or reduce the impact of the ArCl interference, a range of methods have been, and continue to be employed: sector field ICP-MS [22,23], hydride generation techniques [24], membrane desolvation sample introduction techniques [25], electrothermal vaporization [26], mathematical corrections [27] and addition of organic compounds or molecular gas to modify the argon plasma [28,29]. Using high-resolution sector field ICP-MS is one possible method for eliminating the interference because this technique offers the possibility to operate at more steps of resolution (a resolution of $M/\Delta M = 8000$ is required for arsenic determination), but causes a lower signal sensitivity

---

[*] Corresponding author at: Key Laboratory of Biogeology and Environmental Geology of Ministry of Education, Faculty of Earth Sciences, China University of Geosciences, No. 388 Lumo Road, Wuhan, Hubei 430074, PR China. Tel.: +86 010 5222 7517; fax: +86 010 5222 7523.
E-mail address: guowei012345@163.com (W. Guo).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.02.026

due to the increase of resolution (the sensitivity at $M/\Delta M = 7800$ yields an intensity of only 0.5–2% compared with $M/\Delta M = 300$) [23]. The hydride generation technique has been routinely coupled for the determination of As, because spectral interferences are minimized and detection limits are improved by this approach [24]. However, the generation of AsH_3 is normally carried out in the presence of a high concentration of HCl, which may interfere with the determination of As by ICP-MS because of the formation of $ArCl^+$ [29]. Membrane desolvation sample introduction techniques could reduce ArCl interference by minimizing the transportation of chloride to the plasma. Coedo et al. [25] have employed a desolvating microconcentric nebulizer (D-MCN) to improve the determination of As in steels. The isobaric interference of $^{40}Ar^{35}Cl^+$ due to the presence of Cl from the hydrochloric acid was minimized and the background signal intensity of 5% (v/v) HCl reduced from 82,300 cps to 380 cps [25]. The above-mentioned technologies successfully removed the interfering chlorine before introduction into the plasma, however, they are requiring additional expensive equipments. Electrothermal vaporization is another possibility [26], but the complexity of the procedure may prevent this method from being widely used. Some other methods, such as mathematical corrections [27] and addition of organic compounds [28] or molecular gas [29] to modify the argon plasma have been reported, but only with limited success especially when chlorine is present at high concentrations [30].

A potentially better approach based on the ion–molecule reactions in a dynamic reaction cell (DRC) technique has proved to be effective for the alleviation of the ArCl interference [31–34]. This technology may be considered as an interesting alternative to chemical separation or high-mass resolution instrumentation, because it offers different possibilities for the determination of elements in different matrices [35–37], by the use of ion molecule reactions with various reaction gases under the optimized instrumental parameters.

In this work, a valid method based on ion–molecule reactions to improve trace As determination in high chlorine food samples by ICP-MS was studied. Our work has centered on the elimination of the ArCl interference using two different reaction gas CH_4 and O_2 in the DRC, and the improvement of arsenic poor sensitivity by addition of methanol modifier. The optimization of this technique, and its analytical performances, as well as its application to the trace As determination in 119 high chlorine food samples for the market monitoring are presented in this work.

2. Material and methods

2.1. Instruments and apparatus

A PerkinElmer SCIEX ELAN DRC-e (dynamic reaction cell) ICP-MS instrument was used in this work and it was described in detail elsewhere [38,39]. ICP and DRC conditions were selected that maximized the ion signals of the elements studied while reducing the background to a minimum. The operating parameters of the DRC-ICP-MS used for this work are summarized in Table 1. The DRC gas O_2 and CH_4 was purchased from Praxair (China) Investment Co., Ltd. (99.999% purity). A CEM MARS X-press (CEM, Matthews, NC, USA) microwave apparatus equipped with Teflon vessels was used to digest the samples.

Table 1
Instrument operating parameters.

ICP-MS instrument	Perkin–Elmer Sciex Elan DRC-e
RF power (W)	1300
Plasma gas flow ($L\,min^{-1}$)	16
Auxiliary gas flow ($L\,min^{-1}$)	1.0
Nebulizer gas flow ($L\,min^{-1}$)	0.80 for $^{75}As^+$; 0.84 for $^{75}As^{16}O^+$
CH_4 reaction gas flow ($mL\,min^{-1}$)	0.30
O_2 reaction gas flow ($mL\,min^{-1}$)	0.50
Rejection parameter, q	0.50 for $^{75}As^+$; 0.40 for $^{75}As^{16}O^+$
Rejection parameter, a	0.017 for $^{35}Cl^+$; 0 for other ions
Axial field potential (AFP) (V)	200
Autolens	On
Dwell time (ms)	50
Sweeps	20
Readings	1
Replicate	3
Monitored ions	$^{75}As^+$, $^{75}As^{16}O^+$, $^{35}Cl^+$, and $^{103}Rh^+$

2.2. Reagents and materials

High purity water (18.2 $M\Omega\,cm^{-1}$) was used for the preparation of all blank, standards and sample solutions was obtained from a Millipore water purification system (Millipore, France). The single element stock solutions (As, Zr, Cl and Rh) were purchased from the National Center for Analysis and Testing of Steel Materials, China. Nitric acid (65–70%, w/w, 99.9999%), hydrogen peroxide (35%, w/w), hydrofluoric acid (99.99%), hydrochloric acid (99.9999%) and methanol (Semiconductor grade, 99.9%) were purchased from Alfa Aesar (Tianjing) Ltd. The standard reference materials of GBW08573 (Yellow croaker) and GBW08517 (Seaweed) were purchased from National Research Center for Certified Reference Materials (China).

2.3. Sample preparation

Approximately 250 mg of the homogenized sample was weighed into the Teflon vessel, then 3.0 ml of HNO_3 and 2.5 ml of H_2O_2 and 0.5 ml of HF were added and the vessel was sealed. A microwave digestion procedure was applied as following: the temperature was ramped to 120 °C within 10 min at 800 W power, holding for 5 min, and then ramped to 160 °C within 10 min at 800 W power, holding for 10 min, finally ramped to 200 °C within 10 min at 1600 W power, holding for 20 min. After cooling, 2.0 mL methanol and 0.5 mL of 1 $mg\,L^{-1}$ Rh internal standard solution were added, and the final analytical solution was diluted to 50 ml with high purity water. With each digestion run, two samples were randomly chosen for quality control measurements. One sample was digested in duplicate to check for reproducibility of the digestion and analysis.

3. Results and discussion

3.1. Interference of $^{40}Ar^{35}Cl^+$ on $^{75}As^+$

It is well known that accurate determination of trace arsenic in the presence of high Cl is difficult due to the significant $^{40}Ar^{35}Cl^+$ interference on the only used isotope ^{75}As in ICP-MS analysis. In our experiments, this spectral interference was evaluated under the conventional standard mode ICP-MS, the mass spectral scan (72–77, m/z) for 1% (v/v) HNO_3 blank, 0.1% (v/v) HCl matrix, 1.0% (v/v) HCl matrix and 1.0 $ng\,mL^{-1}$ As were monitored in Fig. 1. The signal intensity of m/z 75 was 1010 cps for 1.0 $ng\,mL^{-1}$ As. However, the signal contribution from 0.1% (v/v) HCl and 1.0% (v/v) HCl was high at 1806 cps (equal to 1.8 $ng\,mL^{-1}$ As) and 10,044 cps (equal to 9.9 $ng\,mL^{-1}$ As), respectively. Therefore, the ArCl interference, especially for high chlorine matrix foods, such as salted egg, soy fermented bean curd and cooked meat products, could result in significant positive bias for trace As determination, and it should be eliminated or reduced for the accurate analysis.

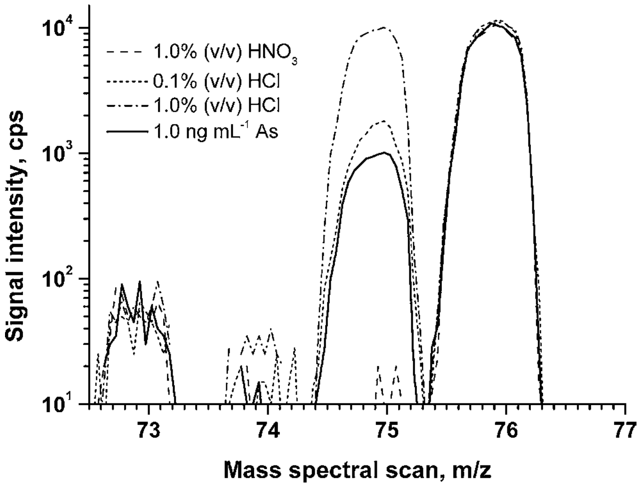

Fig. 1. Mass spectral scan for 1% (v/v) HNO_3 blank, 1 ng mL^{-1} As, 0.1% (v/v) HCl matrix and 1.0% (v/v) HCl matrix under the standard mode ICP-MS operating conditions. The scanning mass were m/z = 72–77.

3.2. Reduction of $^{40}Ar^{35}Cl^+$ interference by CH_4 charge transfer reaction

In order to eliminate the $^{40}Ar^{35}Cl^+$ interference for As determination, a strategy based on ion–molecule reaction with molecule methane to reduce the interference in a DRC was used, in combination with the appropriate DRC rejection parameter q (Rpq). The background equivalent concentration (BEC) value was used as a criterion for ^{75}As monitoring. The flow rate of the reaction gas could be the crucial operating parameter for the DRC system. Fig. 2a shows the effects of CH_4 flow rate on the signals of 1.0 ng mL^{-1} As + matrix and matrix blank at m/z 75. A solution of 0.1% (v/v) HCl was treated as the matrix blank in this experiment to simulate the interfering elements on As determination in the high chlorine food samples. At low CH_4 flow rate there was a significant decrease of the signals of interfering species at m/z 75. The optimized CH_4 flow rate was selected at 0.30 mL min^{-1} and the interference signal intensity was reduced by up to 100-fold. This may be explained by the charge transfer reactions between interfering ion $^{40}Ar^{35}Cl^+$ and molecule methane in the DRC. The Rpq values are important to filter out unwanted precursors of interfering species from the ion beam to eliminate interferences created in the cell by reaction gas. As shown in Fig. 2b, the optimized Rpq value was 0.50 for ^{75}As and the BEC of ^{75}As was 0.10 ng mL^{-1}.

3.3. Oxidation of $^{75}As^+$ to $^{75}As^{16}O^+$ by O_2 oxygenation reactions

Another alternative is to find that use of the MO^+ products of oxidation of M^+ with O_2 in the DRC as analyte ion reduced the effect of isobaric interferences [36]. Fig. 3a shows the effect of O_2 cell gas flow rate on the $^{75}As^{16}O$ signal (1 ng mL^{-1} As), 0.2 ng ml^{-1} Zr + 0.1% (v/v) HCl was treated as the matrix blank, and the Rpq fixed at the optimized value of 0.40 (Fig. 3b). The profile (Fig. 3a) indicates that at low O_2 flow rate there was a significant increase signal at m/z 91, which was mainly from $^{75}As^{16}O^+$ (Fig. 4a). Meanwhile the signal of matrix blank decreased rapidly at m/z = 91 (Fig. 3a). The AsO:As intensity ratio is higher than 10 and shows a flat roof as the O_2 flow rate exceed 0.5 mL min^{-1}, indicating the chemical yield of AsO is high and stable (Fig. 4a). Based on the results, the 0.5 mL min^{-1} O_2 flow rate was chosen for the following experiments. For the arsenic oxide at the m/z of 91, the other interference originating from ^{91}Zr should also be considered. Fig. 4b shows the effect of the O_2 cell gas flow rate on the signals of 1 ng mL^{-1} Zr at m/z 91 and 107. As shown in Fig. 4b, with increasing O_2 flow rates, the $^{91}Zr^+$ signal intensity decreased, while the signal intensity at m/z = 107 increased and then decreased in the same trend with signal at m/z = 91. This indicates the reduction of the interfering $^{91}Zr^+$ is based upon the generation of $^{91}Zr^{16}O^+$, and the Zr concentration of 1 ng mL^{-1} has low interference on AsO in ICP-MS determination. Under the optimized DRC conditions (O_2 flow rate = 0.5 mL min^{-1} and Rpq = 0.4, as shown in Fig. 3), the ratio of Zr:ZrO was less than 0.04 (Fig. 4b). The presence of the Zr is the only spectral interference for AsO at m/z 91, while As at m/z 75 suffered from $ArCl^+$, Nd^{2+}, Eu^{2+} and Sm^{2+} interferences. Because of the concentration of Zr in the analyzed solutions of the interest foods range from 0.01 to 0.2 ng mL^{-1} (dilution factor 200), at these concentration levels, the interference of $^{91}Zr^+$ can be easily eliminated by the reaction with molecule oxygen.

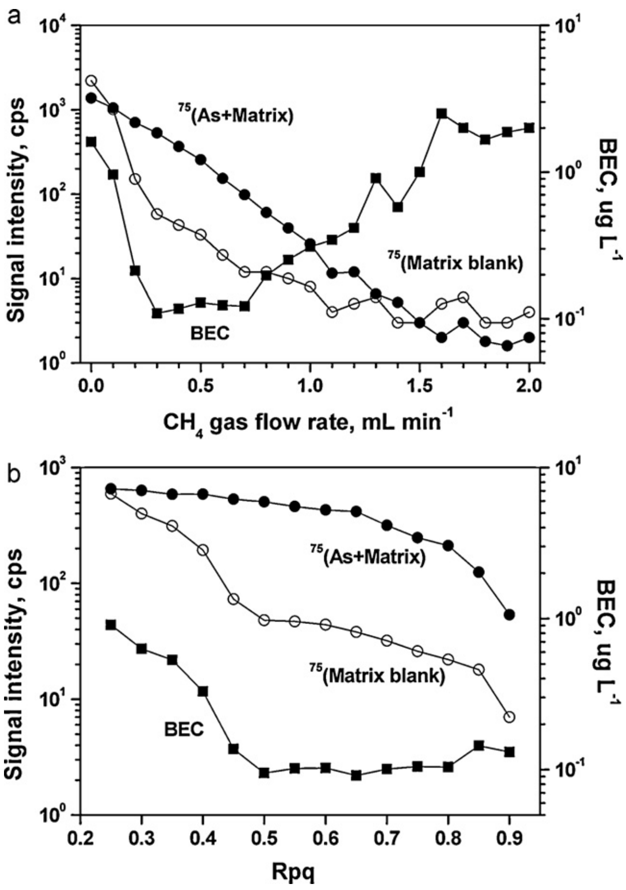

Fig. 2. Effects of CH_4 gas flow rate (a) and Rpq value (b) on the signal intensity of ^{75}As + matrix, matrix blank and background equivalent concentration (BEC). The concentration of As was 1 ng mL^{-1}. A solution of 0.1% (v/v) HCl was treated as the matrix blank.

3.4. Signal improvement with methanol addition

The first ionization energy of arsenic is high (9.81 eV) resulting in low ionization efficiency in the plasma and consequently, low signal intensities. Fortunately, some researchers have reported that addition of organic compounds to the analytical solution could increase signal intensity of the high ionization energy elements by ICP-MS detection [40–42]. In order to improve the poor signal intensity of $^{75}As^+$ or $^{75}As^{16}O^+$, the addition of a certain amount of methanol to the analytical solution was investigated. Because the plasma temperature can be affected by the introduction of organic matrix, the nebulizer flow rate and the methanol concentration should be considered in our experiments. Fig. 5a shows signal intensities as a function of nebulizer gas flow rate in 4% (v/v) methanol and 1% (v/v) HNO_3 solutions for $^{75}As^+$ and $^{75}As^{16}O^+$ at

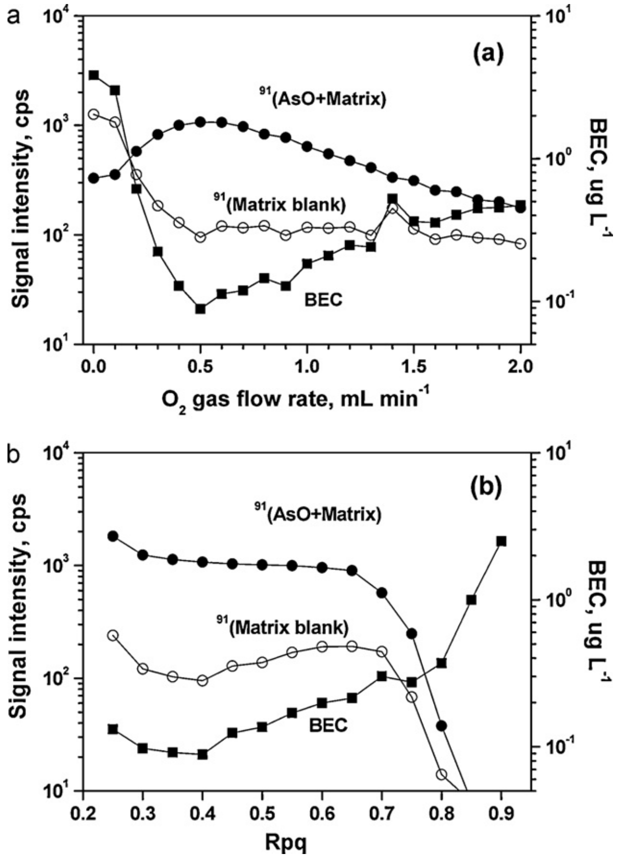

Fig. 3. Effects of O_2 gas flow rate (a) and Rpq value (b) on the signal intensity of $^{75}As^{16}O$ + matrix, matrix blank and background equivalent concentration (BEC). The concentration of As was 1 ng mL^{-1}. A solution of 0.2 ng ml^{-1} Zr + 0.1% (v/v) HCl was treated as the matrix blank.

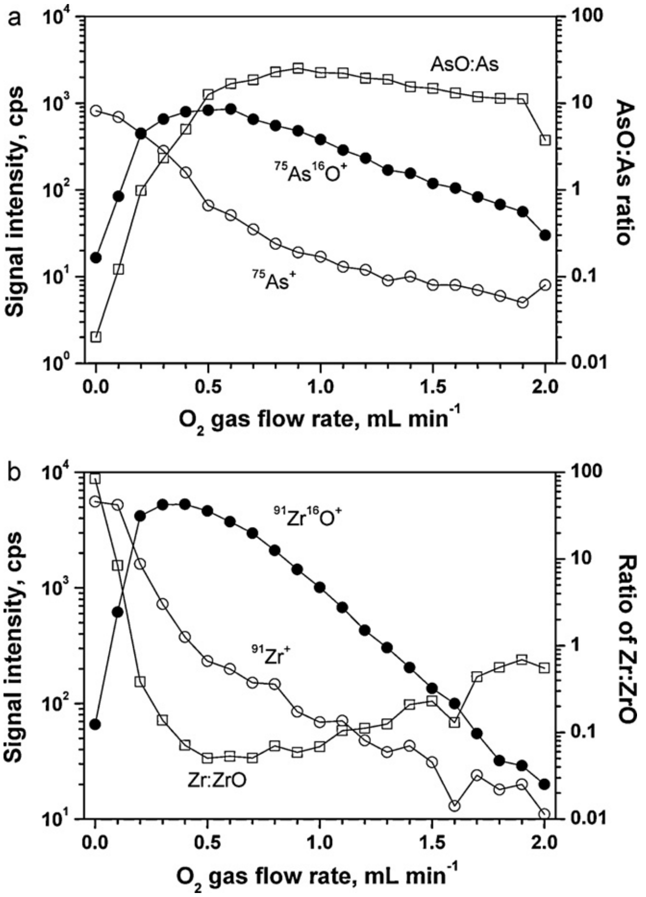

Fig. 4. Effects of O_2 gas flow rate on ion signal intensities of $^{75}As^+$ and $^{75}As^{16}O^+$ (a) and $^{91}Zr^+$, $^{91}Zr^{16}O^+$ (b). The concentration of As and Zr was 1 ng mL^{-1} and 0.2 ng mL^{-1}, respectively. The Rpq value is 0.40.

a fixed power of 1300 W. The optimized nebulizer gas flow rate for $^{75}As^+$ and $^{75}As^{16}O^+$ in 4% (v/v) methanol solution is 0.80 and 0.84 L min^{-1}, which lower by about 0.12 and 0.06 L min^{-1} than 1% (v/v) HNO_3, respectively. Lower rate of the nebulizer flow gas in 4% (v/v) methanol solution is due to the compensation of the plasma cooling effects [41]. After blank corrections, the signal intensities were normalized to values obtained with 1% (v/v) HNO_3 solution. The normalized signal intensities of $^{75}As^+$ and $^{75}As^{16}O^+$ as a function of methanol concentrations are illustrated in Fig. 5b. The results show that maximum sensitivities for $^{75}As^+$ and $^{75}As^{16}O^+$ in 4% (v/v) methanol are higher than those in 1% (v/v) HNO_3 solution by a factor of 2.9 and 3.8. Under the respective optimized conditions, the mass spectral scans (m/z = 73–77, 88–93) for 4% (v/v) methanol + 1% (v/v) HNO_3, 10 ng mL^{-1} As + 1% (v/v) HNO_3 and 10 ng mL^{-1} As solution + 4% (v/v) methanol + 1% (v/v) HNO_3 matrix using CH_4 DRC-ICP-MS method and O_2 DRC-ICP-MS method were shown in Fig. 6. The signal intensity of $^{75}As^+$ and $^{75}As^{16}O^+$ improved by a factor of 3 (from an initial 3560 to 10,700 cps) and 4 (from an initial 5080 to 20,500 cps) with addition of 4% (v/v) methanol, respectively. At the same time, the background signals for m/z 75 and 91 were nearly no variation in this experiment. A similar increase (3.6-fold) was also observed for $^{75}As^+$, which was as expected, since the enhancement of the arsenic signal intensity with the presence of organic solvent is well documented [41]. This phenomenon of signal enhancement is explained by a charge transfer reaction occuring between positively charged carbon species and the high ionization energy arsenic (9.81 eV) in the central channel of the plasma [42].

3.5. Analytical performance

The limit of quantitation (LOQ, ten times to the standard deviation of procedure blank) was 0.8 ng g^{-1} (CH_4-DRC method) and 0.3 ng g^{-1} (O_2-DRC method) for As, respectively. The LOQ is expressed as the concentration in the samples, thereby taking into account the dilution factor (200). This sensitivity is sufficient for the trace As monitoring in food samples where they are often found at 0.001–0.40 μg g^{-1}. Reproducibility (RSD) was calculated based on triplicate sample digestions and analyses, and was generally less than 10%. The accuracy of the two methods was assessed using two high chlorine food standard reference materials (GBW08573 yellow croaker and GBW08517 seaweed). The results of these SRMs were listed in Table 2. The reported value of As for GBW08573 was 5.10 ± 0.20 (CH_4-DRC method) and 5.08 ± 0.16 (O_2-DRC method), and 14.0 ± 0.13 (CH_4-DRC method) and 13.9 ± 0.12 (O_2-DRC method) for GBW08517, which was in good agreement with the certified value of 5.08 ± 0.39 and 13.9 ± 0.24, respectively.

3.6. Application to high chlorine food samples

For the market monitoring of toxic arsenic in food samples, a total of 119 food samples (salted duck egg, fermented bean curd and cooked meat products) were collected from eight markets of Beijing at October 2010. They were analyzed by the proposed methods at the Laboratory of Circulation Industry Promotion Center of the Ministry of Commerce of China. Table 2 summarizes

Table 2
Recovery values of arsenic in standard reference materials by DRC-ICP-MS.

SRM	Name	Recovery values ($\mu g\,g^{-1}$) (mean ± SD)		Certified values ($\mu g\,g^{-1}$)
		CH_4-DRC[a]	O_2-DRC[b]	
GBW08573	Yellow croaker	5.10 ± 0.20	5.08 ± 0.16	5.08 ± 0.39
GBW08571	Seaweed	14.0 ± 0.13	13.9 ± 0.12	13.9 ± 0.24

[a] Results using CH_4 as reaction gas in DRC-ICP-MS.
[b] Results using O_2 as reaction gas in DRC-ICP-MS.

the results for 119 high chlorine food samples, the As concentration ranges between 0.028 and 0.335 mg kg^{-1} with the proposed method (CH_4 DRC-ICP-MS or O_2 DRC-ICP-MS), however, the results of As concentration with standard mode ICP-MS (Non DRC) ranges between 0.096 and 1.672 mg kg^{-1} (31% of the values exceed the maximum residue level, 0.5 mg kg^{-1}). Although the value of Cl/As for FBC-17 was high at 2.97×10^6, our reported value of As was 0.044 ± 0.002 mg kg^{-1} by CH_4 DRC-ICP-MS, which agreed with the value of 0.042 ± 0.003 mg kg^{-1} by O_2 DRC-ICP-MS method. However, the value of the standard Mode ICP-MS determination was over estimation with 0.908 ± 0.045 mg kg^{-1}, which was 22 times higher than that of the DRC method. Fig. 7 shows the differences of As concentration for 119 food samples in our laboratory using standard mode ICP-MS and CH_4 DRC-ICP-MS plotted as a function of the food chlorine concentration. The linear relativity ($R = 0.962$) between the differences of As values obtained by two methods and the chlorine concentrations showed that the Cl based interference may cause a severe positive bias on trace As results. However, the polyatomic interference can be successfully improved using the proposed methods (Table 3).

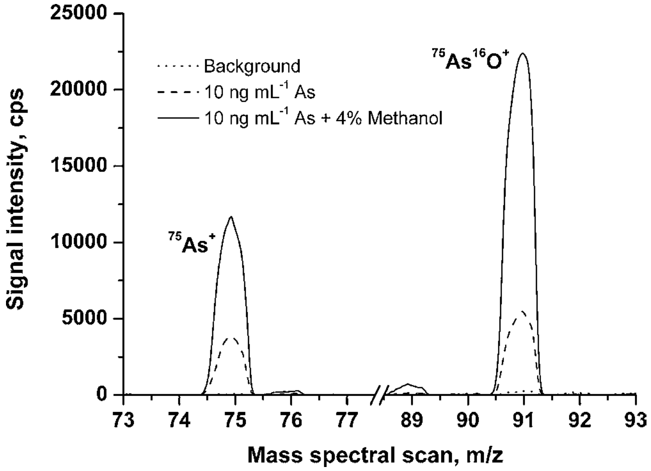

Fig. 6. Mass spectral scans (m/z = 73–77, 88–93) for background (4% (v/v) methanol + 1% (v/v) HNO_3), analyte (10 ng mL^{-1} As + 1% (v/v) HNO_3) with and without 4% (v/v) methanol addition for CH_4 DRC-ICP-MS method and O_2 DRC-ICP-MS method. The nebulizer gas flow rate was set at the respective optimized values.

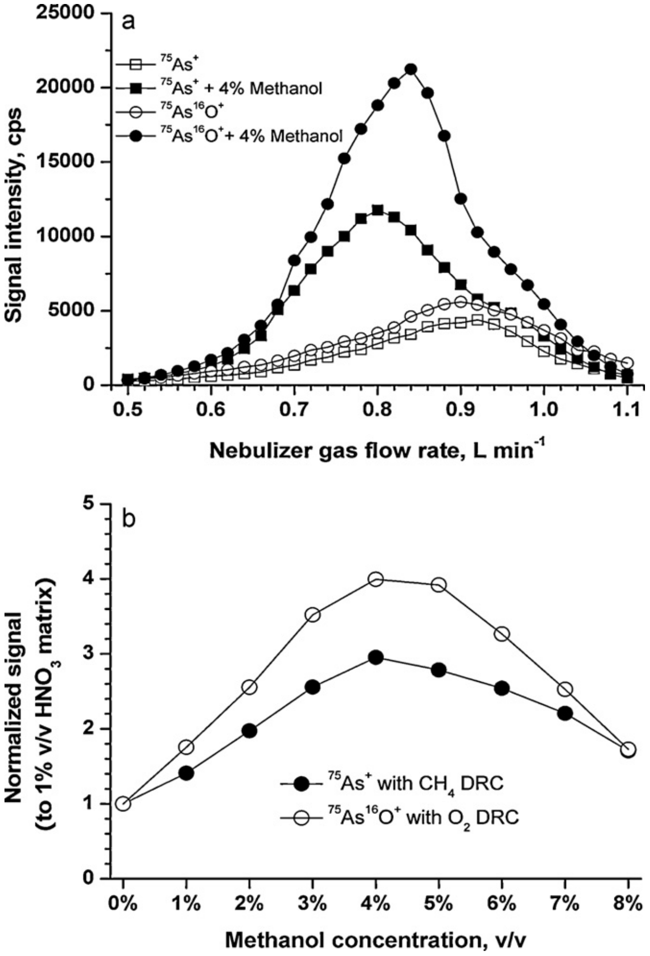

Fig. 5. (a) Signal intensities of $^{75}As^+$ and $^{75}As^{16}O^+$ as a function of nebulizer gas flow rate in 4% (v/v) methanol and 1% (v/v) HNO_3 solutions. (b) $^{75}As^+$ and $^{75}As^{16}O^+$ signals normalized to values in 1% (v/v) HNO_3 matrix as a function of methanol concentration. The concentration of As was 10 ng mL^{-1}.

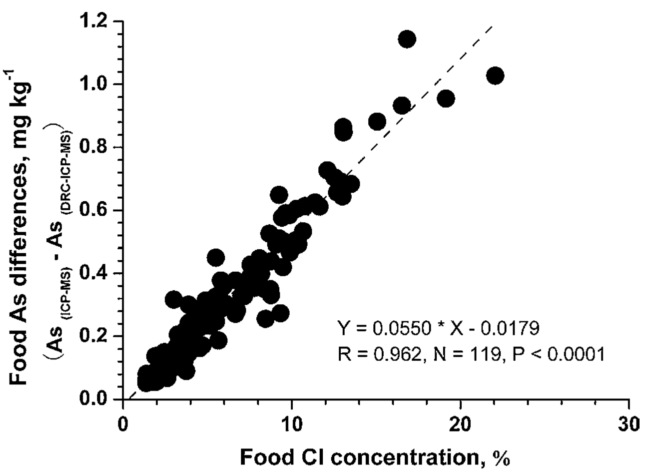

Fig. 7. Difference of As concentration (mg kg^{-1}) between standard mode ICP-MS and DRC-ICP-MS (CH_4 as the reaction gas) as a function of food chlorine concentration (%) in foods (N = 119).

Table 3
Mean values ($n = 5$) of Arsenic in 119 food samples by standard mode ICP-MS and DRC-ICP-MS.

No.	Name	Cl/As	Zr/As	As ($\mu g\, g^{-1}$) (mean ± SD)		
				ICP-MS	CH_4-DRC[a]	O_2-DRC[b]
1	SDE-01	1.31E+06	0.08	0.381 ± 0.019	0.053 ± 0.002	0.054 ± 0.003
2	SDE-02	3.24E+05	0.03	0.114 ± 0.007	0.058 ± 0.003	0.064 ± 0.003
3	SDE-03	3.09E+05	0.04	0.096 ± 0.006	0.044 ± 0.003	0.038 ± 0.002
4	SDE-04	1.13E+06	0.05	0.508 ± 0.022[c]	0.074 ± 0.003	0.070 ± 0.004
5	SDE-05	4.62E+05	0.09	0.148 ± 0.009	0.047 ± 0.002	0.045 ± 0.002
6	SDE 06	3.14E+05	0.09	0.151 ± 0.011	0.083 ± 0.004	0.081 ± 0.003
7	SDE-07	3.31E+05	0.06	0.152 ± 0.009	0.060 ± 0.002	0.064 ± 0.004
8	SDE-08	1.13E+06	0.07	0.554 ± 0.024	0.087 ± 0.005	0.089 ± 0.007
9	SDE-09	1.22E+06	0.08	0.511 ± 0.021	0.072 ± 0.007	0.063 ± 0.005
10	SDE-10	7.63E+05	0.09	0.422 ± 0.012	0.094 ± 0.005	0.095 ± 0.006
11	SDE-11	1.12E+06	0.11	0.472 ± 0.025	0.073 ± 0.003	0.069 ± 0.005
12	SDE-12	1.41E+06	0.08	0.331 ± 0.018	0.048 ± 0.003	0.042 ± 0.002
13	SDE-13	4.89E+05	0.06	0.162 ± 0.011	0.048 ± 0.004	0.047 ± 0.003
14	SDE-14	1.29E+06	0.08	0.399 ± 0.016	0.068 ± 0.005	0.068 ± 0.004
15	SDE-15	3.97E+05	0.05	0.185 ± 0.007	0.048 ± 0.005	0.046 ± 0.002
16	SDE-16	1.28E+06	0.07	0.199 ± 0.012	0.036 ± 0.003	0.037 ± 0.003
17	SDE-17	5.42E+05	0.07	0.096 ± 0.008	0.037 ± 0.003	0.042 ± 0.004
18	FBC-01	1.19E+06	0.07	0.623 ± 0.035	0.090 ± 0.007	0.087 ± 0.006
19	FBC-02	1.80E+06	0.05	0.759 ± 0.043	0.075 ± 0.005	0.073 ± 0.004
20	FBC-03	7.92E+05	0.03	1.672 ± 0.088	0.244 ± 0.013	0.226 ± 0.009
21	FBC-04	1.95E+06	0.03	1.230 ± 0.075	0.086 ± 0.007	0.084 ± 0.004
22	FBC-05	2.32E+06	0.09	1.004 ± 0.059	0.071 ± 0.006	0.071 ± 0.005
23	FBC-06	8.47E+05	0.11	0.532 ± 0.039	0.112 ± 0.009	0.107 ± 0.005
24	FBC-07	6.63E+05	0.02	0.477 ± 0.033	0.127 ± 0.008	0.134 ± 0.012
25	FBC-08	5.86E+05	0.04	0.322 ± 0.031	0.088 ± 0.011	0.091 ± 0.007
26	FBC-09	1.14E+06	0.02	0.833 ± 0.042	0.106 ± 0.007	0.093 ± 0.004
27	FBC-10	9.35E+05	0.09	0.728 ± 0.024	0.115 ± 0.005	0.098 ± 0.008
28	FBC-11	1.08E+06	0.01	0.664 ± 0.033	0.087 ± 0.007	0.080 ± 0.005
29	FBC-12	8.61E+05	0.02	0.617 ± 0.054	0.108 ± 0.009	0.100 ± 0.007
30	FBC-13	5.65E+05	0.04	1.348 ± 0.046	0.320 ± 0.013	0.310 ± 0.007
31	FBC-14	1.20E+06	0.11	0.591 ± 0.037	0.085 ± 0.007	0.083 ± 0.004
32	FBC-15	2.38E+06	0.05	0.711 ± 0.024	0.053 ± 0.003	0.056 ± 0.005
33	FBC-16	6.88E+05	0.05	0.445 ± 0.022	0.104 ± 0.006	0.108 ± 0.008
34	FBC-17	2.97E+06	0.11	0.908 ± 0.045	0.044 ± 0.002	0.042 ± 0.003
35	FBC-18	9.91E+05	0.05	0.980 ± 0.063	0.132 ± 0.011	0.120 ± 0.006
36	FBC-19	7.28E+05	0.04	1.218 ± 0.057	0.263 ± 0.027	0.277 ± 0.013
37	FBC-20	9.04E+05	0.01	0.622 ± 0.043	0.096 ± 0.005	0.096 ± 0.010
38	FBC-21	1.40E+06	0.07	0.322 ± 0.021	0.048 ± 0.005	0.052 ± 0.004
39	FBC-22	2.39E+06	0.10	0.757 ± 0.039	0.052 ± 0.004	0.050 ± 0.003
40	FBC-23	1.34E+06	0.10	0.995 ± 0.065	0.113 ± 0.007	0.104 ± 0.006
41	FBC-24	6.73E+05	0.04	0.837 ± 0.047	0.048 ± 0.008	0.052 ± 0.007
42	FBC-25	7.18E+05	0.11	0.872 ± 0.064	0.179 ± 0.005	0.164 ± 0.014
43	FBC-26	6.08E+05	0.09	0.812 ± 0.026	0.187 ± 0.012	0.174 ± 0.009
44	FBC-27	1.25E+06	0.08	0.664 ± 0.077	0.079 ± 0.007	0.078 ± 0.006
45	FBC-28	1.01E+06	0.05	0.707 ± 0.037	0.102 ± 0.008	0.106 ± 0.007
46	FBC-29	4.72E+05	0.05	0.712 ± 0.054	0.220 ± 0.013	0.211 ± 0.007
47	FBC-30	2.61E+05	0.05	0.685 ± 0.030	0.335 ± 0.014	0.325 ± 0.010
48	FBC-31	1.10E+06	0.05	0.416 ± 0.026	0.067 ± 0.005	0.061 ± 0.003
49	FBC-32	1.71E+06	0.08	0.648 ± 0.065	0.056 ± 0.004	0.052 ± 0.005
50	FBC-33	1.25E+06	0.03	0.578 ± 0.033	0.076 ± 0.007	0.073 ± 0.004
51	FBC-34	5.35E+05	0.06	0.339 ± 0.024	0.088 ± 0.005	0.083 ± 0.007
52	FBC-35	1.07E+06	0.06	0.499 ± 0.045	0.071 ± 0.004	0.059 ± 0.004
53	FBC-36	1.45E+06	0.08	0.318 ± 0.011	0.046 ± 0.003	0.042 ± 0.002
54	FBC-37	7.50E+05	0.05	0.167 ± 0.007	0.046 ± 0.004	0.050 ± 0.003
55	FBC-38	5.48E+05	0.04	0.163 ± 0.010	0.058 ± 0.003	0.066 ± 0.002
56	FBC-39	4.96E+05	0.02	0.197 ± 0.022	0.074 ± 0.007	0.085 ± 0.005
57	CMP-01	1.12E+06	0.04	0.287 ± 0.014	0.040 ± 0.003	0.042 ± 0.002
58	CMP-02	1.09E+06	0.02	0.734 ± 0.044	0.085 ± 0.006	0.091 ± 0.007
59	CMP-03	1.19E+06	0.04	0.320 ± 0.022	0.038 ± 0.002	0.033 ± 0.001
60	CMP-04	7.89E+05	0.04	0.305 ± 0.016	0.058 ± 0.003	0.056 ± 0.002
61	CMP-05	6.88E+05	0.07	0.309 ± 0.011	0.061 ± 0.002	0.056 ± 0.004
62	CMP-06	6.49E+05	0.05	0.196 ± 0.017	0.048 ± 0.003	0.048 ± 0.005
63	CMP-07	1.16E+06	0.11	0.428 ± 0.023	0.050 ± 0.004	0.055 ± 0.003
64	CMP-08	4.52E+05	0.01	0.572 ± 0.037	0.122 ± 0.006	0.127 ± 0.004
65	CMP-09	9.11E+05	0.04	0.285 ± 0.019	0.043 ± 0.003	0.044 ± 0.003
66	CMP-10	8.47E+05	0.10	0.244 ± 0.015	0.038 ± 0.003	0.037 ± 0.003
67	CMP-11	7.82E+05	0.12	0.293 ± 0.027	0.050 ± 0.002	0.046 ± 0.004
68	CMP-12	4.84E+05	0.11	0.184 ± 0.013	0.044 ± 0.003	0.037 ± 0.002
69	CMP-13	2.15E+05	0.09	0.212 ± 0.019	0.102 ± 0.005	0.097 ± 0.002
70	CMP-14	2.81E+05	0.07	0.138 ± 0.012	0.064 ± 0.004	0.066 ± 0.005
71	CMP-15	2.01E+05	0.02	0.151 ± 0.009	0.070 ± 0.005	0.067 ± 0.003
72	CMP-16	2.58E+05	0.02	0.117 ± 0.013	0.053 ± 0.003	0.050 ± 0.004
73	CMP-17	1.94E+06	0.03	0.412 ± 0.030	0.034 ± 0.004	0.030 ± 0.002
74	CMP-18	7.16E+05	0.07	0.262 ± 0.014	0.056 ± 0.005	0.058 ± 0.003

Table 3 (*Continued*)

No.	Name	Cl/As	Zr/As	As ($\mu g\,g^{-1}$) (mean ± SD)		
				ICP-MS	CH $_{rmbox4}$-DRC[a]	O_2-DRC[b]
75	CMP-19	1.11E+06	0.04	0.521 ± 0.035	0.073 ± 0.006	0.072 ± 0.004
76	CMP-20	7.71E+05	0.08	0.266 ± 0.023	0.048 ± 0.002	0.046 ± 0.002
77	CMP-21	1.11E+06	0.07	0.334 ± 0.027	0.046 ± 0.005	0.044 ± 0.003
78	CMP-22	6.43E+05	0.06	0.217 ± 0.018	0.049 ± 0.002	0.048 ± 0.004
79	CMP-23	3.02E+06	0.07	0.330 ± 0.023	0.016 ± 0.001	0.017 ± 0.002
80	CMP-24	1.66E+06	0.10	0.465 ± 0.045	0.046 ± 0.002	0.042 ± 0.003
81	CMP-25	6.53E+05	0.04	0.631 ± 0.021	0.139 ± 0.012	0.143 ± 0.007
82	CMP-26	2.85E+05	0.01	0.602 ± 0.016	0.328 ± 0.013	0.310 ± 0.011
83	CMP-27	1.15E+06	0.05	0.363 ± 0.014	0.050 ± 0.003	0.047 ± 0.002
84	CMP-28	8.71E+05	0.09	0.297 ± 0.028	0.053 ± 0.003	0.048 ± 0.003
85	CMP-29	1.82E+06	0.07	0.676 ± 0.033	0.064 ± 0.003	0.063 ± 0.005
86	CMP-30	8.53E+05	0.05	0.444 ± 0.020	0.091 ± 0.004	0.104 ± 0.007
87	CMP-31	7.64E+05	0.06	0.320 ± 0.017	0.072 ± 0.005	0.073 ± 0.004
88	CMP-32	9.56E+05	0.07	0.275 ± 0.021	0.047 ± 0.002	0.052 ± 0.003
89	CMP-33	8.24E+05	0.11	0.431 ± 0.028	0.072 ± 0.007	0.063 ± 0.005
90	CMP-34	1.65E+06	0.10	0.359 ± 0.018	0.033 ± 0.002	0.032 ± 0.001
91	CMP-35	1.24E+06	0.09	0.305 ± 0.011	0.038 ± 0.003	0.037 ± 0.003
92	CMP-36	5.96E+05	0.05	0.359 ± 0.020	0.033 ± 0.004	0.032 ± 0.002
93	CMP-37	5.16E+05	0.09	0.297 ± 0.014	0.079 ± 0.007	0.070 ± 0.004
94	CMP-38	7.16E+05	0.12	0.265 ± 0.027	0.053 ± 0.002	0.057 ± 0.005
95	CMP-39	1.59E+06	0.07	0.435 ± 0.014	0.047 ± 0.003	0.042 ± 0.002
96	CMP-40	7.87E+05	0.10	0.242 ± 0.022	0.043 ± 0.004	0.048 ± 0.004
97	CMP-41	9.65E+05	0.03	0.330 ± 0.025	0.057 ± 0.003	0.052 ± 0.002
98	CMP-42	9.38E+05	0.04	0.350 ± 0.008	0.062 ± 0.002	0.056 ± 0.005
99	CMP-43	1.43E+06	0.08	0.279 ± 0.021	0.031 ± 0.003	0.028 ± 0.001
100	CMP-44	7.83E+05	0.03	0.328 ± 0.013	0.061 ± 0.004	0.062 ± 0.005
101	CMP-45	1.18E+06	0.06	0.338 ± 0.019	0.043 ± 0.005	0.049 ± 0.002
102	CMP-46	3.98E+05	0.07	0.457 ± 0.035	0.152 ± 0.006	0.139 ± 0.005
103	CMP-47	4.39E+05	0.09	0.277 ± 0.023	0.077 ± 0.004	0.081 ± 0.006
104	CMP-48	6.06E+05	0.11	0.312 ± 0.017	0.065 ± 0.004	0.064 ± 0.002
105	CMP-49	2.41E+05	0.02	0.306 ± 0.033	0.160 ± 0.005	0.169 ± 0.008
106	CMP-50	3.17E+05	0.02	0.208 ± 0.019	0.118 ± 0.010	0.110 ± 0.005
107	CMP-51	5.82E+05	0.08	0.132 ± 0.008	0.045 ± 0.003	0.049 ± 0.002
108	CMP-52	7.11E+05	0.12	0.159 ± 0.011	0.038 ± 0.003	0.034 ± 0.003
109	CMP-53	4.62E+05	0.06	0.158 ± 0.009	0.061 ± 0.002	0.056 ± 0.005
110	CMP-54	8.09E+05	0.05	0.141 ± 0.013	0.035 ± 0.002	0.033 ± 0.002
111	CMP-55	5.73E+05	0.08	0.104 ± 0.004	0.032 ± 0.003	0.028 ± 0.002
112	CMP-56	3.97E+05	0.08	0.393 ± 0.025	0.076 ± 0.005	0.081 ± 0.006
113	CMP-57	5.95E+05	0.12	0.242 ± 0.012	0.064 ± 0.003	0.057 ± 0.005
114	CMP-58	7.57E+05	0.07	0.183 ± 0.017	0.032 ± 0.002	0.036 ± 0.003
115	CMP-59	3.77E+05	0.01	0.208 ± 0.011	0.082 ± 0.007	0.075 ± 0.005
116	CMP-60	9.38E+05	0.04	0.346 ± 0.022	0.090 ± 0.002	0.087 ± 0.007
117	CMP-61	8.23E+05	0.05	0.228 ± 0.013	0.057 ± 0.003	0.062 ± 0.004
118	CMP-62	5.24E+05	0.06	0.375 ± 0.021	0.074 ± 0.007	0.068 ± 0.003
119	CMP-63	7.84E+05	0.06	0.259 ± 0.012	0.072 ± 0.002	0.069 ± 0.006

[a] Results using CH_4 as reaction gas in DRC-ICP-MS.

[b] Results using O_2 as reaction gas in DRC-ICP-MS.

[c] The biased values exceed MRL of As (>0.5 mg kg^{-1}).

4. Conclusions

The spectral interference of ArCl on As monitoring in high chlorine food samples was successfully eliminated using two different strategies based on ion–molecule reactions in ICP-MS analysis. One is direct elimination of the ArCl interference by the reactions with molecule methane. Another method is converted $^{75}As^+$ to $^{75}As^{16}O^+$ that could be detected at m/z 91 which is free interfered. The low sensitivities of As or AsO are improved 3–4 times by addition of 4% (v/v) methanol in the analysis solutions. The proposed method has been used as the laboratory routine method to determinate trace arsenic in various high chlorine food samples for market monitoring.

Acknowledgments

This work is supported by the grants from the National Nature Science Foundation of China (No. 40973021 and 40821061) and the Monitoring Program for Central Meat Reserves (CRC) from the Ministry of Commerce of the People's Republic of China.

References

[1] Environmental Health Criteria 224 Arsenic and Arsenic Compounds, 2nd ed., World Health Organization, Geneva, 2001, pp. 168–345.

[2] WHO, Food Additives Series No. 24, Food and Agriculture Organization, World Health Organization, Geneva, Switzerland, 1998.

[3] Ministry of Health of People's Republic of China and Standardization administration of the People's Republic of China, National Standard of the People's Republic of China – Hygienic standard for fermented bean product (GB 2712-2003), 2003.

[4] Ministry of Agriculture of People's Republic of China, Agricultural Industrial Standard of the People's Republic of China – Pollution-free food for salted duck egg (NY 5144-2002), 2002.

[5] M. Ghambarian, M.R.K. Zanjani, Y. Yamini, A. Esrafili, N. Yazdanfar, Talanta 81 (2010) 197–201.

[6] Z. Ajtony, N. Szoboszlai, E.K. Susko, P. Mezei, Talanta 76 (2008) 627–634.

[7] L. Zhang, Y. Morita, A. Sakuragawa, A. Isozaki, Talanta 72 (2007) 723–729.

[8] C.G. Bruhn, C.J. Bustos, K.L. Saez, J.Y. Neira, S.E. Alvarez, Talanta 71 (2007) 81–89.

[9] M.N.M. Reyes, M.L. Cervera, R.C. Campos, M.D.L. Guardia, Talanta 75 (2008) 811–816.

[10] M.J. Mato-Fernandez, J.R. Otero-Rey, J. Moreda-Pineiro, E. Alonso-Rodriguez, R. Lopez-Mahia, S. Muniategui-Lorenzo, D. Prada-Rodriguez, Talanta 71 (2007) 515–520.

[11] R.M.W. Nano, R.E. Bruns, S.L.C. Ferreira, N. Baccan, S. Cadore, Talanta 80 (2009) 559–564.

[12] C.M. Xiong, M. He, B. Hu, Talanta 76 (2008) 772–779.

[13] S.G. Salgado, M.A.Q. Nieto, M.M.B. Simon, Talanta 75 (2008) 897–903.
[14] K. Boutakhrit, R.C.F. Bolle, J.M. Degroodt, L. Goeyens, Talanta 66 (2005) 1042–1047.
[15] U. Arroyo-Abad, J. Mattusch, S. Mothes, M. Moder, R. Wennrich, M.P. Elizalde-Gonzalez, F.M. Matysik, Talanta 82 (2010) 38–43.
[16] S. Ciardullo, F. Aureli, A. Raggi, F. Cubadda, Talanta 81 (2010) 213–221.
[17] W.H. Geng, R. Komine, T. Ohta, T. Nakajima, H. Takanashi, A. Ohki, Talanta 79 (2009) 369–375.
[18] L.H. Reyes, J.L.G. Mar, G.M.M. Rahman, B. Seybert, T. Fahrenholz, H.M.S. Kingston, Talanta 78 (2009) 983–990.
[19] G.D. Yang, J.H. Xu, J.P. Zheng, X.Q. Xu, W. Wang, L.J. Xu, G.N. Chen, F.F. Fu, Talanta 78 (2009) 471–476.
[20] T. Narukawa, K. Inagaki, T. Kuroiwa, K. Chiba, Talanta 77 (2008) 427–432.
[21] S. Catarino, A.S. Curvelo-Garcia, R.B.D. Sousa, Talanta 70 (2006) 1073–1080.
[22] V.G. Mihucz, G. Silversmit, I. Szaloki, B.D. Samber, T. Schoonjans, E. Tatar, L. Vincze, J. Yao, G. Zaray, Food Chem. 121 (2010) 290–297.
[23] H. Wildner, J. Anal. Atom. Spectrom. 13 (1998) 573–578.
[24] B. Klaue, J.D. Blum, Anal. Chem. 71 (1999) 1408–1414.
[25] A.G. Coedo, T. Dorado, I. Padilla, Appl. Spectrosc. 53 (1999) 974–978.
[26] G. Grindlay, J. Mora, L. Gras, M.T.C.D. Loos-Vollebregt, Anal. Chim. Acta 652 (2009) 154–160.
[27] R.J.C. Brown, R.E. Yardley, A.S. Brown, M.J.T. Milton, J. Anal. Atom. Spectrom. 19 (2004) 703–705.
[28] Z.C. Hu, S. Gao, S.H. Hu, H.L. Yuan, X.M. Liu, Y.S. Liu, J. Anal. Atom. Spectrom. 20 (2005) 1263–1269.
[29] J. Wang, E.H. Evans, J.A. Caruso, J. Anal. Atom. Spectrom. 7 (1992) 929–936.
[30] K. Neubauer, U. Vollkopf, Atom. Spectrosc. 20 (1999) 64–68.
[31] I. Jayawardene, R. Saper, N. Lupoli, A. Sehgal, R.O. Wright, C. Amarasiriwardena, J. Anal. Atom. Spectrom. 25 (2010) 1275–1282.
[32] S. D'Ilio, N. Violante, M.D. Gregorio, O. Senofonte, F. Petrucci, Anal. Chim. Acta 579 (2006) 202–208.
[33] D.E. Nixon, K.R. Neubauer, S.J. Eckdahl, J.A. Butz, M.F. Burritt, Spectrochim. Acta B 59 (2004) 1377–1387.
[34] R.Y. Wang, Y.L. Hsu, L.F. Chang, S.J. Jiang, Anal. Chim. Acta 590 (2007) 239–244.
[35] S.D. Tanner, V.I. Baranov, D.R. Bandura, Spectrochim. Acta B 57 (2002) 1361–1452.
[36] J.W. Olesik, D.R. Jones, J. Anal. Atom. Spectrom. 21 (2006) 141–159.
[37] S.D. Tanner, V.I. Baranov, U. Volkopf, J. Anal. Atom. Spectrom. 15 (2000) 1261–1269.
[38] W. Guo, S.H. Hu, Y.F. Xiao, H.F. Zhang, X.J. Xie, Chemosphere 81 (2010) 1463–1468.
[39] W. Guo, S.H. Hu, J. Zhao, S.S. Jin, W.J. Liu, H.F. Zhang, Microchem. J. 97 (2011) 154–159.
[40] P. Allain, L. Jaunault, Y. Mauras, J.M. Mermet, T. Delaporte, Anal. Chem. 63 (1991) 1497–1498.
[41] Z.C. Hu, S.H. Hu, S. Gao, Y.H. Liu, S.L. Lin, Spectrochim. Acta B 59 (2004) 1463–1470.
[42] E.H. Larsen, S. Stürup, J. Anal. Atom. Spectrom. 9 (1994) 1099–1105.