



## Reduction of acid effects on trace element determination in food samples by CH<sub>4</sub> mixed plasma-DRC-MS

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### ABSTRACT

A robust method for trace element determination in food samples by addition of methane to the plasma of a dynamic reaction cell mass spectrometer (CH<sub>4</sub> mixed plasma-DRC-MS) was developed. Addition of 3 mL min<sup>-1</sup> methane to Ar-plasma eliminates the signal suppressions of various elements (As, Se, Hg, etc.) due to the high concentration of nitric acid (10%, v/v). The CH<sub>4</sub>-Ar mixed plasma may compensate for the plasma cooling effects due to the highly concentrated nitric acid. The interfering polyatomic ions <sup>40</sup>Ar<sup>12</sup>C<sup>+</sup>, <sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup> and <sup>40</sup>Ar<sup>40</sup>Ar<sup>+</sup> on <sup>52</sup>Cr<sup>+</sup>, <sup>75</sup>As<sup>+</sup> and <sup>80</sup>Se<sup>+</sup> determination were removed effectively using the DRC with CH<sub>4</sub> as the reaction gas. The limits of quantification (LOQ, 10σ) were 0.35 ng g<sup>-1</sup>, 0.07 ng g<sup>-1</sup>, 0.35 ng g<sup>-1</sup>, 0.07 ng g<sup>-1</sup>, 0.15 ng g<sup>-1</sup>, and 0.07 ng g<sup>-1</sup> for As, Cd, Cr, Hg, Pb and Se, respectively. The proposed method was applied to the determination of these trace elements in four food standard reference materials (NIST1577b, GBW10018, NIST1570a and GBW10016), and the results were in good agreement with the certified values.

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### 1. Introduction

The technique of microwave-assisted acid digestion followed by inductively coupled plasma mass spectrometry (ICP-MS) is probably one of the most versatile methods for the analysis of trace elements in food samples [1–8]. It has the advantages of high analytical throughput, less potential contamination and loss of volatile elements, excellent detection limits, multi-element capability and the ability to measure isotope ratios [9]. However, one of the most significant limitations is acid matrix effects, which mainly lead to signal suppression [10], especially if the analyzed solution has high acid concentrations.

In ICP-MS analysis, acid matrix effects are known to cause signal suppression with increased acid concentrations [11,12]. The signal depression is related to the effect of the acid on the aerosol generation [13], transport processes [14] as well as a change in plasma conditions [15]. Some methods have been employed to minimize the interference of mineral acids: (a) matrix matching [16], (b) internal standards [17], (c) standard addition [18] and (d) modification of the sample introduction system (i.e. using cyclonic-type spray chamber [19], desolvation [20], direct injection nebulizers [21] and sample introduction via electrothermal vaporization [22]). Nevertheless, because of the acid content and the large different

signal suppression between the analyte elements and internal standard elements, the methods of (a) matrix matching and (b) using of internal standards could be difficult to apply, respectively [23]. Other methods are time consuming or require additional expensive equipment. The advantages and disadvantages of these methods were evaluated in detail by Todoli and Mermet [10].

Some research reports that the addition of organic solvent can significantly improve the sample nebulization-transport efficiency or ionization efficiency in plasma [24–29]. The introduction of small amounts of organic solvents into the plasma modifies the physicochemical properties of the nebulized solution, compared to the aqueous sample, contributing to an overall smaller droplet size, which favors nebulization and transport into the plasma [30]. The increased population of carbon or carbon-containing ions in the plasma can contribute to the improvement of the ionization equilibrium in the plasma [31]. Recently, Hu et al. [32] found that addition of 4% (v/v) ethanol to analyzed solution could alleviate the acid suppression effects on arsenic determination. However, the study of the effects of acid suppression with the addition of carbon as methane to the plasma on the Se, Cr, Cd, Pb and Hg determination by DRC ICP-MS has not been reported so far.

The aim of this paper is to describe a simple method to eliminate the suppression effects of high nitric acid concentrations. This method is based on CH<sub>4</sub>-Ar mixed plasma to improve the plasma cooling effect due to the highly concentrated nitric acid. Addition of 3 mL min<sup>-1</sup> methane to the normal Ar-plasma, the 10% (v/v) nitric acid can directly introduce to the ICP without signal

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intensity changes. In addition, the eliminations of spectral interferences of  $^{40}\text{Ar}^{12}\text{C}$ ,  $^{40}\text{Ar}^{35}\text{Cl}$  and  $^{40}\text{Ar}^{40}\text{Ar}$  on  $^{52}\text{Cr}$ ,  $^{75}\text{As}$  and  $^{80}\text{Se}$  determination by  $\text{CH}_4$  as the reaction gas in a DRC were also studied. The developed method was validated by analyzing four food standard reference materials (SRMs).

## 2. Material and methods

### 2.1. Instrumentation

A PerkinElmer SCIEX ELAN DRC-e (dynamic reaction cell) ICP-MS instrument was used and is described in detail elsewhere [33–35]. Methane (99.999% purity) gas was added to an additional port in the cyclonic spray chamber ( $\text{PC}^3$ , Elemental Scientific, USA) via a calibrated mass-flow controller (32907, Cole-Parmer, USA), capable of regulating minute (measuring range  $0\text{--}10\text{ mL min}^{-1}$ , precision  $0.01\text{ mL min}^{-1}$ ) flows of the gas. The operating parameters of the DRC-ICP-MS used for this work are summarized in Table 1. A CEM MARS X-press (CEM, USA) microwave apparatus equipped with Teflon vessels was used to digest the samples.

### 2.2. Reagents and standards

The single element stock solutions of As, Cd, Cr, Hg, Pb, Se, In and Bi were purchased from National Center for Analysis and Testing of Steel Materials (China). Nitric acid (65–70%, 99.9999%), hydrogen peroxide (35%, 99.999%), and hydrochloric acid (99.9999%) were purchased from Alfa Aesar (Tianjing) Ltd. The methane gas (99.999% purity) was purchased from Praxair (China) Investment Co., Ltd. (99.999% purity). High purity water ( $18.2\text{ M}\Omega\text{ cm}^{-1}$ ) was obtained from a Millipore water purification system (Millipore, France). The SRMs of NIST1577b (Bovine liver) and NIST1570a (Spinach leaves) were purchased from National Institute of Standards and Technology (USA), and the SRMs of GBW10018 (Chicken) and GBW10016 (Tea) were purchased from National Research Center for Certified Reference Materials (China).

### 2.3. Sample preparation

Approximately 0.2000 g of sample was accurately weighed into the microwave Teflon vessel, and 5 mL of  $\text{HNO}_3$  were added. After the sample was pre-digested for 0.5 h at room temperature, 2 mL

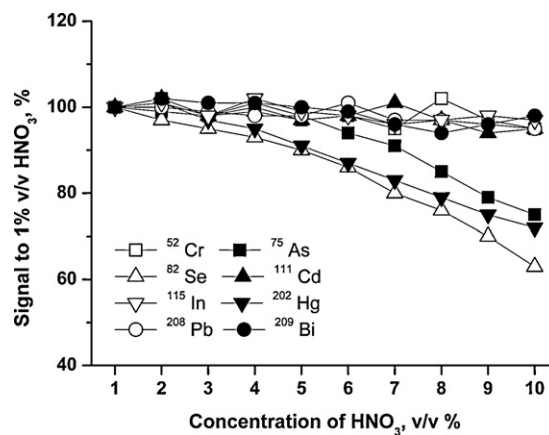


Fig. 1. Effects of nitric acid concentration on normalized signals of  $10\text{ ng mL}^{-1}$  As, Bi, Cd, Cr, Hg, In, Pb, and Se (to 1%, v/v  $\text{HNO}_3$ ) by normal plasma. The nebulizer gas flow is  $0.76\text{ L min}^{-1}$ .

of  $\text{H}_2\text{O}_2$  was added, and then the vessel was capped. Microwave digestion was applied as follows: the temperature was ramped to  $160^\circ\text{C}$  within 10 min at 800 W, holding for 5 min; then ramped to  $200^\circ\text{C}$  within 10 min at 1600 W, holding for 25 min. After the vessel had cooled down, the digestion solution was diluted to 50 mL with high purity water.

## 3. Results and discussion

### 3.1. Signal suppression in high concentration nitric acid

It is widely known that the introduction of nitric acid in ICP-MS causes serious signal suppression phenomenon [10,36]. The suppression effect of nitric acid is dependent on the element's mass number [37] and first ionization potential [38]. In order to investigate the signal suppression in different concentrations of nitric acid, As, Se, Hg, Pb, Cr, Cd, In and Bi were selected, and the nitric acid concentration was varied from 1 to 10%. The normalized signal intensities (to 1%  $\text{HNO}_3$ ) as a function of nitric acid concentration at the optimization instrument parameters are shown in Fig. 1. The signal intensities of  $^{75}\text{As}$ ,  $^{82}\text{Se}$  and  $^{202}\text{Hg}$  are reduced about 30–40% with increasing nitric acid concentration (from 1% to 10%). These three elements have high first ionization potentials ( $\text{IP} > 9\text{ eV}$ ). However, the signal suppression of low first ionization potential elements ( $\text{IP} < 9\text{ eV}$ )  $^{52}\text{Cr}$ ,  $^{114}\text{Cd}$ ,  $^{115}\text{In}$ ,  $^{208}\text{Pb}$  and  $^{209}\text{Bi}$  is less than 10%. These results are in good agreement with those obtained by Stewart and Olesik [13] and Hu et al. [32]. The large relative signal suppression between 1% and 10%  $\text{HNO}_3$  for As, Se and Hg suggests that there is a significant plasma cooling effect due to introduction of the high concentration nitric acid. It was also proved that the method based on normal internal standards (such as Rh, In or Bi) or modification of the sample introduction system was not valid for overcoming the acid suppression effect.

### 3.2. Reduction of acid effect with methane addition

To eliminate the suppression effects of high concentration nitric acid,  $3\text{ mL min}^{-1}$  methane was added to plasma used to investigate the compensation effects for elemental signal suppression. In addition, as more matrices ( $\text{HNO}_3$  and methane) are introduced to the plasma, more time is required in the plasma for vaporization, atomization and ionization prior to sampling by the mass spectrometer [39]. Therefore, in order to increase the robustness of the plasma, the nebulizer gas flow rate was decreased from 0.76 to  $0.72\text{ L min}^{-1}$ . Fig. 2 shows the effects of nitric acid concentration on normalized signals of  $10\text{ ng mL}^{-1}$  As, Bi, Cd, Cr, Hg, In, Pb and

Table 1  
Instrument operating parameters.

ICP-MS instrument	PerkinElmer Sciex Elan DRC-e
Sample introduction	PFA-400 MicroFlow nebulizer
Spray chamber	Cyclonic spray chamber ( $\text{PC}^3$ Peltier Chiller)
Injector tube	1.0 mm id Quartz
RF power, W	1300
Plasma gas flow, $\text{L min}^{-1}$	16
Auxiliary gas flow, $\text{L min}^{-1}$	1.0
Nebulizer gas flow, $\text{L min}^{-1}$	0.76 (normal plasma); 0.72 (methane mixed plasma)
$\text{CH}_4$ reaction gas flow, $\text{mL min}^{-1}$	$^{75}\text{As}^+$ , 0.40; $^{80}\text{Se}^+$ , 0.60; $^{52}\text{Cr}^+$ , 1.0; other elements, 0
Rejection parameter, $q$	$^{75}\text{As}^+$ , 0.30; $^{80}\text{Se}^+$ , 0.60; $^{52}\text{Cr}^+$ , 0.75; other elements, 0.25
Rejection parameter, $a$	0
Axial field potential (AFP), V	250
Autolens	on
Dwell time, ms	50
Sweeps	20
Readings	1
Replicate	3
Monitored ions	$^{52}\text{Cr}^+$ , $^{75}\text{As}^+$ , $^{80}\text{Se}^+$ , $^{111}\text{Cd}^+$ , $^{202}\text{Hg}^+$ , $^{208}\text{Pb}^+$ , $^{115}\text{In}^+$ and $^{209}\text{Bi}^+$

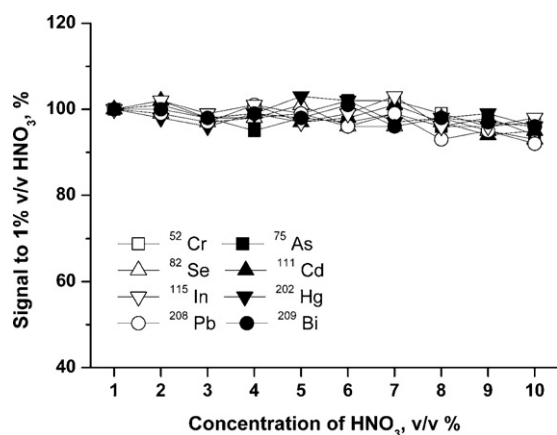


Fig. 2. Effects of nitric acid concentration on normalized signals of 10 ng mL<sup>-1</sup> As, Bi, Cd, Cr, Hg, In, Pb, and Se (to 1%, v/v HNO<sub>3</sub>) by CH<sub>4</sub> mixed plasma. The addition of CH<sub>4</sub> flow rate was 3 mL and the nebulizer gas flow rate was 0.72 L min<sup>-1</sup>.

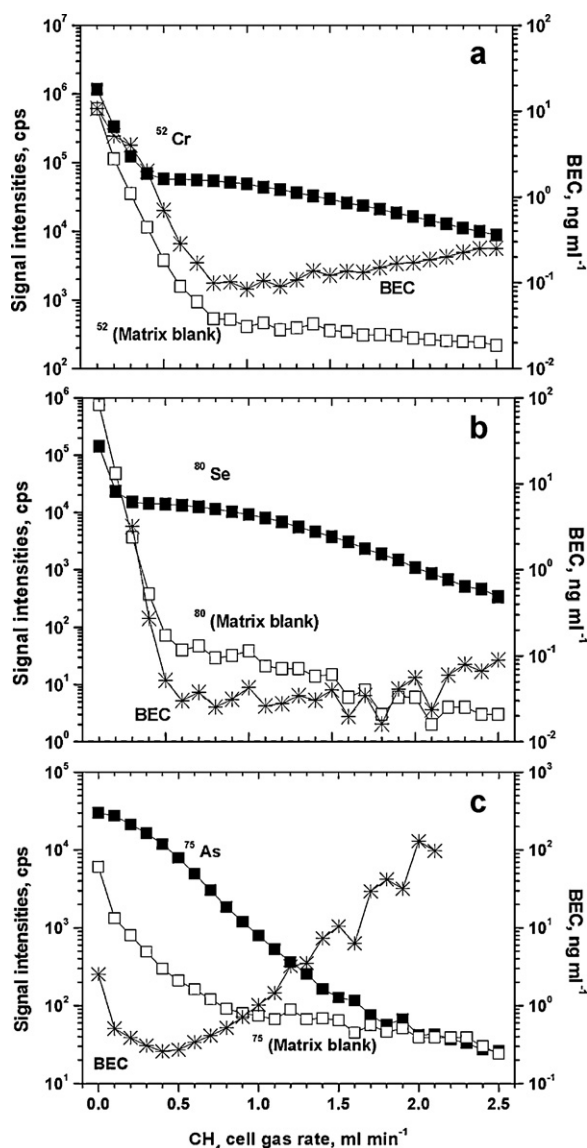


Fig. 3. Effects of CH<sub>4</sub> cell gas flow rate on elemental signal intensity, matrix blank and background equivalent concentration (BEC). (a) 10 ng mL<sup>-1</sup> Cr; (b) 10 ng mL<sup>-1</sup> Se; (c) 10 ng mL<sup>-1</sup> As. Rpq = 0.60.

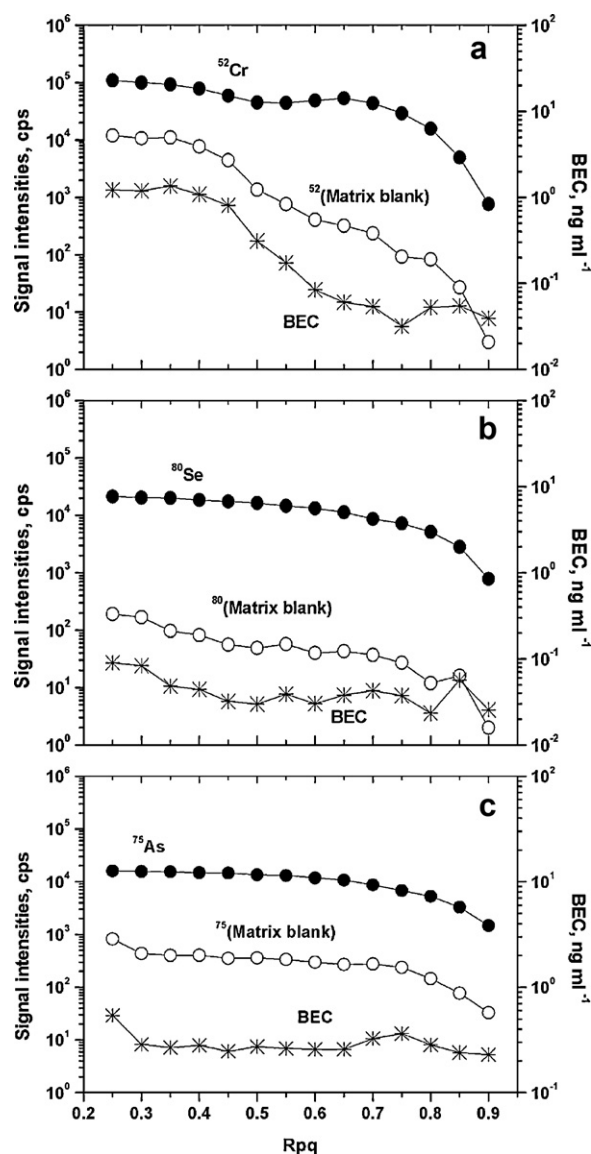


Fig. 4. Effects of the Rpq value on elemental signal intensity, matrix blank and background equivalent concentration (BEC). (a) 10 ng mL<sup>-1</sup> Cr, CH<sub>4</sub> gas flow rate 1.0 mL min<sup>-1</sup>; (b) 10 ng mL<sup>-1</sup> Se, CH<sub>4</sub> gas flow rate 0.6 mL min<sup>-1</sup>; (c) 10 ng mL<sup>-1</sup> As, CH<sub>4</sub> gas flow rate 0.4 mL min<sup>-1</sup>.

Se (to 1%, v/v HNO<sub>3</sub>) in CH<sub>4</sub>-Ar mixed plasma. As shown in Fig. 2, the signal suppressions of high first ionization potential elements (such as Se (9.75 eV), As (9.81 eV) and Hg (10.07 eV)) are successfully reduced in the CH<sub>4</sub>-Ar mixed plasma. The methane addition could improve the plasma cooling effect, and the analytes could tolerate 10% (v/v) nitric acid matrix without signal intensity changes. This method needs no precise nitric acid match and Rh, In or Bi can be adopted as internal standards for the determinations of As, Se and Hg in various food samples.

### 3.3. Elimination of mass spectral interferences by DRC

The dynamic reaction cell (DRC) technology was used to eliminate the spectral interferences of <sup>40</sup>Ar<sup>12</sup>C, <sup>40</sup>Ar<sup>35</sup>Cl and <sup>40</sup>Ar<sup>40</sup>Ar on <sup>52</sup>Cr, <sup>75</sup>As and <sup>80</sup>Se, respectively. The operation of the DRC could be mainly controlled by the cell gas type, flow rate of the reaction gas and values of the rejection parameter *q* (Rpq) of the DRC system [40]. In this experiment, CH<sub>4</sub> was selected as the universal reaction gas for eliminating the effect of these spectral

**Table 2**  
Results for six trace elements in four food standard reference materials ( $n = 3$ ,  $\text{mg kg}^{-1}$ ).

SRMs	Analysis method	Element					
		As	Cd	Cr	Hg	Pb	Se
NIST1577b (Bovine liver)	Regular method <sup>a</sup>	0.036 ± 0.005	0.46 ± 0.02	0.23 ± 0.01	0.0012 ± 0.0011	0.121 ± 0.005	0.56 ± 0.07
	This method <sup>b</sup>	0.045 ± 0.003	0.51 ± 0.01	0.24 ± 0.01	0.0018 ± 0.0010	0.130 ± 0.003	0.75 ± 0.03
	Certified value	(0.05) <sup>c</sup>	0.50 ± 0.03	– <sup>d</sup>	(0.003)	0.129 ± 0.004	0.73 ± 0.06
GBW10018 (Chicken)	Regular method	0.089 ± 0.009	0.005 ± 0.002	0.56 ± 0.04	0.0022 ± 0.002	0.10 ± 0.01	0.37 ± 0.03
	This method	0.103 ± 0.007	0.005 ± 0.001	0.64 ± 0.05	0.0030 ± 0.001	0.11 ± 0.01	0.53 ± 0.02
	Certified value	0.109 ± 0.13	(0.01)	0.59 ± 0.11	0.0036 ± 0.0015	0.11 ± 0.02	0.49 ± 0.06
NIST1570a (Spinach leaves)	Regular method	0.056 ± 0.008	2.80 ± 0.05	1.06 ± 0.06	0.017 ± 0.003	0.18 ± 0.03	0.101 ± 0.013
	This method	0.070 ± 0.005	2.87 ± 0.03	1.19 ± 0.05	0.025 ± 0.002	0.22 ± 0.01	0.117 ± 0.010
	Certified value	0.068 ± 0.012	2.89 ± 0.07	–	0.030 ± 0.003	(0.20)	0.117 ± 0.009
GBW10016 (Tea)	Regular method	0.064 ± 0.004	0.056 ± 0.005	0.41 ± 0.05	0.0019 ± 0.0005	1.36 ± 0.05	0.79 ± 0.009
	This method	0.091 ± 0.003	0.062 ± 0.003	0.47 ± 0.04	0.0031 ± 0.0003	1.46 ± 0.04	0.108 ± 0.003
	Certified value	0.09 ± 0.01	0.062 ± 0.004	0.45 ± 0.10	0.0038 ± 0.0008	1.5 ± 0.2	0.098 ± 0.008

<sup>a</sup> Conventional Ar-ICP-DRC-MS after microwave digestion method.

<sup>b</sup> CH<sub>4</sub> mixed plasma-DRC-MS after microwave digestion method.

<sup>c</sup> Reference value or information value.

<sup>d</sup> Not available.

interferences, and the background equivalent concentration (BEC) values were used as the criterion for optimization of the DRC parameter settings. Fig. 3 shows the effect of flow rate of CH<sub>4</sub> in the DRC on the signals of 10 ng mL<sup>-1</sup> <sup>52</sup>Cr, <sup>80</sup>Se, and <sup>75</sup>As. A solution of 10% HNO<sub>3</sub> + 0.4% HCl + 2% H<sub>2</sub>O<sub>2</sub> + 1% HF was treated as the matrix blank. The significant decrease of the signal intensities at  $m/z = 52$ , 75 and 80 for the matrix blank are obtained when the flow rate of CH<sub>4</sub> is less than 1.0 mL min<sup>-1</sup> with the fixed RPq value (RPq = 0.60). This signal profile indicates that polyatomic ion interferences at  $m/z = 52$ , 75 and 80 could be eliminated at a low CH<sub>4</sub> flow rate ( $\leq 1.0$  mL min<sup>-1</sup>). The optimized CH<sub>4</sub> flow rates were selected at 1.0 mL min<sup>-1</sup>, 0.6 mL min<sup>-1</sup> and 0.4 mL min<sup>-1</sup>, and the interfered ions were reduced by up to 1000, 10,000 and 100 fold for Cr, Se and As, respectively. 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. The optimized RPq values (Fig. 4) were selected at 0.75, 0.60 and 0.30 for Cr, Se and As, and the best BEC was obtained for <sup>52</sup>Cr (0.03 ng mL<sup>-1</sup>), <sup>80</sup>Se (0.03 ng mL<sup>-1</sup>), and <sup>75</sup>As (0.3 ng mL<sup>-1</sup>), respectively.

#### 3.4. Determination of trace elements in food SRMs

The limits of quantitation (LOQ, 10 $\sigma$ ) were 0.35 ng g<sup>-1</sup>, 0.07 ng g<sup>-1</sup>, 0.35 ng g<sup>-1</sup>, 0.07 ng g<sup>-1</sup>, 0.15 ng g<sup>-1</sup>, and 0.07 ng g<sup>-1</sup> for As, Cd, Cr, Hg, Pb and Se, respectively. The proposed method was applied to determination of the trace elements in two food SRMs (NIST 1577b and GBW 10018) of animal origin and two food SRMs (NIST 1570a and GBW 10016) originating from vegetables; the results are shown in Table 2. The results show clearly that five of the elements of interest (As, Cr, Cd, Pb, Se, etc.) are in good agreement with the certified values. The results of ultra-trace levels of Hg show a little negative bias, which is similar with the findings of Zbinden and Andrey [41], who found that Hg recoveries were low when adding 2% (v/v) isopropanol to the analyzed solution in ICP-MS. This is due to the well-known Hg memory effect: low concentrations of Hg can adhere to the walls of the spray chamber and the transfer tubing of the sample introduction system [42,43].

#### 4. Conclusions

An accurate method for the determination of trace elements in food samples by CH<sub>4</sub> mixed plasma-DRC-MS was developed. Using 3 mL CH<sub>4</sub> addition to plasma, the suppression effects of high concentration nitric acid were successfully reduced. The mass spectral interferences of <sup>40</sup>Ar<sup>12</sup>C, <sup>40</sup>Ar<sup>35</sup>Cl and <sup>40</sup>Ar<sup>40</sup>Ar on <sup>52</sup>Cr, <sup>75</sup>As and <sup>80</sup>Se determination were successfully eliminated by DRC with CH<sub>4</sub>

as the reaction gas. This method has great potential for the trace elements in various food samples.

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