



Analytical Methods

Solidified floating organic drop microextraction for speciation of selenium and its distribution in selenium-rich tea leaves and tea infusion by electrothermal vapourisation inductively coupled plasma mass spectrometry



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ABSTRACT

Solidified floating organic drop microextraction was combined with electrothermal vapourisation inductively coupled plasma mass spectrometry for Se species in Se-rich tea leaves and tea infusion, including total, suspended, soluble, organic and inorganic Se as well as Se(IV) and Se(VI). Ammonium pyrolydinedithiocarbamate was used as both chelating reagent and chemical modifier in this study. Se(IV) and Se(VI) were separated at pH range of 2.0–5.0. An enrichment factor of 500 was obtained for Se(IV) from this method. Under the optimum conditions, the detection limits for Se(IV) and Se(VI) were 0.19 and 0.26 $\mu\text{g mL}^{-1}$, respectively. The relative standard deviations were less than 5.5% ($c = 0.1 \text{ ng mL}^{-1}$, $n = 9$). This method was applied for Se species, its content and distribution in Se-rich tea leaves and tea infusion with satisfactory results. The recoveries of spike experiments are in the range of 92.2–106%. A certified reference material of tea leaves was analyzed by this method, and the results were in agreement with certified values.

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1. Introduction

In recent years, selenium-rich agricultural products have received considerable attention. Selenium (Se) is the only trace element to be specified in the genetic code as selenocysteine (Rayman, 2002). The study showed that Se has a very narrow concentration range from sufficiency to deficiency and toxicity (Sun, Liu, & Wu, 2013). Se deficiency can lead to heart disease, hypothyroidism and a weakened immune system, but excess exposure to Se often results in gastrointestinal disturbances, hair and nail changes and neurologic manifestations (Colangelo et al., 2014; Zhang, Fu, Fang, Feng, & Ke, 2011). In addition, essentiality and toxicity of Se depend on its chemical forms (Chandrasekaran, Ranjit, Karunasagar, & Arunachalam, 2008). In general, inorganic species of Se are more toxic than its organic forms, and the toxicity of Se(VI) is more severe than Se(IV) (Gangher, Levander, & Baumann, 1996; Zhang, Gao, Guo, & Wang, 2013). Due to its medicinal, refreshing and mild stimulant effects, tea has become one of the most widely popular nonalcoholic beverages in the world. Se exists as organic and inorganic forms in tea leaves, but some low

molecular weight organic Se and inorganic Se can be extracted into tea infusion. Hence, knowledge of Se speciation, especially inorganic form with higher toxicity, and its distribution in Se-rich tea leaves and tea infusion are of great importance to food production, nutrition and safety.

It is well known that elemental speciation can be carried out by combining a reliable separation method with a sensitive detection technique. The separation techniques for speciation generally include chromatographic (Georg et al., 2012; Joanna, Henryk, Halina, & Ewelina, 2014; Matusiewicz & Ślachciński, 2012; Moreira et al., 2011; Zhang et al., 2013) and non-chromatographic methods (Chen, Guo, He, & Lu, 2013; Escudero, Martinis, Olsina, & Wuilloud, 2013; Güler, Maden, Bakirdere, Ataman, & Volkan, 2011; Soylak & Kizil, 2013; Wang, Song, Ma, Ma, & Liang, 2000). For a simple elemental speciation like different oxidation states, non-chromatographic procedure is often more diffused than chromatographic technique due to their more accessibility, easy availability, low cost and competitive detection limit (Vieira, Grinberg, Bobeda, Reyes, & Campos, 2009). Recently, solidified floating organic drop microextraction (SFODME), as a new liquid phase microextraction technique, has been used widely for the analysis of trace elements owing to its unique merits of simplicity, rapidity, low cost, consumption of small organic solvent and high enrichment factor

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(Durukan, Şahin, & Bektaş, 2011; Fazelirad & Taher, 2013; Liang, Yu, Yang, & Peng, 2014; Ma, Zhang, Du, Lei, & Li, 2010; Mahnaz, Yadollah, & Ali, 2013; Yi, Wu, & Jiang, 2013). However, the use of SFODME for the determination of selenium speciation has received little attention so far.

Up to date, inductively coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) still represent the most important routine techniques for elemental analysis. Relatively, ICP-MS is the most favourable choice for elemental analysis owing to its high sensitivity, wide linear range, rapid multi-element detection capability and no line-rich spectrum interference encountered in ICP-AES. It is predicted that SFODME coupled with ICP-MS may be a powerful detection tool for elements. Unfortunately, liquid nebulization sample introduction procedure for conventional ICP-MS is not compatible with SFODME because of its large sample consumption. Therefore, a lot of works on SFODME for separation and preconcentration of trace elements have been done by AAS, but only few researches were reported using ICP-MS (Chen, Cheng, He, Zhu, & Lu, 2013; Guo, He, Chen, & Hu, 2012).

Electrothermal vapourisation (ETV), as a sample introduction device for ICP-MS, has the merits of high introducing efficiency, small sample requirement, low absolute detection limit. Moreover, use of chemical modifier in ETV could greatly improve the analytical performances of method (Chen, Zhu, & Lu, 2013). With its ability of micro-sampling, ETV could be conveniently combined with a miniaturized sample pretreatment procedure such as SFODME. However, to the best of our knowledge, study on SFODME-ETV-ICP-MS for elemental speciation has not been reported in literature.

The aim of the present work was to develop SFODME coupled with ETV-ICP-MS for speciation and quantification of Se, including total, suspended, soluble, organic and inorganic Se as well as Se(IV) and Se(VI) in Se-rich tea leaves and tea infusion. Ammonium pyrrolidinedithiocarbamate (APDC) was used as both a chelating reagent in SFODME and a chemical modifier in ETV-ICP-MS. Main factors affecting separation, preconcentration and determination of the analytes were investigated in detail. A certified reference material was analyzed to validate the accuracy and feasibility of this method.

2. Materials and methods

2.1. Chemicals

All reagents in this study were of high purity available or at least of analytical grade, and bidistilled deionized water obtained from Milli-Q® A10 system (Millipore Corporation, USA) was used throughout this work. The stock standard solutions of Se(IV) and Se(VI) (1.0 mg mL^{-1}) were prepared by dissolving appropriate amount of sodium selenite and sodium selenate (Shanghai Reagent Factory, Shanghai, China) in bidistilled deionized water, respectively. Working solutions were prepared daily by appropriate dilution of the stock solutions. APDC solution was prepared by dissolving proper amount of APDC (Shanghai Reagent Factory, China) in 1-undecanol (Shanghai Reagent Factory, China). All glass and polypropylene wares were kept in 2.0 mol L^{-1} HNO_3 solution for at least one night, and then rinsed with 0.1 mol L^{-1} HNO_3 solution and subsequently with bidistilled deionized water.

2.2. Apparatus

An X-7 ICP-MS system (Thermo Elemental Corporation, USA), equipped with a modified commercially available WF-4C graphite

furnace (Beijing Second Optics, China) as an electrothermal vapourizer, was used for the determination of analytes. The operation parameters of ICP-MS were optimized with a concentric glass nebulizer prior to connection with ETV device. Pyrolytic graphite tube was used throughout this work. The working conditions of ETV-ICP-MS were summarized in Table S-1. The pH value of solution was controlled with a pH metre (Thermo Orion Corporation, USA) supplied with a combined electrode. An Ethos T microwave digestion device (Milestone, Italy) was used for sample digestion.

2.3. Sample pretreatment

For the determination of total Se in tea leaves, an accurately weighed sample portion of 0.1000 g (Se-rich green tea leaves obtained from Enshi, Hubei, China) was mixed with 4.0 mL concentrated HNO_3 and 2.0 mL H_2O_2 in a Teflon pressure vessel. The vessel was closed and left to stand overnight. The vessel was then placed into a microwave oven. After that, the samples were digested in the microwave oven at 180°C for 15 min . After cooling, the obtained solution was heated to near dryness. The residues were dissolved with 0.1 mol L^{-1} HNO_3 solution, and then diluted to the desired volume with bidistilled deionized water.

Tea infusion was prepared by a conventional method (generally, infuse tea three times). 2.000 g of dried tea leaves was placed into a 100 mL beaker, and then soaked with 20 mL of boiling bidistilled deionized water (95°C) for 5 min . After cooling, the solution was transferred into polypropylene beaker. The residues were re-leached two times, following the former procedure. The three combined extracts were mixed for the future use.

For sample preparation of suspended and soluble Se, a desired volume of tea infusion was taken, and then filtered through a $0.25 \mu\text{m}$ membrane filter. The insoluble residues attached to the membrane were carefully rinsed down with bidistilled deionized water. The insoluble residues and filtrate were digested by the method mentioned above for the determination of total amount of suspended and soluble Se in tea infusion, respectively.

The filtrate obtained through a $0.25 \mu\text{m}$ membrane filter was also used for the direct determination of Se(IV) without digestion. To obtain the content of Se(VI), the filtrate was heated in a boiling water bath for 20 min after the addition of 5.0 mol L^{-1} HCl to reduce Se(VI) into Se(IV) (Sun et al., 2013). The obtained solution was used for the determination of the sum of Se(VI) and Se(IV). The content of Se(VI) was calculated by subtracting Se(IV) from the sum. The content of organic Se was achieved from the difference between soluble Se and sum of Se(VI) and Se(IV). The blanks were exactly prepared in the same way.

2.4. SFODME extraction

SFODME device used in this work for extraction of analytes was similar to that described in literature (Zanjani, Yamini, Shariati, & Jonsson, 2007). The sample solution containing analytes was adjusted to the desired pH values using diluted HNO_3 solution. Then 10 mL of resulting solution was transferred into an 11 mL vial, and a stir bar and $20 \mu\text{L}$ of APDC in 1-dodecanol were added. The magnetic stirrer was turned on, and the solution was stirred for a fixed time. In this step, analytes react with APDC to form hydrophobic complexes, and were extracted into 1-undecanol. After the extraction process was out, the sample vial was transferred into an ice bath until organic solvent was solidified. The solidified solvent was then transferred into a conical vial where it melted immediately at room temperature. The extract was diluted to $100 \mu\text{L}$ with tetrahydrofuran (THF). Finally, $10 \mu\text{L}$ of the extract was injected into the graphite tube for ETV-ICP-MS determination.

2.5. ETV–ICP–MS procedure

After ETV unit had been connected to ICP–MS, 10 μL of analytes was injected into graphite furnace. During the drying and charring process, the dosing hole of graphite furnace was kept open to remove water and organic vapour. Then it was sealed with a graphite probe in the range of 5–10 s prior to vapourisation step, the vapourized analytes were swept into the plasma excitation source by a carrier gas, and the peak-hop transient mode for data acquisition was used for the detection of the analytes. The recoveries of the analytes were calculated from the ratio of the concentration found by this method to that of the initial sample.

3. Results and discussion

3.1. Investigation on vapourisation behaviour of Se(IV) and Se(VI)

As a powerful chelating reagent, APDC can react with Se(IV) to form stable chelates (Kamada, Shiraishi, & Yamamoto, 1978). This fact encourages us to try to develop a method for Se speciation by low temperature ETV–ICP–MS with APDC as chemical modifier. Fig. 1 shows the typical signal profiles of Se(IV) and Se(VI) with APDC. It can be seen from Fig. 1 that there is an intensive and sharp signal profile for Se(IV) in the presence of APDC (b). On the contrary, no signal was recorded for Se(VI) with APDC (c). In addition, a blank signal of corresponding solution was not detected in this experiment (a). These results indicated that in the presence of APDC, the volatile and thermally stable Se(IV)–APDC complex can be formed, and then vapourized and transported from graphite furnace to ICP. Thus, APDC was used as a suitable chemical modifier in this work.

3.2. Separation of Se(IV) and Se(VI) with SFODME

In order to separate Se(IV) from Se(VI) by SFODME, the selection of chelating reagent and extraction solvent is of great importance. Fig. 2 shows signal profiles of Se(IV) and Se(VI) with SFODME extraction. It can be seen from Fig. 2 that the signal of Se(IV) can hardly be detected in the absence of APDC–1-dodecanol (Fig. 2a). However, a strong signal (Fig. 2b) was detected after APDC–1-dodecanol extraction of Se(IV) solution containing the same concentration of Se(VI). Fig. 2c is the signal profile obtained from the mixture solution mentioned above after reducing Se(VI) to Se(IV). It is worth noting that the signal intensity of Fig. 2b is about 50%

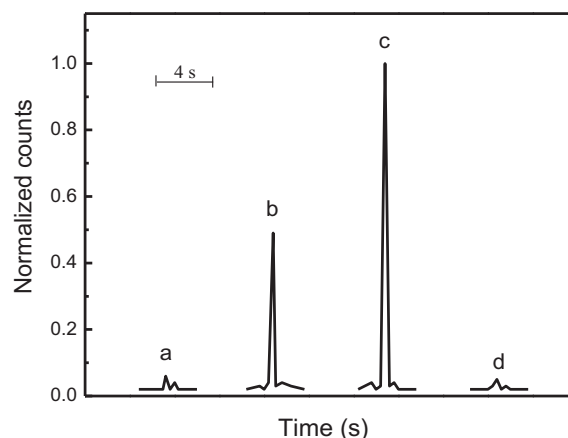


Fig. 2. Separation of Se(IV) and Se(VI) with SFODME extraction. (a) Se(IV) solution; (b) Se(IV) solution containing the same concentration of Se(VI) with APDC–1-undecanol extraction; (c) 1.0 ng mL^{-1} Se(IV) + 1.0 ng mL^{-1} Se(VI) with APDC–1-undecanol extraction after reduction; (d) Se(VI) solution. Se(IV) and Se(VI): 1.0 ng mL^{-1} ; vapourisation temperature: 1300 $^{\circ}\text{C}$.

of that of Fig. 2c. In addition, the signal of Se(VI) was not observed without APDC–1-dodecanol (Fig. 2d).

The facts mentioned above showed that Se(IV) and APDC form a complex and can be extracted into the organic phase of 1-dodecanol, whereas Se(VI) can not form APDC complex at the same conditions, and it can be not extracted by 1-dodecanol. Thus, APDC and 1-dodecanol were used as both a chelating reagent and an extraction solvent for the separation of Se(IV) from Se(VI) for the subsequent experiment, respectively.

3.3. Effect of pH

In this work, the pH value plays an essential role in metal–APDC complex formation and subsequent extraction with 1-dodecanol. Thus, the effects of sample pH on the signal intensity of Se(VI) and Se(IV) were investigated in the pH range of 1.0–7.0. As shown in Fig. 3, the maximal signal intensity of Se(IV) was obtained in the pH range of 2.0–5.0, whereas no signal intensity of Se(VI) was observed in the same pH range. Based on these results, a pH of 4.0 was used for SFODME of Se(IV).

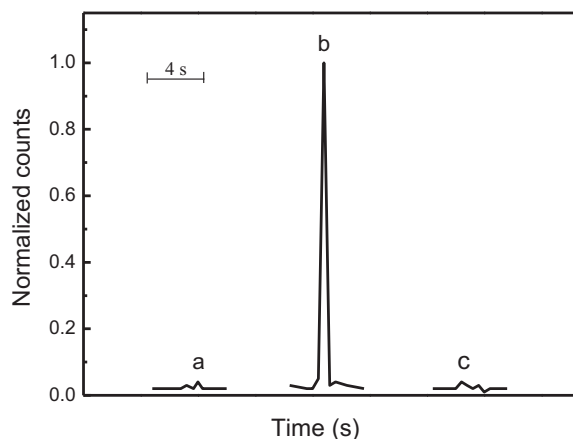


Fig. 1. Signal profiles for Se(IV) and Se(VI) with APDC. (a) APDC in 1-undecanol and THF; (b) Se(IV) with APDC in 1-undecanol and THF; (c) Se(VI) with APDC in 1-undecanol and THF. Se(IV) and Se(VI): 1.0 ng mL^{-1} ; vapourisation temperature: 1300 $^{\circ}\text{C}$.

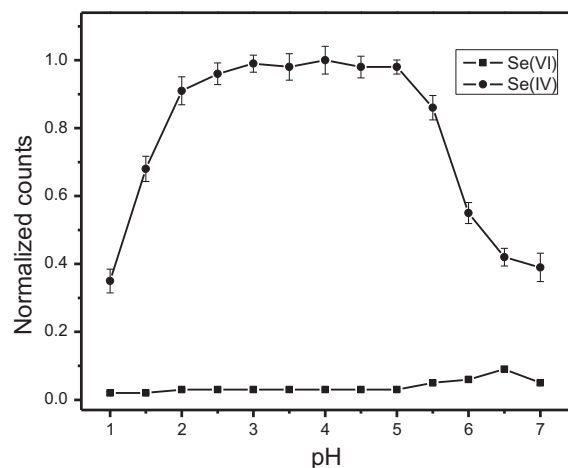


Fig. 3. Effect of pH on signal intensity of Se(IV) and Se(VI). Se(IV) and Se(VI): 1.0 ng mL^{-1} .

3.4. Effect of APDC concentration

The effect of APDC concentration on the signal intensity of analyte was studied by preparing Se(IV) solutions containing APDC in the concentration range of 0.1×10^{-2} – 4.0×10^{-2} mol L⁻¹. The results showed that the signal intensity of analyte increased with the increase of APDC concentration from 0.1×10^{-2} to 1.5×10^{-2} mol L⁻¹, and then kept nearly constant when the amount of APDC had changed between 1.5×10^{-2} mol L⁻¹ and 4.0×10^{-2} mol L⁻¹. Taking into account that APDC could be consumed by interfering ions, the concentration of 2.0×10^{-2} mol L⁻¹ APDC was used in the sequent determination.

3.5. Influence of extraction time

In order to obtain a good extraction efficiency and analysis speed, the effect of extraction time on signal intensity of Se(IV) was investigated in the time range of 10–50 min. The results showed that the signal intensity of Se(IV) firstly increased with the increase of extraction time, and then reached a plateau after 25 min. Therefore, an extraction time of 30 min was selected for further study.

3.6. Influence of extraction temperature

In SFODME, temperature has an important effect on both phase equilibrium and mass transfer. The results showed that the signal intensity of Se(IV) increased by rising the sample temperature up to 40 °C. However, the signal intensity of Se(IV) decreased with the increase of temperature higher than 50 °C. This result may be due to the decrease of distribution ratio of Se(IV)–APDC complex at the higher temperature. Thus, the sample temperature was adjusted to 45 °C in the present work.

3.7. Optimization of stirring rate

To enhance the mass-transfer of analyte from aqueous to organic phase and reduce the extraction time, the effect of stirring rate on extraction was studied in the range of 400–1200 rpm. The results displayed that the signal intensity of the analyte increased rapidly with increasing the stirring rate from 400 to 800 rpm. However, the increasing rate of signal intensity decreased obviously when the stirring rate exceeded 1000 rpm owing to the loss of floating solvent drop. Therefore, a stirring rate of 900 rpm was employed for analysis.

3.8. Effect of sample solution volume

Sample solution volume is an important parameter evaluating preconcentration capability of method. On one hand, an increase in the volume ratio of aqueous to organic phase can result in a significant increase of enrichment factor. On the other hand, an increase in sample volume may lead to a decrease in extraction efficiency in a given time. Accordingly, the effect of sample solution volume on the extraction of 0.1 ng of Se(IV) in different sample volume ranging from 2.0 to 30 mL was investigated. The results indicated that when the sample volumes were lower than 15 mL, the signal intensity of analyte was maximal and remained constant, whereas the decrease of the signal intensity was observed with the continuous increase of sample volume. Considering two factors of analysis time and enrichment fold, 10 mL sample volume was used for the analysis of real samples. As described in previous section, the analyte was quantitatively extracted using the volume of 20 μ L solvent drop. Thus, an enrichment factor of 500 was obtained for Se(IV) in this work.

3.9. Interference study

The effect of potential interference ions in food and agricultural samples on the extraction and determination of analyte was investigated. In this experiment, 10 mL solution of 1.0 ng mL⁻¹ Se(IV) containing the various amounts of interfering ions was tested according to this procedure. The tolerance limit of coexisting ion is defined as the largest amount making variation of less than 10% error in the recovery of analyte (Table S-2). Results in Table S-2 could be explained by the following facts. This method has high tolerance limits to alkaline, alkaline earth metal ions, and anions since they have negligible interaction with APDC. On the contrary, Se(IV) can form stable and hydrophobic Se(IV)–APDC complex, which can be extracted by 1-dodecanol. It is worth noting that the tolerance limits of Al³⁺, Zn²⁺, Cu²⁺ and Fe³⁺ were not as high as other interference ions, mainly because they can react with APDC, and then enter the competitive reaction with Se(IV). Therefore, the excessive chelating reagent (2.0×10^{-2} mol L⁻¹) was used for this experiment. In addition, the concentrations of interference ions were generally at trace levels in food and agricultural samples. Thus, this method may be applicable to analysis of Se speciation in tea sample.

3.10. Optimization of ETV conditions

In order to obtain good sensitivity and accuracy, ETV temperature program was optimized. During drying step, a drying temperature of 100 °C and a drying time of 10 s were used for removal of water vapour. The experimental results showed that the signal intensity of Se(IV) decreased obviously with the increase of charring temperature higher than 300 °C due to the thermal decomposition of Se(IV)–APDC complex. Thus, a charring temperature of 200 °C and a charring time of 30 s were used for in-situ removal of extraction solvent from furnace.

The effect of vapourisation temperature on the signal intensity of Se(IV) was studied at optimum vapourisation time of 4 s. It can be seen from Fig. S-1 that the signal of Se(IV) could only detected at

Table 1
Analytical results of analytes in tea infusion.

Selenium speciation	Determined ^a (ng mL ⁻¹)	Se(IV) added (ng mL ⁻¹)	Se(IV) found ^a (ng mL ⁻¹)	Recovery (%)
Total	14.3 ± 0.89	5.0	4.73 ± 0.21	94.6
Suspended	0.35 ± 0.034	5.0	5.10 ± 0.35	102
Soluble	13.7 ± 0.63	5.0	4.89 ± 0.28	97.8
Organic	11.5 ± 0.48	5.0	4.61 ± 0.31	92.2
Inorganic	2.18 ± 0.19	5.0	5.25 ± 0.46	105
Se(IV)	2.08 ± 0.15	5.0	4.97 ± 0.38	99.4
Se(VI)	0.10 ± 0.012	5.0	5.30 ± 0.42	106

^a Mean value ± standard deviation, *n* = 5.

Table 2
Distribution of analytes in tea leaves and tea infusion.

Sample	Selenium	Determined (μ g g ⁻¹)	Percentage (%)
Tea leaves	Tea leaves	2.35 ± 0.15	–
	Tea soup	0.43 ± 0.027	18.3
	Tea residue	1.86 ± 0.11	79.1
Tea infusion	Total	0.43 ± 0.027	–
	Suspended	0.011 ± 0.001	2.44
	Soluble	0.41 ± 0.019	95.3
	Organic	0.34 ± 0.014	80.2
	Inorganic	0.065 ± 0.006	15.1
	Se(IV)	0.062 ± 0.005	14.4
	Se(VI)	0.003 ± 0.0004	0.7

Mean value ± standard deviation, *n* = 5.

Table 3

Analytical results and recoveries of analytes in certified reference material of tea leaves.

Added ($\mu\text{g g}^{-1}$)		Found ^a ($\mu\text{g g}^{-1}$)		Total Se	Certified ($\mu\text{g g}^{-1}$)	Recovery (%)	
Se(IV)	Se(VI)	Se(IV)	Se(VI)			Se(IV)	Se(VI)
0	0	0.081 \pm 0.007	Nd ^c	0.081 \pm 0.007	0.072 ^b	–	–
0.1	0	0.186 \pm 0.015	Nd ^c	0.186 \pm 0.015	–	105	–
0	0.1	0.075 \pm 0.008	0.103 \pm 0.010	0.178 \pm 0.013	–	–	103
0.2	0.2	0.274 \pm 0.019	0.182 \pm 0.016	0.456 \pm 0.029	–	96.5	91.0
0.5	0.5	0.572 \pm 0.035	0.474 \pm 0.039	1.046 \pm 0.054	–	98.2	101

^a Mean value \pm standard deviation, $n = 5$.^b Reference value.^c Nd: not detection.

about 1000 °C without APDC, and no signal plateau was obtained by increasing the vapourisation temperature to 2000 °C. However, the situation was changed greatly after APDC was added. A weak signal for Se(IV) appeared at 350 °C. The maximum signals were obtained at 1000 °C for Se(IV), and then the signals were kept constant with the further increase of vapourisation temperature to 1600 °C. In addition, the signal intensity of Se(IV) with APDC is much more intense than that without APDC. Therefore, a vapourisation temperature of 1300 °C was used in this work.

3.11. Analytical performance

Under the optimized conditions, the important parameters of this method, including precision, linear range of calibration curve and detection limits, were validated. The detection limits of Se(IV) and Se(VI), based on three-times the standard deviation of blank solution, were 0.19 pg mL^{-1} and 0.26 pg mL^{-1} , respectively, with an enrichment factor of 500-fold. The linear range of this method was found from 0.01 to 10 ng mL^{-1} with correlation coefficient better than 0.9957. The relative standard deviations were 4.7% and 5.4% for Se(IV) and Se(VI) ($c = 0.1 \text{ ng mL}^{-1}$, $n = 9$), respectively. The comparison of the analytical performances in this work with those reported in the literatures was given in Table S-3. As can be seen, this method offers higher enrichment factor and lower detection limits, but the relative standard deviations are comparable to those reported in the literatures (Corinne, Olivier, & Martine, 2002; Xia et al., 2006; Zhang, Duan, He, Chen, & Hu, 2013; Zhao et al., 2011).

3.12. Sample analysis

To evaluate the feasibility and applicability of this method, Se species, including total, suspended, soluble, organic and inorganic Se as well as Se(IV) and Se(VI), were determined in Se-rich tea infusion (Table 1). The reliability was checked by spiking experiments with satisfactory recoveries.

Table 2 gives the distribution of Se in tea leaves and tea infusion. The total Se content (2.35 g g^{-1}) obtained by this method is higher than its average value (1.5 g g^{-1}) in Se-rich tea leaves reported by the literature (Gong, Ouyang, & Cai, 1996). In addition, it can be seen in Table 2 that the total concentration of Se in the tea residues is much higher than that in the tea infusion after extraction three times, the content of organic Se is much higher than that of inorganic Se in the tea infusion, and the content of Se(IV) is much higher than that of Se(VI) in the tea infusion. These conclusions are consistent with those of the literature (Gong et al., 1996).

In order to validate the accuracy of this method, a certified reference material of tea leaves (GBW 07605) was analyzed by SFODME-ETV-ICP-MS. It can be seen from Table 3 that the analytical results of this method are in agreement with certified value. The recoveries are in the range of 91.0–105%.

4. Conclusions

In conclusion, a novel method was developed for Se species and distribution in Se-rich tea leaves and tea infusion by SFODME combined with ETV-ICP-MS, including total, suspended, soluble, organic and inorganic Se as well as Se(IV) and Se(VI). The analytical results of Se-rich tea and its infusion showed that the minority of Se can be transferred into tea infusion after extraction three times, Se exists mainly as organic Se with low toxicity in the tea infusion, and content of Se(IV) is very much higher than that of Se(VI) in the infusion. In addition, this method has also the features of high enrichment factor, low detection limit, simple operation, good precision and accuracy. Although the number of samples is limited in this work, the present study may provide a potential technique for Se speciation and its distribution in different food, biological and agricultural products.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.foodchem.2014.07.147>.

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