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Preliminary results on the determination of ultratrace amounts of cadmium in tea samples using a flow injection on-line solid phase extraction separation and preconcentration technique to couple with a sequential injection hydride generation atomic fluorescence spectrometry

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Abstract

In this work, a method was developed for determination of ultra-trace levels of Cd in tea samples by atomic fluorescence spectrometry (AFS). A flow injection solid phase extraction (FI-SPE) separation and preconcentration technique, to on-line couple with a sequential injection hydride generation (SI-HG) technique is employed in this study. Cd was preconcentrated on the SPE column, which was made from a neutral extractant named Cyanex 923, while other matrix ions or interfering ions were completely or mostly separated off. Conditions for the SPE separation and preconcentration, as well as conditions for the HG technique, were studied. Due to the separation of interfering elements, Cd hydride generation efficiency could be greatly enhanced with the sole presence of Co^{2+} with a concentration of 200 $\mu g\,L^{-1}$, which is much lower than those in other works previously reported. Interferences on both the Cd separation and preconcentration, and Cd hydride generation (HG) were investigated; it showed that both the separation and preconcentration system, and the HG system had a strong anti-interference ability. The SPE column could be repeatedly used at least 400 times, a R.S.D. of 0.97% was obtained for 6 measurements of Cd with 0.2 $\mu g\,L^{-1}$ and a correlation coefficiency of 1.0000 was obtained for the measurement of a series of solutions with Cd concentrations from 0.1 to 2 $\mu g\,L^{-1}$. The method has a low detection limit of 10.8 $ng\,L^{-1}$ for a 25 mL solution and was successfully validated by using two tea standard reference materials (GBW08513 and GBW07605).

Keywords: Cd; Tea sample; AFS; On-line preconcentration and separation; Hydride generation; Cyanex 923

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1. Introduction

Cadmium is considered to be of as highly toxic as ‘probably carcinogenic for humans’ [1]. Though naturally present at very low levels in common biological and environmental matrices related tightly with human living, its strong tendency to accumulate in organism makes it one of the most dangerous metals to humans. For tea products, the strict control of Cd content that is critical, results in a number of analytical methods being established for this purpose [2,3].

The vapor generation technique has attracted great attention for Cd determination since the early papers by D′Ulivo and Chen [4]. However, a literature survey has revealed that compared with other vapor generation elements such as As and Hg, Cd was much less studied in this aspect, only about 20 more studies being searched out up to 2003 [5]. And some of these literature data were much inconsistency or even contradictory. The reason was that Cd vapor generation required very critical conditions and was subjected to severe

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interferences; it was found that Cd vapor could only be generated over a very narrow acidic range (0.1–0.3 M HCl, for example), and could be severely depressed by Au, Ag, Cu, Bi, Ni, Pb and some other transition elements with levels low to μg L^{-1} [6,7]. Thus, most applications of the vapor generation technique for Cd determination were limited on samples of simple matrices such as water samples [8–10].

When relatively more complex samples, such as sewage or biological samples, were analyzed, a masking reagent, such as KCN [6,11] or thiourea [7,12], was used for eliminating or alleviating the severe interferences. However, KCN was such a toxic reagent that its availability was much inconvenient and great care should be taken when using it in experiments, while the masking effectiveness of thiourea was much limited [5]. On-line introducing in a separation technique for interfering element removal is undoubtedly an ideal choice for interference elimination. Much strangely, within our knowledge, there are rare studies on on-line combining separation techniques with the Cd vapor generation technique up to now. The reason may be that it is difficult to have optimal conditions, which are suitable for both separation technique and vapor generation, especially the limitation of the acidity for vapor generation.

Cyanex 923 (TRPO), a mixture of straight-chain alkylated phosphine oxides, mainly (92.4%) with normal hexyl and octyl groups, is a new neutral extractant appeared in the last decade mainly for hydrometallurgical purpose. It has several excellent properties including little tendency to hydrolysis, low solubility and high stability in both acid and basic solutions. Applications of Cyanex 923 for extraction of Cd have been only studied in L–L (liquid–liquid) extraction mode [13]. Therein, it was concluded that (1) Cyanex 923 could effectively extract mg L^{-1} levels of Cd in 2 M HCl medium as the form of $CdCl_2$, while co-existing elements such as Co, Ni, Pb, Cu were not extracted; (2) 0.01 M HCl as a back-extractant could completely recover Cd; and (3) 1 M H_2SO_4 could be used to renew the extractant. These valuable properties suggest that Cyanex 923 is promising for use in a renewable solid phase extraction (SPE) column for Cd preconcentration and/or separation.

In most works, the Cd HG technique was carried out in an HCl system. In this work, an investigation was made on incorporating a separation and preconcentration technique into the Cd hydride generation technique, which was carried out in a H_2SO_4 system, for on-line interference element removal, avoiding the use of masking reagents. A SPE min-column made from Cyanex 923 was used for the on-line separation and preconcentration purpose. Since the FI system was more flexible in operation and was not limited by sample volumes, while the SI system was more stable in solution transferring, the separation and preconcentration was performed in a FI system while the Cd vapor generation was performed in a SI system. The feasibility of the method was evaluated by analyzing two tea standard reference materials containing tens of ng g^{-1} levels of Cd and a good agreement between the found and certified values was obtained.

2. Experimental

2.1. Instrumentation

An AFS-920 atomic fluorescence spectrometer (Beijing Titan Instrumentals Co. Ltd., Beijing, China) equipped with a sequential injection hydride generation sampling system SIS-100 (Beijing Titan Instrumentals Co. Ltd.) was used for Cd measurement. The instrumental parameters were in Table 1. A FIA-3110 flow injection system (Beijing Titan Instrumentals Co. Ltd.) with a 12-channel valve and two pumps was adopted for Cd separation and preconcentration. Fig. 1 shows the schematic diagram of the manifold for on-line separation and preconcentration in this study. A microwave-assisted digestion oven (Xin Tuo Microwave Decomposition and Testing Technology Co. Ltd., Shanghai, China) was used for sample pretreatment. And an ICP-MS was used for off-line determination of Cd to obtain optimizing conditions for the SPE minicolumn separation and preconcentration. Operation conditions for the ICP-MS were the same as elsewhere [14].

2.2. Reagents

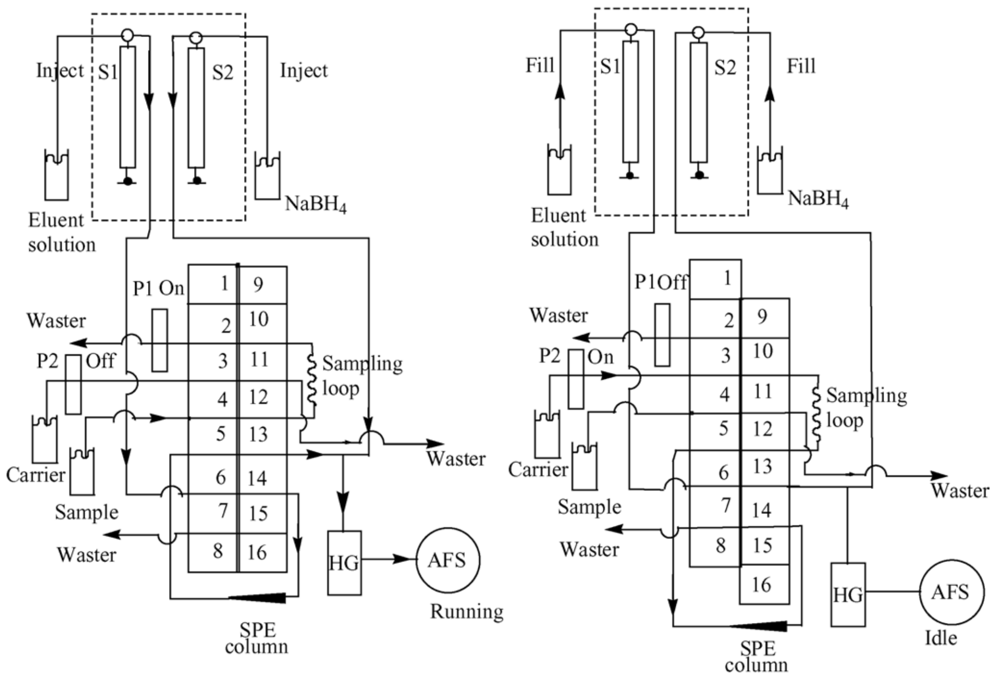
All reagents used were of highest available purity, and of at least analytical grade. Water was de-ionized and then sub-boiling distilled. 5% (v/v) HCl used for carrier solution and dilution medium and 25% (v/v) HCl used in sample treatment was prepared from high purity grade and was further purified by streaming through a SPE column at 6 mL min^{-1}. Both HNO_3 and H_2SO_4 were of high purity grade. The Cd stock solution of 1.000 g L^{-1} was prepared by dissolving 1.1423 g of CdO (Merk) in 20 mL of 5 mol L^{-1} HCl, and diluting to 1000 mL with water. Working standard solutions of Cd were prepared by stepwise dilution of the stock solution with 5% HCl just before use.

Cyanex 923 used to prepare the SPE column was supplied by Cytec (Canada). It was dissolved in heptane (Hongxing Chemical Plant, Beijing) to obtain a 30% (v/v) solution and the solution was purified as elsewhere [15]. Silanized PTFE powder of 60-mesh size was purchased from The First Chemical Plant (Shanghai, China).

The $NaBH_4$ solutions were daily prepared by dissolving proper amounts of this reagent (Tianjin Institute of Chemical

Table 1
Parameters of the HG-AFS instrument

PTM voltage (V)	300
Atomizer temperature (°C)	200
Atomizer height (mm)	16
Main lamp current (mA)	80
Lamp ancillary electrode current (mA)	30
Flow rate of carrier gas (Ar) (mL min^{-1})	400
Flow rate of shield gas (Ar) (mL min^{-1})	800
Read mode	Peak area
Gas–liquid separator (quartz) volume (mL)	About 30



(1)Sampling and desorption

(2)Absorption and rinsing

Fig. 1. Schematic diagram of the manifold for on-line FI-SPE–SI-HG–AFS. P1, pump 1; P2, pump 2; S1, syringe 1; S2, syringe 2; HG, hydride generation gas–liquid separator.

Reagent, Tianjin) in 0.5% (m/v) NaOH solution. The ascorbic acid solution of 10 g L^{-1} was prepared by dissolving 0.5000 g ascorbic acid (Beijing Chemicals) in 50 mL of 5% HCl and was purified like that of the 5% HCl solution. An amount of 50 g L^{-1} of thiourea solution was prepared by directly dissolving the proper amount of thiourea (Beijing Chemicals) in water. An amount of 100 mg L^{-1} of Co stock solution was prepared by dissolving a precisely weighted amount of high pure Co metal (Merk) in concentrated HNO_3 and the excess of HNO_3 was removed to obtain a final solution containing 1% (v/v) HNO_3.

2.3. SPE resin and minicolumn preparation

The preparation of the SPE resin was simple: some amounts of PTFE powder, some volumes of the 30% Cyanex 923 solution and some volumes of heptane were well mixed in a glass beak and then heptane as the solvent was completely removed by heating with a hair-drier. The obtained resin by this way should contain a Cyanex 923 content of about 20% (w/w).

To prepare the SPE minicolumn, a proper amount of the SPE resin was packed into a sampling tip of a pipettor with a total volume of about 100 μL by dry packing method. The resulted conical minicolumn was about 1.5 mm inter-diameter in one-end, 5 mm in another-end and about 2.5 cm long. Both ends of the column were placed with some quartz cotton to prevent losing of the resin.

2.4. Sample pretreatment

Approximately 0.1000 g of the tea sample was accurately weighted into the microwave digestion vessel and 4 mL concentrated HNO_3 was added. The vessel was sealed and microwave digested according to the programme recommended by the manufacturer. After cooling, the vessel was open and heated at 180 °C to dryness to completely removing HNO_3. Five milliliters of 25% HCl was then added, followed by gentle heating until a clear solution was obtained. The solution was transferred into a 25 mL volume of flask and was adjusted to volume with water.

2.5. Analytical procedure

To develop the FI-SPE–SI-HG–AFS system, a flow injection system with two pumps was connected with a two-syringe sequential injection system through a 12-channel rotary valve. The SI system was already connected with a gas–liquid separator, through a three-way commutation valve, forming the HG system. When running, the generated Cd hydride was carried by Ar gas from the gas–liquid separator to the AFS for measurement. In the FI system, a loop about 1.9 mL was assembled on the rotating valve for volume-based sampling. The SPE mini-column was also assembled on this valve, for Cd preconcentration, and matrix and interfering ions separation.

The analytical procedure is described as follows: At step (1), the rotary valve was at Inject position; Pump P1 was off, P2 was on, pumping the sample solution into the sampling loop at 12 mL min^{-1}; at the same time, both the two syringes were in movement, S1 injected a 2 mL volume of elution solution containing 200 μg L^{-1} Co and 1% (v/v) H_2SO_4, through the SPE column at 6 mL min^{-1} and S2 injected 2.6 mL of 5% $NaBH_4$ solution at 8.4 mL min^{-1}, both to the gas–liquid separator to produce Cd hydride; And the AFS at this step was in running status and the Cd hydride brought in by Ar gas from the gas–liquid separator was measured. At step (2), the rotary valve was at Fill position; Pump P1 was activated, pushing the sample solution onto the SPE column for Cd absorption with the 5% (v/v) HCl carrier solution at a flow rate of 6 mL min^{-1}, while P2 was off; S1 and S2 were loaded with solutions and were ready for injection; and the AFS this time was in standby status. The schematic diagram for the whole procedure can be seen in Fig. 1.

3. Results and discussion

3.1. Study of AFS parameters

3.1.1. Instrumental parameters for AFS

Three main parameters, including the main lamp current, the flow rate of carrier gas, and the atomizer height, influence the analytical performance greatly and hence must be optimized.

Increasing the main lamp current resulted in an increase in signal intensity, however, the signal noise also increased, and working at high lamp current would be dangerous for shortening the lifetime of the lamp. Changing the main current lamp from 40 to 100 mA, it was observed that the ratio of signal to noise reached the highest at 80 mA. Thus an 80 mA of main lamp current was used.

The flow rate of the carrier gas was supposed to influence the Cd signal intensity by influencing the transportation of Cd hydride and its residue in the atomizer. When changing the flow rate from 100 to 400 mL min^{-1}, the Cd signal intensity increased rapidly. Though an apparent increase was also observed when the flow rate increased from 400 to 500 mL min^{-1}, the shape of the Cd signal deteriorated badly. Thus, to achieve a stable signal, the carrier gas flow rate was finally set at 400 mL min^{-1}.

The atomizer height imposed great influence on the signal noise, though the signal intensity changes slightly, when the atomizer height was over 8 mm. The noise signal intensity decreased sharply from around 700 to around 200 and then kept constant, when the atomizer height increased from 8 to 16 mm. Higher than 16 mm would result in unstable signals. So 16 mm was chosen as the optimal atomizer height.

The atomizer temperature was fixed at 200 °C by the manufacture, so it was not able to be changed. Other parameters, such as the lamp ancillary electrode current and the shield gas flow rate, were also optimized. It was found that the lamp ancillary electrode current at 30 mA and the shield gas flow rate at 800 mL min^{-1} were optimal.

3.1.2. Acidity effects on Cd HG

HNO_3 has ever been used as the acidic medium, most of the works employed HCl. However, there were almost rare reports on the use of H_2SO_4 as the acidic medium. In both HNO_3 and HCl systems, acidity of the solution was a very important parameter that has great influence on the hydride generation, and even critic. In this study, the use of H_2SO_4 as the acidic medium and its concentration effects on Cd hydride generation was investigated. The use of H_2SO_4 instead of HNO_3 was based on the consideration that H_2SO_4 could act as a more effective back-extractant in the following SPE system, as indicated elsewhere [13]. For which the reason was deduced to be that H_2SO_4 could be more strongly extracted by Cyanex 923 than HNO_3, as a result of extraction competition, extracted metal ions could be more easily back-extracted by H_2SO_4. HCl could not be use as the acid medium because of the formation of Cd chloride complexes, which were the absorption forms of Cd by the SPE column. As can be seen in Fig. 2, Cd hydride can also be generated in H_2SO_4 system, and the concentration of H_2SO_4 imposed similar influence with those in HNO_3 and HCl systems. Namely, the concentration of H_2SO_4 was also critic; about 1% (v/v) H_2SO_4 was the most suitable acidity.

3.1.3. Influence of $NaBH_4$ concentrations on Cd HG

The concentration of $NaBH_4$ was another parameter of very importance for Cd hydride generation. In the H_2SO_4 system, at the optimal acidity, when $NaBH_4$ solution concentrations were increased from 1% to 4% (m/v), the Cd signal intensity increased sharply (in Fig. 3). This increment slowed down when $NaBH_4$ concentrations were higher than 5%. On the other hand, higher $NaBH_4$ concentrations than 5% (m/v)

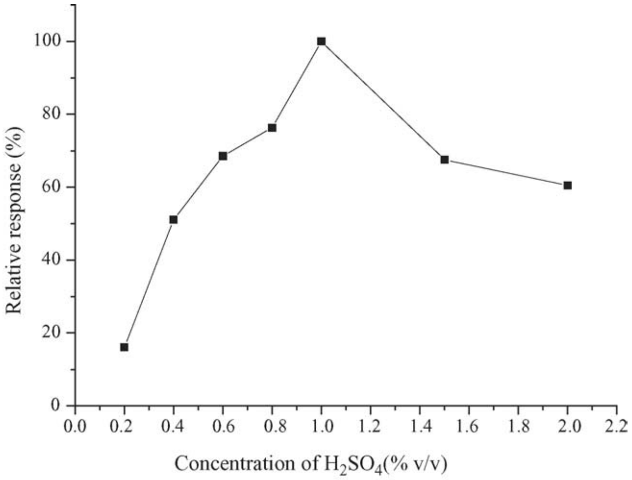


Fig. 2. Effect of H_2SO_4 concentration on Cd HG. Reductant solution, 5% $NaBH_4$; Cd solution, 1 μg L^{-1}, containing 200 μg L^{-1}of Co; injection rate of carrier solution, 6 mL min^{-1}; and injection rate of reductant solution, 7.8 mL min^{-1}.

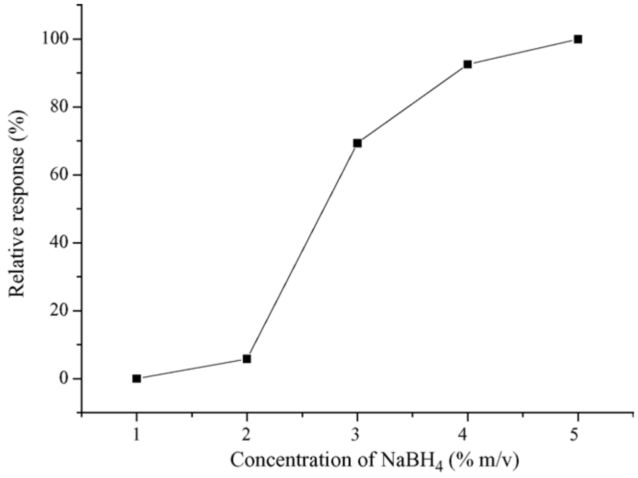


Fig. 3. Effect of $NaBH_4$ concentrations on Cd HG. Carrier solution, 1% (v/v) H_2SO_4; Cd solution, 1 $\mu g\,L^{-1}$ in 1% (v/v) H_2SO_4, containing 200 $\mu g\,L^{-1}$of Co; injection rate of carrier solution, 6 mL min^{-1}; and injection rate of reductant solution, 7.8 mL min^{-1}.

would result in a violent reaction in the gas–liquid separator and eventually lead to an unstable signal. Thus 5% (m/v) of $NaBH_4$ solution was used as the optimal reductant solution.

3.2. *Cd hydride generation efficiency enhancement*

In previous works, it was widely reported that, in an HCl or HNO_3 system, thiourea together with Co, acting as a catalyzer that would enhance the Cd hydride generation efficiency to a great extent [6,7]. In this study, since a different reaction system was chosen, it was necessary to re-investigate the roles of thiourea and Co on the Cd hydride generation efficiency enhancement. Much different from HCl or HNO_3 system, the presence of thiourea hardly gave an enhancement effect on Cd hydride generation; though the presence of Co also significantly enhanced the Cd hydride generation efficiency, however, a maximum enhancement was reached at 200 ng L^{-1} of Co, compared to those of 1 $\mu g\,L^{-1}$ in other systems [6,7]. Since thiourea had no effect on Cd signal enhancement, it was therefore not necessary to introduce thiourea in following experiments.

3.3. *Study of SPE parameters*

The following experiments were carried out with off–line determination of Cd by ICP-MS.

3.3.1. *Effects of HCl concentration on Cd absorption*

Since Cd was extracted as a neutral complex as $CdCl_2$ in HCl medium by the neutral extractant Cyanex 923 and the concentration of HCl determines the form of $[CdCl_x]^{2-x}$, consequently, the concentration of HCl would affect the absorption efficiency. Over the HCl concentration range from 5% to 25% (v/v), Cd was completely absorbed. This result indicates an enhanced Cd absorption efficiency in the SPE mode compared with in the L–L extraction mode, as revealed in Bina's work [13], where an extraction efficiency lower than 10% was obtained at 5% (v/v) HCl. Five percentage (v/v) of HCl was then set as the optimal concentration, since higher concentrations potentially caused higher blank values.

3.3.2. *Effects of sample solution loading rate on Cd absorption*

The absorption of Cd by the SPE column was a very rapid kinetic process. At 5% (v/v) HCl, when the sample flow rate is varied from 2 mL min^{-1} to 10 mL min^{-1}, the absorption efficiency for 10 $\mu g\,L^{-1}$ of Cd kept constant at almost 100%. However, flow rates higher than 6 mL min^{-1} would produce undesirable high backpressure on the column, while a lower flow rate prolong the analytical cycle. Accordingly, 6 mL min^{-1} of sample solution flow rate was chosen. At this flow rate, two solutions with 1 $\mu g\,L^{-1}$ of Cd and 100 $\mu g\,L^{-1}$ of Cd, respectively, were also tested, recoveries of Cd for both solutions were complete.

3.3.3. *Influence of concentration of H_2SO_4 as the elution solution on Cd desorption*

H_2SO_4 concentrations in the range of 0.1–4% (v/v) were tested for their desorption ability. Higher and lower concentrations were not considered, since the subsequent hydride generation required a narrow acidity range around 1% H_2SO_4, as mentioned above. Much fortunately, H_2SO_4 at concentrations over the whole selected range could function as a good desorption reagent. Complete desorption was achieved at all the experimented concentrations, which means that no subsequent on-line addition or dilution was needed to adjust the acidity to satisfy the optimal hydride generation conditions.

3.4. *Condition adjustment for on-line combination of the FI-SPE and SI-HG systems*

When on-line combining, the elution solution in the FI-SPE system was also the carrier solution in syringe 1 in the SI-HG system. The injection rate and volume of H_2SO_4 thus both influenced Cd desorption and hydride generation and therefore must be adjusted to achieve the best match between the two systems. Keeping other conditions unvaried, when the injection rate varied from 4 to 10 mL min^{-1}, the peak area of Cd signal changed little. A 6 mL min^{-1} of injection rate was finally used as a compromise between shortening the analytical time and avoiding high backpressure in the column. It was found that a 2 mL of injected volume of 1% (v/v) H_2SO_4 could both guarantee a full desorption of Cd and the completeness of Cd hydride generation. However, from a point of eliminating memory effect arisen from the solution transmitting tubes, a 3 mL of injected volume would be more preferable.

When the injection rate and volume of H_2SO_4 was adjusted, the injection rate and volume of $NaBH_4$ should be accordingly adjusted. It was found that the injection rate at

7.8 mL min^{-1} and the injected volume of 2.6 mL were the most suitable for a high and stable Cd fluorescence signal.

3.5. Interference studies

3.5.1. Interference on Cd absorption

Recovery tests were carried out for 10 μg L^{-1} of Cd in a mixture solution containing 1 g L^{-1} of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, $Fe^{2+}$and Al^{3+} and single solutions containing 0.1 g L^{-1} each of Ti^{4+}, Fe^{3+}, Pb^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Sn^{4+}, Mn^{2+} and Cr^{3+}, at least 10 mg L^{-1} each of $Zn^{2+}$and V^{5+} and 1 mg L^{-1} each of Mo^{6+} and Cr^{6+}. It can be concluded that the SPE system has a strong anti-interference ability. Though high level of Fe^{3+} do not affect the Cd absorption, it was observed that this ion could be also absorbed onto the column and not be easily eluted completely, judging from the color change of the column. In this case, the capability of the column might possibly decrease after a long time of analysis, due to the accumulation of Fe^{3+}. To avoid the absorption of Fe^{3+}, an effective way was to reduce Fe^{3+} to Fe^{2+}. The addition of several drops of 1% (m/v) ascorbic acid solution into the sample solution could be adopted for this purpose.

Co^{2+} was specially experimented. It was found that absolutely no absorption of this element happened both in 5% (v/v) HCl and 1% H_2SO_4, which enabled Co, acting as the catalyzer for Cd hydride generation, to be directly added into the 1% H_2SO_4 elution solution, avoiding complicating the FI manifold by adding an additional route to on-line introducing in Co.

3.5.2. Interference on Cd hydride generation

Transition elements were reported to severely depress Cd hydride generation. Among which Pb, Cu, Ni, Sn and Zn, should be paid with special attentions, because they were known as the common elements existed at relatively high concentration in biological samples and would cause severe interference even at 10 μg L^{-1} levels [6,7]. Degrees of depression by these elements were in the order of Cu > Pb > Sn > Ni > Zn [16]. It was reported that even with the presence of thiourea, 10 μg L^{-1} of Cu, 100 μg L^{-1} of Pb, 500 μg L^{-1} of Ni and 1000 μg L^{-1} of Zn, respectively, caused a severe depression by about 60% [7]. In this work, since these interference elements were possibly isolated by the SPE column, anti-interference ability of the established method might be enhanced. In the FI system, the carrier solution also served as the rinse solution, as mentioned above. It was found 10 mg L^{-1} of Cu and Ni and 2 mg L^{-1} of Sn could not cause any interference, providing that a complete rinse was made. A 70 s of rinsing time, equivalent to a 5 mL of rinsing volume, was proved to eliminate completely the interference from the experimented concentration of Cu, Sn and Ni. The complete rinse of Pb from the SPE column was a little difficult. Even after a 120 s of rinsing time, 1 mg mL^{-1} of Pb still had a 20% depression on the Cd signal. However, a 80 s of rinsing time could guarantee no depression from 100 μg L^{-1} of Pb. Unfortunately, Zn was also preconcentrated on the column along with Cd, so the isolation of Zn could not be realized. However, Zn imposed the least influence on Cd hydride generation among the five common elements, as reported by other workers. It was found that 1 mg L^{-1} of Zn did not cause significant change in Cd signal intensity in this study. Obviously, the rinse time could be further reduced in real sample analysis, since concentrations of these elements in real samples were much lower than the experimented concentrations; a total 40 s was proved sufficient for a complete rinse plus the sample loading.

As mentioned in Section 3.2, thiourea gave no contribution to the improvement of Cd signal in this work. In fact, thiourea was deduced to act as a masking reagent more than a catalyzer. However, a 5% (m/v) or even 10% (m/v) of thiourea solution would be a very effective rinsing reagent. Compared with the use of water for rinse, the use of thiourea solution could greatly shorten the rinsing time. Obviously, the effectiveness of thiourea as the rinsing reagent resulted from its strong masking ability.

4. Analytical performance

Even the column had been repeatedly used at least over 400 times, no significant change in its separation performance was observed, which proved a long lifetime of this column.

A 20 s was required for sampling plus the AFS measurement, while a 40 s was required for sample loading plus complete rinse, and considering that recalibration was carried out every 20 sample analysis, thus, a sample throughput of up to 40 samples per hour was obtained. A successive measurement of a 0.2 μg L^{-1} of Cd solution gave a RSD of 0.97% for six runs, which indicated good reproducibility of the proposed method. The analysis of a series solutions containing 0.1, 0.2, 0.5, 1.0, and 2.0 μg L^{-1} of Cd, respectively, gave a calibration function of $I_f = 3327C + 39$ (I_f, the signal intensity and C, the concentration of Cd, expressed in μg L^{-1}), of which the correlation coefficiency is 1.0000. The detection limits (DLs), defined as 3 s of the standard deviation for six measurements of the procedure blank solution, was 10.8 ng L^{-1}.

Finally, the feasibility of the method was evaluated by analyzing two standard reference materials. The results listed in Table 2 reveal that this method is of high accuracy and precision.

Table 2
Analysis of standard reference materials ($n = 5$)

Sample	Certified (μg g^{-1})	Found (μg g^{-1})
Tea (GBW08513)	0.023 ± 0.004	0.024 ± 0.002
Tea leaf (GBW07605)	0.057 ± 0.010	0.055 ± 0.001

5. Conclusions

This work demonstrated the feasibility of on-line combining a FI-SPE separation and preconcentration technique with a SI-HG-AFS technique for determination of ultra-trace levels of Cd in tea samples. The HG technique was studied in a H_2SO_4 system and it was found that thiourea produced no positive effect on the Cd hydride generation, while Co enhanced the hydride generation efficiency at a much lower concentration than those in HCl or HNO_3 systems. Masking reagents were not necessarily added, since common elements causing severe interference on Cd hydride generation, such as Cu, Ni, Sn and Pb, were completely or mostly removed. The developed method is precise, accurate and of high sample throughput, and so is promising for routine analysis of trace of Cd in other biological materials and even may be extended to other more complex materials with high Cu, Ni, and Sn contents.

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