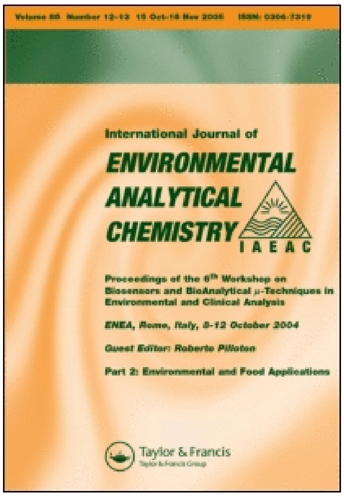

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A sensitive and accurate method for the determination of ultra-trace level of cadmium in environmental waters by atomic absorption spectrometry with *in situ* trapping hydride in iridium coated graphite tube

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A sensitive and accurate method is described for the determination of ultra-trace level of cadmium in environmental waters by atomic absorption spectrometry with *in situ* trapping hydride in iridium coated graphite tube. Effects of the conditions for the generation and collection of cadmium hydride were investigated. Phenanthroline–Co^{2+} was selected as an enhancement reagent for hydride generation with good enhancing effect, and iridium coating was an effective adsorbent for *in situ* trapping cadmium hydride in graphite tube at 300°C. Under the optimal conditions, the calibration curve was linear from 10 to $1\,\mu g\,L^{-1}$ with correlation coefficient of 0.9991, the detection limit (3σ) was $3\,ng\,L^{-1}$, and the relative standard deviation (RSD) for 11 replicate analyses of $500\,ng\,L^{-1}$ Cd standard solution was 1.4%. The results found by the proposed method are not significantly different from the values of four plant certified reference materials (CRMs, $p = 0.05$). The proposed method was applied for the determination of ultra-trace Cd in tap, river water, lake water, wastewater and fish tank water with the recovery in the range of 95.6–99.7% with RSD ($n = 7$) of 0.5–16%. The contents of cadmium in these water samples were in the range of $9–521\,\mu g\,L^{-1}$.

Keywords: hydride generation; *in situ* trapping; graphite furnace atomic absorption spectrometry; cadmium; plant CRMs; environmental waters

1. Introduction

Cadmium is highly toxic even at very low concentrations, causing damages to organs such as the kidneys, liver and lungs [1]. Cadmium empoison has arose increasing interest. The determination of trace or ultra-trace cadmium in environmental water is of great interest. For this reason, years of effort have been devoted for the development of more approaches to the determination of this element in environmental and biological materials.

Graphite furnace atomic absorption spectrometry (GFAAS) has been used to determine cadmium in a large variety of biological, clinical, food and environmental samples [1,2]. Several pre-concentration techniques have been used for the determination of cadmium by GFAAS. A new procedure, based on hollow fibre supported liquid membrane pre-concentration coupled with GFAAS detection, was developed for the

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determination of trace cadmium in seawater samples [3]. Dispersive liquid–liquid microextraction technique was used as a sample preparation method for GFAAS with detection limit of $0.6\,\mathrm{ng\,L^{-1}}$ [4]. Cloud point extraction-GFAAS was reported for the determination of cadmium in biological samples [5], and in urine samples [6]. The hydride generation (HG) offers significant advantages of pre-concentration and separation [7].

The concept of *in situ* trapping of a volatile hydride in a pre-heated graphite furnace with subsequent atomisation was first reported by Drasch *et al.* [8]. Atomic spectrometric detection of hydride forming elements following *in situ* trapping within a graphite furnace was reviewed [9,10]. The *in situ* trapping volatile hydride in a pre-heated graphite furnace was used for the determination of cadmium in river water and tea infusions [11]. Vapour generation combined with on-line pre-concentration on a resistively heated W-coil was reported for the determination of cadmium in seawater by AAS using an unheated quartz absorption cell [12]. The 'in-atomiser trapping' technique has the advantages of high sensitivity, decrease or elimination of the interference effects and easy integration with flow injection methodology for the atomisation of hydride-forming elements over the use of conventional heated quartz cells. The pre-concentration technique was used for the determination of cadmium in environmental samples by different atomic spectrometric methods, such as GFAAS with the limit of detection (LOD) of $60\,\mathrm{ng\,L^{-1}}$ [13], $4\,\mathrm{ng\,L^{-1}}$ [14] and $10\,\mathrm{ng\,L^{-1}}$ [15], and ICP-MS with LOD of 3.5–7 pg [16], and quartz furnace AAS with LOD of $8\,\mathrm{ng\,L^{-1}}$ [17]. Under different concentration levels the relative standard deviations (RSDs) of these methods were in the range of 1.3–12%.

The main purpose of this work was to develop an accurate methodology suitable for rapid and sensitive determination of ultra-trace level of cadmium in tap water, river water, wastewater, and fish tank water samples by GFAAS with *in situ* trapping hydride.

2. Experimental

2.1 *Equipments*

A Perkin-Elmer 1100B GFAAS (Beijing Haiguang Instrument Co., China) combined with a HGA-700 graphite furnace and a deuterium lamp background corrector was used to measure the integrated absorbance over a 4 s atomisation time. The Cd hollow cathode lamp was operated at 10 mA. The most sensitive line (228.8 nm) with a 0.7 nm band pass was typically used.

A HG system (Shenyang Zhaofa Automation Analysis Institute, China) was used for the HG and *in situ* trapping in the graphite furnace [18]. Inner surface of gas–liquid separator was alkylation-treated with 5% (v/v) toluene solution of dimethyl dichlorosilicane (DMCS) in order to set up hydrophobic surface and decrease adsorption losing. A 40 mm long of quartz capillary was used for sampling.

An AFS-230 double-channel non-dispersive atomic fluorescence spectrometer with a quartz furnace atomiser in a shielding mode (Beijing Haiguang Instrument Company, China) was used for investigating the optimal conditions of HG at fluorescence line of 228.8 nm.

2.2 *Reagents and solutions*

A cadmium standard solution GBW(E)080400, National Steel Material Test Centre, Beijing, China with a Cd concentration of $1000\,\mathrm{\mu g\,mL^{-1}}$ in 1% HNO_3 was diluted with 0.1% HNO_3 to provide a working stock solution of $10\,\mathrm{\mu g\,mL^{-1}}$. Working standard solutions were prepared daily by further dilution. High-quality hydrochloric acid (HCL) and nitric acid were purchased from Merck (Darmstadt, Germany). All other chemicals (phenanthroline, 8-hydroxyquinoline, etc.) were at least of analytical-reagent grade. Doubly distilled water (DDW) obtained from quartz distillation apparatus, was used throughout. Iridium modifier, 2.50 g L^{-1}, was prepared by dissolving 0.5973 g $(NH_4)_3IrCl_6$ in 10 mL of 0.1 mol L^{-1} HNO_3 and diluting to 100 mL with DDW. Zirconium modifier, 2.50 g L^{-1}, was prepared by dissolving 0.8831 g $ZrOCl_2 \cdot 8H_2O$ in 10 mL of 0.1 mol L^{-1} HCl and diluting to 100 mL with DDW. The palladium modifier solution (1.00 mg mL^{-1}) was prepared by dissolving 0.8336 g $PdCl_2$ in 10 mL of 0.1 mol L^{-1} HNO_3 and diluting to 500 mL with DDW. KBH_4 (Merck) solution, 0.5–40 g L^{-1}, was prepared fresh daily by dissolving the appropriate amount of KBH_4 in 0.1% NaOH and filtered through a 0.45 µm membrane filter. Cobalt stock solution (1.00 g L^{-1}) was prepared by dissolving metal cobalt in 50 mL of 0.5 mol L^{-1} nitric acid by heating in a water bath and diluting to 1000 mL with 0.1 mol L^{-1} nitric acid. Phenanthroline solution (0.5 mg L^{-1}) was prepared by dissolving the reagent with water through gentle heating.

The four kinds of certified reference materials (CRMs), peach leaf (GBW 08501), tea (GBW 08505), wheat powder (GBW 08503) and rice powder (GBW 08502), were purchased from the National Standard Material Research Center (Beijing, China).

2.3 *Coating procedure*

The coating procedure was based on that described by Haug and Liao [19]. A 50 µL of iridium modifier was injected into the graphite tube, slowly dried at 110–130°C for 50 s and heated in a reduction step at 1200°C for 20 s and 2000°C for 3 s. The complete injection and heating cycle were repeated, the total mass on the graphite tube was 500 µg Ir. The same procedure using a 0.1% m/v of Zr or Pd solutions gave 500 µg Zr or Pd on the graphite tube.

2.4 *Sample treatment*

A 0.5 g standard was digested with 10 mL aqua regia for 10 h, followed by the addition of 5 mL perchloric acid and gentle heating on an electric hot plate to dryness. Then, 5 mL of 1% nitric acid was added, and the solution was heated and centrifuged. The obtained solution was transferred into a 25 mL volumetric flask and diluted to the volume with DDW. A 10 mL sample of wastewater, river and tap water was acidified with 1–2 mL of 1% nitric acid and then filtered through a 0.45 µm membrane filter. A 1.0 g reference material was digested with 10 mL aqua regia for 10 h, followed by the addition of 5 mL perchloric acid and gently heating on an electric hot plate to dryness. Then, 5 mL of 1% nitric acid was added, and the solution was heated and centrifugated. The obtained solution was transferred into a 25 mL volumetric flask and diluted to the volume with DDW. Final sample solutions were adjusted to contain 0.35 mol L^{-1} HCl for the generation of cadmium hydride. The sample blank was prepared in the same way.

2.5 *Procedure*

Sample solution containing 0.5 mg L^{-1} phenanthroline, 1.0 mg L^{-1} Co^{2+} and 0.37 mol L^{-1} HCl was introduced by means of a peristaltic pump at 8 mL min^{-1}, then 20 g L^{-1} KBH_4

Table 1. Furnace temperature programme.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Inner gas flow ($mL\,min^{-1}$)	Read	Performance
1	120	1	10	300		Dry
2	300	10	40–100	0		Trap
3	1600	0	4	0	Yes	Atomise
4	2300	4	4	300		Clean

solution was pumped through another passage at 4 $mL\,min^{-1}$ into the *Y* mixing block. The volatile hydrides generated in mixing tube were separated at the gas–liquid separator and transported to the graphite furnace by a stream of argon with 400 $mL\,min^{-1}$.

A quartz capillary was used for transmitting the hydride into the graphite tube, and the trapping temperature was set at 300°C. After collecting the gases for 40–100 s (depending on the analyte content), the atomiser was purged with argon in order to ensure complete flushing of the reaction gases from the graphite furnace. The quartz capillary was removed by handwork from the furnace after collecting hydride. The determination of the collected analyte was performed using the furnace temperature programme shown in Table 1.

Under the optimal conditions, a series of standard solutions (10–500 $ng\,L^{-1}$) were analysed by *in situ* trapping hydride-GFAAS. The special concentration range of standard solutions was selected according to Cd content in real samples. The calibration curves were protracted based on the absorbance *versus* the concentration of Cd.

3. Results and discussion

3.1 *Choice of HG conditions*

For operational convenience, the optimisation of the conditions for the generation of cadmium hydride was carried out with atomic fluorescence detection. The most sensitive atomic fluorescence line (228.8 nm) of analyte was chosen for the investigation.

The result showed that the fluorescence intensity increased in the range from 0.10 to 0.35 $mol\,L^{-1}$ HCl, and when higher to 0.375 $mol\,L^{-1}$ it decreased fleetly. So, 0.35 $mol\,L^{-1}$ HCl was selected as the optimal concentration.

A series of KBH_4 solutions were prepared covering the range 0.5–40 $g\,L^{-1}$ concentration. The Cd signal increased continuously with increasing reductant concentration up to 15 $g\,L^{-1}$, and in the range of 15–25 $g\,L^{-1}$, the signal reached to the most intensity and retained to be stable. Beyond 25 $g\,L^{-1}$, the Cd signal experienced only slight variations and offered no practical advantages for increasing the reductant concentration. In addition, a significant increase of the blank signal was observed as this reagent concentration increased.

In this work, no significant signal was observed when the experiment of HG was carried out at laboratory temperatures below 10°C. In order to evaluate the effect of temperature on HG, the sample vessel and mixing coil were immersed in water bath and the temperature was varied between 10 and 90°C. The results showed that the efficiency of HG was poor at lower temperatures, but increased by 10% at 60°C. However, no further enhancement was shown at temperatures over 65°C. Certainly, the higher temperature facilitated the kinetic process of the Cd vapour generation, while much higher temperature

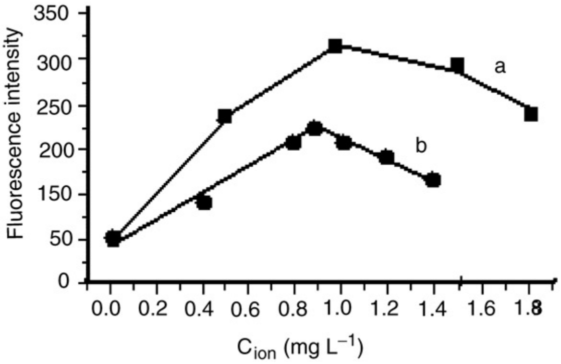

Figure 1. Effect of (a) Co^{2+} and (b) Ni^{2+} concentration on Cd fluorescence intensity. Data point is the average value of three measurements with <2% of RSD.

caused the hydride reaction products to decompose before phase separation could be accomplished. For simplicity, the measurements were carried out at ambient temperature (18–25°C).

Cadmium hydride generated in the reactor was directly introduced into the quartz furnace by using argon carrier gas. The fluorescence signal increased obviously with the increase of the flow rate from 100 to 500 mL min^{-1}, and decreased gradually with the increase of the flow rate from 500 to 700 mL min^{-1}. So an argon flow rate of 500 mL min^{-1} was used throughout for fluorescence measurements to increase transport efficiency.

Otherwise, the trapping efficiency of the coating graphite tube to cadmium hydride increased with the increase of the argon flow rate from 100 to 400 mL min^{-1}, and decreased with the increase of the argon flow rate from 400 to 700 mL min^{-1}. Therefore, the argon flow rate should be changed from 500 mL min^{-1} for AFS to 400 mL min^{-1} for *in situ* trapping hydride with higher trapping efficiency. And the above selected other conditions of HG for AFS can be applied for *in situ* trapping hydride GFAAS with higher sensitivity.

3.2 *Effect of enhancement reagent*

In our previous work [20], by comparing the enhancing effects of some organic reagents it was found that 8-hydroxyquinoline and phenanthroline individually showed excellent performance for the simultaneous vapour generation of Zn and Cd. The enhancing effects of Co^{2+} and Ni^{2+} on generation of cadmium hydride were investigated. Figure 1 shows that cadmium signal in the absence of enhancement reagent was much weaker, and Co^{2+} presents a better enhancing effect. Figure 2 shows that cadmium signal was improved in the presence of phenanthroline and 8-hydroxyquinoline with and without Co^{2+}. It was shown that both phenanthroline and 8-hydroxyquinoline have enhancing effect and synergistic effect with Co^{2+} for cadmium signal. A mixture of 1.0 mg L^{-1} Co^{2+} and a 0.4 mg L^{-1} phenanthroline was selected as the enhancement reagents in this work. The generation of volatile species could be considered as a hydrogenation process [20]. Phenanthroline could form complexes with Cd. The formed complex (ML) produced

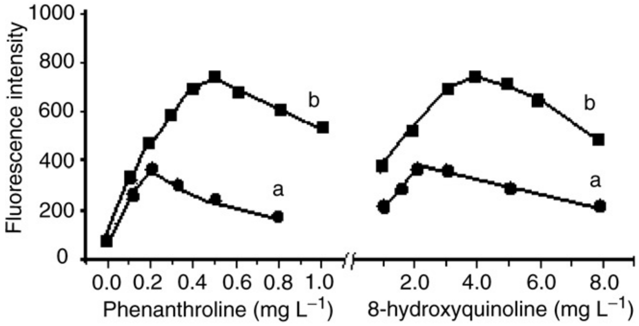

Figure 2. Effect of enhancement reagent on Cd fluorescence intensity in 0.37 mol L^{-1} HCl medium (a) with and without (a) Co^{2+} and (b) with 1.0 mg L^{-1} Co^{2+}. Data point is the average value of three measurements with <2% of RSD.

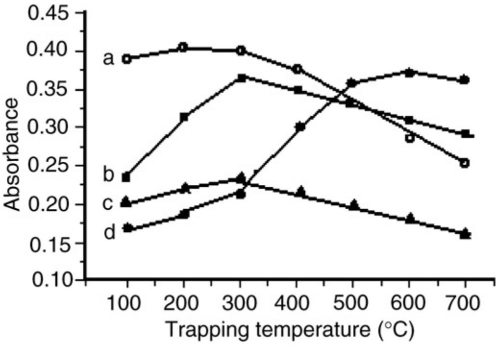

Figure 3. Effect of collection temperature on absorbance of cadmium using different coating: (a) palladium coating, (b) iridium coating, (c) without coating, (d) zirconium coating. Data point is the average value of three measurements with <2% RSD.

a reactive transient intermediate $H\cdots M\cdots L$ with KBH_4, which changed the thermodynamic reaction constant and facilitated the generation of M–H bond. The decomposition of cobalt hydride could restrain decomposition of cadmium hydride, it was increasing transmission efficiency of cadmium hydride [21].

3.3 *Effect of different coatings of graphite tube on* in situ *trapping*

The effects of the graphite tubes coated with iridium, palladium or iridium–palladium on *in situ* trapping cadmium hydride were compared at different temperatures in the range of 100–700°C, as shown in Figure 3.

It was noted that collection efficiency for graphite tubes without coating was much weaker than that for graphite tubes with coating. The palladium-coated graphite tube showed the highest collection efficiency; however, it needs to be re-coated before each collection. The zirconium coated graphite tube showed better collection efficiency under higher temperatures of 500–800°C. The iridium coated graphite tube exhibited better stability under temperatures of 250–350°C, and the same coating can be used up to 200 times.

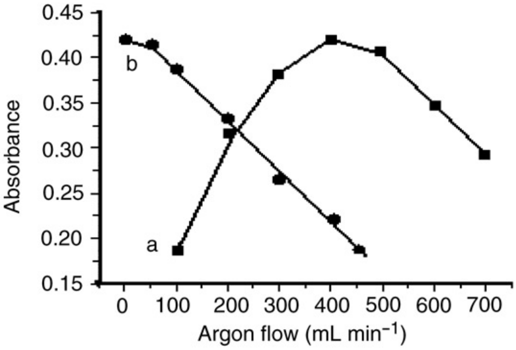

Figure 4. Effect of the flow rate for (a) carrier gas in generation system and (b) inner gas in graphite tube on collection purpose of cadmium hydride. Data point is the average value of three measurements with <2% of RSD.

So iridium coating (500 µg Ir) was used for *in situ* trapping cadmium hydride and a temperature of 300°C was selected with better efficiency.

3.4 *Effect of trapping time*

The effect of trapping time from 10 to 160 s on response of cadmium hydride was further examined. It was noted that absorbance increased obviously with increasing trapping time from 10 to 100 s, and higher absorbance was reached for collection for 100 s, after which the absorbance retained to be stable due to saturation effect. A time of 100 s was selected in our work in order to ensure all the hydride to be stripped from solution and transferred into the furnace.

3.5 *Effect of carrier gas and inner gas flow rate*

Cadmium hydride generated in the reactor was directly introduced into graphite tube by using argon carrier gas. The integrated absorbance of cadmium significantly depends on the gas flow rate. The results indicate that the cadmium hydride can completely be stripped from the hydride generator (as confirmed by direct solution sampling) and adsorbed in the graphite tube in the carrier gas flow rate of 400 mL min^{-1} with a 30 s collection time. The integrated absorbance of cadmium hydride decreases with the increase of flow rate over 500 mL min^{-1}, as shown in Figure 4. Therefore, an argon flow rate of 400 mL min^{-1} was optimal and was used throughout subsequent experiments.

The flow rate of inner argon gas in a graphite tube also influenced the trapping efficiency. Under a 400 mL min^{-1} of carrier gas flow rate, the integrated absorbance of cadmium decreased remarkably with the increase of inner gas flow rate. Therefore, inner gas flow rate at trapping step should be kept low to obtain higher collection efficiency of cadmium hydride.

3.6 *Interference studies*

If the determination procedure established is to have any practical utility, it is essential that it can tolerate the presence of pertinent ions. Thus, the influences of common interferents on the absorption signals were investigated using the recommended conditions. The tolerance content is defined as the interferent concentration reducing the analyte signal by 5%. The result showed no interference with following matrix components, which is as follows (tolerance content in parentheses expressed in milligrams per litre): Fe(III), Mn(II) and Zn(II) (20); Cr(III) (5); Sn(II), As(III) and Sb(III) (2); Te(IV), Hg(II) and Co(II) (1); Se(IV), Cu(II) (0.5); Bi(III), Pb(II), Ni(II) (0.2); Ag(I) (0.1); $0.3\,\mathrm{mol\,L^{-1}}$ NO_3^- and $2\,\mathrm{mol\,L^{-1}}$ Cl^-.

3.7 *Performance of the method*

The quantity of volatile cadmium species trapped in iridium-coated graphite tube is depended on: HG efficiency transmission efficiency and trapping efficiency in graphite tube. The overall efficiency of the *in situ* trapping and generation processes was evaluated by a comparison of the integrated response from the direct injection of a 10 µL volume of aqueous Cd standard solution containing the same mass of Cd on the same tube surface and subjected to an identical thermal programme.

The overall efficiency of HG, transportation and trapping efficiency was calculated from the cadmium quality of the procedure developed technique and that calculated from the signal obtained direct injection of the same quality cadmium. The over all calculated efficiency was 41% in our system. This result is higher than the value of 30% [13], and equals the value for HG, transportation and trapping process [22], and approaches the value of 43.5% for HG plus transport process [11].

The calibration equation and the other performance were examined. The calibration equation followed $A = 0.837C + 0.0018$, the linearity from 10 to $1000\,\mathrm{ng\,L^{-1}}$ was good with correlation coefficient of 0.9991. The LOD was calculated as the concentrations that give signals equal to three times the standard deviations of the blanks. The LOD of $3\,\mathrm{ng\,L^{-1}}$ was obtained for a sample volume of 10 mL, which can be improved further by pre-concentrating larger volumes of sample. The observed RSD value for 11 replicate analyses at $0.5\,\mathrm{ng\,mL^{-1}}$ was 1.4%. The existing data on cadmium HG-atomic spectrometry were reviewed in 2003 [22], and the LOD and RSD values reported in the literature were in the range of 8–1 $\mathrm{\mu g\,L^{-1}}$ and 0.2–4%, respectively. The LODs of *in situ* trapping hydride atomic spectrometric techniques were in the range of 4–1 $\mathrm{\mu g\,L^{-1}}$ [13–17]. The LOD of the proposed method was lower than these values reported, and nears to that of cloud point extraction-GFAAS [6].

The slope of standard solution calibration curve and standard addition curve was investigated, no remarkable difference was observed between the slopes, showing no interference with matrix, and a Cd spiked before the digestion procedure could be recovered quantitatively. Therefore, analyses can be performed using a direct standard solution calibration method.

3.8 *Analysis of reference materials*

The *in situ* trapping hydride-GFAAS method was used for the determination of Cd in the CRMs of wheat, rice, peach leafage and tea in order to evaluate the accuracy. The result is given in Table 2.

Table 2. Determination of cadmium in the reference materials.

Reference material	Certified value ($\mu g\, g^{-1}$)	Determined value ($X \pm SD$, $n = 7$) ($\mu g\, g^{-1}$)
Wheat powder (GBW08503)	0.031 ± 0.002	0.028 ± 0.007
Rice powder (GBW08502)	0.020 ± 0.002	0.024 ± 0.009
Peach leafage (GBW08501)	0.018 ± 0.004	0.016 ± 0.004
Tea (GBW08505)	0.023 ± 0.004	0.019 ± 0.006

Table 3. Validation of cadmium analysis in real samples with *in situ* trapping hydride-GFAAS.

Sample	Content in sample	RSD* (%)	Added value	Average recovery (%)*
Tap water-1 ($ng\, L^{-1}$)	9	16	10, 15, 20	98.3
Tap water-2 ($ng\, L^{-1}$)	12	14	10, 15, 20	96.8
River water-1 ($ng\, L^{-1}$)	18	13	10, 15, 20	95.6
River water-2 ($ng\, L^{-1}$)	30	10	20, 30, 40	96.2
Wastewater-1 ($\mu g\, L^{-1}$)	478	0.5	200, 400, 600	99.7
Lake water-1 ($\mu g\, L^{-1}$)	390	0.6	100, 200, 300	95.6
Fish tank water-1 ($ng\, L^{-1}$)	32	9.0	10, 20, 30	97.5
Fish tank water-2 ($\mu g\, L^{-1}$)	524	1.3	200, 300, 400	96.6
Fish tank water-3 ($\mu g\, L^{-1}$)	521	0.5	200, 400, 600	98.8

Note: $^*n = 7$.

The results obtained for the determination of cadmium in four standard reference materials, are not significantly different from the certified values (*t*-test, $p = 0.05$). It is indicated that the proposed methods is reliable.

3.9 *Analysis of environmental waters*

The proposed method was applied for the determination of Cd in environmental samples, such as tap, river water, wastewater and fish tank water, with direct standard solution calibration. In addition, the recovery experiments were carried out, and the results are shown in Table 3. The recoveries in the range of 95.6–99.7% were reasonable for trace analysis. The contents of cadmium in these water samples were in the range of 9–521 $\mu g\, L^{-1}$ with RSD ($n = 7$) of 0.5–16%. Among them, the highest cadmium content was observed in fish tank waters, it overstepped the water quality standard. This was aroused by using a high-performance oxygenate (calcium peroxide powder) in the fish tank waters, which had been contaminated by a mass of impurities (cadmium and arsenic) in calcium peroxide powder.

4. Conclusions

The proposed method has good sensitivity for the determination of cadmium in environmental waters. Phenanthroline–Co^{2+} was found to be an effective enhancement reagent for generation of cadmium hydride with good enhancing effect, and iridium coating of graphite furnace was an effective adsorbent for trapping cadmium hydride. The proposed method has low-detection limit and high accuracy. This approach provides a viable alternative to the conventional GFAAS technique.

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