Determination of cadmium in water samples by electrochemical hydride generation atomic fluorescence spectrometry using series graphite tubes as electrolytic cells under constant voltage

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The two new graphite tubes were pyrolytic graphite coated tubes without platforms, which used the GFAAS atomizer and were connected via an insulated plastic pipe. The distance between the two graphite tubes (i.e., the gap between the cathode and the anode) was 4 mm. The solution inlet end of the anode graphite tube was connected to the entrance tube by 5 ml plastic pipette tips. The solution outlet of the cathode graphite tube was directly connected to the thin connecting tube by a small rubber plug matching the inner diameter of the graphite tube. In addition, the connecting tube length between the outlet of the graphite tubes and the GLS solution inlet was 3.5 cm in order to reduce the retention time of the electrolytic solution in the pipeline and to reduce the decomposition of cadmium hydride. The central holes of every graphite tube were sealed using rubber bars to prevent solution leaks.
Abstract
An electrochemical vapor generation (EcHG) system to determine the cadmium content using atomic fluorescence spectrometry has been established. The EcHG system uses two serially-connected graphite tubes as two electrolysis cells and an AC to DC power wall plug adapter with the constant voltage mode as a power supply. The system did not have an ion exchange membrane and only needed a pump to transport the feed solution and waste. Under these optimized conditions, the detection limit (3σ) and the relative standard deviation were 0.05 ng ml$^{-1}$ and 3.2%, respectively. The EcHG efficiency was 38.4±2.2%. The proposed technique has been successfully applied to determine the cadmium in three certified reference materials for environmental water and two drinking water samples.

**Keywords:** Cadmium, graphite tube, electrochemical vapor generation, atomic fluorescence spectrometry
Introduction

As a highly toxic environmental element, the maximum contaminant level of cadmium established by US EPA is 0.005 ppm,\(^1\) and this strict permissible level requires very sensitive instruments for the determination of the trace amounts of cadmium in food and environmental samples. For this purpose, at present, the most suitable instruments for the determination of trace cadmium are graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS) due to its suitable detection limits.\(^2,3\) However, both instruments are expensive and complex to operate. Therefore, the continued development of new analytical methods for the determination of trace cadmium using other atomic spectrometer instruments is necessary to reduce instrument costs and operational complexity.

Although chemical vapor generation (CVG) based on tetrahydroborate(III)(THB) combined with three other atomic spectrometers, namely, inductively coupled plasma - atomic emission spectroscopy (ICP - AES),\(^4,6\) atomic fluorescence spectrometry (AFS),\(^7,9\) atomic absorption spectrometry (AAS),\(^10,11\) can provide excellent detection limits, this method has two imperfections in the determination of trace cadmium. First, the range of acid concentration is very narrow at the maximum CVG signal of cadmium,\(^5,9,12,13\) and a small change in acidity will lead to a great change in the signal value at the best acidity.
Thus, it is very difficult to obtain good, reproducible results. Second, serious interferences can be found for the determination of cadmium in the presence of Fe, Cu, Ni and Co.\textsuperscript{4,11-13} In addition, the high costs of THB and its instability in solutions are also the imperfections of this method.

It is well known that electrochemical hydride generation (EcHG) has also been used as a sampling technique for atomic spectrometry.\textsuperscript{14-16} EcHG can overcome the inherent imperfections of THB-based CVG. Because no THB reagent is used, EcHG has low analytical costs and can reduce the contamination of reagents. However, the existing EcHG apparatuses are usually complex and have high costs. First, most of existing EcHG apparatuses generally use two “parallel electrodes”; hence, an ion exchange membrane and two pumps are generally required for the separation of two electrolyte solutions. Although the EcHG apparatus without a membrane was also developed,\textsuperscript{17,18} it still needs the careful fabrication and use of various materials due to the adoption of “parallel electrodes” and a DC unit with the constant current mode, which had relatively high power supply costs. Second, the electrode was usually made of a metal or alloy such as lead, cadmium, titanium, platinum or tin-lead due to their high hydrogen overvoltage. Since these metal electrodes could usually be dissolved during EcHG (except for platinum electrodes), the method has high costs, and the dissolution of electrodes
may affect the stability of EcHG efficiency. Third, the influence of the acidity change and the interference of coexisting ions are still serious.

At present, EcHG has mainly been applied for the determination of As, Hg, Cd, Ge, Sb, Se and Sn, etc. For the determination of trace cadmium using EcHG, the above mentioned defects still exist.

Recently, we reported a new EcHG apparatus for the determination of total inorganic arsenic using AFS. The new EcHG apparatus used two serially-connected graphite tubes (from GFAAS) as two electrolysis cells, which is called the “serial electrodes EcHG”, and an AC to DC power wall plug adapter as the power supply without an ion exchange membrane. As a result, its fabrication and assembly was very simple and easy for the fast determination of elements that can form hydrides.

The present study continues to examine the feasibility of the further application of the “serial electrodes EcHG” apparatus and expand its application scope by developing a simple, fast procedure for the determination of the trace amounts of cadmium in samples using AFS.

**Experimental**

*Reagents and materials*

All chemicals that were used were of analytical grade. Hydrochloric acid (HCl) of high purity were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Thiourea of analytical purity was purchased from Tianjin Guangfu Fine Chemical Research Institute.
(Tianjin, China). 1000 µg ml⁻¹ inorganic ions for the interference study were purchased from Beijing General Research Institute for Nonferrous Metals (Beijing, China). Deionized water (Tianjin Yongqingyuan Distilled Water Co., Tianjin, China) was used in the whole experiment.

A 1000 µg ml⁻¹ stock standard solution of cadmium (National Standard Material Center of China) was used for the preparation of the working standard solutions of cadmium. Three certified reference materials (CRMs), GBW08608 (Batch No. 17081), GSB07-1185-2000 (Batch No. 201431) and GSB07-3186-2014 (Batch No. 200933), for environmental water were purchased from the Institute for Environmental Reference Materials of the National Ministry of Environmental Protection (Beijing, China). Among them, 07-1185-2000 was prepared using pure water and does not truly represent an environmental matrix material.

Instrumentation and apparatus

A model PF6 non-dispersive atomic fluorescence spectrometer (Beijing Puxi General Instrument Co., Beijing, China) fitted with an EcHG apparatus was used in this work. The main current/auxiliary current of the cadmium hollow cathode lamp was 60 mA; the high voltage for the photomultiplier tube was 300 V; the carrier gas flow rate was 250 ml min⁻¹, the shield gas flow rate was 1000 ml min⁻¹; and the hydrogen flow rate 350 ml min⁻¹. The other operating conditions for AFS were exactly
the same as those described in our previous report.\textsuperscript{24}

The EcHG system in this work, which includes two pyrolytic graphite-coated graphite tubes (28.4 mm length, 8 mm od, 6 mm id and 1 mm wall thickness; Beijing Beifen-Ruili Analytical Instruments Co., Ltd., China) in series\textsuperscript{24} and the GLS,\textsuperscript{27} was identical to the one recently described in the literature,\textsuperscript{24} except for the following three changes. (1) To prevent the decomposition of the cadmium hydride, the connecting pipe length between the outlet of the graphite tubes and the GLS solution inlet was 3.5 cm, which is the minimum distance available, and the solution outlet of the cathode graphite tube was directly connected to the thin connecting tube by a small rubber plug matching the inner diameter of the graphite tube to reduce the retention time of the solution in the connecting pipe. (2) An AC 220 V to DC 18 V 2 A regulated power supply adapter was used throughout this work. (3) The distance (gap) between the two graphite tubes (the cathode and the anode) was 4 mm. A schematic diagram for the EcHG system is shown in Fig. S1 (Supporting Information).

**Results and discussion**

**Distance between the two graphite tubes electrodes**

The first feature of this study is to use two graphite tubes in series as two electrolysis cells without an ion-exchange membrane. Such an EcHG apparatus is very easy to assemble using conventional insulated plastic
pipe as a connecting tube. It can be seen from Fig. S2 (Supporting Information) that the cadmium signal intensity increases with the decrease of the distance between the two graphite tube electrodes. When the distance was less than 0.2 cm, the EcHG reaction was very intense, a large number of bubbles was produced in the gap between the two electrodes and the corrosion of the graphite tubes is more serious, which would shorten the lifespan of the graphite tubes. When the distance was greater than 0.4 cm, it can be seen that the signal intensity decreases rapidly. In view of this, the distance between the two graphite tube electrodes was set as 0.4 cm, as a compromise. Using this distance, the lifespan of the graphite tubes was greater than 150 hours. Additionally, it was also found that the order of the two electrolysis cells (the cathode is below, the anode is above, ) had no significant effect on signal intensity.

**Power adapter**

The second feature of the proposed technique is to use the constant voltage mode power adapter instead of the traditional special power supply with the constant current mode. A power adapter is cheap and easy to purchase and use. Because the common power adapters for portable computers and mobile phones in the market are 6 V, 12 V, 15 V and 18 V, a power adapter larger than 20 V is not easy to buy. To systematically study the influence of the voltage on the signal under the constant voltage
mode, a DC Power supply for a traditional EcHG (Model DH1719A-3 with the constant current and voltage mode, Beijing Da Hua Wireless instrument Co., China) in the constant voltage mode was used in this work. Fig. S3 (Supporting Information) shows the effects of different constant voltages on the signal intensity of cadmium. It can be found that when the voltage from the DC Power supply was greater than 20 V, the signal intensity decreased rapidly with the increase of the voltage. To highlight the features of this work, an 18 V power adapter was used throughout this work.

*Length of the pipe between the outlet of solution and the GLS*

The third feature of the proposed technique is to use the bubble GLS and the shortest possible the pipe between the outlet of solution and the GLS. In this work, we first measured the intensity of cadmium without igniting the H$_2$–Ar flame. It was found that no cadmium signal was observed, so it proved further that the cadmium volatile species are cadmium hydrides rather than atomic cadmium.$^{23}$ However, it was found that cadmium hydrides were very unstable in the solution. To reduce the retention time of the solution in the connecting pipe, the pipe connecting the graphite pipe and the GLS was a thin plastic pipe with an even diameter (see Fig. S1 (Supporting Information)) instead of the tapered plastic pipette tip, which was used in the previous work.$^{24}$ From Fig. S4,
it can be seen that the signal intensity decreased with the increase of the connecting pipe length between the outlet of the graphite tubes and the GLS solution inlet. Hence, a connecting pipe length of 3.5 cm, which is the minimum distance available, was chosen for the subsequent experiments. It is worth noting that if the distance from the outlet of the graphite tube cathode to the frit plate on the GLS glass was further reduced, including the height from the mixed solution outlet to the bottom of the frit, the signal intensity of cadmium may be further enhanced.

In addition, in order to obtain the best EcHG efficiency, the retention time of volatile cadmium species and avoid the decomposition of volatile cadmium species in solution, the bubble GLS, which had been shown to be very effective for gas-liquid separation, was used throughout this work.

**HCl concentration**

The previous study showed that when sulfuric acid is used as the electrolyte, the corrosion of graphite tubes, especially the corrosion of anodic graphite tubes, is very serious. Therefore, in this work, HCl was still used as the feed solution (i.e., electrolyte). From Fig. 1, it can be observed that the signal increases rapidly with the increase of HCl concentration when the HCl concentration is 2% - 4%. In addition, the maximum signal value can be found in the ~4.5% HCl concentration.
This maximum signal was obtained within a narrow range of HCl concentration and it was not suitable for widespread, accurate measurements. However, when the HCl concentration is 8% - 22%, the signal intensities exhibited an excellent signal plateau in which cadmium can be accurately determined. Thus, a 10% HCl concentration was used in this work. The above results are very exciting. To the best of our knowledge, in the existing CVG techniques for cadmium, it is rare to get such an excellent signal plateau in a wide acidity range. Therefore, the proposed EcHG technique could have good application prospects for the determination of cadmium in real samples.

**Effect and role of thiourea**

From Fig. 1 (dotted line), it can found that when 1% thiourea was added to the 100 ng ml$^{-1}$ cadmium solution, the overall signal for cadmium was lower compared with that without thiourea. Further, it can also be found that the shape of the curve of HCl concentration changed markedly when the HCl concentration changed. When the HCl concentration increased from 0 to 14%, the cadmium responses increased slowly, and when the HCl concentration was varied from 14% to 20%, the cadmium signal remained unchanged. This could indicate that thiourea can partially complex cadmium so that it cannot be completely reduced to cadmium hydride by electrolysis. When in low HCl concentration, thiourea had
larger complexation ability with cadmium and the signal for cadmium was low (and vice versa). In addition, the experimental results of Section “Interferences” showed that the addition of thiourea can eliminate the interference of 10 µg ml\(^{-1}\) of Cu\(^{2+}\), Fe\(^{3+}\), Mn\(^{2+}\), Ni\(^{2+}\) and Zn\(^{2+}\). This may be that thiourea can form more stable complexes with these ions or suppress these ions interferences through other reactions.

*Effects of the solution and carrier argon flow rate*

Fig. 2 and Fig. S5 (Supporting Information) showed the effects of the solution and carrier argon flow rate on the signal intensities, respectively. It can be seen that the maximum signal was obtained at the carrier gas flow rate of 250 ml min\(^{-1}\) and the solution flow rate of 3 ml min\(^{-1}\). Thus, the above two flow rates were selected for the subsequent experiments.

*Efficiency*

The efficiency of EcHG for cadmium was evaluated by determining the residual cadmium content in the waste using inductively coupled plasma-atomic emission spectrometry (ICP-AES) with the standard addition method. The solutions containing 400 ng ml\(^{-1}\) cadmium were used as the feed solution (the calibration curve of cadmium was linear at 400 ng ml\(^{-1}\), see section “figures of merit” ). The results showed that the average efficiency (n=3) was found to be 38.4±2.2% when thiourea is absent. This efficiency is similar to that of arsenic in our recent report.\(^{24}\) It
is notable that the calculated efficiency is related only to the cadmium hydride formation, and the losses of the cadmium hydride in the transfer line from the GLS to the AFS atomizer were not taken into account.

When compared to the existing EcHG technique, in which the dissolution of the metal (or alloy) electrode may affect the stability of EcHG efficiency, the proposed EcHG technique has a more stable EcHG efficiency because the graphite tube electrode was hardly corroded during the proposed EcHG.

Interferences

The interferences were examined by measuring the recovery in the presence of interferent ions. Ten percent of the change in the recovery was considered to be interference from foreign ions. The experimental results showed that: (1) when thiourea were absent, it was found that when 5 µg ml\(^{-1}\) of Fe\(^{3+}\), Mn\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\) and Zn\(^{2+}\) and 0.5 µg ml\(^{-1}\) of As(III) were added to the 100 ng ml\(^{-1}\) cadmium solution, no significant interference was found; however, 10 µg ml\(^{-1}\) of Cu\(^{2+}\), Fe\(^{3+}\) Zn\(^{2+}\) and Ni\(^{2+}\) can reduce the signal by 30%, 21%, 36% and 42%, respectively. (2) when thiourea was added, it was found that the interferences from 10 µg ml\(^{-1}\) of Cu\(^{2+}\), Fe\(^{3+}\) Zn\(^{2+}\) and Ni\(^{2+}\) were eliminated. Therefore, when sample solutions contain high concentration of above mentioned interfering ions, the addition of thiourea would be a good method for masking in order to accurately determine the trace cadmium in samples, which would be
another feature of the proposed technique.

Analytical figures of merit

The analytical figures of merit were obtained using the optimized conditions. When there was no addition of 1% thiourea, the calibration curve of cadmium was linear in the range of 0.15 – 400 ng ml\(^{-1}\) with an \(R^2 = 0.9981\). The detection limit (3\(\sigma\), n = 10) was 0.05 ng ml\(^{-1}\). The relative standard deviation (RSD, %, n=10) for 60 ng ml\(^{-1}\) of cadmium was 3.2. In the presence of thiourea, the calibration curve of cadmium was linear in the range of 1.23 – 400 ng ml\(^{-1}\) with an \(R^2 = 0.9944\). The detection limit (3\(\sigma\), n = 10) was 0.41 ng ml\(^{-1}\). The relative standard deviation (RSD, %, n=10) for 60 ng ml\(^{-1}\) of cadmium was 3.6. In addition, in order to obtain a better understanding of the proposed EcHG method, Table 1 also compares the analytical performance of the proposed EcHG method with other CVG-AFS methods.

Analysis of CRMs and real samples

To verify the accuracy of the presented method, cadmium contents were determined in three CRMs samples of environmental water, tap water (from our lab) and bottled water (purchased from supermarkets). The cadmium contents were obtained using the external standard method without the addition of thiourea. The analytical results for the samples are presented in Table 2. From Table 2, it can be seen that the analytical
results obtained by this method were in good agreement with the certified values and the student t test shows there is no significant difference between the two values at the confidence level of 95%. The recovery rates for tap water and bottled water were 95%–109%.

Conclusions

In this work, we developed a new EcHG system for Cd determination in samples. The new EcHG system is simple, low cost, and easy to implement, and it also has very good analytical performance (LOD of 0.05 ng ml\(^{-1}\)) for cadmium and a better interference tolerance. In addition, when the HCl concentration varies in a wide range (v/v, 8%-20%), the signal can remain stable and cadmium can be determined accurately, which is also an important advantage of this method. Hence, the proposed EcHG apparatus could have good application prospects.

Although the proposed technique has the above advantages, the EcHG efficiency of cadmium could not yet reach the optimal value. If several key factors affecting the cadmium signal can be further optimized, the sensitivity and detection limit of cadmium will undoubtedly be further improved. These factors include the size of the graphite tube, the EcHG voltage, and the distance between the solution outlet of the graphite tube and the surface of the frit in the GLS. Among them, when the voltage and the distance between the graphite tubes are fixed, the retention time between the outlet and the surface of the frit plate in the GLS is the most
important factor, since cadmium hydride is unstable and easily decomposes in the solution. Hence, it is necessary to reduce this retention time as much as possible. This includes further reducing the length of the connecting pipeline between the solution outlet of the graphite tube cathode and the inlet of the GLS, as well as the distance between the solution inlet in the GLS and the frit plate in the GLS.

Supporting Information

Supplementary data associated with this article can be found in the online version.

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### Table 1
LOD, RSD and efficiency of proposed method compared to other CVG methods

| Method                   | LOD, ng ml⁻¹ | RSD, % | Efficiency, % | Ref.   |
|-------------------------|--------------|--------|---------------|--------|
| This work               | 0.05         | 3.2    | 38.4 a        |        |
| Traditional EcHg        | 0.15         | 3.0    | 44.5 a        | [22]   |
| CVG–based on THB         | 0.03         | 0.9    | -             | [25]   |
| Photo-CVG               | 2.0          | 30     | 90 a          | [26]   |

* a Determination of residual cadmium in waste solution.
Table 2. Analytical results of cadmium in water samples (mean ± SD, n = 4)

| Sample                  | Certified, ng ml\(^{-1}\) | Found, ng ml\(^{-1}\) | Added, ng ml\(^{-1}\) | Recovery, % |
|-------------------------|----------------------------|------------------------|------------------------|-------------|
| GBW08608\(^a\) (No. 17081) | 12.0 ± 0.5                 | 12.1 ± 0.5             | 12.0 ± 0.5             |             |
| GSB07-3186-2014\(^b\) (No. 200933) | 140 ± 8.0                 | 139 ± 7.7              | 140 ± 8.0              |             |
| GSB 07-1185-2000\(^c\) (No. 201431) | 15.0 ± 1.0                 | 15.0 ± 0.9             | 15.0 ± 1.0             |             |
| Tap water               | ND                         | 2                      | 2                      | 109 ± 3     |
| Bottled water           | ND                         | 2                      | 95 ± 2                 |             |

\(^a\) The main matrix elements (mg l\(^{-1}\)): K 2.2, Na 23, Ca 39, Mg 11, Pb 0.051, Cu 0.051, Cr 0.033, Zn 0.091, and Ni 0.061

\(^b\) The main matrix elements (mg l\(^{-1}\)): K 4.5, Na 10, Ca 20, Mg 5.0, Cu 0.4, Pb 0.152, Zn 0.493, Ni 0.157, and Cr 0.303

\(^c\) The main matrix elements (mg l\(^{-1}\)): pure water

**Figure captions**

**Fig. 1.** Effects of the volume concentrations of HCl on the fluorescence intensity of a 100 ng ml\(^{-1}\) cadmium solution

(■ HCl, ● HCl + 1% (m/v) thiourea, solution flow rate of 3 ml min\(^{-1}\), Ar carrier gas flow rate of 250 ml min\(^{-1}\), and an 18 V 2 A power adapter). The error bars are the standard deviations of n = 3.

**Fig. 2.** Effects of the solution flow rate on the fluorescence intensity of a 100 ng
ml⁻¹ cadmium solution
(carrier Ar flow rate of 250 ml min⁻¹, 10% of HCl, and an 18 V 2 A power adapter).
The error bars are the standard deviations of n = 3.