Efficient generation of volatile species for cadmium analysis in seafood and rice samples by a modified chemical vapor generation system coupled with atomic fluorescence spectrometry

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HIGHLIGHTS

- We develop a modified chemical vapor generation method coupled with AFS for the determination of cadmium.
- The response of Cd could be increased at least four-fold compared to conventional thiourea and Co(II) system.
- A simple mixing sequences experiment is designed to study the reaction mechanism.
- The interference of transition metal ions can be easily eliminated by adding DDTC.
- The method is successfully applied in seafood samples and rice samples.

GRAPHICAL ABSTRACT
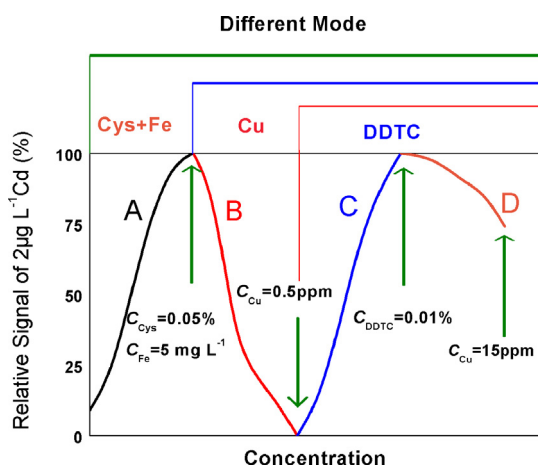
ABSTRACT

A vapor generation procedure to determine Cd by atomic fluorescence spectrometry (AFS) has been established. Volatile species of Cd are generated by following reaction of acidified sample containing Fe(II) and L-cysteine (Cys) with sodium tetrahydroborate (NaBH$_4$). The presence of 5 mg L^{-1} Fe(II) and 0.05% m/v Cys improves the efficiency of Cd vapor generation substantially about four-fold compared with conventional thiourea and Co(II) system. Three experiments with different mixing sequences and reaction times are designed to study the reaction mechanism. The results document that the stability of Cd(II)–Cys complexes is better than Cys–THB complexes (THB means NaBH$_4$) while the Cys–THB complexes have more contribution to improve the Cd vapor generation efficiency than Cd(II)–Cys complexes. Meanwhile, the adding of Fe(II) can catalyze the Cd vapor generation. Under the optimized conditions, the detection limit of Cd is 0.012 µg L^{-1}; relative standard deviations vary between 0.8% and 5.5% for replicate measurements of the standard solution. In the presence of 0.01% DDTC, Cu(II), Pb(II) and Zn(II) have no significant influence up to 5 mg L^{-1}, 10 mg L^{-1} and 10 mg L^{-1}, respectively. The accuracy of the method is verified through analysis of the certificated reference materials and the proposed method has been applied in the determination of Cd in seafood and rice samples.

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1. Introduction

An accurate and rapid analytical technique to detect Cd has been widely concerned, due to the toxicological importance of this ubiquitous element even at trace levels [1]. Generally, the combination of chemical vapor generation (CVG) with a specific and sensitive detector including atomic absorption spectroscopy (AAS) [2–4], atomic fluorescence spectrometry (AFS) [5–7], and inductively coupled plasma mass spectrometry (ICP-MS) [8,9] has been considered as an efficient approach for determination of Cd. The volatile cadmium species can be generated by using the reaction of Cd(II) and sodium borohydride ($NaBH_4$). It also can be generated by other borides. For instance, D'Ulivo and Chen reported the generation of volatile cadmium species from aqueous solution by using the reaction of Cd(II) and sodium tetraethylborate ($NaBEt_4$), which can be determined by non-dispersive AFS with a detection limit of $0.2\,ng\,mL^{-1}$ [10]. Recently, some new vapor generation techniques including electrochemical vapor generation [11,12] and photochemical vapor generation [13] are also reported to generate volatile cadmium species.

Whether it is obtained by chemical, electrochemical or photochemical methods, the vapor generation efficiency of Cd can be influenced by experimental settings, apparatus, quenching or interferences in solution [10–13]. Hence, numerous attempts have been made to improve the vapor generation efficiency of Cd or alleviate the interferences of the transition metal ions by preconcentration techniques including solid-phase extraction (SPE) [14], cloud point extraction (CPE) [15], and trapping [16,17]. It can be further increased by using organic media or adding masking agents. For example, Cacho et al. [18] reported a vapor generation method for Cd determination based on the reaction between Cd diethyldithiocarbamate (DDTC-Cd) in acidic dimethylformamidine (DMF) and borohydride in DMF. Sanz-Medel et al. [19] found that the surfactants, specifically didodecyldimethylammonium bromide (DDAB) could enhance the efficiency of Cd vapor generation. Guo and Guo [20] pointed out that thiourea (TU) and cobalt could greatly improve the generation efficiency of Cd. This synergistic effect has also been found between thiourea/8-hydroxyquinoline and other transition metal ions, such as iron and nickel [21,22]. We also reported that the efficiency of Cd electrochemical vapor generation can be highly increased by using organic media (HCOOH) as electrolytes [11]. Although its inherent advantages in providing better sensitivity and lower detected limit for Cd, these masking agents cannot overcome serious suppression from transition metal ions adequately. Chuachuad and Tyson found that thiourea/L-cysteine and cobalt in nitric acid increased the sensitivity of the determination [23]. The transition metal ions such as Cu(II) and Fe(III) suppressed the signal of Cd by 60–100% even at low concentrations ($0.1–1\,mg\,L^{-1}$). Manzoori et al. [24] reported that Cu(II) and Bi(III) had no significant influence when the interferent-to-Cd ratios were 20 and 100. Chen et al. [14] used a cellulose fiber packed micro-column to absorb the pre-concentrated Cd and the results showed that the detection limit of $3\,ng\,L^{-1}$ was derived, while the interferences from Cu did not beyond 100-fold. Li et al. [25] considered that sodium iodate ($NaIO_3$) as an additive can enhance the generation of volatile Cd species in acidic medium. Yet the performance of this procedure is still unknown in the presence of the interfering metal ions. Liva et al. [26] and Yilmaz et al. [27] reported that the volatile species of Cd were generated effectively by adding potassium cyanide (KCN). The deeply study displayed that Cu (II) and Pb(II) has no significant influence up to $1.0\,mg\,L^{-1}$ and $0.1\,mg\,L^{-1}$, respectively. However, a possible problem of this procedure is the toxic hydrogen cyanide.

Taking into account the actual concentration of cadmium in the sample is low and the concentration of transition metal ions is about at least 100–1000 times over the concentration of Cd. An effort is made in this work to find suitable CVG system for the determination of ultra-trace Cd in complex samples. Another purpose is to minimize the interference of transition metal ions contamination, to sensitive monitor the Cd pollution of the rice, kelp and lobster samples

2. Experimental

2.1. Apparatus

A double-channel non-dispersive atomic fluorescence spectrometer, AFS-230E (Beijing Haiguang Instrument Company, China), is used and controlled through computer. The light source, coded hollow cathode lamps (HCLs) of Cd (228.8 nm), is operated in a double-modulated pulsed mode to offer stable and high intensity radiation. The atomizer is a quartz furnace in a shielding mode, which is composed of a concentric inner tube (7 mm i.d × 14 mm length) and outer shielding tube (10 mm i.d × 18 mm length). Around the top of quartz furnace outlet is a resistance wire to ignite the gas mixture of argon, hydrogen and volatile analysts produced from the vapor generation. The flame is maintained without addition of any auxiliary hydrogen. Two sequential gas–liquid separators (GLS) are used to separate the gases from liquid. Instrument settings and operational parameters used for the experimental AFS system are summarized in Table 1.

2.2. Reagents and samples

All reagents used are of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Doubly deionized water (DDW) is used throughout. Cd standard stock solution is prepared by dissolving 0.2500 g of high-purity cadmium powder in 10 mL concentrated nitric acid and subsequently transferring to 250 mL flask and diluting to the mark with DDW. Working standard solution is obtained daily by stepwise dilution of standard stock solution with $0.6\,mol\,L^{-1}$ HAc. 2.0% (m/v) $NaBH_4$ solution is prepared by dissolving $NaBH_4$ in 0.3% (m/v) sodium hydroxide solution. Cysteine solution is prepared by dissolving L-cysteine in $0.1\,mol\,L^{-1}$ HCl solution. The stock solution of Fe(II) is prepared by dissolving a suitable amount of $FeCl_2$ in $0.1\,mol\,L^{-1}$ HCl solution. The DDTC solution is prepared by dissolving the sodium salt in DDW. Mixture of enhancement reagent solution is obtained by stepwise adding of Cys Fe and DDTC in $0.6\,mol\,L^{-1}$ HAc.

For interference studies, the different stock solutions are prepared by dissolving the proper amount of their chloride or nitrate salts (for cation) and sodium salt (for anion) in the HAc or HCl; working solutions are prepared by dilution with HAc and adjustment of the final acid concentration.

Three certified reference materials (CRMs) including dogfish liver (NRCDOLT-3), rice (GBW08510) and kelp (GBW08517) obtained from China National Research Center for Certified

Table 1
Operating parameters.

Parameter	Setting
Determination system	
High voltage of PMT (V)	−290
Peak current of lamp (mA)	30
Sample flow rate ($mL\,min^{-1}$)	8.0
Flow rate of carrier gas (Ar) ($mL\,min^{-1}$)	300
Flow rate of shield gas (Ar) ($mL\,min^{-1}$)	1000
Reaction system	
Cys (m/v)	0.05%
Fe(II)	$5\,mg\,L^{-1}$
$NaBH_4$ (m/v)	2.0%
Sample media	$0.6\,mol\,L^{-1}$ HAc