Room-temperature Chelate Vapor Generation of Lead Using Ammonium $O,O$-Diethyl Dithiophosphate as a Chelating Reagent and Determination by Atomic Fluorescence Spectrometry in Environmental Water Samples

Shuai LIU,* Jinsheng SUN,* Jianzhong HUO,** Xuchuan DUAN,*† and Yue LIU**†

*College of Life Sciences, Tianjin Key Laboratory of Animal and Plant Resistance, Tianjin Normal University, Tianjin 300387, China
**Key Laboratory of Inorganic-Organic Hybrid Functional Materials Chemistry (Tianjin Normal University), Ministry of Education, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, College of Chemistry, Tianjin Normal University, Tianjin 300387, China

A novel gas-liquid separator (GLS) system for chelate vapor generation (Che-VG) combined with AFS was developed for the determination of trace Pb. It was shown that Pb can form a volatile chelate by mixing of Pb with ammonium $O,O$-diethyl dithiophosphate (DEDTP) in various aqueous solutions. Under the optimal conditions (frit pores of the GLS, 5 – 15 μm; solution pH, 6.7; DEDTP concentration, 0.4%; flow rate of the two feed solutions in the on-line mode, 1.2 mL min$^{-1}$; and carrier gas flow rate, 150 mL min$^{-1}$), the calibration curve was linear up to 100 ng mL$^{-1}$ Pb. The limit of detection (LOD) was 1.1 ng mL$^{-1}$. The relative standard deviation was 5.6% for eleven replicate determinations of 10 ng mL$^{-1}$ Pb. The efficiency of Che-VG was estimated to be 12%, and the volatile Pb species was preliminarily studied by ICP-OES. This method was applied to determine trace Pb in water samples.

Keywords Chelate vapor generation, atomic fluorescence spectrometry, Pb

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Introduction

Pb is one of the heavy metals with unquestionable toxicity and one of the most hazardous elements to human health. Many nations and international organizations have a maximum allowable limit for Pb in various foods and water.1 Nowadays, methods based on atomic spectrometry are widely applied in the determination of Pb in various samples.2 However, the determination of trace Pb in food and environmental samples usually requires highly sensitive and specific instruments, which include graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS).3,4 In addition, as one of the most important branches of chemical vapor generation (CVG),5,6 a quartz tube consisting of an electrothermal vaporizer and a quartz tube atom trap coupled with atomic fluorescence spectrometry (QT-ETV-QTAT-AFS),7,8 hydride generation (HG) in combination with a heated quartz tube atomizer atomic absorption spectrometer (HG-QTA-AAS),9 atomic fluorescence spectrometry (HG-AFS)10 and inductively coupled plasma atomic emission spectrometry (HG-ICP-AES)11 are alternatives to ETA-AAS or ICP-MS for the determination of trace Pb. CVG based on sodium tetrahydroborate (THB) has been proven to be an effective approach for the determination of some elements due to its high sample introduction efficiency and low detection limit.12-15 In addition, photo-induced CVG for the determination of Pb has also been reported.16-18 Recently, room-temperature chelate vapor generation (Che-VG) as a new CVG technique for atomic fluorescence spectrometry was developed in our group. The performance and characteristics of Che-VG with several metal ions were studied including Zn$^{2+}$, Au$^{3+}$, Cd$^{2+}$ and Ni$^{2+}$. Further Che-VG was applied in the determination of Zn$^{2+}$, Au$^{3+}$, Cd$^{2+}$ and Ni$^{2+}$ in several types of samples.19-22 It was shown that some transition and precious metal elements can generate a volatile metal chelate by a chelating reaction with diethyldithiocarbamate (DDTC). It was reported that the Che-VG efficiency depended on not only the properties of the elements, but also the gas-liquid separator (GLS) parameters and other experimental conditions, such as flow rate, concentrations of acid and DDTC, efficiency-enhancing reagent, etc.22 In addition to DDTC, it was found that $O,O$-diethyl dithiophosphate (DEDTP) is also a promising reagent for the Che-VG technique.23 In this study, the effect of GLS was further investigated on the Che-VG efficiency for Pb using DEDTP as a chelating reagent. Furthermore, the developed method was assessed for the determination of Pb in environmental water samples.

† To whom correspondence should be addressed.
E-mail: skydxc@tjnu.edu.cn (X. D.); nkcmliu@yahoo.com (Y. L.)
## Experimental

### Reagents and materials

All solutions were prepared using distilled water. Working standard solutions were prepared daily by the stepwise dilution of a 1000 mg L⁻¹ stock solution of Pb (National Research Center for Certified Reference Materials, China). Sodium diethyldithiocarbamate (DDTC) and ammonium O,O-diethyl dithiophosphate (DEDTP) were obtained from Sigma-Aldrich Chemicals Ltd., Shanghai, China, and both chelating reagents were of analytical-reagent grade. Other chemicals used were of at least analytical-reagent grade.

Borate buffer solution at a pH of 7.4, which was used for sample analysis, was prepared with 9 mL of 0.2 M of H₃BO₃ and 1 mL of 0.05 M of Na₂B₄O₇.

### Instrumentation and apparatus

A non-dispersive atomic fluorescence spectrometer (Model RGF-6200, Beijing Bohui Innovation Technology Co., Ltd., Beijing, China) with a Pb hollow cathode lamp was used throughout. A Model GCH-500 hydrogen generator (Beijing BFHP Analytical Instruments Co., Ltd., Beijing, China) at a flow rate of 230 mL min⁻¹ was used to ignite the H₂–Ar flame of the atomizer of the AFS. The detailed working conditions for AFS are listed in Table 1. Model Avio200DV ICP-OES (Perkin-Elmer, USA) was used to study the mechanism and efficiency of Che-VG of Pb.

### Chelate vapor generation system

A continuous Che-VG system was used throughout the experiments. The core of the Che-VG consisted of two GLSs, made in house. The larger one had 5 - 15 μm frit pores in it, and the smaller one was used for the thorough separation of gas from the solution and waste drain. A schematic diagram of the Che-VG manifold is shown in Fig. 1. The larger GLS was designed on the right: height from the mixed solution inlet to the bottom of the frit, 10 mm; and height from the outlet of the mixture for carrier argon and solution to the bottom of the frit, 4 mm. The small GLS was placed on the left: height from the inlet of the mixture from the larger GLS on the right to the bottom of small rubber stopper, 10 mm. The length of the connecting pipe between the two GLSs: 10 mm. A 1.5-m silicone rubber pipeline (i.d. = 5 mm between the carrier outlet of the small GLS and the inlet of the atomizer) was used to transport steam. In addition, two old GLSs with 15 – 40 and 5 – 15 μm frit pores, which had been described in our previous work,²⁰ were used for a comparison with the new GLS. The detailed working parameters for the Che-VG system are summarized in Table 1.

### Results and Discussion

#### Performance of the new GLS

When a 0.4% DEDTP solution and 50 ng mL⁻¹ Pb was mixed in neutral distilled water without the addition of any acid and
pumped into the larger GLS at a 1.2 mL min⁻¹ feed rate on the right in Fig. 1, it was shown that very fine bubbles were produced, and the solution became very fine with a homogeneous foam phase with a milk-white color on the frit. When the height between the bottom of the rubber stopper and the surface of frit was 2 cm, the height of the foam phase in the GLS was approximately 1.5 cm from the frit, and the distance between the bottom of rubber stopper and the foam phase surface was approximately 0.5 cm. Such a homogeneous foam phase was then pushed immediately to the small GLS on the left in Fig. 1 by continuous foam phase steam coming from the rear. The volatile Pb chelate was separated from the solution by the argon carrier gas due to the smaller balance pressure in the small GLS. It was found that the position of the rubber stopper in the larger GLS was needed to keep a height of 2 cm from the bottom of the rubber stopper to the frit. When the height was higher than 2 cm, the mixture retention time and memory effect increased in the larger GLS. When the height was lower than 2 cm, the signal intensity decreased due to the low separation efficiency of the volatile Pb chelate by the argon carrier gas. Therefore, a height of 2 cm from the bottom of the rubber stopper to the frit was fixed in this work.

In order to further investigate this new Che-VG system in Fig. 1, three contrast experiments were carried out under the same experimental conditions (0.4% DEDTP, 50 ng mL⁻¹ Pb in neutral distilled water, 1.2 mL min⁻¹ feed solution flow rate, and 150 mL min⁻¹ argon carrier gas flow rate) by using the old different GLSs used in our previous work. As shown in Table S1 (Supporting Information), a 160 net fluorescence intensity of Pb was observed when the old GLS with 15 – 40 μm frit pores (A device) was used. A 170 net fluorescence intensity of Pb was observed when the old GLS with 5 – 15 μm frit pores (B device) was used. However, when the new GLS was used, a 240 net fluorescence intensity of Pb was observed. It was proposed that the new GLS with 5 – 15 μm frit pores (C device) could produce a finer liner carrier steam, and had a greater contact area, which lead to a higher separation efficiency for volatile Pb species. However, for the A device, since it had larger frit pores, the ability to separate volatile Pb species was worse than that of the C device. As for the B device, since the mixed solution became a very fine and homogeneous foam phase, which failed to be quickly drained even when the waste solution flow rate was 5 mL min⁻¹, the ability to separate volatile Pb species was limited. Therefore, a smaller frit was better than a larger one for the volatile Pb species. As shown in Fig. S1A (Supporting Information), a height of 2 cm from the frit to the exit was enough for separation, owing to the "zigzag flow direction" style design for the C device. Both A and B devices (Fig. S1B, Supporting Information) with a height of 6 cm were "linear flow direction" style design. It was inferred that the flow direction was also an important factor, besides the frit pores.

Since that chelate of DEDTP with Pb was stable in aqueous solutions with various pH values, an off-line mixing procedure for the Che-VG of Pb by DEDTP would be possible. In order to verify this inference, equal volumes of 0.4% DEDTP and 50 ng mL⁻¹ Pb standard solution (in neutral water) were mixed in a beaker, the mixture was pumped at a flow rate of 2.4 mL min⁻¹ into the C device, and a stable Pb signal was observed similar to that obtained by on-line mixing the same two solution. This result indicated that the volatile Pb DEDTP chelate species could be generated by either on-line or off-line mixing and separation. To simplify the operation, reduce investigation time, minimize the risk of contamination and improve accuracy, the on-line mixing procedure was chosen in the subsequent work.

**Effect of the type of chelating reagent and pH on the signal intensity**

In order to investigate the effects of different chelating reagents and pH on the signal intensity of Pb, two chelating reagents, DDTC and DEDTP, were tested. The investigation was conducted under a 0.4% chelating reagent concentration and 50 ng mL⁻¹ Pb solution, with feed rate of 1.2 mL min⁻¹ for chelating reagent. It was found no signal intensity for DDTC in various pH conditions, including various hydrochloric and nitric acid concentrations. However, under weak alkaline, neutral and low concentration nitric acid solution conditions, a relatively higher signal intensity of Pb obtained by DEDTP can be observed, which was shown in Fig. 2. It showed that pH values corresponding to the two maximum signals were approximately neutral (distilled water, pH 6.7) and 2 < pH < 5. Therefore, the effect of pH on the signal intensity of Pb was very harsh, and accurate regulation of the pH should be implemented in real sample analysis by the addition of borate buffer solution.
The above experimental results, Pb²⁺, i.e., and Ni can mainly exist in the form of cation ions, and these anions, possible coexisting metal ions were also investigated as interfering ions. No interference was observed.

**Effect of the DEDTP concentration**

In a neutral distilled water solution (pH of approximately 6.7), a 1.2 mL min⁻¹ feed rate for DEDTP and a 50 ng mL⁻¹ Pb solution were used to study the effect of the DEDTP concentration on the signal intensity of Pb. As shown in Fig. 3, as the DEDTP concentration increased, the intensity of the lead signal first increased, with the concentration of DEDTP reaching 0.4%, and then decreased. Thus, the concentration of 0.4% for DEDTP was used for subsequent experiments.

**Effect of the solution flow rate**

In this experiment, an interesting phenomenon was observed. As shown in Fig. S2A (Supporting Information), as the flow rate of the two feed solutions increased, the signal intensity rose. No optimum rate plateau was observed where the largest signal intensity existed, as described in our previous report for Zn, Au, Cd and Ni. This might be attributed to the fact that the volatile Pb-DEDTP chelate was very stable and had a long life span in aqueous solution due to the high stability of DEDTP in volatile Pb species was at least composed of sulfur, phosphorus, and likely in the form of Pb[(C₂H₅O)₂PS₂].

Furthermore, it was found that the features demonstrating the relationship between the signal and the pH was in a similar way to that of Ni. This could be caused by the fact that both Pb and Ni can mainly exist in the form of cation ions, i.e., Pb²⁺, [Pb(OH)]⁺ and [Ni(OH)]⁺ in neutral and weak alkaline aqueous solutions, respectively. The above experimental results further indicated that DEDTP could be a better reagent for Che-VG of some metal ions than DDTC. Thus, the study of DEDTP for Che-VG should be conducted in the near future.

**Effect of the argon carrier gas flow rate**

As shown in Fig. 4, the signal decreased as the argon flow rate increased. The maximum signal intensity was obtained at 150 mL min⁻¹. Based on this observation, a flow rate of 150 mL min⁻¹ was selected in this work.

**Efficiency and mechanism**

The efficiency of Che-VG for Pb was estimated by comparing the net signal intensity obtained by the proposed Che-VG procedure to that by conventional solution nebulization. The two calibration equations obtained by conventional solution nebulization and Che-VG using six Pb standard solutions (ng mL⁻¹: 5, 10, 20, 40, 60, and 80) were $I = 400.5631 \rho + 300.26$ and $I = 1670.52 \rho + 500.67$, respectively. Based on the enhancement in the sensitivity, about 12% Che-VG efficiency of Pb was estimated (assuming 3% efficiency for the conventional solution nebulization).

A preliminary study on the mechanism for the formation and release of volatile Pb species was conducted by ICP-OES with the same Che-VG apparatus used in AFS. The Pb standard (0, 2 and 4 mg L⁻¹ Pb²⁺) and 0.4% DEDTP solution were prepared using CO₂-free distilled water to avoid dissolved CO₂ from interfering with the determination of carbon in volatile species. According to the composition of ligand DEDTP⁻ = (C₂H₅O)₂PS₂⁻, the emission intensities of the elements that came from the ligand DEDTP were measured at 213.60 nm for P, 181.98 nm for S, 247.80 nm for C and 220.35 nm for Pb. Figure S3 (Supporting Information) showed a significant correlation between the normalized emission intensity for each element and Pb concentration. Although we do not know the exact contents of P, S, C and Pb in the gas phase, such a result indicated that volatiles Pb species was at least composed of sulfur, phosphorus, and likely in the form of Pb(C₂H₅O)₂PS₂.

**Interferences**

Individual ions were deemed not to cause interference if the signal intensity for the added foreign ion is within ±5% of that from 50 ng mL⁻¹ Pb in aqueous solution. First, the two most common anions in water samples, i.e., Cl⁻ and SO₄²⁻, were studied due to the fact that Pb can form complexes and precipitate with these two anions, respectively. In this work, it was found that the interfering limits of Cl⁻ and SO₄²⁻ are approximately 300 and 80 μg mL⁻¹, respectively. In addition to these anions, possible coexisting metal ions were also investigated as interfering ions. No interference was observed from 5 μg mL⁻¹ solutions of the following main group metal ions: Ca²⁺, Mg²⁺, K⁺, Na⁺ and Al³⁺. Furthermore, it also was found that several of the most common transition metal ions, Fe³⁺, Mn²⁺, Zn²⁺, Ni²⁺ and Bi(III) (as Bi(NO)₃), did not produce interference when their concentrations were at 1000 ng mL⁻¹ (no maximum allowable level). However, it was found that Cu²⁺ can suppress the signal of Pb at a 60 ng mL⁻¹ level. Obviously, the interference from common transition elements was
The 3 GLS was rinsed with deionized water for 1 min until the Pb to eliminate the memory effect in the sampling interval, the I occurring between these metal ions such as Fe³⁺, Mn²⁺, Zn²⁺, aqueous solution, and thus, no competitive reaction with DEDTP that DEDTP was very stable and did not decompose in neutral chelating reagent in an acidic solution. One reason might be eliminated in comparison with Che-VG using DDTC as a chelating reagent in an acidic solution. One reason might be that DEDTP was very stable and did not decompose in neutral aqueous solution, and thus, no competitive reaction with DEDTP occurred between these metal ions such as Fe³⁺, Mn²⁺, Zn²⁺, Ni²⁺, Bi(III) and Pb²⁺. Thus, the interference from these transition elements was relieved. Another reason could be that some transition metal ions could not exist in the form of cations in neutral and weak alkaline aqueous solutions, and thus, DEDTP would not chelate with these ions. This result indicated that Che-VG in neutral and weak alkaline solutions had better selectivity toward some metal ions.

Analytical figures of merit

Under the optimum experimental conditions (Pb solution pH, 6.7; DEDTP concentration, 0.4%; two feed solutions flow rates in an on-line format, 1.2 mL min⁻¹; and carrier gas flow rate, 150 mL min⁻¹), the calibration curve obtained using 6 standard Pb solutions at concentrations ranging from 5 to 100 ng mL⁻¹ was linear with an equation of \( I = 4.1775\rho - 4.1479 \) and a correlation coefficient of 0.998, where \( I \) is the peak area and \( \rho \) is the concentration of the Pb standard (ng mL⁻¹). Considering to eliminate the memory effect in the sampling interval, the GLS was rinsed with deionized water for 1 min until the Pb signal fell down to the background. The sample throughput was 30 h⁻¹. The 3σ limit of detection was 1.1 ng mL⁻¹ (n = 11). The relative standard deviation (RSD, %) of ten replicated measurements for a 20 ng mL⁻¹ Pb solution was 5.6. Table 2 showed the comparison of LOD between the developed method above to some published methods for the determination of Pb.

**Pb determination in real water samples**

Three types of water samples, from a river near our campus and a lake in our campus, respectively, were immediately analyzed after collection by first filtration with a 0.45-μm filter and then Che-VG treatment. In order to keep the pH of the water sample consistent with that of the standard solution and to eliminate the analytical errors produced by the pH, a buffer solution was added. It showed that a borate buffer solution at a pH of 7.4 was satisfactory for this analytical requirement. The results of an analysis of the samples and the recoveries from spiking them with Pb are given in Table 3. From this table, the added Pb can be quantitatively recovered from the water samples by the developed procedure.

**Conclusions**

Although a preliminary comparative experiment proved that the new GLS system was effective for the Che-VG of Pb, an in-depth study of the system should be continued. In this study, a GLS with 5 – 15 μm frit pores was promising for further enhancing the efficiency of Che-VG. It could be easier to strip volatile chelate species of the elements and to obtain a higher analytical sensitivity in Che-VG.

The present experimental results showed that the volatile Pb chelate can only be generated with DEDTP in wide pH range from pH 2 to 10 by on-line or off-line mixing of sampling. In addition, since the chelates between Pb and DEDTP showed a higher stability, and did not decomposed in various pH conditions, the Che-VG technique can be implemented in the batch sampling mode, and in this manner.

Compared with the hydride generation of Pb, this method showed advantages in avoiding introducing other toxic and dangerous reagents, such as potassium hexacyanoferrate(III), ammonium persulfate, hydrogen peroxide, etc., which were commonly used in hydride generation for the determination of Pb. Hence, the reported method saved analysis time, decreased the possibility of sample contamination as well as eliminated potential danger during analysis. Although analytical grade DEDTP has a similar price as analytical grade sodium tetrahydroborate, DEDTP is more stable in solution as well as air, and only a low concentration is required for Che-VG. Thus, DEDTP costs less than that of sodium tetrahydroborate. Furthermore, Che-VG combined with AFS can be obtained at a very low cost, and the developed method will be more convenient and suitable for use in a small-scale laboratory.

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**Supporting Information**

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

**References**

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