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Photochemical vapor generation of lead for inductively coupled plasma mass spectrometric detection

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ABSTRACT

Photochemical vapor generation (PCVG) of lead was successfully achieved with a simplified and convenient system, in which only low molecular weight organic acid and a high-efficiency photochemical reactor were needed. The reactor was used to generate lead volatile species when a solution of lead containing a small amount of low molecular weight organic acid was pumped through. Several factors, including the concentration of acetic acid, the concentration of hydrochloride acid, and the irradiation time of UV light were optimized. Under the optimal conditions, including the addition of 0.90% (v/v) acetic acid and 0.03% (v/v) hydrochloride acid, and irradiation time of 28 s, intense and repeatable signal of lead volatile species was successfully obtained and identified with inductively coupled plasma mass spectrometry (ICPMS). In addition, the effects from inorganic anions and transition metal ions, including Cl^-, NO_3^-, SO_4^{2-}, Cu^{2+}, Fe^{3+}, Co^{2+} and Ni^{2+}, were investigated, which suggests that their suppression to the PCVG of lead was in the order of $Cl^- < SO_4^{2-} < NO_3^-$ for anions and Ni^{2+}, $Co^{2+} < Fe^{3+} < Cu^{2+}$ for transition metal ions. Under optimized conditions, relative standard derivation (RSD) of 4.4% was achieved from replicate measurements ($n = 5$) of a standard solution of 0.1 μg L^{-1} lead. And, the limit of quantitation (LOQ, 10σ) of 0.012 μg L^{-1} lead was obtained using this method and the method blank could be easily controlled down to 0.023 μg L^{-1}. To validate applicability of this method, it was also employed for the determination of lead in tap water, rain water and lake water.

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1. Introduction

Lead is widely known as a poisonous metal, which especially has neurotoxic effects on the nervous system of the developing children and fetuses [1–3]. Meanwhile, lead is ubiquitous because of its countless sources in the environment, such as food, water, air and soil [4]. Due to its toxicity and the greatest possibility for exposure, lead has been considered to be one of the most severe "heavy metals" and has attracted the greatest attention of the scientists, general public, and environmental agencies in many countries. Therefore, developing accurate analytical methods for lead determination is both necessary and significant.

Inductively coupled plasma mass spectrometry (ICPMS) has been considered as the most favorable instrumental approach among the widely used techniques for the determination of trace element for its powerful sensitivity and outstanding detection limit [5–8]. In spite of these superior analytical performances, ICPMS suffers from inevitable interference problems especially in the presence of complex matrices [9], which usually have negative effects on sensitivity and repeatability. To deal with this, efforts to develop new sample pre-treatment procedure or sampling introduction method for matrix separation remain fascinating in ICPMS technique.

Chemical vapor generation (CVG) is widely used as an online separation method and has been coupled with atomic spectrometry and mass spectrometry for trace level element analysis [10–13]. Compared to conventional direct solution nebulization, CVG technique offers improved detection capability because of the high analyte transport efficiency, the increased mass flux of sample, and the efficient matrix separation. Since Thompson and Thomerson [14] first reported the generation of lead hydride, namely plumbane, about four decades ago, hydride generation (HG) has been applied in lead determination for various samples and the analytical figures of merit have been improved constantly [15–19]. Nonetheless, this technique still has its own limitation including relatively high blanks resulting from the oxidizing agent addition and interferences of transition metals and hydride-forming elements.

As one of superior CVG techniques, photochemical vapor generation (PCVG) could be a potential method for lead analysis, due to its unique advantages over traditional CVG, such as elimination of the need for fresh tetrahydroborate (THB) solution, decreased generation of

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hydrogen, elevated stability of the plasma source, potentially interference-free feature due to weakly reducing chemical reagents, relatively low blanks level, and large elemental scope [20–22]. However, the research is merely limited to the initial deduction of the potentiality of PCVG of lead by Guo et al. [23], an assessment of relative intensity enhancement factor by Sturgeon et al. [24], and an evaluation on the volatile lead generation efficiency of near to zero by Zheng et al. for many years [25]. For the latest development, an extremely high efficiency PCVG of lead was proposed by Gao et al. [26] using 5.0% formic acid medium with 3.0 µg g^{-1} Ni^{2+} addition. The method sensitivity was improved compared to the traditional methods for Pb analysis and the shortage of relatively higher detection limits of multicollector-ICPMS (MC-ICPMS) was also compensated.

According to our previous work for PCVG of tin [27], which was in the same IVA group with lead in the periodic table, good method performance was achieved with a simple PCVG system consisting of only a small amount of low molecular weight (LMW) organic acids, a similar high-efficiency photochemical reactor with ref. [26] and a quadrupole ICPMS. Herein, the main objective of this work was to develop a relatively simple and convenient method for the lead determination with online PCVG technique.

In this work, lower concentration of LMW organic acid was used to avoid the potentiality of any extra contamination and then to reduce the method blank. With a laboratory-built flow-through photochemical reactor with remarkably high transmissibility of UV light [28–30], the volatile product of lead generated from PCVG was then separated with a gas–liquid separator (GLS) prior to ICPMS detection. Hence, characteristic of this method for lead determination and quantitative analysis of trace levels of lead were investigated. To evaluate the applicability of the new method, water samples were tested and relatively good results were achieved.

2. Experimental

2.1. Reagents

All solutions were prepared using ultrapure water (18.2 MΩ cm) from a Milli-Q system (Millipore Filter Co., Bedford, MA, USA). Working solutions were prepared daily by stepwise dilution of the 1000 mg L^{-1} stock solution of lead (Fisher Scientific Co. Fair Lawn, NJ, USA) with diluted hydrochloric acid (Merck). The concentration of hydrochloric acid spiked in the working standard solutions was 0.03% (v/v). Solutions of LMW acids were prepared with guaranteed grade formic acid, acetic acid and propionic acid purchased from Sinopharm Chemical Regent Co., Ltd. (Shanghai, PR China). The guaranteed grade KCl, KNO$_3$ and MgSO$_4$·7H$_2$O were also purchased from Sinopharm Chemical Regent Co. Stock solution of Cu, Fe, Co and Ni was made of their transition metal nitrates (spectroscopic pure) and diluted nitric acid (Merck, 5%, v/v) for the investigation of the effect of these transition metals, respectively. The argon gases used in this study were of high-purity grade (≥99.999%).

2.2. Apparatus

As shown in Fig. 1, the whole instrumental setup was mainly consisted of a photochemical reactor, a peristaltic pump (LEAD-1, Baoding Longer Precision Pump Co., Ltd., PR China), a six-port injection valve (VICI 24VDC RoHS, Valco Instruments Co. Inc., USA) and an Agilent 7700× ICPMS (Agilent Technologies Inc., USA), which was programmable-controlled with a laboratory-developed operating system. The ICPMS was optimized daily to obtain a stable sensitivity, less doubly charged ions (≤2.0%) and oxides (≤1.2%) with 1 µg L^{-1} tuning solution of ^{7}Li, ^{89}Y, ^{140}Ce and ^{205}Tl in the pneumatic nebulization (PN) mode. For the PCVG procedure, data were collected in the Time Resolution Analysis (TRA) mode for real-time monitoring. The optimized conditions for PCVG and ICPMS are listed in Table 1 and Table 2.
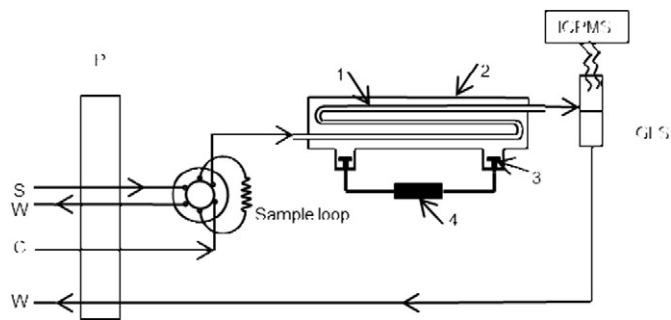

Fig. 1. Schematic illustration of the experimental system. 1, quartz tube for reaction; 2, low-pressure mercury lamp chamber; 3, tungsten electrode; S, sample; C, carrier flow solution; W, waste; P, pump; FI, flow injection; GLS, gas–liquid separator.

The photochemical reactor was composed of a 19-W low-pressure mercury lamp (Beijing Titan Instrument Co. Ltd., Beijing, China) and an internal reaction tube with an active volume approximately of 720 µL (1019 mm in length × 0.3 mm i.d.). A pair of tungsten electrodes was used to electrically connect the low-pressure mercury lamp to a 220 V, 50 Hz AC power source. The reaction tube, made of synthetic quartz, was used as a sample channel for high-efficiency irradiation with UV light.

With a polytetrafluoroethylene (PTFE) sample loop of 800 µL (fixed), the analyte solution was loaded and injected using a carrier flow of ultrapure water and then irradiated with UV emission in the photochemical reactor. The irradiation time of the lead solution with UV emission was controlled by changing the revolutions of the peristaltic pump. The conventional argon carrier gas of ICPMS was used as the carrier flow for the GLS. The volatile vapor generated in the PCVG reaction was directly transported into the ICPMS spray chamber at 2 °C via a quartz tube adaptor for removal excess water vapor.

2.3. Procedure

Briefly, volatile lead species were generated when standard or sample solutions of lead containing different kinds of LMW organic acids were introduced into the photochemical reactor for a typical irradiation time of 28 s with the sample flow rate of 1.5 mL/min. The solution was then flushed with carrier flow of ultrapure water to the GLS wherein the volatile lead species were rapidly separated from the liquid phase and transported into ICPMS by the carrier gas flow for lead detection in the TRA mode. Considering the radiogenic property of lead, which was always utilized to derive the provenance of materials [31], the isotopes of ^{206}Pb, ^{207}Pb and ^{208}Pb were simultaneously monitored and their peak signals were integrated and added up to avoid random error from isotopic abundance difference between various types of samples and standard solution.

To verify the method applicability, three types of samples including tap water, rain water and lake water were collected and stored in polytetrafluoroethylene (PTFE) bottles after filtration with 0.45 µm filter (mixed cellulose ester, Millipore) and acidification with optimal acetic

Table 1
Optimized operating conditions for PCVG.

Parameter	Condition
Acetic acid concentration	0.90% (v/v)
Hydrochloric acid concentration	0.030% (v/v)
Sample flow-rate	1.53 mL min^{-1}
Sample loop	800 µL
Dead volume of photochemical reactor	720 µL
Irradiation time	28 s
Carrier gas flow-rate for GLS	0.90 L min^{-1}