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Saturated Solution of PbSO_4 as Standard Stock Solution and Its Applications in Analytical Spectroscopy: Screening Analysis of Lead in Natural Water and *Usnea longissima*

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Abstract: A saturated PbSO_4 aqueous solution, which was prepared by dissolving commercially available solid PbSO_4 in doubly distilled water, was employed as a standard stock solution of lead for the visual colorimetric determination of lead in water and atomic fluorescence spectrometric determination of lead in whole *Usnea longissima* (i.e., Methuselah's beard lichen). The concentration of lead in this saturated solution is theoretically calculated to 27.8 mg/L by using the solubility product constant of PbSO_4 at 25°C. The standard solution series is by further dilution of the saturated solution. A validation experiment proved the feasibility of using the saturated solution as the standard stock solution of lead. The experimental conditions, mainly the temperature, that affect the equilibrium of precipitation–dissolution in the saturated solution were

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investigated. The saturated PbSO_4 solution was proved to be accurate enough for the purpose of screening analysis of lead in these samples.

Keywords: Atomic fluorescence spectrometry, hydride generation, lead sulfate, *Usnea longissima*, visual colorimetry, water

INTRODUCTION

Lead is one of the heavy metals frequently evaluated for its concentrations in various samples because of its great toxicity. By exposure to lead-contaminated foods, infants and children can suffer serious physical or mental retardation,^[1,2] while adults may suffer kidney problems or high blood pressure.^[2] Because of its numerous industrial applications,^[3–5] lead could pose high risks to the environment either by inadequate manufacturing process or by accident, therefore, monitoring lead levels in the environment is of significance.

Traditionally, to obtain a standard solution series, one needs to dilute the commercially available standard stock solution or to weigh and dissolve the high-purity metal or its compounds with a strong acid. Furthermore, a standard solution expires in a limited period of time compared with a solid standard. Also, high-purity metals or their compounds are expensive products, and the dissolution may be labor- and time-consuming. Therefore, Panichev et al.^[6] proposed a new way for preparation of standard solution, that is, a saturated solution of PbCrO_4 as a calibration reference material for Cr(VI). Without an accurate weight of PbCrO_4 , the concentration of Cr(VI) in the saturated solution of PbCrO_4 can be known simply by theoretical calculation. In this work, a saturated solution of PbSO_4 was used as a standard stock solution of lead, with the concentration of lead in the saturated solution theoretically calculated to 27.8 mg/L by using the solubility product constant of PbSO_4 at 25°C. Then it was successfully applied to the field screening analysis of lead in water by visual colorimetry and the screening of lead pollution in *Usnea longissima* by hydride generation atomic fluorescence spectrometry.

MATERIALS AND METHODS

Instruments

A commercial hydride generation atomic fluorescence spectrometer (HG-AFS) (AFS-2202, Beijing Haiguang Instrument Co., Beijing, China) was used to validate the feasibility of using the saturated solution of PbSO_4 as the standard stock solution and for the determination of lead in the *Usnea longissima* samples. The optimized instrumental parameters were as

follows: voltage of photomultiplier tube, -290 V; current of hollow cathode lamp, 60 mA; carrier (Ar) flow rate, 400 mL/min; shield gas (also Ar) flow rate, 1000 mL/min; height of atomizer, 9 mm; quantification mode, peak area; and read time, 20 s. The operation program for the intermittent flow reactor consisted of four steps. The first step is merely 6 s in duration for starting the measurement. The second step is to sample the analyte solution: duration, 10 s; pump rotation speed, 100 rpm. The third step: duration, 6 s; pump rotation speed, 0 rpm. The fourth step is to take a reading: time, 16 s; pump rotation speed, 120 rpm.

A common household cooking microwave oven (WP800T, Galanz Microwave Oven Corporation, Foshan, China) with five shifts (37% power, 40% power, 66% power, 85% power, and 100% power) was used for the closed-vessel (70-mL Teflon containers) microwave sample digestion. The full power for the microwave oven is 800 W. An electric hot plate (EH20A, LabTech Corporation, Beijing, China) with a controllable temperature range from 40°C to 250°C was used for the evaporation of the digests. The operating program of the microwave oven was composed of five steps: 3 min, 296 W; 3 min, 320 W; 3 min, 528 W; 3 min, 800 W; and 2 min, 680 W.

A flame atomic absorption spectrometer (GGX-9, Beijing Haiguang Instrument Co.) equipped with a flame quartz furnace (FF-AAS) was used to verify the accuracy of the lead concentrations in water samples determined by the proposed visual colorimetric procedure. The whole apparatus was similar to Berndt's^[7] but with a quartz tube instead of a nickel tube. Its working conditions were as follows: voltage of the photomultiplier tube, -540 V; current of lead hollow cathode lamp, 6.0 mA; acetylene flow rate, 1.5 L/min; air flow rate, 5.0 L/min; height of atomizer, 7.0 mm; current of deuterium lamp, 191 mA; slit bandwidth, 0.2 nm; and analytical wavelength, 283.3 nm.

Reagents and Standard Solutions

All solutions were prepared using doubly distilled water (DDW) made with a quartz sub-boiler (Guoqiang Glass Instrument Corporation, Jintan, China). Lead sulfate (A.R., Chengdu Kelong Chemical Reagent Factory, Chengdu, China) was used to prepare the saturated solution. Lead standard stock solution (National Standard Reagent Center, Beijing, China) was used to obtain standard series solutions for the purpose of comparison. Hydrochloric acid (Reagent Grade, Chengdu Kelong Chemical Reagent Factory), sulfuric acid (A.R., Chengdu Kelong Chemical Reagent Factory), potassium borohydride (A.R., Lianhe Chemical Reagent Research, Chengdu, China), sodium hydroxide (A.R., Changlian Chemical Reagent Co., Chengdu, China), and potassium ferricyanide (A.R., Lianhe Chemical Reagent Research) were used in the validation experiments and for the measurement of lead in *Usnea longissima* samples by HG-AFS (hydride generation atomic

fluorescence spectrometry). In addition, nitric acid (A.R., Kelong Chemical Reagent Factory, Chengdu, China), hydrofluoric acid (A.R., Institute of Organic Chemistry, Shanghai, China) and 30% hydrogen peroxide (A.R., Kelong Chemical Reagent Factory) were used for the digestion of the *Usnea longissima* samples.

Dithizone 0.0050 g (A.R., The Third Reagent Factory, Shanghai, China) was dissolved and diluted to 50 mL with ethanol (A.R., Chengdu Kelong Chemical Reagent Factory) as the colorization reagent. Phenanthroline 0.0875 g (A.R., Kemiu Chemical Reagent Development Center, Tianjin, China) was dissolved and diluted to 25 mL using DDW. Thiourea (A.R., East Reagent Factory, Chongqing, China) was prepared as a saturated aqueous solution. Potassium thiocyanate 0.6375 g (A.R., Chengdu Chemical Reagent Factory) was dissolved and diluted to 25 mL with DDW. Phenanthroline, thiourea, and potassium thiocyanate were used as masking reagents.

Experimental Procedures

Preparation of Standard Lead Solutions by Using a Saturated Solution of PbSO_4

Preparation of saturated solution of PbSO_4 : At 25°C, excessive PbSO_4 was put in a clean beaker (100 mL), 50 mL DDW was then added, and the solution was stirred sufficiently. The solution was then left for one-half hour to reach the precipitation–dissolution equilibrium prior to use. Finally, the solution was filtered with a piece of filter paper (0.2 μm). According to the formula of the solubility product constant,^[8] the concentration of Pb^{2+} in the saturated solution of PbSO_4 can be calculated as follow:

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = 1.8 \times 10^{-8}$$

$$[\text{Pb}^{2+}] = [K_{\text{sp}, \text{PbSO}_4}]^{1/2} \text{ (mol/L)}$$

$$M_{\text{Pb}} = 207.2 \text{ g/mol}$$

thus, the concentration of Pb^{2+} in the saturated solution at 25°C is theoretically 27.8 mg/L.

Standard calibration series: The working lead solution of 1.0 mg/L was from dilution of the saturated solution. For the purpose of comparison, a working standard solution of 1.0 mg/L was then made from step dilutions of a standard stock solution purchased from National Standard Reagent Center of China. The two working solutions were used to obtain two different series of working solutions, which were used to construct two five-point calibration curves by HG-AFS under the optimized experimental conditions. The lead concentrations of the two series were 10, 20, 40, 60, and

80 ng/mL, respectively, each of which contained 2% (v/v) hydrochloric acid and 10% (m/v) potassium ferricyanide.

Determination of Pb in Water Samples by Visual Colorimetry

First, a working standard solution of 5 mg/L, which was obtained by diluting the saturated solution, was used for the preparation of a standard series containing 0.5, 1.0, 1.5, and 2.0 mg/L Pb²⁺ in four 10-mL cuvets, respectively, each including 0.5 mL saturated thiourea, 0.2 mL phenanthroline (3.5 g/L), 0.5 mL potassium thiocyanate (25 g/L), and 1 mL dithizone (0.1 g/L). For the sample analysis, instead of the lead working standard solution, 7 mL water from Funan River and 7 mL water from Hehua Pool were used. The masking reagents were added and reacted with interference ions for 3 min prior to the addition of dithizone. The three masking reagents were used to mask Cu²⁺, Fe²⁺, Zn²⁺ by coordinating effects.^[9] These metal ions are common in natural water, and they cause the major interferences. Visual comparison was carried out when the color of the solutions had stabilized.

Determination of Lead in *Usnea longissima* Samples

Sample collection and sample handling: *Usnea longissima* is also called Methuselah's beard lichen, and it is widely found in the southwest of China. In this experiment, samples of *Usnea longissima* from Kalonggou Ravine in Heishui county of Sichuan Province of China were collected from a variety of trees of the scenic mountain areas at different altitudes. The total *Usnea longissima* samples were cleaned with DDW and dried at 60°C in an oven for 6 hr, and the samples were ground to 80-mesh powder. Finally, the powder was kept in clean polyethylene bags in a desiccator.

Aliquots of 0.1 g of the *Usnea longissima* powder were accurately weighed into Teflon vessels, to each of which 2 mL HNO₃, 0.5 mL H₂O₂, and 0.5 mL HF was added, and the vessels were slightly shaken to mix the sample and liquid. The Teflon vessels were closed tightly prior to the microwave digestion procedure. After the microwave heating, they were taken out of the microwave oven and cooled to the ambient temperature before being opened. The contents in the containers were quantitatively transferred into small Teflon beakers and heated to near dry on an electric hot plate at 150°C. The residues obtained were dissolved and transferred to 10-mL volumetric flasks with a mixture of 10% K₃Fe(CN)₆ and 2% HCl for the determination of lead by HG-AFS. Reagent blank was also prepared under the same conditions. Essential safety precautions must be taken during the whole digestion procedure, and an adequate ventilation system is necessary because HF is involved.

RESULTS AND DISCUSSION

Validation of the Saturated PbSO_4 Solution as Lead Standard Solution

Figure 1 shows that the two calibration curves, one by using a PbSO_4 saturated solution as a standard solution and another by a regular standard solution, are in good agreement in terms of sensitivity (i.e., the slope, 74.0 and 76.6, respectively) and correlation coefficient (0.9904 and 0.9957, respectively). Thus, it is feasible to employ the PbSO_4 saturated solution as the standard stock solution.

Factors that Affect Precipitation–Dissolution Equilibrium

Salt effect, pH, and temperature can affect the solubility of PbSO_4 . In this work, high-purity PbSO_4 and DDW were used for the preparation of the standard solution, so salt effect and pH are not considered as affecting factors. In this work, the temperature is the only major factor affecting the PbSO_4 solubility. According to the solubility and coefficients of activity data published in the literature, when the temperature variation is within $25 \pm 5^\circ\text{C}$, the concentration of lead in the saturated solution is $27.8 \pm 2.6 \text{ mg/L}$, that is, about 9% relative variation.^[10] This should be good enough for a standard solution for screening purpose. Further, it is not difficult to control the temperature within $25 \pm 1^\circ\text{C}$, and this means that the concentration of lead can be more accurate. Nevertheless, clean vessels and DDW of 25°C are recommended for preparation of the saturated PbSO_4 solution, and it should be filtered at the same temperature before use.

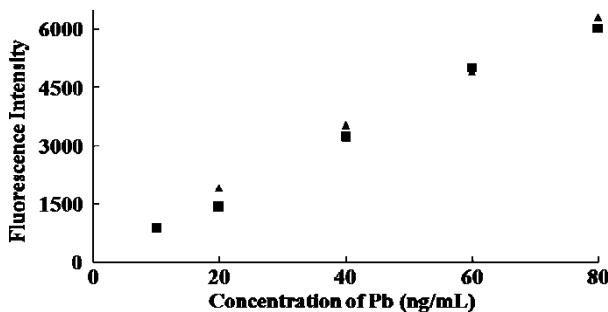


Figure 1. The agreement of the two calibration curves (■ prepared from the standard solution, $Y = 74.0X + 138$; and ▲ from the saturated solution, $Y = 76.6X + 290$). Here Y is the fluorescence intensity, and X is the lead concentration (ng/mL).

Application I: Field Screening of Lead Pollution in Natural Water by Visual Colorimetry

One of the applications of the saturated solutions of PbSO₄ is to use it as a lead standard solution for field screening of lead pollution in natural water. A traditional visual colorimetric method was chosen for the field use because it does not require a complicated instrument. For a colorimetric method, concentrations of colorization reagent, masking reagent, and buffer solution are essential. To reduce secondary environmental pollution from the screen analysis, it is important for one to use minimal amounts of reagents. According to Liu's work,^[11] the absorbance reaches the maximum when pH is 7. Without adding a buffer solution, the pH value in this work was already approximately 6, and the absorbance was large enough to identify the color scale of the standard series. So a buffer solution was not adopted for the reason of simplicity and environmental cleanliness. Surfactants have been used to enhance the solubility of colorization reagents in aqueous solutions for better interaction among analytes and reagents,^[12] but we were pleased to find that a surfactant was not a must for the proposed procedure. A reagent box including the necessary reagents can be prepared for field use, without the need of any analytical instruments.

The steady state of lead in its compounds is Pb(II),^[13] and the dominating state of lead in water is also Pb(II).^[14,15] Consequently, the total lead concentration in natural water can be estimated approximately by monitoring of Pb(II) concentration. The concentrations of Pb(II) in both samples from Funan River and Hehua Pool (prefiltered with 0.2 μm filter paper) were found to be about 0.5 mg/L by visually comparing them with the standard series, thus the water samples were not lead-contaminated, as the total lead in dischargeable wastewater must be lower than 1 mg/L according to National Standard (GB 8978-1996) in China. The analytical results were further validated by FF-AAS.

Application II: Determination of Lead in *Usnea longissima* by HG-AFS

The study of the lead-contamination of *Usnea longissima* may provide environmental pollution information of the studied area. By using the proposed method for the preparation of lead standard solutions, lead in *Usnea longissima* samples were determined by HG-AFS and compared with those by ICP-MS (inductively coupled plasma mass spectrometry), as shown in Table 1. It can be seen that the results by HG-AFS and by ICP-MS were generally comparable, considering the low level of lead contamination. Samples 1 through 5 were collected from the same area at different altitude, from high to low. No apparent trend for the lead concentration was found for the samples from different altitude. However, sample 6, which was collected from a different mountain area about 200 miles away, has much higher lead concentration. The high

Table 1. The analytical results of lead in the *Usnea longissima* samples

<i>Usnea longissima</i>	HG-AFS (Pb \pm 3 SD), $\mu\text{g/g}$	ICP-MS (Pb \pm 3 SD), $\mu\text{g/g}$
Sample 1		
Trial 1	3.9 \pm 0.1	2.8 \pm 0.1
Trial 2	3.3 \pm 0.2	
Sample 2		
Trial 1	2.1 \pm 0.3	2.5 \pm 0.1
Trial 2	2.1 \pm 0.2	
Sample 3		
Trial 1	3.3 \pm 0.1	2.6 \pm 0.1
Trial 2	3.2 \pm 0.1	
Sample 4		
Trial 1	2.4 \pm 0.2	2.7 \pm 0.1
Trial 2	2.6 \pm 0.4	
Sample 5		
Trial 1	3.0 \pm 0.3	3.2 \pm 0.1
Trial 2	3.1 \pm 0.3	
Sample 6		
Nos. 1–4	24.3 \pm 5.6	26.0 \pm 5.3 ^a

SD, standard deviation of three measurements.

^aMeasured with GF-AAS, and for four samples.

standard deviation originated from the sample heterogeneity (i.e., four original samples from the same mountain area). This difference could have originated mainly from the difference in the environment for its growth, such as the contamination level of the soil, the water, and the air. Unfortunately, we do not have the relevant information, so further conclusions can not be made at this point.

CONCLUSIONS

In this investigation, saturated PbSO₄ solution, which was prepared by using commercially available solid PbSO₄, was employed as standard stock solution of Pb. The concentration of Pb in this saturated solution was theoretically calculated via the solubility product constant of PbSO₄. It was successfully applied to the field screening analysis of lead in water by visual colorimetry and the screening of lead pollution in *usnea longissima* by HG-AFS.

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