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Determination of Pb(II) in natural water with dibromo-*p*-methyl-sulfonazo by the light-absorption ratio variation approach

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Abstract: Pb ions can react sensitively with dibromo-*p*-methylsulfonazo (DMSA) to form a blue complex, whose absorption is maximal at 630 nm. By means of the light-absorption ratio variation approach (LARVA), the direct determination of Pb was developed in 0.3 M nitric acid and plots of ΔA_r^{-1} vs. c_{Pb}^{-1} are linear where ΔA_r is the light-absorption ratio variation and c_{Pb} Pb(II) concentration is between 0 and 5.0 mg/L. The limit of detection (3σ) of Pb(II) is only 0.02 mg/L. This method was applied to direct analysis of natural water with satisfactory results.

Key words: Light-absorption ratio variation, spectrophotometry, dibromo-*p*-methylsulfonazo, determination of Pb(II), natural water

1. Introduction

Pb(II), one of the most topically toxic metals, is widely distributed in water and soil with recognized accumulative and persistent characteristics¹ When accumulated in the human body, Pb(II) causes damage to organs and other systems (especially in young children)²⁻⁴ In recent years, water pollution has caused blood lead accidents in children frequently in China. Although many sophisticated techniques for the determination of trace Pb(II) have been developed, including MS, ICP, AAS, chromatography, and chemiluminescence,⁵⁻⁹ factors such as the low cost of the instrument, easy handling, lack of requirement for consumables, and almost no maintenance have caused spectrophotometry to remain a popular technique, particularly in laboratories in developing countries with limited budgets¹⁰ Various spectrophotometric reagents such as sodium diethyldithiocarbamate,¹¹ dibromo-methyl-carboxysulfonazo,¹² 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol,¹³ and dibromo-*p*-chloro-arsenazo¹⁴ have also been reported for the spectrophotometric determination of lead in various complex materials and samples. Meanwhile, the further development in analytically significant chromophoric systems and methodology offers new possibilities for a variety of analytical applications. As a sensitivity increasing spectrophotometric method, the light-absorption ratio variation approach (LARVA) was established by Gao's group,¹⁵ based on the sensitive variation in the light-absorption ratio of a complexation system. The analytical sensitivity and accuracy have been greatly improved^{16,17} For example, Tang et al. used bromopyrogallol red to determine iron ions at pH 6.23 by LARVA¹⁸ Zhao et al. synthesized the MSCPA chromophore to react with copper ions at trace level¹⁹ As an asymmetric bisazo derivative of chromotropic acid with one *o*-sulfonic functional group (Figure 1), dibromo-*p*-methylsulfonazo (DMSA) was reported as a good sensitive and selective chromogenic

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reagent to barium, strontium, and lead^{20,21} However, the excessive DMSA co-existing in the reaction solution often interfered with the accurate determination of the DMSA-Pb(II) complex. In this work, the LARVA was applied to the direct determination of trace amounts of Pb(II) in water using the DMSA-Pb(II) complexation so as to raise the analytical accuracy and sensitivity. The parameters influencing the determination were evaluated. The applicability is in the linear range from 0 to 5 mg/L Pb(II) and the detection limit only 0.02 mg/L. The method was successfully applied to determine trace amounts of Pb(II) from natural water samples and certified reference material.

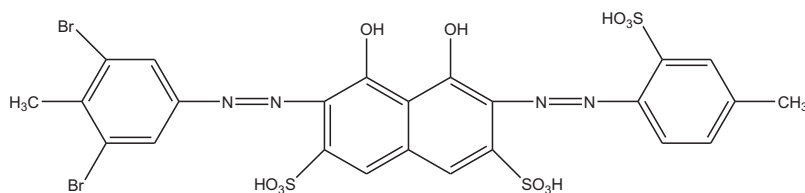


Figure 1. Structure of dibromo-*p*-methylsulfonazo (DMSA).

2. Experimental section

2.1. Apparatus and reagents

A Lambda-25 spectrometer (PerkinElmer Instruments, USA) was used to record the absorption spectra. A BS110S electronic balance (Sartorius Instruments, Beijing, China) was used to accurately weigh the standard substances and DMSA. A stock standard Pb(II) (1000 mg/L) solution was purchased from the National Research Center for Certified Reference Materials (Beijing, China). Both 0.100 and 1.00 mg/L Pb(II) standard use solutions were prepared by diluting the above solution. A 0.6407 mM DMSA was prepared by dissolving 50 mg of dibromo-*p*-methylsulfonazo (content >99%, Jameskin Reagents Institute of Shanghai, China) in 100 mL of deionized water. It was used to complex Pb(II). An Optima 2100 DV inductively coupled plasma optical emission spectrometer (ICP-OES) (PerkinElmer, USA) was used to verify the accuracy of the method. The wavelength of Pb(II) was 220.23 nm, which was recommended by the manufacturer. The standard reference material (GBW 08571) was pretreated according to the literature²²

2.2. Recommended procedures

A solution containing less than 50 μg of Pb(II) was transferred into a 10-mL calibrated flask. Then 3 mL of 1 M HNO_3 and 0.60 mL of 0.6407 mM DMSA were added. The solution was diluted to 10 mL with deionized water and mixed well. By the same method, a reagent blank without Pb(II) was prepared. After 10 min, the absorbances (A_{λ_1} and A_{λ_2}) of the sample solution and those ($A_{\lambda_1}^0$ and $A_{\lambda_2}^0$) of the blank were measured at 525 and 630 nm with a 1-cm cell against water reference. The ΔA_r was calculated by $\Delta A_r = A_{\lambda_2}/A_{\lambda_1} - A_{\lambda_2}^0/A_{\lambda_1}^0$. According to the standard equation, $\Delta A_r^{-1} = pc_{Pb}^{-1} + q$, the concentration (c_{Pb} , mg/L) of Pb may be calculated, where both p and q are the regression constants. Because the sensitivity factor p^{-1} is the inverse ratio to the concentration of DMSA added,¹⁵ the less DMSA added may bring out higher analytical sensitivity. Nevertheless, too low DMSA will result in an obvious error, e.g., increasing the fraction of instrument noise signal. It is appropriate for the addition of chromophore to produce a peak absorbance between 0.05 and 0.2.

3. Results and discussion

3.1. Absorption spectra

The complex reaction between DMSA and Pb(II) occurred in the acid medium because the reagent will form a 1:2 blue complex with lead ions under acid conditions²³. The absorption spectra of the Pb(II)–DMSA solutions in various acid concentrations are shown in Figure 2. All of the curves showed that the absorption peaks of the solutions are located at 630 nm and the valleys at 525 nm. These 2 wavelengths were used in the determination of Pb(II) by LARVA. Curve 2 indicated that the absorbance difference between the peak and the valley approaches its maximum in 0.3 M HNO₃.

Effects of the reaction time on the absorption spectra of the Pb(II)–DMSA complex were determined. The absorbance difference between the peak and the valley indicated that the reaction is complete in 5 min. Moreover, the light absorption of the complex solution is stable for at least 180 min.

3.2. Effect of DMSA, calibration graphs, and LOD of Pb(II)

From variation in ΔA_r of the solutions with the initial constant molar ratio of Pb(II) to DMSA at 10 $\mu\text{g}/\mu\text{mol}$ (Figure 3), ΔA_r approaches a maximal constant when DMSA is more than 0.050 mM. The sensitivity $\Delta A_r/c_{Pb}$ becomes higher with decreases in DMSA concentration. However, the noise of the spectrometer becomes serious if the DMSA concentration is too low. In order to optimize the addition of the DMSA solution, the determination of replicated reagent blanks, i.e. without Pb(II), was carried out.

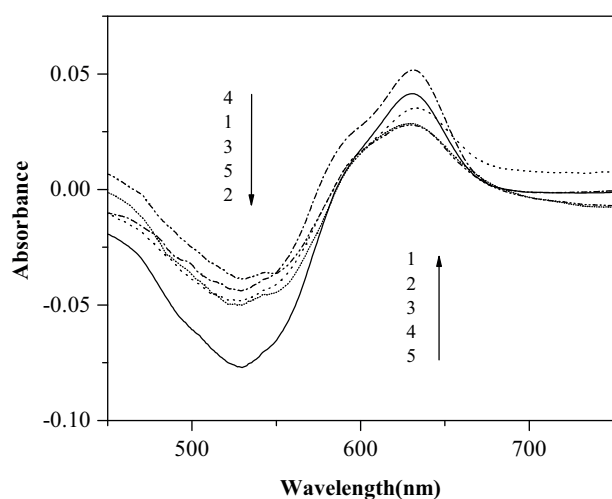


Figure 2. Absorption spectra of the Pb(II)-DMSA solutions in various acid concentrations. 1 to 5: 0.2, 0.3, 0.4, 0.5, and 0.6 M HNO₃.

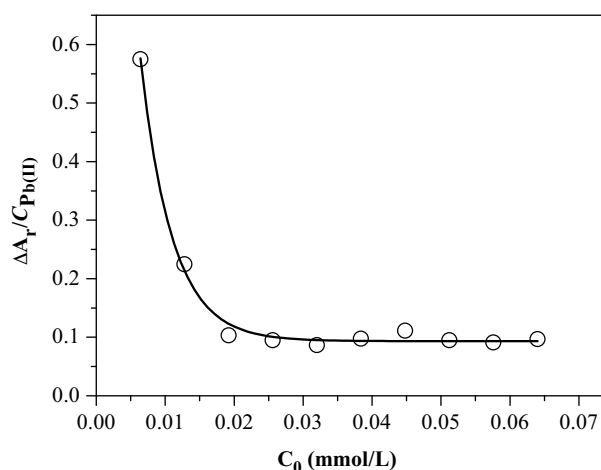


Figure 3. Variation in $\Delta A_r/c_{Pb(II)}$ of the solutions with the same ratio of Pb(II) to DSMA at 10 $\mu\text{g}/\mu\text{mol}$.

Four series of standard Pb(II) solutions between 0 and 3.0, 0 and 2.0, 0 and 5.0, and 0 and 8.0 mg/L were prepared and 0.40, 0.50, 0.60, and 0.80 mL of 0.6407 mM DSMA were added, respectively. The absorbances of each solution were measured at 525 and 630 nm against water reference and ΔA_r was calculated according to the recommended procedures. Their regression equations are given in Table 1. Simultaneously, 12 replicated blanks of each series were determined and their standard deviations (σ) are shown in Table 1. The LOD of Pb(II), defined as 3σ , was calculated and series 3 has the lowest LOD at 0.02 mg/L Pb. Therefore, 0.60 mL of 0.6407 mM DSMA added is suitable for analysis of water samples.

Table 1. Calibration equations for determination of Pb(II) with DMSA.

Series	DSMA, mM	c_{Pb} , mg/L ^a	Standard equation	R ^b	σ^c	LOD, mg/L
1	0.0256	0–3.0	$\Delta A_r^{-1} = 19.4c_{Pb}^{-1} + 5.92$	0.9971	0.0100	0.06
2	0.0320	0–2.0	$\Delta A_r^{-1} = 35.0c_{Pb}^{-1} - 0.946$	0.9977	0.0033	0.04
3	0.0384	0–5.0	$\Delta A_r^{-1} = 15.3c_{Pb}^{-1} + 3.67$	0.9958	0.0034	0.02
4	0.0512	0–8.0	$\Delta A_r^{-1} = 16.3c_{Pb}^{-1} + 3.61$	0.9901	0.0036	0.02

^a Every series contained 9 lead concentrations; ^b Linear correlation coefficient; ^c Standard deviation from 12 replicated blanks.

3.3. Effect of foreign ions

Fourteen foreign ions including 12 kinds of metal ions and PO_4^{3-} and Cl^- were added in order to investigate the selectivity of this method in the presence of HNO_3 and Pb(II). Their effects on ΔA_r are shown in Table 2. The foreign ions did not affect the direct determination of 2.00 mg/L Pb(II) (error < 10%). The recommended method is highly selective and suitable for the direct monitoring of natural water.

Table 2. Calibration graphs for determination of Pb(II) with DMSA.

Solution no. (<i>i</i>)	Ions added	Added, mg/L ^a	Error, % ^b
1	Pb(II)	2.00	
2	Ca(II)	10.0	8.8
3	Zn(II)	50.0	-0.7
4	Fe(III)	50.0	0.4
5	Co(II)	50.0	-1.3
6	Mn(II)	50.0	3.2
7	Ni(II)	50.0	-4.7
8	Cd(II)	50.0	-3.4
9	Cr(III)	50.0	4.9
10	Cu(II)	250.0	-1.2
11	Mg(II)	250.0	-1.9
12	K(I)	250.0	-3.9
13	Al(III)	250.0	4.5
14	PO_4^{3-}	250.0	0.1
15	Cl^-	250.0	0.3

^a 2.00 mg/L Pb(II) added into each solution from no. 2 to 15; ^b Error = $(\Delta A_r^i - \Delta A_r^1) / \Delta A_r^1 \times 100$ (*i* from 2 to 15).

3.4. Analysis of samples

Three types of surface water were analyzed. They were sampled from Huangpu River (Shanghai, China), Nanxi River (Zhejiang, China), and tap water. A known volume of a sample was transferred into a 10-mL calibrated flask and then treated according to the recommended procedures. The results for Pb are listed in Table 3. The recovery rates of Pb(II) are between 100% and 110%.

In order to establish the validity of the proposed procedure, the method was applied to the determination of the content of Pb(II) in certified reference material GBW08571. The determined values by the LARVA ($1.87 \pm 0.22 \mu\text{g g}^{-1}$) were in good agreement with the certified value for the analyte ($1.96 \pm 0.09 \mu\text{g g}^{-1}$) (mean value \pm standard deviation, *n* = 3).

Comparative information from some studies on spectrophotometric determination of Pb(II) by various methods is given in Table 4. The suggested method possesses advantages with respect to sensitivity, selectivity, acidity range, and ease of operation.

Table 3. Determination of Pb(II) in natural water.

Sample from	Pb(II) added, mg/L	Pb(II) found, mg/L ^a	Recovery, % ^b	Pb(II) found by ICP, mg/L
Huangpu River	0	0.05	100	0.048
	0.05	0.10		0.112
Nanxi River	0	0.02	100	0.026
	0.01	0.03		0.031
Tap water	0	0.07	110	0.078
	0.10	0.18		0.181

^a Three replicated determinations; ^b calculation e.g. 110% = (0.18 - 0.07)/0.10 × 100%.

Table 4. Comparison of the present method with other spectrophotometric methods for the determination of Pb(II).

Reagent	Media	λ_{\max} /nm	Remarks	Ref
Pyridine-2-acetaldehyde-salicyloylhydrazone	Benzene	380	1. Poor sensitive, 2: salting-out agent used,	24
2,5-Dimercapto-1,3,4-thiadiazole	HCl	375	1: Sensitive, 2: Fe, Mn interfere	25
Benzil Amonoxime Isonicotinoyl Hydrazone	Aqueous	405	1: Low sensitive, 2: small acidity range	26
N-Hydroxy-N,N-diphenylbenzamidine	CHCl ₃ + Methanol	525	Cu interferes	27
2-(2Thiazolylazo)- <i>p</i> -cresol	pH 9.0–10.0	650	Ni, Co, Zn, Fe, Cu interfere	28
Dibromo- <i>p</i> -methylsulfonazo with LARVA	Aqueous	630	Rapid and wide acidity range, selectivity	This work

4. Conclusion

DMSA was selected as a chromophore for determination of trace amounts of Pb(II) in nitric acid medium by LARVA. Under the optimal conditions, the light-absorption ratio variation is linear in the range of Pb(II) between 0 and 5.0 mg/L and LOD of Pb(II) only 0.02 mg/L. The detection results are accurate in comparison with those detected by the classical method and the applicability was also estimated by the determination of the standard material and environmental samples. As a result, there is potential for this method to provide field detection of Pb(II) ions in natural water.

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