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Spectrophotometric Determination of Lead in Tea Leaf Sample with Dibromo-*p*-chloro-arsenazo

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This work reports the use of dibromo-*p*-chloro-arsenazo (DBC-ASA) as a chromogenic agent to develop a new spectrophotometric method for the determination of lead using Pb^{2+}-(DBC-ASA) complex. In the medium of 0.10 mol L^{-1} phosphoric acid, the maximum absorption wavelength of Pb^{2+}-(DBC-ASA) violet-red complex formed is located at 614 nm. At this wavelength a good linearity is presented between the concentration range of 0.1-3.5 μg mL^{-1} of lead(II) and absorbance and its linear regression equation is: A = 0.130 C (C:μg/mL) + 0.007. The apparent moler absorption coefficient of the method is 3.33×10^4 L mol^{-1} cm^{-1} and its detection limit is 0.225 μg mL^{-1}. The method was used to determine lead in some tea leaf samples and the obtained results are in good agreement with those of atomic absorption spectrometry. The relative standard deviation of 13 replicate determinations was (0.43-0.80) %. The recovery of the standard addition of the method was (96.0-98.5) %.

Key Words: Dibromo-*p*-chloro-arsenazo, Lead, Tea leaf sample, Spectrophotometry.

INTRODUCTION

Lead is one of metals whose applied techniques mankind at the earliest time mastered. Its use is extensive but lead has a definite toxicity. Usual contact and no taking caution against it, may result in lead toxicosis. Lead is a toxic substance from head to foot and has high cumulation property and multi-affinity. It can be absorbed by body by digestion, breath approach, *etc*., and has not any physiological functions. Lead can bring ill influences on many apparatus of human body, especially on lung, kidney, procreation system, heart vein system[1,2]. Commonly used methods for the determination of lead have spectrophotometry, cool atomic absorption spectrometry, atomic fluorescent method, chromotography, *etc*.[1]. In these methods,the needed apparatuses of cool atomic absorption spectrometry, atomic fluorescent method and chromotography are valuable and the operations are complex. Spectrophotometric determination of strontium has the advantages of operation simplicity, cheap instrument price, *etc*. Therefore, spectrophotometric method is one of commonly used methods in the analysis of lead at present[3]. Dithizone extraction spectrophotometric method is a commonly used method for lead determination, but dithizone itself is not stable and the organic solvent such as CCl_4, 1,1,1-trichloroethane, *etc*., is needed for extractive comparison[4]. Also, in the determination of lead by this method, various interfering ions and at the operation virulent potassium cyanide is needed for masking interfering

ions and the reaction conditions are strictly mastered. Although some researchers used new chromogenic agents and proposed some spectrophotometric methods for the determination study of lead such as dibromo-*p*-methyl-carboxysulfonazo[5], chloro-phosphonazo(III)[6], the selectivity of the methods are poor. Development of a new spectrophotometric method for the determination of lead still has an important significance.

Dibromo-*p*-chloro-arsenazo (DBC-ASA),is a chromogenic agent and its molecular formula is $C_{22}H_{14}N_4O_{11}S_2Br_2ClAs$ (Fig. 1).
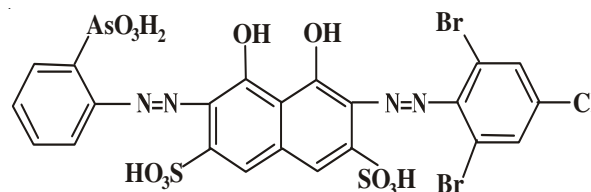

Fig. 1. Molecular structure of DBC-ASA

It can be known from Fig. 1 that the aromatic ring in DBC-ASA carries -OH, $-SO_3H$ and $-AsO_3H_2$ and multiligands containing N,O. The reagent has stronger complex ability and can form the complexes of water-solubility with metal ions. DBC-arsenazo has ever been used as the chromogenic agent of rare earth elements[7,8]. This paper investigated a colour reaction of the reagent with lead(**II**). The results showed that in a dilute phosphoric acid medium between DBC-ASA and

Pb^{2+} a complex reaction occurs and a violet-red complex forms. A simple, fast and sensitive spectrophotometric method for the determination of lead was developed. The article used the DBC-arsenazo spectrophotometry for successful determination of the lead contents in tea samples with satisfactory results.

EXPERIMENTAL

A 722S spectrophotometer (Shanghai Linggunag Technique Co. Ltd., China) equipped with 1.0 cm cell was used for measuring the absorbance. Distilled water was used in this work and analytical reagent grade chemicals were used for this study.

Pb^{2+} standard solution: 0.1599 g $Pb(NO_3)_2$ (Wuzhou Beijing Century Star Chemical Co. Ltd., China) was placed in a 50-mL beaker. After 1 mL of concentrated nitric acid and a small amount of water were added to dissolve it, the solution was transferred to a 100-mL volumetric flask. It was diluted to the mark with water and 1 mg/mL stock solution of Pb^{2+} was obtained. Before use, the working solution, 20 μg/mL, was obtained by dilution of the stock solution with distilled water. DBC-arsenazo (DBC-ASA, Shanghai Changke Research Institute for Reagents, China) solution : 2 g/L. Phosphoric acid (Beijing Chemical Plant, China) solution : 2 mol/L.

Recommended procedure: In a 10 mL volumetric flask, 0.5 mL of 2 mol/L H_3PO_4 solution, 1 mL of 2.0 g/L DBC-ASA solution, 1 mL of 20 μg/mL Pb^{2+} working solution was added in turn. The solution was diluted to the mark with water, shaken well. After 15 min, the solution was added to a 1-cm cell and the absorbance value of the system containing lead was determined at 614 nm using the blank solution of no addition of Pb^{2+} as reference.

Procedure for the determination of lead in tea sample: An appropriate amount of tea leaf sample was accurately weighed and placed in a ceramic crucible and dried at 100 ºC for 2 h and incinerated in a muffle oven at 550 ºC for 12 h. After cineration was complete, a few drops of water were added to wet it. Along the wall of utensil 5 mL of hydrochloride acid solution (1:1, v/v) was dropped to dissolve the leftover. It was transferred into a 25 mL volumetric flask and then diluted with distilled water to the mark of the volumetric flask as test solution. An appropriate amount of the above-stated test solution was taken and placed in a10 mL volumetric flask for lead determination according to the general procedure. Then, recovery determination experiments were made and atomic absorption spectrometry was used for contrast determination. The above analytical results are given in Table-1.

RESULTS AND DISCUSSION

Absorption spectra of complex: DBC-ASA and Pb^{2+} form a violet-red complex in the phosphoric acid medium.

Curve (a) in Fig. 2 is the absorption curve of reagent blank against water and there is an absorptive peak at 474 nm. Curve (b) is the absorption curve of complex against reagent blank and for the curve at 614 nm the absorbance is maximum and the experimental sensitivity is the highest. The contrast is 140 nm. This paper selected 644 nm as the experimental measurement wavelength to carry through absorbance measurement.
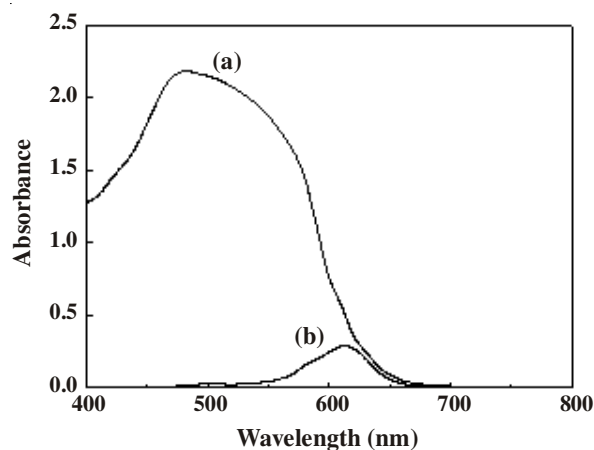

Fig. 2.   Absorption spectra. (a) Reagent blank (against water); (b) complex (against reagent blank); $[Pb^{2+}] = 9.65 \times 10^{-6}$ mol/L; [DBC-ASA] = 2.37×10^{-4} mol/L; $[H_3PO_4] = 0.10$ mol/L

Optimization of experimental variable: According to the general procedure, phosphoric acid concentration was variable and the other experimental conditions were kept optimization. Absorbance of the systems were tested under the situation of 0.0040, 0.040, 0.10, 0.16, 0.30, 0.40 mol/L phosphoric acid concentration, respectively. The results showed that as phosphoric acid concentration increased, absorbance value of the systems continuously increased between 0.0040-0.10 mol/L and decreased between 0.10-0.40 mol/L. When phosphoric acid concentration was between 0.040-0.16 mol/L, the absorbance was maximum and steady. Thus, phosphoric acid medium concentration selected was 0.10 mol/L.

The experimental results indicated that when amount of 2 g/L of DBC-ASA chromogenic agent was in the range of 0.8-1.2 mL, the absorbance was maximum and stable. The present study selected 1.0 mL.

Order of addition reagent has not effect on the experimental results of complex formation. The order used in the experiment was: H_3PO_4 + (DBC-ASA) + Pb^{2+}.

Complex composition and stability: DBC-ASA and Pb^{2+} form a violet-red complex in the phosphoric acid medium. Molar ratio method and equal molar continuous variation method were respectively used to determine the composition ratio of complex to be $n_{(DBC-ASA)} : n_{Pb}^{2+} = 2 : 1$.

	TABLE-1 ANALYTICAL RESULTS OF SAMPLES						
Sample	Found (n = 13, μg/g)	Average (μg/g)	Relative standard deviation (%)	Added (μg/g)	Recovered (μg/g)	Recovery (%)	Atomic absorption spectrometric method (μg/g)
No.1	0.25, 0.23, 0.23, 0.23, 0.25, 0.25, 0.23, 0.25, 0.25, 0.23, 0.23, 0.25, 0.25	0.24	0.43	0.400	0.384	96.0	0.24
No.2	0.12, 0.14, 0.12, 0.12, 0.14, 0.14, 0.14, 0.14, 0.14, 0.12, 0.14, 0.14, 0.12	0.13	0.80	0.400	0.394	98.5	0.12

The experimental results of complex stability showed that at room temperature lead complex formed within 15 min and the absorbance reached a maximum. Within 1 h a variation of absorbance of the complex was less than 5 % and the complex kept stable.

Working curve and analytical characteristics: Under the optimum experimental conditions calibration graph was established from spectrophotometric measurements performed. The results showed that the calibration graph was linear in the range of 0.1-3.5 µg/mL of Pb^{2+}. The calibration equation is $A = 0.130\,C$ (C:µg/mL) + 0.007 with a correlation of $\gamma = 0.9990$, where A is the absorbance determined at 614 nm and C is the concentration of Pb^{2+} in the sample solution in µg/mL. According to the working curve, the apparent molar absorptivity calculated is $\varepsilon_{614\,nm} = 3.31 \times 10^4$ L mol^{-1} cm^{-1}. The relative standard deviation (R.S.D.) for determination of 2.0 µg/mL of Pb^{2+} was 1.77 % (n = 11), indicating that the precision of the method is excellent. The limit of detection, defined as $C_L = 3S_b/m$, where C_L, S_b and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph, respectively, was 0.225 µg/mL.

Selectivity of method: The effect of presence of various co-existing substances with a measurable amount of 20 µg Pb^{2+} in a 10-mL system was studied, allowing relative errors within ± 5 %. The following co-existing substances do not interfere with the determination (µg): Ni^{2+} (30000); Cd^{2+} (20000); Mg^{2+}, Mn^{2+} (20000); Li^+ (10000); Zn^{2+} (4000); Si(IV), Cr(VI) (2000); Hg^{2+} (400); Cu^{2+}, W(VI) (200); Fe^{2+}, Zr^{4+}, Bi^{3+} (40); Ti^{4+}, V(V), Mo(VI) (20); Cr^{3+}, Hf^{4+} (4); Al^{3+} (4, 40*); Ba^{2+}, Th^{4+} (0.4); Sr^{2+} (0.2), Fe^{3+} (0.2); Ca^{2+} (0.2, 0.4*); Cl^- (20000); SO_4^{2-} (4000); CH_3COO^- (2000); Br^- (1600); F^- (1000); I^-, CO_3^{2-} (200); NO_2^- (100); S^{2-} (10); ascorbic acid (2000); citric acid (140); tartaric acid (100); oxalic acid (40); glucose (40); human serum albumin (20) (2 mL of 1.0 mg/mL EDTA solution was added).

Sample analysis: In order to evaluate the analytical applicability of the proposed method, it was applied to the determination of lead in tea samples. The results are given in Table-1 which shows the excellent recoveries are obtained from the proposed method. The obtained results are in good agreement with those obtained by atomic absorption spectrometry. The obtained relative standard deviation values were 0.43-0.80 % for 13 replicate measurements and the obtained recoveries were in the ranges of 96.0-98.5 %.

Conclusion

This work reports the optimum reaction conditions of spectrophotometric determination of lead(II) with DBC-arsenazo and studied the properties of system. It was found that the maximum absorption of complex is at 614 nm and lead(II) content over the range of 0.1-3.5 µg/mL and absorbance obey Beer's law. Its linear regression equation is: $A = 0.130\,C$ (C:µg/mL) + 0.007, with a correlation coefficient of $\gamma = 0.9990$. The limit of detection of the method is 0.225 µg/mL. The present method has been successfully determined the lead content in some tea leaf samples.

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