

Determination of Lead using 2, 5-Dimercapto-1, 3, 4-Thiodiazole (DMTD)

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Summary: A new spectrophotometric method which is fairly selective, non extractive, is described here for the determination of lead based upon its colour reaction with 2,5- dimercapto-1, 3,4- thiodiazole (DMTD). According to this lead (II) can be determined within the range from 1.0 to 50 μg per mL in a slightly acidic media (0.005 M HCl), to give a greenish yellow chelate complex, which has an absorption at 375 nm. The reaction proceeds fastly and color remains stable. While no special conditions are followed. The method is recommended for its routine use and is quite accurate, precise, and sensitive. Effect of Foreign ions is also studied at 40 $\mu\text{g}/\text{mL}$ of lead.

Introduction

Lead is one of the environmentally hazardous elements because, along with cadmium, mercury, copper, zinc and chromium it poses a particularly high risk of disturbing the chemical balance in the ecosystem [1]. Lead is distributed widely in nature. It is found in many ores, galena, angles tic Cero site, storage batteries, alloys, cable sheaths, solder, X-ray equipments and radiation shielding. The most widespread uses, which have led to environmental and health problems, have been the use of lead in gasoline as antiknock agent and paint pigments [2]. This is also of great importance to human health, as lead belongs to toxic elements which can accumulate in the human organism (the maximum daily dose of lead which does not lead to accumulation is 0.50 μg . Excessive amounts of this element cause disorders in the metabolism [1].

Lead is a serious cumulative body poison [3]. It enters our body system through air, water and food. The toxicity of lead has been studied extensively [4]. 2, 5-Dimercapto-1, 3, 4-thiadiazole is utilized in a variety of applications synthesizing polymers, and as a chelating agent in the analysis of metals; in purifying and treating waste [5].

Varieties of methods are available in the literature for determination of lead. Trace amount of lead is usually determined by the colorimetric methods with Dithizone Tetra Hydroxy Quinone method [6] and Tetra Hydroxy Benzo Quinine [7]. 2, 5-Dimercapto-1, 3, 4-thiadiazole is used to determine metals in industrial, environmental, and biological samples [8-10].

Spectrophotometry is essentially a trace analysis technique and is one of the most powerful tools in chemical analysis. DMTD has been reported as a potentiometric reagent [7]. The method is based

on the reaction of non- absorbent DMTD in slightly, acidic solution (0.005 M HCl) with lead (II) to produce a highly absorbent greenish yellow chelate product, followed by direct measurement of the absorbance in aqueous solution. DMTD is known as a specific reagent for spectrophotometric determination of metals such as Lead, Copper, and Nickel.

Result and discussion:

In this paper attempt has been made to determine lead in a trace levels by spectrophotometric technique which has obvious advantages of simplifying the instrumentation and decreasing the cost per test.

The color reaction between Lead (II) and DMTD has maximum absorbance at 375 nm. Fig. 1 and 2, hence all absorbance measurements were carried out at this wavelength.

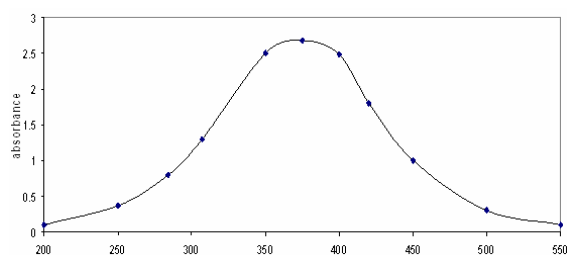


Fig. 1: Wavelength in nm Absorbance spectra of Pb DMDT Maximum at 375nm in aqueous solution.

Effect of Temperature

Since the color intensity remains constant at room temperature Fig. 3 all absorbance measurements were made at room temperature ($25 \pm 5^\circ\text{C}$).

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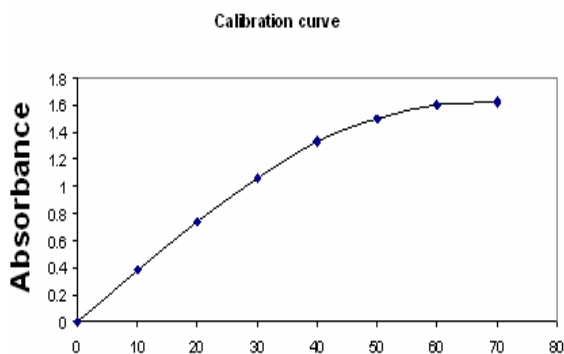


Fig. 2: Concentration of Lead (II).

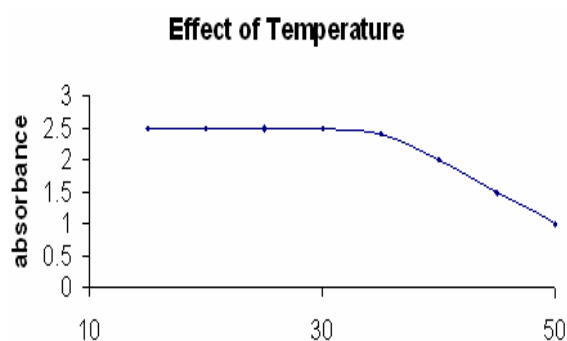


Fig. 3: Temperature.

Effect of pH

The color intensity is stable at pH range 2-4.5. Hence all absorbance measurements were made at this pH. For all measurements, 1 mL 0.005 M Hydrochloric acid was added to achieve the required pH range.

The results for the determination of lead are shown in Table-1 which shows the reliability of the method. The color reaction is specific for lead, and no other cation or anion gives any color with the color producing reagent. The reaction between lead and di-mercapto thiodiazol is very fast and color developed within a few seconds and remains stable for 24 hours Fig. 4.

Table-1: Results of synthetic mixture recovery study using spectrophotometric method for lead determination.

Sr. No.	Lead added µg/mL	Lead measured µg/mL	Recovery % µg/mL
1	1.00	1.03 ± 3.00	103.00
2	2.00	1.98 ± 0.02	99.00
3	4.00	3.96 ± 0.04	99.00
4	6.00	5.92 ± 0.08	98.66
5	8.00	7.96 ± 0.50	99.50
6	10.00	10.02 ± 0.20	100.02
7	15.00	15.05 ± 0.33	100.33
8	25.00	25.06 ± 0.24	100.24
9	30.00	30.08 ± 0.26	100.26
10	40.00	40.01 ± 0.25	100.02
11	50.00	50.35 ± 0.70	100.70

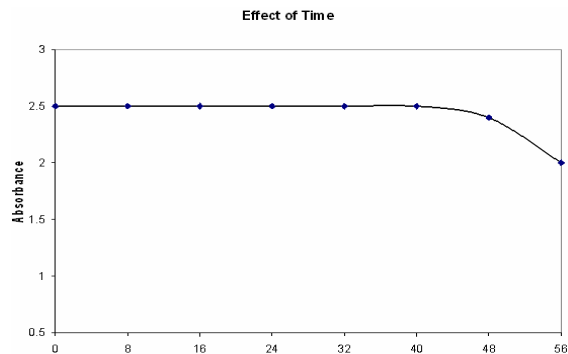


Fig. 4: Hours effect on DMDT complex.

Experimental

Apparatus and Instruments

All absorbance measurements for the determination of lead were made with UV - VIS spectrophotometer Specord 200 with PC version (Germany). pH meter (Crison 2001 Spain) for the measurement of pH respectively. All other volumetric glass ware used was of A grade.

Chemical and Reagent

All chemicals used were of Analytical grade, double distilled water was used. All glass ware were cleaned by soaking acidified solution of $K_2Cr_2O_7$, followed by washing with concentrated nitric acid and then rinsed with double distilled water and oven dried.

Colour Producing Reagent (DMDT) Solution

4.42×10^{-3} M Di-mercapto thiodiazol (Aldrich ACS) was made by dissolving it in a known volume of double distilled water. More dilute solutions were prepared as required.

Lead (II) Standard Solution

Stock standard solution of lead nitrate 4.83×10^{-3} M (Merck) was prepared by dissolving 159.9 mg of lead nitrate in 100 mL double distilled water. One mL of nitric acid was added to prevent Hydrolysis. Dilute solutions were prepared as required.

Synthetic Mixture

Synthetic mixtures of possible interfering inorganic ions such as Barium, Zinc, Chromium and Bismuth were prepared in double distill water [11].

Method

A volume of 1 mL neutral aqueous test solution containing 1 to 100 μg of lead in 10 mL was mixed with 1 mL DMTD reagent solution, followed by the addition of 1 mL 0.005 M hydrochloric acid. The mixture was diluted to the mark with double distilled water. After one to two minutes, absorbance was measured at 375 nm against a blank which contains all the reagents except lead. Blank was tested under the same conditions. The accuracy of the results was also examined by preparing the synthetic mixture containing the known amount of pure chemicals and analyzing it. The well known equation for spectrophotometric analysis in very dilute solutions derived from Beer's law. The effect of lead concentration was studied over 1 to 100 $\mu\text{g}/\text{mL}$. The absorbance was linear at 375 nm up to 50 $\mu\text{g}/\text{mL}$ of lead solution. The calibration curve was prepared and color reaction obeys Beers law [11]. The same samples were also tested by the Atomic Absorption AA.240 Varian Australia for the comparison of results. This method showed good accuracy with the AA. The results of water and synthetic mixture are given in the Table-2.

Table-2: Analytical data of lead determination of a tap water and the prepared synthetic sample analyzed by atomic absorption.

Sr.No.	Material	Samples Lead added ($\mu\text{g mL}^{-1}$)	Measured ($\mu\text{g mL}^{-1}$)	Recovery (%) $\mu\text{g}/\text{mL}$
1	Tap water	20.00	19.05 \pm .14	95.25
		30.00	28.73 \pm .16	95.77
		40.00	39.12 \pm 0.23	97.80
2	Synthetic mixture	40.00	38.11 \pm 0.14	95.27
		60.00	59.09 \pm .19	98.48

Interference Study

The effect of 8 interfering ions on the determination of 40 $\mu\text{g}/\text{mL}$ of lead (II) was studied. They form strongly colored complexes with DMTD at same pH and wavelength. The criterion for interference was an absorbance value varying from the expected value of lead alone. Table-3.

The synthetic mixture containing lead and all the above mentioned foreign ions was analyzed. Table-3 shows that lead can be determined in solution in their presence with a minimum error of 2.5 $\mu\text{g}/\text{mL}$ due to iron for 40 μg of lead and maximum error of 3.75 $\mu\text{g}/\text{mL}$ due to copper for 40 μg of lead. Barium, Cobalt, Zinc, Tin, Chromium and Bismuth do not interfere. While iron and copper interferes seriously with this reagent, which can be eliminated by making it with tartrates or thiocyanide.

The precipitates were removed by centrifugation [12].

Table-2: Effect of Interfering Ions on the recovery study of synthetic mixture using spectrophotometer method for lead determination.

Sr. No.	Interfering ions added $\mu\text{g}/\text{mL}$	Lead added $\mu\text{g}/\text{mL}$	Lead measured $\mu\text{g}/\text{mL}$	Recovery % $\mu\text{g}/\text{mL}$
1	Barium	40.00	40.05 \pm 0.12	100.12
2	Zinc	40.00	40.02 \pm 0.05	100.05
3	Chromium	40.00	40.07 \pm 0.17	100.17
4	Bismuth	40.00	40.05 \pm 0.12	100.12
5	Cobalt	40.00	40.06 \pm 0.15	100.15
6	Tin	40.00	40.04 \pm 0.10	100.10
7	Iron	40.00	41.00 \pm 0.50	102.50
8	Copper	40.00	41.50 \pm 3.75	103.75

Conclusion

In this paper a new simple selective accurate, sensitive, convenient and practical method of lead (II) with DMTD complex was developed. Therefore, it is recommended for the routine use in the determination of lead at trace levels in industrial, environmental and soil samples for continuous monitoring.

In this study the complex formation is one into one ratio for metal to ligands formation. The method was also tested by analyzing several interfering mixtures and diverse ions (Table-3). Although many sophisticated techniques such as AAS, ICP- AES, are available for the determination of lead at trace levels in samples, yet spectrophotometry is still a popular technique because of easy handling and low cost of instrument. Hence, the precision and accuracy of the method is excellent.

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