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Lead in collyrium and silver foils by absorbance modification, stability of lead thymol blue complex and comparison of different methods

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ABSTRACT

This study was undertaken to investigate collyrium and silver foils for lead contents by using an absorbance modification technique (Visible spectroscopy) and its comparison with gravimetry and atomic absorption spectroscopy. Lead-thymol blue complex was studied for stability with reference to (pH, temperature, time and concentration) and the interference of ionic impurities (silver, ferrous, zinc, copper, aluminum, magnesium and cadmium) on lead recovery. Both collyrium and silver foil samples were found to contain lead in different concentration. Lead thymol blue complex was found to be stable at pH 1 and temperature below 80°C for 30 minutes. Aluminum, ferrous and zinc do not interfere at concentration 10 µg/ml while others interfere at this level. The lead contents by visible spectroscopy were similar to atomic absorption spectroscopy (P < 0.05). This method can be used for routine analysis of lead contents. The use of collyrium and silver foils can contribute in lead toxicity.

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KEYWORDS

Lead toxicity;
Collyrium;
Silver foils;
Stability;
Lead thymol blue complex.

INTRODUCTION

Some metals are essential biochemically, some have no biological significance and some have potential to produce toxicity. From toxicological point of view no metal has been investigated more other than lead (Pb) due to multiplicity of route of entry and spectrum of damage to body organs. Lead toxicity is apparent if blood lead level is 40 µg/dl. Side effects have also been reported at very low levels^[1]. Continuous exposure leads to its deposition in bones and causes osteonecrosis^[2]. Some of the common sources of Pb are automo-

bile exhaust, lead battery recycling plants, lead smelting, lead based paints and pigments, printing press, ceramic glazes and lead containing cosmetics^[3-5] and folk medicines^[6-8]. Pb toxicity is increasing while efforts are less and the some factors for slow pace to address this problem have been discussed^[9]. Therefore, it is important to evaluate different contributing factors and to develop sensitive method for routine use in industry.

Collyrium (Surma) is a traditional eye cosmetic and also applied on umbilicus at birth. It is prepared from Antimony sulfide (Sb₂S₃)/Galena (PbS) alone or in combination with vegetable ashes, charcoal and inorganic

compounds. It may contain lead as an adulterant or accidental impurity. The small particle size helps in absorption of lead from conjunctival membrane. This eye cosmetic was found to increase blood lead levels^[10-13].

Silver foils are frequently used to decorate certain eatables and as apart of many eastern pharmaceutical preparations. There are doubts regarding purity and even the basic nature of such materials. Whether these foils are prepared from silver or other material, there is no way of proving this by physical means with authenticity

A diverse range of analytical methods have been used to quantify lead. Among these, gravimetric method was reported^[14]. UV/VIS spectroscopy has an important place due to rapidity, sensitivity and accuracy. This mode of analysis provided basis for accurate determination of lead contents. Since 1980 Atomic Absorption spectroscopy is being used quite frequently for lead contents^[15]. One of the absorbance modification techniques was employed here to determine traces of lead. Thymol blue was used to form a complex with lead to shift λ -max from ultra violet to visible region and compared with other methods. So far, there is no report for the quantification lead contents in silver foils and stability studies on lead thymol blue complex according to our information.

Keeping in view lead toxicity, consumer and occupational safety, it is important to investigate collyrium and silver foils and to provide sensitive, reliable, robust and easily available method of analysis.

EXPERIMENTAL

Chemicals

All the chemicals were of Analytical grade. Thymol blue, Silver nitrate, Aluminum chloride, Zinc acetate, Copper sulphate, Ferrous sulfate, Cadmium chloride, Magnesium sulphate, chloroform and acetate buffer.

Instruments

Oven Memmert type U-10(W-Germany), Balance Sartorius L 420P(W-Germany). Spectrophotometer (Hitachi Model U-2000), pH meter(CG-820 Scott and Gerate), Zeeman Absorption spectrophotometer (Hitachi model Z-8000) and other glass wares.

Analysis by gravimetry

1. Analysis of collyrium

Collyrium 0.5gm was taken in Kjeldhal flask and mixed with 5gm sodium sulphate. After adding 10ml concentrated sulfuric acid and 0.5gm tartaric acid, mixture was heated until carbonized. Few drops of hydrogen peroxide were added and the melt was allowed to cool. It was dissolved in 50ml 50% HCl by gentle warming. The contents were transferred to Erlenmeyer flask. Precipitates were collected, dried in oven for 2 hours at 120°C to calculate the amount of lead sulfate formed.

2. Analysis of silver foil

Silver foil 0.5gm and 5ml of conc. nitric acid were taken in a beaker. The contents were dissolved in 25ml distilled water and conc. HCl was added till no further precipitates of AgCl were formed. The mixture was filtered and to filtrate conc. H_2SO_4 was added to form precipitates of lead sulfate. The precipitates were collected, dried in oven at 120°C for 2 hours to calculate the amount of lead sulfate.

Analysis by visible spectroscopy

1. Standard solution of lead

Washed dried lead(0.1 gm) was taken in a beaker and 25ml of 3N nitric acid was added. Contents were heated on water bath till dried. This process was repeated till the metal changed into white powder. It was dissolved in 100ml volumetric flask with distilled water along with 2 to 3 ml of conc. nitric acid and volume was made. Further dilutions were made from this stock solution.

2. Preparation of collyrium samples

Collyrium(0.5gm) was taken in Kjeldhal flask. Nitric acid(10ml) was added and heated till decolorized. Conce. HCl(5ml) was added and heated strongly. The contents were allowed to cool and dissolved in 50ml of 50% HCl and volume was made to 100ml with distilled water.

3. Preparation of silver samples

Silver foil(0.5gm) was taken in a beaker. Nitric acid(10ml) was added and allowed the contents to cool. The contents were dissolved in 25ml distilled water. Then conc. HCl was added till no further precipitates of AgCl were formed. Filtered and filtrate was taken in 100ml volumetric flask and volume was made with distilled water.

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4. Lead extraction as Pb-thymol blue complex

Sample solution(5ml), nitric acid(1ml) and thymol blue in chloroform(5ml) were taken in a separating funnel. The contents were shaken and lower violet layer was collected. Extraction was repeated thrice with 5ml thymol blue in chloroform. Final extraction was done with 10ml pure chloroform. Extracts were pooled in 50ml volumetric flask and volume was made with chloroform. Calibration curve was made from Pb-thymol blue complex having various concentrations of lead with correlation coefficient $R^2=0.9947$.

Atomic absorption spectroscopy

The procedure for making sample solution was same as for visible spectroscopy. The samples were analyzed in triplicate at 283.3 nm using blue acetylene flame. Amount of unknown was calculated from standard curve having with correlation coefficient $R^2=0.9981$.

Stability studies of lead thymol blue complex

1. Effect of pH

Samples of Lead Thymol Blue complex were prepared in triplicate and maintained at pH(1,4,7,10 and 14) and scanned from 800 to 200nm.

2. Effect of temperature, time and concentration

Samples of lead thymol blue complex were maintained at pH1 and kept at different temperature (20to100°C) and absorbance was measured at 544nm. Results are presented in figure 3. Samples were kept at room temperature and analyzed at 544nm at different intervals. Samples were prepared with increasing amount of thymol blue(100 to 1000 μ g) and absorbance was measured at 544nm.

3. Effect of cationic impurities

Lead thymol blue complex containing 50 μ g lead was mixed with various concentrations (10, 20, 30, 40, 50 μ g) of $AlCl_3$, $FeSO_4$, $Zn(CH_3COO)_2$, $CuSO_4$, $AgNO_3$, $MgSO_4$ and $CdCl_2$ at pH 1. Absorbance was measured at 544nm.

Statistical analysis

All analysis was performed in duplicate/triplicate and averaged. Data was analyzed by analysis of variance and multiple comparison was performed by Post hoc test.

RESULTS AND DISCUSSION

Lead is not essential nutritionally and its toxicity is well documented. Toxicity is increasing with a great pace due to atmospheric pollution. Therefore, it is important to monitor Pb levels in the surroundings. Attempt has been made to determine traces of Pb in collyrium (raw and finish product) and silver foils, which are being used routinely in many parts of the world.

Molecules having higher degree of conjugation require less energy and absorb radiation in longer wavelength. Thymol in reduced form is red but in oxidized form show absorption in blue region of visible spectrum. In this work, thymol blue is used to shift the absorption maximum of Pb from UV to visible region. Lead absorbs at 223nm in near UV region and thymol blue has λ_{max} 435nm in the visible region. Whereas, Pb-thymol blue complex via oxygen lone pair coordination results in red or bathochromic shift 544nm. Results are given in figure 1(supplementary material).

The behavior of Pb- thymol blue complex at different pH gives a pH dependent peak at 544nm in addition to pH independent reagent peak around 435nm as shown in figure 2(supplementary material). The results revealed that the lead thymol blue complex is unstable in weak acid, strongly alkaline and at neutral pH. At these pH values, complex dissociates which is indicated by the absence of peak of the complex at 544nm in acidic medium and 580nm in alkaline medium. The pH of maximum of complex formation was 10 but the complex was unstable and metal precipitated after few minutes. Therefore, analysis was carried out at 544nm at pH1.

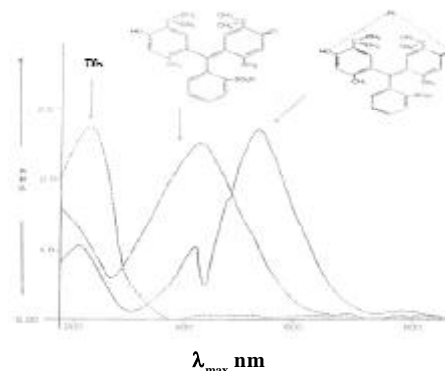


Figure 1: Wavelength scan of lead ($\lambda_{max}=223$ nm), thymol blue($\lambda_{max}=438$ nm) and lead thymol blue complex ($\lambda_{max}=544$ nm) at pH 1

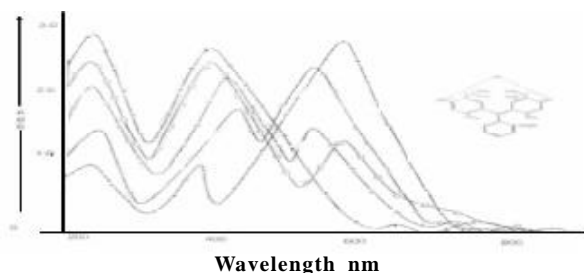


Figure 2 : Effect of pH on absorbance characteristics of Pb- thymol blue complex; o- pH 1, Δ- pH 4, ▲- pH 7, *- pH 10, □-pH14

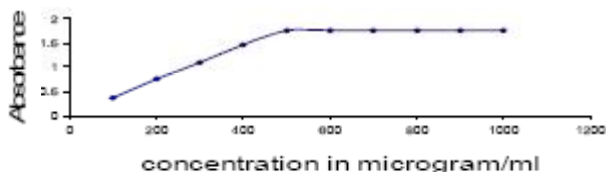


Figure 3: Effect of concentration of thymol blue on the extinction coefficient of Pb-thymol blue complex (pH 1)

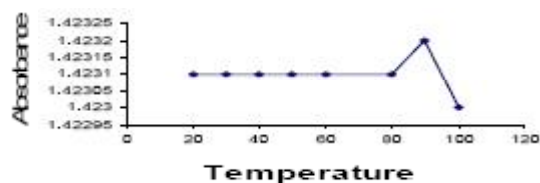


Figure 4 : Effect of temperature on Pb- thymol blue complex at pH1

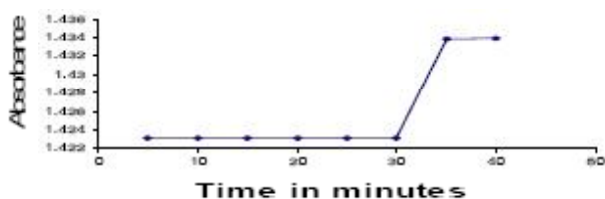


Figure 5 : Shelf life of Pb- thymol blue complex at pH 1

Results shown in figure-3, 4, 5(supplementary material) indicate the stability data of lead thymol blue complex. It was found to be stable till 80°C. Therefore, complex can be kept at moderate temperature for study. There was a slight positive deviation from Beer Lambert relationship after 35minutes. Hence, it is better to take readings within 30minutes of its preparation. On increasing the amount of thymol blue and keeping the amount of lead constant Beer Lambert relationship was valid till 400ppm. Above, this critical value negative deviation was observed.

The results shown in TABLE 1 indicate the fluctua-

tions in concentration of lead in various samples of collyrium by gravimetric, visible and atomic absorption spectroscopy. It is clear from the results that the lump(raw) collyrium samples contain large amounts of lead contents where as some varieties of powder samples contain less, except the powder sample (imported from Saudi Arabia). The higher levels may be attributed to the natural contamination of Pb with collyrium rocks. The results of visible spectroscopy clearly indicate that it is better in sensitivity compared to gravimetry. The micro quantification of minute amounts of lead by AAS sharply compromise with the results obtained from visible spectroscopy.

The most striking feature of AAS method is that it is excellent in reproducibility which is obtained upon successively aspirating the same sample solution. The atomic absorption is also virtually free from spectral interferences, because a particular element can only absorb light of its own characteristic frequency. Interferences are confined mainly to the formation of refractory compounds due to ionization and matrix interference phenomenon. Light scattering effect manifests itself as an apparent enhancement of the Pb measurements. It is significant at wavelength below about 2500Å for the determinations of the metals in media that contain heavy loading of foreign ions particularly NaCl. The interference occurs with the direct estimation of Pb in samples at the 2170Å line. To avoid possible interferences estimation is carried out at 2833Å.

The results of lead contents in various silver foils are also shown in TABLE 1. The majority of samples

TABLE 1 : Percentage of lead contents collyrium by different methods

Sample	Form	Sampling area/brand	Gravi-metric method	VIS spectroscopy	AA spectro-spectroscopy
1	Lump	Saudi arabia (Imported)	1.36	1.82	1.70
2*	Lump	Local market	2.38	2.50	2.26
3	Lump	Local market	2.04	2.04	2.23
4	Powder	Local market	0.00	0.60	0.63
5	Powder	Local surmi,	0.00	0.25	0.24
6	Powder	Latif Surma sada	0.00	0.30	0.29
7	Powder	Latif surma special	1.53	1.42	1.25
8*	Powder	Saudia arabia (Imported)	2.21	2.00	2.08
9	Powder	Hashmi surma	1.70	1.90	1.95

*Sample with maximum lead contents

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TABLE 2 : Effect of cations (Al^{+3} , Fe^{+2} , Zn^{+2}) on Pb contents by visible spectroscopy at pH1

Lead $\mu\text{g/ml}$	Impurity $\mu\text{g/ml}$	Pb recovery with $AlCl_3$	Error	Pb recovery with $FeSO_4$	Error	Pb recovery with $Zn(CH_3COO)_2$	Error
50	10	50.00	0.00	50.00	0.00	50.00	0.00
50	20	50.20	0.20	50.20	0.20	51.00	2.00
50	30	50.20	0.20	50.50	0.50	52.00	4.00
50	40	50.30	0.30	50.70	0.70	52.00	4.00
50	50	50.40	0.40	50.70	0.70	52.25	4.50

TABLE 3 : Effect of cations (Cu^{+2} , Ag^{+1} , Mg^{+2} , Cd^{+2}) on Pb contents by visible spectroscopy at pH1

Impurity $\mu\text{g/ml}$	Pb recovery with $CuSO_4$	Error	Pb recovery with $AgNO_3$	Error	Pb recovery with $MgSO_4$	Error	Pb recovery with $MgSO_4$	Error
10	52.00	4.00	52.00	4.00	52.50	5.00	52.50	5.00
20	54.00	8.00	54.00	8.00	54.00	8.00	54.00	8.00
30	54.00	8.00	56.00	12.0	54.50	9.00	54.50	9.00
40	55.00	11.0	56.00	12.0	56.00	12.0	56.00	12.0
50	55.60	12.0	56.00	12.0	58.00	16.0	58.00	16.0

analyzed by gravimetric method contain no detectable lead contents. This negative response of the method is due to low sensitivity of the method. Only a single sample found to contain lead 1.19% which may be due to high adulteration. This sample was dull silvery white as compared to other samples. Response of different methods was same as in collyrium.

The results of TABLE 2 and 3 (supplementary material) indicate the effect of various cationic impurities on the absorbance of Pb-thymol blue complex at 544nm. The impurities like (Al^{+3} , Fe^{+2} , Zn^{+2}) do not interfere below 10ppm but heavy loading has a proportional effect. Whereas, Impurities like (Cu^{+2} , Ag^{+2} , Mg^{+2} , Cd^{+2}) interfere even below 10ppm. Hence, these ions affect the accuracy of the method and should be taken in consideration during analysis.

By applying one way ANOVA, it is found that methods of analysis differ from each other ($P > 0.05$). The multiple comparison by Post hoc test shows, gravimetric method differ from visible spectroscopy ($P = 0.037$), ($P = 0.022$) and AAS ($P = 0.063$), ($P = 0.005$) for collyrium and silver foils respectively. AAS differ from visible spectroscopy ($P = 0.781$), ($P = 0.437$) for collyrium and silver foils respectively. Hence, instrumental methods are alike and are best for the determination of lead contents.

CONCLUSION

The manufacturing process of collyrium and silver foils should be monitored to minimize the lead contents. Visible spectroscopy using lead thymol blue complex can be applied to quantify lead for routine analysis.

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