

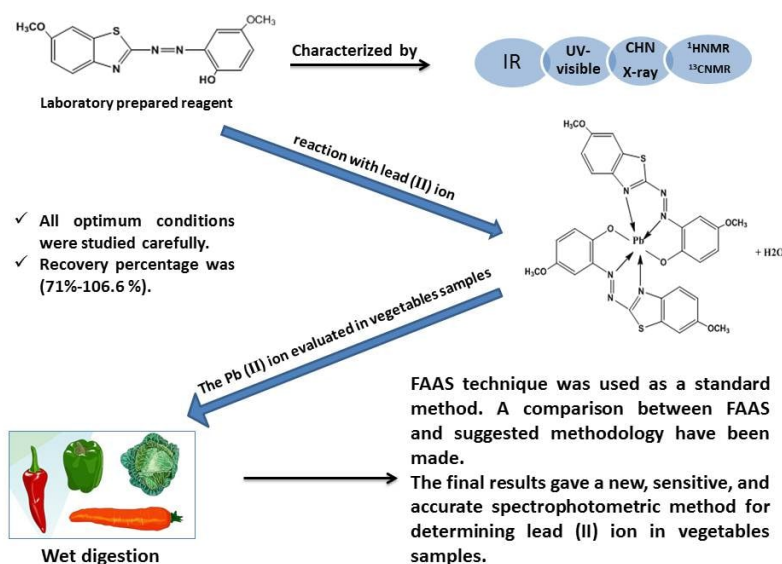
ARTICLE

A New Spectrophotometric Method to Determine Lead (II) Ion in Vegetables with 2-[(6-Methoxy-2-benzothiazolyl)azo]-4-methoxy phenol as a New Reagent

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A new, sensitive, and accurate spectrophotometric method for determining lead (II) ion in vegetable samples, using laboratory prepared reagent (6-MBTAMP) is developed. The reagent and Pb^{+2} complex characterization included infrared spectroscopy (IR), ultraviolet-visible spectrophotometry (UV-vis), elemental analysis (CHN), energy dispersive X-ray spectroscopy (EDX), and nuclear magnetic resonance spectroscopy (1H NMR & ^{13}C NMR) techniques. The method depends on the reaction of lead (II) with the 6-MBTAMP reagent in a neutral medium to form a green-red complex which showed a maximum absorbance at 670 nm. The optimum conditions such as pH of the

medium, reagent volume, reagent concentration, and time effect were also investigated carefully. Limit of detection (LOD), limit of quantification (LOQ) and Sandell's sensitivity were calculated to be 0.181 mg L^{-1} , 0.604 mg L^{-1} and $0.03 \mu\text{g cm}^{-2}$ respectively. The proposed method obeyed Beer's law at the range of $0.6\text{-}10 \text{ mg L}^{-1}$ and the recovery percentage of the vegetable samples ranged from 71% to 106.6%. The suggested spectrophotometric technique is proved to be simple, fast and sensitive for the determination of Pb (II) ion in vegetable samples.

Keywords: 6-MBTAMP, metal ions, spectrometry, toxic ions, vegetable samples

INTRODUCTION

Heavy metal is increasingly present in our surroundings; lead is one of the most well-known toxic heavy metals that can be found in everyday life,¹ including food and water. Any excessive presence of these

Cite: Ali, K. J.; Al-Zubaidi, F. L.; Mohammed, L. A. A New Spectrophotometric Method to Determine Lead (II) Ion in Vegetables with 2-[(6-Methoxy-2-benzothiazolyl)azo]-4-methoxy phenol as a New Reagent. *Braz. J. Anal. Chem.*, 2023, 10 (39), pp 88-99. <http://dx.doi.org/10.30744/brjac.2179-3425.AR-50-2022>

Submitted 20 June 2022, Resubmitted 07 August 2022, 2nd time Resubmitted 21 August 2022, Accepted 22 August 2022, Available online 26 September 2022.

toxic materials in the environment can lead to serious consequences to the ecosystem.² Hearing loss, anemia, brain damage, behavioral issues, learning disabilities, cancer, and even death are examples of such impacts on humans.^{2,3}

Lead has an effect on humans when it accumulates in the body over time; this is due to the daily needs for food and drink, as well as, breathing processes that may contain even small amounts of lead.⁴ Lead contamination has a significant influence on the ecosystem; therefore, this hazardous heavy metal is now considered a global issue due to its negative effects on health and the environment, which originate from its long half-time and difficulties in degrading.⁵ Because of its chemical and physical qualities, lead and its compounds were widely used in industry, and numerous items containing lead metal in their chemical structure exist, including cosmetics, ceramic solders, pipes, paints, gasoline, and batteries.⁶ According to the World Health Organization, the content of lead in water should not exceed $10 \mu\text{g L}^{-1}$, and the US Environmental Protection Agency recommends $15 \mu\text{g L}^{-1}$.⁷ As a result, monitoring the lead concentration is essential, particularly in environmental biological samples.⁸

For determining the trace amounts of lead in various substances, many standard techniques have been utilized, including electro-thermal atomic absorption spectrophotometry, atomic fluorescence method, chromatography, flame atomic absorption spectrometry, inductivity coupled plasma mass spectrometry, and spectrophotometry.⁹⁻¹²

Spectrophotometry has become a popular approach because of its advantages over other techniques, such as precision, simplicity, accuracy, and speed, especially in developing countries.¹²

A few work were done on estimating the lead in everyday human life especially in food. Khalaf (2011)¹³ carried out a new technique based on the lead (II) reaction with alizarin red(S) to estimate the lead in human hair. The reaction was conducted in a basic medium which produced a pink red water soluble complex with a maximum absorbance value at 518 nm. The author has taken optimum conditions such as the impact of nitric acid and hydrogen peroxide on medium pH, time effect, heating effect, and reagent concentration. El-Shahawi et al. (2020)¹⁴ used the chromogenic reagent 2-(5-bromo-2-pyridylazo)-5-(diethyl amino) phenol (5-Br-PADAP) to create a simple methodology for detecting Pb^{2+} ion in natural water samples. The study was carried out using Whatman filter paper that has been treated with commercially available nail polish (NP). The reaction was carried out under the optimum values and it was obtained an LOD value of $0.01 \mu\text{g mL}^{-1}$.¹⁴ Klamtet et al. (2007)¹⁵ used an analysis depending on flow injection technique with spectrophotometric detection in order to estimate lead in aqueous samples. The suggested reagent for this analysis was 4-(2-pyridylazo) resorcinol (PAR). The ideal parameters of the pre-concentration system, chemical and FIA variables were studied. The used technique obtained value of lead ranging from 50 to $90 \mu\text{g L}^{-1}$ with a detection limit of $11 \mu\text{g L}^{-1}$ and 102% recovery. Qing et al. (2013)¹⁶ used dibromo-p-chloro-arsenazo (DBC-ASA) as a reagent in determination of lead in tea leaf samples by spectrophotometric technique, phosphoric acid (0.10 mol L^{-1}) was used as a reaction medium. They obtained a result of linearity over the range $0.1\text{-}3.5 \mu\text{g mL}^{-1}$ of lead (II) with a high value of regression whereas the molar absorptivity coefficient was $3.33 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and the limit of detection was $0.225 \mu\text{g mL}^{-1}$. They compared their results with atomic absorption spectrometry technique with a low error percentage. A recovery of 96.0-98.5% was obtained from the standard addition of their technique.

In the current work, the suggested approach will use new reagent derivatives from thiazole to give a simple, fast and sensitive way to estimate lead ions and to identify the optimal reaction conditions to achieve the best results.

MATERIALS AND METHODS

Apparatus

All absorbance measurements were tested using the Biochrom Libra S60 double beam spectrophotometer. The pH value was measured using the Oakton 2100 Series pH/mV/Ion/OC/OF Meter. All samples were weighed using an Ohaus PA214 Pioneer Analytical Balance. The maximum wavelength was selected by using Shimadzu UV-1700 spectrophotometer. Flame atomic absorption

spectrometry was used as the standard method in this study. Infrared spectroscopy (IR), Ultraviolet-Visible spectrophotometry (UV-vis), Elemental analysis (CHN), Energy dispersive X-ray spectroscopy (EDX), Proton nuclear magnetic resonance spectroscopy (^1H NMR) and Carbon-13 nuclear magnetic resonance (^{13}C NMR) techniques were used to diagnose the reagent and lead (II) complex.

Chemicals

Except of the reagent 6-MBTAMP, all chemicals were analytical grade and were used without additional purification. The solutions in this study were prepared using distilled water.

Preparation of the azo dye 2-[(6-methoxy-2-benzothiazolyl)azo]-4-methoxy phenol (6-MBTAMP)

Diazonium chloride solution was prepared by dissolving 3.60 g, 0.02 mol from thiazole amine derivative in 30 mL of water and 3 mL of concentrated HCl.¹⁷ The solution was treated with 5 mL of aqueous 1.4 g, 0.02 mol sodium nitrite drop wise and stirred for 30 min at 0 °C. This diazonium chloride solution was added drop-wise with stirring to the alkaline solution of paramethoxy phenol 2.48 g, 0.02 mol which dissolved in 30 mL of ethanol, and 80 mL of 10% sodium hydroxide was added. Then, the mixture was stirred for 1 h at 0-5 °C. The product was filtered, air dried, and recrystallized twice from hot ethanol and then dried in the oven at 50 °C for two hours. The melting point of the reagent is 90-95 °C. The preparation steps of the 6-MBTAMP reagent are shown in Figure 1.

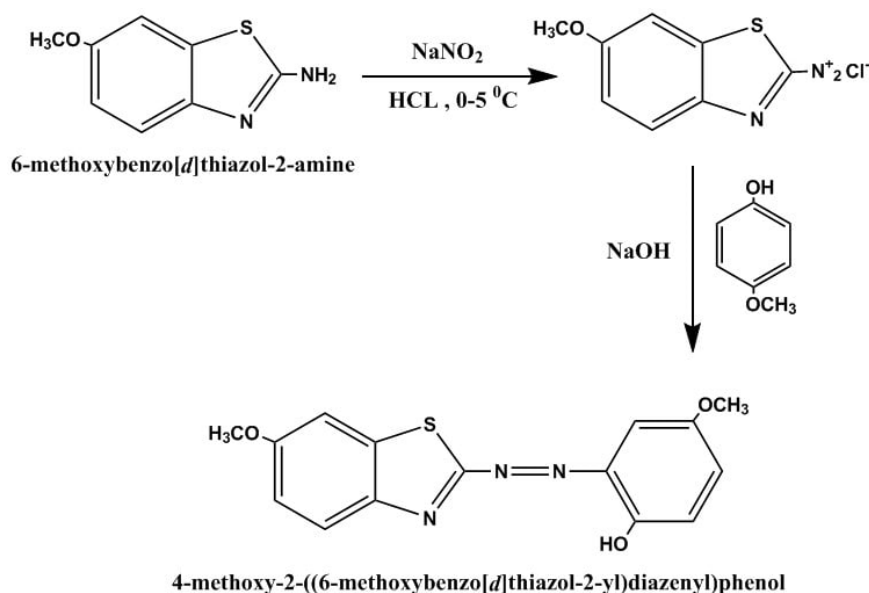


Figure 1. Preparation steps of the 6-MBTAMP reagent.

Preparation of standard stock solutions

Lead (II) ion solution 100 mg L⁻¹: a stock solution was prepared by dissolving 0.0159 g of lead nitrate in 100 mL of distilled water with adding a few drops of nitric acid. Working solutions were obtained by further dilution. Lead nitrate standard was purchased from B.D.H (England).¹⁸

New organic reagent 6-MBTAMP solution 1 × 10⁻³ mol L⁻¹: a stock solution was prepared by dissolving 0.0315 g of the organic reagent in 100 mL of ethanol. More diluted solutions of the reagent were prepared as required.

Interference solutions: all interference ions solutions were prepared in 100 mg L⁻¹ concentration, by dissolving amounts (0.0268, 0.0208, 0.0404, 0.036, 0.0403, 0.0483, 0.0159, 0.0221, 0.0138, 0.0164 and 0.0147 g) of CuCl₂·2H₂O, ZnCl₂, NiCl₂·6H₂O, MnCl₂·4H₂O, CoCl₂·6H₂O, FeCl₃·6H₂O, SnCl₂, NaF,

CH_3COONa , NaCl and Na_2SO_4 , respectively in distilled water (pH=6.8) and completing the volume to 100 mL to get on Cu^{+2} , Zn^{+2} , Ni^{+2} , Mn^{+2} , Co^{+2} , Fe^{+3} , Sn^{+2} , F^- , CH_3COO^- , Cl^- and SO_4^{2-} as interference ions. Each foreign ion was tested in two concentrations. The first test was in low concentration of interference ion at 5 mg L^{-1} , whereas, the second test was in a high concentration of interference ion at 50 mg L^{-1} .

Masking agent: all masking agents have been prepared in 100 mg L^{-1} concentration, by dissolving the suitable quantities of the chemical in distilled water and bringing the total volume to 100 mL. The masking agents included sodium thiosulfate, ammonium thiocyanate, sodium oxalate and sodium fluoride and their weight were 0.0141, 0.0131, 0.0152 and 0.0221 g respectively. The masking agent for each interfering ion was added as drop by drop until reach the appropriate amount needed to remove the interfering effect.

Sample collection

The suggested method was applied on vegetable samples collected from two heavy traffic and industrial reigns in Iraq. The first area was Al-Mothana Street, and the second area was Al-Ansar Street at Al-Najaf Province. Six samples were collected including one sample of carrots, potato, beet, celery, and two samples of pepper. All samples were prepared using the wet digestion method and the concentration of lead (II) ion on these samples was determined by Flame Atomic Absorption Spectrometry (FAAS) as a standard method, and this value was considered as a real value of lead in samples for comparison with the suggested method.

Sample preparation

The wet digestion method was used to prepare the samples in this study and the steps were as follows:¹⁹

- 5 g of sample was weighed and then transferred to a 200 mL beaker.
- 10 mL from concentrated nitric acid (HNO_3) was added and the mixture was heated up by using a boiling water bath until the total remnant volume of the mixture became 2-3 mL.
- The mixture cooled down.
- 10 mL of concentrated HNO_3 , 5 mL of concentrated H_2SO_4 and 4 mL of H_2O_2 were added and the mixture was heated up for another time.
- After completing the digestion process, 10 mL of distilled water was added and the mixture was heated up to discard all extra acids. (Repeat this step as needed until remove all extra acids).
- Finally, the mixture cooled down, then filtered in a 100 mL volumetric flask, and the solution was diluted to the mark with distilled water.

RESULTS AND DISCUSSION

The proposed spectrophotometric method in this study was depending on the complexation of lead (II) ion with (6-MBTAMP) as shown in Figure 2, which gave a green-red complex having an absorbance maximum at 670 nm. The optimum conditions for this reaction were studied carefully in order to increase the accuracy of the results.

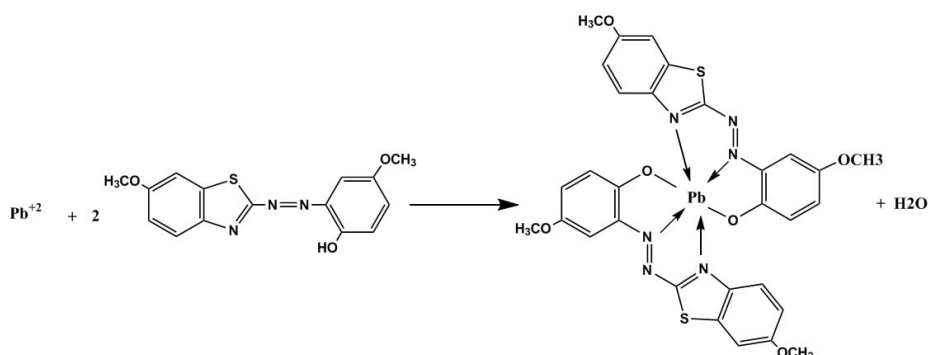


Figure 2. Proposal mechanism between lead (II) ion and the 6-MBTAMP reagent.

Elemental analysis (CHN) of the reagent (6-MBTAMP) and lead (II)-6-MBTAMP complex

When the experimentally collected information is compared to the theoretically estimated data in Table I, a high degree of convergence is observed, demonstrating the correctness of the (6-MBTAMP) reagent composition and for the lead (II)-6MBTAMP complex.

Table I. Results of analysis of elements (CHN) of the reagent (6-MBTAMP) and lead complex

Compound	C (%)		H (%)		N (%)	
	Practical	Theoretical	Practical	Theoretical	Practical	Theoretical
6-MBTAMP	57.14	56.91	4.17	4.12	13.28	13.33
Pb(6-MBTAMP) ₂ .H ₂ O	46.0	42.20	2.574	3.05	8.079	9.85

Infrared spectrometry

The reagent and its lead complex were analyzed by FTIR in the range of 400-4000 cm⁻¹. The spectra obtained were interpreted to clarify the mode of bonding and the effect of the metal ion on the reagent. The complexation process between Pb (II) ion and the reagent causes the change in bonding mode for N=N and C-N, as well as disappearance of O-H bond. The wide peak at 3415-3545 cm⁻¹ belongs to crystallized H₂O molecular at complex which appears usually at 3200-3550 cm⁻¹, as shown in Table II.

Table II. Characteristic FTIR absorption bands of the reagent and lead complex

Compound	$\nu(\text{N}=\text{N}) \text{ cm}^{-1}$	$\nu(\text{O}-\text{H}) \text{ cm}^{-1}$	$\nu(\text{C}-\text{N}) \text{ cm}^{-1}$	$\nu(\text{Pb}-\text{C}) \text{ cm}^{-1}$
6-MBTAMP reagent	1435.04	3390.86	1639.49	-----
Lead (II) complex	1442.75	-----	1600.92	414.70

¹HNMR of the lead (II) complex

The ¹HNMR spectra for the lead (II) complex showed a singlet signal at positions 3.71 ppm and 3.89 ppm, which belong to methoxy protons (O-CH₃) due to the effect of electronic inductive of oxygen atom, which cause decreasing in the numbers of electrons around protons. Whereas the signals at position 6.6 ppm to position 8.03 ppm refers to phenyl rings protons that are found in various environments as shown in Figure 3.

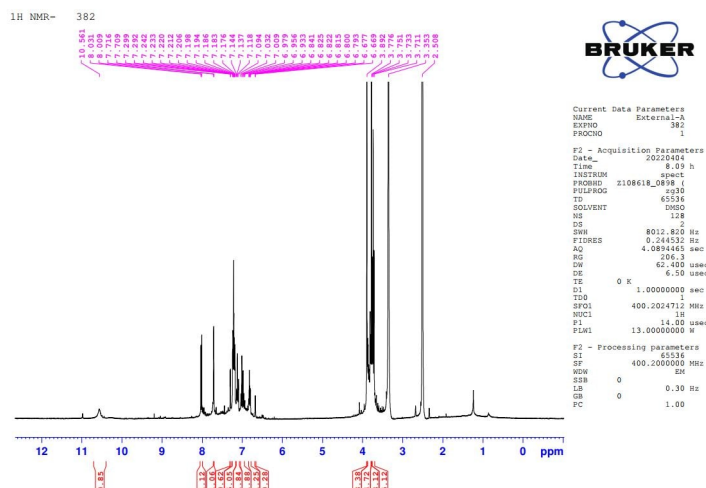


Figure 3. ¹HNMR of lead (II) complex.

¹³CNMR of the lead (II) complex

The spectrum obtained by ¹³CNMR analysis (Figure 4) shows a signal at position 55.8 ppm that belongs to the carbon atom of the methoxy group. The singlets at positions 105 - 125 ppm refer to carbon atoms at phenyl rings, as well as, the signal at position 135 ppm refers to carbon atoms at C=N group which located inside the ring.

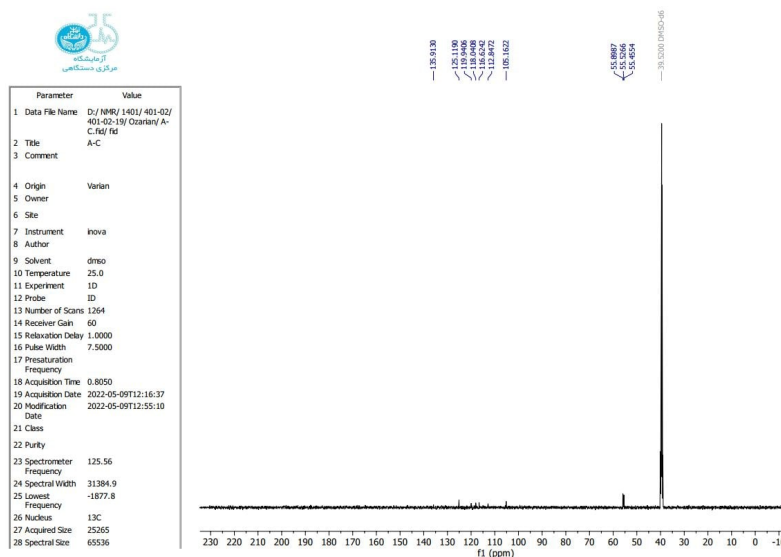


Figure 4. ¹³CNMR of the lead (II) complex.

Energy dispersive X-ray spectroscopy (EDX) for lead (II) complex

The EDX result proved the existence of C, O, H, Pb, N and S in the chemical structure of the lead (II) complex, as shown in the SEM-EDX in Figure 5. This result indicates the formation of the complex.

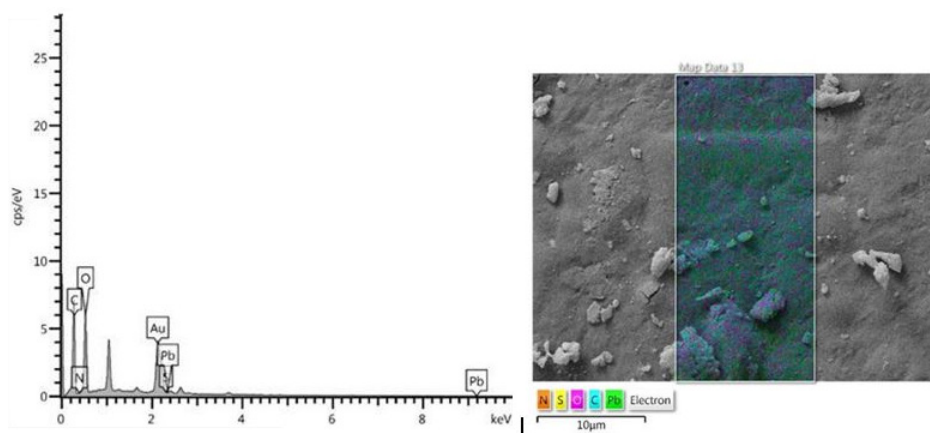


Figure 5. Energy dispersive X-ray spectroscopy (EDX) of the lead (II) complex.

The wavelength of the maximum absorbance of 6-MBTAMP and its complex

Using a Shimadzu UV-1700 spectrophotometer, the maximum absorbance of 6-MBTAMP and its complex with lead (II) was tested in different mediums in order to achieve the greatest sensitivity. The results showed that the best spectra were in neutral medium. The maximum absorbance of the lead (II) complex appeared at 670 nm and the maximum absorbance of the reagent was found at 429 nm, as seen in the Figure 6. According to these results, the 670 nm was chosen as a maximum wavelength (λ) in this study.

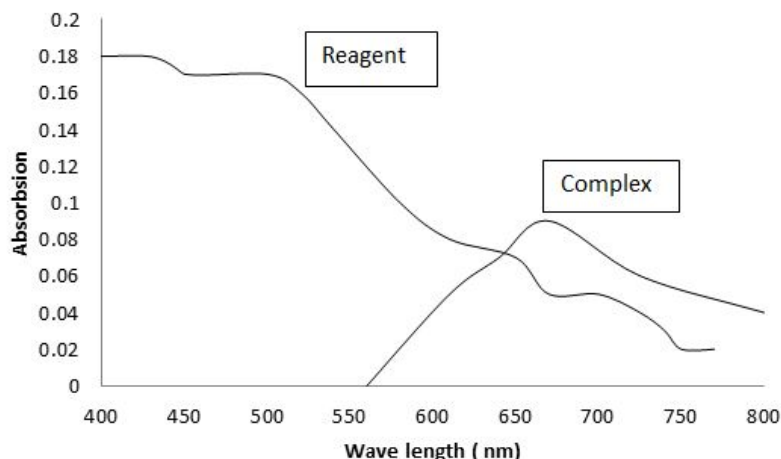


Figure 6. The absorption spectrum of lead (II) complex and the reagent in neutral medium.

Determination of the best solvent for the 6-MBTAMP reagent

The influence of the solvent on the reagent solubility was thoroughly investigated. The solvents involved in this test included absolute ethanol, absolute ethanol:water (1:1), absolute ethanol:water (1:4), and water (the reagent shows no solubility in water).

Absolute ethanol was the best solvent among all solvents tested, due to the high solubility of the reagent in it compared to the other solvents. The absorbance signal of the lead complex in ethanol is around 30% higher than in ethanol:water at a proportion 1:1, v/v.

Optimal parameters of lead complex formation

Effect of reagent concentration on the production of Pb (II) complex

The effect of reagent concentration was tested in the range of 0.002-0.0001 mol L⁻¹, with constant concentration and volume of ion at 10 mg L⁻¹ and 4 mL respectively. The results showed that the absorbance increased rapidly without any precipitate in solution up to 0.001 mol L⁻¹. Above 0.001 mol L⁻¹ the precipitate started to appear. Thus, 0.001 mol L⁻¹ was chosen as the optimum reagent concentration (Figure 7).

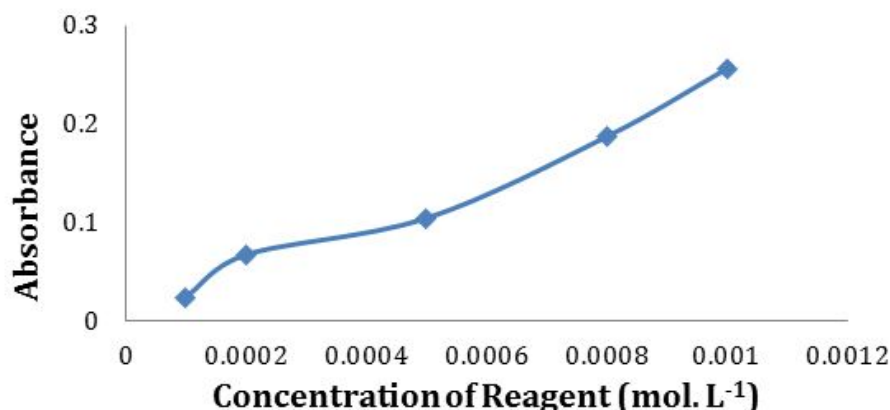


Figure 7. The effect of reagent concentration on the production of Pb (II) complex.

Effect of pH on the formation of the Pb (II) complex

This test was performed with 10 mg L⁻¹ and 4 mL of lead (II) ion, and 0.001 mol L⁻¹ and 0.5 mL of reagent. To determine the optimal pH for complexation, the pH of the medium was changed from 3 to 9

using NaOH and HCl. The formation of the complex is clearly favored by pH 6.8 as shown in Figure 8. Consequently, this value was selected as the suitable pH for the test.

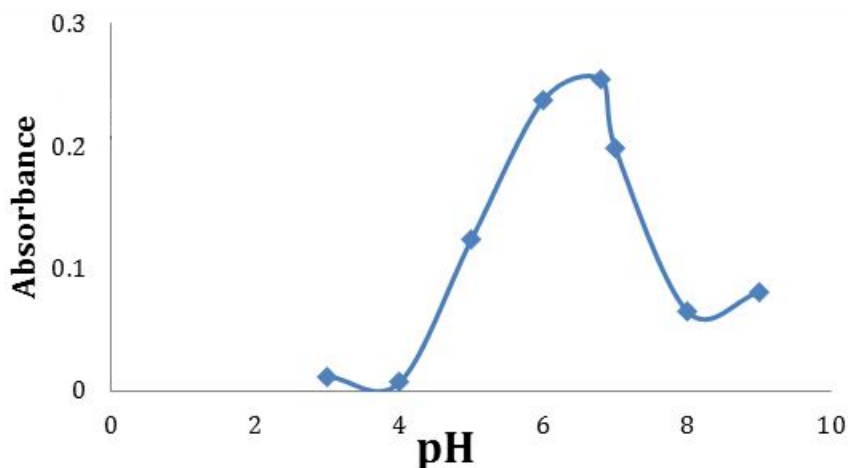


Figure 8. The effects of acidity function on the formation of the Pb (II) complex

Effect of time

The effect of time on the production and stability of Pb (II) complex was studied under the optimum conditions in order to define the suitable time of absorbance measurement. The absorbance of the complex was measured at different times: directly after the complexation process, after 5, 10, 15, 30, 45 and 60 min, and the result indicated that Pb (II)-6-MBTAMP complex was formed and remain nearly stable for 60 min. According to the results, the suitable time for taking absorbance measurement of the complex was directly after preparing it.

The effect of reagent volume on the formation of the Pb (II) complex

The effect of the reagent volume at optimum condition was investigated over the range of 0.1-1.2 mL. During this test, the concentration of lead (II) ion was 10 mg L⁻¹, and the volume was 4 mL. The volume of reagent that gave the greatest absorbance in solution without any precipitation was found to be 0.8 mL, as shown in Figure 9. Therefore, this value has been chosen as the optimal value through this study.

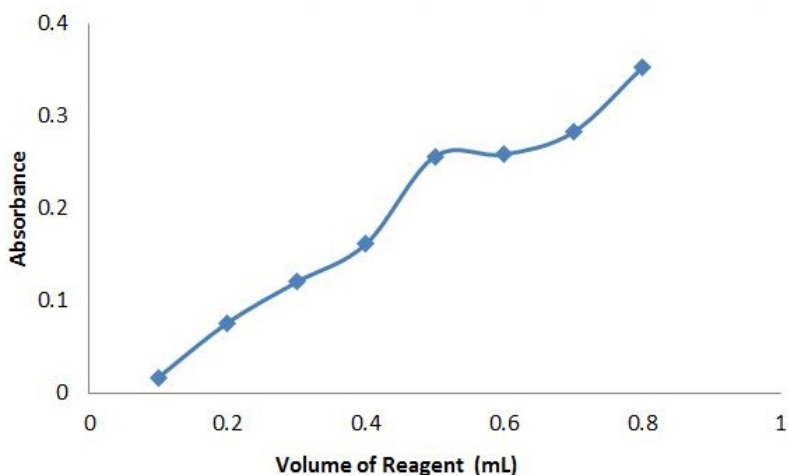


Figure 9. The effect of reagent volume on the formation of the Pb (II) complex.

Stoichiometry of lead (II)-6-MBTAMP complex

A series of solutions were made. The reagent (6-MBTAMP) volume was regularly varied from 0.25 to 2.75 mL with constant concentration at $1 \times 10^{-3} \text{ mol L}^{-1}$, while the Pb (II) ion concentration was held constant at $1 \times 10^{-3} \text{ mol L}^{-1}$ in fixed volume at 1.00 mL. The absorbance of these solutions was measured at 670 nm with all optimum conditions. The metal-reagent mole ratio was confirmed to be 1:2 as shown in Figure 10.

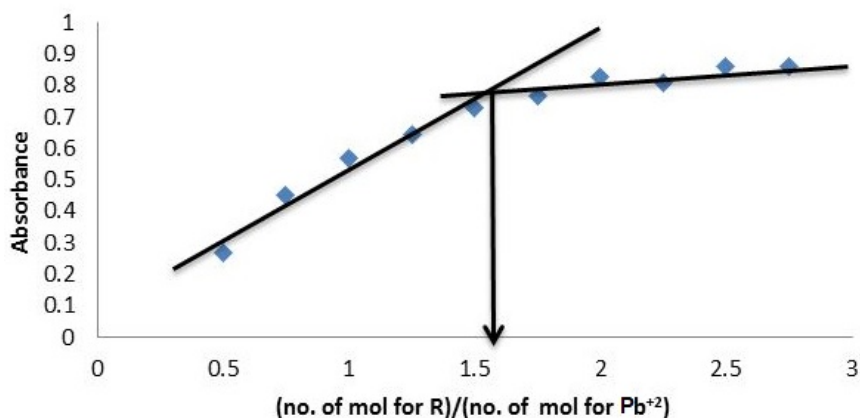


Figure 10. Mole ratio method to study stoichiometric for Pb (II) complex.

Calibration curve for Pb (II) complex

A series of Pb (II) ion solutions ranging from 0.1 to 25 mg L^{-1} were prepared using distilled water at $\text{pH}=6.8$. A 0.8 mL of reagent at 0.001 mol L^{-1} was added to form the green-red complex. The absorbance of the Pb (II) complex was measured at 670 nm. Beer's law is obeyed over the range of 0.6-10 mg L^{-1} as shown in Figure 11. Limit of detection (LOD), limit of quantification (LOQ), molar absorption coefficient and Sandell's sensitivity were calculated to be 0.181 mg L^{-1} , 0.604 mg L^{-1} , $6.8517 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 0.030 $\mu\text{g cm}^{-2}$ respectively.

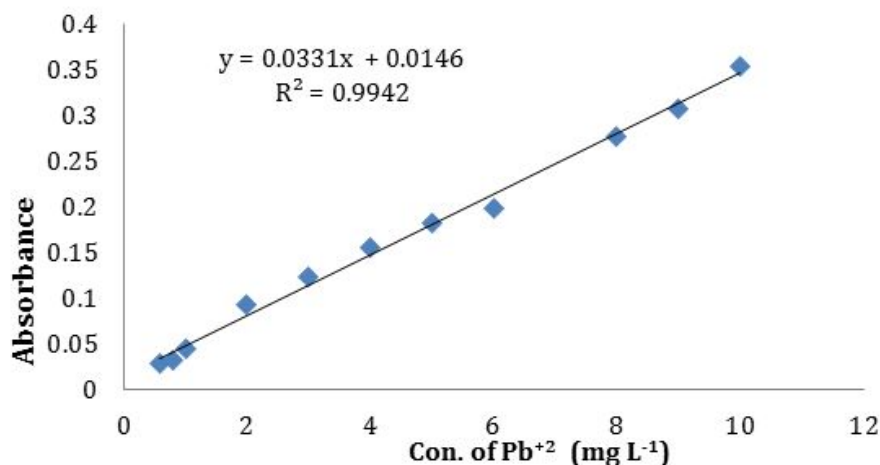


Figure 11. Calibration curve of Pb (II) complex using 6-MBTAMP as new reagent.

The results of this study were compared with other studies, such as a study that used 5,7-dibromo-8-hydroxyquinoline (DBHQ) as a reagent in the determination of Pb²⁺ in several standard reference materials (natural water, alloys and steels, bovine liver, hair and human urine), biological samples, food samples, and soil samples and found the Sandell's sensitivity and the average molar absorption

coefficient to be 5 ng cm^{-2} of Pb^{+2} and $6.16 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ respectively.²⁰ In addition, a study using 4-(2-pyridylazo) resorcinol as a reagent for detecting Pb^{+2} ions obtained a LOD value equal to 11 mg L^{-1} .¹⁵ A further investigation that utilized Alizarin red S as a reagent to estimate the Pb^{+2} ion in human hair found LOD equal to 0.2 mg L^{-1} , LOQ equal to 0.67 mg L^{-1} , and the molar absorptivity equal to $3.2523 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$.¹³ Finally, a study used 2-(5-bromo-2-pyridylazo)-5-(diethyl amino) phenol (5-Br-PADAP) as a chromogenic reagent to detection lead (II) ion in natural water samples and obtained LOD equal to $0.01 \text{ } \mu\text{g mL}^{-1}$.¹⁴

The effect of interference ions

The effect of various cations and anions on the detection of Pb (II) ion was studied extensively in low and high concentrations. The taken amounts of foreign ions were 5 mg L^{-1} at low concentration and 50 mg L^{-1} at high concentration, while the concentration of Pb (II) ion remained constant throughout the experiment at 5 mg L^{-1} . The results indicated that the cations Cu^{+2} , Co^{+2} , Mn^{+2} , Sn^{+2} , Fe^{+3} , Zn^{+2} , Ni^{+2} interfered at both concentrations, Mn^{+2} interfered only at high concentration, and Zn^{+2} , Ni^{+2} appeared no interfere at both concentrations. At the same time, the results confirmed that the anions CN^- , CH_3COO^- , Cl^- , SO_4^{-2} , PO_4^{-3} , F^- showed interfering in high and low concentrations, and CN^- , CH_3COO^- , Cl^- , SO_4^{-2} showed no interfering in low concentrations. Most of the cations and anions investigated interfered in the detection of Pb^{+2} , therefore, it was necessary to use masking agents to reduce the interference effect and increase the accuracy of Pb^{+2} determination.

At low concentrations, the masking agent for Cu^{+2} , Co^{+2} , Mn^{+2} and Sn^{+2} was 3 mL of S_2O_3 , 1 mL of SCN , 1 mL of C_2O_4 and 5 mL of F^- respectively. Whereas, the masking agent for Cu^{+2} , Co^{+2} and Mn^{+2} at high concentrations were 5 mL of S_2O_3 , 10 mL of C_2O_4 and 10 mL of C_2O_4 , respectively. The concentration of all masking agent solutions used in this study was 100 mg L^{-1} .

Applications

The proposed methodology was applied to the determination of the Pb (II) ion in six vegetable samples and the results were compared with the results obtained by flame atomic absorption spectroscopy as standard method. The comparison between the suggested method and FAAS method gave good accuracy with recovery percentage between 71 and 106.6% as shown in the Table III.

Table III. Accuracy of proposed method compared with FAAS method for determination of lead

Sample	Concentration of lead found by FAAS (mg L^{-1})	Concentration of lead found by proposed method (mg L^{-1})	Error %	Recovery %
Carrots 1 ^a	0.296	0.265	-10.47	89.53
Potato 2 ^b	1.105	1.100	-0.45	99.54
Beet 2	0.347	0.278	-19.88	80.12
Pepper 1	3.935	2.788	-29	71
Celery 2	0.347	0.370	6.6	106.6
Pepper 2	0.296	0.292	-1.351	98.65

^aNumber 1: refers to the samples which have been taken from traffic number 1 at Al-Mothana Street in Najaf.

^bNumber 2: refers to the samples which have been taken from traffic number 2 at Al- Ansar Street in Najaf.

CONCLUSION

A new spectrophotometric method has been suggested to determinate lead (II) ion in vegetable samples with 6-MBTAMP as a new reagent. The suggested spectrophotometric method has proved to be simple,

rapid and sensitive for determination of Pb (II) ion in vegetable samples. The proposed method obeyed Beer's law over a wide range of concentrations, 0.6-10 mg L⁻¹, therefore it is suitable for quantitation of Pb (II) ion in samples which have trace level of Pb (II) ion, as well as, those with high level of Pb (II) ion. The interference of Cu⁺², Co⁺², Mn⁺², Sn⁺² have been reduced by using a suitable amount of sodium thiosulfate, ammonium thiocyanate, sodium oxalate and sodium fluoride respectively as masking agents. However, Zn⁺² and Ni⁺² showed no interfering effect with lead (II) ion in this study. The proposed method was more sensitive comparing with other studied which used the same method but different reagents. The limit of detection (LOD), the limit of quantification (LOQ) and Sandell's sensitivity were calculated to be 0.181 mg L⁻¹, 0.604 mg L⁻¹ and 0.03 µg cm⁻² respectively. The proposed method obtained a recovery percentage of the vegetable samples ranging from 71% to 106.6%.

Conflicts of interest

We declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to thank Dept. of Chemistry, Faculty of Education for Girls, University of Kufa for their support during this study.

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