

## Green flow injection spectrophotometric system for lead ion (II) evaluation in vegetables samples using new azo reagent

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**Abstract:** A new, sensitive, and reliable flow injection methodology was investigated for the determination of lead ion (II) in vegetables' samples using a laboratory-prepared reagent 2-[(6-methoxy-2-benzothiazoly)azo]-4-methoxy phenol (6-MBTAMP). Infrared spectroscopy, UV-visible spectrophotometry, Energy dispersive X-ray spectroscopy (EDX), Elemental Analysis (CHN), nuclear magnetic resonance spectroscopy <sup>1</sup>HNMR, and <sup>13</sup>CNMR techniques were used to characterize the reagent and lead (II) complex. The method is based on lead ion (II) reacting with the reagent (6-MBTAMP) in a neutral solution to produce a green-red complex with a maximum absorbance at 670 nm. The optimum conditions, such as flow rate, lead ion (II) volume, reagent volume, medium pH, reagent concentration, and reaction coil length were thoroughly examined. The limits of detection (LOD) and quantification (LOQ) were determined to be 0.621 mg·L<sup>-1</sup> and 2.069 mg·L<sup>-1</sup>, respectively, while Sandell's sensitivity was determined to be 0.345 µg·cm<sup>-2</sup>.

**Key words:** flow injection, metal ions, vegetables' samples, 6-MBTAMP, toxic ions

### 1. Introduction

Lead is a poisonous heavy metal ion that is commonly found in aquatic ecosystems and causes long-term harm to human health and the environment.<sup>1</sup> Even at low levels, it can harm the nervous and digestive systems, causing memory loss, dizziness, and gastrointestinal ulcers.<sup>2</sup> Furthermore, Pb<sup>2+</sup> is toxic to the blood and interferes with the normal activity of enzymes.<sup>3</sup> It also acts as an enzyme inhibitor by binding to the -SH group in enzymes or proteins.

Lead, in its inorganic form, disrupts calcium

metabolism, causing to accumulate Pb<sup>2+</sup> in the bones. Tetramethyl lead and other organic lead compounds are extremely dangerous, because they are easily absorbed by the body through the skin and mucus membranes.<sup>4</sup> The World Health Organization (WHO) set a lead limit in drinking water to not exceed 10 µg·L<sup>-1</sup>.<sup>5</sup>

The degree of contamination in the environment may rise as a result of human activities; this is coming, for example, from the wide use of lead in gasoline antiknock chemicals and paint pigments.<sup>6</sup>

Inductively coupled plasma,<sup>7</sup> molecular spectroscopy,<sup>8</sup>

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atomic emission spectrometry (ICP-AES), inductively coupled anodic stripping voltammetry, and reversed-phase high-performance liquid chromatography coupled with UV-Vis or fluorescence detection techniques have all been used to determine  $\text{Pb}^{2+}$  in the environment and biological samples.<sup>4,9</sup>

These techniques have two advantages: high sensitivity and reproducible detection, however, due to the high cost of their instrument and the tight operational training requirement, it is difficult to meet the need of rapid real-time detection. As a consequence, developing additional detection techniques for the qualitative and quantitative evaluation of lead in polluted samples is required.<sup>10</sup>

María S. Di Nezio *et al.* (2006)<sup>11</sup> used flow injection technique to determine heavy metals by using Dithizone as a reagent. The detection limit and the percent of relative standard deviation (%RSD) of lead ion (II) was  $5.0 \text{ mg}\cdot\text{L}^{-1}$  and 4.5 % respectively. Jintana *et al.* (2007)<sup>12</sup> have applied the flow injection analysis technique to evaluate lead ion (II) in aqueous samples. 4-(2-pyridylazo) resorcinol was used as a reagent. The measured detection limit (3S,  $n=20$ ) was  $11 \text{ mg}\cdot\text{L}^{-1}$  with a recovery rate of 102 %, whereas the linearity of the calibration curve was at range of 0.05-0.90  $\text{mg}\cdot\text{L}^{-1}$  of lead. There were 12 determinations made with each hour of sampling. The technique has been used with a pre-concentration factor of 3 to identify lead in actual water samples. Rogelio Rodriguez *et al.* (2020)<sup>13</sup> used a totally automated examination of the multi-syringe flow injection technique in order to detect lead ion (II) in drinking water using 4-(2-Pyridylazo) resorcinol (PAR) as a reagent. The limit of detection obtained by this method was  $0.79 \text{ }\mu\text{g}\cdot\text{L}^{-1}$  with recovery rates of almost 100 %. Wirat *et al.* (2010)<sup>14</sup> used a simple flow injection colorimetric method to determine lead ion (II) in water samples by using 1,5-diphenylthiocarbazone as a reagent. The optimum conditions for detecting of lead ion (II) were studied. Under optimum conditions, the detection limit (LOD) was  $0.027 \text{ }\mu\text{g}\cdot\text{mL}^{-1}$ , and the range of linear calibration curve was  $1.0\text{-}12.0 \text{ }\mu\text{g}\cdot\text{mL}^{-1}$ . Dinezio *et al.* (2004)<sup>15</sup> designed a flow injection (FI) system with a pre-concentration stage and spectrophotometric

detection for the evaluation of  $\text{Pb}^{2+}$  trace levels in natural, well, and drinking water samples. The suggested technique gave detection limit equal to  $5.0 \text{ ng}\cdot\text{mL}^{-1}$  and a linearity range at  $(25\text{-}250 \text{ }\mu\text{g}\cdot\text{L}^{-1})$ .

This study aims to determine lead ion (II) at vegetables samples with a new reagent (2-[(6-methoxy-2-benzothiazoly)azo]-4-methoxy phenol) (6-MBTAMP) using a flow injection analytical method, along with spectrophotometric detection in a sensitive, easy, fast, economical, and reliable way.

## 2. Experimental

### 2.1. Apparatus

The Oakton 2100 Series pH/mV/Ion/OC/OF Meter was used to determine the pH value. Analytical Balance (Ohaus PA214 Pioneer) was used to weigh all of the samples. Shimadzu UV-1700 spectrophotometer was used to determine the maximum wavelength. The true value of lead ion (II) in vegetables samples was calculated using flame atomic absorption spectrometry (FAAS). Materials were loaded via Teflon pipes 0.5 mm. The flow cell employed was  $450 \text{ }\mu\text{L}$ , and the solutions were pushed using an Ismatic peristaltic pump. UV-Visible detector (OPTIMA SP300) was used to obtain the resulting peak. Signal Pen Siemens C1032 Hitter Ardeas was also used as a recorder. Infrared spectroscopy I.R (Shimadzu FT-IR 8400), Elemental analysis CHN (Micro analytical unit, 1108 CHN-O Elemental analyzer), Ultraviolet-Visible spectrophotometry (Shimadzu UV-1700), Energy dispersive X-ray spectroscopy EDX (Shimadzu Europe-EDX-700HS/800HS/900HS), nuclear magnetic resonance spectroscopy <sup>1</sup>HNMR (Burcker Biospin Gmph, 500MHz, DMSO as a solvent) and <sup>13</sup>CNMR (Varian INOVA-500 NMR Spectrometer, DMSO as a solvent) techniques were used to diagnose the reagent and lead (II) complex in this study.

### 2.2. Materials

All compounds, with the exception of the reagent 6-MBTAMP, were analytically graded and utilized without further purification. The solutions in this

experiment were made with distilled water at pH 6.8.

### 2.3. Preparation of standard stock solutions

- Solution of lead ion (II) ( $100 \text{ mg}\cdot\text{L}^{-1}$ ): Stock solutions were obtained by dissolving 0.0159 g of  $\text{Pb}(\text{NO}_3)_2$  in 100 mL of distilled water, whereas, working solutions were prepared by further dilution. The lead nitrate standard was provided by B.D.H. (England).
- New organic reagent 6-MBTAMP solution ( $1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ ): 0.0315 g of the organic reagent was dissolved in 100 mL of ethanol to prepare a stock solution. More diluted solutions of reagent were made as needed.
- Interference solutions: All interference ion solutions were made at a concentration of  $100 \text{ mg}\cdot\text{L}^{-1}$  by dissolving the suitable amount of the interfering substance in distilled water at pH 6.8 and diluting it to 100 mL.  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ ,  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ ,  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ ,  $\text{SnCl}_2$ ,  $\text{NaF}$ ,  $\text{CH}_3\text{COONa}$ ,  $\text{NaCl}$ , and  $\text{Na}_2\text{SO}_4$  are all prepared by dissolving (0.0268, 0.0208, 0.0404, 0.036, 0.0403, 0.0483, 0.0159, 0.0221, 0.0138, 0.0164 and 0.0147 g) respectively. Each foreign ion was evaluated in two concentrations. The first test was performed with a low concentration of interference ion at  $5 \text{ mg}\cdot\text{L}^{-1}$ , while the second test was performed with a high concentration of interference ion at  $50 \text{ mg}\cdot\text{L}^{-1}$ .

### 2.4. Samples collection

Vegetables' samples subjected to the proposed method were gathered from two industry and high-traffic areas of Najaf city in Iraq. Al-Mothana Street was the first area, while Al-Ansar Street was the second area. Five samples were taken, including one sample of carrot, celery, beet, and two samples of pepper. All samples were prepared using the wet digestion method. The concentration of lead ion (II) on these samples was evaluated by using flame atomic absorption spectrometry (FAAS) as standard method, and these values were used to compare with the values of lead ion (II) concentration in samples which obtained by the suggested method.

### 2.5. Preparation of samples

The samples in this investigation were prepared using the wet digestion method, and the processes were as following<sup>16</sup>:

5 g of sample was weighed and placed in a 200 mL beaker. 10 mL of concentrated nitric acid  $\text{HNO}_3$  was added, and the mixture was boiled in a water bath until the total remaining volume was 2-3 mL. The mixture then cooled down, and 10 mL of concentrated  $\text{HNO}_3$ , 5 mL of concentrated  $\text{H}_2\text{SO}_4$ , and 4 mL of  $\text{H}_2\text{O}_2$  were added, after that, the mixture was heated up again. When the digesting process was completed, 10 mL of distilled water was added, and the mixture heated up again to remove any remaining acids (Repeat this step as necessary until remove all extra acids). Finally, the mixture was cooled down before being filtered in a 100 mL volumetric flask and diluted to the mark using distilled water.

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

Diazoinumchloride salt solution was prepared<sup>17</sup> by dissolving 3.60 g, 0.02 mol from thiazoleamine derivative in 30 mL of water and 3 mL of concentrated hydrochloric acid  $\text{HCl}$ . The solution was treated with 5 mL of aqueous 1.4 g, 0.02 mol sodium nitrite dropwise and stirred for 30 min at  $0^\circ\text{C}$ . This diazonium chloride salt solution was added dropwise with stirred to alkaline solution of paramethoxy phenol 2.48 g, 0.02 mol which dissolved in 30 mL of

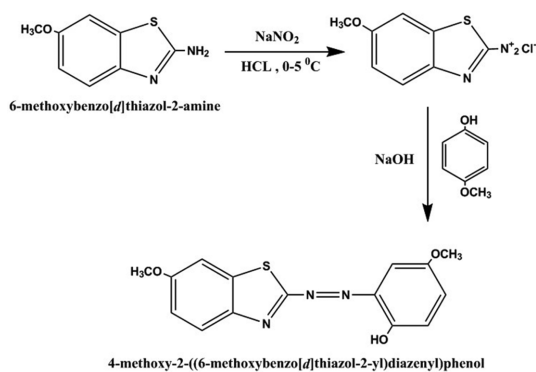


Fig. 1. Preparation steps of the 6-MBTAMP reagent.

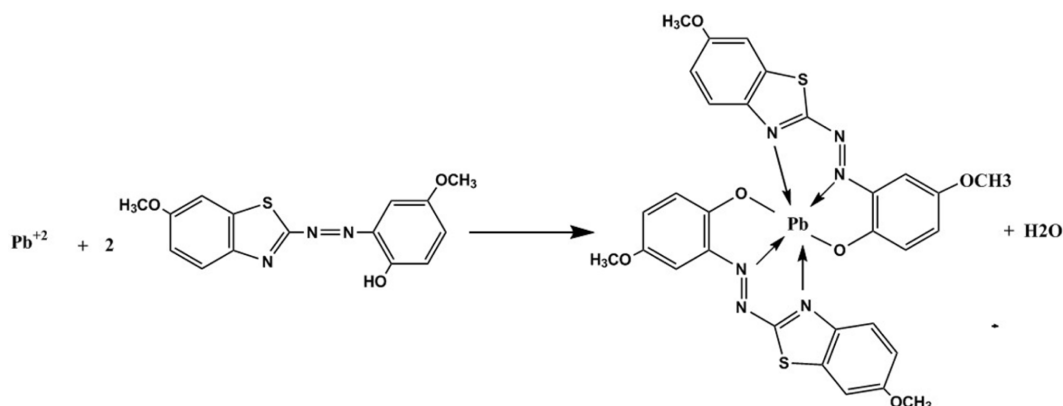


Fig. 2. Proposal mechanism between lead ion (II) and the reagent (6-MBTAMP).

ethanol, and 80 mL of 10 % sodium hydroxide was added. After the mixture had been stirred for 1h at 0-5 °C, the final compound was filtered; air dried, and recrystallized two times from hot ethanol and then dried in the oven at 50 °C for two hours, melting point of the reagent was found to be 90-95 °C. The preparation steps of the 6-MBTAMP reagent are shown in (Fig. 1).

In this study, the proposed flow injection technique (Fig. 3) was governed by the complexation of lead ion (II) with 2-[(6-Methoxy-2-benzothiazolyl) azo]-4-methoxy phenol (6-MBTAMP), which produced a green-red complex with a maximum absorbance at 670 nm as shown in Fig. 2. To improve the accuracy of the data, the optimum conditions for this reaction were extensively examined.

### 2.7. Suggested Procedure

After a very carefully studying for the optimum conditions for the suggested design of FIA system which consists of a peristaltic pump, a valve of two channels, reaction coil, spectrophotometric detector, and recorder as shown in (Fig. 3). The sample or the standard solutions of  $Pb^{2+}$  was loaded in the first channel with 6 cm (47.1  $\mu$ L) whereas the reagent (6-MBTAMP) at 0.0001 mol·L<sup>-1</sup> was loaded in the second channel with 10 cm (78.1  $\mu$ L). The sample and reagent were passed through the manifold tubes by the carrier stream (distilled water at the optimal value of pH) with a flow rate of 7 mL·min<sup>-1</sup>. The complexation

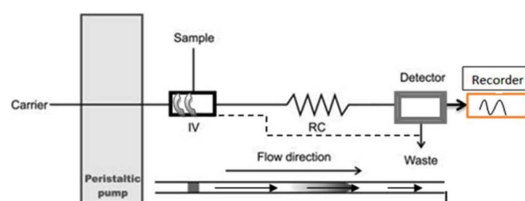


Fig. 3. Proposed FIA manifolds: **Carrier**, distilled water at pH 6.8; **IV**, injection valve it included two loops the first loop for samples and standard solution of  $Pb(NO_3)_2$  and the second loop for reagent; **RC**, reaction coil.

process between  $Pb^{2+}$  and the reagent (6-MBTAMP) occurred in the reaction coil (20 cm) before reaching the detection unit. The spectrophotometric detector was employed to monitor the signal at 670 nm and the signal recorded as an absorbance values.

## 3. Results and Discussion

### 3.1. The maximum absorbance wavelength ( $\lambda$ ) of 6-MBTAMP and its complex with lead ion (II)

To determine the wavelength of maximum absorbance of reagent and study the effect of lead (II) complex formation on the wavelength and maximum absorbance, samples were examined in different media using Shimadzu UV-1700 spectrophotometer in order to obtain the greatest sensitivity; the findings showed that the best spectra were in neutral medium. The lead(II) complex had a maximum absorbance at 670 nm, while the reagent had a maximum absorbance

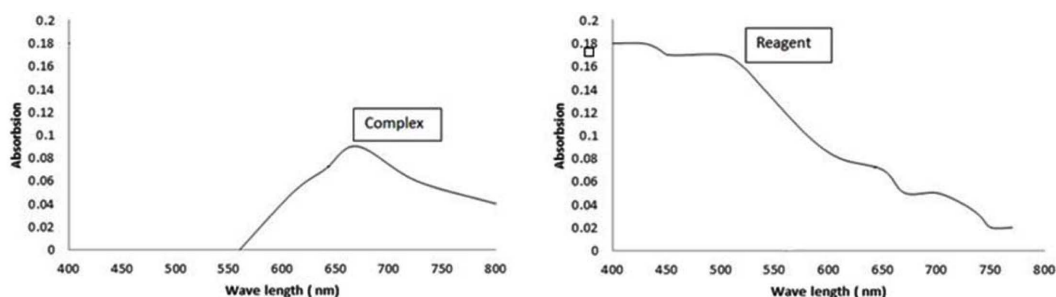


Fig. 4. The absorption spectrum of lead (II) complex and the reagent in neutral medium.

of 429 nm. As a result of the coordination of some functional groups of the reagent with the lead ion (II), a bathochromic effect was seen in the spectrum of the lead ion (II) - 6-MBTAMP complex, as shown in (Fig. 4). According to these results, the maximum wavelength ( $\lambda$ ) in this investigation was chosen at 670 nm.

### 3.2. Determination of the best solvent for the reagent 6-MBTAMP

The effect of the solvent on the solubility of the reagent has been thoroughly studied; the results are presented in (Table 1). Due to the high solubility of reagent in absolute ethanol compared to the other solvents tested in this study (Absolute ethanol, absolute ethanol: water 1:1, absolute ethanol: water 1:4, and water), it was chosen as the best solvent for the reagent. Moreover, the absolute ethanol considers as nontoxic, available, and green chemistry solvent.

### 3.3. Characterization of reagent (6-MBTAMP) and lead (II) complex

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

When comparing the analytical data which was obtained in practice with the theoretically calculated data provided by using Elemental Analysis CHN (Micro analytical unit, 1108 CHN-O Elemental analyzer) which is listed in (Table 2), a high degree of convergence can be seen, demonstrating the correctness of composition for (6-MBTAMP) reagent and lead (II)-6-MBTAMP complex.

#### 3.3.2. Infrared spectrum

The FT-IR technique showed clear absorption bands in the IR spectrum. The free azo dye was indicated in a band at  $1435.04\text{ cm}^{-1}$  due to the azo group of the thiazoleamine derivative while it shifted to  $1442.75\text{ cm}^{-1}$  in the lead (II) complex. The band at  $3390.86$

Table 1. Effect of solvent on solubility of reagent

NO	Solvent	Absorbance			Mean	SD	RSD%
1	Ethanol	0.199	0.197	0.198	0.198	0.001	0.505
2	Ethanol:water 1:1	0.129	0.130	0.130	0.130	0.001	0.769
3	Ethanol:water 1:4	0.003	0.003	0.003	0.003	0.000	0.000
4	Water	The reagent shows no solvation in water					

Table 2. Results of analysis of elements (CHN) of the reagent (6-MBTAMP)

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) <sub>2</sub> ·H <sub>2</sub> O	46.0	42.20	2.574	3.05	8.079	9.85

Table 3. Characteristic FTIR absorption bands of the reagent and lead complex

Compound	$\nu$ (O-H) $\text{cm}^{-1}$	$\nu$ (N=N) $\text{cm}^{-1}$	$\nu$ (C-Pb) $\text{cm}^{-1}$	$\nu$ (C-N) $\text{cm}^{-1}$
6-MBTAMP reagent	3390.86	1435.04	-----	1639.49
Lead (II) complex	-----	1442.75	414	1600.92

$\text{cm}^{-1}$  which appeared in the reagent spectrum refers to OH group; this band disappeared in complex spectrum which confirms its contribution in the coordination bond. In the lead (II) complex, the weak band (Pb-C) vibrations were seen at  $414 \text{ cm}^{-1}$ . The wide peak at  $3415\text{-}3545 \text{ cm}^{-1}$  belongs to the crystallized  $\text{H}_2\text{O}$  molecular at the complex which appears usually at  $3200\text{-}3550 \text{ cm}^{-1}$  as shown in (Table 3).

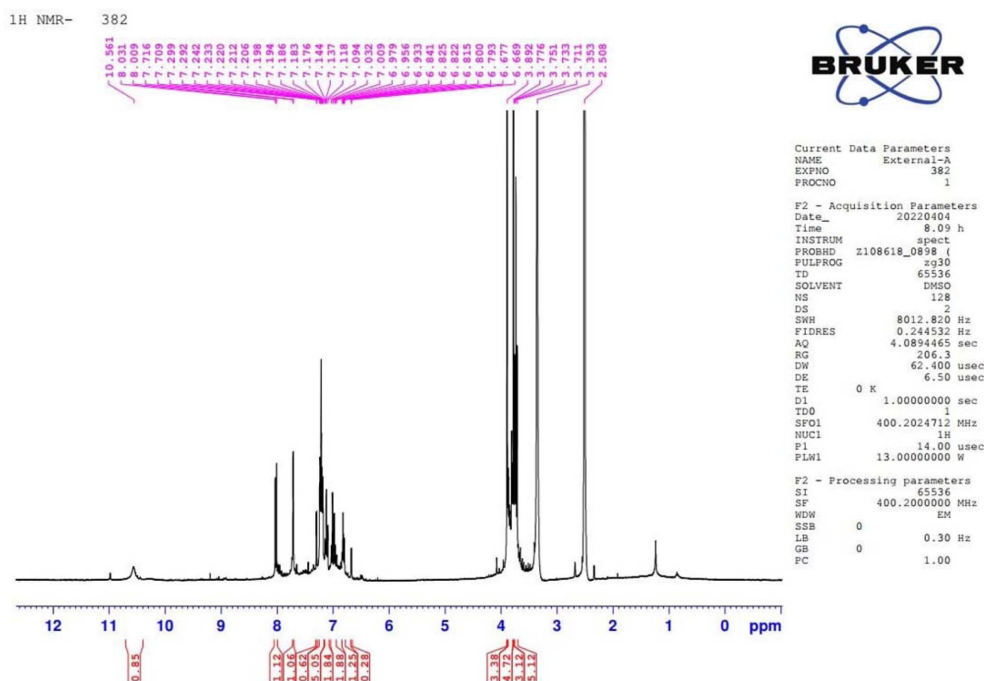
### 3.3.3. $^1\text{H}$ NMR of lead (II) complex

The  $^1\text{H}$ NMR spectrum of the lead (II) complex has cleared all the signals within their expected and indicated ranges as shown in (Fig. 5), the multiple signals at the chemical shift  $\delta=3.71 \text{ ppm}$  and  $3.89 \text{ ppm}$ , belong to methoxy protons (O- $\text{CH}_3$ ) due to the effect of electronic inductive of oxygen atom, which

cause decreasing in the numbers of electrons around protons, whereas, the signals at  $\delta=6.6\text{-}8.03 \text{ ppm}$  refers to phenyl rings protons that are found in various environments. The spectrum also showed a mono signal at the chemical shift  $\delta=2.530 \text{ ppm}$  due to the solvent protons DMSO- $d_6$ .

### 3.3.4. $^{13}\text{C}$ NMR of lead (II) complex

The results of  $^{13}\text{C}$ NMR spectrum were as following: The carbon atom of the methoxy group is responsible for the signal at position  $55.8 \text{ ppm}$ . The singlets at positions  $105\text{-}125 \text{ ppm}$  refer to carbon atoms at phenyl rings, while the signal at position  $135 \text{ ppm}$  refers to carbon atoms at C=N group that is placed inside the ring as indicated in the  $^{13}\text{C}$ NMR spectrum shown in (Fig. 6).

Fig. 5.  $^1\text{H}$ NMR of lead (II) complex.

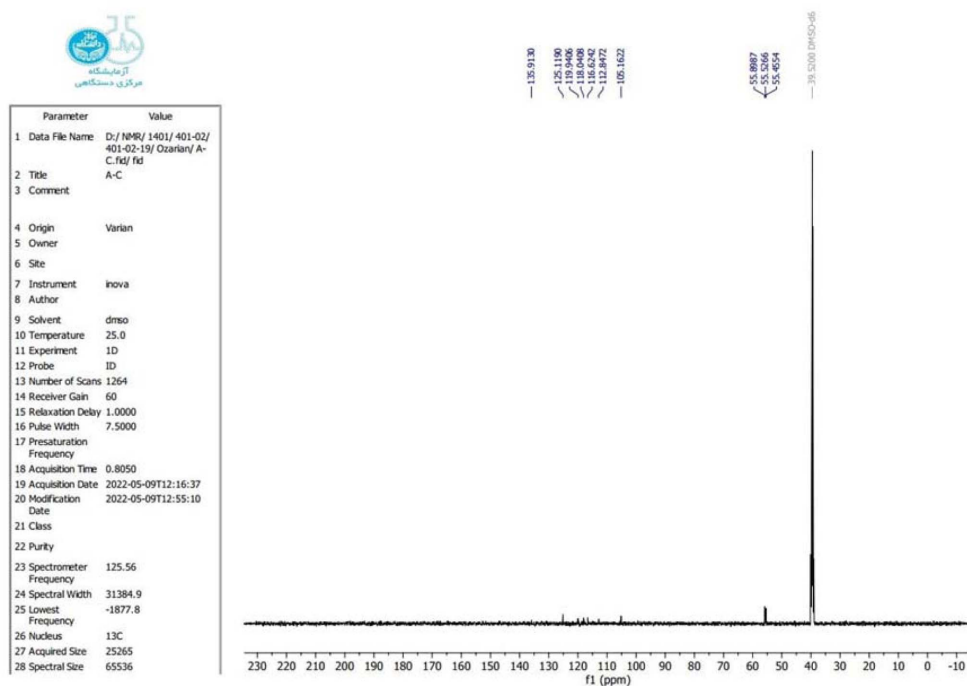


Fig. 6. <sup>13</sup>CNMR of lead (II) complex.

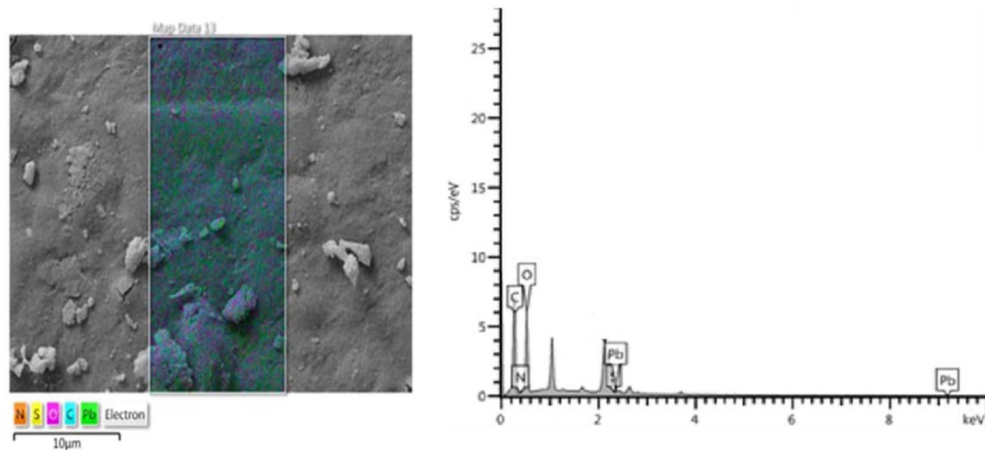


Fig. 7. Energy dispersive X-ray spectroscopy (EDX) for lead (II) complex.

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

The EDX results of the lead (II) complex proved the existing of C, O, H, Pb, N, and S in the chemical structure of the complex as shown in (Fig. 7). This result indicates the veracity of complex formation.

### 3.4. Optimal conditions of lead (II) complex formation using a new flow injection system

Carrier flow rate, reaction coil length, pH, reagent volume, reagent concentration, and sample volume, were examined carefully to determine their optimal values in the flow system.

Different values of carrier flow rates were tested to

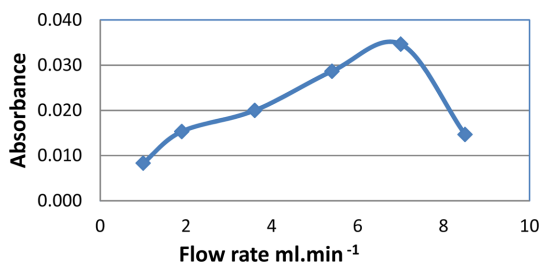


Fig. 8. The effect of flow rate on the production of lead (II) complex.

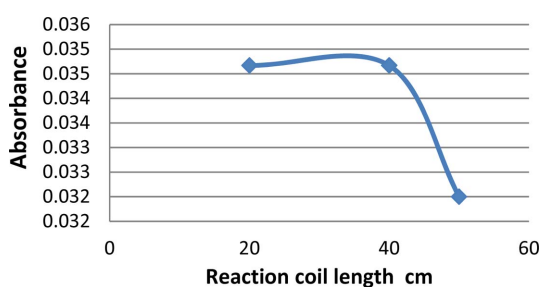


Fig. 9. The effect of reaction coil length on the production of lead (II) complex.

determine the impact of the carrier flow rate on the analytical signal, including (1, 1.9, 3.6, 5.4, 7, and 8.5 mL·min<sup>-1</sup>). The highest analytical signals, as shown in (Fig. 8), were obtained at a flow rate of 7 mL·min<sup>-1</sup>, which was chosen as the ideal value, this result of flow rate was in agreement with the result of flow rate in the reference number.<sup>18</sup>

The influence of reaction coil length on the absorbance value was also evaluated. The test is included 20, 40 and 50 cm. The reaction coils with length of 20 and 40 cm have produced the highest values of absorbance when compared to the reaction coil with 50 cm. According to the obtained results, the reaction coil with length of 20 cm was selected as the best reaction coil length, because it caused less desparation and required less time than the reaction coil with 40 cm as presented in (Fig. 9).

After choosing the optimum values of flow rate and reaction coil length, the pH effect was studied due to the acidic function effects on the lead complex formation. The values of the pH which studied in this test were 4, 5, 6, 6.8 and 8 using NaOH and HCl to identify the ideal complexity pH. As seen in (Fig.

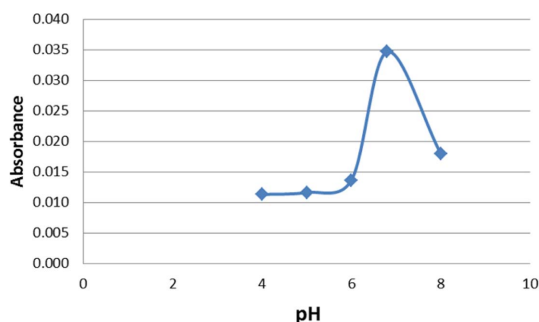


Fig. 10. The effect of pH on the formation of the lead (II) complex.

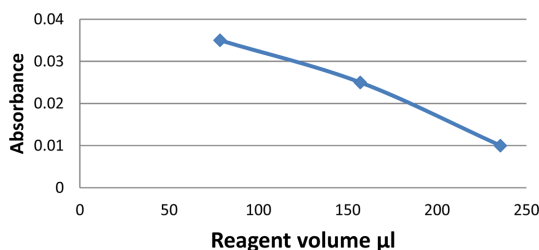


Fig. 11. The effect of reagent volume on the formation of the lead (II) complex.

10) the pH value at 6.8 was the optimum value of pH for the complex formation. At this test, the lead ion (II) concentration was 10 mg·L<sup>-1</sup> in a volume of 47.1 μL, whereas the reagent concentration was 0.0001 mol·L<sup>-1</sup> in a volume of 78.1 μL.

The effect of reagent volume on absorbance value was tested in different volumes including 78.1, 157 and 235.5 μL which are equivalent to 10, 20 and 30 cm of reagent loops respectively. This test was at (10 mg·L<sup>-1</sup>, 47.1 μL of lead (II) ion and 0.0001 mol·L<sup>-1</sup> of reagent). The maximum value of analytical signal has appeared with reagent volume at 78.1 μL as shown in (Fig. 11), thus this volume was selected as an optimum value of reagent volume in this study.

To determine the appropriate lead ion (II) volume in this work, three different loops were employed in this test. The lengths of loops were 6, 16, and 26 cm which is equivalent to 47.1, 125.6, and 204.1 μL of lead ion (II), respectively. During this test, the concentration of the reagent was 10<sup>-4</sup> mol L<sup>-1</sup>, and the volume of the reagent was 78.1 μL. (Fig. 12) shows that the highest absorbance of lead (II) complex was



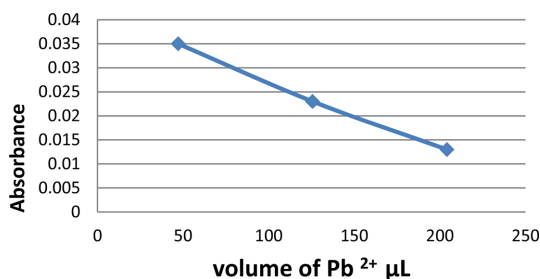


Fig. 12. The effect of lead ion (II) volume on the formation of the lead (II) complex.

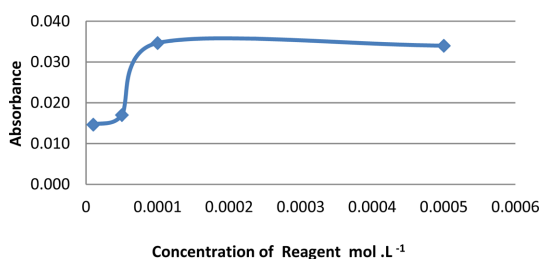


Fig. 13. The effect of reagent concentration on the production of lead (II) complex.

at a loop with a length of 6 cm (47.1 μL). This value was considered to be the best loop length of lead ion (II) in this test.

The effect of reagent concentration on the analytical signal was studied between  $1 \times 10^{-5}$  and  $5 \times 10^{-4}$  mol·L<sup>-1</sup> at pH (6.8). The analytical signal increased with the increases of reagent concentration up to  $1 \times 10^{-4}$  mol·L<sup>-1</sup>. Due to the results, reagent concentration at  $1 \times 10^{-4}$  mol·L<sup>-1</sup> was selected for further experiments as an optimal value as shown in (Fig. 13). this result of the reagent concentration solution was in agreement with the result of reagent concentration in the reference number.<sup>19</sup>

### 3.5. Calibration curve for lead (II) complex

After examining the various conditions and their impact on the absorbance value of the lead (II) complex, calibration curves for the lead complex were constructed under optimal conditions using distilled water at pH 6.8 and a series of lead ion (II) solutions ranging from 0.5 to 30 mg·L<sup>-1</sup>. Beer's law was observed by measuring the lead (II) complex absorbance at 670 nm over the concentration range of 1-20 mg L<sup>-1</sup> as

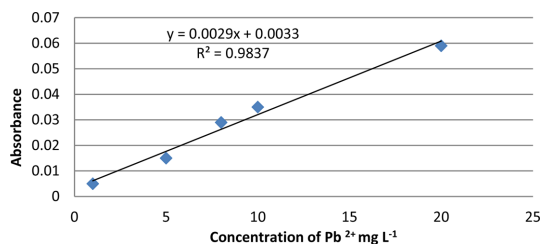


Fig. 14. Calibration curve of lead (II) complex.

illustrated in (Fig. 14). The Sandell's sensitivity, the limit of detection (LOD), and the limit of quantification (LOQ) were founded to be  $0.345 \mu\text{g}\cdot\text{cm}^{-2}$ ,  $0.621 \text{ mg L}^{-1}$ , and  $2.069 \text{ mg}\cdot\text{L}^{-1}$ , respectively.

The results of the suggested method have been compared with two previous studied, the first comparison was with Rodríguez *et al.* (2020),<sup>13</sup> where the recovery rates were found from 91 % to 105 % and the limit of detection (LOD) of this method was  $0.00079 \text{ mg}\cdot\text{L}^{-1}$  in drinking water samples. The linearity range was  $0.0026\text{-}0.24 \text{ mg L}^{-1}$  and the value of %RSD was 4.2.

The second comparison was with Wirat *et al.* (2010)<sup>14</sup> in this study the same methodology of the suggested method was used but with a different reagent. The linear calibration curve was  $1.0\text{-}12.0 \text{ mg}\cdot\text{L}^{-1}$  and the value of the limit of detection (LOD) was  $0.027 \text{ mg L}^{-1}$  in water samples.

### 3.6. Dispersion coefficient

The dispersion coefficient (D) used widely as an experimental factor for determining the degree of sample dilution from the injection point to the detector. Due to the outcomes displayed in (Table 4), the type of dispersion in this study was limited dispersion.

Table 4. Desperation coefficient values

Pb <sup>2+</sup> Conc. mg·L <sup>-1</sup>	Response		Dispersion D = A°/A <sub>max</sub>
	A°	A <sub>max</sub>	
10	0.074	0.034	2.176

A°: Absorbance with absent of dilution (outside the FIA system).  
A<sub>max</sub>: Absorbance with the presence of dilution (inside the FIA system).

Table 5. Repeatability of lead ion (II) at a concentration of 10 mg·L<sup>-1</sup> in FIA unit

Samples Readings	1	2	3	4	5	6	Mean	SD	%RSD
Absorbance	0.033	0.031	0.035	0.036	0.034	0.034	0.034	0.002	5.882

Table 6. Accuracy of suggested method compared with FAAS technique for evaluation of lead ion (II)

Sample	True value (FAAS) mg·L <sup>-1</sup>	Measured value (suggested method) mg·L <sup>-1</sup>	E%	Recovery %
Carrots 1 <sup>a</sup>	0.296	0.230	-0.220	99.780
Pepper 2 <sup>b</sup>	0.296	0.302	2.030	102.030
Beet 2	0.347	0.282	-18.73	81.270
Celery 2	0.347	0.332	-0.040	99.960
Pepper 1	3.935	4.130	4.950	104.950

<sup>a</sup>Number 1: refers to the samples which have been taken from traffic number 1 at Al-Mothana Street in Najaf.

<sup>b</sup>Number 2: refers to the samples which have been taken from traffic number 2 at Al- Ansar Street in Najaf.

### 3.7. Repeatability

In order to measure the precision of the FIA unit, the experiment was repeated six times for lead ion (II) at a concentration of 10 mg·L<sup>-1</sup>. The results are shown in (Table 5).

### 3.8. Effect of foreign metal ions on the absorbance of lead (II) complex

Effect of foreign metal ions was investigated by preparing low and high concentrations of interference ions, the influence of various cations and anions on the detection of lead ion (II) was thoroughly tested. Foreign ions concentrations were 5 mg·L<sup>-1</sup> at low concentration and 50 mg·L<sup>-1</sup> at high concentration, while lead ion (II) concentration remained constant at 5 mg·L<sup>-1</sup> throughout the experiment. All cations (Cu<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Sn<sup>2+</sup>, Fe<sup>3+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup>) interfered at both concentrations, with the exception of Mn<sup>2+</sup>, which interfered only at high concentrations; however, Zn<sup>2+</sup>, Ni<sup>2+</sup> did not appear to interact at both concentrations (CN<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> and F<sup>-</sup>) showed interference in both high and low concentrations, with the exception of (CN<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) which had no interference in low concentrations. The majority of the cations and anions under examination interfered with the detection of Pb<sup>2+</sup>, which requires the use of masking agents to minimize the interfering effect and improve Pb<sup>2+</sup> evaluation accuracy. At low concentrations, the masking agent

for Cu<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup> and Sn<sup>2+</sup> were 3 mL of S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, 1 mL of SCN<sup>-</sup>, 1 mL of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> and, 5 mL of F<sup>-</sup> respectively. Whereas, the masking agent of Cu<sup>2+</sup>, Co<sup>2+</sup> and, Mn<sup>2+</sup> at high concentrations, were 5 mL of S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, 10 mL of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> and 10 mL of C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, respectively. The concentration of all masking agent solutions which used in this study was 100 mg L<sup>-1</sup>.

### 3.9. Applications

Five vegetable samples were tested to determine lead ion (II) using the suggested method. According to FAAS, the concentration of Pb<sup>2+</sup> in the samples of pepper 1 was located at the linearity range (1-20 mg L<sup>-1</sup>), thus this sample was measured directly. However, the rest of the samples (carrot 1, pepper 2, beet 2, celery 2 and pepper 2) were found to have a Pb<sup>2+</sup> concentration of less than 1 mg·L<sup>-1</sup>, therefore the standard additions method was utilized in these samples. The recommended method gave good accuracy in comparison with the FAAS method, recovery rates were ranged from 81 to 104.95 % as indicated in (Table 6).

## 4. Conclusions

The suggested green flow injection spectrophotometric system of lead ion (II) which is evaluation in vegetables samples using laboratory-prepared reagent (6-MBTAMP) has been found to be new, reliable,

simple, and economic for lead ion (II) determination. This suggested methodology has a wide linearity range which is located at a range of 1-20 mg·L<sup>-1</sup> therefore, it is considered an appropriate method for detecting lead ion (II) in samples containing relatively large amounts of it, such as waste water or industrial discharges, but it is unsuitable for trace concentrations of lead ion (II) in natural water which usually is less than 0.1 mg·L<sup>-1</sup>. The solvent used to dissolve the reagent in this study was absolute ethanol which considers as green chemistry and less cost compared to other organic solvents. The interference of Cu<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup> and, Sn<sup>2+</sup> has been decreased by utilizing the appropriate concentrations of sodium thiosulfate, ammonium thiocyanate, sodium oxalate, and sodium fluoride as masking agents. In this investigation, lead ion (II) did not interfere with Zn<sup>2+</sup> and Ni<sup>2+</sup> ions. According to calculations, the limit of detection (LOD), limit of quantification (LOQ), and Sandell's sensitivity was 0.621 mg·L<sup>-1</sup>, 2.069 mg·L<sup>-1</sup>, and 0.345 µg·cm<sup>-2</sup> respectively. The recovery percentage of lead ion (II) in the vegetable samples using the suggested method was ranged from 81.27 % to 104.95 %.

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