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Synthesis of Schiff Base Unsaturated Oligomeric Polyester for Determination of Trace Lead

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Abstract

A new very sensitive and selective chromogenic reagents prepared by the reaction of Schiff base with maleic anhydride (MA) and 1,4-butane (I), ethylene (II), 1,6-hexamethylene (III) and 1,2-propane diol (IV), respectively, were synthesized and studied for the determination of trace lead in detail. In 0.1molL^{-1} NaOH medium, lead reacts with polyester to form a yellow complex, which gives a maximum absorption at 462, 478, 482 and 495 nm using I, II, III and IV respectively. Beer's law is obeyed over the concentration ranges $0.04\text{--}1.20\mu\text{g mL}^{-1}$, whereas optimum concentration ranges as adopted from Ringbom method was $0.10\text{--}1.05\mu\text{g mL}^{-1}$. The molar absorptivity, Sandell sensitivity, detection and quantification limits are also calculated Ca (3500-fold), Mg (2250-fold), Sr (1250-fold), Ba (1000-fold), Al (1500-fold), Bi (800-fold), Fe (2500-fold) Co (1100-fold), Ni (1000-fold), Cu (900-fold), Zn (1300-fold), Cd (2500-fold), and Ag (750-fold) do not interfere with the determination of lead. The chromogenic system is remarkably superior to other reagents, especially porphyrin compounds. The influence caused by oxygen in air or in solution can be easily eliminated by adding Na_2SO_3 . The reaction is very stable, the stability constant of the complex being 1.44×10^{45} . The chromogenic reaction is completed within 2.0 min at room temperature. The proposed method has been applied to the direct determination of trace lead in clinical samples. The accuracy and precision are both very satisfactory.

Keywords: Unsaturated polyester; Spectrophotometry; Lead determination; Clinical analysis

Introduction

It is well known that absorbed superfluous lead is vital to human, but people would also sicken serious diseases such as encephalopathy, kidney damage, and memory loss even if exposure a small quantity of it due to its cumulative characteristic in organism and bones [1,4]. Lead and its compounds are hazardous, lead poisoning was cumulative and its toxic effects are many and severe [5,6]. Because of environmental pollution (especially in developing countries), clinical lead analysis is becoming increasingly important. Analysis of clinical samples must be reliable, are simple and quick as possible. Flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), flow injection (FI) [7-10], and electrochemical sensor [11-13] were used for the analysis of lead. However, FAAS was reliable down to about $0.2\mu\text{g L}^{-1}$ and so was not always suitable for the analysis of lead in clinical samples ETAAS and FI are generally used to determine lead at low concentrations, but they were complex to use; moreover, some type of preconcentration or extraction step must be used to meet the requirement of accuracy and precision. Spectrophotometric methods were versatile and economical.

Dithiazone [14], diethyldithiocarbamate [15-17], arsenazo III [14], 4-(2-pyridylazo)-resorcinol (PAR) [18], malachite green [19], butylrhodamine-B [20], xylenol orange [21], 2-(2-thiazolylazo)-p-cresol, dithiodibenzoic acid [22], dithiodibenzoic acid iodide-ethylene violet- polyvinyl chloride [23], and a copolymer consisting of protoporphyrin disodium salt and acrylamide [24] were suitable for the trace analysis of lead in clinical samples due to their low detection limit. Dibromo-p-methylsulfonazo [25] was sensitive, but Ca^{2+} and Mg^{2+} , which exist in clinical samples were reasonable amounts, interfere with the determination of lead and require prior separation with potassium iodide-methylisobutylketone extraction.

Polymers having the amino acid moiety in the main chain or in the side chain find a variety of useful applications, such as chelating agents for metal ions, ion-exchange resins, polymer catalysts with enzyme like behavior, and promotes for preparing polymeric carrier's

drugs [26-31] polyesters with pendant amino groups and carbonyl oxygen of the ester group as donor sites per unit may yield metal-coordinated polymers with interesting properties. However, few investigations had been reported on the synthesis of polyesters having amino acid moieties in the main chain. Earlier, reported the synthesis and characterization of poly (ethyleneaspirate)-metal complexes [32] which were found to be thermally more stable than the polyesters itself.

The present investigation aimed to synthesize polyester based on Schiff base derived from amino acid have attached much attention as analytical reagents owing to their very high sensitivity, however, certain problems seriously effect their application, such as solubility and selectivity (especially transition metal ions interfere with the determination of lead).

All foreign ions studied in reasonable amounts do not interfere with the determination of trace lead. The proposed method has been applied to the direct determination of lead in clinical samples with good precision and accuracy. The method is one of the most sensitive and efficient techniques for the determination of trace lead at the present time.

Experimental

Materials

DL aspartic acid (Aldrich Comp), salicylaldehyde (WIN LAB, U.K.)

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anhydrous sodium acetate, maleic anhydride (Oxford Lab., Mumbai) pure-grade of Merk Co. (Germany) and were used directly, Glycols 1,4-butane, ethylene, 1,6-hexamethylene and 1,2-propylene were reagent grade and used without further purification product of Merk, darmstade, all solvents used were of A.R. or all solutions were prepared with distilled water. A stock solution of Pb^{2+} was prepared by dissolving 0.2g of $Pb(NO_3)_2$ in 250mL of distilled water containing 0.5mL of concentrated nitric acid. The solution was standardized complexometrically using ethylenediaminetetraacetic acid (EDTA), and a working solution of $10\mu g Pb^{2+} mL^{-1}$ was about prepared by suitable dilutions.

Preparation of azomethine schiff base

The Schiff base monomer was prepared by reacting 1.22g (0.01mol) of salicylaldehyde with 1.33g (0.01 mole) of aspartic acid in 15mL of methanol in the presence of 0.5g of anhydrous sodium acetate. The mixture was refluxed for 3.0hr at $60^\circ C$ under nitrogen atmosphere [33], poured into ice-cold water and then allowed to stand for 1.0hr. The precipitated solids were filtered off, washed repeatedly with demineralized water and recrystallized from ethanol. The Schiff base was isolated as yellow solid. The yield was about 70%.

Preparation of unsaturated polyesters

Polycondensation were carried out by the reaction of maleic anhydride (0.5mol) and different Glycols (1.0mol) at temperature of $140-170^\circ C$ about (4.0hr) using traces of p-toulene sulphonic acid as acidic catalysis in reaction flask which dipped in an oil bath (thermostatically controlled), provided, with mechanical stirrer and Dean-Stark trap to collect the water, stream of dry nitrogen insert in the flask to facilitate the removal of water [34]. 0.5mol of Schiff base added in the second step and the temperature raised gradually $180-210^\circ C$ (6-8hr). The unreacted monomer and other by-product were removed from the reaction mixture by evacuation for 0.5–1.0hr. at the end of the reaction. The copolymer was purified by dissolving in DMF and precipitating into large amount of rapidly stirred petroleum ether ($40-60^\circ C$). The precipitated viscous copolymer dried in a vacuum oven at $40^\circ C$ for 6.0hr.

Characterization of polyesters

Viscosity measurements were carried by Ostwald viscometer using 1.0% solution in dioxane at $30^\circ C$. the mean molecular weight of the prepared polyesters were determined by the end-group analysis for COOH using alcoholic potassium hydroxide. The infrared were recorded by Beckman 4220 infrared spectrophotometer. The

Polyester	Nature of polyester polyester	Acid value	Mean M. wt.	N*	η_{int} (dL g ⁻¹)
I	Viscous material	12.5	7392	16	0.54
II	Viscous material	25.0	4872	12	0.73
III	Viscous material	21.0	7773	15	0.36
IV	Viscous material	19.5	7552	9	0.47

N* = Degree of polymerization

Table 1: Physical properties of saturated polyester.

Polymer	THF	DMF	DMSO	CHCl ₃	Acetone	HCOOH	Conc. H ₂ SO ₄
I	-	+	+	-	±	+	+
II	-	+	+	-	±	+	+
III	-	+	+	±	±	±	+
IV	-	+	+	-	±	+	+

(+) Soluble; (±) Partially soluble; (-) Insoluble

Table 2: Solubility characteristics of polyesters (I-IV).

proton magnetic resonance spectra (in DMSO-d₆ solvent using TMS as reference) were measured with a Varian EML 390 spectrometer operating at 200MHz.

The absorption spectra were recorded and measured using JASCO 530V spectrophotometer, equipped with 1.0cm quartz cells.

Synthesis of reagents

0.05% reagent solutions were prepared by dissolving 0.05g of reagent in 100mL of N, N- dimethylformamide (DMF).

General procedure

A solution containing no more than $12.0\mu g$ of Pb^{2+} was transferred into a 10mL calibrated flask, 2.0mL of 0.1M NaOH, 0.5mL of 2.0% Na_2SO_3 and 0.5 mL of 0.05% reagent were added successively; after standing for 2.0min, 0.5mL of 2.0% Triton X-100 solution was added and diluted to the mark with water and mixed well. The absorbance was measure at λ_{max} , against the reagent blank in a 1.0cm cell was recorded.

Clinical analysis

Clinical samples were weighed (blood samples, 1.0g, hair samples, 0.5g; urine samples, 50g, dried and carbonized in an electric furnace; this was followed by ashing in a muffle furnace at $550-600^\circ C$ and dissolving the ash in 3.0mL of 0.1mol L⁻¹ HNO_3 . This solution was transferred into a 10mL calibrated flask, 2.0mL of 0.1 M NaOH, 0.5mL of 2% Na_2SO_3 and 0.5mL of 0.05% polyester were added successively; after standing for 5.0 min, 0.5mL 2.0% Triton X-100 was diluted to the mark with water and mixed well. The absorbance was measured at the corresponding λ_{max} against the same reagent as blank.

Results and discussion

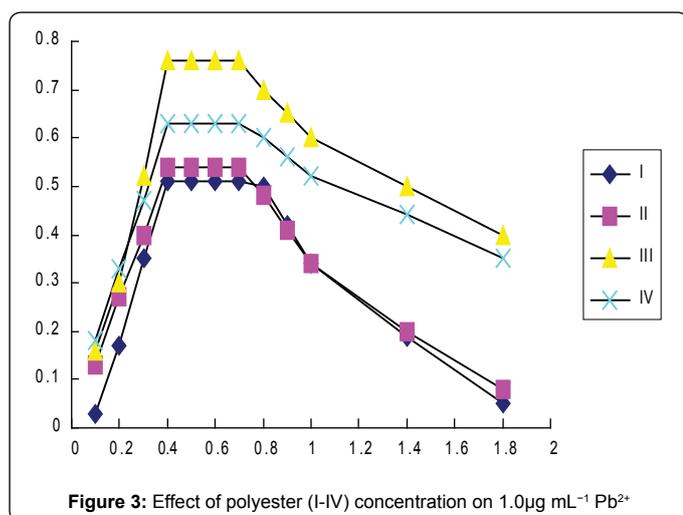
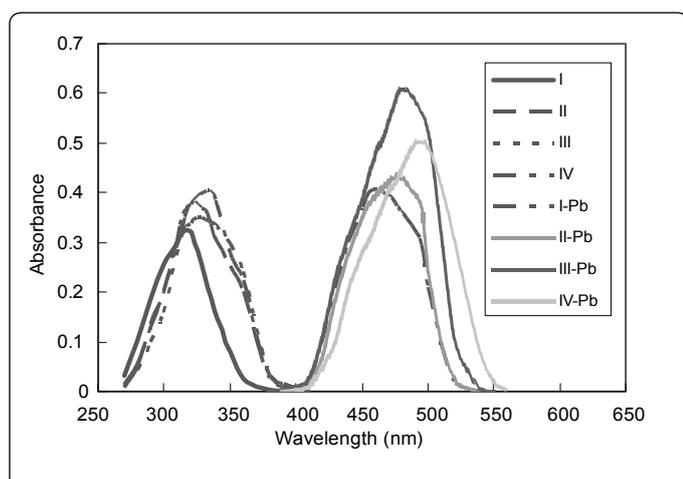
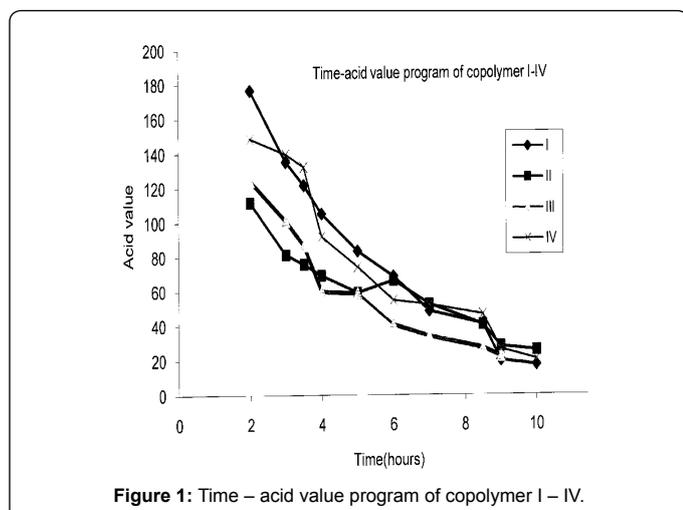
Physical and chemical properties of polyesters

The physical properties of the prepared unsaturated polyesters (I-IV) were listed in Table (1). The study of Table (1) indicate that the degree of polymerization, mean molecular weight and acid value were determined by the end group analysis and calculation of the mean M. wt. were in the range 4872–7773 by the standard method [35–36] and degree of polymerization range 9–16 unit which give copolymer with medium molecular weight. All polyesters are yellowish viscous. The inherent [37] viscosities of the polymer solutions in DMSO were determined at 30C depending on the solubility of polyester. The η_{int} values of the polyesters (I–IV) were in the range of (0.36–0.73dl/g). The solubility characteristics of the polyesters (I–IV) are shown in Table (2). It can be seen from Table 2 that all polyester was insoluble in halogenated solvents such as chloroform and tetrahydrofuran (THF). Most of the polyester were soluble in dimethylformamide (DMF), dimethylsulphoxide (DMSO) and partially soluble in acetone.

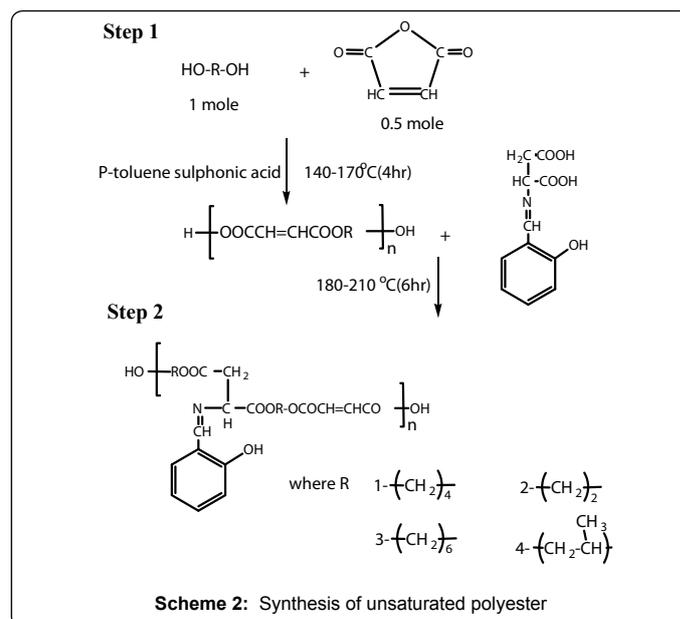
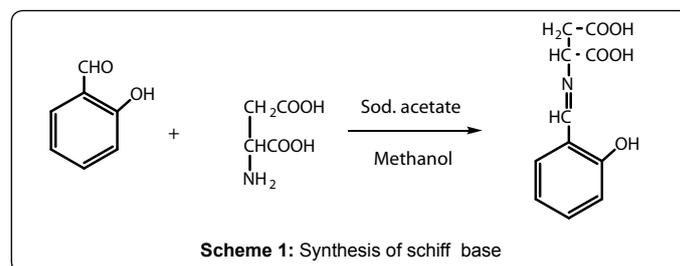
The relation between acid value and time of the polyester preparation by raise the temperature circuly after each one hr and calculate the progress of polymerization by acid value determination at the end of this temperature as shown in Figure (1). Finally, we operate the polymerization till the least degree of acid value which indicate that almost all moles of acids react with glycol.

The unsaturation of copolymer give high degree of stability and extend conjugation which help for the accuracy of this ligand in spectrophotometric determination of traces metal under application.

The structure of the prepared copolyesters (I–IV) were established from IR and ¹H NMR spectra. The IR spectra of the prepared Schiff



base showed sharp band at 3410 cm^{-1} due to stretching vibration of OH group, sharp band at $1700\text{--}1705 \text{ cm}^{-1}$ $\nu\text{C=O}$ of acid group, C=N stretch at $1610\text{--}1630 \text{ cm}^{-1}$, band at 2950 cm^{-1} stretching CH_2 . The IR spectra of the prepared copolyesters (IV) showed bands around 3430 cm^{-1} (νOH), 2950 cm^{-1} (νCH_2), 1720 cm^{-1} ($\nu\text{C=O}$) of ester and 1635 cm^{-1} ($\nu\text{C=N}$).



The $^1\text{H-NMR}$ of the copolyesters I-IV were illustrated in Table 3. The method of Baddar, [38] was used in this present work for the qualitative but quantitative analysis of these copolyesters by the $^1\text{H-NMR}$ spectroscopy. The results of both qualitative and quantitative were clear the molar ratios of the glycol to the acid from Table 3, also the study of $^1\text{H-NMR}$ indicate the formation of the copolyester and also indicate the relation between the calculated amount of moles of acid and glycol were almost the same from quantitative analysis of the $^1\text{H-NMR}$ spectra of the product copolyesters.

Chromogenic reaction of polyester with metal ions

Polyesters were found to react mainly with Zn^{2+} and Pb^{2+} . Zn^{2+} reacts with reagent to form complex in pH 10 (borax buffer solution) with λ_{max} 462, 478, 482 and 495 nm [Figure 2] and molar absorptivity are 1.05×10^5 , 1.12×10^5 , 1.57×10^5 and $1.31 \times 10^5 \text{ Lmol}^{-1}\text{cm}^{-1}$. The highly sensitive reagent with Pb^{2+} is examined now.

Effect of medium

The influence of the pH on the absorbance of the Pb^{2+} reagent complex was studied. At pH > 9.0, the complex absorbance remained almost constant. The final pH was controlled by adding 2.0 mL of 0.1 mol L^{-1} NaOH to 10 mL calibrated flask in order to keep the colour reaction reproducible, constant and sensitive.

Effect of polyester concentration

Under the conditions employed, the volume of 0.05% reagent solution required to obtain a maximum and constant absorbance for $1.0 \mu\text{g}$ of lead was 0.4-0.7 mL. Therefore, 0.5 mL of 0.05% reagent solution was introduced (Figure 3).

Polymer	Component	Chemical shift δ (ppm)	Assignment	No. of proton	Peak areas	Relative Mole amount	Mole %
I	G*	1.7, 3.7 and 4.2	$(8H)_2(CH_2)_2(H)(CH_2OCO)_2$	16	110.2	6.88	55.57
	A*	1.9, 3.9, 4.3, 5.2, 6.2, 7.1 and 7.5	$(2H) CH_2COO, (1H) CH=N, (1H)CH=N, (1H)OH(2H)=, (4H) Ar$	11	70.2	5.5	44.42
II	G	4.2	$(8H) COOCH_2$	8	102	8.5	53.4
	A	1.7, 3.6, 4.1, 5.2, 6.1, 7.3 and 7.8	$(2H) CH_2COO, (1H) CH=N, (1H)CH=N, (1H)OH(2H)=, (4H) Ar$	11	81.4	7.4	46.54
III	G	1.7 and 4.2	$(16H)_2(CH_2)_4H_2(4H)(COOCH_2)_2$	24	198.9	8.29	51.82
	A	1.8s, 3.8, 4.2, 5.2, 6.3, 7.3 and 7.7	$(2H) CH_2COO, (1H) CH=N, (1H)CH=N, (1H)OH(2H)=, (4H) Ar$	20	84.8	7.71	48.18
IV	G	0.9, 4.1, and 4.3	$(6H)_2CH_3, (4H)COOCH_2$ and $(2H)(COOCH)_2(CHOCO-)$	12	85.6	7.2	48.0
	A	1.7, 3.7, 4.0, 5.2, 6.1, 7.1, and 7.7	$(2H) CH_2COO, (1H) CH=N, (1H)CH=N, (1H)OH(2H)=, (4H) Ar$ $CH_2COO(2H) (1H)-CH=N, CH-CO, \text{ and } (1H)HO$	11	113.8	7.8	52.0

G: Glycols

A: Diacid

Table 3: ¹H-NMR Spectral data of unsaturated polyester I-IV.

Parameter	Reagent			
	I	II	III	IV
λ_{max}	462	478	482	495
Beer's law, $\mu\text{g mL}^{-1}$	0.05-1.20	0.05-1.00	0.5-1.10	0.05-1.15
Ringbom conc, $\mu\text{g mL}^{-1}$	0.15-1.05	0.20-0.85	0.1-1.0	0.15-1.05
Molar absorptivity, $\text{L mol}^{-1}\text{cm}^{-1}$	1.05×10^5	1.12×10^5	1.57×10^5	1.31×10^5
Sandell sensitivity ng cm^{-2}	1.97	1.85	1.32	1.58
Detection limit, ng mL^{-1}	15	14	16	17
Quantification limit, ng mL^{-1}	48	45	50	54
Stability up to bray	7.0	7.0	9.0	10.6
Regression equation *				
(a) intercept	- 0.013	0.009	0.012	- 0.008
(b) slope	0.51	0.54	0.76	0.63
Correlation coefficient ^a	0.9992	0.9990	0.9996	0.9988
Standard deviation %	0.38	0.61	0.72	0.54
Relative standard deviation %	0.87	1.13	1.27	0.96
Error %	± 1.3	1.6	± 1.7	± 1.5

^aA = a +bC where C is the concentration of Pb²⁺ in ng mL^{-1}

Table 4: Physical and analytical parameter for Pb - complexed with polyester I-IV.

Effect of surfactants and organic solvent

The effects of various surfactants and organic solvents on the Pb²⁺-reagent chromogenic system were studied. It was found that the absorbance increased remarkably in the presence of non-ionic surfactants. The order of the increase was Triton x 100 > Tween 80 > octylphenyl ether > polyethyleneglycol. Cationic surfactants such as cetyltrimethyl ammonium bromide and cetylpyridinium chloride were added; the absorbance of the complex obviously diminished.

The addition of appropriate amounts of various organic solvents did not affect the absorbance of the complex. Hence, Triton X-100 is the best sensitizing agent and 0.3-0.7mL of 2.0% Triton X-100 solution gives a constant and maximum absorbance. Therefore, 0.5mL of 2.0% Triton X-100 was adopted.

Stability of the system

Oxygen in air or in the solution can affect the absorbance of the polymeric reagent and the complex. We have found that this easily be eliminated by adding 0.5 mL of 2% Na₂SO₃ solution. The absorbance of the Pb²⁺-reagent complex then remains stable for at least one week at room temperature.

Calibration graph

According to the properties of the complex, Beer's law was obeyed for 0.04-1.20 $\mu\text{g mL}^{-1}$ of lead, whereas optimum concentration ranges as adopted from Ringbom method was 0.1-1.05 $\mu\text{g mL}^{-1}$. The calculated molar absorptivity and Sandell sensitivity are recorded in Table 4. The IUPAC detection limit (K=3) and the quantification limits (k=10) [39] were calculated for each sample system (Table 4) Ten replicate analysis of a test solution containing 1.0 $\mu\text{g mL}^{-1}$ of lead using general procedure gave a mean of 2.01, 2.007, 1.994, 1.996 with a relative standard deviation of 0.87, 1.13, 1.27 and 0.96% using polyester I, II, III and IV, respectively.

Effect of interfering ions

Under the optimum conditions, the effects of various foreign ions on the determination of 1.0 $\mu\text{g mL}^{-1}$ of Pb²⁺ were examined separately, with a relative error of less than $\pm 5.0\%$. According to the data provided in Table 5, the tolerance for ions Zn²⁺, Mo⁶⁺, Cr⁶⁺, V⁵⁺, W⁶⁺, Ag⁺ and Hg⁺ should be low. All the foreign ions studied can be tolerated in considerable amounts.

Analytical applications

The proposed method was applied to the determination of Pb²⁺ in



Foreign Ions	Tolerance limits $\mu\text{g mL}^{-1}$			
	I	II	III	IV
Na ⁺ , Li ⁺	12500	12000	11000	13000
K ⁺ , Mg ²⁺	10000	10000	9000	10500
Ca ²⁺ , Sr ²⁺	8000	7500	7000	8000
Ba ²⁺ , Sn ²⁺	5000	4000	4000	4500
Al ³⁺ , Bi ³⁺	2500	2000	2250	2500
Ti ⁴⁺ , Sn ⁴⁺	1000	200	900	1100
Mn ²⁺ , Ca ²⁺	600	500	600	700
Fe ³⁺ , Cr ³⁺	400	375	360	450
Cu ²⁺ , Ni ²⁺	240	200	225	300
Cd ²⁺ ,	130	120	120	150
Ag ⁺ , Hg ⁺	80	75	70	20
V ⁵⁺ , W ⁶⁺	50	40	45	60
Mo ⁶⁺ , Cr ⁶⁺	25	20	25	30
Zn ²⁺	8	10	12	15
Cl ⁻ , I ⁻	7500	7000	7250	8000
C ₂ O ₄ ²⁻ , CO ₃ ²⁻	5000	6200	6000	2200
SO ₄ ²⁻ , NO ₃ ⁻	5000	5000	4700	5500
B ₄ O ₇ ²⁻ , P ₂ O ₄ ²⁻	10000	9000	9500	10000

Table 5: Effect of foreign ions, tolerance limits in the determination of $\mu\text{g mL}^{-1}$ of Pb²⁺ using polyester (I-IV).

Sample ^a	Found ^b $\mu\text{g g}^{-1}$				
	I	II	III	IV	ETAAS
I	0.155 ± 0.003	0.153 ± 0.002	0.157 ± 0.004	0.159 ± 0.005	0.16 ± 0.004
II	0.212 ± 0.004	0.210 ± 0.005	0.215 ± 0.002	0.220 ± 0.003	0.21 ± 0.006
III	0.114 ± 0.002	0.109 0.003	0.117 ± 0.005	0.110 ± 0.004	0.12 ± 0.005
IV	0.445 ± 0.003	0.450 0.004	0.447 ± 0.003	0.444 ± 0.005	0.45 ± 0.007

^aThe samples, which were taken from persons who were seriously suffering from lead poisoning, were provided by Benha University Hospital.

^bResults expressed as: $\bar{x} \pm \frac{St}{\sqrt{n}}$ where \bar{x} is the mean of n observations of x, s is the standard deviation, t is a distribution value chosen for the desired confidence level.

Table 6: Determination of Pb²⁺ in clinical samples.

clinical samples. The results are in good agreement with those found for lead by ETAAS with a prior separation by potassium iodide-methyl isobutyl-ketone (KI-MIBK) (Table 6). The performance of the proposed method was assessed by comparison with the ETAAS method. Mean values were obtained with a student's test for accuracy and F-values for precision at 95 % confidence limits for five degrees of freedom [40]. The results showed comparable accuracy and precision, since the calculated values were less the theoretical values.

Conclusion

The present investigation aimed to synthesize oligomeric polyester based on Schiff base derived from amino acid which have attached much attention as analytical reagents owing to their very high sensitivity. The proposed procedure gives a simple, very sensitive and low cost spectrophotometric procedure for the determination of trace quantities of lead. Beer's law is obeyed over the concentration ranges 0.04–1.20 $\mu\text{g mL}^{-1}$, whereas optimum concentration ranges as adopted from Ringbom method was 0.10–1.05 $\mu\text{g mL}^{-1}$. The chromogenic system is remarkably superior to other reagents, especially porphyrin compounds. The influence caused by oxygen in air or in solution can be easily eliminated by adding Na₂SO₃. The method is, safe, simple, rapid and inexpensive for the determination of trace quantities of lead in clinical samples.

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