Spectrophotometric determination for micro amount of Lead(II) in environmental and vital samples by 2-[Benzo thiozolyl azo]-4-Benzyl phenol

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Abstract:-

2-[Benzo thiozolyl azo]-4-Benzyl phenol (BTABP)was used as an organic reagent to form complex with Lead(II) having maximum absorbance at (λ=393 nm) and molar absorbency ε=2121 L $mol^{-1}cm^{-1}$.The optimum condition studies about complexation reaction demonstrated PH=9, 25minutes shaking time, stoichiometry shows the complex have a structure of 1:2(metal:ligand) $[Pb^{+2}(BTABP^{-})_2]$,as well complexation reaction was endothermic reaction without any effect for polarity of organic solvent on extraction method but there is effected for organic solvent structure ,in addition of used this organic reagent as spectrophotometric reagent for determination of Lead(II) in different samples of plants soils and water at different position in Al- Najaf governorate, with RSD%=1.2 , DL=3.492×10^{-6} and Sandell's sensitivity *S*=9.77×10^{-7}mg cm^{-2}.

Introduction:-

The Lead is not necessary for living and consider as very important pollutant for vital systems[1,2].Lead supply to the environment by different ways[3-5]. Kostenko used Chromazurol S as organic reagent for spectrophotometric determination of Lead in drinking water[6],Pellerano et al used (5-Br-PADAP) as organic reagent for spectrophotometric determination of Lead(II) in surface water[7],Sonawala et al used TBPO for extraction Pb(II) and Cu(II) also carry out this method for determination Cu(II) and Pb(II) in casts natural and pharmaceutical samples[8],Farid et al determined the concentration of some trace elements in cow's milk[9] ,Tintana et al determination Pb(II) in aqueous samples used aflow injection analysis system[10],Suparna et al used 2-amino thiazole as organic reagent for dertermination of Lead in environmental samples[11].The goal of this study about determination spectrophotometricaly for Lead(II) by use new organic reagent in different samples.

Experimental

Apparatus

For absorbance measurements shimadzu UV-1700 spectrophotometer is used 1cm quarts cells(Japan),pH-measurements were carried out using WTW, listed 8f93(Germany),For shaking used HY-4 vibrator with AD just about speed multiple(Italy), Atomic absorption AA6300.

Materials and Solutions:-

All chemical materials received from commercial sources with high purity and used as received ,Pb(II) 1mg/ml aqueous solution was prepared by dissolving o.1598 gm from $Pb(NO_3)_2$ in 100ml of distilled water contain 1ml conc.HNO_3,BTABP 1×10^{-2}M in Chloroform prepared by dissolving 0.3450gm from BTABP in 100ml of $CHCl_3$,Dithizone 1×10^{-2}M prepared by dissolving 0.2560gm from Dithizone in 100ml of CCl_4.

Adoption procedure

Prepared the complex of Lead(II) with organic reagent BTABP in Chloroform at optimum conditions of pH=8 and shaking time 25 minutes giving maximum absorbance at (λ=393nm) and molar absorptivity 2121 L $mol^{-1}cm^{-1}$,for determination Pb(II) in environmental and vital samples ,digest by moist method[12],after complete the aqueous volume to 25 ml ,for 5ml portion of sample solution added 3ml of 10% KCN and adjust acidity of solution to pH=8 added 5ml of 10^{-4}M BTABP dissolved in Chloroform after complete extraction and separated two layers take absorbance of organic phase at λ=393nm vies organic reagent solution as blank after resort of calibration curve Fig(1) determine amount of Pb(II) in the sample .And to the aqueous phase determine remainder quantity Pb(II) according to Dithizone method[13] as well calculate distribution ratio (D) depended calibration curve Fig(2).According to results at Fig(2) show the method have RSD%=1.2 , DL=3.492×10^{-6},S=9.77×10^{-7}mg cm^{-2}, (λ=393nm) and ε=2121 L $mol^{-1}cm^{-1}$.

Results and Discussion:-

Effect of pH

5 ml aqueous solution contain 100µg Pb(II) at different pH shaking with 5ml of 1×10^{-4}M BTABP in Chloroform ,after separated the two layers measure the absorbance of organic phase at (λ=393nm) also calculate distribution ratio (D) according to Dithizone method[13] , the results shows pH=8 was optimum value as in Figs(3,4).

Effect of metal ion concentration

5ml aqueous solutions containing different quantity of Pb(II) (5µg-150µg) adjust all solutions of pH=8 ,then added 5ml 1×10^{-4}M BTABP in Chloroform ,after completed shaking and separated two layers measure absorbance of organic layer at (λ=393nm) as well calculate distribution ratio (D) dependence on Dithizone method[13],the results in Figs(5,6) show 100µg giving higher distribution ratio (D).

Shaking time effect

5ml aqueous solution contain 100µg Pb(II) at pH= 8 after added 5ml of 1×10^{-4}M BTABP in Chloroform ,shaking for different times (5-30) minutes after separated the layers then measure the absorbance of organic phase at (λ=393nm) then calculate distribution ratio as in Dithizone method[13],the results at Figs(7,8) demonstrate 25 minutes is favorable shaking time.

Organic solvent effect

Used different organic solvent for BTABP to extracted Pb(II) from aqueous solutions at optimum condition, afterward calculate distribution ratio according to Dithizone method[13],the results show in Table(1) illustrated 1,2-DCE was the best organic solvent.

Temperature effect

Optimum conditions extracted Pb(II) by 1×10^{-4}M BTABP in Chloroform at temperature range (5-60) C°,after determine distribution ratio (D) by Dithizone method[13]calculate extraction constant K_{ex}.

$$K_{ex} = \frac{D}{[Pb^{+2}][BTABP]} \dots\dots(1) \qquad Slope = \frac{-\Delta H_{ex}}{2.303R} \dots\dots(2)$$

$$\Delta G_{ex} = -RTLnK_{ex} \dots\dots(3) \qquad \Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex} \dots\dots(4)$$

Fig(9)shows the complexation reaction was endothermic reaction with ΔH_{ex}= -0.0337KJ.mol^{-1} , ΔG_{ex}=-48.40 KJ.mol^{-1} and ΔS_{ex}=165.101 J.mol^{-1}.K^{-1}.

StoichiometrySlope
analysis method

At conditions of extraction ,extracted Pb(II) by 1×10^{-6}M-5×10^{-3}M BTABP in Chloroform .The slope value of straight relation Fig (10) shows the more probable structure of complex extracted was 1:2 [$Pb^{+2}(BTABP^{-})_2$].

Mole ratio method

Solution of 1×10^{-6}M-1×10^{-3}M BTABP in $CHCl_4$ used to extracted Pb(II) from aqueous solution at optimum condition ,afterward determine absorbance of organic phase at (λ=393)nm against CHCl3 ,the results at Fig (11) illustrated the complex was 1:2[$Pb^{+2}(BTABP^{-})_2$].

Continuous variation method

Aqueous solution of Pb(II) at 1×10-4M and BTABP in Chloroform at the same concentration, mixed different volume to total volume 10 ml, after complete shaking, determine absorbance for organic layer at λ=393nm ,Fig (12) show the structure of complex extracted was 1:2 [Pb+2(BTABP-)2].

Synergism effect

5 ml aqueous solutions contain 100µg Pb(II) at pH=8 shaking for with 5ml of (1×10^{-4}M) BTABP in Chloroform contain different concentration of Tributyl phosphate(TBP) or Methyl Iso Butyl Ketone (MIBK) (1×10^{-5}-1×10^{-2}M),then separate the two layers and used spectrophotometric method[13]for determination distribution ratio(D),and plot log D vies log[TBP] or log[MIBK] graphs were constricted Fig(14).

The results were show that the existence of TBP or MIBK with ligand in organic solution effect increasing distribution ratio (D) with concentration increase .The slope of straight line was show there is one molecule of TBP or MIBK participate in complex extracted as [$Pb^{+2}(BTABP^{-})_2$(TBP)], [$Pb^{+2}(BTABP^{-})_2$(MIBP)],occupied one position in coordination number instade water molecule and enhanced distribution ratio.

Applications about determination of Pb(II) in different samples

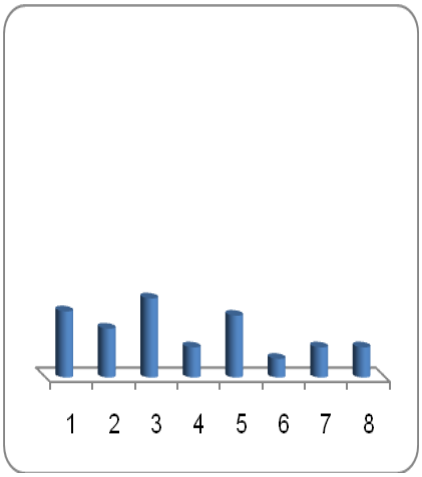
By used BTABP dissolved in Chloroform as spectrophotometric reagent determined Pb(II) in environmental and vital samples, after digested the sample according to moist method [12], after that dealing the sample as evident in adoption method, the results demonstrated at Tables 2,3,4,5 for plant leaves and Tables 6,7,8 for different soils as well as results at Table 9 for water at different samples.

Table(1)Effect of organic solvent on Pb(II) extraction

Organic Solvent	Dielectric Constant (ε)	Distribution ratio (D)	Percentage of extraction %E
Nitrobenzene	35.470	1.7	63
Amylalchohol	15.800	1.6	62
1,2-dichloro ethane	10.650	4.8	83
Chloro benzene	5.708	0.8	44
Chloroform	4.806	4.3	81
Benzene	2.804	2.1	68

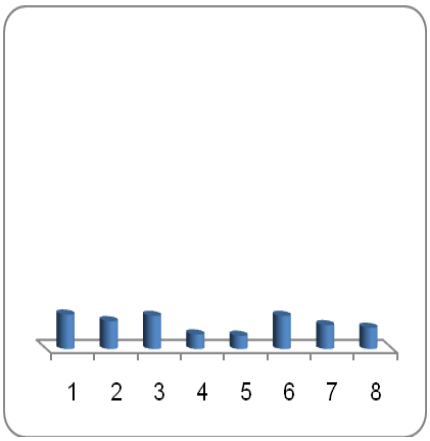
Table(2) Plant leaves in different positions at Al-Najaf governate.

	The position	[BTABP] method ppm	RSD %	AAS method ppm
1	Said Jawad stream	1.21	0.4	1.20
2	Al-manathira faraway from street	1.09	0.9	1.11
3	Al-mishkhab near the street	1.30	0.8	1.28
4	Aal aissa territory	0.96	1.4	1.01
5	Al-manathira near the street	1.18	0.8	1.20
6	Near Al-sahla mosque	0.88	0.6	0.89
7	Al-mutanabbi district	0.96	1.0	0.98
8	Plantation in Al-mishkhab	0.96	1.2	0.97



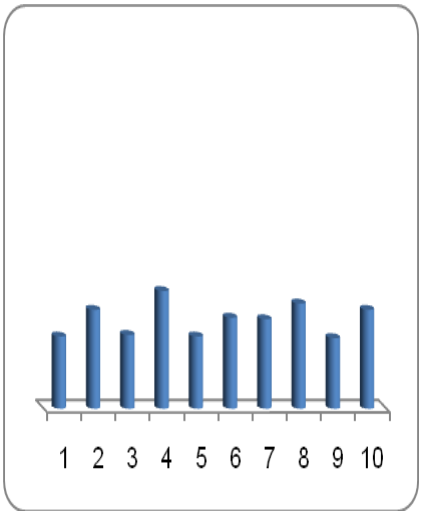
Table(3) Plant leaves from market near street at Al-Zahraa quarter

	Kind of leaver	[BTABP] method ppm	RSD %	AAS method ppm
1	Radish leaves	1.01	0.5	1.0
2	Lettuce leaves	0.96	1.4	0.98
3	Spinach leaves	1.00	0.8	1.1
4	Madanos leaves	0.86	1.2	0.90
5	Peppermint leaves	0.85	1.1	0.88
6	Leek leaves	1.00	0.5	1.05
7	BarBeen leaves	0.93	1.1	0.96
8	Celery leaves	0.91	0.6	0.9



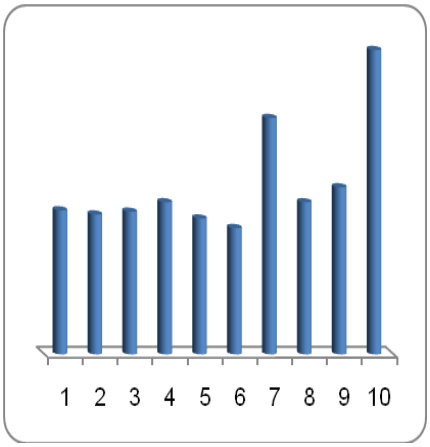
Table(4) Plant leaves from different quarter in Al-Najaf city

	The position	[BTABP] method ppm	RSD %	AAS method ppm
1	Al-Milad quarter	1.21	0.4	1.2
2	Al-Garry quarter	1.38	0.6	1.4
3	AL-Sihha quarter	1.22	1.0	1.25
4	Al-Zahraa quarter	1.50	0.8	1.6
5	Al-Wafaa quarter	1.21	0.5	1.22
6	Al-Anssar quarter	1.33	0.4	1.3
7	Al-Nasser quarter	1.32	0.2	1.32
8	Al-Asskary quarter	1.42	0.8	1.41
9	Al-Kuddos quarter	1.20	0.2	1.22
10	Al-Swak quarter	1.38	0.5	1.4



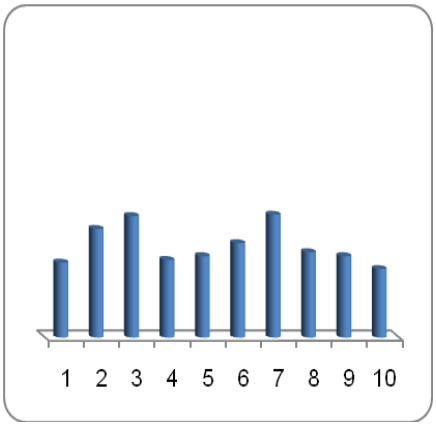
Table(5) Plant leaves from different positions along Al-Kufa street.

	The position	[BTABP] method ppm	RSD %	AAS method ppm
1	Al-Ashreen squar	1.81	0.4	1.80
2	Traid room	1.78	0.8	1.80
3	Al-Najaf court	1.80	1.0	1.81
4	Al-Sadrien squar	1.87	0.4	1.86
5	Education Gollege	1.75	0.5	1.75
6	Al-Sader hospital	1.68	0.6	1.66
7	Al-Waeli group	2.49	1.2	2.5
8	Mjles Al-Ashaer	1.87	0.6	1.88
9	Al-Kufa court	1.98	1.1	1.97
10	Al-kufa mosque	2.99	0.6	3.0



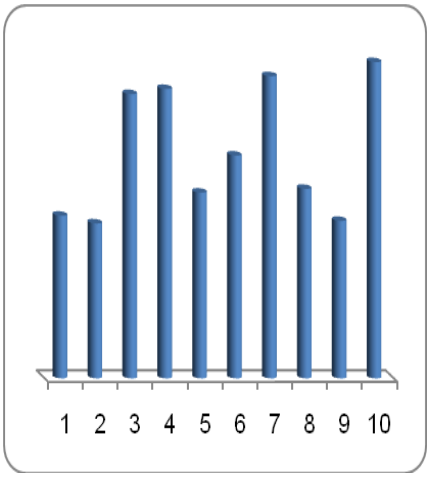
Table(6) Soil samples from many quarters at AL-Najaf city

	The position	[BTABP] method ppm	RSD %	AAS method ppm
1	Al-Milad qurter	1.33	0.4	1.3
2	Al-Garry qurter	1.59	0.8	1.31
3	AL-Sihha qurter	1.69	1.2	1.7
4	Al-Zahraa qurter	1.35	0.6	1.37
5	Al-Wafaa qurter	1.38	0.6	1.40
6	Al-Anssar qurter	1.48	0.5	1.49
7	Al-Nasser qurter	1.70	0.2	1.72
8	Al-Asskary qurter	1.41	0.4	1.42
9	Al-Kuddos qurter	1.38	1.0	1.40
10	Al-Swak quter	1.28	0.5	1.3



Table(7) Soil samples from different positions along Al-Kufa street.

	The position	[BTABP] method ppm	RSD %	AAS method ppm
1	Al-Ashreen squar	2.02	0.5	2.0
2	Traid room	1.96	0.8	1.98
3	Al-Najaf court	2.97	1.4	2.99
4	Al-Sadrien squar	3.01	0.6	3.03
5	Education Gollege	2.20	0.2	2.21
6	Al-Sader hospital	2.49	0.4	2.5
7	Al-Waeli group	3.11	0.6	2.99
8	Mjles Al-Ashaer	2.23	0.5	2.25
9	Al-Kufa court	1.98	1.2	2.0
10	Al-kufa mosque	3.22	0.6	3.24

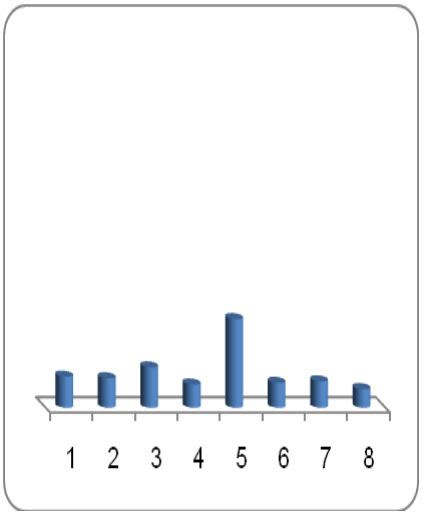


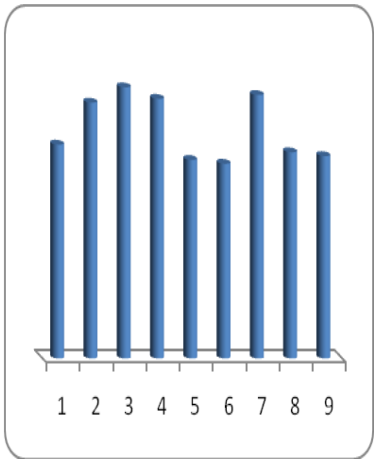
Table(8) Soil samples from different locutions at Al-Najaf governorate

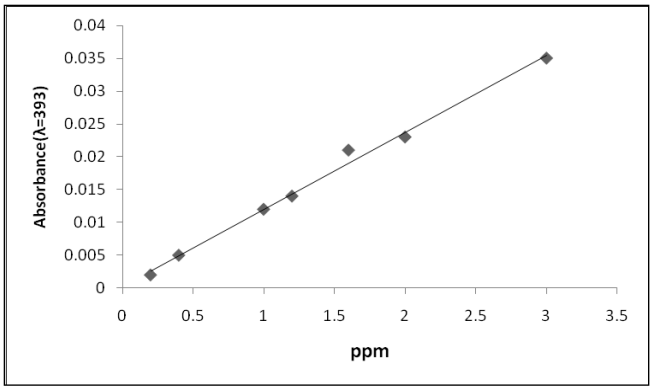
	The position	[BTABP] method ppm	RSD %	AAS method ppm
1	Al-Zarka group	0.056	0.2	0.055
2	Al-Asam machine	0.067	0.4	0.067
3	Al-Kufa old water group	0.071	0.2	0.071
4	Iron bridge	0.068	0.2	0.067
5	Al-Zorfat territory	0.052	0.4	0.053
6	Aal aissa water group	0.051	0.2	0.051
7	Al-Esement factory	0.069	0.8	0.068
8	Al-manathira territory	0.054	0.6	0.054
9	Al-mishkhab territory	0.053	0.4	0.053

Table(9)Water samples from different locution of Al-Forat river.

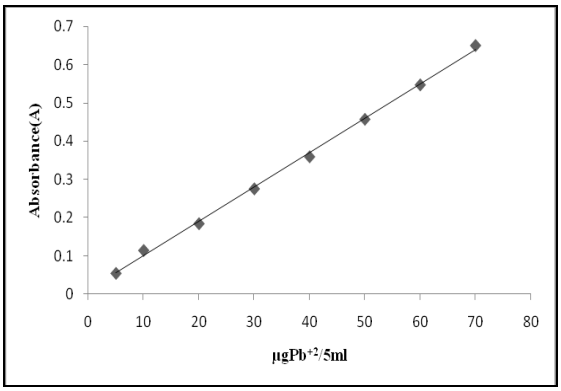
	The position	[BTABP] method ppm	RSD %	AAS method Ppm
1	Said Jawad stream	0.95	0.8	1.0
2	Al-manathira faraway from street	0.94	0.5	0.96
3	Al-mishkhab near the street	1.01	1.2	1.03
4	Aal aissa territory	0.90	1.2	0.91
5	Al-manathira near the street	1.32	0.5	1.34
6	Near Al-sahla mosque	0.91	0.2	0.91
7	Al-mutanabbi district	0.92	0.6	0.94
8	Plantation in Al-mishkhab	0.87	0.4	0.9



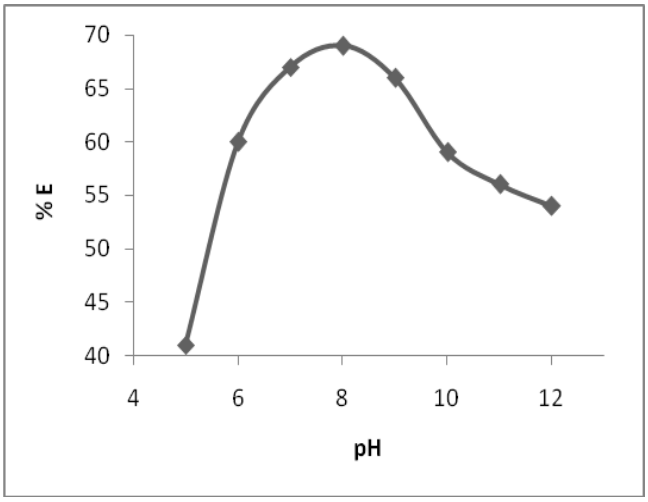




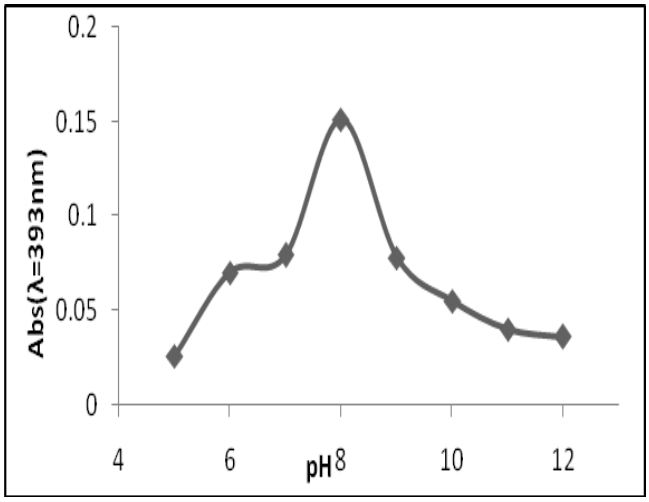
Fig(1)Calibration curve of Pb(II) with Pb(II) with BTABP in $CHCl_3$



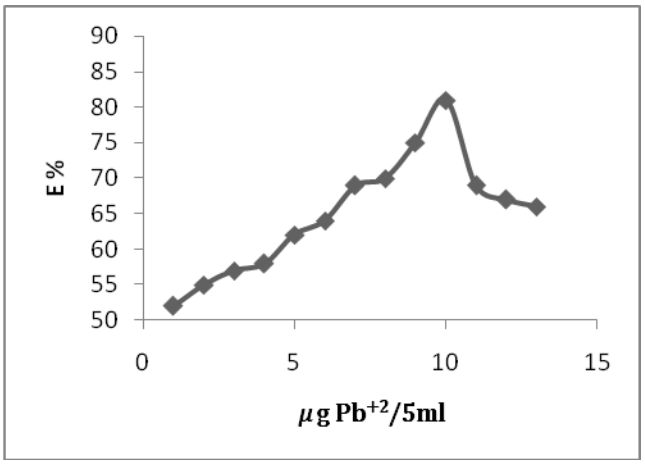
Fig(2) Calibration curve of Dithizon



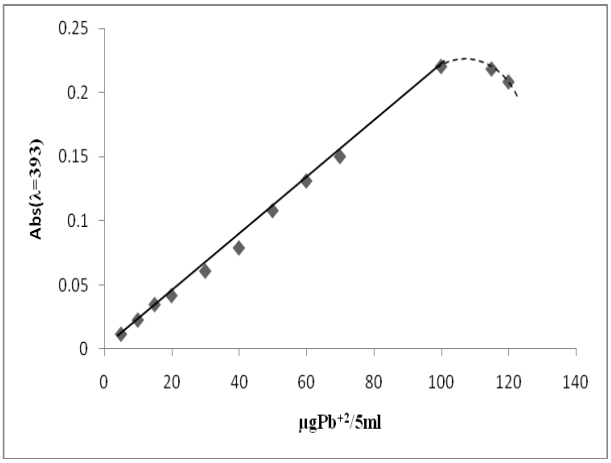
Fig(3) Effect of pH on the percentage formation in of extraction



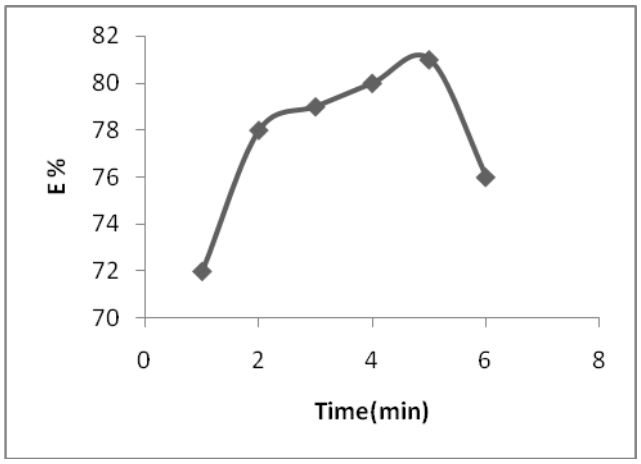
Fig(4) Effect of pH on complex the organic phase



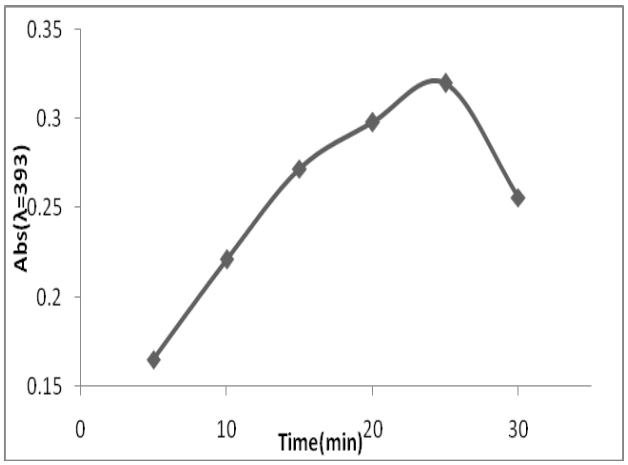
Fig(5) Effect of metal ion concentration of %E



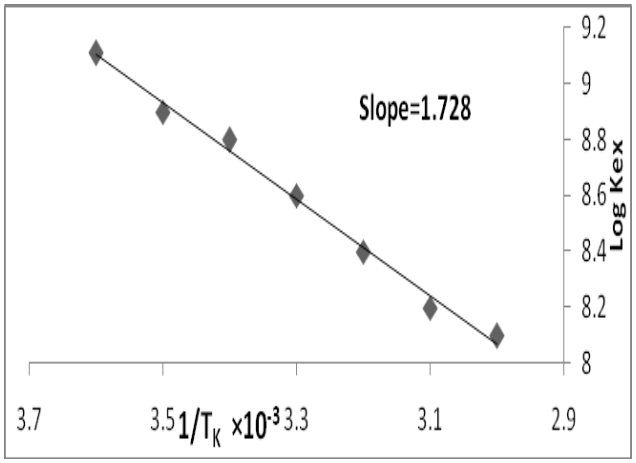
Fig(6)Effect of metal ion concentration on complex formatio in the organic phase



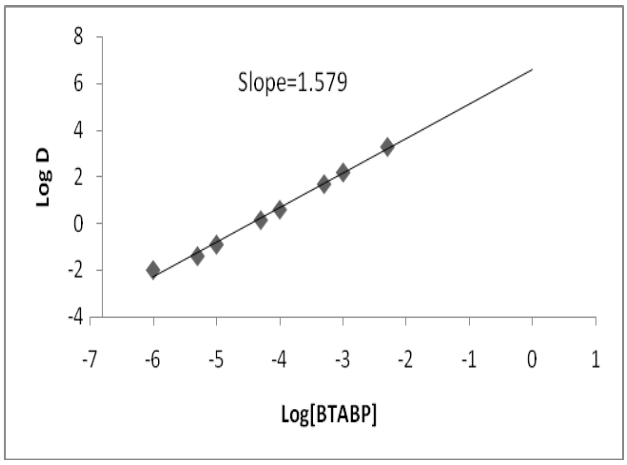
Fig(7) Effect of shaking time on the E %



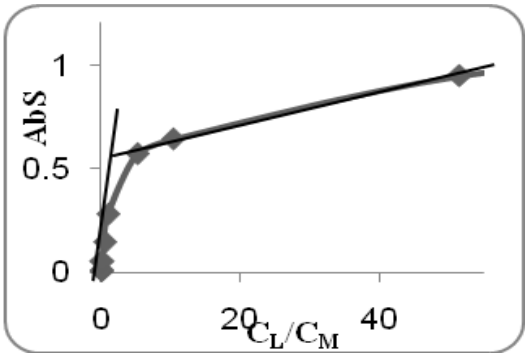
Fig(8)Effect of shaking time complex on formation in the organic phase



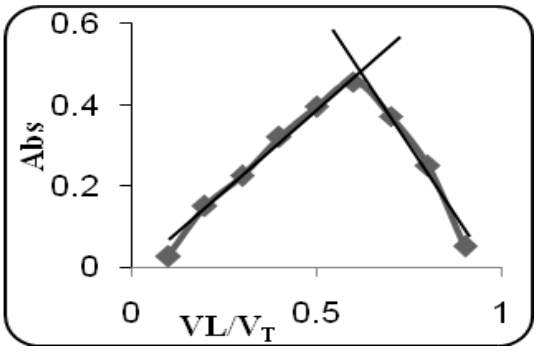
Fig(9) Temperature effect on extraction



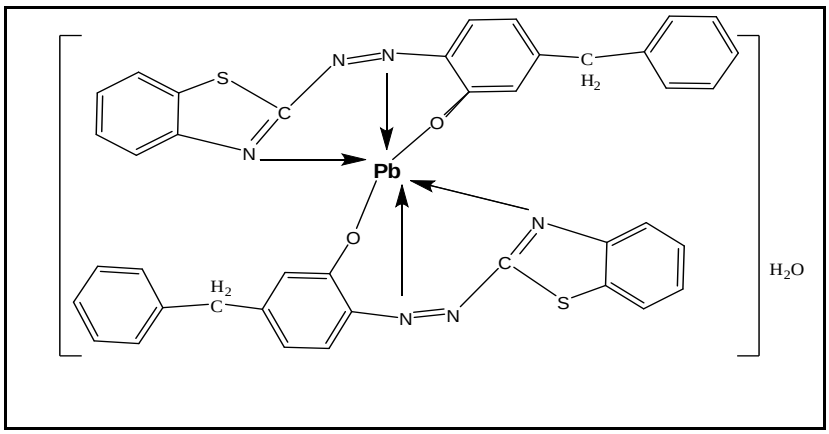
Fig(10) The slope analysis method constant K_{ex}



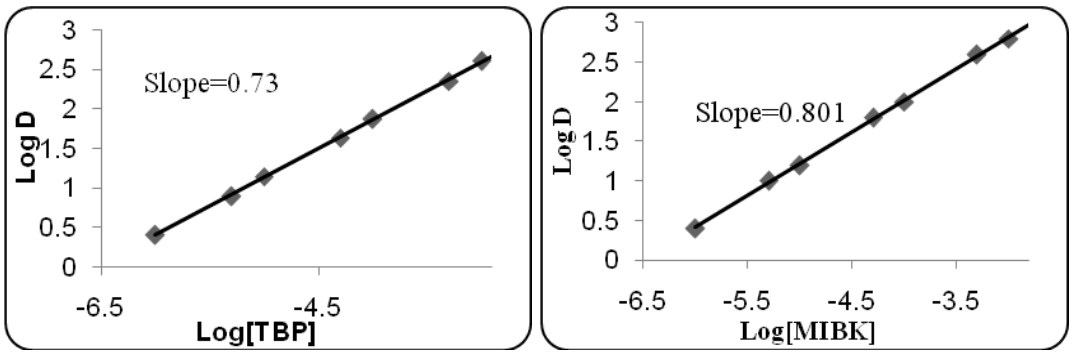
Fig(11)Mole ration method



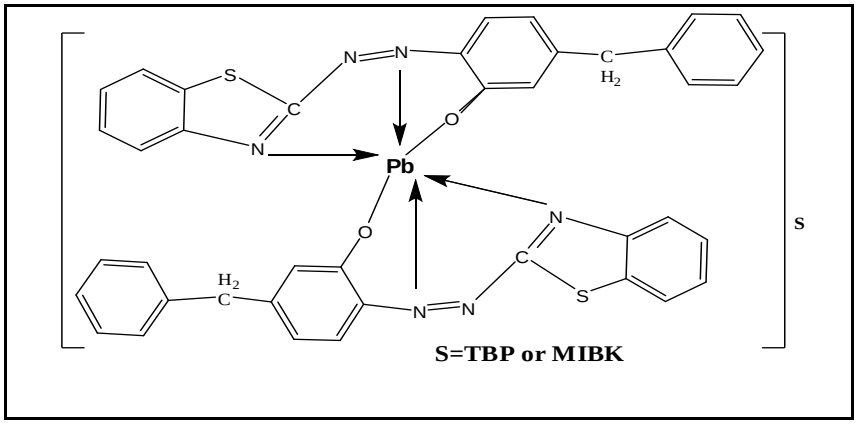
Fig(12) Continuous variation method



Fig(13)The suggested structure of complex[$Pb^{+2}(BTABP^{-})_2$]



Fig(14) Synergism effect for TBP & MIBK on distribution ratio (D)



Fig(15) Structure of complex[$Pb^{+2}(BTABP^{-})_2$] with occupied of TBP or MIBK

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التقدير الطيفي للكميات المايكروية للرصاص(II) في النماذج البيئية والحياتية باستعمال 2-[بنزو ثايوزوليل ازو]-4-بنزايل فينول

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الخلاصة:-

استعمل 2-[بنزو ثايوزوليل ازو]-4-بنزين فينول ككاشف عضوي لتكوين معقد مع الرصاص (II) له امتصاصيةعظمى عند الطول الموجي (λ=393) وامتصاصية مولية ε=2121 L $mol^{-1}cm^{-1}$،وقد درست الظروف المثلى لتفاعل التعقيد وقد كانت PH=9 وزمن الرج 25دقيقة ،اما دراسة تركيب المعقد اوضحت ان للمعقد الصيغة التركيبية هي$[Pb^{+2}(BTABP^{-})_2]$ (metal:ligand)1:2كذلك فقد اوضحت النتائج ان تفاعل التعقيد هو تفاعل ماص للحرارة مع عدم وجود أي تاثير لقطبية المذيب على عملية الاستخلاص ولكن وجد ان هناك تاثير لتركيب المذيب العضوي.كما انه قد استخدم الكاشف العضوي ككاشف تقدير طيفي للرصاص (II) في نماذج للنباتات والتربة والماء في مواقع مختلفة في محافظة النجف وكانت المعالجة الاحصائية للنتائج اظهرت RSD%=1.2، $DL=3.492\times10^{-6}$ وحساسية ساندل $S=9.77\times10^{-7}$mg cm^{-2}.