Optimization of a new cloud point extraction procedure for the determination of trace amounts of total Barium (II) in some environmental samples by turbidimetric

الاستفادة المثلى من الإجراء الجديد استخراج نقطة السحابة لتحديد كميات ضئيلة من مجموع الباريوم في بعض العينات البيئية من خلال قياس التعكرية

Shamaa Ibrahem sead
Chemistry department-College of Science-University of kerbala-kerbala-Iraq
-alzafaaranysh@gmail.com

Abstract:

A new, simple, and rapid cloud point extraction (CPE) procedure system, combined with turbidity was created for particular partition, preconcentration, and determination of follow measures of aggregate barium in some ecological specimens. The methodology depends on the complexation of Ba(II) particles with chlorazol clear reagent within the sight of SDS as a non-ionic surfactant. The ideal conditions for the CPE of Ba(II) particles were explored as for a few trial parameters, for example, order addition , pH of the solution, SDS and chlorazol blank concentrations, incubation time and temperature, and effect of intervirrnses and time .

The detection limit for Ba(II) ions taking into account the 8 times the standard deviation of the blanks (N:8) was found to 0.004554µg mL^{-1}, while the relative standard deviation (RSD) was 0.041514 . The proposed strategy was broke down for soil and water tests, which assembled from Environment Iraq , as guaranteed reference materials , were utilized, and spike tests were connected to accept the technique. The technique was connected to some genuine ecological examples to assess their aggregate barium levels. With respect to accomplished information, water and soil of contextual analysis is dirtied

Key word: Barium , SDS (Sodium dodecyl sulfate) , Turbidity , CPE (Cloud point extraction)

الخلاصة :

الاستخلاص بنقطة الغيمة (CPE) هو نظام جديد يمتاز بسرعة والبساطة وقد طورة جانبا الى جانب مع قياسات التعكرية لتقدير وانتقائية كميات ضئيلة من تركيز الباريوم الكلي في بعض العينات البيئية. ويستند هذا الاجراء على تعقيد ايون الباريوم الثنائي مع كاشف كلوروزول وبوجود SDS باعتباره غير الأيونية .

وحددت الظروف المثلى لتكوين معقد من الباريوم الثنائي مع الكلوروزول وبوجود SDS حيث تضمنة دراسة اضافة التعاقب للمكونات ,تركيز الكاشف المستخدم ,تركيز SDS والدالة الحامضية للمحلول , درجة الحرارة , زمن الاحتضان , مدة استقرارية المعقد المتكون وتأثير الايونات المتداخلة وبعض المعالجات الاحصائية .

كما اوجد منحني المعايرة واستخدمه مع الانحراف المعياري للمحلول المرجع و 8 مرات (N: 8) في اجاد حد الكشف عن الباريوم الثنائي ضمن هذه الطريقة والذي يساوي (0.004554 ملغرام /لتر) في حين كان الانحراف المعياري النسبي (RSD) للمنحني المعايرة لهذه الطريقة يساوي 0.041514 . بعد تحديد الظروف الفضلى طبقة الطريقة المقترحة في تقدير مجمل مستويات الباريوم في بعض العينات البيئية الحقيقية حيث شملت العينات ثلاثة عينات من المياه وثلاث عينات من التربة التي تم جمعها من البيئة العراق لمحافظة كربلاء . أجريت مقارنة بواسطة المعالجة بتحليل المتغيرات بطرق الاحصائية عند حدود ثقة 95 % بين الطريقة المستحدثة والطريقة التقليدية الطيفية لتقدير ايون الباريوم وعلى هذا الاساس بالإمكان قبول الطريقة الجديدة كطريقة تحليلية بديلة

مفتاح الكلمات :ايون البزموث , الصوديوم دوديسيل كبريتات , التعكرية , الاستخلاص بنقطة الغيمة

1.Introduction

Barium is a delicate, brilliant white metal, with a slight brilliant shade when ultrapure (1) The shimmering white shade of barium metal quickly vanishes upon oxidation in air yielding a dim oxide layer. Barium has a medium particular weight and great electrical conductivity .Barium is artificially like magnesium, calcium, and strontium, being much more receptive. It generally shows the oxidation condition of +2(1). Responses with chalcogensare profoundly exothermic (discharge vitality); the response with oxygen or air happens at room temperature, and in this manner barium is put away under oil or idle gas atmosphere. The plenitude of barium is 0.0425% in the World's crust and 13 µg/L in ocean water. The primary business wellspring of barium is barite (additionally called barites or overwhelming fight), whichis a barium sulfate mineral (1) . In view of the high reactivity of the metal, toxicological data are accessible just for compounds (2) .

Water-solvent barium mixes are harmful. At low dosages, barium particles go about as a muscle stimulant, while higher measurements influence the sensory system, bringing on cardiovascular abnormalities , tremors, shortcoming, nervousness, dyspnea and loss of motion. This may be because of the capacity of Ba2+ to square potassium ion channels, which are basic to the best possible capacity of the nervous system(3) . Barium is not carcinogenic , and it doesn't bioaccumulate. (4 , 5)

In any case, breathed in dust containing insoluble barium mixes can aggregate inthe lungs, bringing about a kindhearted condition called baritosis.(6) .For correlation with the solvent toxic substances, the insoluble sulfate is nontoxic and is subsequently not named a dangerous good (1) .

Ba has not been accounted for as a crucial follow component for plants, and it was incorporated into a rundown of components that represent a danger to human wellbeing and are most usually found in instances of soil defilement (11) . Ba retention by plant species developed in contaminated territories has been seen by Abreu et al. (12) . That Ba substance of 200 mg/kg could be modestly lethal and that 500 mg/kg could be viewed as dangerous for plants (13) . Along these lines, there is expanding concern with respect to Ba in plants, particularly in eatable plants, since Ba can bring about inconvenience or harm in the human body. The ingestion of Ba can bring about a few human wellbeing issues: strong loss of motion, gastrointestinal unsettling influences, heart harm, hypertension, and, at times, even passing (14, 15) . Along these lines, the observing of Ba aggregation in soil and plants merits consideration in neighborhood and global ecological enactment.

The instrument of barium poisonous quality is identified with its capacity to substitute for calcium. Danger results from incitement of smooth muscles of the gastrointestinal tract, the cardiovascular muscle, and the deliberate muscles, bringing about loss of motion (7) . Harmfulness can likewise come about because of barium going about as a physiological rival to potassium particles, which have a comparable viable ionic sweep. Hypokalemia is connected with the capacity of barium particles to square potassium channels (8) . The deliberate or unintentional ingestion of dissolvable barium mixes can bring about intense barium poisonous quality. Systemic impacts of barium lethality incorporate stomach torment, sickness, regurgitating and looseness of the bowels, hypertension, cardiovascular arrhythmias, muscle loss of motion and demise. (9 ,10) . Hypokalemia is a key component of barium danger (8).

2. Experimental :

2 – 1 - Apparatus

turbidity measurements were carried out on a lovibond Turbidiract Germeny BP 3001 TRANS . A Jenway 3305 pH meter was used for pH measurements. UV-Vis absorbance spectra were recorded on a Shimadzu 1800 UV-Vis spectrophotometer using 1cm quartz cells.

2 -2 - Reagent and standard solutions

All chemicals were used of analytical-reagent grade while distilled water was used to prepare the Solutions . A Stock solutions of barium (1000ppm) From ($BaCl_2.9H_2O$) was set up by dissolving 0.2696 g in 100 ml distilled water (1). A stock solution (0.001 $mol.L^{-1}$) of Chlorazol Black was set up by dissolving 0.0781 g in 100 ml of distilled water. A Stock solutions of SDS (4%w/v) were set up by dissolving 4 g in 100 mL distilled water (2). The acid solution was prepared by A 1 $mol.L^{-1}$of hydrochloric acid solution (35% , 1.19 $g.ml^{-1}$) were set up by transferring 8.5 mL of concentrated hydrochloric acid and finished of the volume with distilled water in 100 mL volumetric carafe and 0.1M Sodium hydroxide was set up by dissolving 0.4 g in 100 ml distilled water . Exact pH of the solution was measured using a pH meter. All other chemical obtained from different company with high purity.

2-3- Recommended procedure of CPE :

For the cloud point extraction, 10mL aqueous solution containing Ba(II) ion 25 µg . mL^{-1}, 0.1 mL of 1.0×10^{-3} Chlorazol Black solution and 0.5 mL of 4.0% (w/v) SDS solution and the volume of solution was finished to 10 mL by distilled water .The extraction was carried out at room temperature and the solution was transferred into a cell to turbidimeter to measure its turbidity .

2-4- Preparation of real samples

2-4-1 - Water samples :

The water tests were separated at first through filter paper to isolate the coarse particles and suspended matter and keep in a refrigerator in a dark bottle. 10 ml water test was used to the CPE methodology as described above

2- 4 -2 - Soil samples :

Precisely weighed 1.0 g of soil tests and desiccated at 100 °C were put in to a 250-ml beaker and 10 ml concentrated nitric corrosive was added to it. The blend was gradually warmed under a hood till drying. After complete drying and cooling to room temperature, a second 10-ml part of concentrated nitric corrosive was included and the strategy was rehashed. At that point 10 ml concentrated hydrochloric corrosive was added to the container and the blend was gradually warmed until complete drying. Subsequent to cooling, the deposit was disintegrated in 10 ml of 1 M HCl and the arrangement was then sifted. The example was killed by appropriate measures of a 1 M NaOH arrangement lastly arranged by purposed method

3. Result and discussion

3-1- Optimization of the CPE procedure :

In order to attain maximum extraction efficiency by CPE method, several parameters lead a substantial role in the performance and collecting of the surfactant system. The most important are: Order addition, pH of the solution, ligand concentration, SDS concentration, effects of equilibrium ration temperature and time and effect of the interfering ions.

3 –1 -1 -Effect of order addition :

The orders of addition of solution are examined and the results are shown in Table (1) .

Table(1) : Effect of order addition [Conditions: 25mgL^{-1}metal ion; 0.05 mmol L^{-1} of reaguent ; 0.2% w/v SDS]

No. of Solution	Order addition	Turbidity /NTU
I	M+L+S	190
II	L+S+M	186
III	L+M+S	177
IV	L+S+M	171
V	S+M+L	179
VI	S+L+M	177

*Barium(M) , SDS(S) , Chlorazol Black reagent(L)

From the results above, order (I) has been used for a subsequent experiment, due to the highest sensitivity.

3 -1 -2- Effect of chlorazol black concentration :

The effect of concentration of Chlorazol Black on the CPE in determination the Ba(II) was investigated in the concentration range of (0.005- 0.07) mmol L^{-1}. Table 2 summarizes the results obtained and figure 1 shows that 0.01 mmol.L^{-1} of Chlorazol Black is the optimum concentration. As it is seen for the turbidity of complex, the signal increases up to a known concentration of chlorazol black, reaching a plateau, which is considered as the top determination to ion .

Table.2- Shows that the measured turbidity with the concentration of reaguent Conditions : Ba (II) = 25 µg mL^{-1} , 0.5 ml of0.2% w/v SDS]

Concetration of ligaind mmol.L^{-1}	Turbidity measurement (n=3)	RSD%	Confidence interval at(95%) $\bar{y} \pm t_{0.05/2}\,\sigma_{n-1}/\sqrt{n}$ (n=3)(NTU)
0.005	181.33	0.84	181.33±3.79
0.01	226.00	0.44	226.00±2.48
0.02	220.67	0.26	220.67±1.43
0.03	204.67	0.75	204.67±3.79
0.05	191.00	0.52	191.00±2.48
0.06	180.00	0.56	180.00±2.48
0.07	173.00	0.58	173.00±2.48

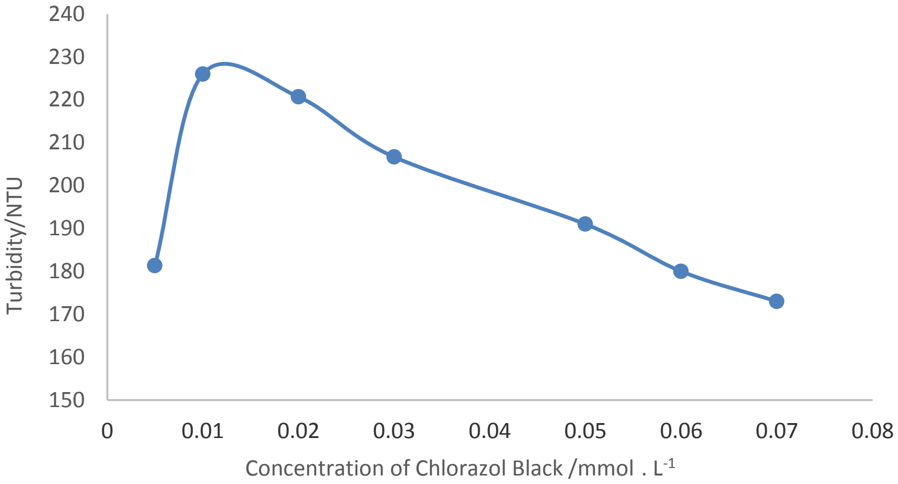
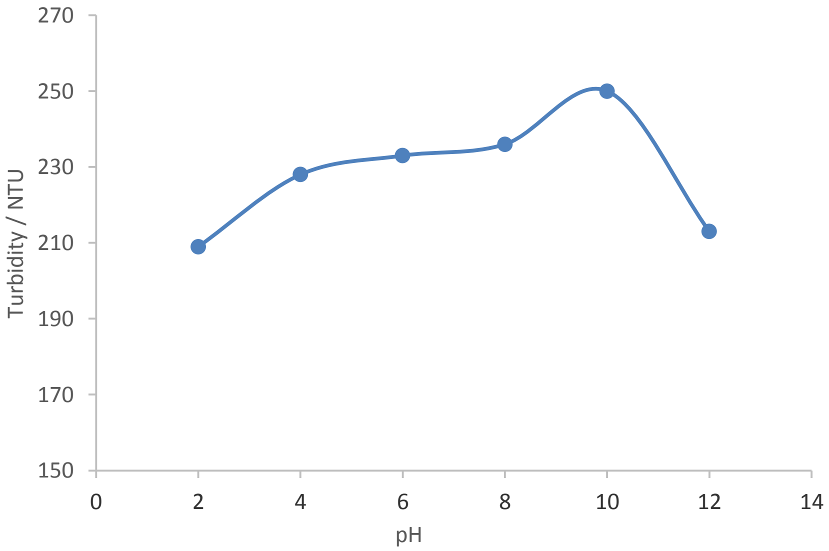


Figure .1 : Effect of concentration of Chlorazol Black on the measurement of turbidity for the determination of Ba(II).

3-1-3- Effect of pH :

The development of metallic complex and its synthetic strength are the two critical components required in the partition and determination of metal particles by cloud point extraction (CPE). They have to exhibit adequate hydrophobicity to be separated into the little volume of the surfactant-rich stage. The pH assumes a basic part on metallic complex development and consequent extraction and has been a huge parameter for CPE. Along these lines, extraction yield relies on upon the pH at which complex arrangement is researched. An arrangement of comparable tests was completed in the pH scope of 2.0–12.0 by utilizing diverse pH arrangements (1N HCl and 0.1M NaOH). As appeared in Figure 2 that the turbidity initially expanded strongly with expanding pH and achieved a greatest at pH 10.6 demonstrating extraction proficiency was accomplished .

The turbidity was diminished in light of halfway separation of the edifices at higher pH, which may bring about a fragmented extraction of complex.Therefore, pH 10.6was picked as the ideal working pH for complete arrangement of Ba(II)- Chlorazol Black complex and thus a decent extractability



.

Figure 2.: Effect of pH on the formation of Chlorazol Black - Ba(II) complex.[Conditions : Ba (II) = 25 µg mL^{-1} ,of 0.1 ml of Chlorazol Black= 1 x 10^{-3}M , 0.5 mL of 4 % (w/v) SDS]

3-1-4-Effect of SDS concentration :

The grouping of surfactant utilized as a part of the CPE is an imperative element. SDS was picked in view of its business accessibility in a high-decontaminated homogeneous structure, low cloud point temperature, low toxicological properties and expense. Likewise, the high thickness of the surfactant-rich stage encourages stage. The impact of surfactant fixation on the determination of Ba (II) was analyzed inside the SDS focus range from to % (W/V) . Table.3 and fig. 3 demonstrates that the deliberate turbidity increments with increasing concentration of the surfactant, and then decreases when the surfactant concentration is more than 0.20% (W/V) SDS . Therefore was used achieve the highest determination efficiency .

Table.3: Shows that the measured turbidity with the concentration of the surfactant [Conditions : Ba (II) = 25 µg mL^{-1} , 0.1 ml of 1 x 10-3M Chlorazol Black]

Concetration of SDS%	Turbidity measurement (n=3)	RSD%	Confidence interval at(95%) $\bar{y} \pm t_{0.05/2}\,\sigma_{n-1}/\sqrt{n}$ (n=3)(NTU)
0.04%	210.00	0.48	±2.48210.00
0.08%	207.67	0.74	207.67±3.79
0.12%	201.67	0.57	201.67±2.87
0.20%	225.00	0.44	225.00±2.48
0.24%	192.67	0.60	192.67±2.87 .
0.28%	181.00	0.55	2.48181.00±

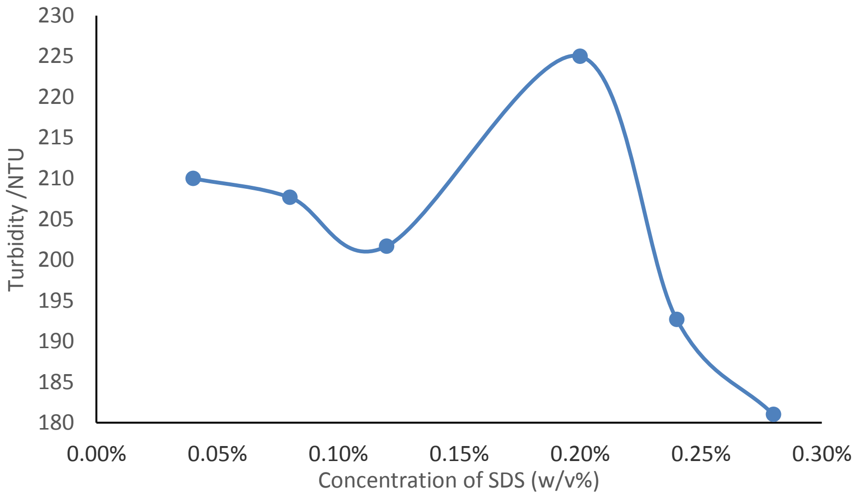


Fig. 3 : Shows the measured turbidity with the concentration of the surfactant [Conditions : Ba (II) = 25 µg mL^{-1} ,of 0.1 ml of Chlorazol Black= 1 x 10^{-3}M]

3-1-5-Effects of equilibrium ration temperature and time:

It was alluring to use the most constrained equilibration time and the minimum possible equilibration temperature, as an exchange off between completing of extraction and capable separation of stages. Thusly, the effect of equilibration temperature in the extent of 25-95°C was analyzed. It was found that 50°C is agreeable and sufficient to achieve complete extraction and determination of Ba(II). The dependence of extraction adequacy upon equilibration time was in like manner focused on for a period break of 5-45 min. An equilibration time of 20 min was picked as a perfect quality. The effect of temperature and time on the extraction and determination of Ba(II) by turbidity methodology is showed up in figures (4,5).

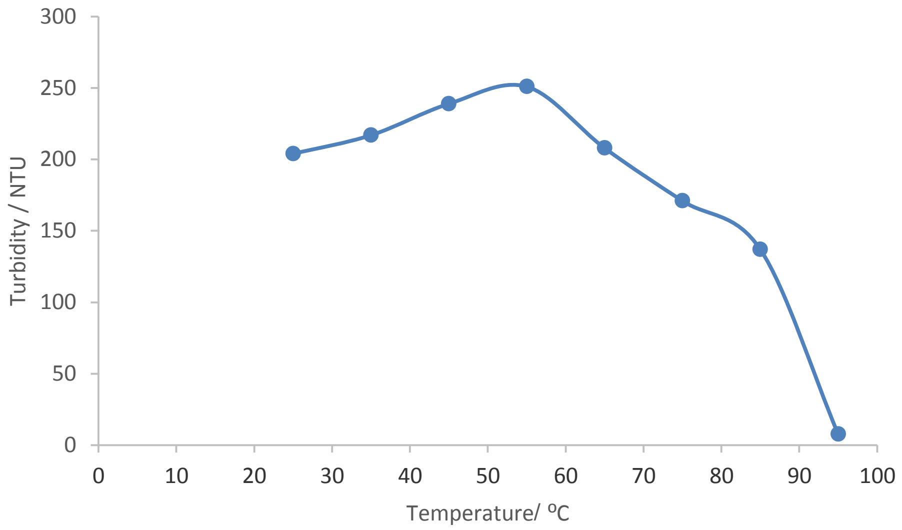


Fig. 4 Shows the measured turbidity with the temperature [Conditions : Ba (II) = 25 µg mL^{-1} ,of 0.1 ml of Chlorazol Black= 1 x 10^{-3}M , 0.5 ml of 4% (w/v) SDS]**.**

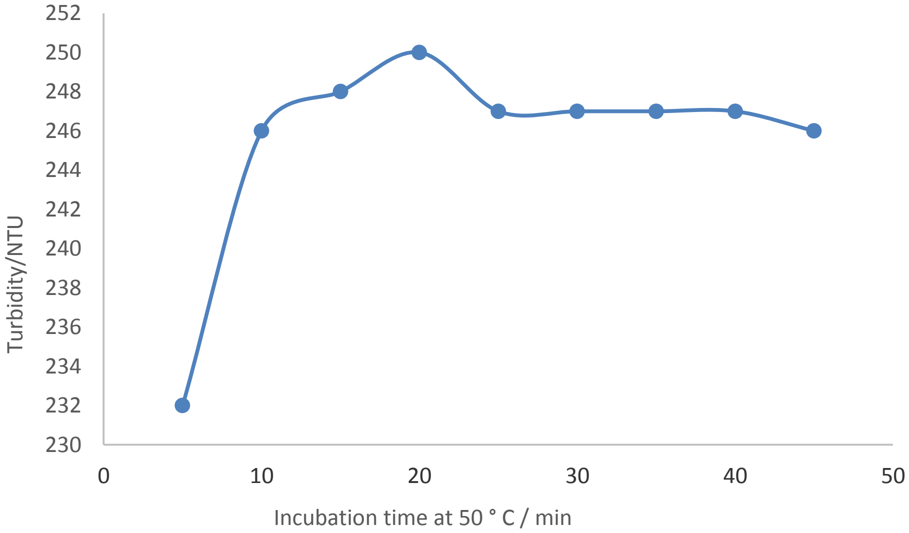


Fig. 5 : Shows that the measured turbidity with the equilibration time[Conditions : Ba (II) = 25 µg mL^{-1} ,of 0.1 ml of Chlorazol Black= 1 x 10^{-3}M , 0.5 ml of 4% (w/v) SDS, at 55° C].

The stability of the complex that study by measuring with time leaving as illustrated in Figure. 6, it is show that the stability of the complex for long time.

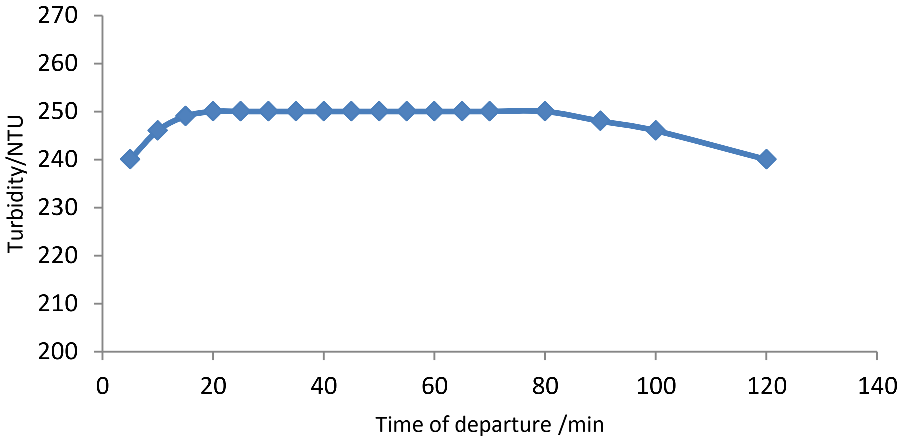


Figure . 6: Effect of time of leaving after heating on the measurement of attenuation of incident light [Conditions : Ba (II) = 25 µg mL^{-1} ,of 0.1 ml of Chlorazol Black= 1 x 10^{-3}M , 0.5 ml of 4% (w/v) SDS, at 55° C].

3-1-6-Effect of the interfering ions :

The efficiency of the suggested method in the extraction and determination of the barium ion in the presence of anions different cations and anions was examined by using a solution containing $25mgL^{-1}$ of Ba with addition of same concentrations of potential interferences . It is concurred that an incidental particle esteemed to meddle genuinely when it gives a relative blunder percent of more than ± 5%. It was demonstrated that all the monovalent cations (M^{+}) have no consequences for investigative reaction or percent recuperation , however divalent cations (M^{2+}) have surpassed the permissible furthest reaches of obstructions on value turbidity barium except Fe(II) and Ca(II) does not appear affect the value of barium turbidity , while the anions does not appear affect except SO_4^{2-} ,shown in Table 4.

Table 4 :. Effect of divers ions on the turbidity value of Ba(II) ($25mg.L^{-1}$ an 250.00 turbidity unit at 55 °C) by CPE turbidimetry

Interferances	Turbidity measurement (n=3)	RSD%	Confidence interval at(95%) $\bar{y} \pm t_{0.05/2}\, \sigma_{n-1}/\sqrt{n}$ (n=3)(NTU)	Eerre%
Mg^{2+}	201.67	0.29	201.67±1.44	19.33%
Fe^{2+}	248.67	0.61	248.67±3.80	0.53%
Sr^{2+}	226.33	0.26	226.33±1.44	9.47%
Cd^{2+}	212.33	0.27	212.33±1.44	15.07%
Hg^{2+}	210.00	0.48	210.00±2.49	16.00%
Ca^{2+}	244.67	0.24	244.67±1.44	2.13%
K^{1+}	249.00	0.00	249.00±0.00	0.40%
Na^{1-}	252.00	0.40	252.00±2.49	-0.80%
$NO_3^{\ 1-}$	247.67	0.23	247.67±1.44	0.93%
SO_4^{2-}	232.33	0.25	232.33±1.44	7.07%
$S_2O_3^{\ 2-}$	249.00	0.40	249.00±2.49	0.40%

3-2- Characteristics of the Method

A calibration curve of turbidity versus concentration was was built by gathering the systematic signs of various volumes of Ba(II) standard arrangements submitted to the strategy proposed. Under the ideal trial conditions , the calibration curve for Ba(II) ion is linear from 0.5 to 30.0 μg/mL with a relationship coefficient (R^2) of 0.9976. Table 5 gives the parameters of the calibration curve, the relative standard deviation acquired subjected to the complete system and the detection limit. The detection limit for Ba(II) ions based on the 8 times the standard deviation of the blanks (N:8) characterized as 3Sb/m (where Sb is the standard deviation of the blank and m is the slope of the calibration curve) is 0.004554μg mL^{-1} (3σ).

Table 5: show the parameters of the calibration curve

Parameter	Value
RSD	0.041514
Accuracy	100.4664± 4.170791
Slope (k = Turbidity Coefficient)	9.806
Intercept	0.3188
Correlation coefficient (R^2)	0.9976
Range of concentration	0.5 -30 μg.ml^{-1}
SD of intercept	2.622
LOD3.3 (SD of intercept / Slope)	8.2855
LOQ (10 ×SD of intercept / Slope)	2.7883
t_{cal}	8.4494 57.665>>> **t_{tab} at 95%** (2.365)

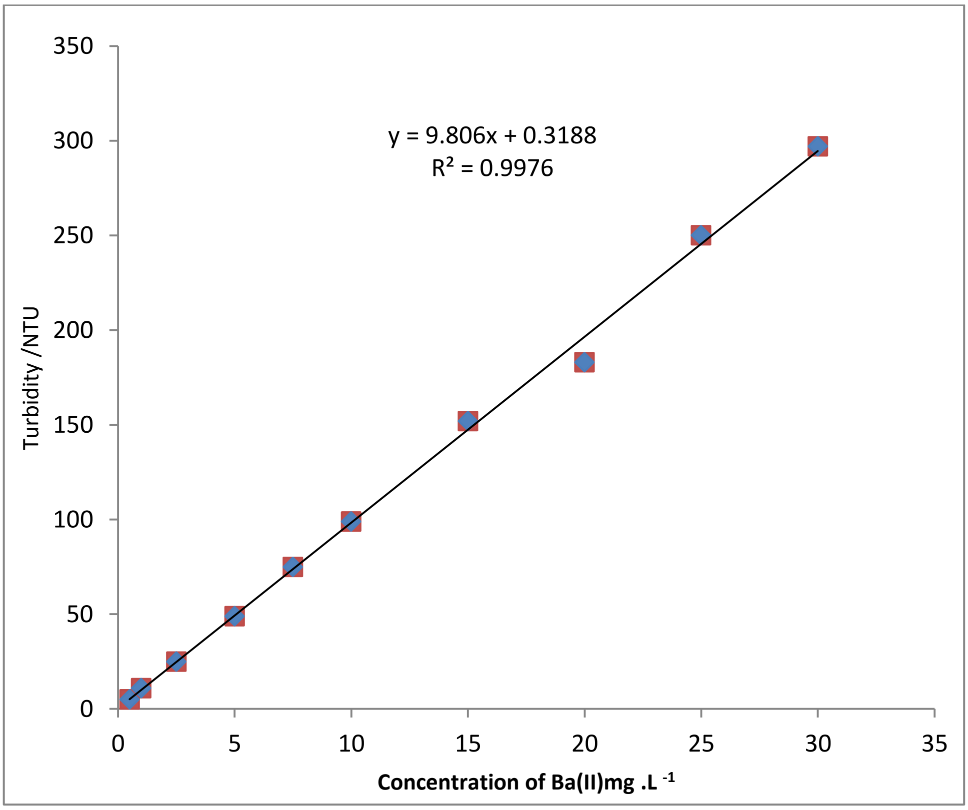


Fig.7: Calibration graph for the variation of Ba(II I) ion concentration on NTU by linear equation using turbidity instrument.

3-3-Repeatability :

The estimation of the relative standard deviation (RSD%) for Ba (II) 0.05mg.L-1 was classified in Table.6. The rate relative standard deviation under 1 % was acquired demonstrating a dependable estimation can be accomplished utilizing this technique .

Table.6: Repeatability of Ba (II) at optimum parameters.

[Ba] µg.mL^{-1}	Average response n*=8	RSD %	Confidence interval at 95% $\bar{y}i \pm t_{0.05/2,n-1}\ \sigma_{n-1}/\sqrt{n}$
0.5	5.02	0.67%	5.02±0.03
25	250.25	0.28%	250.25±0.59

n* =Number of repeated measure , $t_{0.05/2,7}$= 2.365

3-4- Application :

Two techniques were utilized to the determination of barium ion in an arbitrary river and soil tests from Karblaa suberb. The techniques were firstly utilizing Turbidimetric (new) strategy while the second strategy was to utilized the traditional estimation for Spectro strategy. Table .7 demonstrates the synopsis of results from the six specimens in water and soil tests and the two-path investigation of change to test the impacts of the two techniques utilized for examination and the sort of water and soil tests supplied from various land locations .

Table . Results for determination of Ba(II) in genuine example by two strategy and the two-route examination of difference.

Type of methods	Concentration of Ba/ppm					
	Hosseinieh River	Indian River	Maqam River	Hosseinieh Soil	Indian Soil	Maqam Soil
Turbidimetric method (new)	0.7906	0.6717	0.7397	0.7382	0.6517	0.8737
Spectro method$^{(26)}$	0.8200	0.6400	0.7600	0.7400	0.6600	0.8600
Sum	1.6106	1.3117	1.4997	1.4782	1.3117	1.7337
$\bar{X}_{i\ Avarage}$ mean of Sum	0.8053	0.65585	0.74985	0.7391	0.65585	0.86685
$\bar{X}_{Avarage}$ Grand Value	0.745467					
V_B	0.034436					
V_{within}	0.001271					
Total variation	0.070143					
F- test	6.5024<<4.3874					

4- Conclusions :

Cloud point extraction was utilized toward the preconcentration of baruim in various examples. The strategy, which depends on the cloud point extraction of the complex of barium with chlorazol dark , permits the determination of baruim as low a0.5 µg.ml - 1 The proposed technique requires cheap instrumentation and offers great selectivity, exactness and accuracy that can be connected to the determination of bismuth in genuine specimens. The surfactant has been utilized for preconcentration of barium as a part of tests, and in this manner lethal dissolvable extraction, has been maintained a strategic distance from.

.

5- References :

1- R. Kresse , U. Baudis, P.Jäger , H. Riechers , H. Wagner, J. Winkler and H.Wolf, “Barium and BariumCompounds”. In Ullman, Franz. Ullmann’s Encyclopedia of Industrial Chemistry. WileyVCH(2007)03_325.pub2.

2- F. Baldi, M. Pepi, D. Burrini, G. Kniewald, D. Scali and E. Lanciotti, Dissolution of barium from barite in sewage sludge and cultures of Desulfovibrio desulfuricans,Appl. Environ. Microbiol. 62 (1996) 2398–2404.

3- J.A. Ippolito and K.A. Barbarick, Biosolids affect soil barium in a dryland wheat agroecosystem, J. Environ. Qual. 35 (2006) pp2333–2341.

4- H. Choudhury and R. Carey, Barium and barium compounds, in: ConciseInt. Chem. Assessment Doc. 33. Int. Progr.Chem. Safety, World Health Organ., Geneva, 2009.

5- CETESB, Environmental Agency of the State of Sao Paulo, Report establishment of guiding values for soils and groundwater of the State of Sao Paulo, São Paulo,Brazil, 2001.

6- T. A. Nogueira , W. J. Melo, I. M. Fonseca ,M. O. Marquesb, Z. He . Journal of Hazardous Materials .181 (2010) 1148–1157 .

7- A. K . Pendias and A.B. Mukherjee, Trace Elements from Soil to Human, Springer, Berlin, 2007.

8- CETESB, Environmental Agency of the State of Sao Paulo, 195-2005-E, November 23, 2005.

9- A.L. Reeves, Barium, in: L. Frrieberg, G.F. Nordberg, V. Vouk (Eds.), Handbook on the Toxicology of Metals, Elsevier Science Publishers Biomedical Press, Amsterdam, 1986, pp. 84–94.

10- S .Srbislav, R. Rudolf ,V. Ivana . I. Marina and M. Vojislava M. Matica Srpska J. Nat. Sci. Novi Sad ,No 129, 27—34,2015 .

11- O. Hemobayo and I.Kolade , Journal of Environmental Science and Technology 1 (1): 19-26, 2008.

12- R.B. Oliveira, L.C. Cunha, M.C. Valadares, M.J. Peres Filho, D.M. Araújo, Celobar accident: the experimental toxicology as a tool in establishing causation of mass drug intoxication, R. Eletrôn. Farmácia Suplemento 2 (2005) 140–142.

13- P.M. DiBello, J.L. Manganaro, and E.R. Aguinaldo. Barium compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology. 4th edition, vol. 3. John Wiley and Sons, New York, Chichester, Brisbane, Toronto and Singapore1991.. pp. 909-931.

14- M. Llugany, C. Poschenrieder, and L. Barcelo. Assessment of barium toxicity in bush beans. Archives of Environmental Contamination and Toxicology, v. 39, n. 4, 2000, p. 440-444.

15- S. Jourdan, M. Bertoni, P. Sergio, P. Michele and M. Rossi. Suicidal poisoning with barium chloride. Forensic Sci Int 119(2) : . (2001) 263-265.

16- M. Koch, O.Appoloni and V.Haufroid. Acute barium intoxication and hemodiafiltration. J Toxicol/Clin Toxicol. 2003;41: 363–367.

17- Z. Marczenko ,Spectrophotometric determination of elements , E. Horwood, 1986 pp 533-543 .