RESEARCH ARTICLE

Sensitive determination of Lead in Brine water by Cloud Point Extraction-Flame Atomic Absorption Spectrometry Method using Mixed Matrix modifying agents.

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Manuscript Info	*Abstract*
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A cloud point extraction (CPE) method was developed for the separation and preconcentration of trace amounts of lead is combined with flame atomic absorption spectrometry (FAAS) to determine trace amounts of lead in brine water. The method is depended on the formation of the hydrophobic complex between Pb(II) and (APDC) followed by its extraction into a Triton X-114 using surfactant. The parameters such as pH of sample, concentrations ofAPDC and Triton X-114, equilibrium temperature, and equilibrium time, which affect both complexation and extraction, are optimized. Under the selected optimum conditions, and use of matrix modifying agents enable us to develop the direct method for determination Pb in brine water. The accuracy of the method was % (96)while the detection limit was found to be (0.1122 ppm) for   preconcentration of 1.0 ml sample,for the determination of Pb(II) is obtained.

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Introduction:-

Inorganic lead arising from a number of industrial and mining sources occurs in water in the +2 oxidation state.[1].Short-term exposure to high levels of lead can cause vomiting, diarrhea, convulsions, Coma or even death. However, partial contact to even very small amounts of lead can be hazardous, especially to infants and young children. Therefore it is very significant to examine the trace levels of it in environments[2].Presently, the mostcommon analytical methods for the determination of trace amount of lead are the flame atomic absorption spectrometry (FAAS) [3]. The electrothermal atomic absorption spectrometry (ETAAS) [4]and the inductively coupled plasma emission spectrometry (ICP) [5]. Flame atomic absorption spectrometry is by far the most commonly employed technique for analyte determination[6].

 Principles of CPE have been mentioned in some interesting reviews [7]. Non-ionic surfactants in aqueous solutions have an affinity to form micelles and become turbid at a certain temperature, which is called "cloud point temperature." Exceeding the temperature, the micellar solution separates into two phases: a surfactant-rich phase of a small volume and a dilute aqueous phase [8].While metal ions react with a suitable ligand and form an aqueous low solubility complex, they can be extracted from the aqueous solution into the small-volume surfactant-rich phase. This method is an uncomplicated experimental process with, environmental safety, not expensive, high ability for preconcentration of broad variety of analytes, and high improvement factor with good recoveries [9]. In present of

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these advantages, cloud point extraction and name atomic absorption have been united together to determine a variety of metal ions in an environmental samples [10],[11].

Cloud point extraction and atomic absorption spectrometry have been effectively employed for a number of elements in different matrices and it is an interesting option when a complex matrix has to be analyzed [12], [13], [14]. Cloud point extraction CPE complex has become an important branch for the separation and preconcentration of trace metal ions [15],[16]. In this research work CPE combine with matrix modyfing agent enables to a simple sensitive, and accurate method for separation and preconcentration for the determination of Pb^{+2}ions in brine water and waste water using APDC as selective and sensitive complexing agents in basic media was established.

Material and Method:-

Reagents and solutions:-
All solutions were prepared with distilled water, analytical grade used in this study were obtained from international companies and used as received without more purification.The calibration curve for Pb^{+2} ions was established using standard solutions prepared at optimum conditions for each ion. $Pb(NO_3)_2$in purity 99.99% from (B.H.D), Triton-X-114 purity Analer from (B.H.D).

Apparatus:-
Shimadzu AA-630-12 Atomic Absorption /Flame Emision spectrophotometer (Japan) ,pH- meter Adwa AD 1030, Heraeus SEPATECH Labofuge 200 Centerfuge,Thermostatic water Bath.Model YCW-01 , Shaker model KA 500Kika-WERK, Electronic balance model AE ADAM, BWB Flame Emission Spectrophotometer.

Procedure:-
For the cloud point extraction, an aliquots 1 ml of a solution containing lead, are mixed with 0.6 ml of 1N HNO_3, 2 ml Triton X-114 1% (W/V) and 2.5ml of 200 ppmAPDC. The mixture were placed in a volumetric flask,the mixture (1:1) volume ratio of 2 ml Hydroznium sulphat:Amonium nitrite was add and the volume completed by DW,the total amount was transfer to centrifuge tube and heated in a thermostat water bath at 45°C for 20 min.

After heated, the resultant solution was subjected to centrifugation at 3500 rpm for 10 min for phase separation, and then cooled in an ice-water for 10 mint in order to increase the viscosity of the surfactant–rich phase. The supernatant aqueous phase was easily decanted by simple decantation. To decrease the viscosity of the surfactant phase and aspiration in flame, 0.5 ml of ethanol and 2 drops of 1N HNO_3 was added. And mixed well. The resultant solution was introduced into flame by conventional aspiration.

Applications:-
A real water sample from river, sea,waste water and discharge reverse osmosis plant has been used in this work.

Water samples:-
Water samples were collected from certain sampling area(southern shat al arab,Faw,Basrah wast water treatment and revers osmoses discharge water). They were filtered through Watman filter paper No. 42 and stored in a glass bottles at 4°C. Then the samples were ready for analysis.

Results and Discussion:-
For removal of matrix effect and to attain the best performance for the cloud point extraction procedure,the parameters such as pH of sample, concentrations of APDC and Triton X-114. Effects of the using of matrix modyfing dilution agent for the surfactant-rich phase equilibrium temperature, and equilibrium time, which affect both complexation and extraction, are optimized. Under the selected optimum conditions, the preconcentration of 1mL, for the determination of Pb^{+2} ions is obtained.

Effects of matrix modifying agent:-
Brine water with (Salinity 2.7-40%) is a complex matrix. Therefore, there is high matrix effect on the resonance line of Pb element at 217 nm. Therefore, the secondary line 283.1 nm was had been used Pb analysis. Additionally, a matrix modifying agent(hydozonium sulphate 1% M1and ammonium nitrate 1% M2) was used to overcome the interference. Absorbance of 0.5 ppm of lead was studied in the presence of 1 ml matrix (sample) and matrix modifying agents. The result shows the enhancement of lead signal absorbance. (Figure 1). Mixing modifying agents with different ratio was examined as shown in (Figure 2). Diluting by 1:1 mixing modifying agents was chosen for further works.
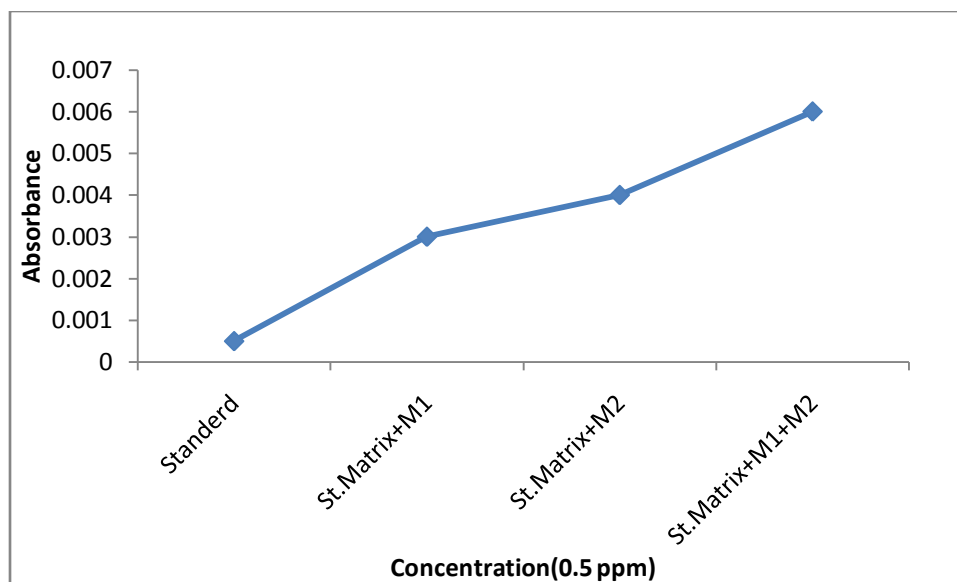
Figure 1 Effect of different modifying agents and mixed modifying agent on Pb atomic absorption signal.
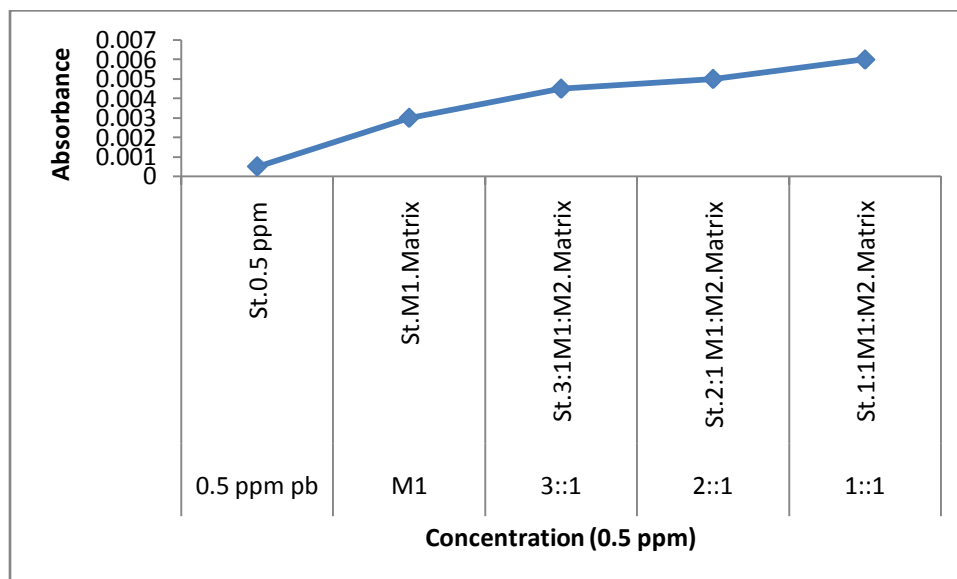

Figure 2 Effect of mixed modifiers of different proportions on the signal of 0.5 ppm Pb

Effect of pH:-

Optimization of pH plays an exclusive role on metal-chelate formation and subsequent extraction, and is proved to be a major parameter for CPE. The influences of pH of the aqueous solutions on yield the extraction of Pb (II) as APDC chelate was investigated in the pH range 1–5 using nitric acid and its found the rang of pH between (1.8-2.5) shows the enhancement of lead signal absorbance (Figure 3).
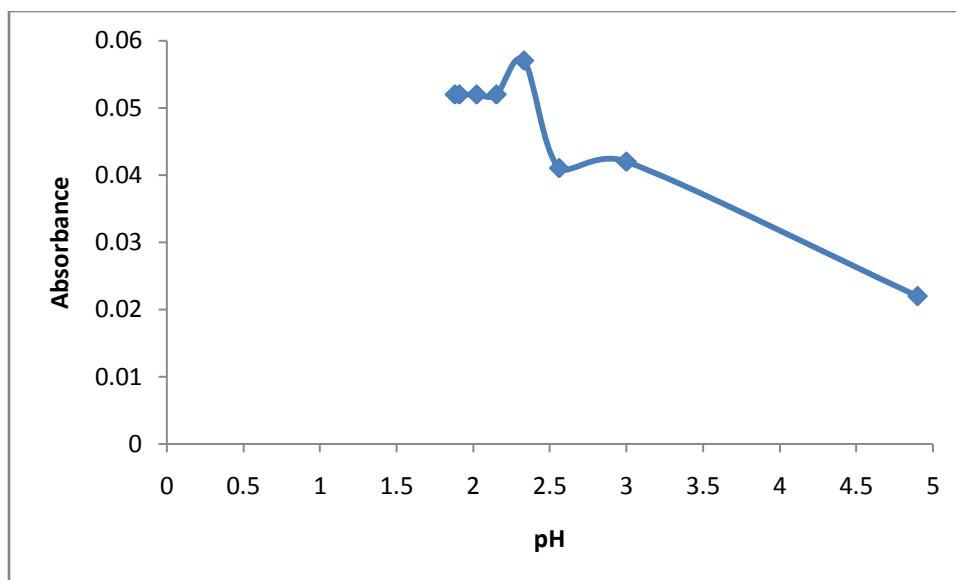
Figure 3 effect of pH variation on signal of 0.5 ppm Pb .

Effect of ligand Concentration

The effect of concentration of APDC on the analytical responses was consequently studied. Therefore, a set of similar experiments under the conditions of 20 ppm Pb(II) ion,1%(v/v)Triton X-114, at pH 2.5 and a different range of amounts of APDC was carried out (0-3)ml.It was observed that the absorbance increased by increasing the ligand volume. The sensitivity increases up to 2 ml of the amount of APDC which reaches a plateau. At this amount, a volume of 2 ml is selected as a suitable amount of APDC for the extraction process in order to make the extraction reaction complete (Figure 4).
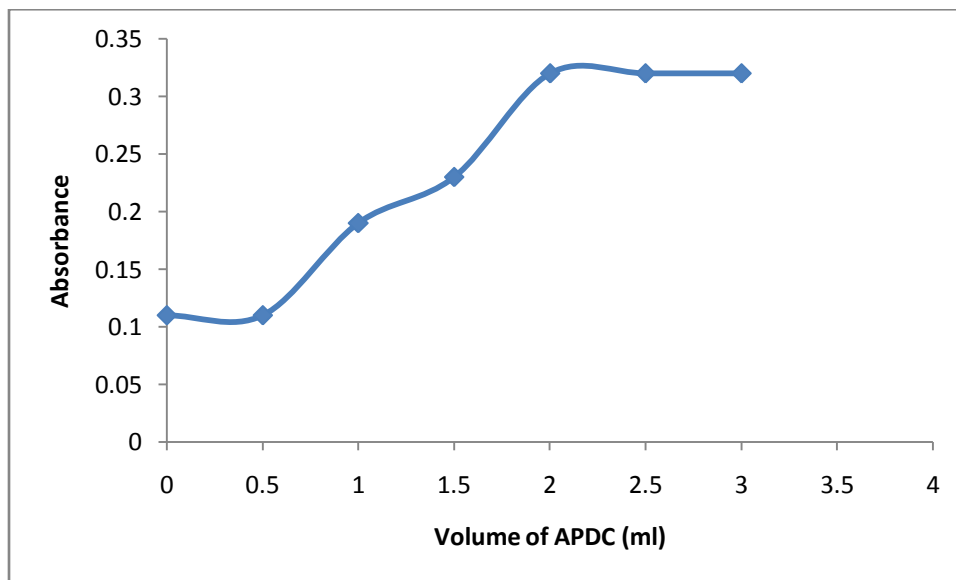

Figure 4 Effect of ligand concentrations on the atomic absorption signal of 20 ppm Pb.

Effect of surfactant concentrations:-

A good cloud point extraction should maximize the extraction efficiency by minimizing the phase volume ratio (Vorg/Vaq), as a result improving the concentration factor. Triton X-114 was select for the formation of the surfactant rich phase due to its low cloud point temperature and industrial availability in a high purified uniform form, low toxicity and low cost and high density of the surfactant rich phase, which simplifies phase separation by centrifugation. Figure 5 shows the effect of Triton X-114 concentrations on the APDC preconcentration of lead. The

signals of lead increased as the Triton X-114 concentration increased from 1% (V/V) Triton X-114 concentration was prepared (0.1-3) ml, the signals was increased by using 0.5 ml and the maximum absorbance in the range (0-2)ml. Hence a low signal was decreased over 2 ml from the surfactant.Therefore,2ml of 1% (V/V) Triton X-114 was employed for the rest of this work as shown in Figure 5.
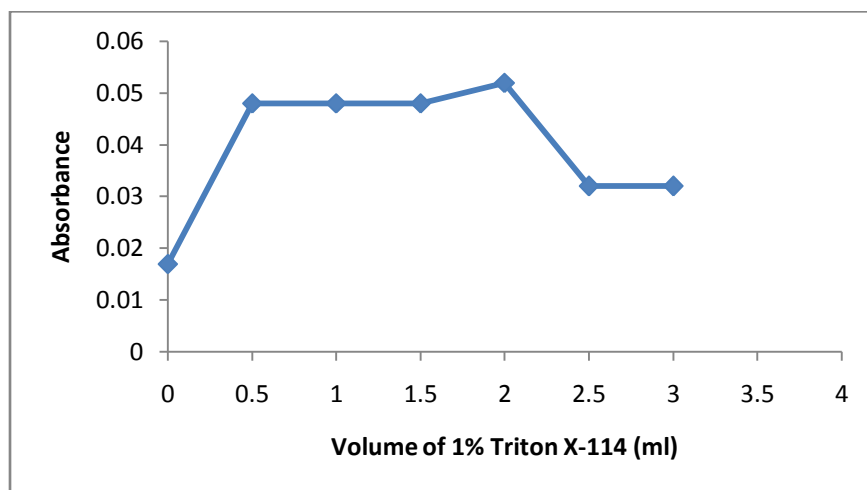

Figure 5 Effects of volumes of surfactant on the atomic absorption signal of 0.5 Pb.

Effects of the diluents agent for the surfactant –rich phase:-
An organic solvent should be low viscosity, low surface tension and easily combustible in flame atomic absorption. Different solvents for the surfactant–rich phase were examined so as to select the one producing the optimal results regarding sensitivity. Acetone, methanol, ethanol water mixture (1:1) (Ethanol: HNO_3) and DMF were tested for this purpose. Ethanol: HNO_3 mixture dissolved completely the surfactants which in its extracted complex of lead -APDC complex and the best recovery were obtained and an optimum volume is 0.5 ml. For more enhancement of the signal, on other hand the use of 0.5 ml of (1N) nitric acid was added in order to release the Pb (II) from the complex (Figure 6.)
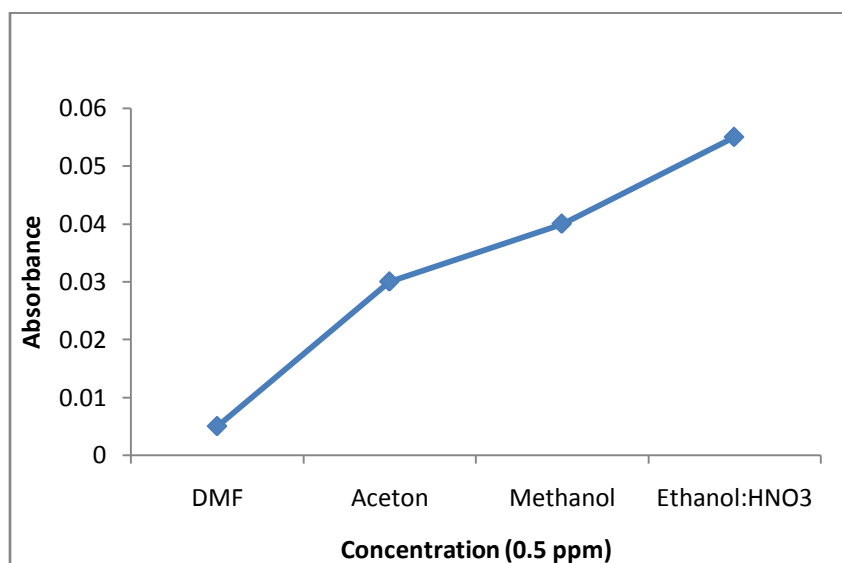

Figure 6 Effect of different diluent agent concentration.

Effect of Temperature:-
Cloud point formation obey to thermodynamic law with Optimum Temperature extraction performed with temperature ranging from 25Cº to 55Cº Shows 45Cº was suitable for Cloud point formation with higher viscosity and easily separated for Pb^{+2}-complex ion at lower temperature the separation of two phases is not complete. At

Higher temperature the decomposition of ion complex and reduction of extraction and micelles formation is happened.
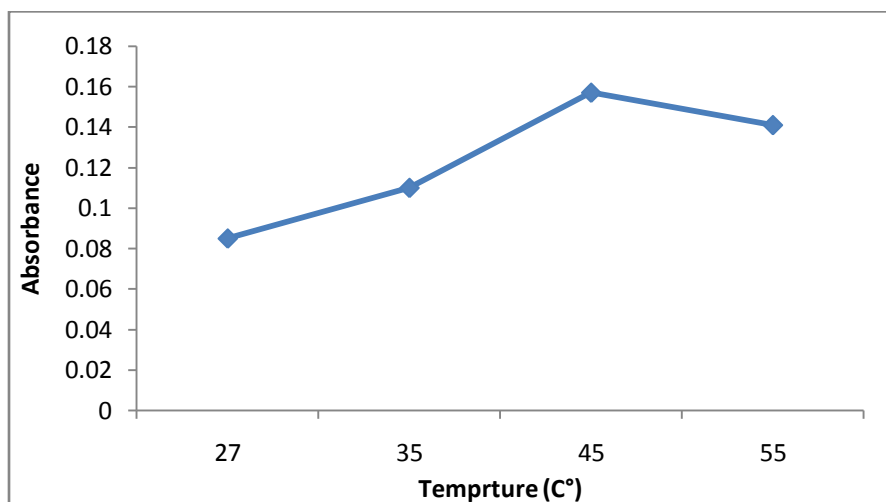

Figure 7 Study the effect of temperature.

Determination of lead in different water samples:-

In order to test the reliability of the proposed methodology suitable for the assaying of lead in different water samples. For this purpose, 1ml of each of the samples were taken with APDC 2 ml concentration of 200 ppm a 2 ml 1% (v/v) Triton X– 114 and, following the proposed procedure. The results show that the sample water from Southren Shat al arab with salinity 2.7 ppt gave a recovery percentage ranging from 96% to 102% whereas water samples from Faw has a salinity of 31 ppt and gave a recovery percentage ranging from 97% to 102% these results shows a affective proposal method for determination of Pb in salinity matrix sample. Although the salinity of waste water is only 3.3 ppt , the recovery percentage was an enhancement matrix (107%) due to the presence of organic compounds. The recovery percentage varies form 100.2% to 102%. The water samples of RO3(reverse osmosis water treatment system) has a salinity 9.4 of and recovery percentage ranging from 100% to 103%. In total the methodology was satisfying for the determination of lead recovery by using mixed modifier, by direct modification as well as standard addition method fig(5).

Table 1 Recovery percentage of the matrix modified procedure of real environment samples.

| Sample	Pb Content µg/L	Pb add µg	Pb Found µg/L	Recovery %	Error%	Mean recovery%
Southren Shat al arab	243.5	2000	23.13.9	96	-4	99.6±0.4
	243.5	6000	6211.18	100.5	0.5	
	243.5	8000	8037.997	102.5	2.5	
Faw	114.4741	2000	2068.539	102.2206	2.22	100.298 ±0.297
	114.4741	4000	4213.166	97.65753	-2.45	
	114.4741	6000	6052.969	101.0161	1.01	
Waste water*						104.854 ±4.854
	492.88	4000	**4473.899**	**100.4243**	0.4243	
	492.88	6000	**6066.304**	**107.0319**	7.031	
	492.88	8000	**7927.356**	**107.1338**	7.133	
RO3**	**281.644**	2000	**2274.864**	**100.298**	0.298	101.657 ±1.657
	281.644	6000	**6066.305**	**103.5498**	3.5498	
	281.644	8000	**8189.511**	**101.125**	1.125	
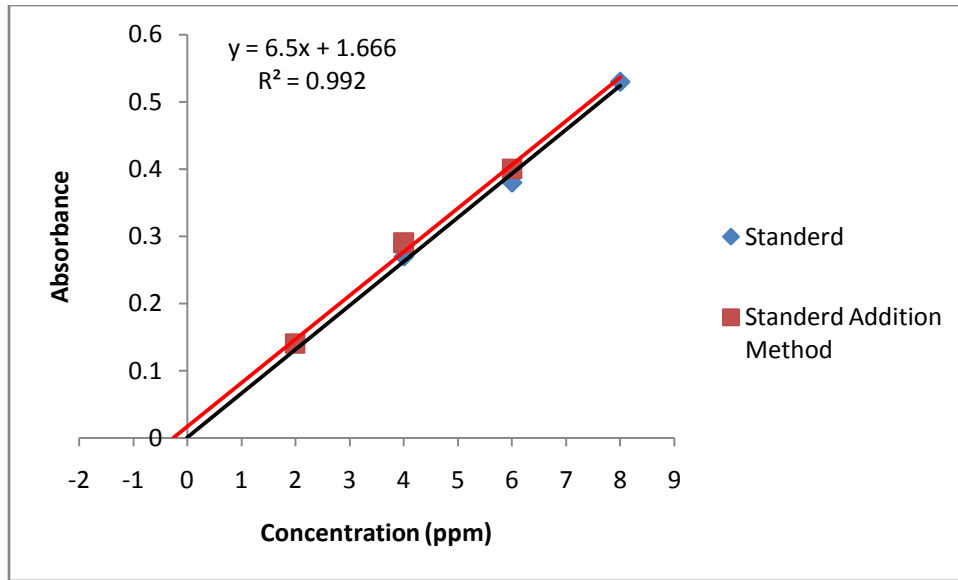
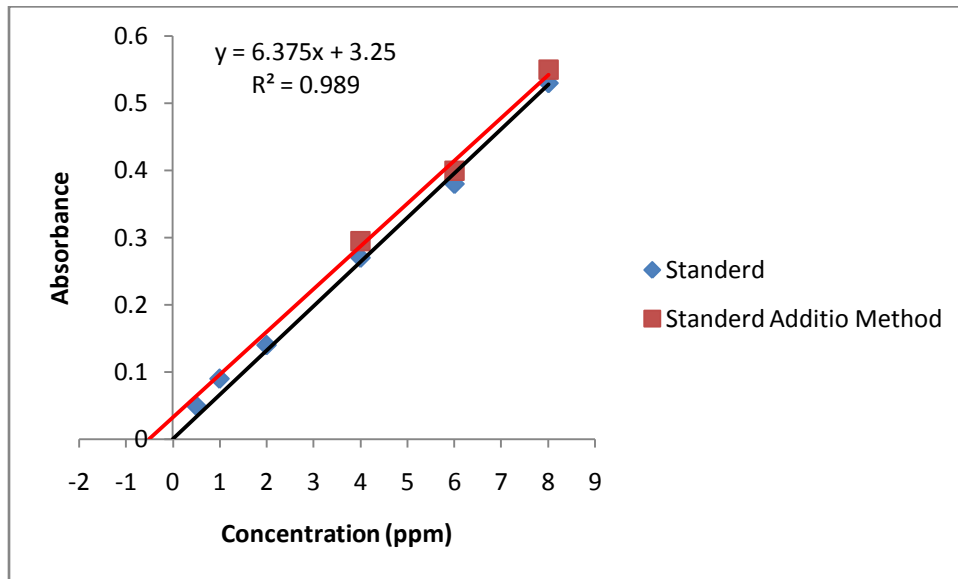Figure 8 Standard Addition Method for determination Pb in FAW Sample

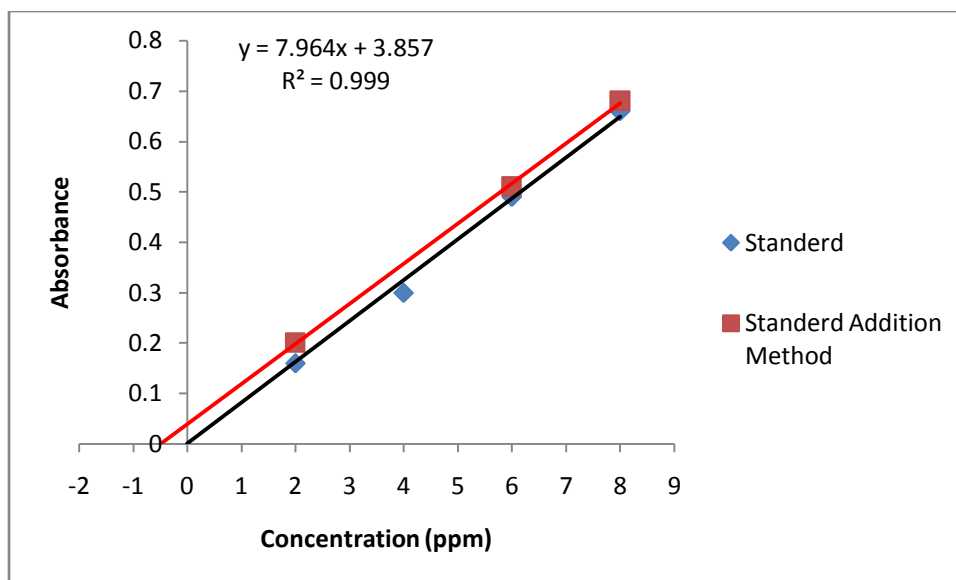Figure 9 Standard additions method and recovery calculation for waste water Sample

Figure 10 Standard eddition method recovery calculation for Southern shatt al Arab Sample (seba)
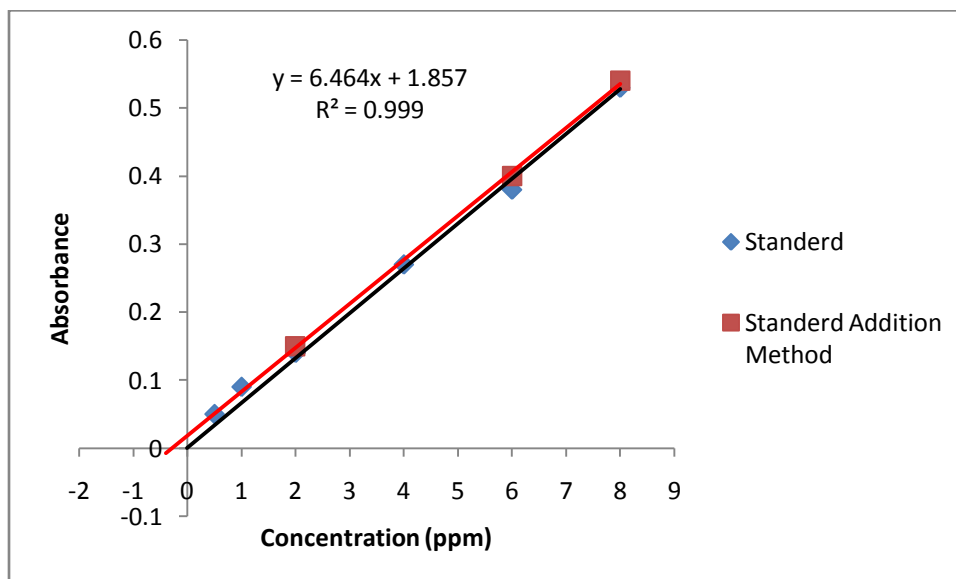

Figure 11 Standard Addition Method for determination Pb in rejection RO plant Sample

Analytical performance:-

Under the optimum conditions, performance characteristics were obtained by processing standard solutions of Pb(II) and the data is illustrated in Table1. Calibration functions were linear at least up to 20 μg ml^{-1}, 0.5 μg ml^{-1} .Figure (7)shows this results. Furthermore, for preconcentration of 1 ml of the working standard solutions based on the slope ratio of calibration curves with and without preconcentration, an enrichment factor of 3.8, was obtained for Pb(II). To test the reproducibility of the proposed extraction method, the suggested procedure was repeated eight times under optimum conditions. The relative standard deviation (R.S.D.) was measured to be 1.31%, for Pb.
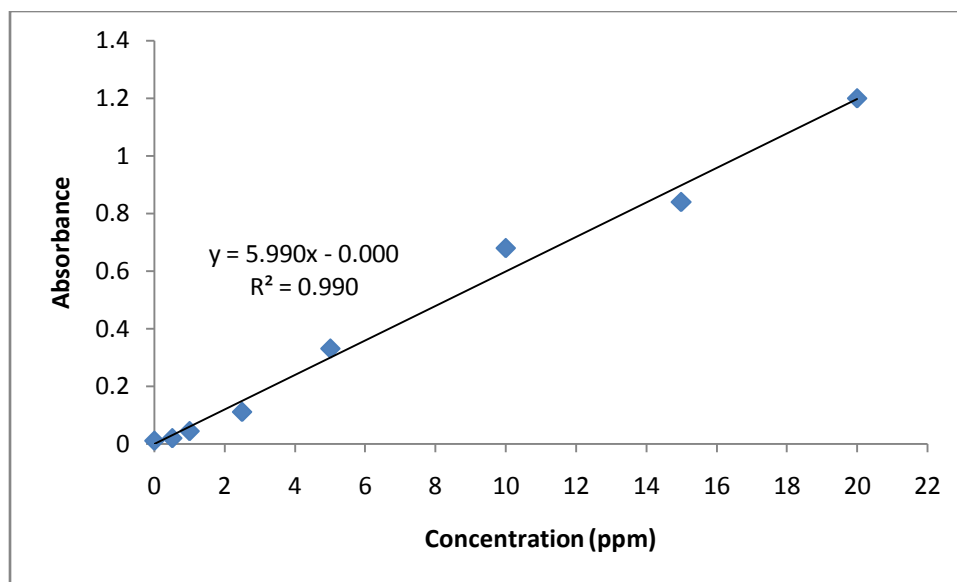
Figure 12 Calibration Curve

Cloud point extraction is asensitive, inexpensive, simple, and rapid system in preconcentration and separation of trace metal. TritonX-114 is used as cloud point extractant because it has the low cloud point temperature and high density, and, more importantly, it is very economical. In the pH 2.5, Pb(II) and APDC can form stable complexation. After extraction preconcentration by neutral surface active agents Triton X114, the element Pb can be measured to the level of $0.5\mu gmL^{-1}$ which is very satisfactory.

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