Article

CPE For Determination Pb $^{+2,}$ Cd $^{+2}$, and Cu^{+2} Prior to Flame AAS Method in Different Types of Water in Basrah City Province

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Abstract

A cloud point extraction (CPE) method was used as a pre-concentration strategy prior to the determination of trace levels of Cadmium, lead and copper in water samples by flame atomic absorption spectrometry (FAAS) The pre-concentration is based on the clouding phenomena of non-ionic surfactant, triton X-114, with Cd (II) ,Pb(II),Cu(II)/ Ammonium pyrrolidine dithiocarbonate (APDC) complexes in which the latter is soluble in a micellar phase composed by the former. When the temperature increases above its cloud point, the Cd (II) Pb (II), Cu (II)/ Ammonium pyrrolidine dithiocarbonate (APDC) complexes are extracted into the surfactant-rich phase. The factors affecting the extraction efficiency including pH of the aqueous solution, concentration of the (APDC), amount of the surfactant, incubation temperature and time were investigated and optimized. Under the optimal experimental conditions, the (CPE) method was successfully applied for the determination of trace levels of Cadmium, lead and copper in different types water samples in Basra city Province

Keywords: CPE , AAS

1. Introduction

Determination of trace analytes at low concentrations in complex matrixes has often been a problem for analytical chemists. The solution to this problem emerged early with the use of extraction- separation techniques, which offered not only the ability to isolate the target analytes from the matrix solution, thus reducing, controlling or even eliminating the interferences originally present.

Cloud point extraction (CPE) is an eco-friendly procedure for pre- concentration and separation of many analytes offering several benefits over the traditional liquid-liquid extraction [1]. The procedure is fast, inexpensive, accurate, selective and precise. It is termed as green ex- traction procedure as it consume no or minimum amount of toxic organic solvents [2]. The classical CPE procedure is based on the property of non-ionic surfactant to form micelles in aqueous media upon heating above definite temperature (called as cloud point or cloud temperature) [3] or by adding salt (salting-out phenomenon) [4]. The separation into two phases (an aqueous phase and a surfactant rich one) is then possible by centrifugation. The analyte is usually separated in the surfactant-rich phase. Fig. (1-1) summarizes the process of CPE of metal ions as an example of the traditional procedure.

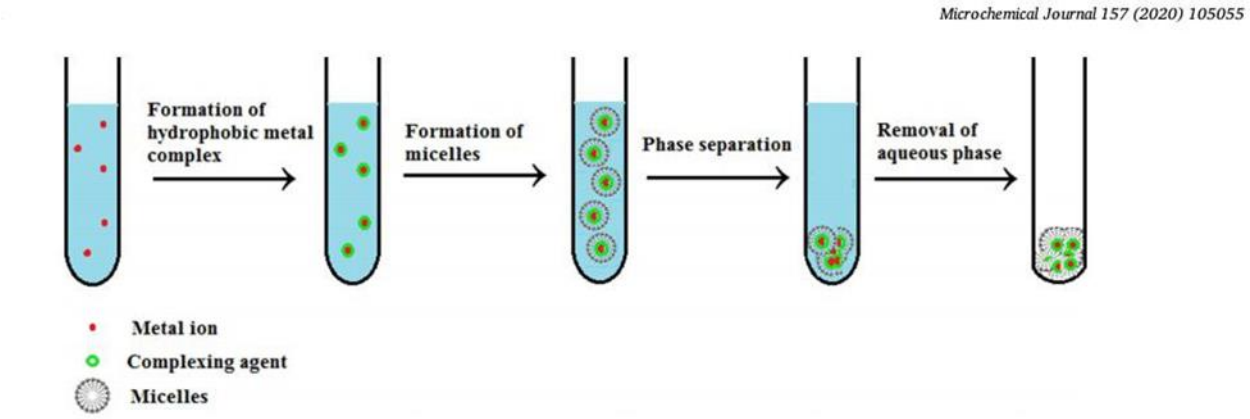

Fig. 1. Cloud point extraction of metal ions.

Fig(1-1) summarizes the process of CPE of metal ions as an example of the traditional procedure.

1.1. CPE for removal of metal ions

Heavy metals are one of the most dangerous pollutants that affect the ecosystem . The continuous domestic, industrial, medical and agricultural uses of metal-based compounds result in increasing emission and deposition of heavy metals in air, water and soil. This have serious implications for human health and other living organisms [5] Chromium, iron, cobalt, copper, zinc and others are required for cellular activities and therefore their nutritional deficiency may lead to many diseases [6]Other metals, such as cadmium, mercury and lead, are termed as toxic metals because they are not required for any bio logical functions and the exposure to them from any source leads to their accumulation in soft tissues such as kidneys, liver and brain[7] The process of CPE of metal ions requires complexation of metal ions with a suitable ligand and the reaction is pH dependent [8]. . Cloud point extraction has been used widely for preconcentration of metal ions from water samples.

1.1.1.Lead is one of the toxic elements - The body contains about 120 mg of lead which is mainly present in skeleton and in smaller amount in hair and blood. It accumulates with age in bones, aorta, kidney, liver and spleen. Lead is a general protoplasmic poison of that is cumulative, Slow acting and subtle and produce a variety of Symptoms. The main source of environmental pollution in urban areas are the use of tetraallyls lead as gasoline additives other sources of land are, plasters, paints, house Just and new prints. The toxic symptoms are anemia, insomnia, headache, dizziness, irritability, weakness of muscles and Kidney damage [9,10]

1.1.2.Cadmium it is also poorest the elements which are toxic to the body. It is present in human body at birth bat accumulates with age. the adverse physiological) effects encountered to high Cd

exposure include depressed growth rate, anemia, hypertension[11]damage of tubules and poor mineralization of bones. [12,13]

1.1.3.Copper - is an essential element for life and plants and plays an important role in Carbohydrate and lipid metabolism. Daily Copper intake (1.5-2) mg is essential and Cu at nearly 40 ng/ml is required for normal metabolism of many living organisms[14,15]Higher levels of Cu is toxic and sever oral in toxification will affect mainly the blood and kidneys. At these levels copper bind to the cell membrane and hinder the transport process through the cell wall. there for the trace Copper should be controlled in water and food, the European Commission has fixed the limit of 2 µg / ml for cu in drinking water and allowed limit of 2 µg / ml cu in USA and that in Canada (1µg/ml) [16]

2. Material and Method

2.1 Reagents and solutions **:-**

All Reagents used in this study are of analytical grade, and the solution where Prepared using distilled water. The reagent APDC(200ppm) of purity 99% from Sigma It was prepare by dissolving 0.01g of APDC in 50 ml distilled water. The standard solution of Pb+2,Cd+2 and Cu+2were from their nitrate salt of purity 99.99% from B.D.H. the surfactant Triton -X114was from B.D.H

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2.2 Apparatus:-

Atomic absorption spectrophotometer model (GBC Savant AAS) PH-meter Adwa AD 1030, Thermostatic water bath model YCW-01 AD shaker model 1 KA 500 kaka-WERK. Electronic balance model AE ADA

2.3 Optimization conditions for CPE

2.3.1 The substance to be separated

The substance to be separated by CPE should be hydrophobic or can be converted to a hydrophobic substance. The hydrophobicity is a necessary condition to ensure its incorporation into the micellar system. Therefore, the direct separation of some water-soluble molecules by CPE is difficult. An example is metal ions that should be converted to hydrophobic complexes by chelation with a suitable ligand prior to CPE . [17]

2.3.2 surfactants

The surfactants are critical reagents in CPE. They are necessary for formation of micelles that capture the material to be separated. They are amphipathic molecules consisting of non-polar chain with a charged or polar non-ionic head. According to the nature of the hydrophilic group, surfactants are classified into four categories (Anionic, Non-ionic ,Cationic, and Amphoteric or Zwitterionic).The concentration of surfactant is also critical in CPE. There is a narrow concentration range within which the phase separation is possible. Increasing in concentration of surfactant leads to decreasing in extraction efficiency due to decrease in preconcentration factor. On the other hand, lower amount of the surfactant causes insufficient uptake of the analyte [18]

Effect of surfactant concentrations a good cloud point extraction should maximize the extraction efficiency by minimizing the phase volume ratio (V_{org}/V_{aq}), 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 (2) 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 2% (V/V) Triton X-114 concentration was prepared (0.1-1) ml, the signals was increased by using 0.8 ml.Therefore,0.8 ml of 2% (V/V) Triton X-114 was employed for the rest of this work as shown in Figure (2)

2.3.3 pH of the solution

The medium pH is a significant parameter that influences CPE especially for ionizable species such as metal ions. Each CPE procedure has an optimum pH range at which extraction of the analyte is quantitative. The pH may also affect the stability constant of the metal complexes and hence critically affects the separation of metal ions by CPE.[19]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 2–6 using buffer solution of Composed of acetic acid and sodium acetate and it’s found the pH range(PH=4 -6) Figure (3)shows the enhancement of lead signal absorbance.

2. 3.4 Temperature and salting-out effect

Temperature is another important factor affecting the CPE. Increasing the temperature above cloud point of the surfactant leads to dehydration of the micelles and formation of turbid solution that result in phase separation [20] In some cases the separation may be occurred at room temperature in the presence of certain salt (salting-out phi noumenon).[21] Addition of a salt to micellar solution increases hydrophobic interactions between micelles due to increase dehydration between them. If the concentration of surfactant is high enough, turbidity is formed and the phase separation is possible The use of salting-out phenom neon in CPE cancels the heating step and so reduces the time needed for the

separation process [22]. Cloud point formation obey to thermodynamic law with Optimum Temperature extraction performed with temperature ranging from 25Cº to 50Cº Shows 40Cº was suitable for Cloud point formation with higher viscosity and easily separated for Pb+2-complex ion. At higher temperature the decomposition of ion complex and reduction of extraction and micelles formation is happened Figure (4). The presence of electrolytes in the extraction process has a significant impact on efficiency. In a 10 ml volumetric cup, a 5 ml aliquot of Pb2+, 2(ml) of APDC(200ppm) was added, along with 0.8 ml of 2% Triton X-114. Additionally, 0.5 ml from a 0.1% solution of various salts including (Lacl3, KCI, NH4NO3, and NaCl). Found(LaCl3) Figure (5) shows the enhancement Extraction Efficiency

2.3.5 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 5(ml) Pb(II) ion, APDC 200(ppm),2%(v/v)Triton X-114, at pH 4-6 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 1.5 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 (6).

2.3.6 Study Speed of centrifuge at(10 min)

The study aimed to determine the optimal speed for extracting metal ions in a viscous organic layer. Different speeds ranging from 1500 to 3800 RPM were tested for a fixed duration of 10 minutes. The results, as shown in Figure(7) indicated that speeds exceeding 3500 RPM resulted in the retention of Pb ions in the layer, hindering the extraction process and preventing access to the dissolved organic layer. This also disrupted the formation of micelles. Therefore, a speed of 3500 RPM was selected for the subsequent steps of the experiment.

2.3.7 Effect of Incubation Time

Study the effect of time in the range of (5-20) min was investigated by taking 5ml aqueous solution and followed CPE procedure Found(10)min Figure (8) shows the enhancement Extraction Efficiency

2.4 General Procedure for CPE for metal ions

To an aliquot of 5 ml of water samples, 1.5 ml of 200 ppm Ammonium pyrrolidine dithiocarbonate (APDC) reagent solution, 2ml of buffer solution of pH(4) Composed of acetic acid and sodium acetate. , 0.8 ml of triton x (114) 2% where mixed in 10ml standard flask and diluted to mark with distilled water. The content of the flask was transferred to a 10 ml centrifuging tube and the phase separation

was induced by heating the content in a water bath at 40 ºC for 10 min. Separation of phases was accelerated by centefuging at 3500 RPM for 20 min. cooling by ice bath for 10 min the surfactant rich phase becomes viscous the aquas phase could be separated by using a syringe subsequently. 0.5ml of ethanol with 3 drops of 1N HNO_3 was added to the surfactant rich phase in order to decrease its viscosity and make the final volume ready to transfer to the ultrasonic device. After that the volume introduced to the conventional Atomic Absorption Spectroscopy. The procedure was applied for the determination of metal ions by flame atomic absorption spectrometry (FAAS) .

2.5 REAL APPLICATION

This study involved: water samples were collected from of different types, including (river water, domestic use water, sewage water, electrical station water) from several different areas of Basra Governorate. illustration the amount heavy metals such as Pb,Cd,Cu and the alulity of the cloud point extraction method to estimate these pollutants.

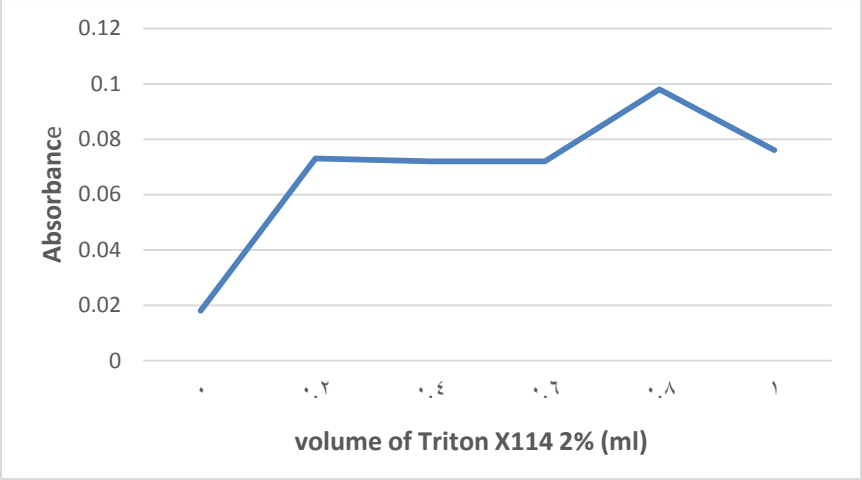
3. Results and discussion

The use of CPE-Complex has complexed an important branch for the separation and preconcentration of trace metals such as pb+2,cd+2and cu+2 using at a ligand ABDC as a sensitive and selective Complexing agent PH =6.

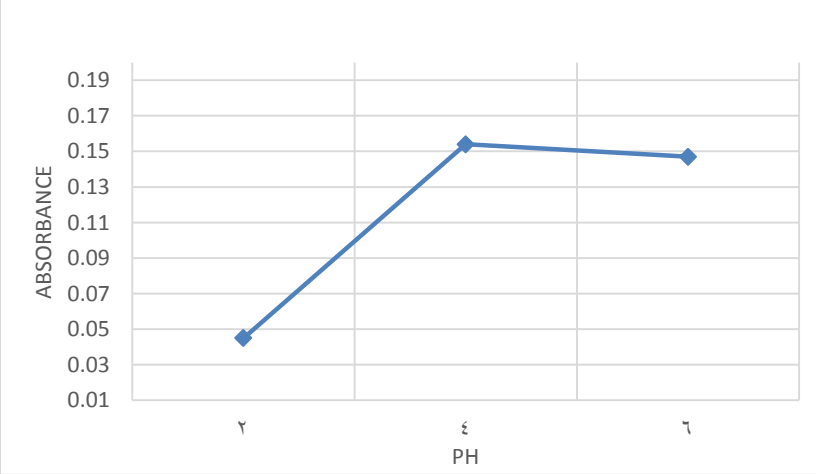
Table[1]show the results of CPE-complexation of metals ion Pb+2, Cd+2and Cu+2 in different types of water. In order to Verifying the results obtained by the direct method CPE ,the standard additions method, used to proved effect of matrix on the results obtained, therefore a three Samples of water selected for the standard. additions method and their results Compared with that Obtained I by direct CPE method. Figures (9,10,11) Show a standard addition calibrations of samples Shatt Albasrh, Waste Water and Shatt Alarab water.

Table [1] show the results obtained by the direct CPE method and Standard additions CPE methods the results show good agreement between them and the direct CPE show accurate results with accuracy of 98.9-113.4% Indicate that method is reliable for determination of heavy metals Pb, Cd and cu in different types of water.

Table[2]:show the values of detection limits and sensitivity for calibration curves for the metal ions that were studied



Fig(2) Effects of volumes of surfactant on the atomic absorption signal



Fig(3) Effect of pH variation

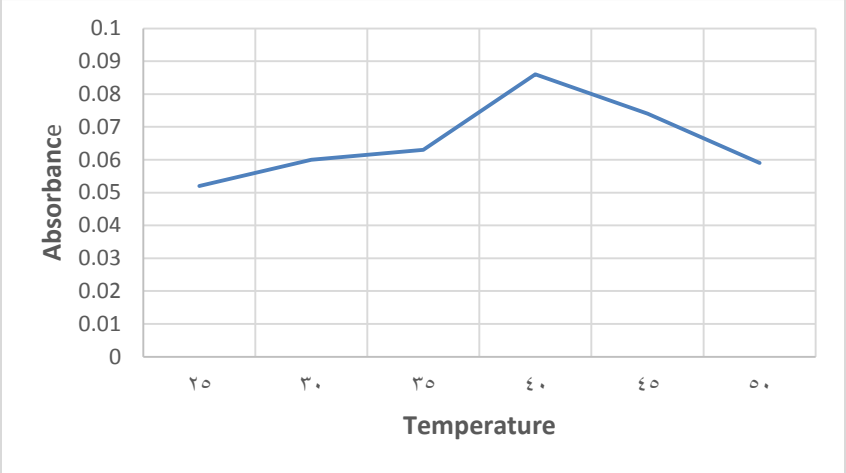


Fig-4-Effect of Equilibrium Temperature

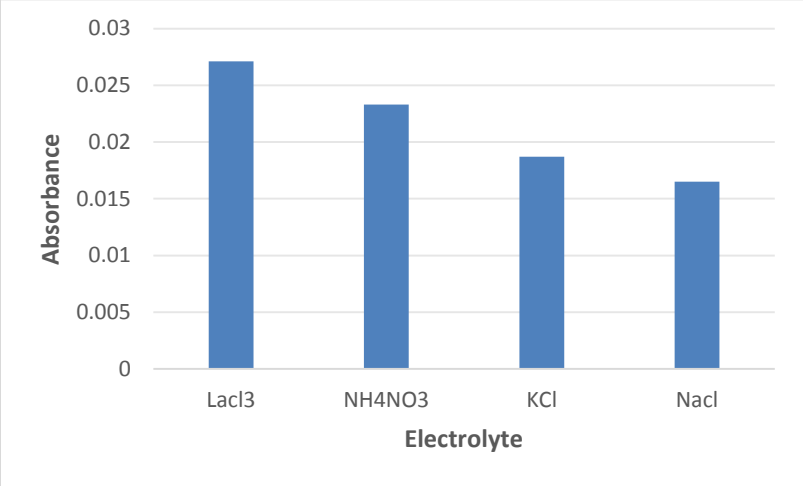
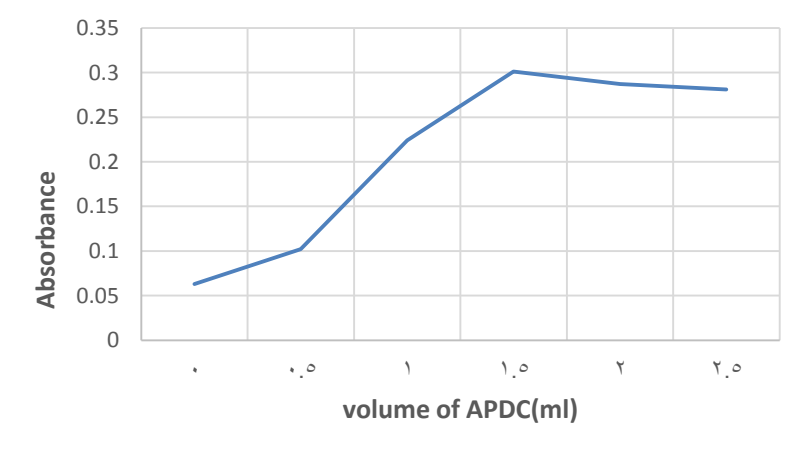
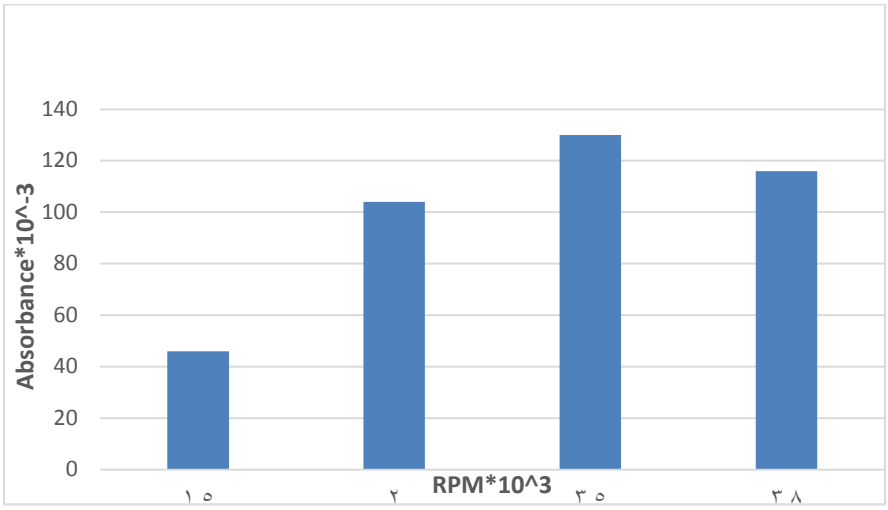


Fig (5) Effect of Type of Electrolyte



Fig(6) Effect of ligand concentrations on the atomic absorption signal .



Fig(7)Effect of Speed of centrifuge

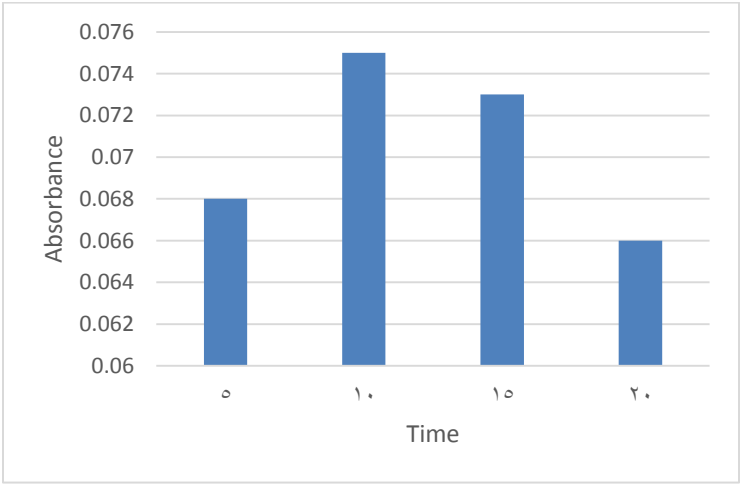


Fig (8) Effect of Incubation Time

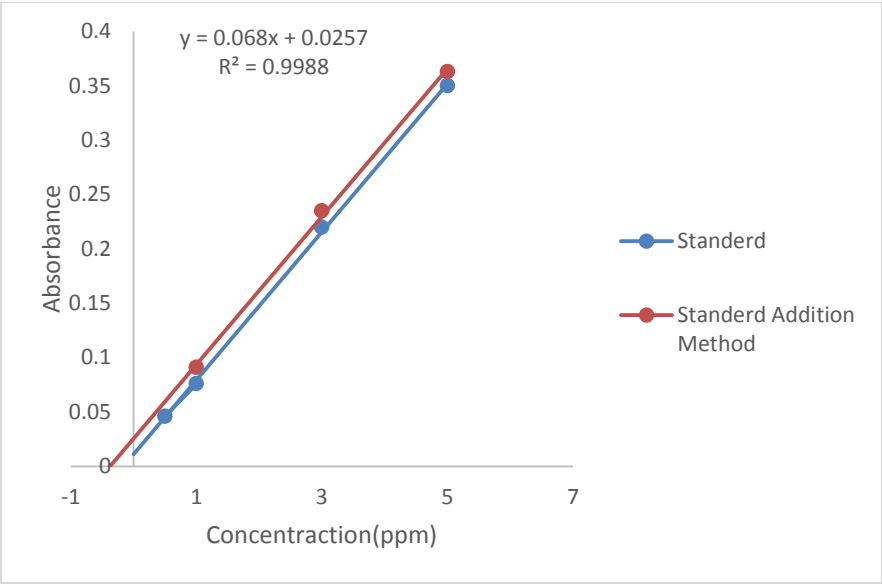


Figure (9) Standard Addition Method for determination Pb in Shatt Al-Arab samples

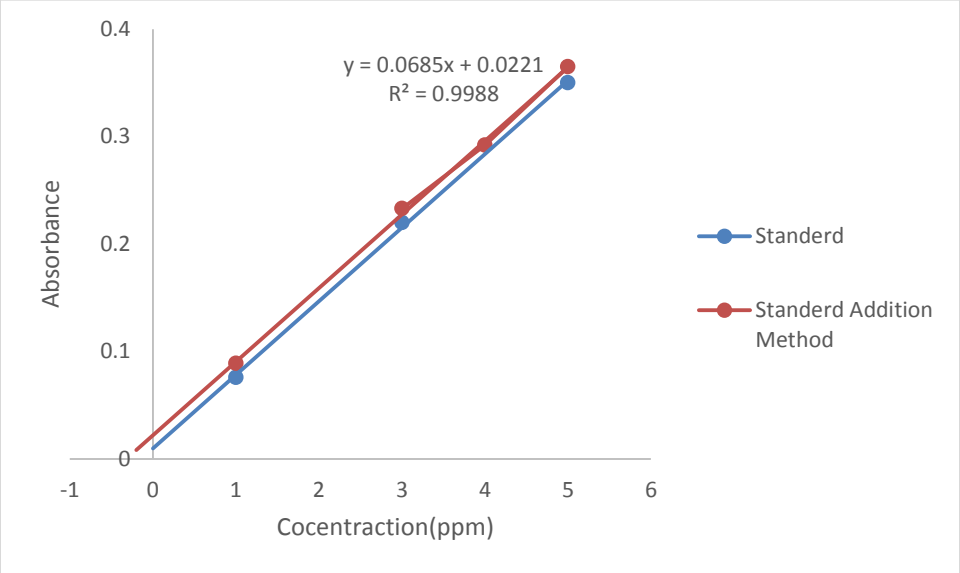


Figure (10) Standard Addition Method for determination Pb in waste water samples

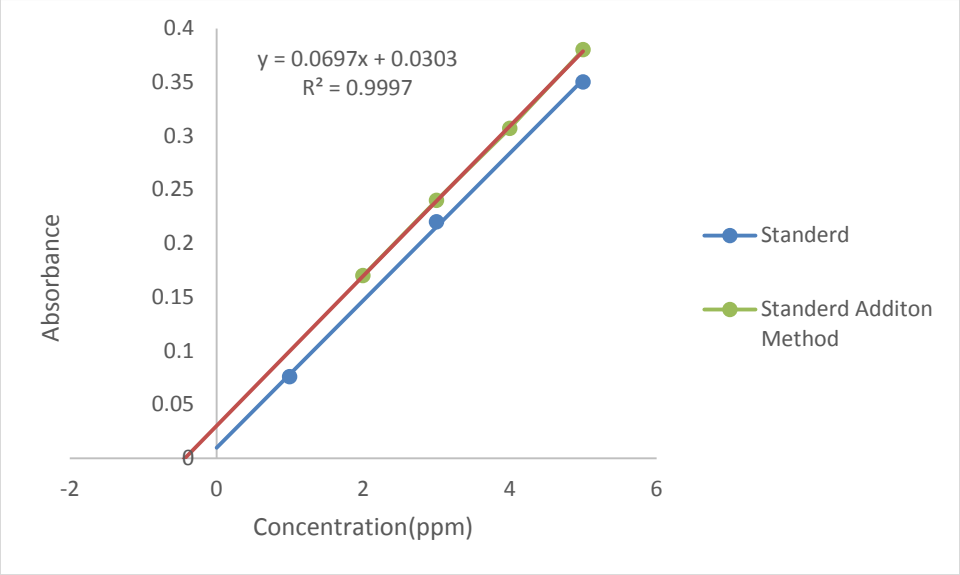


Figure (11) Standard Addition Method for determination Pb in Shatt AI-basrah samples

Table[1]:Determination the concentration Cd+,Pb+2 and Cu2+ in different types of water samples by direct CPE method and standard addition CPE method (µg/ml)

Sample	Pb+2content direct	Standard Addition Method	Cd+2content direct	Standard Addition Method	Cu+2content direct	Standard Addition Method
1	0.2127	0.2012	0.0244	0.0235	0.3104	0.3111
2	0.3803	0.3751	0.0246	0.0236	0.5638	0.5651
3	0.3521	0.3431	0.0293	0.0281	0.4364	0.4253
4	0.2254	0.2164	0.0387	0.0377	0.4428	0.4351
5	0.1409	0.1365	0.0195	0.0186	0.5002	0.4801
6	0.3831	0.3771	0.0824	0.0731	0.0733	0.0741
7	0.1451	0.1362	0.0824	0.0815	0.4301	0.4251
8	0.0845	0.0745	0.0727	0.0656	0.4524	0.4451

The areas for modeling water samples in Basra Governorate are:1- Water Tubs RO ,2- Hertha Thermal Power Station,3- Najabiya Thermal Power Station ,4- Karma Ali Channel ,5- Shatt Al-Basra , 6- Industrial Water -Hamdan ,7- Wastewater ,8- Shatt Al -arab water

Table[2]:show the values of detection limits and sensitivity for calibration curves for the metal ions that were studied

Metal ion	Pb+2	Cd+2	Cu+2
DL	0.0126	0.0112	0.0743
Sensitivity	0.044	0.012	0.013

CONCLUSION

The combined advantages of the cloud point methodology (easy, safe, rapid and inexpensive) and the use of APDC as a reagent (selectivity and sensitivity) for Pb ,Cd, and Cu were and utilized for their determination in. water samples. Using a direct method to extract elements from contaminated and clean water without the need to use standard additive methods due to the ability of CPE to selective extraction under the best conditions studied from the PH' surfactant concentration ---- The main advantage of the method is simultaneous determination of traces of lead ,Cadmium and copper without the need for any chemometric method. The method gives a very low limit of detection. The results. of this study clearly show the potential and versatility of this method, which could be applied to monitoring trace elements spectrophotometrically in various water samples.

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