CLOUD POINT EXTRACTION, PRECONCENTRATION AND SPECTROPHOTOMETRIC DETERMINATION OF MAGNESIUM(II) BY USING 2,4-DIMETHYLPENTAN-3-ONE

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The cloud point extraction (CPE) method has been applied to the extraction and pre-concentration of Mg^{2+} ions. The extracted solvated species showed a maximum absorbance at λ_{max} = 249 nm. The optimum conditions for extraction of solvated species to CPL are the presence of 0.5 M KNO_3 for 50 µg Mg^{2+} ion in 10 ml aqueous solution with 1×10^{-4} M of extractant, 2,4-dimethyl-pentan-3-one (2,4-DMP) and heating up to 90 °C for 15 minutes and addition of 0.5 mL of 1 % Triton X–100 as surfactant. The study showed that different extractant have different extraction efficiency, acetophenone showing higher extraction efficiency but ethyl methyl ketone has a lower efficiency. The effect of different salts and variable concentration of nitrate salts on the extraction efficienct has been studied. Determination of Mg^{2+} in different samples has been studied with a *RSD* = 0.0074, *DL* = 1.84×10^{-5} and Sandel's sensitivity = 3.58×10^{-9} µg cm^{-2}.

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Introduction

The extraction and estimation of Mg(II) by CPE methodology has not been attempted so far though the methodology has been used for extraction of several other elements with high efficiency. One sensitive application is the CPE for extraction Ni(II) by crown ether DB18C6.[1] Separation and micro determination of Pb(II) and Cd(II) by CPE methodology, using 2-[1-benzothiazolylazo]-4-benzylphenol for Pb(II) and 2-[(3-bromophenyl)azo]-4,5-diphenyl-imidazole for Cd(II) have also been reported.[2] Zn(II) was removed from aqueous solution as ion-pair complex by CPE technique with 3-[2-pyridylazo]-1-nitroso-2-naphthol (PANN).[3] Dual detection of drug norfloxacin (NOR) and iron (III) ion have been performed in biological and pharmaceutical samples.[4] CPE methodology and cetyltrimethylammonium bromide (CTAB) surfactant was used for extraction and determination Al^{3+}.[5] Similarly, Triton X-100 and dithizone have been used to determine selenium in kanykony (*ipomoea reptans p*.).[6] CPE methodology coupled with flame atomic absorption spectrometry has been developed for separation, pre-concentration and determination of trace amount of iron in different samples.[7,8] SDS has ben used as surfactant for pre-concentration and spectrophotometric determination of Pb(II) and Cu(II) by N^1,N^2-diphenylhydrazine-1,2-dicarbothioamide (PHCT).[9] CPE methodology was also used to determine Hg(II) with a new complexing agent[10] and Ni(II) with DMG by UV-Vis spectrophotometry.[11]

Experimental

Biochrom model (80-7000-11) Libra s60 Cambridge CB40FJ spectrophotometer with 1 cm quartz cell was used for recording the absorbance spectra and absorbance. Electrostatic water bath (WNB7-45) (England) was used to maintain the temperature.

All chemicals used in experiments are of analytical grade and were used without further purification. Stock solution of Mg(II) (1 mg mL^{-1}) was prepared in a volumetric flask by dissolving 0.6101 g of $Mg(NO_3)_2$ in 100 mL distilled water containing 0.5 mL of concentrated HNO_3. Other solutions were prepared by dilution of the stock solution with distilled water. Buffer solution, pH = 9.6, was prepared by dissolving 60 gm of NH_4Cl in distilled water with 120 mL of concentrated ammonia solution and diluted to 1 L by distilled water. A 0.02 % solution of Eriochrome black-T was also prepared.

Principal method

A mixture of aqueous solution of 10 mL containing 50 µg Mg^{2+} and 0.5 mL of 1 % Triton X–100 with suitable concentration of KNO_3 and 1×10^{-4} M of 2,4-DMP as the extractant was prepared. The mixture was heated at a fixed temperature with lime to form cloud point layer (CPL) which was separated. It was dissolved in 5 mL of ethanol and its absorbance at λ_{max} was measured at against a blank prepared in the same manner without Mg^{2+} ion but treated with Eriochrome black-T.[12] The distribution ratio (DR) was calculated.

In the stripping method, ethanolic CPL solution was shaken with 2 x 5 mL of diluted HNO_3. The results showed that the both the type of analysis gave the identical results.

Result and discussion

The UV-VIS spectrum (Figure 1) of the extracted solvated species, obtained by CPE method showed maximum absorbance at wavelength λ_{max}= 249 nm.

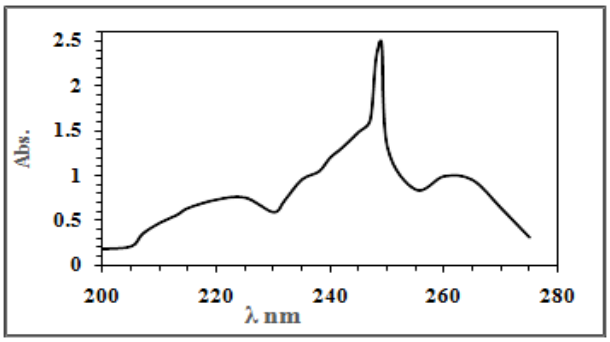

Figure 1. UV-VIS spectrum of the ion-pair complex extracted to cloud point.

Variation of KNO_3 concentration

An aqueous solution (10 mL) was prepared which contained 50 µg Mg(II), 0.5 mL of 1 % Triton X–100, 1×10^{-4} M 2,4-DMP and varying concentration of KNO_3. It was heated at 90 C° for 15 min for the formation of CPL. The CPL was separated from aqueous solution and dissolved in 5 ml of ethanol and its absorbance at 294 nm was measured against a blank, prepared in the similar manner but without Mg(II).[12] By the use of calibration curve (Figure 2), the remaining quantity of Mg(II) ion in aqueous solution after extraction was determined. The transferred amount of Mg(II) was also determined and the DR was calculated according to procedure described above in the section of principal method. The results are presented in Figures 3 and 4.

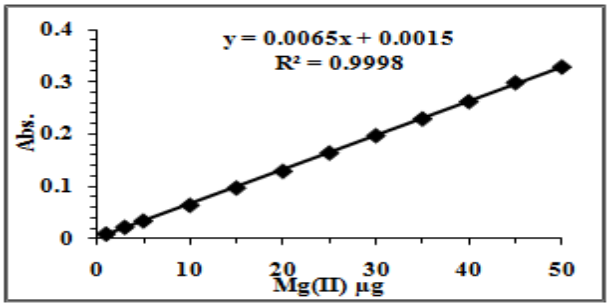

Figure 2. Calibration curve

The results indicate that increase in KNO_3 concentration increases the extraction of the of the solvated species to CPL. The absorbance and DR reach a maximum with 0.5 M KNO_3. The degree of solvation depends on thermodynamic equilibrium of species formed, and in the present case, 0.5 M KNO_3 gives favourable thermodynamic equilibrium for formation, and extraction, but at KNO_3 concentration less than the optimum, the thermodynamic equilibrium of the formation of solvated species is not reached. A high concentration of KNO_3 may hinder the formation of CPL by increasing micelles diffusion to aqueous solution.

Variation of Mg(II) concentration

Aqueous solutions (10 mL each) containing different amounts of Mg(II), 0.5 M KNO_3, 0.5ml of 1 %Triton X–100, and 1×10^{-4} M 2,4-DMP was subjected to the standard procedure to form CPL and their absorbance (Figure 3) were measured and DR were calculated.

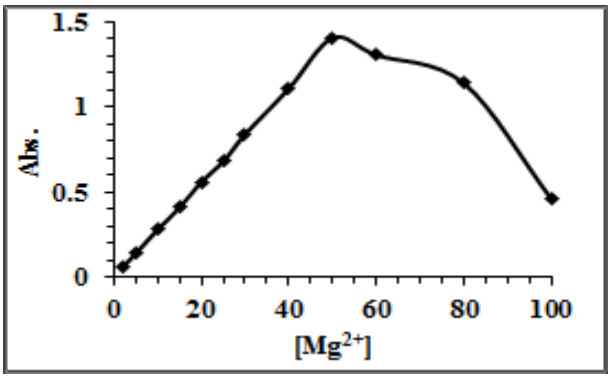

Figure 3. Dependence of absorbance on Mg(II) concentration.

The results show that the optimum value of Mg(II) concentration is 50 µg. At this concentration an optimum value for the following equilibrium is reached.

$$Mg^{2+} + 2NO_3^- + 2,4\text{-DMP} \rightleftharpoons 2,4\text{-DMP-}Mg(NO_3)_2 \qquad (1)$$

Metal ion concentration less than the optimum value is not enough to establish the equilibrium fully and results in a decrease in the extraction efficiency. Similarly, any metal ion concentration more than the optimum value is also not suitable for extraction because it tends to decline the extraction efficiency.

Variation of 2,4-DMP concentration

50 µg of Mg(II) ion from10 ml aqueous solution in presence 0.5 M KNO_3, 0.5 ml of 1%Triton X–100, and different concentrations of 2,4-DMP was extracted according to procedure detailed in principal method.

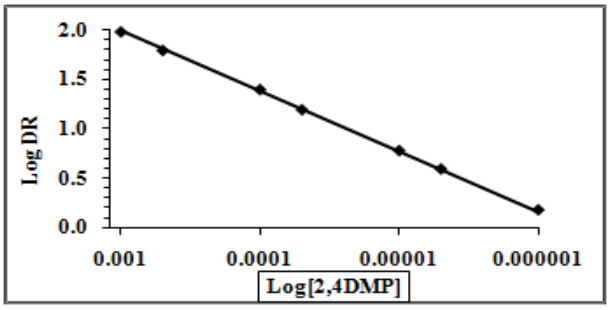

Figure 4. Dependence of distribution ratio on the concentration of 2,4-DMP.

The results show there is linear relation between extraction efficiency and 2,4-DMP concentration, i.e. extraction of the solvated species to CPL increase with an increase in the concentration of 2,4-DMP. Similarly, the DR varies linearly with the concentration of 2,4-DMP (Figure 4).

The slope of straight line in Figure 4 is 0.603, which indicate that one molecule of 2,4-DMP is coordinating with Mg(II) in $Mg(NO_3)_2$ forming 2,4-DMP-$Mg(NO_3)_2$.

Effect of different salts

50 µg of Mg(II) ion from10 ml aqueous solution, under optimum reaction conditions was extracted according to procedure detailed in principal method, in the presence 0.5 M of different salts. The results show extraction efficiency change with nature of salt added, and the best extraction and DR is achieved in the presence of $Al(NO_3)_3$ (Figure 5).

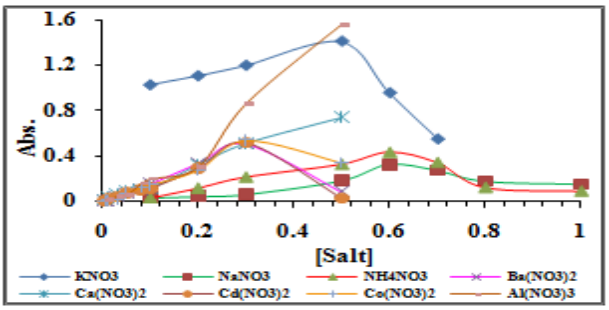

Figure 5. Effect of different salts on the extraction process.

Effect of concentration of different salts

Extracted 50 µg Mg^{2+} ion from10 ml aqueous solution containing varying concentration of different salts was carried out according to procedure detailed in principal method. The results show that for most of the salts, the extraction efficiency and DR increases up to a concentration between 0.5 M to 0.6 M and thereafter either declines or remain constant.

Temperature variation

Extraction of Mg(II), under optimum conditions, was carried out different temperatures between 70 and 95 °C. The results show that CPE is an endothermic process. The absorbance of complex and DR value increase with an increase in temperature up to the optimum temperature of 90 °C but decreases thereafter. The most suitable temperature for attaining the equilibrium of the extraction process and the formation CPL is 90 °C. At lower temperatures, the equilibrium is not fully attained and the extraction efficiency does not reach the optimum value. It seems that at temperature higher than 90 °C, micelles are dehydrated, the density of CPL is reduced and extraction efficiency is also reduced. The extraction constant K_{ex} at each temperature was calculated according to Eqn. (2).

$$K_{ex} = \frac{D}{\left[Mg^{2+}\right]\left[2,4\text{-DMP}\right]} \qquad (2)$$

It was found that a plot of log K_{ex} against reciprocal of temperature is linear with a negative slope. From the slope of the plot, values of thermodynamic parameters for the equilibrium were calculated. The values are ΔH = 0.23 kJ mol^{-1}, ΔS_x = 173.3 J mol^{-1} K^{-1} and ΔG = - 63.1 kJ mol^{-1}. The small value of ΔH indicate a strong binding of 2,4-DMP with $Mg(NO_3)_2$ to form stable solvated species extracted to CPL. The high value of ΔS reflects entropic nature of the extraction process.

Variation of heating time

Extraction of Mg(II), as per the standard, process was carried out while varying the heating period. The results show optimum heating time is 15 min. Heating for 15 min gives favourable aggregation of micelles and complete dehydration to give CPL with smaller volume and higher density to enable extraction of maximum concentration of solvated species to result in higher absorbance and DR values. It seems that heating for 15 min. is required to produce good CPL, less than 15 min. is not sufficient to produce good CPL. More heating time also declines extraction efficiency as it decreases dehydration and increase diffusion of micelles.

Variation of surfactant concentration

Effect of variation in the volume of 1 % solution of Triton X–100 was studied by keeping other reaction condition at the optimum level. The results (Figure 6) showed that the optimum volume of Triton X–100 is 0.5 mL up to which both the absorbance and DR value increase. Less than 0.5 mL of surfactant solution is not sufficient enough to produce good CPL for extraction. Higher concentration of the surfactant than optimum value tend to increase diffusion and decrease dehydration and extraction efficiency.

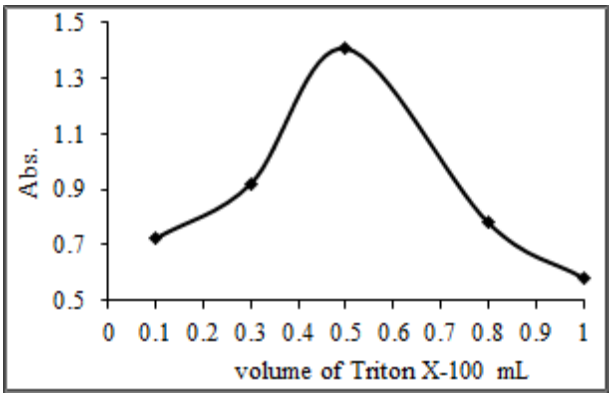

Figure 6. Effect of surfactant concentration on extraction efficiency.

Extractant variation

The extraction process was carried in 2,4-DMP, ethyl methyl ketone, methyl isobutyl ketone (MIBK), tributyl phosphate (TBP) and acetophenone, keeping other optimum reaction conditions constant. The results showed that the best extractant for the present process is acetophenone. The efficiency of the extractants exhibited the following order.

Acetophenone>MIBK>2,4-DMP>TBP>Ethyl methyl ketone

This effect of extractant may be explained on the basis of strength of coordinate bonding between extractant and neutral molecule of magnesium nitrate as well as the stability of the binding between the species extracted into CPL. And extractant.

Spectrophotometric determination

For determination, Mg(II) ion spectrophotometrically, a calibration curve (Figure 7) was prepared by carrying the extraction process as detailed under principal method with varying concentration of the metal ion and recording the absorption at 249 nm. Calculations based on this calibration curve, yielded the values of molar attenuation coefficient, ε = 6710.1 L mol^{-1} cm^{-1}, *RSD* = 0.0074, *D.L*=1.84×10^{-5} and Sandel's sensitivity=3.58 ×10-9 µg cm^{-2}.

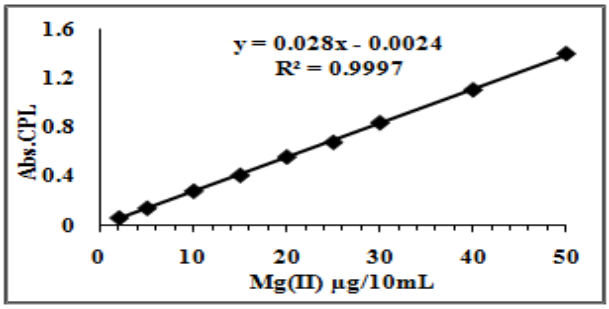

Figure 7. Calibration curve for spectrophotometric determination of Mg(II).

This calibration curve was used for the determination Mg(II) ions in different naturally occurring samples and the results are given in Table 1.

Table 1. Determination of Mg(II) in various samples.

S. No.	Sample	Mg(II)
1	Agriculture soil of Al.mishkab	8.2
2	Unagriculture soil of Al-Mishkab	2.2
3	Chickens meat	9.2
4	Chickens liver	8.4
5	Native beef	8.2
6	Lakes fish	8.6
7	Fish of waste of farms	10
8	Lepidium sativum	4.4
9	Aplum gravealens	5

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