

Solvent Extraction of Cd(II) using *n*-Butylamine-ClO₄⁻-MIBK and *n*-Butylamine-Oxine-MIBK

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ABSTRAK

Pengekstrakan *n*-butilamina-perchlorate-MIBK dan *n*-butilamina-oxine-MIBK didapati lebih berkesan untuk mengekstrakkan ion Cd(II) dalam keadaan alkali kuat ($pH > 10$). Pengekstrakan ini adalah fungsi kepekatan oksin, perklorat, *n*-butilamina dan pH. Isyarat nyalaan spektrometrik (AAS) yang lebih tinggi dapat ditunjukkan dengan menggunakan pengekstrak tersebut. Peningkatan isyarat ini dan % pengekstrakan dapat diterangkan oleh pembentukan aduk amin sinergi.

ABSTRACT

n-Butylamine-perchlorate-MIBK and *n*-butylamine-oxine-MIBK extractants were found to be effective for the extraction of Cd(II) ions under strongly alkaline conditions ($pH > 10$). This extraction is a function of the concentration of oxine, perchlorate, *n*-butylamine and pH. The flame AAS signal for Cd(II) was considerably enhanced by using the above extractants. The signal enhancement and the increase in % extraction of Cd(II) can be attributed to the formation of synergistic amine adducts.

INTRODUCTION

In our previous report (Tan and Wong 1990), we described the advantages of using the primary short chain amine, *n*-butylamine, as a mixed solvent or complexing agent in the ammonium pyrrolidine-dithiocarbamate (APDTC)-methyl isobutyl ketone (MIBK) extraction system. Higher extraction efficiency, higher signal output and greater stability of metal complexes were observed for the extraction of Cd(II) and Zn(II) ions from the *n*-butylamine-APDTC-MIBK system using flame atomic absorption spectrometry for metal analysis. As a continuation of our previous work, we shall report two other species which indicate same effects as APDTC in the presence of *n*-butylamine-MIBK but with increased signal output. These are perchlorate and oxine (8-hydroxyquinoline).

As in the case of APDTC and iodide, the use of oxine as a metal extractant has been widely reported (Marcus and Kertes 1969). However, there have been no reports on work done using

n-butylamine in the oxine-MIBK and perchlorate-MIBK extraction systems.

MATERIALS AND METHODS

Reagent grade MIBK, nitric acid, sodium hydroxide, acetic acid, oxine, and perchloric acid were used without further purification; *n*-butylamine was redistilled before use.

An oxine solution (1% W/V) was prepared by dissolving 1 g of oxine in the minimum amount of acetic acid and adjusting to 100 ml using deionised distilled water. Fresh solutions were prepared as required.

A stock solution of 1000 µg/mL Cd was prepared by dissolving the pure metal in a minimum amount of nitric acid. The solution was standardized using EDTA.

Solvent Extraction

Solutions (40-50mL) containing known concentrations of metal ions and oxine or metal ions and perchlorate with adjusted pH were transferred to

a separatory funnel containing 10 ml of the organic solvent(s). The pH of the solutions was adjusted using NaOH or HNO₃. The ionic strength of solutions was adjusted to 0.1 M with KNO₃ when necessary. The solutions were shaken well for 1 minute and the phases were allowed to equilibrate for 5 minutes before separation was carried out.

A flame atomic absorption spectrophotometer (Model IL 651) was used for metal determination. Absorbances obtained were corrected by using the reagent blanks.

The percentage of extraction was calculated as follows:

$$E = \frac{100 D}{D + V_a/V_o} \%$$

where V_a and V_o refer to the volume of aqueous and organic phase respectively. D is estimated by using the ratio of the absorbances in the organic solvent to that of the aqueous phase. (Brooks *et al.* 1989).

RESULTS

n-Butylamine-C10₄⁻-MIBK

pH Effect

Results in Table 1 show that the extraction of Cd(II) ion by n-butylamine-C10₄⁻-MIBK is strongly favoured under strongly alkaline conditions corresponding to the pK_b of n-butylamine (11.0). Rather poor extraction was observed under slightly alkaline and acidic conditions. Hence it is recommended that the natural pH of n-butylamine be used for chemical analysis. This pH condition was also used in subsequent studies.

TABLE 1
Effect of pH on the extraction of 1 µg/mL Cd(II) using 7% n-butylamine- 40mM C10₄⁻-MIBK

pH	Absorbance	%E
1.8	0	0
4.8	0.10	9
7.0	0.12	10
9.5	0.42	70
10.0	0.53	90
11.4	0.59	100

Effect of Perchlorate Concentration

The results in Table 2 indicate the requirement of a counter ion such as perchlorate for complete extraction of Cd(II) by the n-butylamine - MIBK system. The absorbance and hence the % extraction increases sharply from a low concentration of 1x10⁻⁵ M ClO₄⁻ to near 100% extraction at 4x10⁻²M ClO₄⁻ with a limiting absorbance value of 0.54. The optimum perchlorate concentration for the extraction of 1 µg/mL Cd is 0.04M at a fixed amine concentration of 7%.

TABLE 2
Effect of varying (ClO₄⁻) on the extraction of 1 µg/mL Cd(II) using 7% n-butylamine- C10₄⁻-MIBK extractants at pH 11.4.

(ClO ₄ ⁻) (mM)	Absorbance	% E
0.01	0.01	2
0.10	0.04	9
1.0	0.16	32
5.0	0.44	78
10.0	0.49	89
40.0	0.54	98
70.0	0.54	98
90.0	0.54	99

Effect of n-butylamine Concentration

The data in Fig. 1 show that metal extraction is dependent on the n-butylamine concentration. In the presence of 0.04M ClO₄⁻, 3% amine is sufficient to produce optimum signal output.

n-Butylamine-Oxine-MIBK Extractants

pH Effect

Results in Table 3 show that 1 µg/mL Cd(II) ion appears to be poorly extracted by the 0.01% oxine-MIBK extraction system. Although the efficiency of extraction increased with pH, the optimum pH of 11.4 only corresponds to 22% extraction of Cd(II) ion and 0.18 absorbance. However, in the presence of 0.5% n-butylamine, the extraction of Cd(II) ion increases to 80% which corresponds to an absorbance of 0.51 at pH ≥ 10. It is therefore evident that the extraction of Cd(II) ion by oxine-MIBK is considerably enhanced in the presence of n-butylamine.

Effect of n-butylamine Concentration

The effect of varying the initial concentrations of n-butylamine at a fixed concentration of 0.01% oxine and natural pH of 11.4 was studied. The

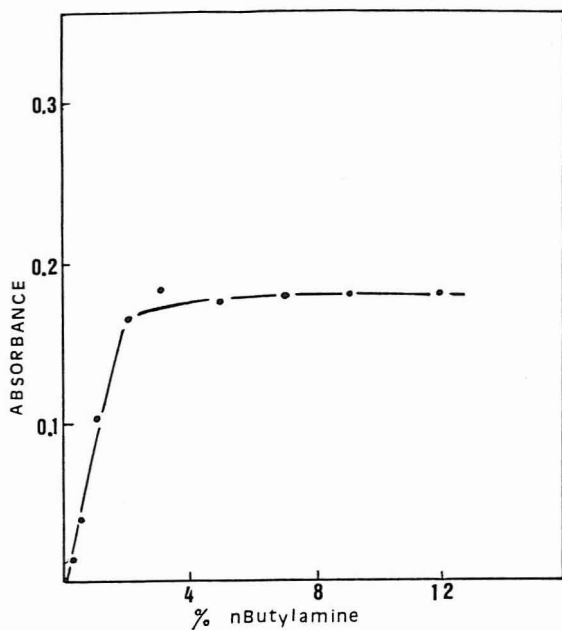


Fig. 1: Effect of varying n-butylamine concentration on the flame AAS signal for the extraction of 1 µg/mL Cd (II) using 0.04M ClO₄⁻-n-Butylamine - MIBK extractants; pH 11.4.

TABLE 3

Effect of pH on the extraction of 1 µg/mL Cd(II) using 0.01% Oxine- MIBK extractants in the presence and absence of n-butylamine.

pH	Without amine		With 0.5% amine	
	absorbance	%E	absorbance	%E
3.4	n.d.	-	0.07	9
4.5	0.02	2	-	-
10.0	0.12	21	0.51	80
11.4	0.18	22	0.51	80

results in Table 4 show that as little as 0.5% amine was sufficient to cause a significantly large AAS signal of 0.51 abs., corresponding to 80% extraction of 1 µg/mL Cd(II) ion. The optimum concentration range for the extraction of Cd(II) appears to be between 0.5-5% amine with 80-100% extraction and signal output of as high as 0.61 abs. The signal output for direct nebulization of 1 µg/mL Cd(II) ion was 0.14 abs.

Effect of Oxine Concentration

The effect of varying oxine concentrations in the presence of 0.5% n-butylamine at its natural pH of 11.4 is summarized in Fig.2. The absorption signal increased sharply from 0.0001% w/v oxine

TABLE 4
Effect of varying n-butylamine concentration on extraction of 1 µg/mL Cd(II) using n-butylamine - 0.01% Oxine-MIBK extractants.

% n-butylamine	Absorbance	%E
0.01	0	0
0.05	0	0
0.10	0.26	52
0.50	0.51	80
1.0	0.54	84
5.0	0.61	100
7.00	0.63	100

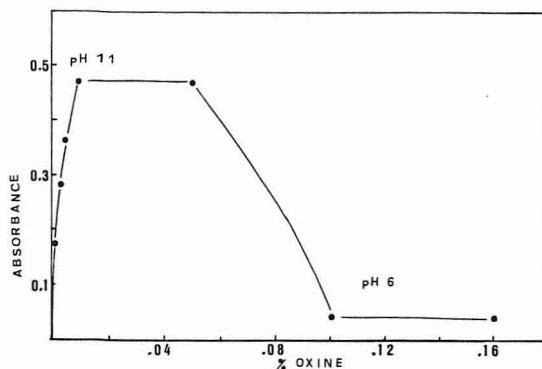


Fig. 2: Effect of varying oxine concentration on the flame AAS signal for the extraction of 1 µg/mL Cd(II) using Oxine - 0.5% n-Butylamine - MIBK extractants.

and levelled off at 0.01 - 0.05%. However, as the oxine concentration increased to 0.1% and beyond, precipitation occurred and the pH of the solution decreased from 11 to 6 and the signal decreased sharply. A near complete extraction was observed at an oxine concentration of greater than 0.01%. In terms of absorption signal output, 0.01% oxine is recommended as the optimum oxine concentration needed. There appears to be no advantage in using > 0.1% oxine since precipitation occurs.

Calibration Curve

The data in Fig. 3 demonstrate the usefulness of a preconcentration step using n-butylamine-ClO₄⁻-MIBK as solvent extractants for Cd(II) compared with the direct nebulization of aqueous samples of Cd(II) ions in flame atomic absorption spectrometry. However, linearity of the calibration curve was observed below 0.4 ppm for the case with solvent extraction. As in the case of the previous study on n-butylamine-APDTC-MIBK, the present studies of ClO₄⁻-MIBK and Oxine-MIBK-in

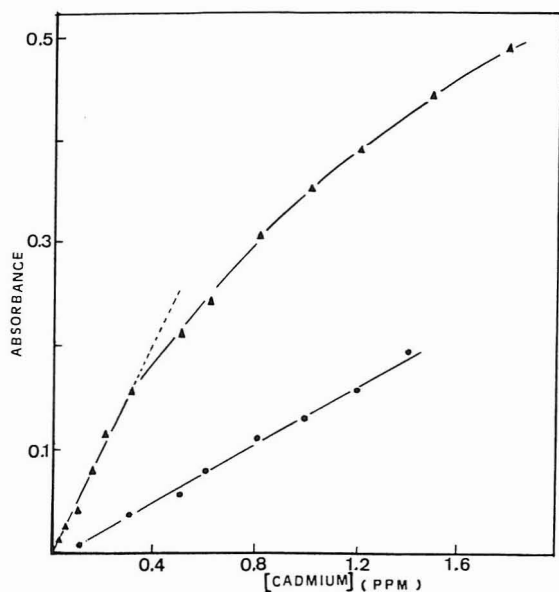


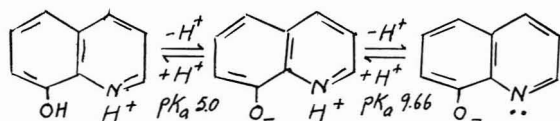
Fig. 3. Calibration graph of Cd(II):
 • aqueous solution (before extraction)
 ▲ nonaqueous solution (after extraction with 7% n-butylamine - 0.04M ClO₄⁻ - MIBK)

the presence of n-butylamine produce similar calibration curves for the extraction of Cd(II). Both systems produce readable signals with a considerable degree of linearity at a range of 0.01 to 0.3 µg/mL Cd(II). Under similar operating conditions, the Cd(II) signal was barely detectable via direct nebulization of aqueous samples containing less than 0.05 µg/mL Cd(II).

DISCUSSION

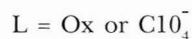
The explanation given previously (Tan and Wong 1990) for the enhanced Cd flame spectrophotometric signal using APDTC-MIBK in the presence of n-butylamine can be extended to the present studies.

Oxine (8-hydroxyquinoline) has pK_a values of 5.0 and 9.66 and its chemical equilibria are as given below :



The phenolate group and the unprotonated N group would be responsible for the chelation of Cd(II) ion forming a five-membered ring chelate with the Cd ion to form the CdOx com-

plex species. The presence of n-butylamine would stabilize the CdOx complex at pH > 9. Under strongly alkaline conditions, the unprotonated amine predominates and could encourage the formation of a more stable amine adduct probably via the following equilibria:



Am = unprotonated n-butylamine

The amine adduct, Cd(Ox)₂ (Am) or Cd(ClO₄)₂ (Am) thus formed would be easily extracted by the MIBK. This effect helps to explain the fairly high flame AAS signal observed for the Cd(II) ion and hence its extractability observed under strongly alkaline conditions rather than the alkaline condition and acidic conditions (Tables 1 and 3).

The present and previous studies (Tan and Wong 1990) illustrate the advantage of adding n-butylamine to commonly used extraction systems such as oxine-MIBK and APDTC-MIBK especially for the extraction of Cd(II). The presence of n-butylamine in these extraction systems enhances the stability and the extractability of the metal ion complex. It allows for the chemical analysis of Cd(II) under strongly alkaline conditions which would otherwise prove impossible due to hydrolysis.

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