

## Enhancement of Cadmium and Zinc Flame Spectrometric Signals by Using APDTC-nButylamine-MIBK Extractants

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### ABSTRAK

Pengekstrakan amonium pirolidina-ditiokarbamat (APDTC) dan metil-isobutil-keton (MIBK) didapati lebih berkesan dengan penambahan n-butylamina terutamanya untuk analisis ion-ion Cd(II) dan Zn(II). Pengekstrakan ion-ion logam bivalen adalah fungsi pH dan kepekatan APDTC dan n-butylamina. Ion-ion Cd(II) dan Zn(II) menunjukkan isyarat nyalaan spektrometrik yang tinggi masing-masing pada julat pH 7 hingga 12 dan 2 hingga 12 apabila pengekstrakan APDTC-n-butylamina-MIBK digunakan untuk menggantikan APDTC-MIBK. Isyarat yang lebih tinggi ini boleh ditafsirkan dalam sebutan pembentukan aduk amin sinergi dan/atau kesan pelarut campuran.

### ABSTRACT

Ammonium pyrrolidine-dithiocarbamate (APDTC) and methyl-isobutyl-ketone (MIBK) extractant were found to be considerably improved by the addition of nbutylamine especially for the chemical analysis of Cd(II) and Zn(II) ions. Solvent extraction of the bivalent metal ions is a function of pH and the concentration of APDTC and nbutylamine. Cd(II) and Zn(II) ions exhibit considerable flame spectrometric signal enhancement for pH ranges from 7 to 12 and 2 to 12 respectively when APDTC-nbutylamine-MIBK was used as the extractant in place of APDTC-MIBK. The signal enhancement observed may be interpreted in terms of the formation of synergistic amine adduct and/or mixed solvent effect.

### INTRODUCTION

Ammonium pyrrolidine-dithiocarbamate (APDTC) and methyl-isobutyl-ketone (MIBK) is one of the most commonly used extraction systems for preconcentration of trace metal for AAS. APDTC was reported to be able to complex with some 30 elements and most of these complexes can be extracted into organic solvents (Kirbright and Sargent 1974; Zolotov *et al.* 1982). Due to the instability of the metal-APDTC complex, back extraction with acid was recommended (Danielson *et al.* 1978; Sturgeon *et al.* 1979). However, its use is limited as it suffers from slow kinetics and non-quantitative recovery of metal ions in organic phase (Sturgeon *et al.* 1979). To overcome these problems, another back-extraction method using a dilute mercury (II) solution instead of mineral

acid was proposed (Lo *et al.* 1982). Back extraction generally requires an extra step in the analytical procedure.

Recently, we added primary amine to APDTC-MIBK extraction system and extracted certain bivalent metal ions. The analysis with flame AAS shows considerable signal enhancement for the extraction of Cd and Zn ions.

The use of alkylamine especially the long chain high molecular weight for the extraction of metal ions has been widely reported (Clark and Viets 1981; Zolotov 1970). The use of short chain amine, however, is rarely reported. Umland and Hoffman (1957) and Luke (1956) reported the use of primary amine n-butylamine as additive to chloroform in order to improve the extraction of alkaline-earth 8-hydroxyquinolates. Scribner and

Kotecki (1965) followed by photometric analysis extracted trifluoro acetylacetonates of bivalent metal ions with chloroform containing some isobutylamine. Zolotov *et al.* (1982) had considered that amines could be used as solvents to extract metals from their iodide solutions.

In this paper, an attempt is made to report work done using n-Butylamine-APDTC-MIBK extractant for the extraction of trace metal ions of Cd, Zn, Pb and Cu, by flame AAS analysis. The emphasis of the work will be on the solvent extraction of Cd(II) ions.

## MATERIALS AND METHODS

### Material and Reagents

MIBK, nitric acid, ammonia solution, sodium hydroxide were of Analar Grade and were used without further purification. Spectrosol Grade APDTC was used directly. N-Butylamine was redistilled before used.

One percent (W/V) APDTC was prepared by dissolving 1 gm APDTC in 100 ml volumetric flask containing 0.5 ml conc.  $\text{NH}_4\text{OH}$ . The solution was then topped up to 100 ml and filtered. The APDTC solutions were prepared fresh daily.

Stock solution of 1000 ppm Cd was prepared by dissolving the pure metal in minimum amounts of nitric acid while 1000 ppm Cu, Pb and Zn were prepared from their nitrate salt (AR Grade). The stock solution was standardized by EDTA titration.

Deionized distilled water was used for all dilution and rinsing purposes.

### Solvent Extraction

Fifty ml of solution containing known concentrations of metal ions and APDTC was transferred to a separatory funnel containing 10 ml of the organic solvent mixture. This mixture contains known amounts of MIBK and n-Butylamine. The solution was hand-shaken for 1 minute and phases were allowed to be equilibrated for 5 minutes before phase separation was carried out. The pH of the solution was adjusted by NaOH or  $\text{HNO}_3$ .

Ionic strength was adjusted to 0.1 M by  $\text{KNO}_3$  when necessary.

Atomic Absorption Spectrophotometer (Model IL 651) was used for metal ions analysis. The absorbance units obtained were background subtracted using the signals output of the reagent blanks.

## RESULTS

### Extraction as a Function of pH

Extraction efficiency of APDTC (0.02%)- n-Butylamine (0.5%) - MIBK for metal ions such as Cd(II), Cu(II), Pb(II) and Zn(II) ions was assessed and compared with those of APDTC (0.1%)- MIBK under various pH conditions. Only the absorbance unit of signal output was used. Results show that APDTC-n-Butylamine-MIBK and APDTC-MIBK extraction systems have similar pH dependence curves for the extraction of Cu(II) and Pb(II) ions between the pH range of 2-12. However, for the case of Cd(II), both extraction systems produce similar pH dependence curves only at a pH range of 2 to 7 (Figure 1). From pH 7 onwards, APDTC -n-Butylamine-MIBK system produces higher relative signal output and the signal increases sharply from pH 10 to 12. As for APDTC - MIBK extraction system, its output signal decreases from pH 7 onwards. A near 4-fold signal enhancement was observed when APDTC-n-Butylamine-MIBK was used at pH 2 as compared with the signal obtained via APDTC-MIBK system (Figure 1).

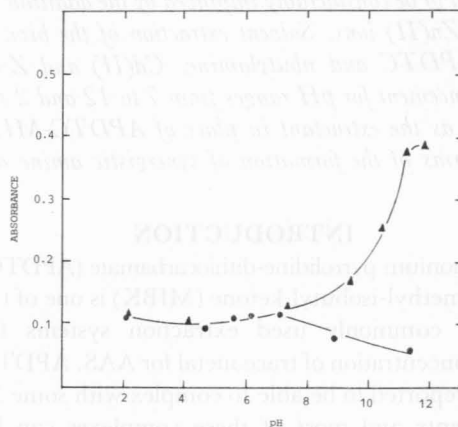


Fig. 1: Effect of pH on the Flame AA Signal for the extraction of 1 ppm Cd(II) using the following extractants:

- (0.1%) APDTC - MIBK,
- △ (0.02%) APDTC - (0.5%) n-Butylamine - MIBK

Figure 2 shows that the extraction curve for Zn(II) ion is also pH dependence. The APDTC n-Butylamine-MIBK system produces enhanced zinc signals output as compared with those derived from APDTC-MIBK system over the pH range of 2-12.

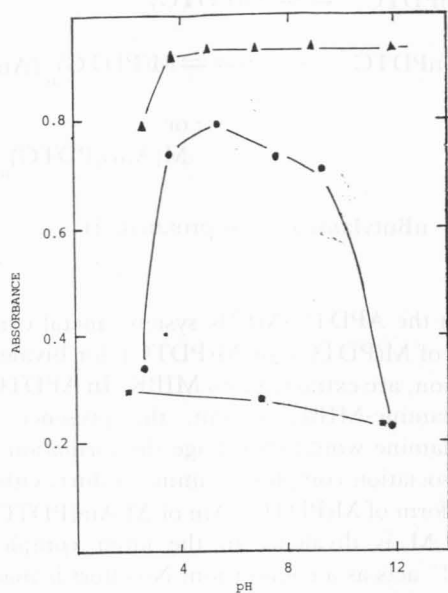


Fig. 2: Effect of pH on the Flame AA signal for the extraction of 1 ppm Zn(II) using the following extractants:

- Aqueous solution (before extraction)
- (0.1%) APDTC - MIBK
- ▲ (0.02%) APDTC - (0.5%) n-Butylamine - MIBK

#### Effect of n-Butylamine

Effect of varying the amine concentration in organic layers was carried out. A sharp increase was observed in the absorbance unit as % amine increases to 1% and levels off as amine concentration increases further. A Langmuir type of concentration isotherm was observed. The variation of amine concentration was similarly carried out in the aqueous layer as a possible complexing agent rather than as a diluent. As expected, a Langmuir isotherm was observed up to a certain amine concentration. After the addition of 5% amine, there was a slight decrease in absorbance unit. It was due to the dilution of the organic layer with increasing amount of amine added to the aqueous layer. The optimum concentration of amine required in the presence of 0.02% APDTC for the extraction of 1 ppm Cd(II) ion is 0.5%.

#### Effect of Varying APDTC

Efficiency of Cd extraction via MIBK was assessed by varying APDTC in the absence and presence of n-butylamine. Results in Table 1 show that in the absence of the amine, the absorbance increases steadily from  $1 \times 10^{-5}$  to  $1 \times 10^{-1}$ . However, in the presence of 0.5% n-Butylamine, the absorbance unit increases sharply from  $1 \times$

$10^{-5}$  to  $5 \times 10^{-4}$ % APDTC and remains constant up to  $1 \times 10^{-1}$ %. The signal output was enhanced by about 80% when amine was used indicating that APDTC-amine-MIBK is a more superior extracting system as compared to APDTC-MIBK. Another advantage is that the amount of APDTC used can be considerably reduced by as much as 3½ fold when 0.5% n-Butylamine is used.

TABLE 1

Effect of varying the amount of APDTC for the extraction of 1 ppm Cd(II) ion in the absence and presence of n-Butylamine at pH 4.5 and 10.0 respectively.

APDTC (%)	Without Amine	With 0.5% Amine
$1.0 \times 10^{-5}$	0.02 Abs.	0.09
$1.0 \times 10^{-4}$	-	0.21
$5.0 \times 10^{-4}$	0.13	0.59
$1.0 \times 10^{-3}$	-	0.60
$5.0 \times 10^{-3}$	0.13	0.60
$1.0 \times 10^{-2}$	0.13	0.60
$5.0 \times 10^{-2}$	0.18	0.60
$1.0 \times 10^{-1}$	0.33	0.60 Abs.

Abs = Absorbance

#### Calibration Curve

Figure 3 depicts the calibration curve for Cd in the concentration range of 0.01-1 ppm with and without a solvent extraction step. The greater sensitivity of the Cd calibration curve using n-Butylamine-APDTC-MIBK system for metal extraction followed by flame AAS analysis as compared to the one obtained directly via aqueous solution is clearly demonstrated. However, caution has to be exercised as linearity of the curve is only below 0.25 ppm.

It is, however, worth noting that the amine system produced readable signals with considerable degree of linearity at a range of 0.01-0.1 ppm while the Cd signal was barely detected via direct nebulization of the aqueous sample containing  $< 0.05$  ppm Cd. This does allow trace analysis of Cd of down to ppb level using Flame AAS via solvent extraction of n-Butylamine-APDTC-

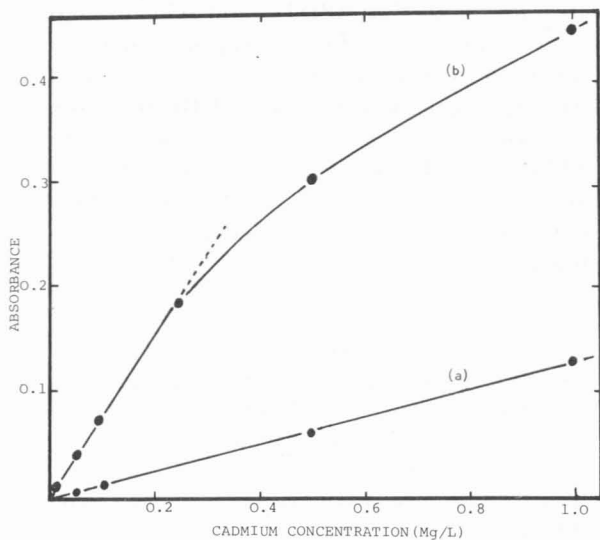


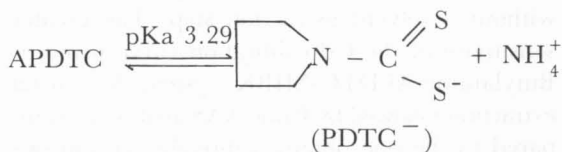
Fig. 3: Calibration graph of Cd(II):  
 (a) aqueous solution (before extraction)  
 (b) (0.02%) APDTC - (0.5%) n-Butylamine - MIBK

MIBK extractants and the use of a preconcentration factor of 5 and more.

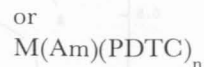
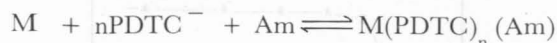
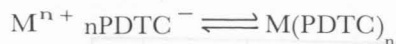
### DISCUSSION

The explanation of the above finding would be aided by an understanding of the complexing properties of the dithiocarbamate in the presence or absence of n-Butylamine and the stability constant of its metal complexes.

The dissociation of APDTC is favored at pH > 3.29 and is as shown



The complexing properties of dithiocarbamates are directly connected with the presence of two donor sulphur atoms which determine the nature of the metal that can be bound and the strength of the complexes formed (Hulanicki 1967). The decomposition of PDTC to CS<sub>2</sub> takes place under strongly acidic condition (Scharfe *et al.* 1973). Solvent extraction of metal complexes can be summarized as follows:



Am = nButylamine (non-protonated)

In the APDTC-MIBK system, metal complexes of M(PDTC)<sub>n</sub> or M(PDTC)<sub>2</sub> for bivalent metal ion, are extracted into MIBK. In APDTC-nButylamine-MIBK system, the presence of nButylamine would encourage the formation of ion association complex of amine adduct: either in the form of M(PDTC)<sub>2</sub>Am or MAm(PDTC)<sub>2</sub> where M is divalent. In the latter complex, PDTC<sup>-</sup> acts as a counter ion. No effort is made to identify the nature of the adduct extracted by MIBK.

For the case of Cu and Pb, the extraction of its metal complexes produce similar results over the pH range of 2-10. It may mean that Cu(PDTC)<sub>2</sub> and Pb(PDTC)<sub>2</sub> complexes are stable and efficiently extracted by MIBK as inferred from its stability constant (Log β<sub>2</sub>: Pb(PDTC)<sub>2</sub> = 16.8; Cu(PDTC)<sub>2</sub> = 29.5) (Scharfe *et al.* 1973; Hulanicki 1967). The presence of nButylamine exerts no significant effect on its extraction.

However, under similar conditions, the extractions of Cd and Zn complexes exhibit a different behaviour (Figures 1-2) probably because of the smaller value of stability constant (log β<sub>2</sub> (Zn-PDTC) = 9.8 - 10.4, β<sub>2</sub> for Cd-PDTC is not reported). Although there is a lack of reliable reports on the stability constant of the amine adduct of bivalent metal ions, certain predictions can be made with regard to the stability of the adduct. The presence of amine probably stabilized with Zn and Cd dithiocarbamate complexes by forming a more stable amine adduct.

These explain why signal enhancement was observed for Cd from pH > 9 where nButylamine (pKa 10.77) are deprotonated and have lone pair electron available for the formation of ion association complex of amine adduct. The observation of the larger than usual signal enhancement at alkaline condition indicates that the amine adduct formed is synergistic in nature. However, the

mechanism of synergism is unclear. In the case of Zn, signal enhancement was observed over a larger pH range (pH 2-12) indicating that besides the synergistic amine adduct formed, other effects may also play a part. This effect may be the mixed solvent effect whereby  $Zn(PDTC)_2$  may be doubly extracted by amine and MIBK diluents. This mixed solvent effect probably exerts a controlling role especially under the acidic condition of pH 2-6 where the formation of amine adduct would not be encouraged.

This work shows that there is an advantage of using APDTC-nButylamine-MIBK system for the extraction and analysis of Cd(II) ions in strongly alkaline conditions. The extraction and analysis of Cd may prove otherwise futile under such a condition since hydrolysis would set in. For the extraction and analysis of Zn(II) ions, enhancement was good over a wide pH range of 2-12 and the signal outputs after background subtraction were excellent when APDTC-nButylamine-MIBK extraction system was used.

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#### REFERENCES

- CLARK, J.R. and J.G. VIETS. 1981. Multielement Extraction System for the Determination of 18 Trace Elements in Geochemical Samples. *Anal. Chem.* **53**: 61.
- DANIELSON, L., B. MAGNUSSON and S. WESTERLAND. 1978. An Improved Metal Extraction Procedure for the Determination of Trace Metals in Seawaters by AAS with Electrothermal Atomization. *Analytica Chimica Acta* **98**: 47.
- HULANICKI, A. 1967. Complexation Reactions of Dithiocarbamates. *Talanta* **14**: 1371-1392.
- KIRBRIGHT, G.F. and M. SARGENT. 1974. *Atomic Absorption and Fluorescence Spectroscopy*. London: Academic Press.
- LO, J.M., J.C. YU, F.I. HUTCHISON and C.M. WAI. 1982. Solvent Extraction of Dithiocarbamate Complexes and Back-Extraction with Hg(II) for the Determination of Trace Metals in Seawaters by AAS. *Anal. Chem.* **54**: 2536-2539.
- LUKE, C.L. 1965. Rapid Photometric Determination of Magnesium in Electronic Nickel. *Anal. Chem.* **28**: 1443.
- SCHARFE, R.R., V.S. SASTRI and C.L. CHAKRABARTI. 1973. Stability of Metal Dithiocarbamate Complexes. *Anal. Chem.* **45**: 413-415.
- SCHRIBNER, W.G. and A.M. KOTECKI. 1965. Solvent Extraction of Metal ions with Trifluoroacetylacetonate-isobutylamine. *Anal. Chem.* **3**: 1304-1306.
- STURGEON, R.E., S.S. BERMAN, A. DESAULNIERS and D.S. RUSSELL. 1979. Preconcentration of Trace Metals from Seawater for Determination of Graphite Furnace AAS. *Talanta* **17**: 85-94.
- UMLAND, F. and W. HOFFMANN. 1957. Photometric Determination of Magnesium. *Analytical Chimica Acta* **17**: 234.
- ZOLOTOV, YU.A., V.A. BODNYA and A.N. ZAGRIZINE. 1982-84. Application of Extraction Methods for the Determination of Small Amount of Metals. *CRC Critical Review in Anal. Chem.* **14**: 102-117.
- ZOLOTOV, YU. A. 1970. *Extraction of Chelate Compounds*, p. 163. London: Ann Arbor-Humphary Science Publishers.

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