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DETERMINATION OF OPTIMUM CONDITIONS FOR LEAD BY SOLVENT EXTRACTION AND ATOMIC ABSORPTION SPECTROPHOTOMETRY

N. ERENTÜRK - Y. SARIKAYA*

Ankara Nuclear Research and Training Center,
Beşevler - Ankara

ABSTRACT

When elemental concentrations are too minute to be determined directly by AAS, pre-concentration by extraction procedures with organic solvent is one of the methods to get the concentration of metals high enough for accurate determinations. Extraction method also enhance the atomic absorption of metals by removing interfering substances. In this study, prior to AAS analysis the optimum conditions for lead chelating with APDC and NaDDC and the solvent extraction of these chelates into MIBK phase are investigated.

ÖZET

Elementel konsantrasyonların AAS ile tayin edilemiyecek kadar az miktarlarda olması durumlarında doğru bir tayin için, elementin yeterli miktarda konsantre edilmesi gereklidir. Bu taktirde çözücü ekstraksiyonu ile ön-konsantrasyon uygulanan metodlardan bir tanesidir. Ayrıca ekstraksiyon yöntemi, girişim veren maddeleri de ortamdan kaldırarak elementin atomik absorpsiyonunu arttırır. Bu çalışmada AAS analizinden önce kurşun elementinin APDC ve NaDDC ile kompleks teşkil ettirilerek MIBK fazına ekstrakte edilmesi işlemindeki optimum şartlar incelenmiştir.

INTRODUCTION

Complex formation is important because it produces species that have more useful characteristics for a particular chemical separation method. The composition of the complexes formed in the aqueous phase is established from the relationship between the distribution ratio (D) of the metal and one of the parameters: pH of the aqueous phase, the concentration of chelating agent, or the concentration of masking agent. In general, the extraction of a simple metal chelate can be described by a plot of logD vs pH at constant reagent concentration $(HL)_o$ in the organic phase. When $D \simeq (Kd)_c$ (the distribution of the metal chelate between the two phases is represented by the partition coefficient, $(Kd)_c$), the neutral metal chelate, ML_n, dominates in each phase. At values $D < (Kd)_c$, the distribution ratio is given aproximately by

$$D \simeq \frac{(Kd)_c \, K_f}{(Kd)_r^n \, (K_{HL})^n} \left\{ \frac{[HL]_o}{[H^+]} \right\}^n \qquad (1)$$

Eq. 1. shows that the distribution ratio is dependent only upon the pH of aqueous phase and the amount of unused chelating

* *University of Ankara, Faculty of Science, Department of Chemistry.*

agent, $(HL)_o$. All other terms are constant for a particular metal chelate-and-solvent pair. Indeed one may write

$$D = K' [HL]^n / [H^+]^n \qquad (2)$$

K' is the extraction constant. If the reagent concentration is maintained constant, the distribution of the metal in a given system is a function of pH alone. For this reason, curves of distribution vs pH at constant reagent concentration are of great analytical significance. Eq. 2 may be written as

$$D = K_1' [H^+]^{-n} \qquad (3)$$

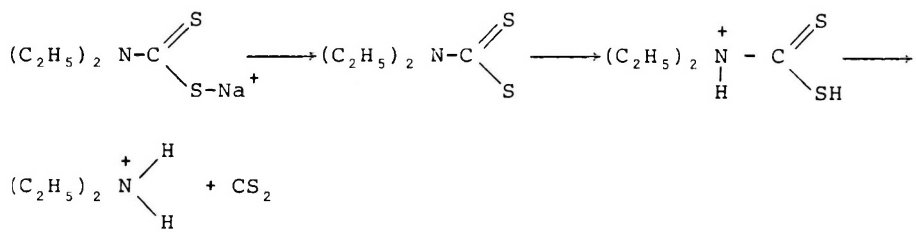
if $[HL]_o$ remains a constant /1,2/ .

EXPERIMENT

In this study lead chelated with ammonium pyrolidine dithiocarbamate (APDC) and sodium diethyl dithiocarbamate (NaDDC) and concentrated with methyl isobutyl ketone (MIBK) by solvent extraction method and analyzed by AAS. Many variables were controlled as extracting lead with organic chelators from an aqueous phase into an immiscible organic phase to increase the sensitivity of the analysis.

a) The effect of pH on the extraction of PbDDC chelate with MIBK.

The aqueous phases containing same quantities of lead were buffered with 20% ammonium citrate buffer solution and the pH were adjusted in the range of 1-9 with 1N NaOH or 1N HCl, lead chelated with 1% NaDDC solution and extracted with MIBK. The separated organic phases were analyzed by AAS. Fig. 1. shows the relation between the pH of the aqueous solution and absorbance. The data shows that maximum absorbance was observed at pH 5. At lower pH values NaDDC is decomposed according to the following scheme.



It is not advised to make chelate with NaDDC below pH5 /3/. At high pH values, decreases were observed in absorbances. This can be explained by the precipitation of $Pb(OH)_2$ in the aqueous phase.

b) The effect of pH on the extraction of PbAPDC chelate with MIBK.

Same experiment was done by APDC as chelating agent. Fig. 2. shows the relation between the pH of the aqueous solution and absorbance. At low pH values, APDC was also decomposed, but it is more stable than NaDDC at lower pH values. If extraction was done rapidly, there was little effect of pH on the extraction of lead

by APDC than by NaDDC.

c) The effect of pH on the extraction of PbDDC + PbAPDC chelates with MIBK.

In this experiment, the mixture of chelating agents was used in the ratio of 1.0:1.0. Fig.3. shows the relation between the pH of the aqueous solution and absorbance. No significant changes at absorbance values were observed as the pH changes.

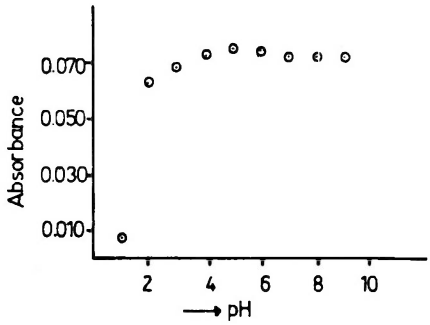


Fig. 1. The effect of pH on the extraction of PbDDC.

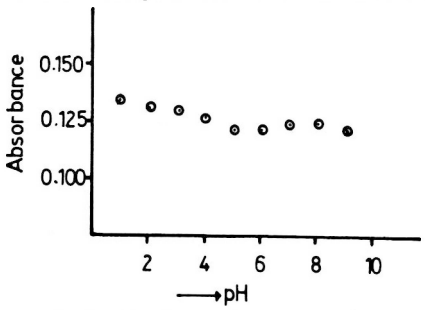


Fig. 2. The effect of pH on the extraction of PbAPDC.

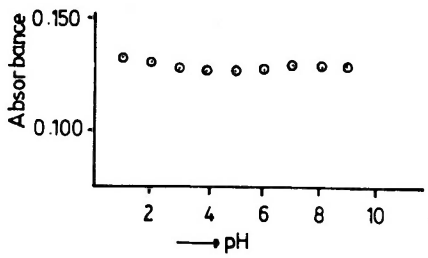


Fig. 3. The effect of pH on the extraction of PbDDC + PbAPDC.

d) The length of time needed for equilibrium for the distribution of the lead chelates between the aqueous and organic phases in PbDDC and PbAPDC systems.

A series of standards were prepared and they were shaken for

periods of 15, 30, 45, 60 seconds after addition of MIBK. Table-1. shows the relation between the time and absorbance.

TABLE-1. The length of time needed for extraction.

Time (second)	Absorbances (n=2) PbDDC-MIBK	PbAPDC-MIBK
15	0.093±0.001	0.093±0.001
30	0.094±0.001	0.094±0.001
45	0.094±0.001	0.093±0.001
60	0.095±0.001	0.093±0.001

The data shows that 15 secs. shaking time was adequate for extraction of lead chelates with MIBK.

e) The effect of the ratio of APDC to NaDDC on the extraction for lead chelates.

Three different mixtures of chelating agents were prepared to determine the effect of variation of the ratio of APDC to NaDDC on the extraction of lead chelates. The pH of the samples containing the same quantities of lead were adjusted to 5. Results are given in Table-2.

TABLE-2. The effect of ratio of reagents on the extraction.

APDC:NaDDC (gr/100 ml)	Absorbances (n = 3)
1.5 : 0.5	0.118±0.004
1.0 : 1.0	0.117±0.002
0.5 : 1.5	0.114±0.001

f) The effect of MIBK solubility on the extraction of lead chelate with varying ratio of aqueous volume to organic volume.

In this experiment, total aqueous volume was 25 ml. Different quantities of Pb standards were added to the aqueousphases so that Pb concentration with the varying volumes of MIBK would be the same in all experiment. The results are given in Table-3.

TABLE-3. The effect of MIBK solubility on the extraction of lead at different ratios of organic to aqueus phases.

MIBK (ml)	Aqu./org.	Added µgPb to the aqu.	Abs (n=2)
2	12.50	10	0.168±0.007
4	6.25	20	0.150±0.001
6	4.17	30	0.138
8	3.13	40	0.138±0.001
10	2.50	50	0.134±0.001
12	2.08	60	0.133±0.001
15	1.67	75	0.131±0.001

Table-3 indicate that the value of absorbance increases as the ratio of organic volume to aqueous volume increases. It can be explained that the solubility of MIBK is the lowest at the smallest aqueous to organic ratio.

g) Stability of lead chelates in MIBK.

The aim of this experiment is to determine the length of time of the extracted metal chelates remaining stable in MIBK. The samples containing the same quantities of lead were prepared and remained 3, 22, 25, 49 and 72 hours at the refrigerator until they were analyzed. Before the stability of these solutions were analyed, new samples were prepared. The absorbances of the new samples and the stability solutions were compared. The results are given in Fig. 4. As it is seen in Fig. 4 all the lead chelates are stable for at least 72 hours.

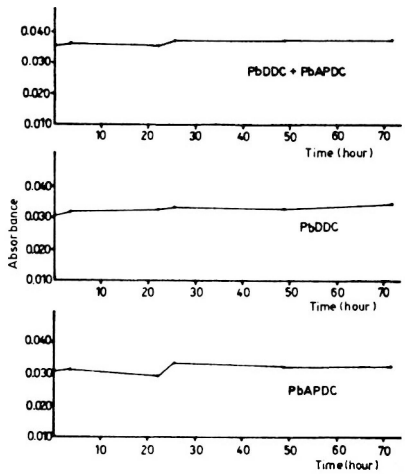


Fig. 4. Stability of the lead chelates.

RESULTS AND CONCLUSION

As is seen in Fig. 3, there is no significant effect of pH on the extraction of PbDDC+PbAPDC mixture. When all the metal ions are complexed by the chelating agent, $D=(K_d)_c$, the maximum degree of extraction has been attained regardless ofchanges in reagent concentration or pH of the aqueous phase /1/. According to the results, the mixture of APDC+NaDDC was found to be the best extraction system for lead, so the accuracy, sensitivity and the detection limit of this method were established.

a) Accuracy

Accuracy of the method was tested on two different concentrations. Ten samples were prepared in each concentration at pH 5, aqu./org=10. Accuracy of the method was expessed by coefficient of variation. Results are given in Table-4.

b) Sensitivity and Detection Limit

To determine the sensitivity, a series of standards were prepared at pH 5, NaDDC+aPDC (1:1), aqu./org=10. Calibration graphs

were prepared from these standards. Average value of sensitivities were determined by these graphs. Also detection limit - Detection Limit in AAS is the concentration corresponding to twice the standart deviation of a series of not less than ten readings taken close to the blank level- was determined and the results are given in Table-5.

TABLE-4. Accuracy

Sample conc. µgPb/ml MIBK	Standard deviation (n=10)	Coefficient of variation (n=10)
0.5	0.001	5%
5	0.002	1%

TABLE-5. Sensitivity and detection limit

Sensitivity µg/ml		Dedection Limit µg/ml
MIBK	0.16	0.10
Corresponding con.in aqu.	0.02	0.01
Aqueous phase	0.20	0.20

Same experiments were done for standard aqueous solutions. Comparison of the aqueous and organic phases are given in Table-1. As seen from the table the sensitivity of lead was increased 10 times and the dedection limit 20 times by this extraction method.

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