

## Evaluation of Two Different Extraction Techniques on Determination of Pb<sup>+2</sup> Contents of Wastes of Dye Manufacturing Industries

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### ABSTRACT

Extraction of trace amounts of toxic heavy metals from complicated environmental matrixes is a challenging task. The aim of this investigation is the comparison of the extraction efficiencies and other related experimental variables (chemicals, effect of pH, potential interfering ions) on the determination of inorganic lead (Pb<sup>+2</sup>) which is present in waste water of dye industries. Compared techniques are liquid liquid extraction followed by UV/Visible spectrophotometric determination (LLE-UV/VIS) and solid phase extraction followed by flame atomic absorption determination (SPE-FAAS). The detection limits are 23 ng.ml<sup>-1</sup> and 0.36 ng.ml<sup>-1</sup> respectively. The effects of sample flow-rate and preconcentration factor are also investigated. The experimental results indicate that preconcentration factor of 300 could be achieved. The techniques are applied for determination of Pb<sup>+2</sup> contents of wastes water of east Tehran regions.

**Keywords:** UV/Visible Spectrophotometry; Lead; Solid Phase Extraction; Flame Atomic Absorption Spectrometry

### INTRODUCTION

Lead is a toxic trace element which causes different undesirable direct and side effects in human and living organism's health. Accumulation of this toxic element in human tissues leads to harmful effects such as hematological damage, anemia, kidney malfunctioning, brain damage, renal hypertension and cancer (IARC has classified Pb as a carcinogen) [1-3]. According to public health service (PHS), the maximum level of inorganic lead in surface and underground water should not be over 0.05 mg.l<sup>-1</sup>.

Hence new approaches to conventional techniques of separation, concentration, and determination of lead have a vital importance and an individual significance in analytical and environmental chemistry. Dye industries use lead as dye pigments. Unfortunately, the amount of this toxic metal in the wastes of these industries is much higher than the allowed level, causing serious problems. The main purpose of this report is a comparison between LLE-UV/VIS and SPE-FAAS techniques on separation and determination of Pb<sup>+2</sup>. Elemental Analysis of the above mentioned wastes revealed that lead is a major constituent component of them.

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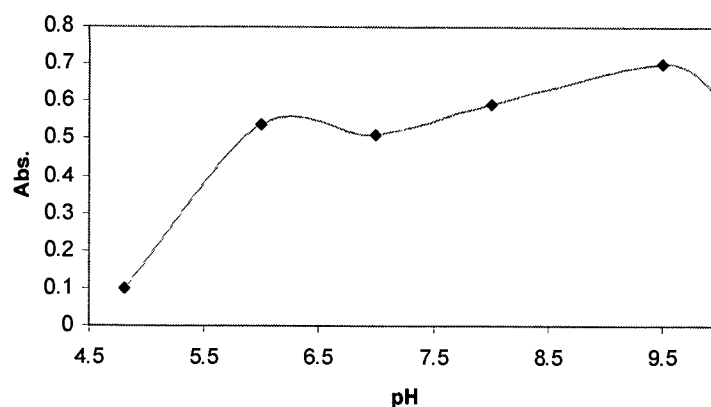


Fig.1. Effect of aqueous phase pH (5ppm) on the absorbance

#### 4. Solid Phase Extraction (SPE)

Sodium diethyl dithiocarbamates (NaDDC) is one of the best ligands for chelation and extraction of traces of inorganic lead. This reagent behaves as a bidentate univalent anionic ligand, having two donor S atoms forming stable complexes. One of the most efficient procedures for determination of trace levels of lead is solid phase extraction flame atomic absorption spectrometry (SPE-FAAS) [5-7]. This technique is fast, inexpensive and simple. Unfortunately in the case of some samples, the detection limit of this technique is not satisfactorily low. However, in the case of very low concentration of the analyte, more sensitive techniques such as electrothermal atomic absorption spectrometry (ETAAS) are recommended. However, ETAAS suffers from restrictions that predominately are: time consuming, expensive instrumentation, high relative standard deviation (RSD), need of more skilled operator and effect of different matrix interferences.

There are numerous numbers of reports concerning retention of the trace amounts of inorganic lead directly or after preliminary chelation with different ligands on solid sorbents in the literature [8-13].

The technique of SPE could be carried out by two different ways:

A) Direct addition of the ligand to the sample. This way is useful for the ligands which are hydrophilic and miscible with water.

B) Modification of the disk surface with the ligand, which is suitable for hydrophobic ligands.

4.1. *Sample Treatment*: the water samples acidified with concentrated nitric acid, the pH adjusted to 2, filtered and 5 ml of methanol was added to a 100 ml portion of each.

4.2. *Disk Cleaning and Conditioning*: after placing the disk in the apparatus, it was washed with 10 ml of methanol. To insure optimal extraction of the analyte, the disk is again washed with 10 ml of methanol immediately followed by 10 ml of water, without letting the surface of the disk to be dried. The results of improper performance of this step would be slow flow-rate

and poor analyte recoveries. It is important to avoid any air contact with the surface of the disk before the addition of sample.

4.3. *Sample Addition*: An accurate volume of the sample solution containing the certain amount of aqueous ligand solution was transferred to the top reservoir of the disk apparatus. At the same time the solution was drawn through the disk by applying a mild vacuum. Application of vacuum was continued until the disk is completely dry (about 5 minute).

4.4. *Analyte Elution*: The analyte must be selectively eluted. The disk was washed with exactly 5 ml of methanol. It was found out that methanol was the best eluting agent. The concentration of  $Pb^{+2}$  in the eluate was then determined by FAAS. The results are tabulated in Table 3.

## RESULTS AND DISCUSSION

Figure 2 shows a typical spectrum of the extracted organic phase of a standard 5 ppm solution of  $Pb^{+2}$  in the visible region. As it is seen the  $\lambda_{Max}$  of the HDZ complexes is at 520 nm. The experiment indicated that there is a linear relationship between the absorbance and concentration in the range of 5 to 25 ppm.

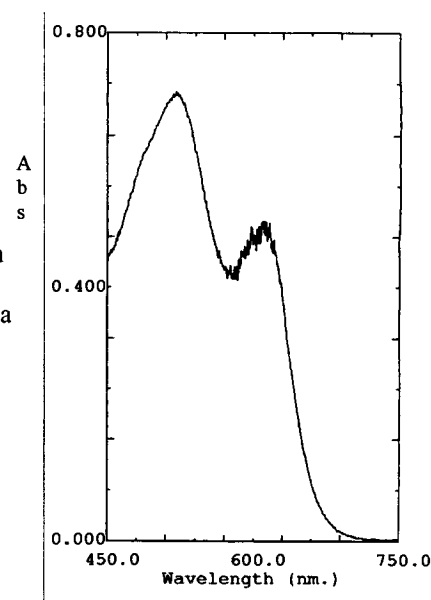


Fig. 2. Spectrum of the extracted organic phase of a standard 5 ppm solution of  $Pb^{+2}$

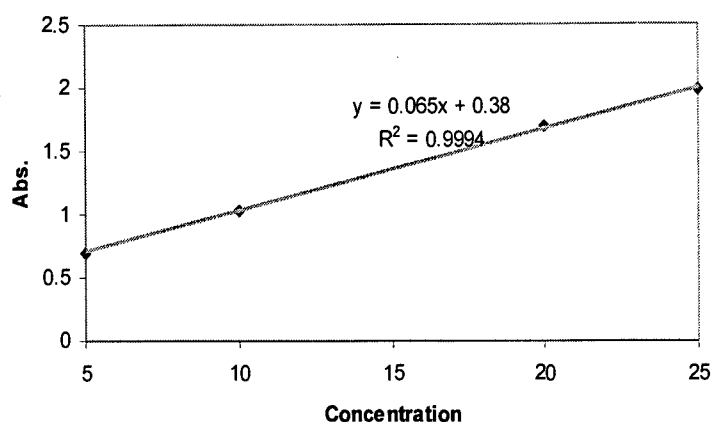


Fig. 3. Calibration curve of the extracted organic phases of HDZ complexed with  $Pb^{+2}$  standard solutions (5 to 25 ppm).

The calibration curve of organic extracted phase of lead complexes is shown in Figure 3.

The calibration curve of standard solutions of  $Pb^{+2}$  obtained by FAAS is shown in Figure 4.

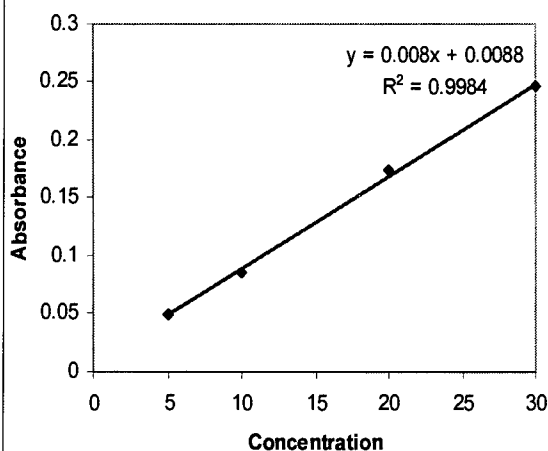


Fig.4. Calibration curve of the standard solutions of  $Pb^{+2}$  (5 to 30 ppm)

The results of the analysis of the real samples "water samples from east regions of Tehran" are listed in Table 2. As it is indicated the level of  $Pb^{+2}$  concentration in these samples are too high. In the case of sample 4 there is no need for preconcentration of  $Pb^{+2}$ .

As the extracting solvent was chloroform, it was not possible to introduce the organic phase to the flame for direct comparison of the two methods.

Solubility of NaDDC in water is 35.1 g per 100 ml at 20°C [14]. In the present work, solutions with different concentration of this ligand were prepared. It was indicated that the solution with the concentration of 0.05 %w.v<sup>-1</sup> of the ligand in water gives the best results. Meanwhile, different volumes of the above solution were checked and it was found out that a 25 ml portion of standard sample containing 125  $\mu g$  of  $Pb^{+2}$  and 1 ml of the ligand solution at pH=9.2 gives the best result.

### *Influence of Flow-Rate*

The dependence of the recovery of  $Pb^{+2}$  retained on the sorbent surface to the flow rate was also investigated.

It was found out that flow rates in the range of 5-20 ml.min<sup>-1</sup> are suitable and lead to reproducible and good recoveries. The flow rate was maintained at 10 ml.min<sup>-1</sup> throughout the experiment.

### *Potential Interfering Ions*

In order to investigate the effect of presence of interfering ions, certain amounts of each were added to the water samples. It was concluded that up to a certain concentration there would be no effect on the recovery of  $Pb^{+2}$  contents of sample. The results are tabulated in Table 4.

### *Preconcentration Factor*

In order to find preconcentration factor, the 5 ppm standard lead solution was diluted step by step to 10 ppb. It was found that a preconcentration factor of about 300 could be achieved.

### *Break through volume*

The break-through volume of the method was determined by dissolving 1.0  $\mu g$  of the  $Pb^{+2}$  in each of the 50, 100, 500, 1000 and 1500 ml portions of water. In all cases, the extraction of  $Pb^{+2}$  was found to be quantitative. Thus, the break-through volume of this method should be about 1500 ml.

### *The Limit of Detection (LOD)*

Under the optimum experimental conditions, the LOD of the two mentioned methods were estimated from  $C_{LOD} = K_b S_b m^{-1}$  where  $S_b$  is the standard deviation of the blank measurements (5 replicates) and  $m$  is the slope of the linear calibration curve. [15-16] for a numerical factor of  $K_b = 3$  the obtained LOD for LLE-UVVIS.SPEC and SPE-FAAS are 23 and 0.36 ng.ml<sup>-1</sup>, considering the preconcentration factor of 300 for the latter technique. The relative standard deviation for a 500 ml sample containing 10  $\mu g$  of

Pb<sup>+2</sup> was found to be  $\pm 2\%$  for five individual replicate determinations.

## CONCLUSION

The advantage of SPE over liquid liquid extraction is that the former is cheaper, faster and gives more accurate results. The point that should be mentioned here is that there are two types of disks. One of them is a kind which is suitable for separation of non polar complexes from mixtures

containing polar or ionic species. In this case, the eluting solvent should be an organic solvent. The second type is suitable for separation of polar species from mixtures containing non polar constituent components. In this case the eluting solvent should be acidic. Meanwhile in the latter case the surface of the disk is usually modified with a ligand.

**Table 2.** Determination of Pb<sup>+2</sup> contents of real samples

number of real sample	determined concentration by FAAS	resulted absorbance of the extracted organic phase in $\lambda_{Max}=520nm$	sampling place
1	0.9 ppm	0.699	Bumehen.Up
2	0.53 ppm	0.3	Bumehen.Down
3	0.53 ppm	0.3	Jajrood
4	21.16ppm	1.72	Tehranpars

**Table 3.** Optimization of SPE – FAAS conditions.

sample volume (ml)	ligand volume (ml)	%w.v <sup>-1</sup> ligand (in water)	pH of the medium	% recovery
25	1	0.05	6.5	70
25	2	0.05	4.8	86
25	1	0.05	9.2	100

**Table 4.** Interfering ions on the recovery of Pb<sup>+2</sup>

interfering ion	added amount ( $\mu g$ )	recovery percentage of Pb <sup>+2</sup>
Li <sup>+</sup>	1000	%99.4
Na <sup>+</sup>	1000	%99.2
K <sup>+</sup>	1000	%100
Rb <sup>+</sup>	900	%98.7
Ca <sup>+2</sup>	1000	%95.4
Sr <sup>+2</sup>	850	%99.2
Ba <sup>+2</sup>	800	%99.9
Zn <sup>+2</sup>	20	%99.9
Cu <sup>+2</sup>	15	%98.2
Ni <sup>+2</sup>	20	%98.4
Co <sup>+2</sup>	25	%99.4

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