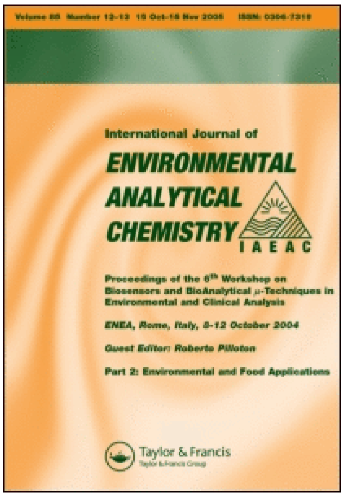

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# The Study of some Organophosphorous Compounds as Extractants for Metal Monitoring in Municipal Wastewater

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# THE STUDY OF SOME ORGANOPHOSPHOROUS COMPOUNDS AS EXTRACTANTS FOR METAL MONITORING IN MUNICIPAL WASTEWATER*

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Three organophosphorous compounds, di-(2-ethylhexyl) phosphoric acid (HDEHP), O-2-ethylhexyl-2-ethylhexyl phosphonate (HEHEHP) and di-(*n*-octyl) phosphinic acid (HDOP), have been tested as extractants for metal monitoring in municipal wastewater. Metals are back-extracted with hydrochloric acid and finally determined by flame atomic absorption spectrometry. Quantitative metal recoveries are obtained with all three extractants tested if the sample is buffered at pHs ranging from 6 to 8. High amounts of calcium, magnesium, iron and COD do not interfere with heavy metal determination.

KEY WORDS: Organophosphorous compounds, liquid–liquid extraction, metal monitoring, municipal wastewater, atomic absorption spectrometry.

## INTRODUCTION

Municipal wastewater usually contains low amounts of metals, but when biological reactors are used for wastewater treatment, an accurate metal control in both influent and effluent is needed because metal effects can range from beneficial to highly toxic for microorganisms. For example, in anaerobic wastewater treatment processes, metals like nickel, cobalt, iron and molybdenum stimulate the bacterial conversion of acetic acid to methane if they are present at low concentrations.[1,2] On the other hand, the toxicity of cadmium and some other heavy metals is well known.

Although atomic absorption spectrometry (AAS) is a powerful tool for determining metals in water, its limit of detection is too high for some environmental purposes and a preliminary sample treatment is usually needed. Liquid–liquid extraction is the most common way to concentrate metals in samples and to remove some interferences.[3] After this treatment, the organic solution is aspirated into the flame. However, the organic matter present in municipal wastewater is also extracted into the organic solvent and metal determination is not possible by the flame method. In addition, metal back-extraction is difficult when chelating reagents such as dithiocarbamates and hydroxyquinoline derivatives are used as extractants.

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Usually a sample treatment involving dry ashing and digestion with mixtures of acids[4] is needed prior to the metal determination. This method is time-consuming and it seems to be unsuitable for routine analysis.

When an acidic extractant is employed, its behaviour as a cationic exchanger allows an easy metal back-extraction by using an acidic aqueous solution, while organic matter remains in the organic phase. Then, metals can be easily determined by flame AAS. Among these acidic reagents, organophosphorous extractants which have been widely used for industrial purposes[5] seem to be appropriate for developing methodologies leading to a simpler sample work-up in metal-monitoring processes.

In the present work, three organophosphorous compounds—di-(2-ethylhexyl) phosphoric acid (HDEHP), O-2-ethylhexyl-2-ethylhexyl phosphonate (HEHEHP) and di-(*n*-octyl) phosphinic acid (HDOP)—were used as metal extractants. HDEHP has been employed for a long time in a number of industrial metal-recovery processes and for that reason it is the best known acidic organophosphorous reagent. In order to compare the behaviour of some compounds belonging to the three main groups of acidic organophosphorous compounds, phosphoric, phosphonic and phosphinic acids, reagents with similar hydrocarbon chains were studied. As no phosphinic acid containing ethylhexyl groups is commercially available, HDOP was chosen because it has been prepared for a long time in our laboratory.

The distribution of metals between the aqueous and organic phase has been studied as a function of pH and extractant concentration. In addition, some mixtures with phase modifiers such as trioctylphosphine oxide (TOPO) and tributylphosphate (TBP) that are reported to enhance extraction[6,7] in some cases, were tested. The following metals were determined: cadmium, cobalt, copper, manganese, nickel and zinc.

## EXPERIMENTAL

### Apparatus

A Cenco Instruments Rotary Mixer and a Cenco Instruments Centrifuge were used in this work.

A Perkin Elmer 2380 Atomic Absorption Spectrometer was used for determining metal concentrations.

### Reagents

All organophosphorous extractants employed were 90% pure. HDEHP was purchased from Merck, HEHEHP was supplied by Shell and HDOP was prepared as described elsewhere.[8] TOPO and TBP were purchased from Merck. Solutions (0.1 M) of the organophosphorous acidic extractants and 0.01 M solutions of the phase modifiers were prepared in toluene.

Buffer solutions: 0.1 M solutions were prepared from sodium acetate at pH 3.5, 4.3 and 5.7 and disodium phosphate at pH 6.0, 6.9 and 7.9 (p.a. reagents from Merck).

Hydrochloric acid: a 0.1 M solution was prepared from hydrochloric acid (Merck p.a.).

All experiments were carried out by using a synthetic water modelled from the Castelldefels (population 20000, located 20 km from Barcelona) municipal wastewater analysis, containing 750 ppm COD (added as phthalic acid), 200 ppm sulphate, 1000 ppm chloride, 100 ppm Mg(II), 50 ppm Ca(II) and 10 ppm Fe(III). Furthermore, 2 ppm Cd(II), Co(II), Cu(II), Ni(II), Mn(II) and Zn(II) were added.

### *Procedure*

Samples (5 ml) were introduced into a stoppered glass tube; next, 10 ml of buffer solution and 15 ml of organophosphorous extractant solution were added. The mixture was shaken mechanically for 30 min and centrifuged at 2000 rpm for 15 min. The aqueous phase was removed and 15 ml of hydrochloric acid solution were added. The mixture was shaken again for 15 min and centrifuged. Metal concentrations in the aqueous phase were determined by AAS at the following wavelengths: Cd, 228.8 nm; Co, 240.7 nm; Cu, 327.4 nm; Mn, 279.5 nm; Ni, 231.2 nm; and Zn, 213.9 nm.

## RESULTS AND DISCUSSION

Metal recoveries as a function of pH for a 0.1 M extractant concentration are shown in Table 1. Quantitative metal extraction was obtained at pH 6.0 for HDEHP, 6.9 for HDOP and 7.9 for HEHEHP. HDEHP was tested over the whole pH range, but as an emulsion is formed at pH values higher than 7, data on metal extraction cannot be given for pH 6.9 and 7.9.

In some cases, recoveries of over 100% are obtained. This is probably due to the reagent distribution between the two phases, since the presence of an extractant in the aqueous phase increases the measured value, a phenomenon for which no correction was made.

When cationic exchangers are used, the optimum extraction pH depends on the acidity constant of the extractant. Thus, HDEHP extracts metals at a lower pH than the other reagents according to the acidity constant sequence: phosphoric > phosphonic > phosphinic. However, the results obtained for HDOP and HEHEHP are not consistent with this prediction. This can possibly be explained by the fact that the hydrocarbon chains of HDOP are slightly different from those of HDEHP and HDOP. As it has been previously reported,[9] a change in the hydrocarbon chains can alter the extraction pH.

The effect of several phase modifiers on the extraction was studied as a function of the pH. The extractant concentration was kept constant at 0.1 M; the phase modifier concentration was 0.01 M. When organophosphorous compounds are

**Table 1** Effect of pH on metal recoveries[a]

| *Metal* | *Extractant* | *pH* | | | | | |
|---|---|---|---|---|---|---|---|
| | | 3.5 | 4.3 | 5.7 | 6.0 | 6.9 | 7.9 |
| Cd(II) | HDHEP | 64 | 98 | 99 | 98 | — | — |
| | HDOP | 15 | 53 | 101 | 102 | 103 | 102 |
| | HEHEHP | * | 9 | 83 | 95 | 99 | 103 |
| Co(II) | HDHEP | 19 | 73 | 93 | 102 | — | — |
| | HDOP | * | 48 | 86 | 99 | 97 | 96 |
| | HEHEHP | * | 81 | 105 | 100 | 96 | 97 |
| Cu(II) | HDHEP | 32 | 83 | 90 | 96 | — | — |
| | HDOP | * | 48 | 90 | 86 | 93 | 86 |
| | HEHEHP | * | 81 | 105 | 96 | 101 | 97 |
| Mn(II) | HDHEP | 90 | 99 | 92 | 98 | — | — |
| | HDOP | 27 | 72 | 99 | 94 | 105 | 86 |
| | HEHEHP | * | 93 | 102 | 98 | 101 | 99 |
| Ni(II) | HDHEP | * | 15 | 82 | 99 | — | — |
| | HDOP | * | * | 21 | 34 | 91 | 102 |
| | HEHEHP | * | * | * | 30 | 63 | 97 |
| Zn(II) | HDHEP | 103 | 101 | 94 | 97 | — | — |
| | HDOP | 16 | 63 | 77 | 81 | 97 | 96 |
| | HEHEHP | 40 | 71 | 82 | 102 | 102 | 104 |

[a] 0.1 M extractant in toluene; total metal ion concentration, 2 ppm; results are mean of 5 determinations.

*Metal recovered <0.1%.

used as extractants and the pH is kept constant, synergism will result in an extraction enhancement; this effect has not been observed in the present study.

The dependence of the metal recovery on the extractant concentration is shown in Figs 1–3. The experiments were carried out at the optimum extraction pH. The results indicate that quantitative metal recovery occurs with at least 0.1 M HDEHP, HDOP or HEHEHP solutions. All metals, except Cd(II), are quantitatively extracted at a 0.05 M HDEHP or HEHEHP concentration, but only Zn(II), Co(II) and Mn(II) are extracted at this concentration with HDOP. Cd(II) and Ni(II) are not easily extracted because organophosphorous reagents are usually designed in order to separate pairs of metals, mainly zinc and cadmium and cobalt and nickel[10] from mineral leachates under specific conditions.

In spite of the somewhat poorer efficiency of HDOP with regard to the extraction of Cd(II), Cu(II) and Ni(II), the differences in the behaviour of the three reagents tested are not really significant. Criteria for selecting one of them should take into account mainly the metals to be determined. High amounts of, e.g., sulphate, chloride, Ca(II), Mg(II), Fe(III) or organic matter were found to have no effect on metal recoveries.

For each metal ion, a set of 10 determinations was carried out with HDEHP at pH 6.0. Relative standard deviations ranged from 1.0 to 1.5% for all metals tested.

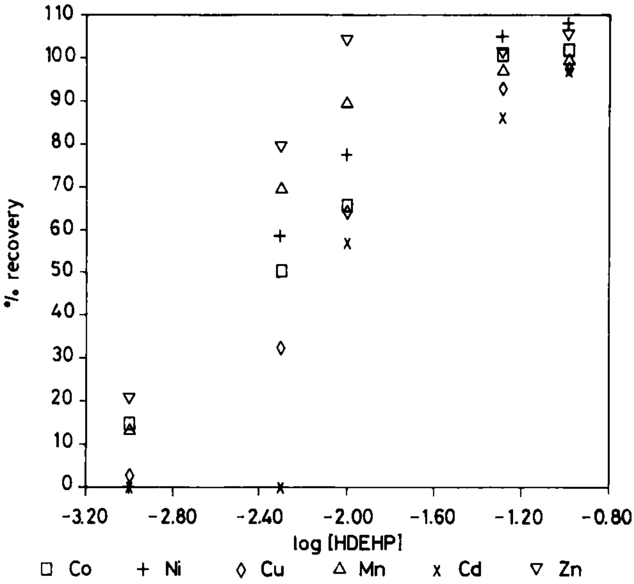

Figure 1 Effect of HDEHP concentration on metal recovery at pH 5.96.

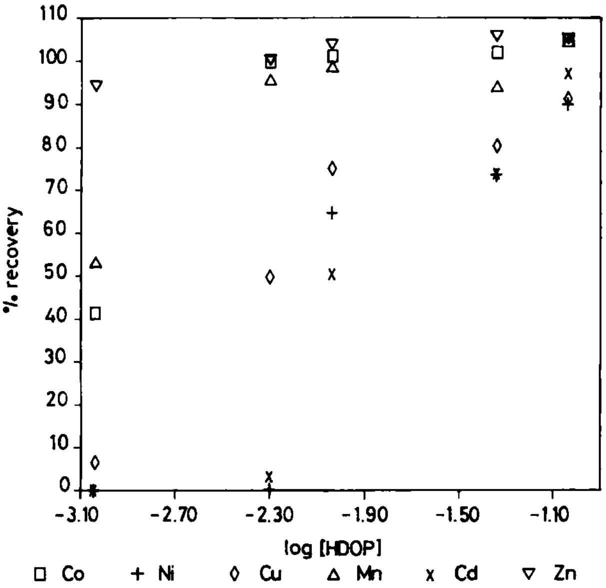

Figure 2 Effect of HDOP concentration on metal recovery at pH 6.88.

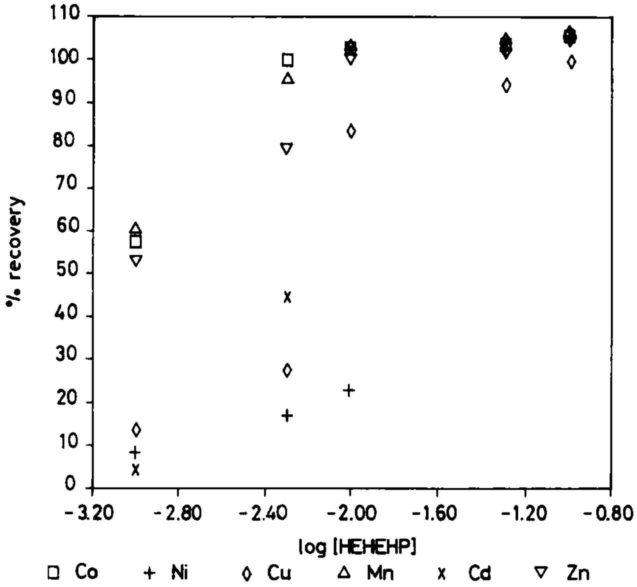

Figure 3 Effect of HEHEHP concentration on metal recovery at pH 7.92.

## CONCLUSIONS

Organophosphorous acidic derivatives are suitable for heavy metal determination in municipal wastewater by using a liquid–liquid extraction work-up procedure. Quantitative metal recoveries are obtained at extractant concentrations from 0.1 M if the sample is buffered; the optimum extraction pH is 6 for HDEHP, 7 for HDOP and 8 for HEHEHP. The addition of phase modifiers has no influence when the extractant-to-modifier concentration ratio is 10. Hydrochloric acid is an adequate reagent in the metal back-extraction process. Furthermore, high levels of foreign species do not interfere with the heavy metal determination.

### *Acknowledgements*

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