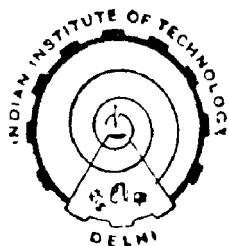


ANALYTICAL APPLICATIONS OF SOME COMMERCIAL CHELATING EXTRACTANTS

by

VISVANATHAN RAMESH

Thesis submitted to
Indian Institute of Technology, Delhi
for the award of the degree of
DOCTOR OF PHILOSOPHY



Department of Chemistry
INDIAN INSTITUTE OF TECHNOLOGY, DELHI.
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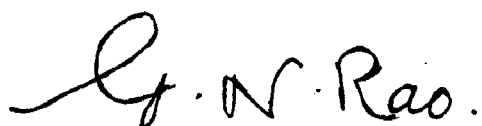
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TO

MY PARENTS

C E R T I F I C A T E

This is to certify that thesis entitled
"ANALYTICAL APPLICATIONS OF SOME COMMERCIAL
CHELATING EXTRACTANTS" by Visvanathan Ramesh
is a record of original bonafide research
carried out under my supervision and has not
been submitted elsewhere for a degree.

A handwritten signature in black ink, reading "G.N. Rao." with a stylized flourish at the end.

(G.N. Rao)

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A C K N O W L E D G E M E N T S

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ABSTRACT

Extraction of some selected metals (Cu(II), Zn(II), Cd(II), Mn(II), Ni(II), Rh(III), Fe(II), Fe(III), Co(II), Pb(II), Pd(II) and Sb(III)) with the following commercial extractants containing different functional groups:

(a) LIX26 (substituted 8-hydroxyquinoline) (b) LIX54 (substituted β -diketone) (c) LIX864 (a mixture of substituted aromatic and aliphatic hydroxyoxime) (d) LIX622 (substituted salicylaldoxime) has been studied. Since both the extractants and their corresponding metal chelates are soluble to a greater extent in various organic solvents, they can be used to extract some of these metals both in macroscale as well as micro scale; $pH_{1/2}$ values and $\log K_{ex}$ values in all the systems wherever it is possible have been calculated. The order of extraction of metals with LIX26 extractant (1% v/v in MIBK):

$Pd(II) < Cu(II) < Sb(III) < Fe(II) < Co(II) < Zn(II) < Ni(II)$
 $< Pb(II) < Mn(II) < Cd(II)$ agrees ^{approximately} with the order of extraction of metals with 0.01 M oxine in chloroform:
 $Fe(III) < Cu(II) < Ni(II) < Co(II) < Zn(II) < Cd(II) < Pb(II)$
 $< Mn(II)$.

Similar trends in the extraction of metals with the other commercial extractants and their corresponding parent analogues has been observed. Quantitative separation

of metals which are feasible using these extractants have been indicated.

LIX26 appears to be very promising extractant for the preconcentration of trace metals present in various samples. Preconcentration of some selected metals present in urine, water, soils, milk and lubricating oils using LIX26 extractant followed by their determination using atomic absorption spectrophotometry have been investigated and the analytical method is found satisfactory.

Synergistic enhancement of manganese(II) extraction of benzoyltrifluoroacetone (BTA) or 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (BMPP) with the auxiliary ligands like pyridine N-oxide (PNO), 2-methyl pyridine N-oxide (2MPNO), 4-methyl pyridine N-oxide (4 MPNO), dibenzylsulfoxide (DBSO) and 8-aminoquinoline (8AQ) has been observed. From the distribution data, extraction constants and adduct formation constants have been computed. The extracted adduct species have been identified.

Mass spectra of chelates of thenoyltrifluoroacetone with copper(II), lead(II), and cadmium(II) have been studied. Since different ion dissociation mechanisms are likely ^{depending} on the nature of the metal, probable fragmentation patterns have been indicated based on the experimental data.

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