بسم الله الرحیم

۲۸۸۶۲

IN THE NAME OF GOD

DETERMINATION OF TRACE AMOUNTS OF SOME
TRANSITION METALS BY ADSORPTIVE AND CATALYTIC
ADSORPTIVE STRIPPING ANALYSIS

&

SELECTIVE AND EFFICIENT UPHILL TRANSPORT OF SOME
TRANSITION METAL IONS THROUGH BULK LIQUID
MEMBRANE

BY

ESMAEIL SHAMS SOOLARI

THESIS

SUBMITTED TO THE SCHOOL OF GRADUTE STUDENT IN
PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY (Ph. D.)

IN

ANALYTICAL CHEMISTRY

SHIRAZ UNIVERSITY

SHIRAZ, IRAN

EVALUATED AND APPROVED BY THE THESIS COMMITTEE AS: EXCELLENT

.... A. Safavi, Ph. D., Prof. of Chemistry (Chairman)

.... S. M. Golabi, Ph. D., Prof. of Chemistry

(Tabriz University)

.... M. Shamsipur, Ph. D., Prof. of Chemistry

(Razi University)

.... A. Abaspour, Ph. D., Asist Prof. of Chemistry

.... M. Akhoond Ph. D., Asist Prof. of Chemistry

JANUARY 1999

۲۵۸۲۸

ABSTRACT

DETERMINATION OF TRACE AMOUNTS OF SOME
TRANSITION METALS BY ADSORPTIVE AND CATALYTIC
ADSORPTIVE STRIPPING ANALYSIS

&

SELECTIVE AND EFFICIENT UPHILL TRANSPORT OF SOME
TRANSITION METAL IONS THROUGH BULK LIQUID
MEMBRANE

BY

Esmaeil Shams Soolari

A sensitive and selective procedure is presented for the voltammetric determination of copper. The procedure involves an adsorptive accumulation of copper pyrogallol red on a hanging mercury drop electrode, followed by a stripping voltammetric measurement of reduction current of adsorbed complex at -0.2 V (vs. Ag/AgCl). The optimum conditions for the analysis of copper include pH ($3.0 - 4.5$), 20 μM pyrogallol red and an accumulation potential of -0.1 V (vs. Ag/AgCl). The peak current is proportional to the concentration of copper over the range $0.4 - 60$ ng.ml^{-1} with a detection limit of 0.07 ng.ml^{-1} with an accumulation time of 60 s. The method was applied to the determination of copper in some analytical grade salts and also in cow's liver tissue.

A very sensitive and selective catalytic adsorptive cathodic stripping procedure for trace measurements of cobalt is presented. The

method is based on adsorptive accumulation of the cobalt-MTB (methyl thymol blue) complex onto a hanging mercury drop electrode, followed by reduction of the adsorbed species by voltammetric scan using differential pulse modulation. The reduction current is enhanced catalytically by nitrite. The optimum conditions for the analysis of cobalt include pH 9.0 (ammonia buffer), 2.0 μM methyl thymol blue, 0.8 M sodium nitrite and an accumulation potential of -0.5 V (vs. Ag/AgCl). The peak current is proportional to the concentration of cobalt over the entire concentration range tested (0.02 – 500 ng.ml^{-1}) with a detection limit of 0.005 ng.ml^{-1} using an accumulation time of 60 s. The method was applied to determination of cobalt in real and spiked samples with satisfactory results. A mechanism for the reaction has been proposed.

A highly selective and sensitive procedure is presented for the determination of ultra-trace amounts of molybdenum by catalytic adsorptive stripping voltammetry. The method is based on adsorptive accumulation of molybdenum –MTB (methyl thymol blue) complex onto a hanging mercury drop electrode, followed by reduction of the adsorbed species by voltammetric scan using differential pulse modulation. The reduction current is enhanced catalytically by chlorate. Optimal analytical conditions were found to be MTB concentration of 0.8 μM, pH of 2.5, a chlorate concentration of 0.5M, and an adsorption potential at 100 mV vs. Ag/AgCl. The peak current is proportional to the concentration of molybdenum over the 0.01 to 150 ng.ml^{-1} range with a detection limit of 0.002 ng.ml^{-1} using an accumulation time of 60 second. The effect of potential interfering ions were studied, and it was found that the proposed procedure is free

from interferences of common interfering ions such as tungsten, iron and etc. The procedure is applied to the determination of molybdenum in a mineral water sample and some analytical grade salts with satisfactory results. It was found that, the cathodic wave in the molybdenum-MTB complex has adsorptive character, and the reduction of complex shows catalytic character in the presence of chlorate.

Methyl red was used as an excellent carrier for the uphill transport of Hg(II) through bulk liquid membrane. By using iodide as a metal acceptor and in the presence of sulfuric acid in receiving phase the amount of mercury transport across the bulk liquid membrane was about 90% after 180 min. By replacement of the above receiving phase with 0.45 M HCl, a simpler and more reproducible system was obtained. Oleic acid was used to overcome a minor leaching of the carrier into the aqueous phase at high acid concentrations. This system was optimized with a simplex optimization program. Under optimum conditions, the amount of Hg(II) transport across the liquid membrane is about 80% after 150 min.· The carrier can selectively and efficiently transport Hg^{2+} ion from aqueous solution containing other cations such as Cd^{2+}, Zn^{2+}, Cu^{2+}, Mg^{2+}, Ca^{2+}, Ag^{+}, Ni^{2+}, Al^{3+}, Na^{+}, Pb^{2+}, Fe^{3+} and Pd^{2+}.

The facilitated transport of Au(III) from cyanide solutions through a bulk liquid membrane is reported. The organic phase consisted of a chloroform solution containing Victoria blue dye as the $Au(CN)_4^-$ carrier. The effects of pH of the source phase, potassium cyanide concentration in source phase, Victoria blue concentration in the organic phase and sodium hydroxide in the receiving phase on the

efficiency of transport process were examined. Under optimum conditions the extent of $Au(CN)_4^-$ transport across the liquid membrane was about 97% after 180 min. The carrier can selectively and efficiently transport $Au(CN)_4^-$ ion from aqueous solutions containing other cations such as alkali and alkaline earth , Zn^{2+} ,Pb^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Ag^+, Co^{2+}, Fe^{2+},Pt^{2+}, Pd^{2+} and Ni^{2+}.

Transport of Ag^+ as $Ag(CN)_2^-$ ions through a bulk liquid membrane is reported. The bulk liquid membrane used is a solution of Victoria blue (VB) in chloroform. The effects of pH of the source phase, cyanide concentration in source phase, sodium hydroxide in receiving phase and VB concentration in organic phase on the efficiency of transport system were studied. The above system has a high selectivity for Ag^+ and can selectively and efficiently transport $Ag(CN)_2^-$ ion from aqueous solutions containing other cations such as alkali and alkaline earth, Zn^{2+}, Pd^{2+}, Cu^{2+}, Cd^{2+},Hg^{2+}, Co^{2+}, Fe^{2+}, Pd^{2+}, Ni^{2+} and Al^{3+}.

ACKNOWLEDGMENT

I whish to acknowledge my indebtedness to Professor Afsaneh Safavi, my supervisor, for her fruitful guidance and inestimable comments.

I would also like to express my appreciation to the members of the thesis committee for their valuable suggestions.

Finally, my special thanks are due all my friends.

DEDICATED TO:

My Teachers

LIST OF CONTENTS

Content	Page

Content   Page

Content

Content

Content