



ANALYTICAL APPLICATIONS OF N-*n*-OCTYLCYCLOHEXYLAMINE (N-*n*-OCA)

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ABSTRACT:

To synthesize the reagent N-*n*-octylcyclohexylamine (N-*n*-OCA) high molecular weight amine using cyclohexylamine and octyl bromide in acetonitrile at room temperature. The synthesized N-*n*-Octylcyclohexylamine (N-*n*-OCA) is characterized by NMR spectrum and GC- MS data. The N-*n*-octylcyclohexylamine used as analytical extractant for the extraction, separation and determination of Cr(VI), Cd(II) and Pb(II). N-*n*-OCA is an ion-pair reagent forming a neutral complex. The optimum extraction conditions were determined from a critical study of effect of acid, concentration of N-*n*-OCA, equilibrium time, study of solvents, loading capacity, and stripping. Stoichiometry of the extracted ion-pair complex determined by slope ratio method. The method has been extended to separation and estimation of Cr(VI), Cd(II), and Pb(II) in the presence of diverse ions, binary mixture of associated metal ions, multicomponent mixture, water samples and sequential.

Keywords: Separation of Cr(VI), Cd(II), and Pb(II); N-*n*-OCA; Real samples analysis

SOLVENT EXTRACTION BY HIGH MOLECULAR WEIGHT AMINES:

Amines are one of the most commonly known classes of solvent extraction technology, having been used industrially for the recovery of many metals. Organic solutions of high molecular weight amines and amines salts have been shown to be excellent extractant for mineral acids, many organic acids and complex metal acids from aqueous solutions. The analytical radio chemist and

process development chemist have been found the technique valuable for a wide variety of separations.

Smith and page [1] first reported that the acid binding properties of high molecular weight amines and amines depend on fact that acid salts of these bases are, in general, essential insoluble in water but rapidly soluble in organic solvents, such as chloroform, xylene, toluene, kerosene or 1,2-dichloroethane. The extraction reactions are of the following ion association type[1-4].

[1] The organic solvent containing amines can extract an a aqueous acid to form an amine salt in the organic phase:



Where,

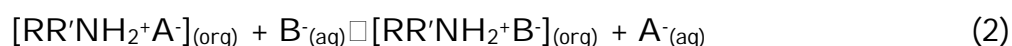
RR'NH = A high molecular weight secondary amine.

A⁻ = Anion of either a single acid or a complex metal acid.

aq = Aqueous phase. org = Organic phase.

In alkaline solution, the extraction is reversed.

[2] An amine salt in the organic phase can undergo anion exchange with an ion in the aqueous phase:



METHODOLOGY:

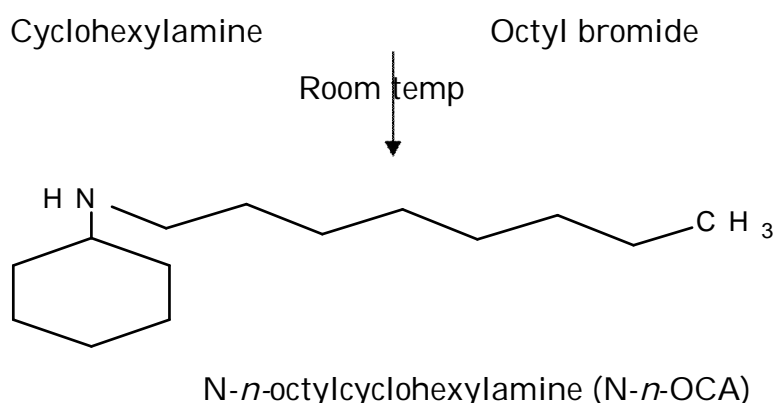
1 Chemicals:

Cyclohexylamine [s. d. fine-chem, A. R grade], acetonitrile (s. d. fine-chem), octyl bromide (s. d. fine-chem), acetone, dichloromethane (DCM) and xylene, are used in the synthesis of N-*n*-octylcyclohexylamine.

2 Synthesis of N-*n*-octylcyclohexylamine (N-*n*-OCA):

Cyclohexylamine (10 mL, 8.65 mole) and octyl bromide (10 mL, 11.18 mole) were mixed in 20 mL acetonitrile at room temperature. The reaction mixture was warmed and stirred for 2 h. The amorphous white product was

precipitated. The product was filtered through Whatmann filter paper no 1 and washed with acetone. The compound was dried and weighed [5-8].



The synthesized N-*n*-Octylcyclohexylamine (N-*n*-OCA) is characterized by NMR spectrum and GC- MS data.

APPLICATIONS:

1 Effective removal of chromium(VI) from electroplating waste water and tannery effluents using N-*n*-octylcyclohexylamine:

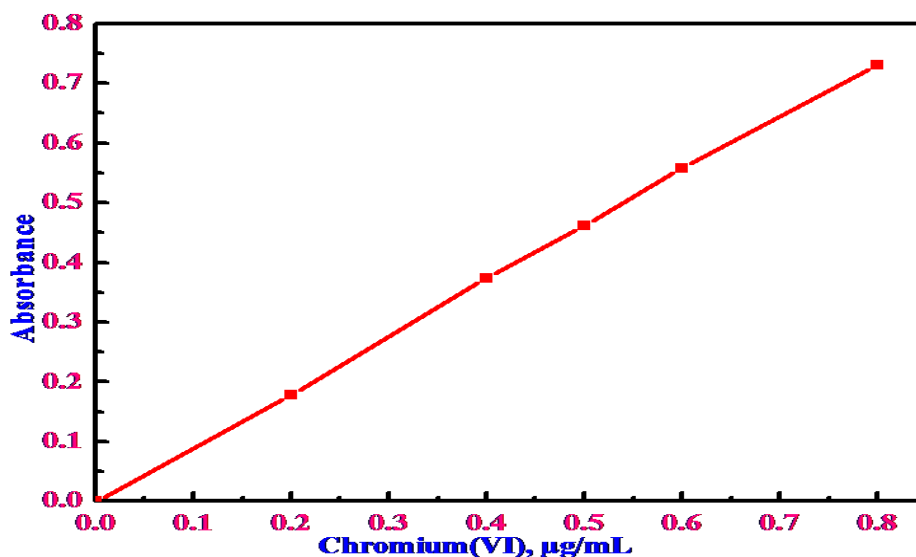
The abundance of chromium in earth crust is 0.014 % [9]. The chromium is most valuable element in various industries like electroplating, metal finishing processes [10], dyes, pigments and tannery industries [11]. Chromium is unreactive or passive at low temperatures because, it is protected by surface coating of oxide. It is because of this passive behavior that chromium is extensively used for electroplating onto iron and other metals to prevent corrosion [12-13]. But on the other side, impact of chromium(VI) pollution is increasing day by day in environment. The toxicity of chromium compounds depends upon its oxidation state [14-15]. The role chromium in biological processes and evidences that chromium is requisite element in human and animal nutrition has been recently reviewed [16]. This evidence poses a need for a rugged and commonly applicable method of measuring the concentration of chromium in foods and other biological materials [17-19]. Chromium(III) is relatively less toxic whereas chromium(VI) has greater potential of toxicity. Human toxicity includes lung cancer as well as kidney, liver and gastric damage.

Therefore the exposure of chromium(VI) has been recognized by national and international organizations. The permissible exposure limits in the air for chromium(VI) is $5.0 \mu\text{g}/\text{m}^3$ [20]. The international agency for research on cancer (IARC) has classified chromium(VI) in group I as a human carcinogen [21]. In environmental air, chromium particulates play a role in the oxidation of sulphur dioxide and the formation acidic aerosols involved in global acid rain [22]. The European commission (Directive 98/83/EC) established $50 \mu\text{g}/\text{L}$ as the maximum permissible limit of total chromium in drinking water, similar to the one established by the world health organization (WHO). The Italian regulation defined a maximum allowable concentration of $2 \text{ mg}/\text{L}$ (on a dry basis) for chromium in soils for private use and a maximum acceptable concentration of $150 \text{ mg}/\text{L}$ for total chromium [23].

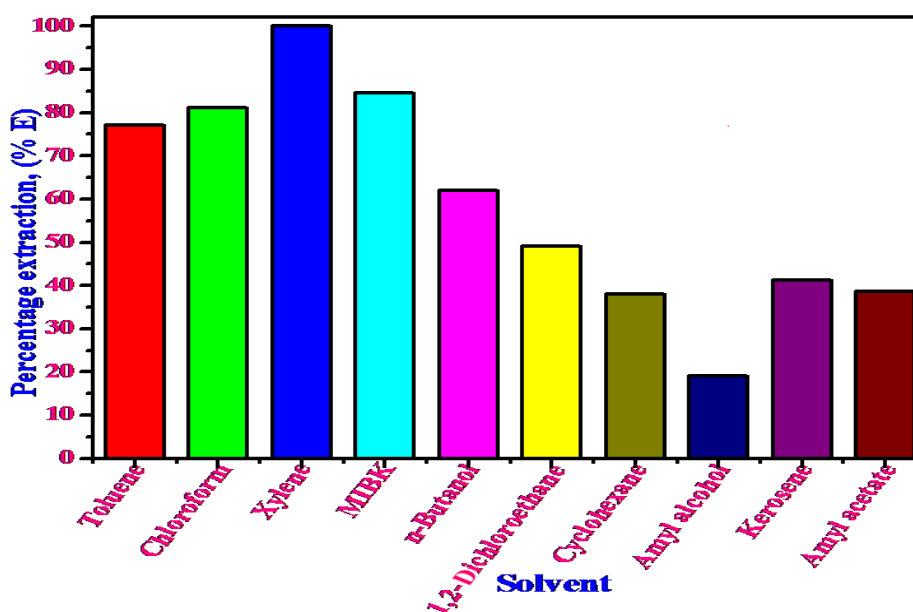
A rapid and selective liquid-liquid extractive system was developed for chromium(VI) by employing *N-n*-OCA reagent and xylene as diluent. Quantitative extraction of chromium(VI) was observed in the concentration range of 0.4 to 0.7 M HCl. The extracted ion-pair complex $[\text{N-n-OCAH}^+ \text{CrO}_3\text{C1}^-]_{(\text{org.})}$ from the organic phase was back extracted by 6.0 M ammonia ($3 \times 10 \text{ mL}$) and spectrophotometrically quantified. Various parameters were explored to study their influence on quantitative extraction of chromium(VI) by varying *N-n*-OCA concentration, equilibration time, effect of diluents, acid concentration and diverse ions. Stoichiometry of the extracted complex showed 1:1:1 ratio of metal, acid and amine. Relative standard deviation of the developed method is 0.09 with respect to calibration range 0.2 to $0.8 \mu\text{g mL}^{-1}$. The validity of the proposed method was checked by applying it to the associated and toxic metals in binary, synthetic mixtures and ternary effluents.

Beer-Lambert law of chromium(VI):

chromium(VI) = 0 to $80 \mu\text{g}$; Wavelength = 546 nm ; Diphenylcarbazide = 0.25%



Effect of solvent on extraction of chromium(VI)



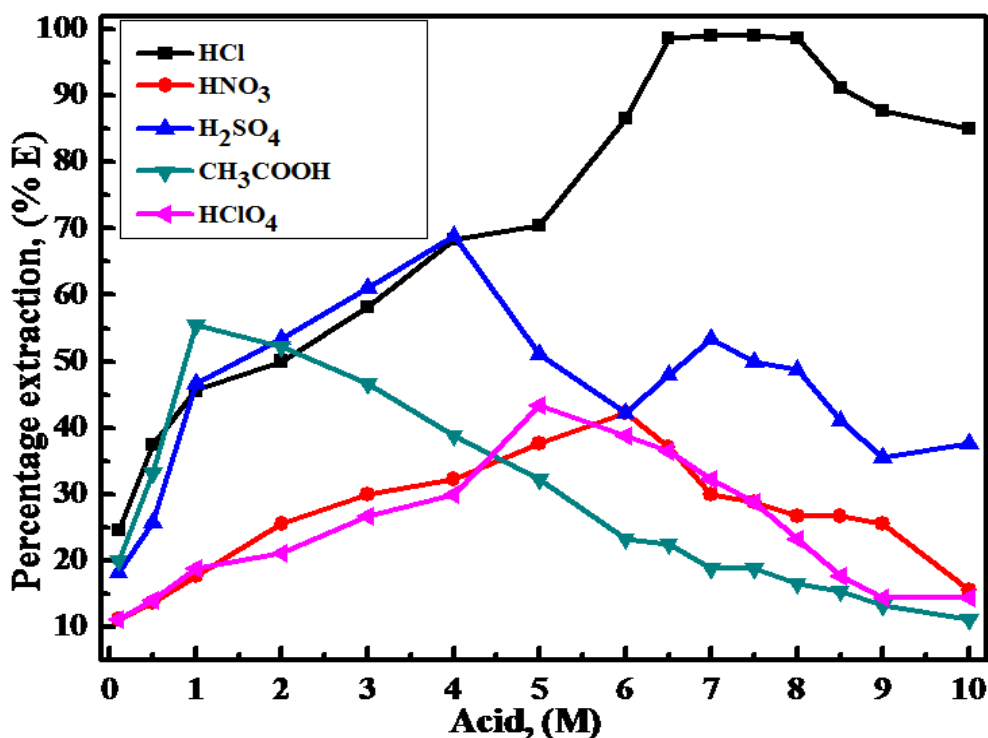
2 Rapid removal of cadmium(II) from real samples by using N-n - octylcyclohexylamine: liquid-liquid extractive anion exchange study:

Environmental pollution is a serious increasing problem that it controlled need necessary against action. A large amount of toxic micro-organic and organic materials has recently discharged into the nature resource from industries waste and cause serious air pollution, soil pollution and water pollution due to contaminated harmful chemical materials [24]. The toxic metals are also commonly manufacturing, paint industries and coating industries, mining, metallurgical processes; nuclear power plants and many other industries [25-26].

The toxic (element) metal separation of waste is compulsory before to discharge in industrial waste in the environment. Among the toxic metal cadmium ion have attention toward it health because it's harmful in nature [27].

Many attempts are being accomplished to investigate power and efficient techniques for separation or keep down the cadmium concentration in the wastewater or industries (sewer water) effluents to save the environment [28]. Based on the concentration of cadmium effluents (waste water) and associated other ion (financial value) cost of treatment, so many processes carried out, e.g., physical treatment (ion exchange) adsorption form (location) and separation process [29] (reverse osmosis, ultra filtration, and solvent extraction). A chemical precipitation technique also used today [30]. Solvent extraction processes or liquid-liquid extraction processes with organic liquid extractant in mixer-settler type reactor (SX) [31] has reported. This technique most used for recovery and removal of the heavy metal in hydrometallurgy processes [32]. It is fascinating technology for separating and enriching metal ion from lower concentration solution based on the exact choice of (highly) extremely selective extractant molecule for in demanded metal [33]. Cadmium has wide application in the manufacturing of alloys, batteries, pigments and metal plating [34]. The recovery and recycling of cadmium from these waste materials is necessary protect the environmental from hazard.

A simple and rapid liquid-liquid extractive system was presented for cadmium(II) with *N-n*-octylcyclohexylamine (*N-n*-OCA) in xylene. Extraction cadmium(II) was found to be quantitative from hydrochloric acid medium (6-9 M). Extracted ion-pair complex was back stripped with 3 M nitric acid (3 × 10 mL) and was determined by EDTA titrimetrically. The stoichiometry of the extracted $[(N-n-OCAH^+)_2.CdCl_4^{2-}]_{(org)}$ ion-pair complex was determined by slope analysis method and it was found as 1:4:2 (metal: acid: extractant). Various parameters like concentration of *N-n*-OCA, equilibrium time, the effect of diluents, acid concentration were optimized for quantitative extraction of cadmium(II). The applicability of the proposed method was studied for diverse ions, binary separation, multicomponent mixtures, alloy samples as well as separation cadmium(II) from cigarette tobacco sample.



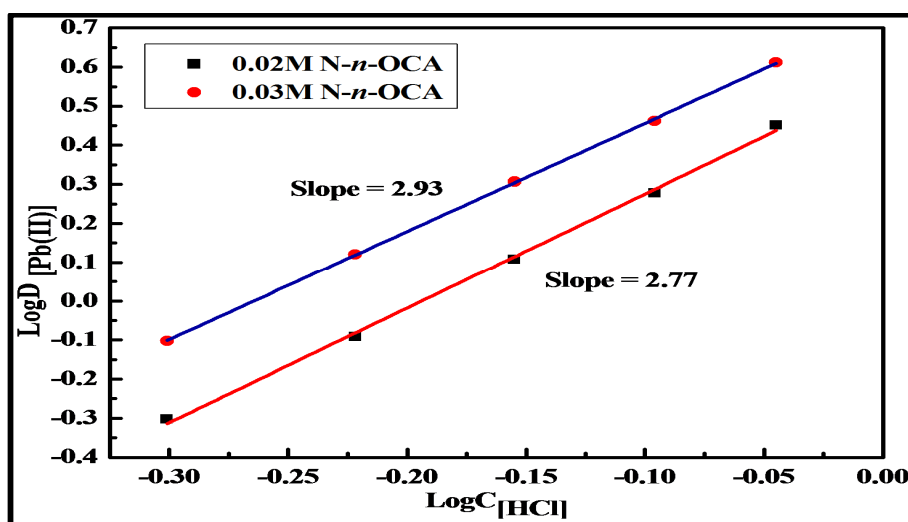
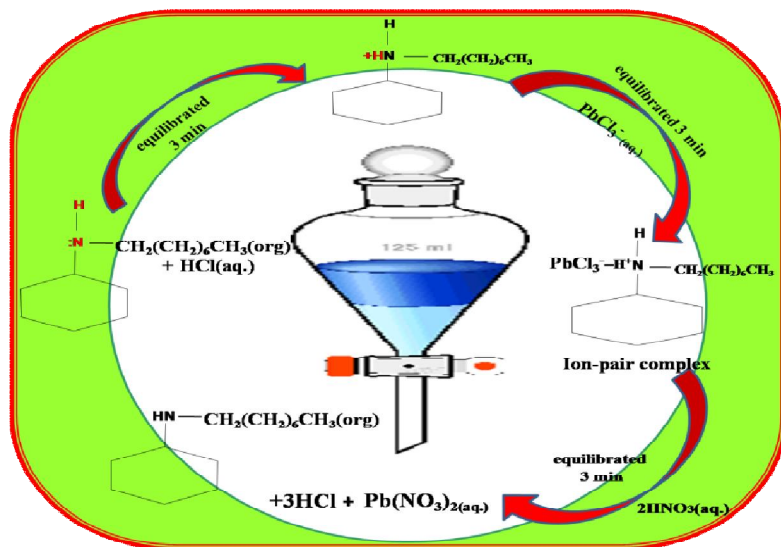
Effect of varying acid concentration

3 Liquid-liquid extraction and separation of lead(II) by using *N-n*-octylcyclohexylamine as an extractant : analysis of real samples:

Now a day's lead(II) and its compounds contamination in the environment is a very important problem of worldwide consulting due to its highly toxic nonbiodegradable in nature [35]. Lead(II) is a well known cumulative poison, found in environment mostly because of mining and smelting, batteries manufacturing and its use as additive in feature [36-38]. Concern about the toxicity of lead(II) brought many substitutions in some application such as plumbing, painting etc [39]. For many years solvent extraction has been one of the most used techniques for the removal and separation of heavy metal ions in pilot plant level as well as industrial skill process. General advantage of solvent extraction over a tridimensional method used as waste waters treatment (chemical precipitation, coagulation-flocculation, ion-exchange, adsorption membrane filtrate) is highly selective metal recovery from aqueous solution during continuous process. It required low inventory of organic phase, low energy consumption, low capital operating cost, good selectivity and mass transfer in one step [40].

Lead can cause the harmful to health even in the trace amount [41]. Lead was highly toxic, damage to nervous system, kidney, many organ and reproductive system [42]. The sulfhydryl group of proteins, metabolism and biological system, it also effects on hemoglobin system [43]. The World Health Organization (WHO) authorities try to control the level of lead in environmental. The Pollution Control Department (PCD) of Thailand allows in ground and drinking water levels are 0.05 mg/L and 0.2 mg/L for industrial effluent, lead pollution was very dangerous to environment, animal, plant, birds and human [44].

A method was discussed for the determination of the micro amount of lead(II). *N-n*-octylcyclohexylamine (*N-n*-OCA) was employed as an ion-pair forming a neutral $[N-n-OCAH^+PbCl_3^-]$ complex from hydrochloric acid medium. The quantitative extraction of lead(II) was observed with *N-n*-OCA (0.03 to 0.055 M) in dichloromethane (DCM) and xylene mixture (1: 4) from hydrochloric acid medium (3.0 to 5.0 M). The extracted ion-pair complex was back stripped with 0.5 M nitric acid and determined by spectrophotometrically with 4-(2-Pyridylazo) resorcinol (PAR). The quantitative extraction of lead(II) was found in DCM : xylene ratio 1: 4 as a mixed solvent system. The various parameters studied like concentration of acid, *N-n*-OCA concentration, equilibrium time, solvent study, back stripping agents, loading capacity were optimized for quantitative extraction of lead(II). The stoichiometry of the extracted ion-pair complex was determined on the basis of the slope analysis method it was found to be the 1: 3: 1 (metal: chloride: extractant). The applicability of the proposed method was successfully applied to the analysis diverse ions, binary mixture of associated metal ions, ternary mixtures, alloys, ayurvedic samples and water samples by using *N-n*-OCA and lead(II) was determined with the 4-(2-Pyridylazo) resorcinol (PAR) and results of analysis were confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-OES).



Determination composition of the extracted species $\text{LogD}_{[\text{Pb(II)}]}$ vs $\text{LogC}_{[\text{HCl}]}$ by slope analysis method

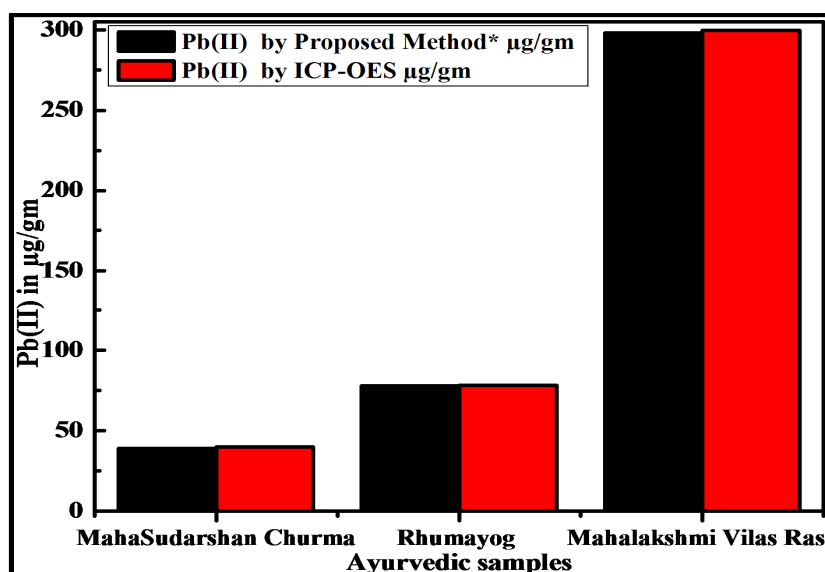


Fig. Separation and determination of lead(II) from ayurvedic samples

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