

**In The Name of God**



Razi University

**Faculty of Chemistry**

**Department of Analytical Chemistry**

## **Ph.D. Thesis**

### **Title of the Thesis:**

*Synthesis and characterization of novel ion-molecular-imprinted polymeric nanoparticles for very fast and highly selective recognition of some metal ions*

**&**

*Determination and extraction of some organic compounds by dispersive liquid- liquid microextraction using high performance liquid chromatography*

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***Beshare Hashemi***

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**Dedicated to:**

**My Mother for all of Her Patience,**

**Love and Wonderful Support.**

## Abstract

### Part One

A new nano-sized silver(I) ion-imprinted polymer (IIP) was prepared via precipitation copolymerization using ethyleneglycol dimethacrylate, as a cross-linking agent in the presence of  $\text{Ag}^+$  and an aza-thioether crown containing a 1,10-phenanthroline subunit as a highly selective complexing agent. The imprint silver(I) ion was removed from the polymeric matrix using a 1.0 M  $\text{HNO}_3$  solution. The resulting powder material was characterized using IR spectroscopy and scanning electron microscopy. The SEM micrographs showed colloidal nanoparticles of 52 nm in diameter and slightly irregular in shape. The optimal pH for quantitative enrichment was 6.0 and maximum sorbent capacity of the prepared IIP for  $\text{Ag}^+$  was  $18.08 \mu\text{mol g}^{-1}$ . The relative standard deviation and limit of detection ( $\text{LOD} = 3S_b/m$ ) for flame atomic absorption spectrometric determination of silver(I) ion, after its selective extraction by the prepared IIP nanobeads, were evaluated as 2.42% and  $2.4 \mu\text{g L}^{-1}$ , respectively.

An analysis method reported for preparation of potassium ion- imprinted nanoparticles using cryptand C222 as a complexing agent, methacrylic acid (MAA) as the functional monomer, ethyleneglycol dimethacrylate (EGDMA) as the crosslinker and 2,2'-azobisisobutyronitrile (AIBN) as the radical initiator. The prepared particles have a diameter of 200-250 nm. The maximum adsorption capacity of potassium IIP particles was  $120 \mu\text{mol g}^{-1}$ . Optimum pH for quantitative extraction was 9.0. Nature of eluent, eluent concentration, adsorption and desorption times, weight of the polymer material, aqueous phase and desorption volumes were also studied. The relative selectivity coefficient values of  $\text{K}^+/\text{Li}^+$ ,  $\text{K}^+/\text{Na}^+$ ,  $\text{K}^+/\text{Rb}^+$  and  $\text{K}^+/\text{Cs}^+$  were 48.07, 4.81, 29.71 and 43.46, respectively. The relative standard deviation (RSD) and limit of detection ( $\text{LOD} = 3S_b/m$ ) of the method were obtained 1.61% and  $4.62 \text{ ng L}^{-1}$ , respectively. Finally, the sorbent was applied for the determination of potassium ion from different samples.

This work reports the first preparation of new lithium ion- imprinted polymer material using benzo-12- crown-4 as a selective crown ether, methacrylic acid (MAA) as the functional monomer, ethyleneglycol dimethacrylate (EGDMA) as the crosslinker, and 2,2'-azobisisobutyronitrile (AIBN) as the radical initiator. The imprinted lithium ion was removed

from the polymeric matrix using a 1.0 mol L<sup>-1</sup> HNO<sub>3</sub> solution. The resulting sorbent was characterized by SEM. The maximum adsorption capacity and preconcentration factor of prepared particles were 1019.27 μmol g<sup>-1</sup> and 80, respectively. The experimental conditions such as nature of eluent, eluent concentration, pH, adsorption and desorption times, weight of the polymer material, sample and eluent volumes were also studied. Finally, selectivity of the prepared IIP particles toward lithium ion was investigated in the presence of some foreign metal ions.

In this work we report the first application of ion- imprinted technology via precipitation polymerization for simple and determination of robidium ion. The Rb- IIP nanoparticles are prepared using dibenzo-21- crown-7 as a selective crown ether, methacrylic acid (MAA) as the functional monomer, ethyleneglycol dimethacrylate (EGDMA) as the crosslinker, and 2,2'-azobisisobutyronitrile (AIBN) as the radical initiator. The resulting powder material was characterized using scanning electron microscopy and showed colloidal nanoparticles of 100–200 nm in diameter and slightly irregular in shape. The maximum adsorption capacity of IIP particles was 63.36 μmol g<sup>-1</sup>. The experimental conditions such as nature of eluent, pH, eluent concentration, adsorption and desorption times, weight of the polymer material, aqueous phase and desorption solvent volumes were also studied. Finally, selectivity of the prepared IIP particles toward robidium ion was investigated in the presence of some foreign metal ions.

This work reports the synthesis of a new Hg<sup>+2</sup>- ion imprinted polymeric nanomaterial by precipitation polymerization technique using 1-(2- acetatophenyl)-3-(4-methylphenyl) triazene as a ligand, ethyleneglycol dimethacrylate as a crosslinker, and methacrylic acid as a functional monomer. The imprint mercury ion was removed from polymer using 1.0 M HCl. The ion-imprinted polymeric nanoparticles were characterized by IR spectroscopy and scanning electron microscopy (SEM). The SEM micrographs showed colloidal nanoparticles of 90-110 nm in diameter and slightly irregular in shape. The maximum adsorption capacity of prepared particles was 13.71 μmolg<sup>-1</sup>. The experimental conditions such as nature of eluent, eluent concentration, pH, adsorption and desorption times, weight of the polymer material, aqueous phase, and desorption volumes were also studied in detail. Finally, selectivity of the prepared IIP particles toward mercury ion was investigated in the presence of some foreign metal ions.

## Part Two

A dispersive liquid-liquid microextraction based on solidification of floating organic drop method combined with solid phase extraction (500 mg C<sub>18</sub> sorbent) was developed for preconcentration and determination of some parabens. The experimental parameters influencing the extraction efficiency such as type of extraction and disperser solvents, as well as their volumes, breakthrough volume, flow rate and salt addition were studied and optimized. The optimum experimental conditions found included: sample volume, 100 mL; KCl concentration, 1% (w/v); extraction solvent (1-undecanol) volume, 20  $\mu$ L and disperser solvent (acetone) volume 250  $\mu$ L. Under the optimum experimental conditions, calibration graphs were linear in the range of 1.0-200  $\mu$ g L<sup>-1</sup> with limits of detection (LODs) ranged from 0.3 to 1.7  $\mu$ g L<sup>-1</sup>. The relative standard deviations (RSDs) were in the range of 1.2-3.1% (n=5). The method was applied to the simultaneous determination of parabens in different matrices. The relative recoveries of water, shampoo and mouth rinse samples, which have been spiked at different levels of parabens, were 87.83-112.25, 82.80-108.40 and 90.10-97.60, respectively.

A simple and practical preconcentration method, dispersive liquid-liquid microextraction (DLLME) based on solidification of a floating organic drop (DLLME-SFO) technique was proposed for the determination of nitrophenols in water samples. The effective experimental parameters on the extraction efficiency such as extraction solvent volume, dispersive solvent volume, and pH were studied using response surface methodology (RSM). Under the optimum experimental conditions, the preconcentration factors of 116 and 84 for 2-nitrophenol and 4-nitrophenol were obtained, respectively. The calibration graphs were linear in the range of 5.0-150  $\mu$ g L<sup>-1</sup> with the detection limit of 1.70  $\mu$ g L<sup>-1</sup>. The proposed method was successfully applied to the determination of nitrophenols in water samples.

Stir bar sorptive extraction (SBSE) combined with dispersive liquid-liquid microextraction based on solidification of floating organic drop (DLLME-SFO) was developed for the extraction and determination of some polycyclic aromatic hydrocarbons (PAHs) in different aqueous samples. The extracted PAHs were separated and determined using high performance liquid chromatography-ultraviolet detection (HPLC-UV). Some important extraction parameters were studied and optimized. The new SBSE-DLLME-SFO method provided high enrichment factors in the range of 1630-2637. The calibration graphs were linear

in the range of 0.02-400  $\mu\text{g L}^{-1}$  and the limits of detection (LODs) were in the range of 0.0067-0.010  $\mu\text{g L}^{-1}$  for this technique. The optimized method exhibited a good precision level with relative standard deviations (RSDs%) values between 2.17% and 6.92%. The proposed method was successfully applied to the extraction of three PAHs in different spiked water samples



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