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# New Methods in the Synthesis of (Meth)Acrylamides and Application Chelating Resin for Determination of Trace Metals in Certified Reference Materials and Waters

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## Abstract

The waste of trace metals are led the pollutions of water, soil and air. That's why the accurate and sensitive identification of amount of trace metals in food samples and environment are gained importance in analytical chemistry because of their toxicity to human health. Besides, the direct determination of trace metals, presented at very low concentration especially in real samples, is difficult. In this content, before determination of trace metals by instrumental methods can be achieved successfully using separation/preconcentration procedures. The different synthesized chelating polymer resin adsorbents are successfully used for the SPE of trace metals. The trace metals, such as Cu, Cr, Co, Mn, Zn and Fe, are necessary for human health, when it has been taken at certain limits. But, the trace metals, such as Hg, Cd, Pb, Ni and As are toxic metals for the human body. About this, there are studies on the determination of trace elements and mineral in food samples and environment. In this study, new methods in the synthesis of (meth)acrylamides and use as a sorbent in the trace metals extraction was identified.

**Keywords:** activated (meth)acrylamides, trace metals, separation/preconcentration, adsorbent, food samples

## 1. Introduction

Heavy metals [Co(II), Cu(II), Ni(II), Pb(II), Cd(II), etc.] have an important place between the water pollutants due to their toxic features. Organic pollutants in the water, biodecomposition at the end of the time may be ruined, heavy metals, biodegradable products are not converted into harmless products. That's why, heavy metals must be removed from the surrounding waters [1, 2]. Due to the toxic features of heavy metals in the environment, researches on these are increasing. One of the most partner and effective methods used to remove heavy metals from wastewater is the adsorption method. This fact that adsorption is a common and effective method has always grown the selection of a good adsorbent. Therefore,

metal oxides, activated carbon, hydrogel polymers, ion exchange resins, and polymeric fibers, microspheres and natural polymers have been used in the literature as adsorbents to remove heavy metals from the aqueous environment. But, the adsorption capacity of some of these adsorbents is very low or a long time is necessary for the adsorption equilibrium. Some adsorbents are also difficult to revive and cannot be reused. Polymer resins with different functional groups and large surface area are broadly used for the separation of metal ions and enrichment of trace elements [3, 4]. Recently, the importance of removing heavy metal ions from aqueous media has been increasing for the purpose of control environmental pollution. Heavy metals in waste water may be removed by adsorption on solid materials. Different adsorbents such as metal oxides, activated carbon, peanut and rice shell, cotton, wool, chitosan, starch, sporopollen and wood shavings [5–14] are used as adsorbents in the removal of heavy metals from the aqueous environment. But, the adsorption capacity of some of these adsorbents is very low or they are broadly used in complexing with them. Recently, copolymer resin with functional groups have been used to remove heavy metal ions from waste waters. In the removal of heavy metal ions from aqueous media and enrichment of trace elements, the use of polymeric adsorbents with high adsorption rates and large surface area is increasing [15–20]. In a very short time, it is cited that the polymers of amidoxime group will find broad usage area as adsorbent in the recovery of uranium from ground water and sea [21–27]. The characteristics of the adsorbent, such as sorption capacity, selectivity to analyte, resistance to physical/chemical conditions, pH range, ease of availability, reusability and cost, are thought. In order to, new sorbents are continuously being examined and these features are expected to be advanced except in the literature [28, 29].

In the removal of heavy metal ions from aqueous media, functional groups such as ester, pyridine, amide, carboxylic acid, amidoxime and hydroxyl at the surface of the adsorbent are substantially effective. Adsorption of heavy metals from aqueous environmental can generally be controlled by functional groups on the adsorbent surface. Polymeric adsorbents containing N-methyl hydroxamic acid groups and amidoxime groups have been selectively used against some trivalent lanthanide metal ions [Nd(III), La(III), Gd(III), Sm(III), Tb(III)] and especially uranium ions.

The concentration range cited as *edit* “work concentration” it has changed over time in parallel with the improvements in artifact analysis techniques. Before 1940s,  $10^{-1}$ – $10^{-2}\%$ , rarely  $10^{-3}\%$  of work sheets,  $10^{-3}$ – $10^{-5}\%$  in the 1950s and  $10^{-6}$ – $10^{-8}\%$  in the 1965s work is cited as *skin*. Kaiser suggested the systematic approach and first naming. Kaiser gave the explanation of ppm and ppb. According to today’s general usage,  $10^{-2}$ – $10^{-6}\%$  concentration range, and concentrations below  $10^{-6}$  are known as *ultra works*.

Recently, the most important parts of analytical chemistry, trace element analysis, soil, water and air pollution, such as pollution effects on the environment, such as the increasing importance of environmental issues, the elements of the human body and metabolism effects, the study of the chemical forms of the heavy metals in natural waters and determination of it has gained importance as the functions in many different areas are. The phrase trace element analysis is used for the determination of very small quantities of elements in the medium formed of large quantities of components. These environments can be minerals, metals, water, compounds, aqueous solutions, biological and organic substances. Often, the environment in which the trace element is available has a reverse effect on the determination. In such environments, accuracy and sufficient precision can not be obtained. The matter starts at the sampling phase in the study analysis. Especially, there may be a non-homogeneous trace element

distribution in solid samples. Limitations at the limit of determination of the instrumental technique to be used in the determination of a suitable sample will be problematic. The concentration of trace element should be above the limit of determination. Otherwise an observable signal is not obtained. In such cases, separation and enrichment processes are carried out in order to concentrate the analyte into the appropriate medium or to collect it in small volumes. Various problems can be encountered during trace element analysis. Some of these problems are as follows;

1. The trace element concentration is too small to be directly determined.
2. In the very small amount of the initial sample, the main component, component and work analysis of elements.
3. Separation of trace elements to be determined from a very large sample.
4. To avoid interference with media and increase the assay capacity, to separate and collect a small volume.

This book chapter includes the synthesis of new acrylamide derived polymer resins and the use of these resins as adsorbents in the removal of heavy metal ions from environmental samples, and the investigation of their adsorption properties. In the literature, various substances are used as adsorbents, but methacrylamide-derived polymer resins are not available for this purpose and how it is used. The sections related to the examples of the studies carried out by our group have been made interesting. With this book chapter, it is aimed to introduce new methods with new adsorbent material for the removal of heavy metal ions from environmental samples. The amount of polymer resins used as adsorbents, their reusability and their ability to quantitatively remove heavy metal ions were the most important positive aspects of the studies.

## **2. Separation and enrichment methods**

Separation of a substance between two phases in contact with varying proportions of distribution basis. In all separation methods solid-liquid, liquid-liquid, liquid-gas and solid-gas, there are two phases in the form. Trace element analysis generally has three separate applications of separation methods. These;

- a. Macro-micro-separation: when the main component is removed from the sample trace components remains in solution.
- b. Micro-macro separation: trace components from solid or thawed sample the main component remains in solution.
- c. Micro-micro separation: the trace components are separated from the other components.

The first application is not used in the work analysis. Because the main component can be dragged along with trace elements. The other two applications are used more in work analysis. The trace elements are separated from the disturbing media components by enrichment methods. It is taken into smaller volume and concentrated. Two important criteria are used in the evaluation of enrichment methods.

The first one is the recovery efficiency. However, it is not always possible to achieve a large recovery value. At low concentrations, 90 or 95% recovery efficiencies are sufficient. The second term is the enrichment coefficient.

The enrichment methods in the work analysis undertake important functions. With enrichment techniques;

1. The ratio of the amount of trace element to the amount of media is increased.
2. Instead of the original media components (matrix), the new and the appropriate technique for the determination technique is created.
3. In the new environment, the analyte shows homogeneous distribution, especially with the enrichment process used in combination with the dissolving process.
4. The standard preparation for calibration is made easier.

The following criteria should be taken into account when selecting trace element enrichment methods;

- The method of determination following the enrichment method
- Minimum concentration limits of trace elements
- Number of desired trace elements
- Enrichment factor
- Recovery value of the method
- Contamination
- Number of samples
- Sample size
- Time for enrichment
- The complexity of the technique
- Price and laboratory conditions.

## **2.1 Enrichment by extraction**

Extraction is the process of passing a chemical compound from a liquid phase into another liquid which is not mixed there with. The extraction of trace element into the organic phase is based on the incorporation of the trace element into a neutral structure. Neutral structures used in such a reaction; chelate, ion pair and covalent structures. In order to accurately measure trace elements, it is very important to separate and enrich the matrix before the analysis. Specific and sensitive methods are required for this.



### 2.1.1 Chelation extraction of trace elements

The trace elements at various levels in natural waters, wastewater, surface water and ground water are converted into chelates at a suitable pH and extracted into a small volume organic phase according to the sample. These elements taken into the organic phase are concentrated back to the aqueous phase directly or again and are determined by various determination techniques. Extraction is used not only in liquid samples but in solid samples to recover from matrix. The first step is to dissolve the sample. In chelate extraction the sample in the first aqueous phase is the appropriate reagent selection depending on the elements it contains. The reagent should form chelates with the desired trace elements and not form chelates with undesirable components. In this regard, chelates are also preferred in the extraction of trace elements, in particular in the alkali and alkaline earth compounds, or in samples containing them. Because chelating ligands do not generally form with alkali and alkaline earth alkalis.

### 2.1.2 Ion pair extraction

Ion pair complexes can also be extracted into organic solvents because they are neutral structures. It is difficult to derive quantitative equivalents or formulas in the extraction of ion pair complexes. Because ion pairs occur in the presence of extremely strong electrolytes. At the same time, a number of different ion strands can be found. Most inorganic complexes are used in extraction from ion pairs. Ion pairs usually occur between the anionic complexes formed by inorganic ligands and the  $H^+$  ion.  $[H^+, ML_{n+1}^-]$ . In the extraction process, selectivity is achieved by utilizing variants such as pH, side reactions in the aqueous phase, ligand, solvent type and temperature. Extraction efficiency is defined as the size of the amount of material passing from the aqueous phase to the organic phase. The dispersion rate is determined by D.

$$D = C_{\text{organic}}/C_{\text{aqueous}} \quad (1)$$

When the balance is established,  $C_{\text{organic}}$ , total concentration of analyte in organic phase;  $C_{\text{aqueous}}$ , denotes the total concentration of the analyte in the aqueous phase. To increase efficiency in extraction processes; synergistic effect, co-extraction and salt effect processes are utilized.

### 2.1.3 Enrichment with co-precipitation

The use of precipitation methods in the separation of elements is based on the different solubility of the compounds in aqueous solutions. Collectors are used in quantitative separation of trace elements in solution by the method of co-precipitation. A large-surface precipitate with inorganic or organic character is formed, so that the adsorbed surface is adsorbed. The mechanism of co-precipitation depends on the physical and chemical properties of the trace element and the carrier and on the experimental conditions. According to this; three mechanisms in the form of confinement, mixed crystal formation or adsorption.

The carrier should be added to the sample solution so that sufficient amount of precipitate is formed. In order to prevent the adsorption of ions that may interfere, the amount of carrier should be as low as possible. Precipitation methods are mostly used for the separation of trace elements into single press as well as separating the main component from trace components. By controlling the precipitation pH, selectivity is ensured.

The use of the precipitation process to separate the main component from the work component is not common. Because when the main component collapses, it can also drag and drop work components together. This leads to substance loss.

#### *2.1.4 Electrolytic enrichment*

The electrolysis method is used to separate trace amounts of heavy metals from various solutions. The composition of the electrolyte and sample, the type and shape of the electrode, the electrolysis cell and other experimental variables greatly affect the electrolytic deposition of an element. Potentially controlled electrolysis, as well as stripping methods, are widely used in the enrichment of trace elements.

#### *2.1.5 Ion exchange*

Ion exchange technique is a method of enrichment of trace elements. The ion exchange method can be practiced in three ways. The first is the rinsing technique that the solution and the ion exchanger interact in the same container. The second is the filtration technique in which the sample solution is held by ion-exchanging paper or membrane filter and the trace elements are kept. The third technique is the column technique which is the most commonly used technique in the application. In the rinsing technique, the solution containing the trace element ion is rinsed with resin. It is expected to establish a balance of time distribution. The resin is separated from the solution by filtration. The resin can be reacted with suitable solutions and trace elements can be determined by solution techniques or directly by solid analysis techniques. In the filtration technique, the sample solution is passed through an ion exchanger paper or membrane filter. Filter elements are determined by direct or degradation. In the column technique, large-volume solutions containing trace elements from the filled column with ion-exchange resin are passed to selectively hold them. These trace elements are attached with a smaller volume of eluent. This final volume can be further reduced by evaporation. Selectivity of the functional groups in the selection of ion exchangers, changing capacity, exchange rate, regeneration of the ion exchanger and use of the appropriate eluent are the considerations.

#### *2.1.6 Enrichment with evaporation*

It is a very convenient method for some elements that can be converted to volatile or easily volatile components. In fly enrichment, the volatility difference between the matrix and the trace element must be large. The separation by blowing can be done in two ways by blowing both the matrix and the trace element. However, in inorganic analysis, it is not common to enrich the trace elements by flying.

#### *2.1.7 Adsorption-enrichment*

The change in the concentration of a solid or a liquid on the boundary surface is called adsorption. This phenomenon arises from the accumulation of molecules or ions of the solute from the gas, liquid or any solution by adhering to the surface of a solid substance. The increase in concentration is called positive adsorption. The decrease in concentration is also called negative adsorption. Physical and chemical properties of adsorbent substances are the most important factors affecting the adsorption process. Solids, metals and plastics have more or less adsorption power. Some natural solids with high adsorption power; coals, clays, zeolites and various

metal sprouts, and artificial solids are activated charcoal, silica gel and special polymers. The amount of adsorbed substance in the solids having high adsorption power varies depending on the surface size and porous structure.

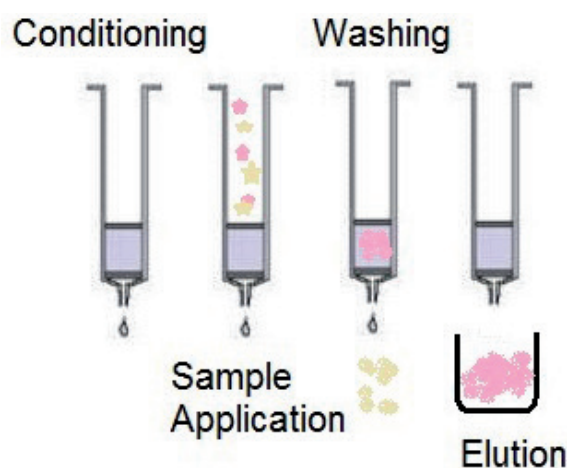
### 2.1.8 Solid phase extraction

The solid phase extraction method is applied in three ways: rinsing technique, semi-permeable retaining disc filtration technique and column technique [30–35].

#### 2.1.8.1 Column technique

Solid phase extraction method is widely used in the column technique. Columns of different sizes can be used. This technique consists of four process steps: These process steps is given in **Figure 1**.

As column filler natural and artificial polymers, silica gel, alumina, florisil, octadecyl (C18); octyl (C8), ethyl (c2), cyano, phenyl, cyclohexyl, amino, diol, quaternary amine, aromatic sulfonic acid, carboxylic acid can be used.



**Figure 1.**  
 Column technique processing steps.

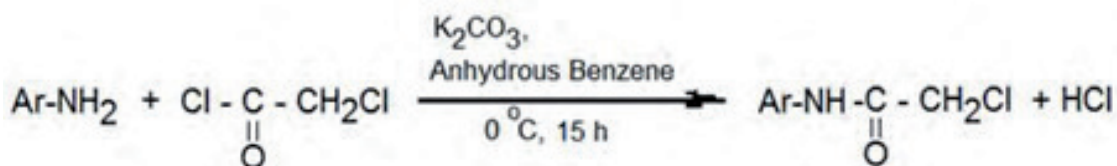
## 3. Functional methacrylates from $\alpha$ -chloro-N-arylacetamides

### 3.1 Synthesis of $\alpha$ -chloro-N-arylacetamide

Synthesis of  $\alpha$ -chloro-N-arylacetamide is as follows: potassium carbonate ( $K_2CO_3$ ) (0.1 mol) and arylamine (1 mol) and are dissolved in 30 mL of anhydrous benzene. The reaction mixture is taken in a three-neck round bottom flask equipped with a magnetic stirrer, thermometer, and cooled to  $0^\circ C$ . After then chloroacetyl chloride (1.1 mol) are added dropwise to the solution and stirred at room temperature for 16 h. The organic layer is washed several times with diethyl ether and separation phase is filtered and dried over  $MgSO_4$ .  $\alpha$ -Chloro-N-arylacetamide is crystallized from methanol. Yield: 80%. The synthesis reaction path is given in **Figure 2**.

The structure of the compound  $\alpha$ -chloro-N-arylacetamide is identified by the FT-IR techniques. FT-IR ( $cm^{-1}$ ): 3340 (NH); 3100–2800 (C–H); 1680 ( $>C=O$ ); 1580 (aromatic, C=C) [36, 37].



**Figure 2.**

Synthesis route of  $\alpha$ -chloro-N-arylacetamide.

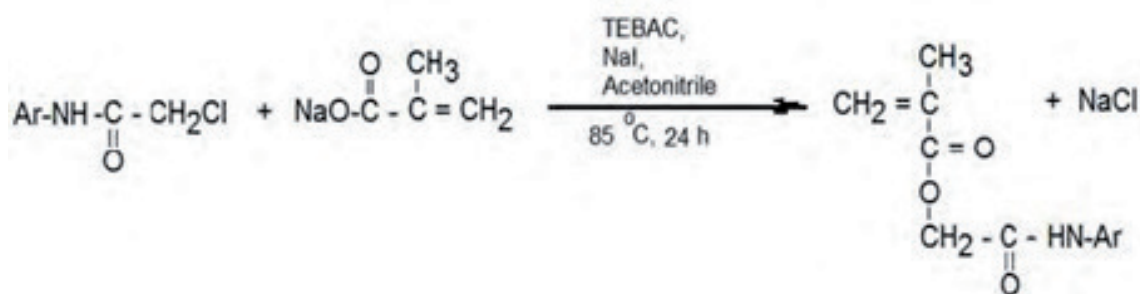
### 3.2 Synthesis of arylamido methyl methacrylate

Arylamido methyl methacrylate is synthesized as follows: 1.1 mol sodium methacrylate, 1 mol  $\alpha$ -chloroacetamide, 0.1 mol NaI, and 0.1 mol TEBAC as catalyst are stirred in 100 mL acetonitrile at 80°C in a reflux condenser for 24 h in the presence of 100 ppm hydroquinone as the inhibitor. Then the solution is cooled to room temperature and neutralized with a 5% KOH solution. The organic layer is washed a few times with water, and the water layer is washed with diethyl ether several times. The diethyl ether layer and acetonitrile layer are aggregated and dried over anhydrous  $\text{MgSO}_4$  overnight. Diethyl ether and acetonitrile are evaporated. The organic layers are collected and the residue was distilled at 130°C at 5 mmHg to give a colorless liquid. (Yield: 80%). The synthesis reaction path is given in **Figure 3**.

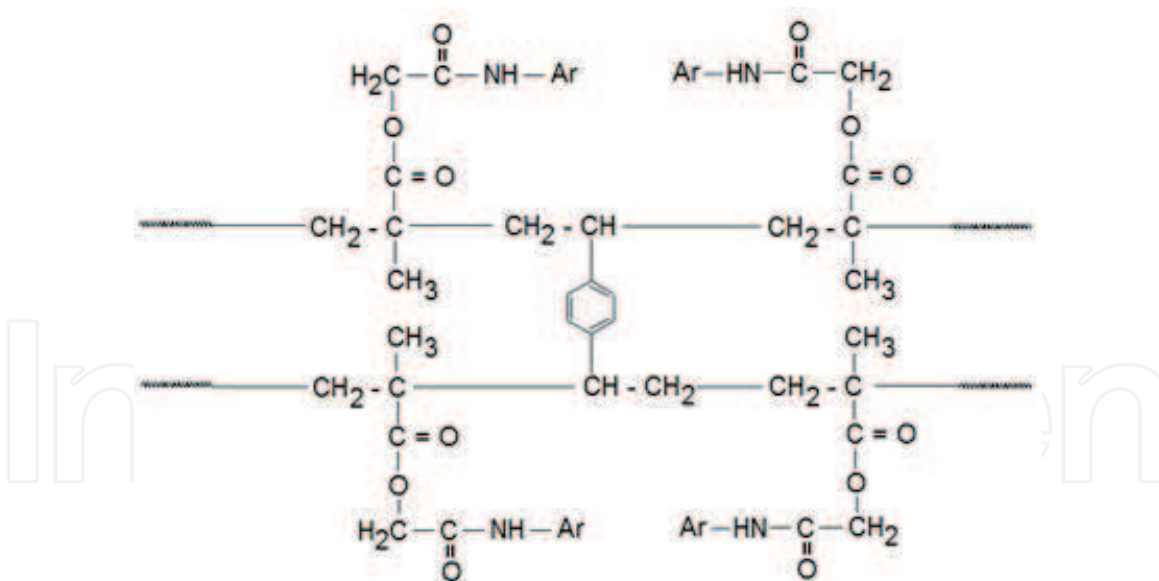
The structure of the monomer is confirmed by the FT-IR and  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopic techniques. FT-IR ( $\text{cm}^{-1}$ ): 3325 (NH); 3100–2800 (C–H); 1680 ( $>\text{C}=\text{O}$ ); 1630 ( $\text{CH}_2=\text{C}$ ); 1580 (aromatic, C=C); 1230 (C–O–C).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , TMS): 9.1 (N–H); 8.0–6.7 (aromatics–H); 6.3–5.43 ( $\text{CH}_2=\text{C}$ ); 1.8 ( $\text{CH}_3$ ).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , TMS): 157.1–113.4 (aromatics–C); 134.4–124.2 ( $\text{CH}_2=\text{C}$ ); 168.1 ( $>\text{C}=\text{O}$ ); 18.1 ( $\text{CH}_3$ ) [38, 39].

### 3.3 Synthesis of polymer resin

Arylamido methyl methacrylate-co-divinylbenzene polymer resin is prepared by copolymerizing of arylamido methyl methacrylate monomer (3.0 mmol) and divinylbenzene (3.0 mmol) as a crosslinker. The polymer resin is designed by the free radical solution polymerization technique in 1,4-dioxane and in a 50 mL sealed pyrex polymerization tube. The azobisisobutyronitrile, AIBN is used at a 1:1 molar ratio as initiator. The reaction mixture is processed with nitrogen gas for 5 min in the polymerization tube and in an oil bath heated at  $70 \pm 1^\circ\text{C}$  for 5 h. Later reaction, the formed polymer resin was kept at 25°C for cooling. The polymer resin was washed with ultra high pressure water, n-hexane and ultra high pressure water, respectively and then dried under vacuum at 40°C. The synthesis reaction path is given in **Figure 4**.

**Figure 3.**

Synthesis route of arylamido methyl methacrylate monomer.



**Figure 4.**  
 Synthesis route of arylamido methyl methacrylate monomer resin.

## 4. Optimization of enrichment separation methods

In the optimization of the methods used in the studies, to the recovery value of the elements to be determined parameters such as pH, amount of carrier element, amount of complexing agent or precipitating reagent, sample volume and effect of matrix components are examined.

### 4.1 Effect of pH

The effect of pH on the precipitation of the studied trace elements such as Ni (II), Co (II), Cu (II), Mn (II), Cd (II), Zn (II), Pb (II) is investigated. The pH value plays an important role in the adsorption of sorbent-related ions and affects the state of sorption of heavy metals. Enrichment of metal ions pH effect is generally examined in the range of 1–8. Binding of analytes to the synthesized polymer resin in solid phase extraction (SPE) is known to be dependent on the pH of the samples solution. The pH value for quantitative SPE of the analytes is fixed by measurements of analytes in final solutions. All of the buffer solutions are prepared the pH 1–2 with 1 mol L<sup>-1</sup> of KCl/HCl, pH 3–5 with 1 mol L<sup>-1</sup> of CH<sub>3</sub>COONa/CH<sub>3</sub>COOH, pH 6–8 with 1 mol L<sup>-1</sup> of CH<sub>3</sub>COONH<sub>4</sub>/CH<sub>3</sub>COOH.

### 4.2 The effect of concentrations of eluents on the efficiency of analytes

Elution of metals from the column is carried out using acids. The influences of various eluents on the recoveries of analytes are usually examined using 1, 2 and 3 M from each of HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> and 10, 20, and 25 mL of these acid solutions.

### 4.3 Effect of flow rates of solutions

The contact time between the analytes and the complexing agent is the effect the recoveries of the analytes and the SPE time. This contact time is supplied to flow rate of the sample. The samples flow rates are usually examined in the range from 2 to 10 mL min<sup>-1</sup>. The increase of sample flow rate, which reduces the interaction time between the analytes and the adsorbent. In order to achieve good precision,

a sample flow rate is generally chosen at  $5 \text{ mL min}^{-1}$ . The analytes desorption on the adsorbent also adhere to on the flow rate of the elution solutions.

#### 4.4 Effect of the amount of the complexing agent

The effects of the amounts of complexing agent on the adsorption of analytes keeping other parameters constant are investigated. For this purpose, the prepared model samples are generally passed through the column containing 1.0, 1.5, 2.0, 3.0 and 4.0 g of the complexing agent. The retained analytes on the complexing agent are usually eluted 10 mL of  $1 \text{ mol L}^{-1} \text{ HNO}_3$ .

#### 4.5 Effect of sample volume

The increase of sample volume will result in important increase in the preconcentration factors. The adsorption of the heavy metals are not affected by sample volume in the range 25–1000 mL of model solutions containing chromium, cadmium, copper, cobalt, iron, lead, manganese, nickel, and zinc ions.

#### 4.6 Effect of matrix ions

The effect of matrix ions in the real samples on the simultaneous separation and preconcentration of heavy metals are generally tested. The model samples (25 mL) containing 2  $\mu\text{g}$  of cadmium, and zinc, 10  $\mu\text{g}$  of copper, cobalt, iron, manganese, nickel, 20  $\mu\text{g}$  of chrome and lead ions. The known concentrations of matrix ions are prepared and work method is implemented to these prepared model samples. The tolerable levels of the matrix ions are given.

### 5. Conclusion

In this paper, reaction pathway for the synthesis of new methacrylamide resin and use as a sorbent in the trace metals extraction was described. This synthesized polymer resin can be used as column filler on the solid phase extraction for the effective separation and preconcentration of the trace elements in dam, waterfall, spring water, and river and dried eggplant, zucchini and tomato samples. The synthesized polymer resin is distinct in terms of precision and particularity for these analytes. The experimental parameters are advanced and the analytical parameters are identified [40–54].

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