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Research Article

Preconcentration of Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+} by Solid-Phase Extraction Using a Recently Developed Mixed-Mode Sorbent

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Abstract: The enrichment and simultaneous analysis of Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+} by solid-phase extraction method were performed using a stationary phase containing amide functional groups, an aromatic benzene ring, and aliphatic groups in a silica-based structure that we had synthesized for HPLC separations in our previous studies. Solid-phase extraction was performed using a column system and the results obtained were analysed by ICP-OES. Effects of pH, amount of sorbent, amount of eluting solvent, sample volume, flow rates of the eluent and the sample, and interfering ions were evaluated in recovery processes for the metals in the sample solutions. Linear range, detection limit, and relative standard deviation (% RSD) values were calculated for each metal. The linear range (ng/mL) was between 0.01 and 0.25 for all ions, while the limit of detection (ng/mL) was found to be 0.64, 1.7, 0.44, and 0.51 and % RSD was 2.8, 2.4, 2.6, and 2.9 for Cu^{2+}, Cr^{3+}, Co^{2+}, ve Ni^{2+}, respectively.

Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+}'nin Son Zamanlarda Geliştirilen Karma Mod Bir Sorbent Kullanılarak Katı Faz Ekstraksiyonu ile Zenginleştirilmesi

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Anahtar Kelimeler
Bakır,
Katı faz ekstraksiyonu,
Kobalt,
Krom,
Nikel,
Silika tabanlı sabit faz

Öz: Daha önceki çalışmalarımızda HPLC ayırmaları için sentezlenen silika tabanlı amid fonksiyonel grupları, benzene halkası ve alifatik gruplar içeren bir sabit baz kullanılarak katı faz ekstraksiyonu yöntemi ile Cu^{2+}, Cr^{3+}, Co^{2+}, ve Ni^{2+}'nin zenginleştirilmesi ve eş zamanlı analizi yapıldı. Katı faz ekstraksiyonu kolon sistemi kullanılarak gerçekleştirilmiş ve elde edilen sonuçlar ICP-OES ile analiz edilmiştir. Örnek çözeltilerdeki metaller için geri kazanım proseslerinde pH, sorbent miktarı, elüsyon çözücü miktarı, numune hacmi, eluent ve numunenin akış hızı ve yabancı iyon etkisi incelendi. Her metal için lineer aralık, dedeksiyon limiti ve bağıl standart sapma değerleri hesaplandı. Dedeksiyon limiti (ng/mL) Cu^{2+}, Cr^{3+}, Co^{2+}, ve Ni^{2+} için sırasıyla 0.64, 1.7, 0.44 ve 0.51 ve bağıl standart sapma 2.8, 2.4, 2.6 ve 2.9 iken, lineer aralık bütün iyonlar için (ng/mL) 0.01 ve 0.25 aralığındadır.

1. Introduction

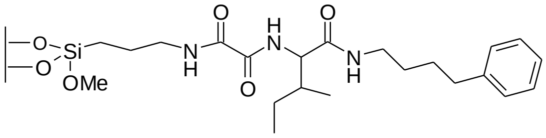
It has been established beyond doubt that heavy metals are pollutants of major significance that exert a multitude of adverse effects for the environment and all present living organisms, in some cases even at the lowest measurable concentrations. Low levels of heavy metals exist naturally within the environment and trace levels of these metals are crucial for the maintenance of human health. However, at higher concentrations, these metals may be hazardous in the long term as well as the short term (Ali et al., 2019). Increasing volumes of industrial activities in many parts of the world have impacted human quality of life both negatively and positively. Unfortunately, the negative effects of these industrial activities can be deadly, as industrial production constitutes a major source of water polluted with heavy metal ions. Heavy metal ions arising from the run-off of industrial processes differ in a critical way from carbon-based or organic pollutants as the former cannot be degraded environmentally. For this reason, increasing heavy metal ion ratios that reach levels above the healthy determined limits may elicit excessive accumulations of metals in living organisms at the cellular level, negatively impacting both their health and the quality of the surrounding environment (Jang et al., 2008). Among the diverse industrial sectors that channel wastes bearing excessive quantities of heavy metals into the natural water cycle, textiles and dyes, mining, electroplating, refineries, tanneries, and the producers of products ranging from pesticides to papers can be named. As the scope of industrial development expands, the volumes of pollution containing heavy metals are also growing, and the resultant accumulations of heavy metals in the cells of both humans and all other organisms trigger many diseases, among which disorders of the skin and the liver are of particular importance (Jang et al., 2008). It is thus no surprise that an increasingly important field of analytical chemistry involves determining the levels of heavy metals in various environmental reservoirs. Numerous practical spectroscopic methods, such as inductively coupled plasma-atomic emission spectrometry (ICP-AES) or inductively coupled plasma-optical emission spectrometry (ICP-OES), may be applied with the aim of measuring the levels of metal ions present in different substances. Measurements of natural samples can be complex and it is difficult to accurately, reliably, and directly detect trace levels of metal ions via approaches such as electrothermal atomic absorption spectrometry or flame atomic absorption spectrometry. Therefore, in trace analysis of environmental matrices performed via methods such as ICP-AES or ICP-OES, separation and enrichment steps are recommended according to the particular samples, analyte concentrations, and measurement techniques (Betiha et al., 2020). Pre-enrichment and matrix elimination steps including solid-phase extraction (SPE) (Khan et al., 2020; Nguyen et al., 2022; Baghaei et al., 2023) solvent extractions (Farajzadeh et al., 2009), co-precipitation (Atanassova et al., 1998), and ion exchange are commonly applied before moving on to begin the instrumental measurements (Liu et al., 2016; Vergara-Barberán et al., 2017; Yan et al., 2017; Liu et al., 2020).

SPE is commonly applied in a wide variety of studies as it offers relatively easy application steps with low costs, does not involve any toxic or otherwise possibly dangerous organic solvents, and is an appropriate technique to be used in preconcentrating or separating a wide array of organic and inorganic compounds (Behbahani et al., 2014). SPE has many other important advantages such as offering higher enrichment factors, straightforward handling processes with high levels of safety, high selectivity, and the ability to be combined with other popular detection techniques (Aydin & Soylak, 2007; Cui et al., 2007; Dakova et al., 2011).

The selectivity of SPE varies in accordance with the particular organic ligands attached to the support material (Fan et al., 2005). The selectivity also depends on variables such as the surface area and activity of the chosen solid support and the properties of the ligand that binds to the solid support (Ghaedi et al., 2013). Surface functionalized inorganic solids possessing assorted organic chelating groups can be feasibly used in processes of adsorption and enrichment of metal ions (Chui et al., 2007; El-Ashgar et al., 2009; Javanbakht et al., 2010). The possible supports include chemically functionalized silica gel, which offers appealing characteristics in terms of its mechanical and thermal stability, while also suffering from very minimal issues of swelling and shrinkage or microbial and radiation degradation (Zou et al., 2009). Silica gel, an effective sorbent often utilized in studies of trace levels of metal ions, usually contains large amounts of internal siloxane groups with active hydrogen atoms and silanol groups suitable for reactions with organosilyl-containing members to impart certain organic characteristics to the precursor inorganic support (Akman et al., 1992). Although such silanol groups can be appropriately applied for complexation or enriching of metal ions, they have rather limited selectivity for binding metal ions as a result of low acidity and other donor properties. However, modifying the silica gel surface by virtue of chemical retention using inorganic and organo-functional members will allow for the increase of the binding capacity and will also improve the selectivity of the silica gel (Liu & Liang, 2008).

Various organic compounds such as fluorescein (Alan et al., 2007), 2,3-dihydroxybenzaldehyde (Ngeontae et al., 2007) and aminothioamidoanthraquinone (Fan et al., 2007), xylenol orange (Jamali et al., 2007), 2-thiophenecarboxaldehyde (Akhond et al., 2006), di(n-propyl)thiuram disulphide (Amarasekara et al., 2009) 4-acylpyrazolone (Ngeontae et al., 2007) aminothioamidoanthraquinone (Goswami & Singh, 2002a), 1,8-dihydroxyanthraquinone (Sadeghi & Sheikhzadeh, 2009), murexide (Gübbük et al., 2012), oxime derivatives (Goswami & Singh, 2002b), resacetophenone and diphenyldiketone monothiosemicarbazone (Sharma et al., 2012) undergo immobilization on silica gel surfaces. The molecules that are most commonly used in these binding processes have the ability to chelate thanks to donor atoms that include nitrogen, oxygen, and sulphur, which have excellent capacity for establishing complexes that possess a number of metal ions, providing ideal features for selective extraction in some cases.

In this study, Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+} were preconcentrated using a stationary phase named IIe-PBA-Mix (Figure 1), which contains aromatic, aliphatic, and amide groups in its silica gel-based structure that we synthesized in a previous study (Aral et al., 2017).



Ile-PBA-Mix

Figure 1. The structure of sorbent used in this study.

2. Material and Methods

2.1. Reagents and solutions

Ultrapure water was supplied from the Milli-Q Millipore device. Chemicals of analytical-grade purity were utilized in the course of all experiments, having been obtained from Merck. All pieces of glassware and plastic equipment were prepared by cleaning them with 2 mol/L HNO_3 and subsequently washing them with ultrapure water before using them. The pH of the medium was changed as needed by adding 0.1 mol/L HNO_3 and/or NaOH. Solutions were readied with the use of ultrapure water, with 1000 ppm Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+} solutions being diluted with ultrapure water to the desired concentration.

2.2. Instruments

An Optima 7000 DV device (PerkinElmer) for ICP-OES experimentation was utilized in measurements of the concentrations of Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+}. Filtering columns (1.0 cm × 10.0 cm) with polypropylene frits were utilized in the course of the SPE experimentation. The solution flow rates were calibrated with the help of a peristaltic pump (BT100-1L). A Thermo scientific Orion 3 Star pH Meter was utilized in the process of adjusting the pH of test solutions.

2.3. Column preparation

A glass column possessing an inner diameter of 0.5 cm and length of 50 cm with porous frits was filled with PBA-MIX to approximately 1.5 cm with preconditioning performed using 1 mol/L HNO_3 before the experimentation began. Following the enrichment experiment, HCl:water (1:4) was used to wash the column and it was stored properly until the next relevant step of experimentation.

2.4. Testing procedures

Analyte solutions of 0.25 µg mL^{-1} concentration and volumes in the range of 250-2000 mL underwent adjustments of their pH values to 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0 using an ammonium formate buffer to achieve the pH values of 3.0 and 4.0, an ammonium acetate buffer to achieve the pH values of 4.0-6.0, and an ammonium phosphate buffer to achieve the pH values of 6.0-8.0. Solutions that had been adjusted in this way were then passed through the column described above at flow rates of 2 mL/min. Metal ions retained by complexation underwent elution via the application of 8 mL of 0.25 mol/LHCl HCl with flows of 2 mL/min. Metal ions were subsequently examined via ICP-OES.

3. Results and Discussion

3.1. pH effects

The process by which metal ions bind to chelating compounds, whether within solutions or by being charged to a solid support, is known to be dependent on many variables, mainly the characteristics of the metal ions themselves, such as their charge and size, as well as the characteristics of the donor elements and their binding properties and buffering variables (Ngeontae et al., 2007). The importance of these characteristics has been thoroughly described in the field of solution chemistry and in the context of the SPE of various metals with chelates that have undergone immobilization on the surfaces of solid supports (Ngeontae et al., 2007). The acidity of the solutions exerts crucial effects in the course of metal adsorption as binding sites of the chelating compounds undergo protonation through the actions of the protons in acidic solutions, while hydroxide can complex or precipitate many metals in basic solutions (Ghaedi et al., 2012). For this reason, the effects of the pH level on the extraction and binding of metal ions of PBA-Mix were investigated in this study in a range from 3 to 8 while ensuring that other parameters remained constant While the adsorption of all ions increased from pH 3 to 7, it then began decreasing due to the stronger interaction of metal ions with mobile phases rich in hydroxyl ions. Therefore, for the following evaluations, a pH of 7 was determined as the optimum value for simultaneous pre-enrichment.

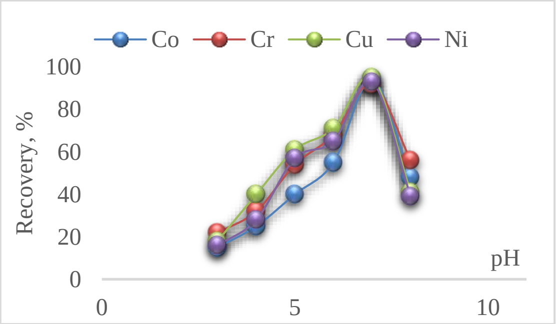


Figure 2. Effects of pH on preconcentration protocol applied for Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+}. Sorbentweight: 0.150 g; sample volume: 50 mL; eluent parameters: 8 mL of 0.25 mol L^{-1} HCl; analyte concentration: 0.25 µg mL^{-1}; sample and eluent flow rate: 2 mL/min.

3.2. Effects of sorbent weight

Impacts of the weighted amount of the solid phase in recovering the metal ions of interest were evaluated using various quantities of the selected solid phase ranging from 50 to 200 mg in weight under conditions wherein all other variables were held at the optimum values. Accordingly, the findings are presented in Figure 3, where it is clear that as the weighted amount of the solid phase increases, the rate of successful recovery also increases and the maximum value is reached when the weighted amount of the solid phase is 150 mg. Therefore, the weighted amount of the sorbent was selected to be 150 mg in the next round of experimentation.

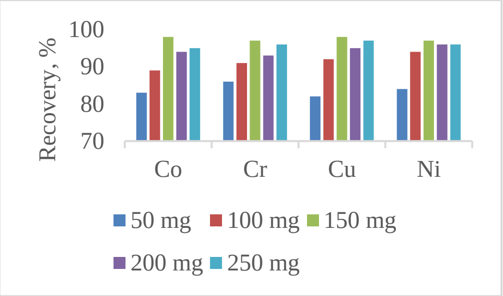


Figure 3. Effects of weighted sorbent amount on the outcomes of the protocol for preconcentrating Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+}. Sample pH: 7, sample volume: 50 mL; eluent parameters: 8 mL of 0.25 mol L^{-1} HCl; analyte concentration: 0.25 µg mL^{-1}; sample and eluent flow rate: 2 mL/min.

3.3. Effects of eluting solvent volumes and concentrations

The concentration of the wash solvent is another important variable in efforts to achieve the quantitative recovery of metal ions from sorbents. In such efforts, the goal is to recover the adsorbed metals of interest while using the smallest possible eluent volume. Ideally, it will be possible to achieve high factors of enrichment using efficiently limited volumes of the selected eluent. In this process, the acid concentration is another variable of significant relevance. At low proton concentrations, some problems arise as a direct result of the inadequacy of protonation occurring at the chelation sites, and when the acid concentrations are particularly high, they will exert significant influence in the course of performing the determination step (Liska, 1993). In general, efficiently performing the elution process for analytes in samples of higher volumes with smaller quantities of the relevant eluent results in higher factors of enrichment (Dakova et al., 2011). Therefore, in the research presented here, the eluting solvent was experimentally investigated by varying its concentration from 0.25 to 3 M and its volume within a range of 5-12 mL. In the course of this experimental process, it was observed that the highest quantitative recovery was achieved as a result of applying 8.0 mL of 0.25 M HCl (Figure 4).

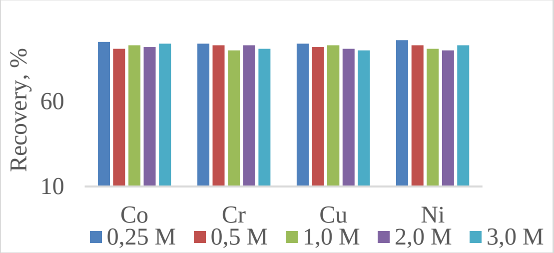


Figure 4. Effects of the applied concentrations of HCl as measured in mol L^{-1} in desorbing Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+}. Sample pH: 7, weighted sorbent amount: 0.150 g; volume of the sample: 50 mL; analyte concentration: 0.25 µg mL^{-1}; flow rates for sample and eluent: 2 mL/min.

3.4. Effects of volume of the sample

Enrichment studies are generally performed with the specific aim of recovering the analyte ions of interest from samples of large volumes. Working with samples of higher volumes makes it possible to obtain higher factors of enrichment. For this reason, determining the optimum value for sample volumes is obviously a step of crucial importance for researchers undertaking extraction studies (Ghaedi et al., 2012). The effect of the volume of the samples in efforts to recover the metallic analyte ions of interest was investigated in the present study while utilizing solutions that ranged from 50 to 250 mL in volume. While increasing the sample volume, the amounts of the selected metal ions were held at a stable level that did not vary in any of the solutions throughout the course of all performed experiments (0.25 µg mL^{-1}) and the metal elements attached to the stationary phase underwent elution via the administration of 8 mL of 0.25 M HCl. Quantitative recoveries were observed for all metal ions at 50 mL.

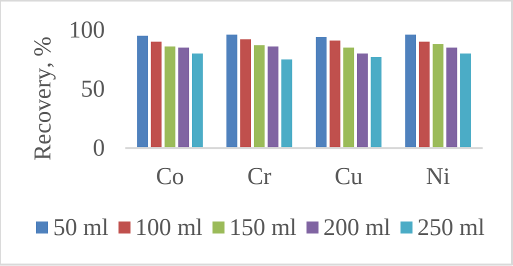


Figure 5. Effects of altering the volume of the samples for absorbance of Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+}. Sample pH: 7, weighted sorbent amount: 0.150 g; eluent parameters: 8 mL of 0.25 mol L^{-1} HCl; analyte concentration: 0.25 µg mL^{-1}, flow rates for eluent and samples: 2 mL/min.

3.5. Effects of flow rates for eluent and samples

For applications involving the use of SPE systems, a variable of particular importance is the sample solution's rate of flow. This variable significantly impacts the rate of recovery of the analytes; furthermore, it is the controlling factor for analysis time. Therefore, the effects of variations in the applied flow rate of the sample on the rate of recovery of the selected metal ions were evaluated within a range from 2 to 10 mL/min under otherwise optimized conditions in terms of variables such as pH and other eluent parameters. The results confirmed that these variations in the rate of flow did not significantly impact recovery rates for Cr^{3+} or Cu^{2+}. However, for all analytes, the most successful retentions were achieved in terms of the best quantitative values when the flow rate applied for the sample was 2 mL/min. Additionally, it was observed that higher recoveries in terms of flow rates were achieved for full binding of Co^{2+} and Ni^{2+} ions but chelation showed decreases due to insufficient time. For these reasons, the value of 2 mL/min was selected as the flow rate to be applied in the subsequent steps of experimentation (Figures 6a and 6b).

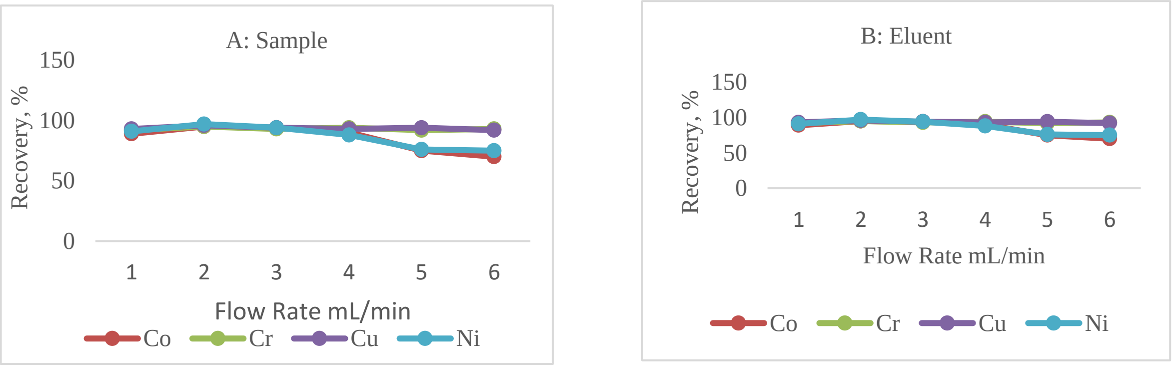


Figure 6. A: Effects of altering eluent flow rates on the outcomes of the protocol for preconcentrating Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+}. Sample pH: 7, weighted sorbent amount: 0.150 g; volume of the sample: 50 mL; eluent parameters: 8 mL of 0.25 mol L^{-1} HCl; analyte concentration: 0.25 µg mL^{-1}; constant, flow rate maintained for sample: 2 mL/min. B: Effects of altering sample flow rates on the outcomes of the protocol for preconcentrating Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+}. Sample pH: 7, weighted sorbent amount: 0.150 g; volume of the sample: 50 mL; eluent parameters: 8 mL of 0.25 mol L^{-1} HCl; analyte concentration: 0.25 µg mL^{-1}; constant flow rate maintained for eluent: 2 mL/min.

3.6. Effects exerted by interfering ions

The possibility of the effects arising from the presence of undesired foreign ions capable of instigating interaction processes with the metal ions of interest was investigated under optimized experimental conditions. Relative error of >5% was accepted in the experimental error range considered in this process. Experimentation was undertaken using model solutions containing Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+}ions at 0.25 µg/L with various amounts of interfering cations at different levels under the previously described optimized experimental conditions. As confirmed by the findings that are offered in figure 7, a mixture of all possible interfering ions was not observed. Recovery rates were not found to decrease with the absence of the analyte upon the experimental application of the selected concentrations (0.25 µg/L) of appropriate interfering ions. It can be reasonably concluded from these experimental findings that the PBA-Mix solid phase possesses excellent selectivity for the metal ions of interest. Furthermore, the protocol proposed here remains valid for the analysis of real-world samples that contain different levels of other ions.

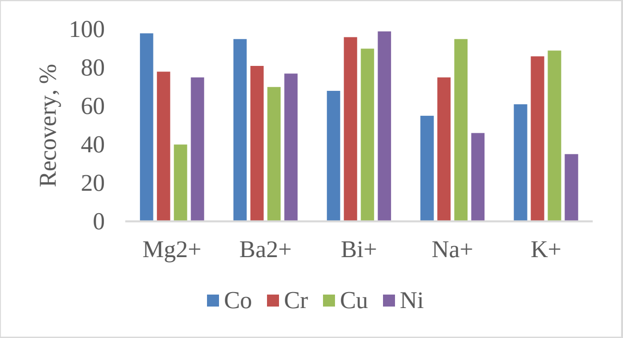


Figure 7. Effects exerted by selected interfering ions on the outcomes of the protocol for preconcentrating Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+}. Sample pH: 7, weighted sorbent amount: 0.150 g; volume of the sample: 50 mL; eluent parameters: 8 mL of 0.25 mol L^{-1} HCl; analyte concentration: 0.25 µg mL^{-1}; constant flow rate maintained for sample and eluent: 2 mL/min.

3.7. Analytical features

Another important factor to be considered in processes such as that described here is the limit of detection, constituting the smallest detectable concentration of the compound of interest causing signals above the noise level as per the definition offered by the IUPAC. The values that are equivalent to three times the standard deviations of the blanks for Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+} ions are 0.64, 1.7, 0.44, and 0.51, respectively. With the intention of investigating the proposed protocol's reproducibility and repeatability under the optimized conditions previously described above, a total of six experiments were undertaken with the same column. The findings are provided in Table 1. Lower relative standard deviation (RSD %) values indicate that the protocol offered in the present work boasts high levels of both repeatability and reproducibility for researchers seeking to undertake the enrichment of trace metal ions.

Table 1. Analysis of the analytical performance of the suggesting protocol under optimized experimental conditions. Sample pH: 7, weighted sorbent amount: 0.150 g; volume of the sample: 50 mL; eluent parameters: 8 mL of 0.25 mol L^{-1} HCl; analyte concentration: 0.25 µg mL^{-1}; constant flow rate maintained for sample and eluent: 2 mL/min

Parameters	Co^{2+}	Cr^{3+}	Cu^{2+}	Ni^{2+}
Linear range (ng/mL)	0.01-0.25	0.01-0.25	0.01-0.25	0.01-0.25
Limit of detection (ng/mL)	0.64	1.7	0.44	0.51
RSD %*	2.8	2.4	2.6	2.9

*RSD=S_r=Sx100/x

4. Conclusion

In this Study, the efficiency of a silica-based amide-derived stationary phase, which we used as the HPLC stationary phase in our previous study, on the enrichment of Cu^{2+}, Cr^{3+}, Co^{2+}, and Ni^{2+} metal ions from aqueous solutions by solid phase extraction method was investigated. In order to determine the optimum experimental conditions, the effects of pH, flow rate, sorbent amount, elution solvent concentration, sample volume and interference ions were studied. All metal ions were highly adsorbed to the stationary phase at pH 7 and were eluted with 8 mL of 0.25 mol/L HCI. It was found that this developed SPE method showed high selectivity towards all metal ions in the presence of interference ions and the low detection limit for all metal ions.

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