

## Modified Sodium Dodecyl Sulfate Coated $\gamma$ -Alumina Nanoparticles with (E)*N'*-(2-Hydroxybenzylidene)Isonicotinohydrazide as New Sorbent for Copper Determination in Real Samples

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### Abstract

In this study, a novel and efficient solid phase extraction method based on the use of  $\gamma$ -alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) nanoparticles coated with sodium dodecyl sulfate and modified with (E)*N'*-(2-hydroxy benzylidene)isonicotinohydrazide (H<sub>2</sub>L) as a new adsorbent was developed for separation and determination of trace amounts of copper(II) prior to flame atomic absorption spectrometry (FAAS). The analyte ions were adsorbed quantitatively on adsorbent due to their complexation with (H<sub>2</sub>L). The separation procedure was studied with regard to experimental parameters such as pH, amount of sodium dodecyl sulfate, ligand's concentration, contact time, type and volume of eluent and stirring rate. The effects of interfering ions on the extraction procedure were also investigated. Under the optimum experimental conditions, the extraction efficiency was 98, 97 and 95.5 with relative standard deviation lower than 5% for Shurabil Lake, the collected water behind the barrier and Baligluchai River, respectively. Noticeably, the method has been successfully applied for the extraction and determination of copper content in some real samples.

### Keywords

Flame Atomic Absorption, Sodium Dodecyl Sulphate,  $\gamma$ -Alumina Nanoparticles.

## 1. INTRODUCTION

Heavy metals released into the environment have posed a regardable danger to the environment and world health because of their toxicity and persistence in environment [1-3]. Copper is one of the several heavy metals, which are essential and significant trace element, its deficiency is one of the causes of anemia, but it is toxic in large amounts. It has been well reported that the accumulation of copper in human body causes brain, skin, pancreas and heart diseases [4]. Domestic and industrial waste discharge, refineries can lead to high copper concentration in plants and water [5]. Furthermore, wastewater from various industries, such as electroplating, plastic, metal finishing, pigments, and mining contains copper. Accordingly, the world health organization and the European water quality directive recommend the concentration of copper in drinking water not to exceed 2 mg L<sup>-1</sup> [6]. Therefore, the amount of copper in water and food must be managed with a sensitive and accurate daily basis method. Various methods have been utilized for the determination of Cu(II) such as spectrophotometry [7,8], inductively coupled plasma mass spectrometry [9], atomic absorption spectrometry (AAS) [10,11], inductively coupled plasma atomic emission spectrometry (ICPAES) [12], and anodic stripping

voltammetry [13]. The common availability of the instrumentation, the ease of the procedure, speed, precision and accuracy of the technique still make flame atomic absorption such an attractive alternative method [14].

Solid-phase extraction of heavy metal ions has come to the forefront to the other preconcentration techniques due to simplicity, consumption of small volumes of organic solvent, and ability to achieve a higher enrichment factor [15], absence of emulsion and safety with respect to hazardous samples [16] and minimal costs [17-22]. It is commonly acknowledged that the adsorption materials determine the analytical sensitivity, precision and selectivity in SPE techniques. Activated carbon [23], SDS coated on alumina [24], modified chromosorb [25] are such most prominent supports have been widely used for the separation of trace metal ions from various matrices. It is regardable that alumina is one of the most widely utilized adsorbents, as it never swells and has proper mechanical strength; small solubility and stability in a broad pH range [26-28]. Immobilization of organic reagents on the surface of surfactant coated on alumina could be aimed at modifying the surface with certain target functional groups for a higher selectivity of the extraction which was introduced by Hiraide et al

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[29-31]. Adsorption of ionic surfactants on mineral oxides is a cooperative process in which organic reagent is participated in the cores of admicelles of sodium dodecyl sulfate attached to alumina surfaces. Because of the amphiphilic character of surfactants, ad-micelles are aggregates in which there are regions of various polarity, and acidity, etc. This feature makes these aggregates extremely versatile extractant because of the different interactions which they can establish with analytes and this approach was triumphfully applied for the pretreatment of different metal ions [32-34], and polyaromatic hydrocarbon as well.

The present research was intended to assess the use of SDS coated on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles modified with (E)N'-(2-hydroxybenzylidene)isonicotinohydrazide (H<sub>2</sub>L) as sorbents for the effective extraction and determination of copper(II) in natural waters.

## 2. EXPERIMENTAL

### 2.1. Instrumentation

The measurements of metal ions were performed with a SensAA GBC atomic absorption spectrometer (Dandenong, Australia) equipped with a hollow cathode lamp as radiation source and deuterium background corrector. The operational conditions of the equipment were set on the base of manufacturer recommendations for each element. The atomization was carried out in an air-acetylene flame. All UV-Vis spectra were recorded on a computerized double-beam 1601pc Shimadzu spectrophotometer (Tokyo, Japan) using two matched 1 cm quartz cells. The Fourier transform infrared (FTIR) spectra were recorded with Shimadzu IRPrestige-21 FTIR instrument (Tokyo, Japan) in the solid state as KBr discs. A Jenway 3510 pH meter (England) with a combined glass-calomel electrode was used for the adjustment of pH.

### 2.2. Reagents and Solutions

All chemicals used in this work, were of analytical reagent grade obtained from Merck (Darmstadt, Germany) and were used without further purification. A stock solution of 1000 mg L<sup>-1</sup> of the understudy element was prepared by dissolving appropriate amount of nitrate salt of the target element in 1% HNO<sub>3</sub> solution. The element standard solutions used for calibration were produced by diluting a stock solution with doubly distilled de-ionized water. All the plastic and glassware were cleaned by soaking in dilute HNO<sub>3</sub> (1 + 9) and were rinsed with de-ionized water prior to use. The pH adjustment was done by the addition of dilute nitric acid or sodium hydroxide to phosphate solution for preparing the desired pH buffer solution.

### 2.3. Preparation of (E)N'-(2-hydroxybenzylidene)isonicotinohydrazide (H<sub>2</sub>L)

(E)N'-(2-hydroxybenzylidene)isonicotinohydrazide was prepared as described in the literature [35]. Briefly, isonicotinohydrazide (10 mmol) was solved in 30 mL ethanol and it was refluxed for half an hour. Then 10 mmol salicylaldehyde was added to the solution and refluxed during 3 to 4 hours on a magnetic mixer so that the sediment formed [36]. After cooling down to room temperature, the final product was separated from the reaction mixture and washed several times with ethanol and dried under vacuum in oven at 60 °C.

### 2.4. Spectrophotometric titration

In order to investigate the complexation process between H<sub>2</sub>L and Cu(II) ions, the spectrophotometric titration was utilized [37]. In a typical procedure, 2 mL of a standard solution of H<sub>2</sub>L (1.0×10<sup>-4</sup> mol L<sup>-1</sup>) in ethanol were placed in the spectrophotometer cell and the absorbance of solution was measured at 25 °C. Then a known amount of the concentrated solution of Cu(II) (1.0×10<sup>-2</sup> mol L<sup>-1</sup>) in ethanol was added in a stepwise manner using a 10  $\mu$ L Hamilton syringe and the absorbance intensity was measured in a range of 200-500 nm.

### 2.5. Preparation of H<sub>2</sub>L-SDS-A

About 0.16 mmol of H<sub>2</sub>L and 0.17 mmol of sodium dodecyl sulfate (SDS) were added to 40 mL of de-ionized water solution containing 1.5 g  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles. The pH was adjusted to 2.0 with 2 mol L<sup>-1</sup> nitric acid to form H<sub>2</sub>L-impregnated ad-micelles on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles while shaking the suspension with a stirrer. After mixing for 20 min, the supernatant was discarded and the remaining was washed by 5 mL of 2 mol L<sup>-1</sup> HNO<sub>3</sub>, and then it was neutralized during the elution process with de-ionized water for several times. The sorbent has been stable at least for 4 weeks if it is kept in a refrigerator. In this study, to avoid formation of micelles in the aqueous solution, the concentration of SDS was fixed below the critical micelle concentration (CMC) of SDS throughout the experimental work.

### 2.6. Recommended procedure

In order to prevent waste of material used for optimization of SPE the following procedure was used. The 10 mL of aqueous sample solutions containing 0.6  $\mu$ g mL<sup>-1</sup> of analyte ions were kept contacted directly with the 0.05 g modified solid phase sorbent after adjusting pH by the buffering of the solution with phosphate buffer solution (pH=7). After a time period of agitation for 60 min at 300 rpm, the suspensions were centrifuged at 4500 rpm for 10 min. The adsorbed ions were then

eluted with 6 mL of 1 mol L<sup>-1</sup> nitric acid and were determined by flame atomic absorption spectrometry. All the investigations were carried out in triplicate to avoid any discrepancy in experimental results with the repeatability and the relative deviation of the order of  $\pm 1.5\%$ .

### 2.7. Analysis of water samples

Three real environmental water samples, including lake water, the collected water behind the barrier and river water were analyzed using this method. The water samples were collected from Shurabil lake, Yamchi barrier and Baligluchai river, Ardabil, Iran. All samples were first passed through 0.45  $\mu\text{m}$  nylon filter in order to remove suspended particles, then enough buffer solution was added to achieve the pH=7. After that, 250 mL of each sample was kept contacted with the 0.5 g modified solid phase sorbent and the analyte ions were quantified as described above.

## 3. RESULT AND DISCUSSION

### 3.1. Characterization of adsorbent

Although a vast number of studies have been reported on the use of bare alumina for metal ion removal from aqueous solution, that were not selective and the recoveries were incomplete, the coating of alumina with organic compounds could increase the adsorption capacity of the analyte ions [24]. The effective prepared adsorbent was chemically characterized by FTIR spectroscopy in order to identify the functional groups at the surface of the modified  $\gamma\text{-Al}_2\text{O}_3$  nanoparticles. The FTIR spectra of pure H<sub>2</sub>L-SDS-A are shown in Fig. 1, which exposure well modified  $\gamma\text{-Al}_2\text{O}_3$  nanoparticles surface with sodium dodecyl sulfate (SDS) and H<sub>2</sub>L.

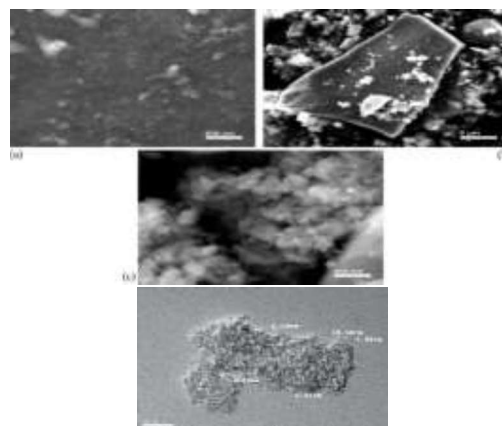


**Fig 1.** The FTIR spectra of H<sub>2</sub>L-SDS-A  
The SEM and TEM image of adsorbent shown in

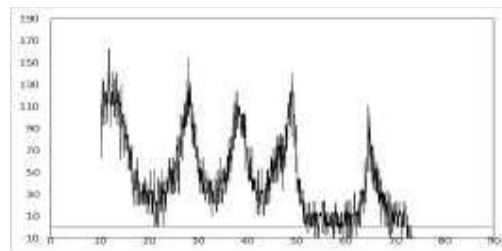
The peak at  $\sim 3446\text{ cm}^{-1}$  is attributed to the stretching vibrations of  $\text{-OH}$ , which is assigned to surface OH groups of  $\gamma\text{-Al}_2\text{O}_3$  nanoparticles. Absorption peaks at almost  $1348\text{ cm}^{-1}$  observed that was attributed to S=O groups of SDS and peaks at 2854 and  $2922\text{ cm}^{-1}$  are assigned to stretching mode of the aliphatic C-H groups of SDS in the final product. Further peaks at 1600 and  $1625\text{ cm}^{-1}$  are attributed to the stretching vibrations of C=C and aromatic C=N, respectively.

FTIR study confirmed the presence of the necessary functional group in the modified  $\gamma\text{-Al}_2\text{O}_3$  nanoparticles.

Fig. 2 the average size of  $\gamma$  Nano alumina is between 5 and 10nm. X-ray diffraction (XRD) analysis of  $\gamma$  Nano alumina show in Fig 3. The pattern confirmed off. Alumina with reference data.



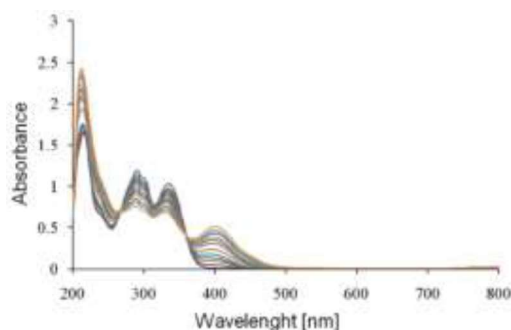
**Fig 2.** SEM image of Nano alumina (a,b,c) and TEM image



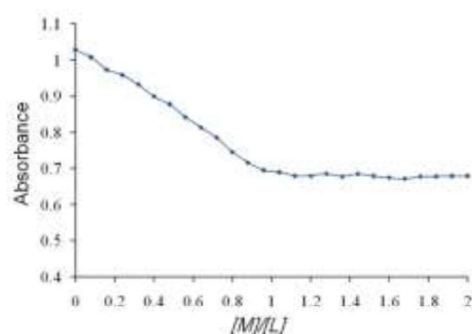
**Fig 3.** (XRD) analysis of Nano alumina

### 3.2. Study of complexation between H<sub>2</sub>L and Cu(II)

We study the complexation between H<sub>2</sub>L and Cu(II) ions using spectrophotometric titration method in ethanol at 25 °C. A typical spectrum was depicted in Fig. 4. According to the obtained results, by addition of Cu(II) ions to the ethanol solution of the ligand, absorbance of the solution at wavelengths of 290 and 335 nm decreased and a new peak at about 400 nm is formed that corresponds to the formation of a Cu(II)-L complex. Also, the observed spectral evolution involved the formation of a well-defined isobestic point at around 355 nm, indicating the presence of an absorbing complex compound between H<sub>2</sub>L and Cu(II) ions. To estimate the stoichiometry of the resulting complex, mole ratio method was used and the plot of the absorbance at 335 nm against [M]/[L] mole ratio is given in Fig. 5. From the sharp inflection point observed at 1:1 [M]/[L] mole ratio, it can be concluded that a stoichiometry of the complex formed between ligand and Cu(II) cation is 1:1.



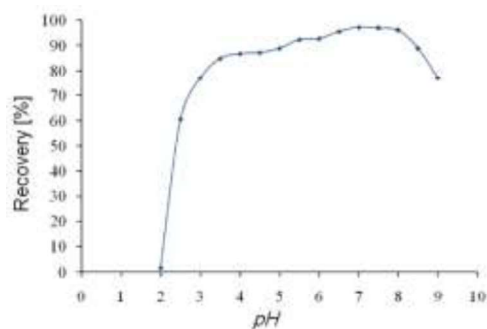
**Fig 4.** Spectrophotometric titration of Standard stock solutions of H<sub>2</sub>L ( $1.0 \times 10^{-4}$  mol L<sup>-1</sup>) with the copper ions ( $1.0 \times 10^{-2}$  mol L<sup>-1</sup>)



**Fig 5.** Mole ratio plots of absorbance as [M]/[L] at 335 nm

### 3.3. Effect of pH

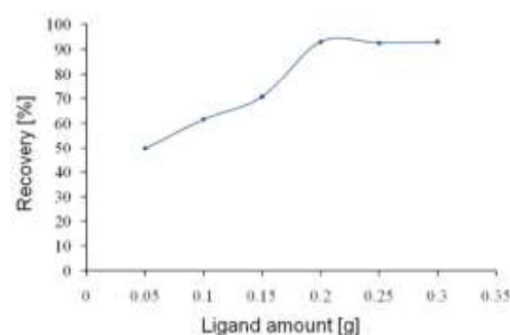
Obviously, pH is a critical parameter on the recoveries of analytes on solid phase extraction. To determine the effect of pH on extraction process, the range from 2-9 was investigated. The obtained results indicated that the copper ions could be quantitatively adsorbed on the modified H<sub>2</sub>L-SDS-A when pH is equal to 7 (in accordance with Fig. 6). The decrease in adsorption observed when pH is higher than 8 due to the precipitation of copper as hydroxide, furthermore, at lower pH values, the positive charge density on the adsorbent surface can lead to the decrease in the recovery. To achieve permissible efficiency and proper selectivity, a pH of 7 was selected for the rest of the experiments.



**Fig 6.** Effect of pH

### 3.4. Effect of ligand concentration

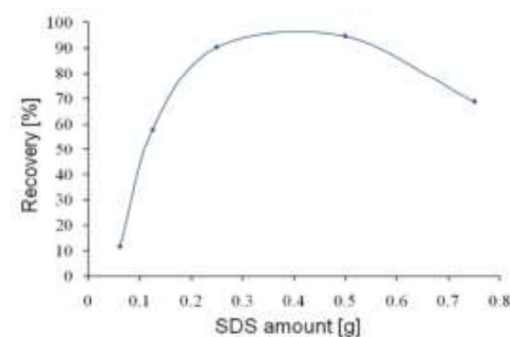
Effect of the quantity of H<sub>2</sub>L as a chelating agent coated on constant amount of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles was also pursued. Quantities of H<sub>2</sub>L around 0.05-0.3 g on the adsorption procedure were tested and the results are shown in Fig. 7. As can be seen, without H<sub>2</sub>L the recovery yields of Cu(II) ions are only about 21%, while the recoveries of the metal ions increased with increasing the amount of H<sub>2</sub>L added and reached a maximum value (95%) with at least 0.2 g H<sub>2</sub>L. Further addition of ligand has no significant change on recovery of ions. On this basis, studies were carried out at 0.2 g of ligand.



**Fig 7.** Effect of the amount of ligand

### 3.5. Amount of SDS

In order to conduct an effective and repeatable solid phase extraction, the composition of solid phase adsorbant must be optimized, so quantitative results were obtained with the addition of different amounts of SDS. A range from 0.06-0.75 g of SDS with 1.5 g  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles and 0.2 g H<sub>2</sub>L as constant amounts were evaluated. The retention of metal ions on admicelles clearly depends on the amount of SDS which forms hemimicelles with hydrophobic surface. According to the Fig. 8, 0.25 g of SDS as a suitable amount which properly can construct hemimicelles selected to continue the procedure. A decrease in the percentage of ions recovery was observed in higher amounts probably due to the formation of micelles in solution [38].



**Fig 8.** Effect of SDS amount

### 3.6. Effect of elution condition on the recovery

There are many different approaches for desorption of analytes on solid phase [39,40]. Nature and amount of the eluent have a great effect on the elution process. A satisfactory eluent must effectively elute the sorbed analytes with small volume, which is needed for acceptable recoveries and should not affect the accurate determination of the analytes and destroy life time and reusability of solid phase. For this reason, various solutions were attempted to be utilized as the eluent. The relative results are presented in Table 1. Also, the effect of eluent volumes on the recovery of copper ions was investigated. As a result, 6.0 mL of 1.0 mol L<sup>-1</sup> HNO<sub>3</sub> was sufficient and quantitative elution consequences could be gained for the curve.

**Table 1.** Effect of elution condition on the recovery

Eluent	Recovery %
H <sub>3</sub> PO <sub>4</sub> (1 M)	52.4
H <sub>3</sub> PO <sub>4</sub> (2 M)	39.5
H <sub>3</sub> PO <sub>4</sub> (3 M)	30.8
H <sub>2</sub> SO <sub>4</sub> (1 M)	60.9
H <sub>2</sub> SO <sub>4</sub> (2 M)	62.9
H <sub>2</sub> SO <sub>4</sub> (3 M)	59.2
HCl (1 M)	75.6
HCl (2 M)	69.0
HCl (3 M)	53.3
HNO <sub>3</sub> (1 M)	99.6
HNO <sub>3</sub> (2 M)	95.4
HNO <sub>3</sub> (3 M)	95.2

### 3.7. Effect of contact time and stirring rate

The complete chelation and deposition of the analyte ions on the sorbent depends on the contact time and stirring rate of the sample solution. To investigate the effect of contact time and stirring rate on the extraction recovery, the amount of 15-60 min and 100-700 rpm were examined respectively. Accordingly, 60 min stirring with the rate of 300 rpm was detected as desirable consequences which depicted the proper contact conditions between analyte and adsorbant.

### 3.8. Sample volume

Sample volume is a main factor for the preconcentration methods. After optimization of SPE conditions, in order to obtain high enrichment factors, sample volume was investigated. To do this several experiments were performed by contacting the sample volumes in the range of 50-500 mL containing 60 µg of copper ions with 0.5 g of modified solid phase. It was indicated that in all cases, adsorption and desorption percent of the copper ions were complete. Therefore, it was concluded that the breakthrough sample volume could be even greater than 500 mL. It should be noted that when the large sample volume was used, the more time was required for deposition of the

copper ions on the sorbent. Due to the high enrichment factor and analytical speed, 250 mL of sample volume is recommended. Since in the proposed procedure, the sample and eluent volumes were 250 and 6 mL respectively, therefore an enrichment factor of 42 was obtained.

### 3.9. Analytical features

Under the optimized conditions, calibration curves of the method were plotted with standard solutions of copper ions at 10 level concentrations. For each level, three replicate extractions were performed. The calibration graph was linear in the range of 0.06-3 µg mL<sup>-1</sup> with correlation coefficient of 0.9993. The limit of detection (LOD) of the method was calculated under optimal conditions after application of the preconcentration method to blank solutions. Detection limits based on the three times the standard deviation of the blank for the copper ions was found to be 3.2 µg L<sup>-1</sup>.

### 3.10. Interferences

In view of the high selectivity which is provided by flame atomic absorption spectrometry, the only interference may be attributed to the extraction process. For this purpose, extraction of copper ions in the presence of some selected metal ions has been carried out. The results were summarized in Table 2. The tolerated amounts of each ion were the tested concentration values that led to error less than 5% of the recovery alteration. The ions normally present in water do not interfere with the determination of analyte under the used experimental conditions.

**Table 2.** Interference

Interfering Ion	Interfering Ion/analyte fold ratio	Recovery %
Ni <sup>2+</sup>	150	95.3
Pb <sup>2+</sup>	100	96.1
Ag <sup>+</sup>	100	96.9
Co <sup>2+</sup>	100	96.2
Zn <sup>2+</sup>	100	97.5
Mn <sup>2+</sup>	100	95.3
Mg <sup>2+</sup>	75	95.1
Na <sup>+</sup>	50	99.8
Fe <sup>3+</sup>	25	98.3
Al <sup>3+</sup>	25	94.4
Hg <sup>2+</sup>	10	96.8
Sr <sup>2+</sup>	10	98.2

### 3.11. Determination of copper in real water samples

In order to assess the applicability of the method for real samples, with different matrices which have a variety diverse ions, it was applied to the separation and determination of copper(II) ions in Shurabil lake, the collected water behind the barrier and Baligluchai river water samples as

different matrices. The results are listed in Table 3. As can be seen, the amount of copper added to the real samples were extracted and determined quantitatively.

**Table3.** Recovery studies of copper extraction from some real samples

Sample	Cu(II) added, $\mu\text{g mL}^{-1}$	Cu(II) found, $\mu\text{g mL}^{-1}$	RSD %	Recovery %
Lake	0.000	0.056	3.1	-
water	0.090	0.144	2.6	98
Barrier	0.000	0.093	3.7	-
water	0.090	0.180	2.9	97
River	0.000	0.071	2.0	-
water	0.090	0.157	1.5	95.5

#### 4. CONCLUSION

A new solid phase extraction technique was developed based on the sufficiently extraction of Cu(II) ions in environmental samples on H<sub>2</sub>L-SDS-A prior to the determination by FAAS. The conditions for quantitative and reproducible preparation and elution with FAAS determinations were evaluated. This approach is simple, accurate, and economical and can be applied for the determination of copper ions in environmental samples. The system depicted reproducibility and reliability in analytical data, with an RSD value of lower than 5% on triplicate experiment. The system was successful in the extraction of analytes from river, lake and barrier water.

#### Acknowledgments

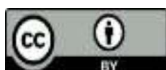
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## اصلاح نانو ذرات گاما آلومینای پوشش داده شده از سدیم دو سدیل سولفات با لیگاند $H_2L$ به عنوان جاذب جدید برای اندازه گیری مس در نمونه های واقعی

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### چکیده

در این مطالعه، یک روش جدید و کارآمد استخراج فاز جامد، مبتنی بر اصلاح نانو ذرات گاما آلومینای پوشش داده شده با سدیم دودسیل سولفات با لیگاند  $H_2L$  به عنوان یک جاذب جدید برای جداسازی و اندازه گیری مقادیر کمی مس (II) توسط طیف سنجی جذب اتمی شعله ای توسعه داده شده است. یون های آنالیت به دلیل کمپلکس شدن با لیگاند به صورت کمی روی جاذب جذب و فرآیند جداسازی به وسیله پارامترهای موثر مانند pH، مقدار سدیم دودسیل سولفات، غلظت لیگاند، زمان تماس، نوع و حجم شوینده و سرعت همزدن مورد بررسی قرار گرفته اند. اثرات یون های مزاحم بر روی روش استخراج نیز بررسی و بهینه شدند. تحت شرایط بهینه راندمان استخراج ۹۷،۹۸ و ۹۵،۵ با انحراف معیار نسبی کمتر از ۵ درصد برای دریاچه شورابیل، آب جمع آوری شده پشت سد و رودخانه بالقلوچای به دست آمد. قابل توجه است که این روش با موفقیت برای استخراج و اندازه گیری مس در برخی از نمونه های واقعی استفاده شد.

### واژه های کلیدی

جذب اتمی شعله ای، سدیم دودسیل سولفات، نانو ذرات گاما آلومینا.