



# Analysis of the Optimal Conditions for the Immobilization of Nitroso-R Salt on Synthetic Fibers

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**\*Corresponding author:** Ashirov MA, PhD, Khorezm Mamun Academy, Uzbekistan

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**Yusupova MR<sup>1</sup>, Ashirov MA<sup>2\*</sup>, Avazyazov AM<sup>3</sup> and Smanova ZA<sup>4</sup>**

<sup>1</sup>2nd year doctoral student, Khorezm Mamun Academy, Uzbekistan

<sup>2</sup>PhD, Khorezm Mamun Academy, Uzbekistan

<sup>3</sup>Master's student, Urgench State University, Uzbekistan

<sup>4</sup>Department of Analytical Chemistry, Faculty of Chemistry, Uzbek National University, Uzbekistan

## Abstract

This study investigates the sorption-spectroscopic method as a contemporary hybrid technique for the quantification of heavy and toxic metals. The research focuses on the immobilization of nitroso-R salt onto solid supports. Optimal conditions for the immobilization of nitroso-R salt on synthetic PPA fiber were established, and the influences of pH and fiber capacity were evaluated. Molar absorptivity coefficients of the colorimetric reactions were determined. Additionally, dissociation constants of nitroso-R salt were calculated colorimetrically at an ionic strength of 0.1-0.5 M and compared with literature data.

**Keywords:** Colorimetry; Spectrophotometer; Molar absorption coefficient; Immobilization; PPA fiber; Nitroso-R

## Introduction

Accurate quantification of metal ions is critical in diverse fields including medicine, ecology, and food science [1]. Conventional techniques such as inductively coupled plasma-mass spectrometry, X-ray absorption spectroscopy, electroanalytical methods, and atomic spectroscopy variants are prevalent for metal ion determination. However, these methods are associated with high costs, complex instrumentation, specialized personnel requirements and reliance on centralized laboratory infrastructure [2-4]. Furthermore, the use of specialized, often volatile, toxic and expensive reagents precludes in situ analysis [5]. Consequently, there is a growing demand for rapid, simple testing systems that enable qualitative and quantitative analysis without complex equipment or extensive sample preparation.

A promising approach involves the immobilization of organic reagents onto solid supports, followed by sorption-spectroscopic detection of metal ions. This hybrid methodology enables a reduction in detection limits while enhancing the selectivity and accuracy of metal ion determination.

Previous studies have demonstrated that the incorporation of surfactants, water-soluble polymers, or their immobilized forms into organic reagent solutions can significantly alter reagent properties [6-14]. Optically transparent polymers, including polymethacrylate [15], triacetylcellulose [16], ethylcellulose [15] and gelatin supported on transparent substrates, have garnered particular interest [8,13-17]. Sensor devices fabricated using these polymers hold promise for simplified photometric analysis. A variety of organic reagents have been investigated, including complexes of 4-(2-pyridylazo)resorcinol with divalent cobalt, copper, cadmium, zinc, lead and nickel [18]; arsenazo III and arsenazo B with trivalent lanthanum, tetravalent thorium, hexavalent uranium, and divalent calcium [14]; nichromazo with divalent vanadium [19] and azo dye formation within the transparent gel layer of commercial photographic films [13,20].

Polymeric materials can serve as either co-matrix with conventional porous substrates or as primary solid supports for immobilization. Essential attributes of the polymeric base include optical transparency, substantial absorptive capacity, straightforward synthesis, ease of handling, chemical inertness, mechanical robustness, stability under acidic and alkaline conditions, and heightened sensitivity to analytical reagents. While many existing polymeric sorbents partially fulfil these criteria, a comprehensive investigation into the analytical characteristics of novel fibrous polymer carriers for sorption-spectrophotometric analytical systems is imperative for broadening the scope of analytical chemistry.

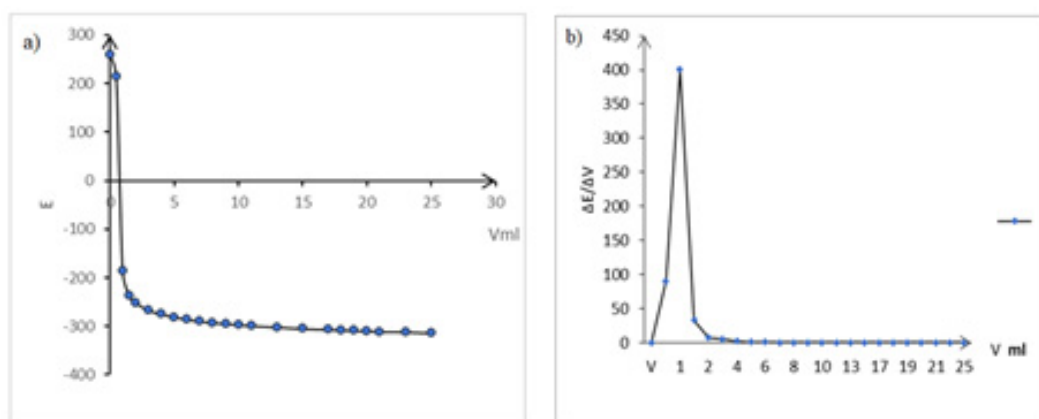
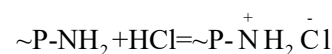
Polyacrylonitrile (PAN) fibers were modified with polyethylene polyamine to produce orange polyamine phosphate (PPA) fibers, a cation-exchange material. Significant interest exists in the immobilization of 1-nitroso-2-naphthol-3,6-disulfonic acid disodium salt (nitroso-R-salt, NRS) onto this synthetic support and the elucidation of the underlying polymer-NRS bonding interactions.

Orange polyamine phosphate (PPA) fiber, a cation-exchange material synthesized from polyacrylonitrile fiber modified with polyethylene polyamine by researchers at the Polymer Chemistry department, National University of Uzbekistan. 1-Nitroso-2-naph-

thol-3,6-disulfonic acid (nitroso-R-salt), a water-soluble analogue of 1-nitroso-2-naphthol [21], is widely employed in analytical chemistry. This study represents the first attempt to immobilize this reagent onto PPA-1 fiber for the development of sorption-spectroscopic methods for the determination of specific metal ions in wastewater. Optimal conditions for this process were investigated.

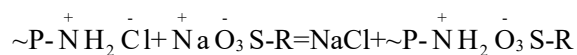
### Immobilization Technique

Carriers were utilized in the form of disks, each with a diameter of 2cm and a mass of 0.2g. The prepared supports were immersed in 10mL of 0.1M hydrochloric acid (HCl) and agitated for 24 hours using a magnetic stirrer. During this process, the amine groups on the fiber bind to the chloride ions present in the hydrochloric acid. Subsequently, the fiber was separated from the solution and rinsed with 50mL of distilled water. The binding of chloride ions to the fiber was quantified by potentiometric titration, measuring the residual hydrochloric acid in the solution with 0.1 M sodium hydroxide (NaOH) (Figure 1). The mechanism of the conversion of the fiber to its chlorinated form is illustrated as follows.



**Figure 1:** Integral (a) and differential (b) curves of potentiometric titration of PPA-1 fiber in aqueous medium.

The washed fiber was maintained in a moist state within Petri dishes. The objective of converting PPA fiber to its chlorinated form is to facilitate the formation of a strong bond between the sulfonate group of the organic reagent and the amine group of the chlorinated fiber. The mechanism underlying this process is as follows.



The effects of pH, buffer mixture and reagent concentration in the solid phase were investigated at a solution flow rate of 10mL/min. The concentration of the reagent in the carrier was quantified spectrophotometrically by measuring the change in absorbance of the solutions at the optimal wavelength for each reagent, both before and after immobilization [22].

From the experiments, it was observed that treating the fiber in a 0.1M hydrochloric acid solution for 24 hours significantly increased the SOE capacity. Increasing the concentration from 25% to

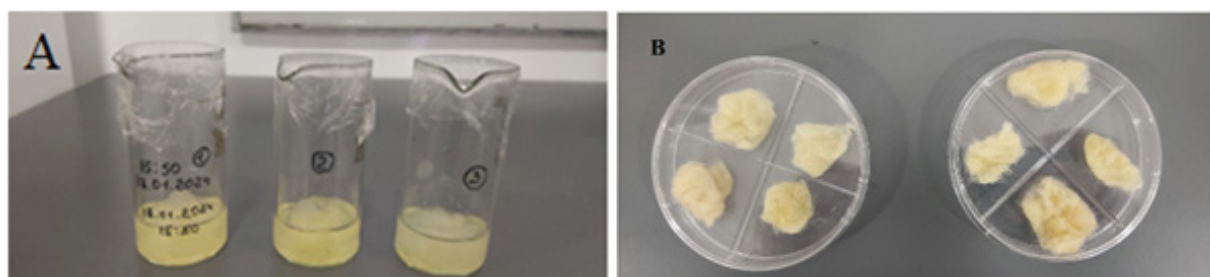
50% resulted in an approximately threefold increase in the degree of polymer conversion. After treatment with hydrochloric acid, PPA-1 fibers were kept moist in Petri dishes (Figure 2) and subsequently immobilized with a solution of the organic reagent nitroso-R salt.

The optimum immobilization conditions, organic reagent concentration, and optical density were measured using a Shimadzu-1900 spectrophotometer. The optimal reaction conditions were determined with a Five Easy pH/mV meter.

We reviewed the literature to analyze the active state of the organic reagent in solution. 1-Nitroso-2-naphthol-3,6-disulfonic acid (nitroso-R-salt) is extensively used in analytical chemistry as a water-soluble analogue of 1-nitroso-2-naphthol. However, there is limited information on the optical characteristics of its various ionic forms, and the dissociation constant of its hydroxyl group is reported inconsistently, ranging from 6.57 to 7.89 (pK units) due to variations in temperature, ionic strength, and ionic environments [23]. This variability complicates the calculation of complex

stability constants. The literature examines the optical and colorimetric characteristics of nitroso-R salt at pH 4-10, determining the dissociation constant of its hydroxyl group using colorimetry at an ionic strength of 0.1-0.5 M, and compares these findings with our

colorimetric results. Based on this literature review, we conducted experiments. Initially, we studied the molar absorption coefficient of the organic reagent at a selected concentration in solution and compared our findings with the literature (Table 1).



**Figure 2:** PPA-1 fiber in acidic medium in 0.1M HCl acid solution (a) and fiber treated with 0.1M HCl acid in Petri dish (b).

**Table 1:** Physical constants of nitroso-R salt.

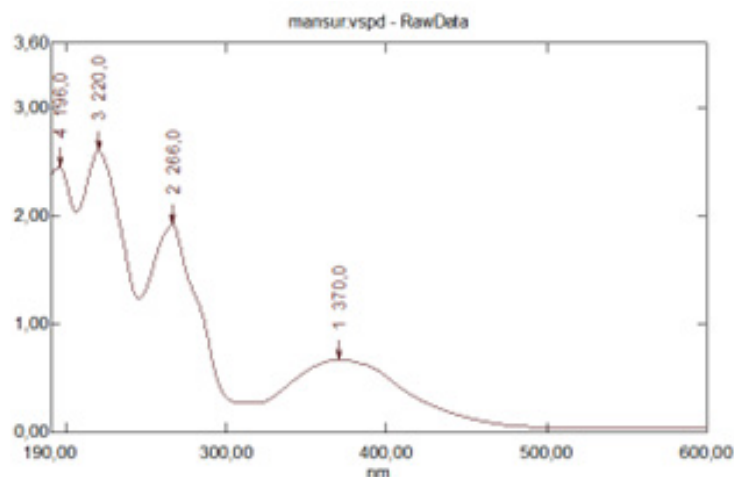
Nº	Reagent	$\lambda_{nm}$	$\epsilon 10^n \text{ L.mol}^{-1}.\text{cm}^{-1}$	$C_M$ concentration	$\lambda_{nm}$	$\epsilon 10^n \text{ L.mol}^{-1}.\text{cm}^{-1}$
1	Nitroso-R	370	$6.61 \cdot 10^3$	$1 \cdot 10^{-4}$	370	$6.48 \cdot 10^3$
		266			265	
		220			240	

### Dissociation Constants

Dissociation constants  $\Delta S/\Delta \text{pH}$  and pH were determined colorimetrically at a concentration of  $1.0 \times 10^{-4}$  M and an ionic strength of 0.1–0.5 (where  $S = \sqrt{A^2 + B^2}$ ) and  $\Delta S/\Delta \text{pH}$  is the specific color difference).

The absorption spectra of the solutions are presented in Fig-

ure 3. At pH 5.09, the solutions exhibit absorption maxima at wavelengths less than 220nm, 266nm, and 370nm (curve 1). As the pH increases, the absorbance at 266nm, corresponding to the absorption maximum of the HR2- form, increases. Concurrently, the absorbance at 370nm decreases slightly, and a more pronounced maximum peak emerges at 425nm.



**Figure 3:** UV spectra of the nitroso-R salt.

After determining the physical constants of the organic reagent, immobilization processes were conducted on the fiber. The capacity of the fiber was then assessed using a spectrophotometric method (Figure 4). The percentage concentration of the organic reagent immobilized on the fiber was measured in a spectrophotometer and calculated using the formula  $R = \Delta A/A_{\text{before}} \cdot 100\%$ .

Immobilization onto 0.2g of fiber resulted in a binding efficiency of 99.76% for the organic reagent at a concentration of  $3.2 \times 10^{-4}$  M, pH 5.09 and room temperature. This immobilized fiber has potential application in the determination of metal ions in various samples, which is currently under investigation. Further studies are ongoing to elucidate the mechanisms of the immobilization process using techniques such as infrared spectroscopy.



**Figure 4:** Immobilized nitroso-R salt.

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## References

- Zolotov YA, Ivanov VM, Amelin VG (2002) Chemical test methods of analysis. In: (1st edn), Elsevier, Volume. 36, ISBN 9780444502612.
- Kamnoet P, Aeungmaitrepirom W, Menger RF, Henry CS (2021) Highly selective simultaneous determination of Cu(ii), Co(ii), Ni(ii), Hg(ii) and Mn(ii) in water samples using microfluidic paper-based analytical devices. *Analyst* 146(7): 2229-2239.
- Bi CC, Ke XX, Chen X, Weerasooriya R, Hong ZY, et al. (2020) Assembling reduced graphene oxide with sulfur/nitrogen- “hooks” for electrochemical determination of Hg (II). *Analytica Chimica Acta* 1100: 31-39.
- Baghayeri M, Amiri A, Moghaddam BS, Nodehi M (2020) u-Based MOF for Simultaneous Determination of Trace Tl (I) and Hg (II) by Stripping Voltammetry. *Journal of the Electrochemical Society* 167: 167522.
- Huang D, Liu X, Lai C, Qin L, Zhang C, et al. (2019) Colorimetric determination of mercury (II) using gold nanoparticles and double ligand exchange. *Microchimica Acta* 186: 31.
- Savvin SB, Shtykov SN, Mikhailova AV (2006) Organic reagents in spectrophotometric methods of analysis. *Russian Chemical Reviews* 75: 341.
- Dzherayan TG, Shkinev VM, Shpigun LK, Kamilova PM, Geckler KE (2002) Water-soluble polymers for spectrophotometric and flow injection determination of cobalt with nitroso-R-salt. *Talanta* 57(1): 7-13.
- Nakashima K, Duhamel J, Winnick MA (1993) Photophysical processes on a latex surface: electronic energy transfer from rhodamine dyes to malachite green. *Journal of Physical Chemistry* 97(41): 10702-10707.
- Bacci M, Baldini F, Scheggi AM (1988) Spectrophotometric investigations on immobilized acid-base indicators. *Analytica Chimica Acta* 207: 343-348.
- Narayanaswamy R, Sevilla F (1986) Reflectometric study of the acid base equilibria of indicators immobilised on a styrene/divinylbenzene copolymer. *Analytica Chimica Acta* 189: 365-369.
- Vachoud L, Zydowicz N, Domard A (2001) Sorption and desorption studies on chitin gels. *International Journal of Biological Macromolecules* 28(2): 93-101.
- D'yachenko NA, Trofimchuk AK, Sukhan VV (2002) Sorption of cobalt as a Nitroso-R-Salt complex on silica gels modified with triphenylphosphonium groups followed by determination in the adsorbent phase. *Journal of Analytical Chemistry* 57: 1022-1024.
- Nikitina NA, Reshetnyak EA, Svetlova NV, Mchedlov Petrossyan NO (2011) Protolytic properties of dyes embedded in gelatin films. *Journal of the Brazilian Chemical Society* 22(5): 857-866.
- Saleem M, Tahira P, Qadeer R (2007) Sorption of acid violet 17 and direct red 80 dyes on cotton fiber from aqueous solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 292(2-3): 246-250.
- Gavrilenko NA, Mokhova OV (2008) Sorption-spectrophotometric determination of iron (II, III) with the use of organic reagents immobilized in a polymethacrylate matrix. *Journal of Analytical Chemistry* 63: 1038-1043.
- Rastegarzadeh S, Rezaei V (2008) A silver optical sensor based on 5(p-dimethylaminobenzylidene) rhodanine immobilized on a triacetylcellulose membrane. *Journal of Analytical Chemistry* 63: 897-901.
- Kuznetsov VV, Sheremet'ev SV (2009) Analytical complexation reactions of organic reagents with metal ions in a solidified gelatin gel. *Journal of Analytical Chemistry* 64: 886-895.
- Reshetnyak EA, Nikitina NA, Loginova LP, Petrossyan NO, Svetlova NV (2005) The protolytic and complex formatting properties of indicators in the gelatinous gel medium. *Kharkov University Bulletin, Chemical Series* 13(36): 67-82.
- Reshetnyak EA, Asmolov VE, Nemetz NN, Nikitina NA (2010) Optical sensor on the basis of hardened gelatinous gel for the photometric determination of sulfates in aqueous media. *Kharkov University Bulletin, Chemical Series* 18(41): 74-81.
- Sheremet'ev SV, Kuznetsov VV (2007) Reactions of the synthesis of azo dyes in solidified gelatin gel and their analytical application in the determination of nitrites. *Journal of Analytical Chemistry* 62: 319-324.
- Peshkova VM, Oksimy (Oximes). (1977) Moscow: Nauka.
- Ashirov MA, Smanova ZA, Gafurova DA (2020) Development of a absorption spectroscopic method for determination. *Universe: Chemistry and Biology* 1(67): 13.
- Ivanova VM, Mamedova AM, Figurovskaya VN, Ershova NI, Barbalat YA, et al. (2006) Photometric, colorimetric and acid-base characteristics of nitroso-R-salt. *Journal of Analytical Chemistry* 61(6): 571-575.