N-heterocyclic azo dyes immobilized on silica gel for solid-phase detection of traces of nickel, cobalt and copper by diffusion reflectance spectrometry

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Introduction

Transition metals, Ni, Co, Cu in particular, play crucial roles in our daily lives, industrial processes, and biological systems. However, even small quantities of these metals can have significant impacts on human health, the environment, and the performance of materials and products. Consequently, the development of precise and sensitive detection methods has become a central focus of scientific investigation and analytical methodologies.

In recent years, the integration of chromophoric organic reagents with silica surfaces has shown promise in creating versatile organo-mineral composites with broad application prospects. Particularly, N-heterocyclic azo dyes like 1-(2-pyridylazo)-2-naphthol (PAN) and 1-(2-thiazolylazo)-2-naphthol (TAN) have garnered significant interest. Previous studies have utilized silica-based sorbents immobilized with these azo dyes to determine metal (M) ions through light adsorption of metal-reagent (MR) complexes. Notably, MR_2, formed by the interaction of metal ions with these dyes, exhibits enhanced stability, higher molar extinction coefficients, and greater affinity to hydroxylation surfaces compared to MR. Consequently, tailoring the sorbent with an optimal arrangement of HR molecules for MR_2 formation has the potential to improve the sensitivity and selectivity of solid-phase determination of metal ions.

Experimental & Results

Modification of the silica gel

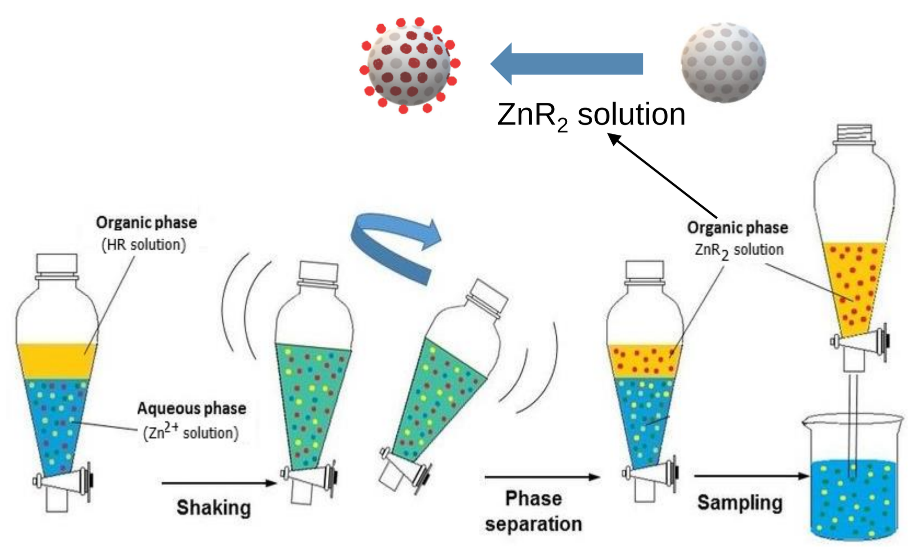
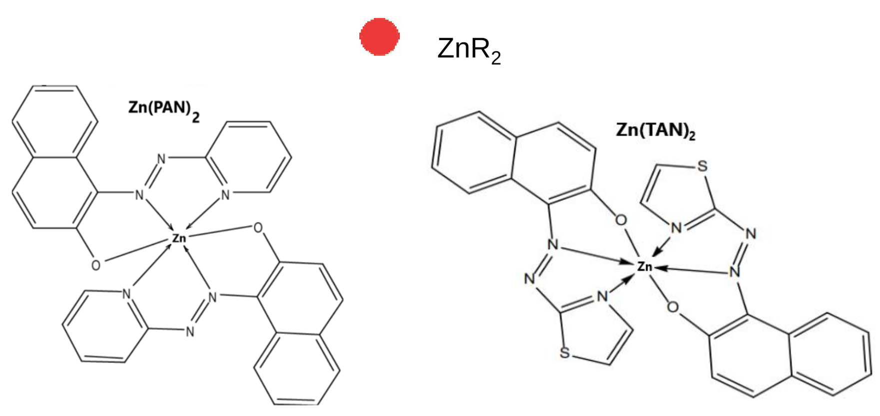


Fig 1. Methodology of $Zn(HR)_2$ immobilization onto SilicaGel surface.



Characterization of modified silica gel

Adsorption

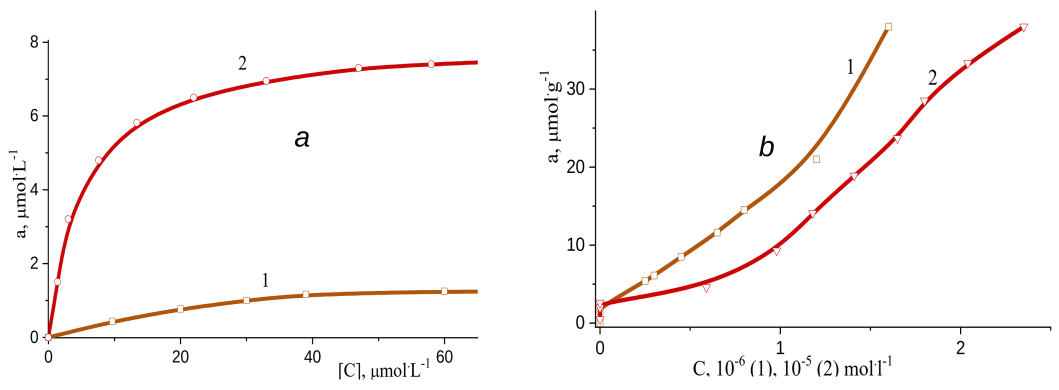


Fig 2. Isotherms of PAN (a) and TAN (b) adsorption onto Silica Gel surface as HR (1) and $Zn(R)_2$

FTIR

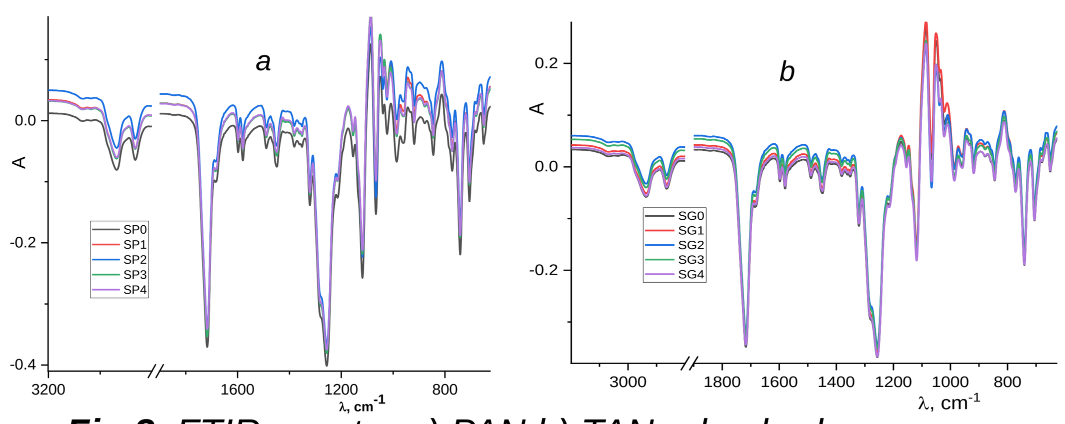


Fig 3. FTIR spectra a) PAN b) TAN adsorbed Fresh Silica gel (0) $a_{Zn(R)2}$, mol/g: $1.2 \cdot 10^{-5}$ (1), $3 \cdot 10^{-6}$ (2), a_{HR}, mol/g: $6 \cdot 10^{-6}$ (3), $2.4 \cdot 10^{-5}$ (4).

SEM

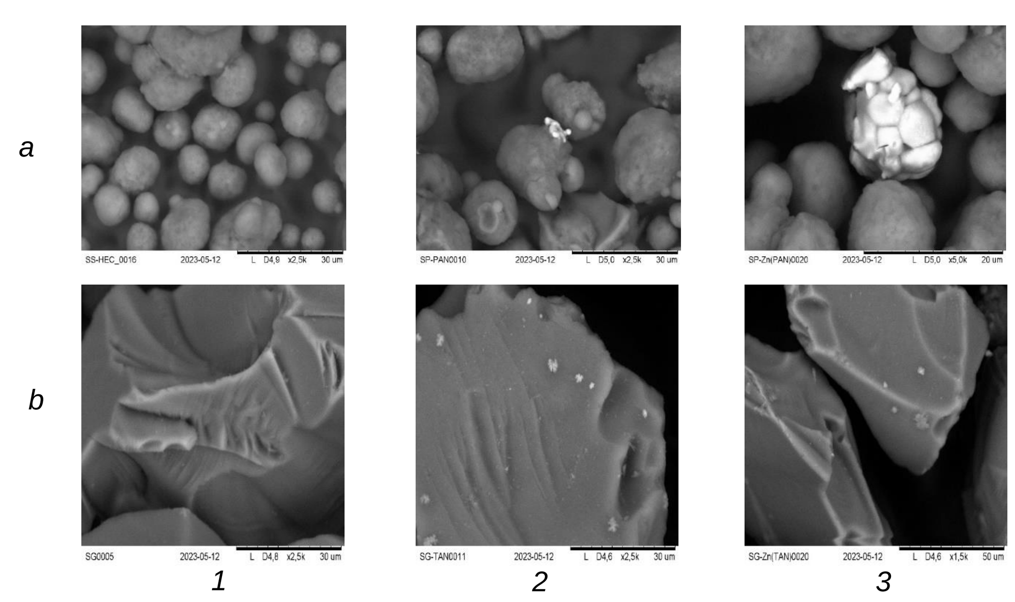


Fig 4. SEM images
(a) SP fresh (1) and with PAN (2) and $Zn(PAN)_2$ (3) adsorbed
(b) SG fresh (1) and with TAN (2) and $Zn(TAN)_2$ (3) adsorbed
a_{HR}, mol/g: $2.4 \cdot 10^{-5}$ (1), $a_{Zn(R)2}$, mol/g: $1.2 \cdot 10^{-5}$ (2)

Analytical application of modified silica gel

Sorbents used were obtained according the scheme

$$SG1,\ a_{ZnTAN_2} = 2.4\ \mu mol/g$$
$$\overline{SG} + ZnTAN_2 \leftrightarrow \overline{ZnTAN_2 - SG}$$
$$SP2,\ a_{ZnPAN_2} = 2.5\ \mu mol/g$$
$$\overline{SP} + ZnPAN_2 \leftrightarrow \overline{ZnPAN_2 - SP}$$
$$SG3,\ a_{TAN_2} = 2.4\ \mu mol/g$$
$$\overline{ZnTAN_2 - SG} + 2H^+ \leftrightarrow \overline{HTAN_2 - SG} + 2Zn^{2+}$$

***Table 1**. The chemical-analytical characteristics of methods developed*

ion	sorbent	t_a, min	analytical signal (y)	calibration equation* y=b+a·C(mg·l^{-1}) (r=0.990÷0.999)		Range of calibration equation linearity, mg/L	Detection limit**, mg/L
				a	b		
Ni(II)	SG1	0.5	$\Delta F(R)_{590}$	0.032	0.02	0.06-1.16	0.002
			ΔA_{590}	1.63±0.09	0	0.005-1.20	0.002
	SP2	10	$\Delta F(R)_{560}$	0.262±0.004	0.032±0.001	0.06-0.58	0.010
Cu(II)	SG3	1.0	$\Delta F(R)_{580}$	0.02	0	0.2-28	0.015
Co(II)	SP2	10	$\Delta F(R)_{595}$	0.216±0.003	0	0.06-0.60	0.015

***Table 2.** The results of Ni(II) determination. n=5, P=0.95*

Sample	Sorbent	Concentration of Ni(II), μg·mL^{-1}		
		Added	Founded x±Δx	
			SS	VT
Standard solution I	SG1	0.29	0.32±0.03	0.29±0.05
Standard solution II	SG1	0.58	0.64±0.12	0.82±0.23
Soil extract	SG1	-	0.50±0.05	0.44±0.12 0.44±0.12*
Soil extract	SG1	0.12	0.58±0.06	0.58±0.14 0.46±0.14*
Soil extract	SG1	0.29	0.82±0.06	-
Natural water	SP2	0.02	-	0.03±0.01
Natural water	SP2	0.06	-	0.06±0.02

Conclusions

- ✓ New solid-phase reagents presented in this work enable the creation of metal ion-organic ligand complexes in a 1:2 ratio on the surface.
- ✓ The hybrid materials produced using the solid-phase reagents were extensively analyzed through Fourier transform infrared spectroscopy, scanning electron microscopy, and adsorption methods. These techniques helped researchers understand the composition, structure, and morphology of the materials.
- ✓ Visual test and diffusion reflectance spectrometry methods for detection of Ni(II), Cu(II) and Co(II) were developed. Detection limits of determination were 2, 15 and 15 µg/l respectively. The successful application of these methods in soil extracts and tap water analysis demonstrates their practical utility for environmental monitoring.

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