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Sorption-Spectroscopic Determination of Cadmium Ions

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ABSTRACT: By immobilization of 1- (2-pyridylazo) -2-oxynaphthalene-3,6-sodium disulfate on a polymer sorbent of polyacrylonitrile type, a carrier was obtained for the determination of cadmium ions. The optimal conditions for immobilization and complexation were found. The data obtained were used to develop a method for the determination of cadmium ions in waters.

KEYWORDS: Immobilization, 1- (2-pyridylazo) -2-hydroxy-naphthalene-3,6-sodium disulfate, cadmium, ammonium acetate buffer, carrier, fibrous material, optical density, spectrophotometer, static mode, infrared spectra (IR), polyacrylonitrile (PAN), modified with hydroxylamine (MX-1 and CMA-1), hexamethylenediamine (CMA-2), ethylenediamine (CMA-3).

I. INTRODUCTION

The development of science and technology, as well as the introduction of new technogenic production processes leads to the anthropogenic impact of human production on the environment. Even today, the scale of this impact is comparable to the global scale of a number of natural processes. The biosphere introduced many alien to the substance, radioactive elements, poisonous chemicals, synthetic detergents and other substances that practically do not decompose, but are able to accumulate in living organisms, etc. [1]. Metal pollution in the water sector has increased particularly with industrialization, anthropogenic sources of which fall into the water during the extraction of oil, coal, ore, as well as industrial waste. A lot of pollution with toxic metals is introduced into the water and with agricultural runoff [2].

Anthropogenic emissions of cadmium, chromium (III), mercury, lead and arsenic are rapidly increasing. Cd found in industrial cities. This is a highly toxic element that falls along with aerosols and precipitation to the ground [3]. Cadmium can cause a violation of enzyme metabolism, the destruction of the nervous and musculoskeletal systems [4]. The development of sensitive, reliable, simple and economical methods for the determination of cadmium is an urgent task of modern analytical chemistry. Many photometric methods for the determination of cadmium have been developed, but the main disadvantage is the low sensitivity and selectivity. One of the developing methods that satisfy modern requirements is reflective spectroscopy using immobilized organic reagents (IMOR) [5, 6]. The use of such reagents allows to lower the lower limits of the determined concentrations of elements, to improve the metrological characteristics of the methods [7, 8].

Currently, fibrous materials are widely used as a matrix for the immobilization of O.R. Unlike other sorbents, polymer fibers have a highly developed specific surface area, the ability to regenerate, and improved kinetic characteristics [8].

The purpose of the work is to study the complexation of cadmium with immobilized 1- (2-pyridylazo) -2-oxynaphthalene-3,6-disulfonic acid sodium (PAR salt) on a fibrous carrier and the development of methods for the solid-state spectroscopic determination of cadmium in natural and waste waters.

II.SIGNIFICANCE OF THE SYSTEM.

Reagents and equipment. A standard solution of cadmium ($T = 1.0 \text{ mg / ml}$) was prepared by dissolving the corresponding cadmium salt ($\text{Cd}(\text{NO}_3)_2$) (chemically pure) in double-distilled water, working solutions were obtained by diluting the original [8].

A solution of an organic reagent-PAR salt with a concentration of $1 \cdot 10^{-3} \text{ mol / l}$ was prepared by dissolving the necessary weighed sample of the drug in double-distilled water.

Buffer solutions were prepared from the corresponding salts and acids of the qualification of chemically pure [9]. Metal salts and other reagents were chemically pure. orch.a. and were not subjected to additional purification, and their diluted solutions were prepared by diluting the original bidistillates before starting the experiment.

The acidity and basicity of the solutions was regulated by acetate-ammonia buffer solutions, the pH of the solutions was measured on an I-130 ionomer and a pH / mV / TEMP Meter P25 EcoMet pH meter made in Korea. Absorption spectra were measured on an SF-46, KFK-2 spectrophotometer, and reflection spectra were recorded on a UV-ViS SPECORD M-40 double-beam recording spectrophotometer equipped with a diffuse reflection attachment. Infrared spectra (IR) of reagents, carriers and immobilized ORs were recorded on an Avatar sistem 360 FT-IR spectrometer (USA).

As the carrier used a fibrous material synthesized according to the procedure [10]. A polyacrylonitrile sorbent modified with an anion exchanger(CMA-1) in the form of a disk, with a diameter of 2 cm and a weight of 20-30 mg, was used. It was washed with a mixture of 50 ml of 0.1 M HCl and 10 ml of acetone, then immersed for 10 minutes. in 10 ml of a $1 \cdot 10^{-3} \text{ M}$ solution of an organic reagent, after which the immobilized sorbent was stored in wet dishes in Petri dishes. The reagent content in the sorbent was determined spectrophotometrically by changing the optical density of the initial reagent solution at 440 nm before and after immobilization (Fig. 1).

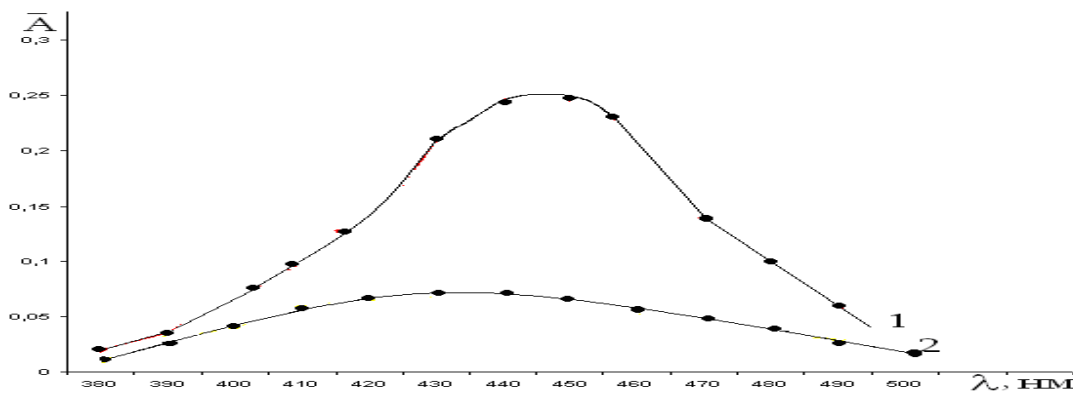


Fig. 1. The absorption spectra of the reagent before (1) and after (2) immobilization on the media SMA-1 at pH = 3-5

The characteristics of the immobilized reagent were determined in a static mode, the disks of which were placed in a glass with the test solution and with some slight stirring they were kept for a certain time. An analytical signal was a change in the coefficient of diffuse reflection of IMPAR salt disks with cadmium ions at 540 nm (Table 1).

Table 1. Spectral characteristics of IMPAR salts

$\lambda_{R, HM}$	$\lambda_{MeR, HM}$	Me:R	pH	mmobilizationtime, min	The concentration of reagent on the carrier, M
440	540	1:1	2.5-3.5	8	$2.5 \cdot 10^{-4}$

Two types of sorbent were used in the work, the initial one (beige color) and the reagent immobilized (colored). Color change due to complexation on the solid phase is detected both instrumentally and visually.

III. EXPERIMENTAL RESULTS.

Various polymeric carriers of industrial production, as well as sorbents synthesized at the Department of Polymer Chemistry of NUUZ, based on polyacrylonitrile (PAN), modified with hydroxylamine (MX-1 and CMA-1), hexamethylenediamine (CMA-2), were tested as a carrier for immobilizing PAR salt), ethylenediamine (CMA-3). It was found that the maximum analytical signal is obtained by immobilizing the reagent on the SMA-1 sorbent. Therefore, for further research, the SMA-1 system was selected: PAR-salt.

CMA-1 fiber was obtained by the action of hydroxylamine sulfate in the presence of hydrazine on PAN fiber [11]. The obtained modified polymer does not dissolve in PAN organic solvents, which indicates a sufficiently good crosslinking with hydrazine. The degree of conversion was evaluated by determining the SOE of the samples by hydrochloric acid, the SOE for the SMA-1 reaches 3.5-5.5 mEq / g.

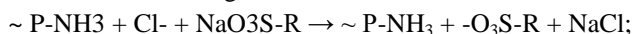
In studying the immobilization mechanism, we proceeded from the assumption that the most electronegative reagent groups and the ionized sorbent group are involved in binding, which is proved by the data of IR spectroscopy and the calculations of the quantum chemical method. The IR spectra of the PAR salt show bands in the regions of 3200–3500 cm⁻¹, 1500–1630 cm⁻¹, 1200–1300 cm⁻¹, and 800–1030 cm⁻¹, which are related to stretching and deformation vibrations –OH, =NH, -N=N- and -SO₃H [12, 13].

A comparison of the spectra of the immobilized reagent and the starting organic reagent showed that the functional-analytical groups responsible for complexation in the immobilized and native reagents are similar, which indicates that the structure of the reagent is preserved in the immobilized state (Table 2).

Table 2. Characteristic frequencies and their assignment in the IR spectra of the reagent and complex (cm⁻¹)

Compound	ν_{-SO_3H}	$\nu_{N=N-}$	ν_{OH}	N_{CN}	ν_{O-Cd}
Reagent	1200	1628	3450	2244	-
Immobilized reagent	1172	1629	3448	2244	-
Complex	1171	1600	3441	2204	598

When immobilizing organic reagents on the surface of sorbents in their IR spectra, a significant change occurs in accordance with the composition and structure of the deposited substances. In the spectrum of the immobilized CMA-1-PAR salt system, band shifts are observed in the region of 3448, 2855, 1648, 1138 cm⁻¹, corresponding to -NH₂, -OH, -COOH and -SO₃H groups. It is obvious that the sulfo groups of the reagent react with the ionized amino group of the sorbent according to the scheme:



where P is the polymer fragment, R-SO₃N is the test reagent.

The shift of the absorption band in the region of 3450 to the region of 2928 cm⁻¹ indicates the formation of strong intermolecular hydrogen bonds. In the complexation of cadmium with IMPAR, the shift of the absorption bands also occurs in the region of 1580-1600, 3200 and 1226 cm⁻¹ ($\Delta\nu = 14-30$ cm⁻¹) and a new absorption band appears in the region of 500-600 cm⁻¹, which is characteristic of the O-Me, which is absent in the IR spectrum of the reagent, is assigned according to [12, 13] to vibrations responsible for the stretching vibrations of the –O-Cd bond.

The absorption spectra of complexes of cadmium with an immobilized reagent on a fibrous sorbent correspond to their spectra in solution. The absorption maxima of the complexes formed in the polyacrylonitrile matrix and in solution practically coincide.

The optimal complexation conditions and the analytical characteristics of cadmium were studied. Cadmium is sorbed by IM-PAR in the pH range from 3-5 for 5-6 minutes. from 100 ml of solution. Quantitative sorption of cadmium is

also possible from large volumes of the studied solutions up to 1000 ml (Table 2). In this case, the phase contact time increases, but the detection sensitivity significantly increases (the detection limit is 0.01 µg / ml).

To establish the possibility of a sorption-spectroscopic method for the determination of cadmium for the analysis of real objects, complex model mixtures of various combinations were compiled that simulated water of different nature (table 3).

Table 3. The results of the sorption spectroscopic determination of cadmium in complex model mixtures
(n = 5; P = 0.95)

The composition of the analyzed mixture, mcg	Found Cd, mcg ($\bar{x} \pm \Delta X$)	S	S _r
Cd(5.0)+Pb(2.0)+Zn(15.0);	4.94±0.09	0.08	0.02
Cd(5.0)+Cu(5.0)+ Fe(15.0)+ Zn(10.0);	4.90±0.68	0.42	0.09
Cd(1.0)+ Cu(1.0)+ Fe(13.0)+ Pb(10.0);	5.04±0.12	0.48	0.10

As can be seen from the table, sorption spectroscopic determination of cadmium using immobilized reagents in model mixtures is quite possible, and the relative standard deviation (S_r) does not exceed 0.10, which indicates good accuracy and reproducibility of the developed methods.

Based on our data, we developed methods for the determination of cadmium using immobilized OR in various waters.

Methodology for the determination of cadmium in waters. In a 50 ml volumetric flask, a sample solution containing 2-50 µg of metal is introduced, a buffer solution with a certain pH, 5.0 ml of a masking mixture is added and passed through an immobilized reagent on a carrier. The metal content is determined by the calibration graph constructed in the coordinates of the reflection coefficient from the concentration $F = f(C)$.

Table 2. Results of testing the methodology for determining cadmium IMPAR on real water samples
(n = 5; P = 0.95)

Water samples	Introduced cadmium, mg / l	Found cadmium, mg / l	S _r	Found cadmium, mg / l *
River	10.0	9.82	0.025	9.92
Sewage	10.0	10.01	0.028	9.89
Natural	10.0	10.40	0.036	10.10

*-atomic absorption method.

IV.CONCLUSION AND FUTURE WORK.

Thus, the high selectivity, simplicity, and concentration rate in combination with instrumental methods of determination without metal desorption directly on the surface of a solid fibrous sorbent determine the expressivity of the analyzes and the possibility of their use in the practice of chemical analysis in the determination of cadmium ions in various objects.

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