

## **Application of Immobilized Arsenazo III for Sorption-Spectroscopic Determination of Mercury**

**M.S. Bobomurodova<sup>1</sup>, Z. A. Smanova<sup>2</sup>**

<sup>1,2</sup>National University of Uzbekistan Uzbekistan

### **ABSTRACT**

The article discusses the credibility of using Arsenazo III immobilized on polyacrylonitrile fiber modified with polyethylene polyamine (PPA) as a reagent for the detection of mercury ions. The optimal conditions for immobilization and complexation have been found. This is due to its high prevalence and stability in the environment, the ability to migrate and bioconcentrate, the high toxicity of most of its compounds.

**KEYWORDS:** Arsenazo III, fiber, polyethylene polyamine, mercury ions, optimal conditions, immobilization, complexation, mercury (II), natural waters, waste waters, toxicant, environment, MAC.

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### **INTRODUCTION**

Ascertainment of track amounts of mercury (II) in natural and waste waters, soils is one of the important analytical tasks in connection with the possible entry of this toxicant into the environment in doses exceeding the MAC.

Metallurgical organizations yearly release a huge amount of various mutagens, carcinogens, toxic metals and their compounds. Currently, up to 5 billion tons of fossil fuels are burned. Almost all metals can be found in coal and oil ash in concentrations that are economically justified for extracting elements from it. One of the common types of anthropogenic pollutants is mercury entering the soil [1, 2].

The basic anthropogenic resources of mercury (II) are industrial waste: emissions from ferrous metallurgy (60% of all mercury emissions), machine building and metalworking (23%), nonferrous metallurgy (9%), numerous small sources, for example, welding [3, 4].

The intake of mercury into the human body in doses exceeding the permissible ones adversely affects the activity of the central nervous system, mercury differ among themselves in the degree of toxicity and in their effect on the nervous, digestive and immune systems, as well as on the lungs, kidneys, skin and eyes. An excess of mercury is manifested by neurotic syndromes, increased fatigue, hypothyroidism, etc. [5, 6, 7, 8].

It is known that mercury is one of the priority environmental pollutants and its definition in many

countries is included in the monitoring program for anthropogenic substances and objects of various natures [7]. This is due to its high prevalence and stability in the environment, the ability to migrate and bioconcentrate, the high toxicity of most of its compounds [8].

These and other techniques (for example, using atomic absorption, atomic emission spectrometry, etc.) have good metrological characteristics, however, they are indirect and laborious to perform or expensive in instrumentation [9].

In recent years, combined methods of analysis have been intensively developed [10], based on a combination of sorption concentration of metals (a necessary procedure not only for concentration, but also the “discharge” of a complex matrix) by polymeric complexing sorbents (ACL) with their subsequent determination in the concentrate after desorption from the sorbent phase by instrumental methods (spectrophotometry, atomic absorption spectrometry. In recent years, adsorption-spectroscopic and test methods have been actively developed, which are simplified techniques using simple devices for the rapid detection and assessment of the content of substances outside the laboratory [11].

It seems urgent to develop a methodology for the determination of mercury (II) in natural and waste waters that is simple to execute, express and does not require the use of expensive equipment. For the determination of

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mercury in natural and waste waters, many photometric methods have been proposed using organic reagents dithizone [9], 4-(2-pyridylazo) resorcinol [12], phthaloxone S [13], rhodamine C [14], dithizone [15], n-phenolazo-3-aminorodanine [16], etc. The disadvantage of these techniques is low sensitivity and selectivity. To improve the selectivity and sensitivity of the determination of mercury with dithizone, a surfactant (surfactant) N-cetylpyridinium chloride was used, while the absorption of the mercury complex is observed at 555 nm. With the addition of cetylpyridinium, the shift of the maximum of light absorption is 75 in comparison with the complex without it [17, 18]. But the addition of surfactants does not always lead to an improvement in metrological characteristics; therefore, the development of simple highly sensitive methods for analytical control over the mercury content in various objects is relevant and necessary.

One of the promising methods for the determination of mercury in objects of complex nature are sorption-spectrophotometric methods of analysis, which make it possible to combine concentration with the subsequent determination of metal on a solid matrix [19-21].

This work shows the advantage of the sorption-spectrophotometric method for the determination of mercury using polyacrylonitrile fiber modified with hexamethylenediamine (PPA 1) as a matrix for immobilization, which, in comparison with various silica gels, is more durable, homogeneous and chemically resistant [22].

### EXPERIMENTAL PART

**Solutions, reagents, sorbents.** The initial 0.01 M mercury solution was prepared by dissolving an accurate weighed portion of 8.57 g of  $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  or 8.34 g of  $\text{Hg}(\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$  is placed in a glass, dissolved in a small amount of distilled water, 1 cm<sup>3</sup> of concentrated nitric acid is added, placed in a 1000 cm<sup>3</sup> volumetric flask and made up to the mark with distilled water. The working solution containing 5 µg / ml Hg (II) was prepared by diluting the initial solution with 0.01 M  $\text{HNO}_3$  [23].

A solution of an organic reagent, Arsenazo III (Ars), was prepared by dissolving its required weighed portion of the drug in bidistilled water, the concentration of which was  $C = 1 \times 10^{-3}$  mol / L.

Buffer solutions were prepared from the corresponding salts and acids of chemically pure grade. [24]. For the experiment, bidistilled water was used. Metal salts and other reagents were of chemically pure grade. or ch.d. and were not subjected to additional purification. Their concentrated solutions were prepared by exact dilution of the starting materials with bidistillate before starting the experiment.

**Equipment.** The acidity and basicity of the solutions were adjusted with acetate-ammonia buffer solutions, the pH of the solutions was measured on an I-130 ion meter and a pH / mV / TEMP Meter P25 EcoMet made in Korea. The absorption spectra were measured on an SF-46, KFK-3 spectrophotometer, the reflection spectrum on a SPEKORD colorimeter. IR spectra of the reagent, carrier, and immobilized OR were recorded on an Avatar system 360 FT-IR spectrometer (Nicolet Instrument Corporation, USA).

Immobilization was carried out by stirring 50-100 mg of a sorbent with 5-10 ml of a reagent solution with a concentration of  $1 \cdot 10^{-4}$  M for 1-10 minutes, followed by washing the carriers with distilled water. The immobilized carriers were kept wet in Petri dishes. The influence of pH, metal concentration, composition of the buffer mixture and reagent content in the solid phase were studied at a flow rate of 5 ml / min.

As a carrier, we used a fibrous material synthesized according to the method [25, 26] modified with various anion-exchange groups (these sorbents were synthesized at the Department of Polymer Chemistry, NUUz). The used polymers do not dissolve in PAN solvents which, indicates the occurrence of crosslinking in them with the participation of modifier molecules. Polyacrylonitrile sorbent weighing 20-30 mg and 2 cm in diameter was washed with 50 ml of 0.1 M HCl, 10 ml of acetone, and immersed for 10 min. in 10 ml of  $1 \times 10^{-3}$  M Arsenazo solution, then the immobilized carrier was stored in Petri dishes in a wet state. The content of the reagent on the support was determined spectrophotometrically by the change in the optical density of the initial reagent solution at 590 nm before and after immobilization. However, in a number of cases, the bathochromic shift of the absorption band of immobilized reagents in comparison with reagents in solution does not worsen the contrast of their reactions with metal ions.

**Research methodology: The work was carried out in static and dynamic modes.** In a static mode, 10.0 ml of a 0.05ml reagent solution (pH 6-7) was introduced into 50.0-ml flasks, the support disk was lowered into it, and stirred for 5-8 min. While holding the support with a glass rod, the reagent was decanted, the immobilized support was washed with distilled water, and it was immersed in the analyzed solution. In the dynamic mode, the analyzed solution was passed through the immobilized carrier at a rate of 10 ml / min, and then the study was started.

### THE MAIN FINDINGS AND RESULTS

Comparison of the diffuse reflectance coefficients of the tablets of the reagent immobilized on various carriers at 540 nm showed that the minimum value of R corresponds to the Ars and PPA system; she was chosen for further research.

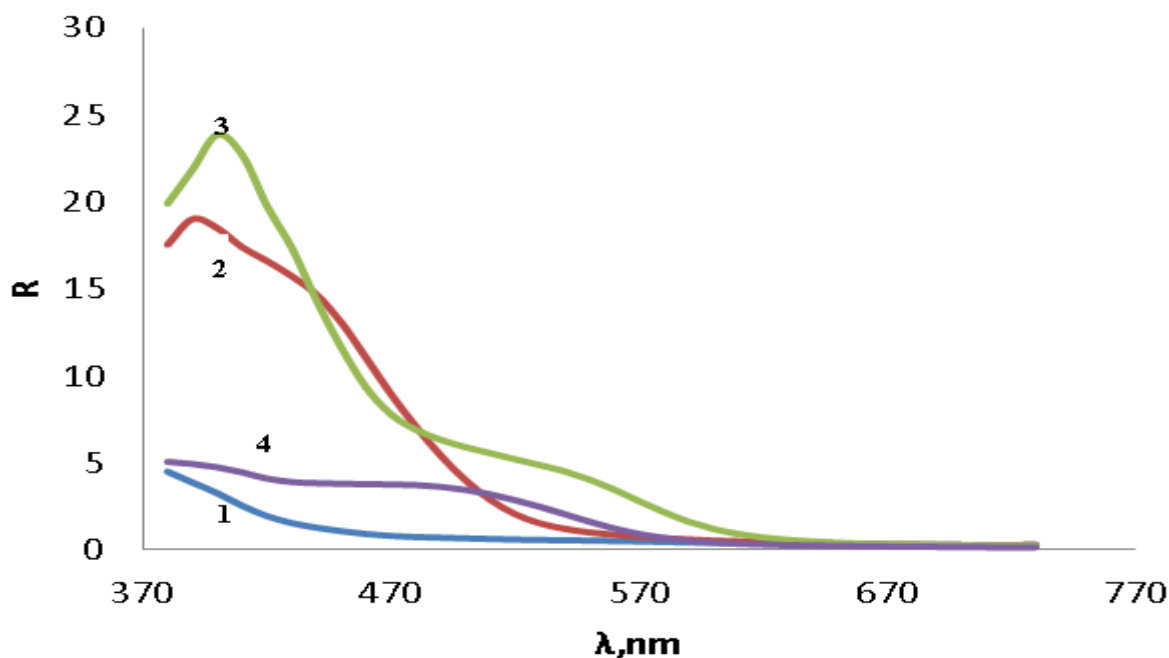
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**Table 1.** The choice of the carrier for the immobilization of Arsenazo III

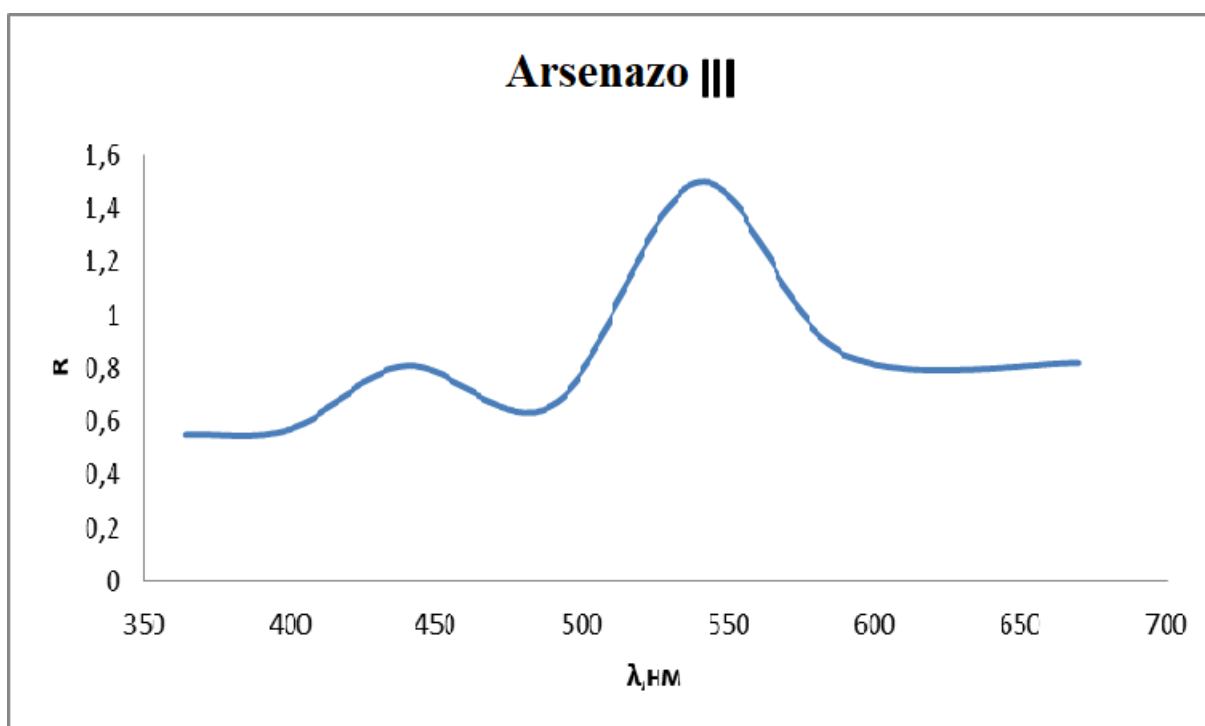
Carriers	R	Carriers	R
MX-1	0,3	SMA-1	0,33
VION-1	0,2	SMA-2	0,4
PPA-1	0,8	ППМ-1	0,7

It was found that Arsenazo III is fixed on all types of carriers (Table 1). The analytical signal was taken as the relative value of the diffuse reflection coefficient (R) or the Kubelka-Munk function F(R) [15]. Comparison of the

relative values of the diffusion reflectance coefficients of immobilized arsenazo III (IMARS III) at 550 nm showed that the minimum R value corresponds to the PPA-1: APC III system, which was chosen for further studies (Fig. 1).



**Figure 1** Reflection spectra of PPA sorbent (1), immobilized reagent (2) and its complex with mercury ions (3)



**Figure 2** Reflectance spectra of the reagent Arsenazo III.

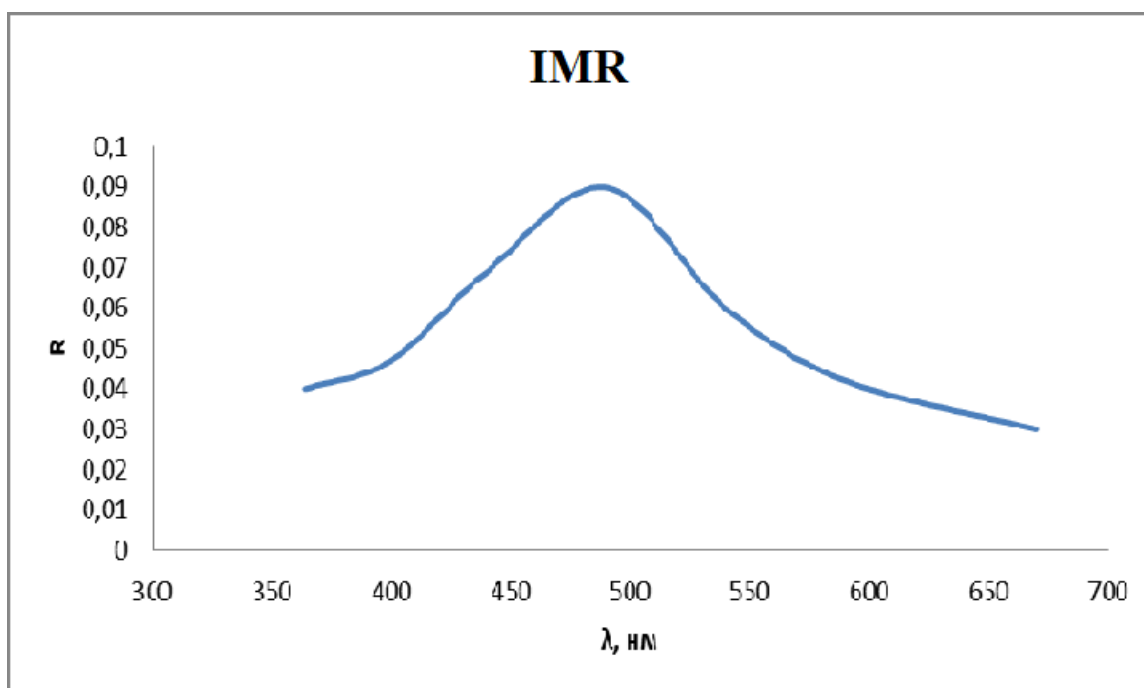


Fig. 3 Reflection spectra of the PPA sorbent of the immobilized reagent

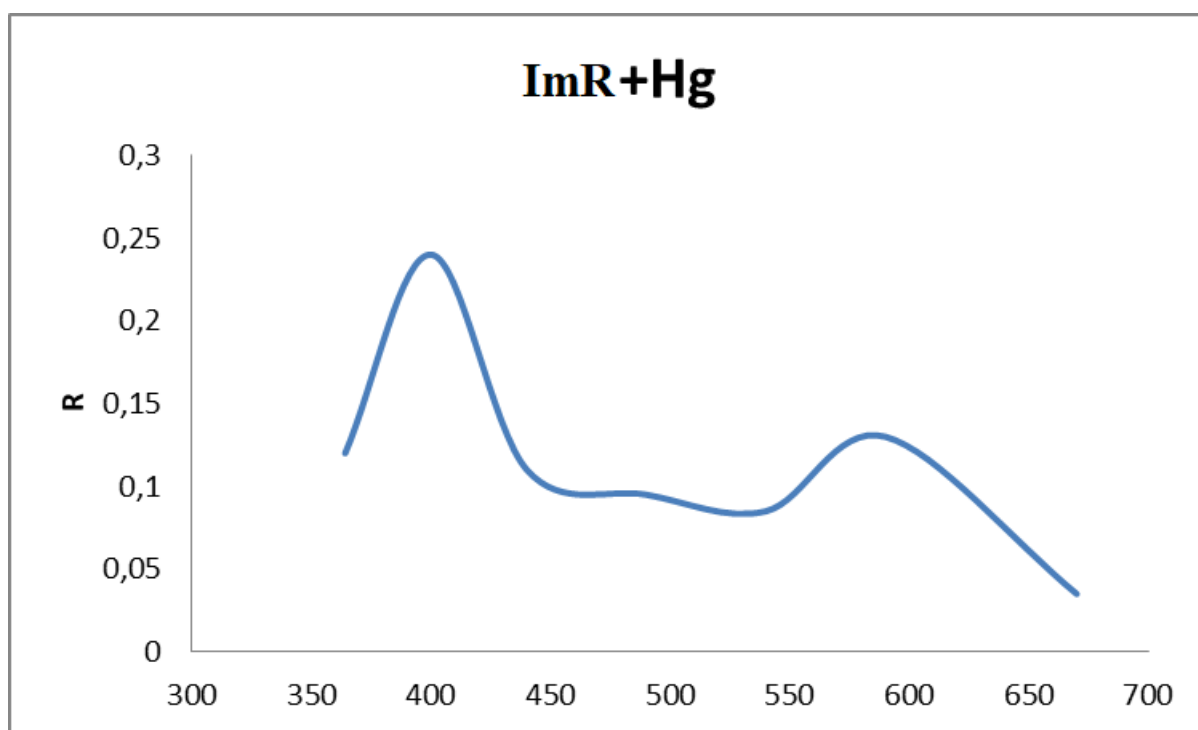


Figure 3 Reflection spectra of a complex with mercury ions.

The concept of “immobilization” as applied to organic reagents in a broad sense includes limiting the mobility of compounds with them through reaction with functional groups of polymeric materials, and in the narrow sense - chemical methods of their fixation [27].

We have tested various variants of determination: sorption of mercury followed by a complexation reaction with a reagent on the solid phase, sorption of complexes formed in solution, and simultaneous sorption and complexation of mercury on a support with immobilized

arsenazo III. In the first case, low results were obtained, in the second and third variants, the values are close. We have chosen the third option for the determination of mercury, because this reduces the number of operations.

In the IR spectra of the initial organic reagent, support and immobilized reagent, it was found that a number of bands shift in the region of 3000-3600  $\text{cm}^{-1}$ , characteristic for bending vibrations of hydroxo and carboxy groups, 1600-1700  $\text{cm}^{-1}$  vibrations of -N = N- groups, 1300-1500  $\text{cm}^{-1}$  for carbonyl and the appearance of characteristic

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vibrations in the range of 600-400  $\text{cm}^{-1}$ , characteristic of O-Me communication [29-30].

The stability of immobilized carriers in solutions of strong electrolytes allows us to conclude that the fixation of the organic reagent on the carrier occurs due to physical

adsorption, and the change in bands in the range of 3000-3400  $\text{cm}^{-1}$ , 1600-1700  $\text{cm}^{-1}$  ( $\Delta n = 40-100 \text{ cm}^{-1}$ ) is associated with the formation of strong intermolecular hydrogen bonds (Fig. 2-4).

	$\nu$ R	$\nu$ IMR	$\nu$ Complex
$\nu^{\text{as}}\text{NH}$	3950	3713	3450,2
$\nu^{\text{s}}\text{N}$	2856	2876	2381
N=N	3451,64	3713	3450,2
CN	2246	2244	2249
O-As	-	825,06	820,72
O-Hg	543,5	547,49	439,75

The influence of the concentration of the reagent in the aqueous phase, the pH-process, the contact time of the sorbent-reagent has been studied. It was found from the data that the best results are achieved when the support is kept in a  $1.0 \times 10^{-4}$  M solution of the reagent at pH = 6.5 for 5 minutes. The found carrier load is 0.20 mg / g.

The dependence of the analytical signal of the immobilized reagent complex with mercury on pH, time, and mercury concentration was studied in static and dynamic modes. The effect of acidity was studied in the pH range from 2 to 10. It was found that there is a shift of the maxima in the spectra of the complexes by 100 nm the diffuse reflection coefficient is minimal at pH 3-6, i.e.

immobilization leads to a shift in the pH of complexation by two units to a more acidic region.

The dependence of the response of the sensitive element on the content of mercury ions was studied in the concentration range 0.02-10.00  $\mu\text{g} / \text{ml}$ . A constant response is generated at various intervals. The graph of the dependence of the diffuse reflection coefficient on the concentration of mercury ions lies in the concentration range of 0.08-10.00  $\mu\text{g} / \text{ml}$ . The detection limit for mercury is 20  $\mu\text{g} / \text{ml}$ . Sr does not exceed  $6,6 \cdot 10^{-2}$ .

The reaction of mercury with IMARs is more sensitive than in solution, and also much more selective (Table 2).

## CONCLUSION

Table 2. Comparative characteristics complexation in solution and on a carrier

System	$\lambda_R$ , nm	$\lambda_{\text{MeR}}$ , nm	pH	$\tau$ , min	$C_H$	Selectivity factor
Ars Mercury	540	610	6-7	-	0,5	Pb(10), Co(20), Fe(80), Co, AI (100)
IMARS III-mercury	490	390	3-5	5	0,0001	Fe(70), Cd(50), Co, AI(1000)

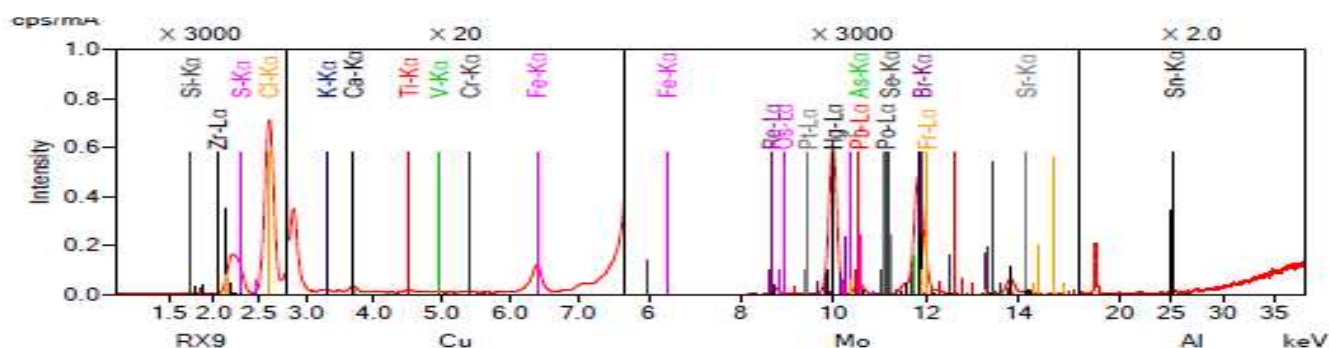


Figure 5 X-ray fluorescence analysis of a complex of mercury with an immobilized reagent.

The results of X-ray fluorescence analysis showed that the tinted fibrous PPA sorbent absorbed 65.8% of mercury ions.

The developed technique is applied to the determination of mercury in model mixtures.

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