Azo Derivative of Pyrogallol as a New Reagent for Spectrophotometric Determination of Molybdenum

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Abstract. An azo derivative of pyrogallol, 4-[(4-fluorophenyl)diazenyl]-1,2,3-trihydroxybenzene, is proposed as a new organic reagent for the spectrophotometric determination of molybdenum(VI) in the presence of antipyrine and 4-aminoantipyrine. The optimal conditions for the formation of the binary Mo–R complex were established as pH 1 and λmax = 490 nm. The addition of antipyrine and 4-aminoantipyrine leads to the formation of mixed-ligand complexes in acidic media, accompanied by bathochromic shifts of the absorption maxima and increased color intensity. In the presence of antipyrine and 4-aminoantipyrine, the absorption maxima are observed at 505 and 510 nm, respectively, in 0.2 N HCl.

The formation of mixed-ligand complexes results in higher molar absorptivity and improved detection limits. Beer's law is obeyed over the concentration ranges 0.384–4.94 µg/mL for the Mo–R complex and 0.294–7.36 µg/mL for the mixed-ligand systems. The proposed method was successfully applied to the determination of molybdenum in standard alloy samples.

Keywords: spectrophotometry; molybdenum determination; pyrogallol azo derivative; 4-[(4-fluorophenyl)diazenyl]-1,2,3-trihydroxybenzene; antipyrine; 4-aminoantipyrine

1 Introduction

The chemical and physical properties of molybdenum determine its wide application in various fields of modern industry. Molybdenum alloys are characterized by high heat resistance, elevated elastic and shear moduli, and significant corrosion resistance in molten alkali metals and their vapors. In addition to its industrial importance, molybdenum plays a crucial biological and physiological role. It is one of the essential trace elements involved in nitrogen metabolism and is known to stimulate the biosynthesis of nucleic acids and proteins. Moreover, molybdenum contributes to increased chlorophyll and vitamin content in plant organisms and is vital for their normal growth and development [1–4].

A wide range of analytical methods has been developed for the determination of molybdenum(VI). Among them, extraction–photometric and electrochemical methods are most commonly applied. However, extraction–photometric methods often require

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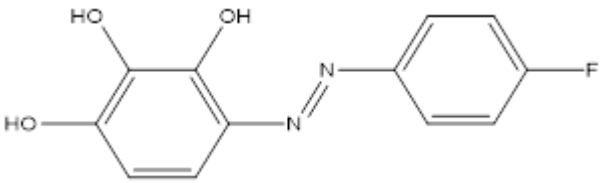
large volumes of organic solvents, while electrochemical techniques frequently involve the use of mercury, which does not meet current environmental safety requirements. Neutron activation analysis and inductively coupled plasma mass spectrometry, although highly sensitive, are rarely used in routine analysis due to their high cost and instrumental complexity. Each analytical method has its own advantages and limitations depending on the specific analytical task.

Among the existing approaches, spectrophotometric methods remain particularly attractive due to their simplicity, sensitivity, and wide applicability. Numerous photometric reagents for molybdenum determination have been reported in the literature. A review of published studies indicates that chelating reagents containing oxygen, nitrogen, and sulfur donor atoms are most commonly employed for the formation of colored molybdenum complexes [5–16]. Consequently, the synthesis of new organic reagents with such donor atoms, combined with a detailed study of their complexation behavior with molybdenum and the improvement of spectrophotometric characteristics through the introduction of an additional component, represents a promising direction in analytical chemistry.

Therefore, the aim of the present work is to develop a new analytical reagent for the spectrophotometric determination of molybdenum and to establish a highly sensitive and selective method suitable for its determination in various samples.

2 Experimental Part

4-[(4-fluorophenyl)diazenyl]-1,2,3-trihydroxybenzene (R) was synthesized by a known method, and its purity was determined by measuring the melting point and using paper chromatography. The ionic strength of the solution was maintained constant by adding a calculated amount of KCl ($\mu = 0.1$) [17]. The composition and structure of the obtained compound were determined by IR and NMR spectroscopy.



C16H13FN2O2 (R) 1H NMR spectrum (DMSO-d6,δ): 2.31 (s, 3H, CH3), 6.77−7.86 (5H, C6H5 and 4H, C6H4), 13.27 (s, 1H, HN). δ: 2.24 15 (s, 3H, CH3), 6.77−7.86 (5H, C6H5 and 4H, C6H4), 14.44 (s, 1H, NH).

13C {1H} NMR spectrum (DMSO-d6,δ): 26,4 (CH3), 112.3 (ArNH-N), 128.4, 128.6, 133.1, 133.7 and 135.5 (Ar-H), 137.8 (C = N), 139.7 (Ar-C = O) , 141.8 (Ar − F), 191.7 və 194.9 (C = O). δ: 31.1 (CH3), 114,6 (Ar − NH − N), 126.5, 128.8, 134.4, 135.2 və 135.9 (ArH), 139,2 (C = N), 141.2 (Ar − C = O) , 145.1 (Ar-F), 196.1 and 198.2(C=O).

2.1 Reagents and Solutions

Reagents of analytical grade (chemically pure or pure for analysis) were used. A 0.01 M sodium molybdate solution was prepared by dissolving weighed portions of $Na_2MoO_4 \cdot 2H_2O$ in distilled water. Working solutions were obtained by diluting the stock solution with distilled water during the experiment. The required pH values were maintained using HCl solutions. Reagent R is well soluble in ethanol. A 1×10^{-3} M ethanolic solution of the reagent and 1×10^{-3} M ethanolic solutions of antipyrine and 4-aminoantipyrine were used [18].

2.2 Apparatus

The pH of solutions was measured using a pHS-25 ionomer with a glass electrode. The optical density of solutions was measured on a KFK-2 photo-colorimeter (l = 1 cm). Absorption spectra were recorded using a Lambda 40 spectrophotometer (Perkin Elmer).

3 Results and Discussion

It was established that the optimal conditions for the formation of the two-component Mo(VI) complex are pH = 1 and λmax = 490 nm. Upon the addition of antipyrine and 4-aminoantipyrine to the solution of the two-component Mo-R complex, the absorption maxima shift to a more acidic medium, accompanied by an increase in color intensity, resulting in mixed-ligand complexes. In the presence of aminopyrine, the maximum complex yield is observed at 0.2 N HCl and λmax = 505 nm, whereas in the presence of 4-aminoantipyrine, it occurs at 0.2 N HCl and λmax = 510 nm. The absorption spectra of the reagent and its complexes in the presence and absence of antipyrine and 4-aminoantipyrine are illustrated in Fig. 1.

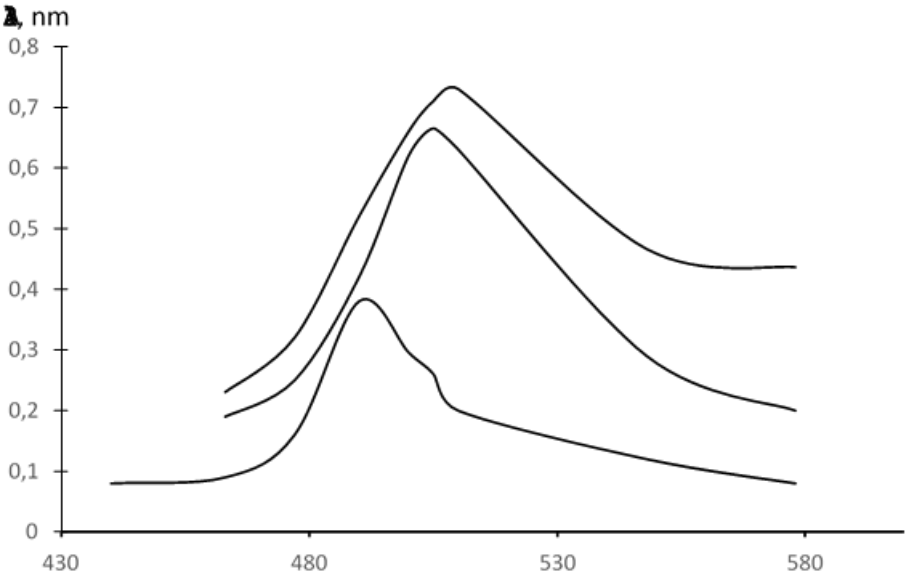


Fig. 1. Absorption spectra of the complexes: 1 – Mo-R, 2 – Mo-R-antipyrine, 3 – Mo-R-4-aminoantipyrine

Performing the determination in a strongly acidic medium does not require strict control of the solution pH, eliminating errors associated with small deviations in acidity. It was established that the addition of antipyrine and 4-aminoantipyrine to the Mo-R complex increases the molar absorptivity and lowers the detection limit. The molar absorptivities of the Mo-R, Mo-R-antipyrine, and Mo-R-4-aminoantipyrine complexes at λ_opt are 16.250, 27.400, and 25.150, respectively. The presence of antipyrine and 4-aminoantipyrine also enhances the sensitivity of the determination.

Beer's law is obeyed within the following molybdenum concentration ranges: 0.384–4.94 μg/mL, 0.294–7.36 μg/mL, and 0.294–7.36 μg/mL for the Mo-R, Mo-R-antipyrine, and Mo-R-4-aminoantipyrine complexes, respectively. The dark-red color of the complexes develops almost immediately upon mixing the components and remains stable for a long period (over 24 hours). The results are reproducible at room temperature, whereas increasing the temperature above 80 °C leads to a decrease in color intensity.

The stoichiometry of the reacting components in the complexes was determined using the methods of isomolar series and continuous variation (Job's method) (Fig. 2). All methods indicated that the component ratio Mo:R in the binary complex is 1:2, while in the mixed-ligand complexes, Mo:R:antipyrine = 1:2:2 and Mo:R:4-aminoantipyrine = 1:2:2 [19].

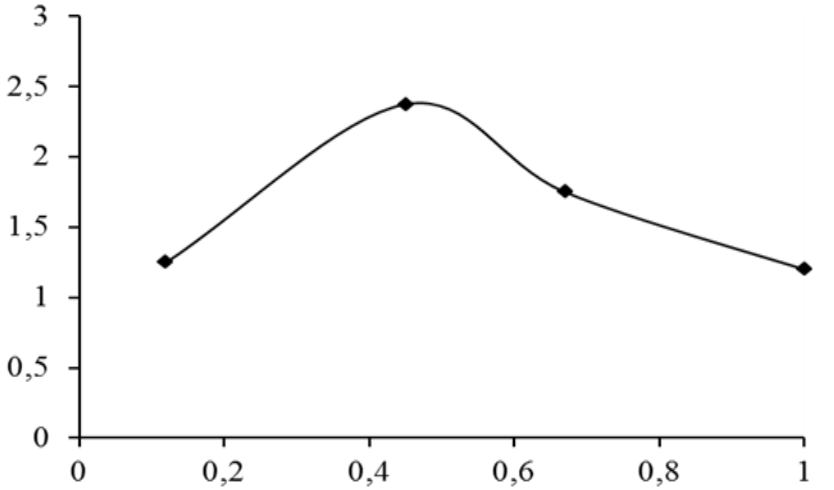


Fig. 2. Composition of Mo-R by the Job's method of continuous variation. [Mo(VI)] = [R]= 1,0 × 10-5M}

The main spectrophotometric characteristics of the complexes are presented in the table1.

Table 1. Main photometric characteristics of molybdenum complexes(VI)

Complex	λ_{max}, nm	pH	ratio Mo: R	ε	Beer's law compliance range, μg/mL
Mo-R	490	1	1:2	16250	0.384-4.94
Mo-R-aminopyrine	505	0.2N HCl	1:2:2	27400	0.294-7.36
Mo-R-4-aminoantipyrine	510	0.2N HCl	1:2:2	25150	0.294-7.36

One of the main factors determining the practical significance of spectrophotometric reactions is their selectivity toward the element being determined. The influence of foreign ions and masking agents on the photometric determination of molybdenum (VI) in the form of binary and mixed-ligand complexes was studied. *The comparative selectivity of the systems is calculated using the following expression and is presented in Table 2.*

Table 2. Permissible excess amounts of foreign substances relative to iron (III) during its determination in the form of binary and mixed-ligand complexes (5%)

Ion or substance	Mo-R	Mo-R-4aminoantipyrine	Mo-R-antipyrine
Alkali metals	1000	2000	6000
Alkaline earth metals	1000	1200	4000
Ni(II)	500	600	1720
Co(II)	400	500	1300
Zn(II)	680	1000	1860
Mn(II)	280	420	1000
Cu(II)	300	1200	1600
Cd(II)	500	1700	3000
Pb(II)	300	440	1200
Al(III)	120	380	420
Bi(III)	15	32	190
Cr(III)	600	1000	1500
Ti(IV)	1	43	430
V(V)	1,4	4,2	27
Sb(V)	180	180	1000
W(VI)	1.8	7.2	280
$C_2O_4^{2-}$	52	110	1035
HPO_4^{2-}	130	240	1000
F^-	125	410	770
Tartrate	312	420	1000
Trilon B	350	1000	1450

Experimental data show that the reaction of molybdenum with R and aminopyrine, as well as 4-aminoantipyrine, is characterized by almost absolute selectivity towards molybdenum, the determination of which is not hindered by more than several hundred-fold excesses of chromium, nickel, cobalt, copper, cadmium, and lead. Anions of mineral acids also do not interfere with the determination, which expands the choice of solvents during sample preparation.

Carrying out the reaction in an acidic medium ensures the high selectivity of the reaction towards Mo(VI) and determines the promise of the Mo-R-aminopyrine complex for developing methods for the determination of molybdenum in various objects.

Spectrophotometric determination of molybdenum in standard alloy samples. A sample weighing 0.2 g was dissolved in 10 mL of a mixture of sulfuric and phosphoric acids (2.3 mL of concentrated phosphoric acid and 15 mL of sulfuric acid were added to 50 mL of distilled water). After dissolving the sample, 1 mL of concentrated nitric acid was added and the solution was heated. After the cessation of the evolution of brown fumes, the solution was transferred to a 100 mL volumetric flask and its volume

was brought to the mark with distilled water. For analysis, an aliquot of the sample solution was transferred to a 25 mL flask and processed according to the calibration curve plotting methodology. [20] The accuracy of the analysis results was assessed by comparing the obtained data with the certified molybdenum content in the standard sample. The determination results are presented in Table 3, from which it is evident that they coincide with the certified molybdenum content.

Table 3. Results of molybdenum determination in standard alloy samples

Standard sample number	Certified content Mo, %	Found $\bar{X} \pm \frac{tp.f \cdot S}{\sqrt{n}}$,%	S_r
236	0.44	0.44±0.02	0.03
259	0.59	0.57±0.02	0.02
102	4.09	4.08±0.03	0.006

Thus, the developed methodology has several advantages, the main one being its high selectivity. In terms of this indicator, it significantly surpasses many methods for molybdenum determination known from the literature. This selectivity is due to the reaction being carried out in an acidic medium and ensures the possibility of direct determination of molybdenum in a wide variety of objects. The important merits of the method also include its simplicity, speed of execution, and the availability of the reagents and equipment used. The results obtained are distinguished by good reproducibility and high accuracy.

4 Conclusion

In this work, a new azo derivative of pyrogallol, 4-[(4-fluorophenyl)diazenyl]-1,2,3-trihydroxybenzene, was proposed as an organic reagent for the spectrophotometric determination of molybdenum(VI). The optimal conditions for the formation of the binary Mo–R complex and mixed-ligand complexes with antipyrine and 4-aminoantipyrine were established. The introduction of a third component resulted in bathochromic shifts of the absorption maxima, increased molar absorptivity, and improved detection limits. The stoichiometric composition of the complexes was determined using the methods of isomolar series and continuous variation. The developed method demonstrated high selectivity toward molybdenum(VI) in acidic media and was successfully applied to the analysis of standard alloy samples, with results consistent with certified values. The simplicity, sensitivity, and selectivity of the proposed approach make it suitable for the determination of molybdenum in various analytical objects.

Disclosure of Interests. The authors declare that they have no competing interests.

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