Russian Chemical Reviews **67** (3) 209 – 224 (1998) © 1998 Russian Academy of Sciences and Turpion Ltd

UDC 543.43

Azorhodanines, azothiopropiorhodanines, and their analytical application

R F Gur'eva, S B Savvin

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Abstract. The methods of synthesis, properties, and reactivities of azo-compounds based on rhodanine and thiopropiorhodanine are examined. The possibilities of the wide scale practical employment of this series of reagents, including their modified and immobilised forms, in the analytical chemistry of platinum and heavy metals are discussed. The bibliography includes 115 references.

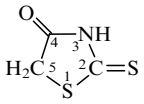
I. Introduction

Azo-compounds based on rhodanine (2-thioxo-4-thiazolidinone), thiorhodanine (2,4-dithioxothiazolidine), and aromatic amines containing salt-forming groups were first synthesised in 1971; these azo-compounds were obtained at the same time as analytical reagents.[1,2] A distinctive feature of these reagents is their ability to enter into highly sensitive, selective, and contrasting colour reactions with noble (NM) and heavy (HM) metals in solutions and in the solid phase.[3–13] Systematic studies on azo-compounds synthesised from 3-substituted derivatives of rhodanine, thiohydantoin (2-thiazolidine), selenoisorhodanine [4-thioxo-2-(1,3-selenazolidinone)], the six-membered analogue thiopropiorhodanine (2,4-dithioxo-1,3-thiazane), as well as bisazo-compounds based on rhodanine resulted in the creation of a whole series of promising analytical reagents.[14–24] By virtue of their exceptionally valuable properties, azorhodanines and azothiopropiorhodanines have found extensive applications in analytical chemistry. For example, various methods for the determination of 17 elements (photometric, differential photometric, extraction-photometric, sorption-photometric, including those using sensitive photometric cells, *etc*.) have been developed using these compounds. The method may be applied in the analysis of objects of different composition and with different contents of the components. It may be that azorhodanines and azothiopropiorhodanines are some of the most promising analytical reagents proposed during the last 25 years.

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Received 24 March 1997
Uspekhi Khimii **67** (3) 236 – 251 (1998); translated by A K Grzybowski

Rhodanine is known as the analytical reagent for the precipitation and gravimetric determination of silver, mercury, and other platinum metals.[25–30]



However, the low sensitivity of rhodanine (as well as the products of its interaction) and the low sensitivity of the reactions precluded the wide scale employment of this reagent for the requirements of analytical chemistry, especially photometry. Because of the enhanced reactivity of the 5-methylene group, rhodanine interacts with compounds of different classes — aldehydes, ketones, and diazo-compounds.[31–42] This leads to the possibility of obtaining from it new reagents containing the chromophoric groups $=C=CH-$ and $-N=N-$. The sensitivity and contrasting properties of the reactions of rhodanine condensation products with metal ions are greatly superior to those of rhodanine. Thus *p*-dimethylaminobenzylidenerhodanine has found fairly extensive applications in the photometric determination of silver and gold.[29,30,43–49]

In contrast to the 5-condensed derivatives, the azo-compounds based on rhodanine and aromatic amines containing salt-forming groups (OH, SO_3H, COOH AsO_3H_2) [1–3,13,14,16,21,24] are of interest for the determination of not only gold and silver but also of platinum, palladium, rhodium, iridium, ruthenium, and heavy metals. Such compounds are more stable in solution, dissolve relatively easily, and their reactions with the elements are characterised by an unusually high sensitivity [the molar absorption coefficient (ε) reaches $(3-9)\times10^5$ in certain cases], good contrasting properties, and high selectivity. The selectivity is based on the sharp differences between the conditions and kinetics of the colour reactions with the elements and the spectroscopic characteristics and stability of the complexes formed.[50–58]

II. Synthesis of the reagents and methods for their identification

About forty 5-azo-compounds based on rhodanine (**1a–m**), thiorhodanine (**2a–c**), thiohydantoin (**3a, b**), pseudothiohydantoin (**4a–d**), 3-aminorhodanine (**5a–f**), N-substituted 3-aminorhodanine (**6a, b**), bisazo-compounds based on rhodanine (**7a–c**), selenoisorhodanine (**8a–d**), a six-membered structural analogue

of rhodanine — thiopropiorhodanine (**9a – d**), as well as aromatic amines containing predominantly salt-forming groups have been synthesised as possible analytical reagents.[1–3, 13, 14, 16, 21, 24] The structural formulae and names of reagents of each group are presented in Table 1.

The azo-compounds are synthesised in accordance with a general scheme: by treating the heterocyclic azo-component with the corresponding diazotised amine under conditions suitable for each reaction (nature of the solvent, pH, time during which the reaction mass is allowed to stand, and the temperature regime). This ensures the preparation of reagents in high yields and reduces to the maximum extent the possibility of the formation of side products. The heterocyclic azo-components are obtained as follows: rhodanine — by the condensation of monochloroacetic acid with ammonium thiocyanate on heating;[25] thiorhodanine — from rhodanine by replacing the carbonyl group by the thiocarbonyl group on treatment with P_2S_5;[1] thiohydantoin — by the reaction of potassium thiocyanate with the hydrochloride of the ethyl ester of glycine;[59] pseudothiohydantoin — by condensing urea with monochloroacetic acid on heating;[25] 3-aminorhodanine — by condensing sodium monochloroacetate with hydrazine dithiocarbazinate;[60, 61] 3-aminobenzylidenerhodanine — by condensing 3-aminorhodanine with aldehydes in acetic acid; thiopropiorhodanine — by treating propiorhodanine with P_2S_5 in dry dioxane;[62] propiorhodanine — by condensing chromotropic acid with freshly prepared ammonium dithiocarbamate and subsequent heating of thiocarbamoyl-β-thiolactic acid with acetic anhydride;[63] selenoisorhodanine — by the interaction of 1,3-selenazolidine-2,4-dione with P_2S_5 in dry dioxane;[64] 1,3-selenazolidine-2,4-dione — by condensing monochloroacetic acid with selenourea on heating.

In order to obtain purer products and higher yields of the main substances, the synthesis is carried out in the presence of metal (calcium, lead) salts, but the solubility of the reagents is then reduced. The azo-compounds based on aminophenols and selenoisorhodanine could not be isolated.

The azo-compounds are identified by paper chromatography, column chromatography, electrophoresis using various buffer systems and also from the characteristic absorption spectra of the reagents themselves (concentrated H_2SO_4, neutral and alkaline solutions) and their complexes. The purity of the preparations is established by the potentiometric titration of the reagents with alkali and by spectrophotometric titration with solutions of metal salts.[3, 7, 16, 65]

The study of 5-azo-compounds based on propiorhodanine [2-thioxo-4-(1,3-thiazanone)] showed that, in contrast to rhodanine, propiorhodanine does not react with diazonium salts even in the presence of activators of the azo-coupling reactions (pyridine, alkoxides). The reduced reactivity of the methylene group in the 5-position is due to the fact that the activating effect of the carbonyl group in the 4-position extends to the 5-methylene group, while the thioxo-group activates the 6-methylene group. On the other hand, in rhodanine the activating effect of the two groups is directed to the 5-methylene group of propiorhodanine. At the same time, the azo-coupling of thiopropiorhodanine with diazonium salts becomes possible as a result of the increase in electron density on the carbon atom in the 5-position as a consequence of enolisation and the formation of a thioenolate anion.[62, 63]

III. Properties of the reagents

The reagents are powdered substances the colour of which varies from yellow to dark-red depending on the nature of the diazo- and azo-components; they dissolve in dioxane, dimethylformamide, ethanol, acetic acid, solutions of alkalis, and concentrated acids. The reagents containing sulfo-groups are readily soluble in water. In a dry form, they retain their analytical properties for more than three years.

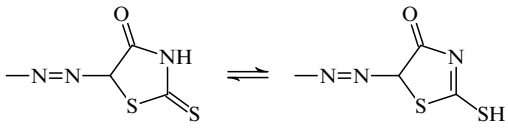
The state of the reagents in solution is one of the principal factors determining the reactivity, the mechanism of the complex formation reaction, and the nature of the colour reactions with the elements. Solutions of the reagents undergo a sharp colour change as the pH is altered, which is due to the dissociation of the acid groups and the protonation of the basic groups as well as tautomeric transformations. For the azo-substituted rhodanines **1a – m**, the diazo-component of which contains a OH group, it is possible to identify several coloured forms: red (conc. H_2SO_4), yellow (pH 1 – 4), orange (pH 4 – 8), red (pH 8 – 10), and violet (pH > 11). For reagents without OH groups, a colour change from lemon-yellow (acid and neutral media) to yellow-orange (pH 9 – 10) and red (pH 11 – 13) is observed. Only three coloured forms have been identified for the azothiorhodanines **2a – c**, which contain an OH group: dark-red (acid and neutral media), violet (weakly alkaline media), and blue (strongly alkaline media). The azothiorhodanines are unstable in strongly acid media.

The above pH values and the sequence in which the acid groups of the reagents ionise have been established on the basis of the results of potentiometric and high-frequency titrations as well as the analysis of the absorption spectra at the pH corresponding to the potential jumps.[3, 7, 16, 22, 65] The nature of the heteroatom (O, S) influences appreciably the pK for the dissociation of the NH group of the heterocycle. In the azothiorhodanines **2a – c**, the NH group is titrated at lower pH; on the other hand, the nature of the substituents in the diazo-component influences the pK of the OH group in the benzene ring.

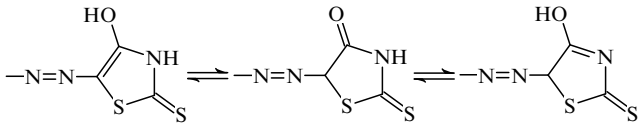
For the majority of azorhodanines, $pK_{NH} < pK_{OH}$. However, in the case of disulfophenolazorhodanine **1b**, the NH and OH groups are titrated simultaneously, whilst in picramineazorhodanine **1e**, containing two strong electron-accepting substituents, the dissociation of the OH group in the benzene ring precedes that of the NH group.

In concentrated H_2SO_4, a shift of the long-wavelength absorption band ($\Delta\lambda$ = 70 nm) is observed for all 5-azo-substituted rhodanines relative to their absorption band in neutral solutions. According to calculated data,[65] the bathochromic shift in strongly acid media is due to the protonation of the reagents: the heteroatoms of the rhodanine ring are protonated but not the hydroxy-group in the benzene ring or the nitrogen atom of the azo- or hydrazo-group, because the highest negative charge is present on the heteroatoms of the rhodanine ring.

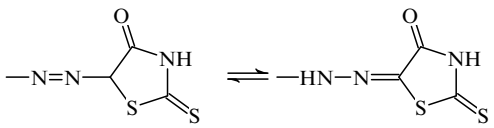
Several types of tautomerism are possible for azo-substituted rhodanines:



thione – thiol



keto – enol



azo – hydrazone

If the reagent contains a OH group in the benzene ring, there is yet another form of tautomerism: hydroxyazoquinone – hydrazone.

Table 1. Structural formulae and names of the reagents.

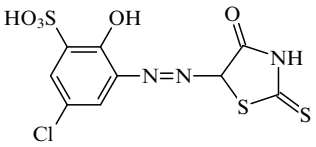
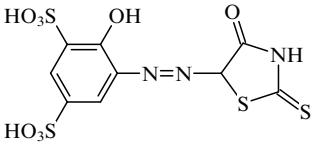
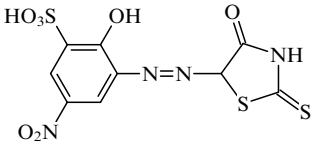
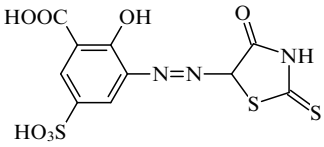
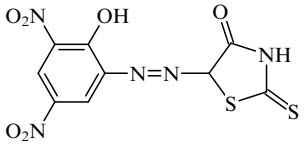
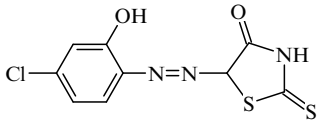
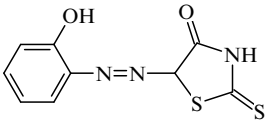
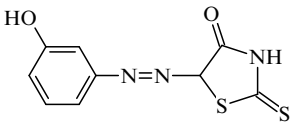
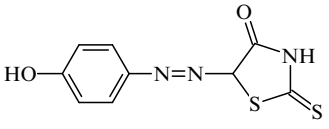
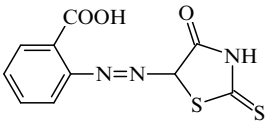
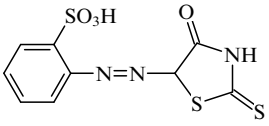
Azo-compound	Number	Name according to IUPAC nomenclature	Trivial name
	**1a**	5-chloro-2-hydroxy-3-[(4-oxo-2-thioxo-5-thiazolidinyl)azo]benzenesulfonic acid	sulfochlorophenolazorhodanine (SCPAR), rhodazol KhS
	**1b**	3,5-disulfo-2-[(4-oxo-2-thioxo-5-thiazolidinyl)azo]phenol	disulfophenolazorhodanine
	**1c**	2-hydroxy-5-nitro-3-[(4-oxo-2-thioxo-5-thiazolidinyl)azo]benzenesulfonic acid	sulfonitrophenolazorhodanine
	**1d**	3-carboxy-2-hydroxy-5-[(4-oxo-2-thioxo-5-thiazolidinyl)azo]benzenesulfonic acid	carboxysulfophenolazorhodanine
	**1e**	3,5-dinitro-2-[(4-oxo-2-thioxo-5-thiazolidinyl)azo]phenol	picramineazorhodanine
	**1f**	4-chloro-2-[(4-oxo-2-thioxo-5-thiazolidinyl)azo]phenol	rhodazol Kh
	**1g**	2-[(4-oxo-2-thioxo-5-thiazolidinyl)-azo]phenol	*o*-phenolazorhodanine
	**1h**	3-[(4-oxo-2-thioxo-5-thiazolidinyl)azo]phenol	*m*-phenolazorhodanine
	**1i**	4-[(4-oxo-2-thioxo-5-thiazolidinyl)azo]phenol	*p*-phenolazorhodanine
	**1j**	2-carboxy-[(4-oxo-2-thioxo-5-thiazolidinyl)azo]benzene	carboxybenzeneazorhodanine
	**1k**	2-[(4-oxo-2-thioxo-5-thiazolidinyl)azo]benzenesulfonic acid	*o*-sulfobenzeneazorhodanine

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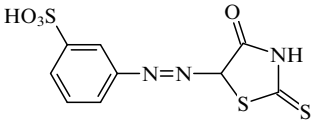
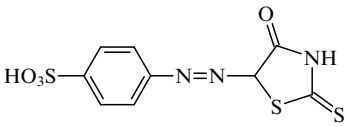
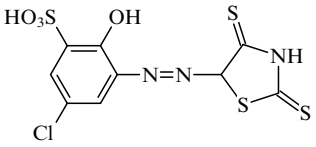
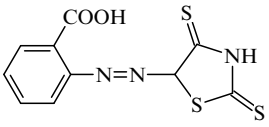
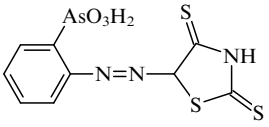
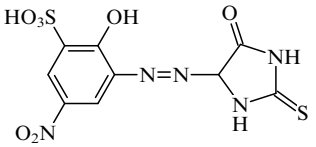
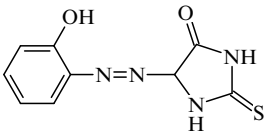
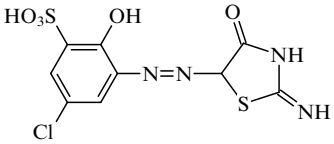
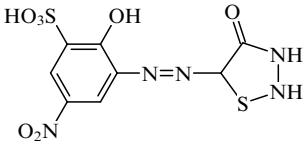
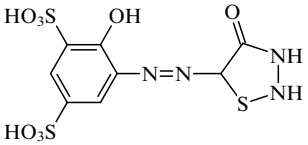
Azo-compound	Number	Name according to IUPAC nomenclature	Trivial name
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	**1m**	4-[(4-oxo-2-thioxo-5-thiazolidinyl)-azo]benzenesulfonic acid	*p*-sulfobenzeneazo-rhodanine
	**2a**	5-chloro-2-hydroxy-3-[2,4-dithioxo-5-thiazolidinyl)azo]benzenesulfonic acid	sulfochlorophenol-azothiorhodanine
	**2b**	2-carboxy-[(2,4-dithioxo-5-thiazolidinyl)-azo]benzene	carboxybenzeneazo-thiorhodanine
	**2c**	2-arsono-[(2,4-dithioxo-5-thiazolidinyl)azo]benzene	arsonobenzeneazo-thiorhodanine
	**3a**	2-hydroxy-5-nitro-3-[(4-oxo-2-thioxo-5-imidazolidinyl)azo]benzenesulfonic acid	sulfonitrophenolazo-thiohydantoin
	**3b**	2-[4-oxo-2-thioxo-5-imidazolidinyl)azo]-phenol	*o*-phenolazothio-hydantoin
	**4a**	5-chloro-2-hydroxy-3-[(2-imino-4-oxo-5-imidazolidinyl)azo]benzenesulfonic acid	sulfochlorophenolazo-pseudothiohydantoin
	**4b**	2-hydroxy-5-nitro-3-[(2-imino-4-oxo-5-imidazolidinyl)azo]benzenesulfonic acid	sulfonitrophenolazo-pseudothiohydantoin
	**4c**	3,5-disulfo-2-[(2-imino-4-oxo-5-imidazol-idinyl)azo]phenol	disulfophenolazo-pseudothiohydantoin

Table 1 (continued).

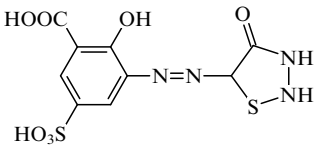
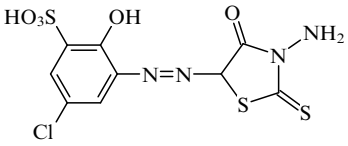
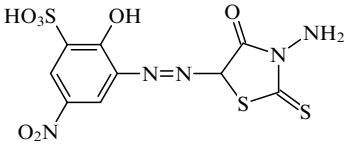
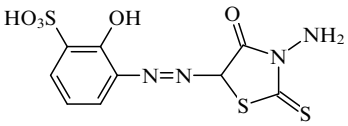
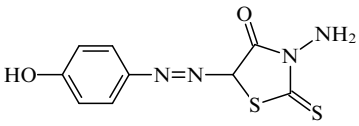
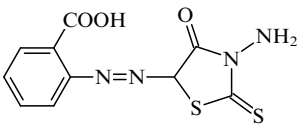
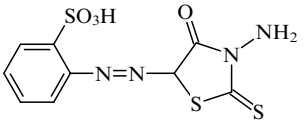
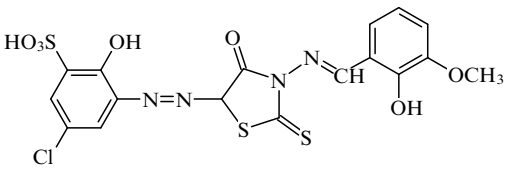
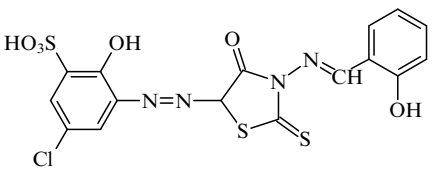
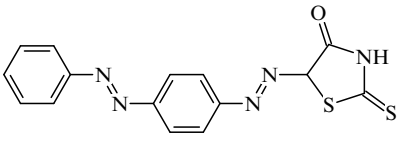
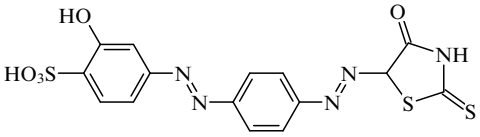
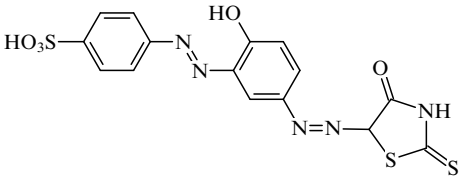
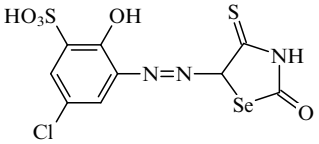
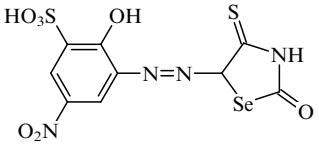
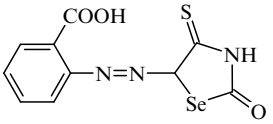
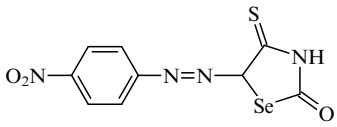
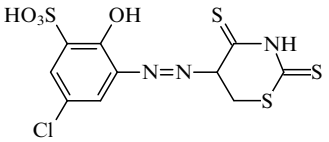
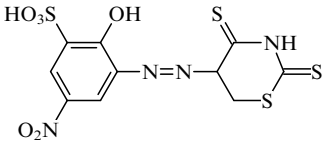
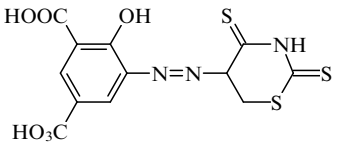
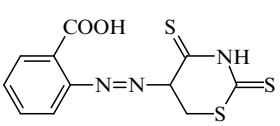
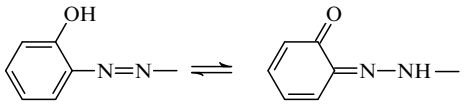
Azo-compound	Number	Name according to IUPAC nomenclature	Trivial name
	**4d**	3-carboxy-5-sulfo-2-[(imino-4-oxo-5-thiazolidinyl)azophenol	carboxysulfophenol-azopseudothiohydantoin
	**5a**	5-chloro-2-hydroxy-3-[(3-amino-4-oxo-2-thioxo-5-thiazolidinyl)azo]benzenesulfonic acid	sulfochlorophenolazo-3-aminorhodanine
	**5b**	2-hydroxy-5-nitro-3-[(3-amino-4-oxo-2-thioxo-5-thiazolidinyl)-azo]benzene-sulfonic acid	sulfonitrophenolazo-3-aminorhodanine
	**5c**	3-[(3-amino-4-oxo-2-thioxo-5-thiazolidin-yl)azo]-2-hydroxybenzenesulfonic acid	sulfophenolazo-3-amino-rhodanine
	**5d**	4-[(3-amino-4-oxo-2-thioxo-5-thiazol-idinyl)azo]phenol	*p*-phenolazo-3-amino-rhodanine (PATAR)
	**5e**	[(3-amino-4-oxo-2-thioxo-5-thiazolidinyl)-azo]-2-carboxybenzene	carboxybenzeneazo-3-aminorhodanine
	**5f**	2-[(3-amino-4-oxo-2-thioxo-5-thiazolidin-yl)azo]benzenesulfonic acid	*o*-sulfonbenzeneazo-3-aminorhodanine
	**6a**	5-chloro-2-hydroxy-3-({2-thioxo-3-[(2′-hydr-oxy-3′-methoxyphenyl)methyleneamino]-4-oxo-5-thiazolidinyl}azo)benzenesulfonic acid	–
	**6b**	5-chloro-2-hydroxy-3-({2-thioxo-3-[(2′-hydr-oxyphenyl)methyleneaminol-4-oxo-5-thiazol-idinyl)azo]benzenesulfonic acid	–
	**7a**	4-[(4-oxo-2-thioxo-5-thiazolidinyl)azo]-benzene	benzeneazobenzeneazo-rhodanine (BABAR)

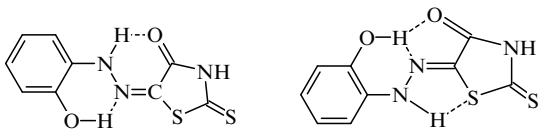
Table 1 (continued).

Azo-compound	Number	Name according to IUPAC nomenclature	Trivial name
	**7b**	3-hydroxy-4-[(4-oxo-2-thioxo-5-thiazolidinyl)azo]benzenesulfonic acid	sulfophenolazobenzeneazorhodanine (SPABAR)
	**7c**	2′-hydroxy-5′-[4-oxo-2-thioxo-5-thiazolidinyl)azo]benzeneazobenzenesulfonic acid	sulfobenzeneazophenolazorhodanine
	**8a**	5-chloro-2-hydroxy-3-[(2-oxo-4-thioxo-5-selenazolidinyl)azo]benzenesulfonic acid	sulfochlorophenolselenoisorhodanine
	**8b**	2-hydroxy-5-nitro-3-[(2-oxo-4-thioxo-5-selenazolidinyl)azo]benzenesulfonic acid	sulfonitrophenolazoselenoisorhodanine
	**8c**	2-carboxy-[(2-oxo-4-thioxo-5-selenazolidinyl)azo]benzene	carboxybenzeneazoselenoisorhodanine
	**8d**	4-nitro-[(2-oxo-4-thioxo-5-selenazolidinyl)azo]benzene	nitrobenzeneazoselenoisorhodanine
	**9a**	5-chloro-2-hydroxy-3-[(tetrahydro-2,4-dithioxo-1,3-thiazin-5-yl)azo]benzenesulfonic acid	sulfochlorophenolazothiopropiorhodanine, tyrodine
	**9b**	2-hydroxy-5-nitro-3-[(tetrahydro-2,4-dithioxo-1,3-thiazin-5-yl)azo]benzenesulfonic acid	sulfonitrophenolazothiopropiorhodanine
	**9c**	2-carboxy-2-hydroxy-5-[(tetrahydro-2,4-dithioxo-1,3-thiazin-5-yl)azo]benzenesulfonic acid	carboxysulfophenolazothiopropiorhodanine
	**9d**	2-carboxy-[(tetrahydro-2,4-dithioxo-1,3-thiazin-5-yl)azo]benzene	carboxybenzeneazothiopropiorhodanine



The molecules of azo-substituted rhodanines exist in aqueous solutions predominantly in the azodiketo-form. On complex formation, the equilibrium shifts towards the enolic form. This is confirmed by data concerning the number of protons liberated on formation of the complex between copper ions and SCPAR **1a**. The formation of a 1 : 1 complex is accompanied by the liberation of two protons.[3] The concentration of the azothiol tautomer is low. Picramineazorhodanine **1e**, for which the contents of the diketo- and thiol forms are approximately the same, is an exception. For the reagents containing a OH group, the first bathochromic shift (pH 6 – 10) is due to the transition from the azo-form of the reagent to the quinone hydrazone form. In strongly alkaline solutions, a shift of the thione – thiol equilibrium towards the thiol azo-tautomer is observed, this being accompanied by a bathochromic shift of the long-wavelength absorption band. The presence of electron-accepting substituents in the benzene ring, for example in compounds such as sulfonitrophenolazorhodanine **1c** and picramineazorhodanine **1e**, 'shifts' the pH of the thione – thiol transition towards lower values.[65]

A series of azorhodanines have been investigated by ^{13}C NMR. It was concluded that the reagents containing OH groups in the benzene ring exist in the form of two isomers in organic solvents (OS) such as CD_3OD, DMSO, and CD_3COOCD_3.[66, 67]



Analysis of IR spectroscopic data for azo-derivatives of rhodanine, 3-aminorhodanine, and thiopropiorhodanine showed that the transition from rhodanine to thiopropiorhodanine entails significant changes in the nature of the interaction of the individual fragments of the heterocycle and a displacement of the equilibrium towards the quinone hydrazone tautomer.[68]

5-Azo-substituted thiohydantoins **3a**, **b** and pseudothiohydantoins **4a** – **d** represent the least investigated series of reagents. Their stability is inferior to that of the azorhodanines **1a** – **m** and azo-3-aminorhodanines **5a** – **f**. The ionisation sequence of the acid groups is retained.

In the case of 5-azo-compounds based on 3-aminorhodanine and *N*-substituted rhodanines **6a**, **b**, the same features of the influence of substituents in the diazo-component on the spectroscopic characteristics and acid – base properties of the reagents are observed as for azorhodanines. For the same sequence of the dissociation of the acid groups, a strengthening of the acid properties of the OH groups in the benzene ring is observed. For example, $pK_{OH} = 8.5$ for sulfochlorophenolazorhodanine **1a**, while $pK_{OH} = 7$ for sulfochlorophenolazo-3-aminorhodanine **5a**. The bathochromic effect in concentrated H_2SO_4 is weaker than in the case of azo-substituted rhodanines.[16]

The introduction of a second areneazo-group into the reagent molecule affects the state of the reagent in acid media. Whereas the protonation of azorhodanines, accompanied by a deepening of the colour † (from 420 to 500 nm), is observed in 10 – 15 M H_2SO_4, the bisazo-compounds based on rhodanines **7a** – **c** are protonated already in 1 – 2 M H_2SO_4 whereupon the colour becomes even deeper (from 420 to 580 nm). The influence of thermochromism — the change in colour on heating in acid media — has been observed for the bisazo-compounds. A sharp change in the colour of benzeneazobenzeneazorhodanines as a function of pH is observed in the presence of surfactants (for example, cetylpyridinium chloride) and certain organic solvents (ethanol, propanol, acetone), provided that the content of the latter exceeds 85%. At least two new coloured forms of the reagents, undetected in aqueous solutions in the absence of organic additives, appear under these conditions. It has also been noted that, in the presence of surfactants, the reagents are protonated in more acid media. The deepening of the colour in alkaline and acid solutions is accompanied by an increase in optical density at the absorption maximum.[21 – 23]

5-Azo-substituted selenoisorhodanines **8a** – **d** are unstable in solutions. When the pH changes, the colour of solutions of the reagents is altered. The nature of the heteroatom (Se) intensifies the acid properties of azoselenoisorhodanines. The protonation of reagents takes place in more dilute acid solutions and is accompanied by a more pronounced deepening of the colour compared with azorhodanines ($\lambda_{max} \simeq 530$ and 490 nm respectively).

5-Azo-substituted derivatives of thiopropiorhodanine have a deeper colour in neutral and alkaline solutions than the corresponding rhodanines ($\lambda_{max} \simeq 540$ and 430 nm respectively). A change in the dissociation sequence of the NH and OH groups has been noted for these reagents. The OH group in the benzene ring is the first to dissociate (at lower pH). This can be due both to the difference between the acid properties of the azo-components themselves ($pK_{NH} = 5.8$ for rhodanine and 8.1 for thiopropiorhodanine) and to the difference between the mechanisms of the tautomeric transformations. A deepening of the colour of the reagents, as in the case of azorhodanines and azo-3-aminorhodanines, is not observed for azothiopropiorhodanines in strongly acid media. The yellow colour of the reagents in weakly acid media, characteristic of the neutral form, is retained even in concentrated H_2SO_4. A strong influence of surfactants and organic solvents on the colour of the reagents over a wide pH range is observed both for azothiopropiorhodanines and for azorhodanines and rhodanine-based bisazo-compounds.[22, 23]

IV. Reactions with metal ions and the properties of the complexes formed

The reagents based on aminophenols give rise to the most sensitive and contrasting colour reactions. In the case of 5-azorhodanines, it is possible to identify three complex-formation pH ranges.[1, 5, 7, 9, 65] Pd, Ag, Cu, Fe, Co, Ni, Zn, Cd, Pb, and Be react in the pH range 6 – 10. The colour then changes from orange (480 nm) to violet (530 – 580 nm); $\varepsilon = 2 \times 10^4$. Cu, Pd, Ag, and Hg interact at pH 1 – 6, the colour changing from yellow (430 nm) to red-orange (430 – 500 nm); $\varepsilon = (1.5 - 3) \times 10^4$. In acid and strongly acid media, noble metals (Pt, Pd, Rh, Ir, Ru, Au, Ag) and Hg interact with the reagent; the reactions are contrasting (430 → 500 – 530 nm) and highly sensitive; $\varepsilon = (2 - 12) \times 10^4$. The reactions in strongly acid media proceed as a rule over a period of time and in the presence of a 30 – 50-fold excess of the reagent. The sensitivity and rate of the reaction as well as the solubility of the reaction products depend on the nature and concentration of the acids (mixture of acids) in which the reaction is performed. Heating increases the rate of the reactions of noble metals with azorhodanines, but the yield of the complexes of certain metals diminishes under these conditions. For example, the chloride complexes between platinum(IV) and SCPAR give rise to a colour reaction in the presence of reductants both in HCl and in a mixture of HCl with H_2SO_4 or H_3PO_4; heating decreases the yield of the complex. The colour development time is 20 and 4 h, while $\varepsilon = 3.3 \times 10^4$ and 1.0×10^5 in HCl and in the HCl – H_3PO_4 mixture respectively (Table 2).

Rhodium and iridium give rise to a colour reaction with azorhodanines in H_3PO_4 and H_2SO_4; in the presence of CH_3COOH, the sensitivity of the reactions increases; heating to 70 and 90 °C respectively increases the rate of the reaction.

† The bathochromic shift of the main absorption band.

Table 2. Analytical characteristics of the colour reactions of azorhodanines and tyrodine.

Initial form of the elements	Reaction conditions	λ_{max} /nm	$10^{-3}\varepsilon$	Ref.
Sulfochlorophenolazorhodanine				
Pt(IV), chloride	3 M HCl, 4 h	500	32	1, 5, 50
	2 M HCl + 2 M H_3PO_4, 4 h [b]	500	100	1, 5, 50
Pt(III), sulfate	2 M H_2SO_4 + 11 M H_3PO_4, 30 min, 50 °C	500	100	18, 51, 54, 74
Pt(III), phosphate	12–15 M H_3PO_4, 50 min, 50 °C	500	100	18, 54, 58
Pd(II), chloride [a]	2 M H_2SO_4 + 8 M H_3PO_4	520	120	1, 5, 75
	1 M HCl	520	50	
Rh(III), chloride	7 M H_2SO_4(H_3PO_4) + 6 M CH_3COOH, 60 min, 70 °C	510	65	4, 5, 51
Rh(II), phosphate	14 M CH_3COOH, 60 min, 70 °C	510	8	8, 9
Rh(II), sulfate	7 M H_2SO_4 + 6 M CH_3COOH, 10 min, 70 °C	510	17	76
Rh(III), acetate	7 M H_2SO_4 + 6 M CH_3COOH, 15 min	510	11	76
Ir(IV), chloride	10 M H_2SO_4 + 6 M CH_3COOH, 1 h, 90 °C	510	45	5, 8, 9
Ir(IV), sulfate, phosphate		weak reaction	< 5	5, 8, 9
Ru(III), Ru(IV), sulfate, phosphate, chloride	2 M HCl + 10 M CH_3COOH, 30 min, 80 °C	500	16	18, 53, 54, 56, 74
Au(III), chloride	1 M HCl, 10 min	530	53	1, 51
Ag, nitrate	pH 2–6	480	16	1, 7, 77
	pH 6–10	560	15	1, 7, 77
	1–6 M H_2SO_4, 30 min	500	40	1, 7, 77
Tyrodine				
Pt(IV), chloride	7.6 M H_3PO_4, 3 h [b]	510	65	14, 16
Pt(III), phosphate, sulfate	3 M H_2SO_4 + 5 M CH_3COOH, 30 min [b]	510	65	18, 74
Ag, nitrate	1 M H_3PO_4 + 10 M CH_3COOH	535	53	16, 17
	Extraction, pH 5 [c]	550–580	450–900	57, 78
Pb(II), nitrate	pH 2–6	590	42	20, 69
Cd(II), sulfate	pH 4–5.5, 10 min	520	30	72
p-Phenolazo-3-aminorhodanine				
Hg(I), Hg(II), nitrate	15 M H_3PO_4 or 7–10 M H_2SO_4	510	20	19, 73
Cu(III), chloride	1 M HCl, pH 1 [b]	520	40	12
Benzeneazorhodanine				
Hg(I), Hg(II), nitrate	pH 7–9, surfactant	570	100	21–23
Cu(II), chloride	pH 7–9, surfactant	570	20	21–23
Au(III), chloride	pH 7–9, surfactant	570	100	21–23
Re(IV)	2 M NaOH + 0.1 M $SnCl_2$	570	c_{min} = 0.052–0.005 μg ml^{-1}	79–81
Sulfobenzeneazophenolazorhodanine				
Pd(II), chloride	pH 1–3, surfactant	540	300	21–23
Au(III), chloride	pH 1–3, surfactant	540	600	21–23
Rh(III), chloride	pH 1–3, surfactant	540	100	21–23
Ru(III), Ru(IV), chloride	pH 1–3, surfactant	540	40	21–23

[a] For the same sensitivities of the reactions of Pd(II) in the form of chlorides and in the form of sulfates, phosphates, and nitrates, the rates of the last three reactions are higher. [b] The reaction is carried out in the presence of reductants. [c] The two reagents 'tyrodine–macrocyclic compound' method.

Gold interacts with azorhodanines in HCl solutions at room temperature, the reaction being completed after 5–10 min. The presence of H_2SO_4 and H_3PO_4 does not affect the sensitivity and rate of the reaction, but the solubility of the complexes increases and the permissible acidity range expands in H_3PO_4. Thus the optical density of solutions of the gold complexes of SCPAR is constant in 2–10 M H_3PO_4 and 0.5–1.3 M HCl, whereas in the absence of H_3PO_4 the maximum development of colour is observed in 1 M HCl.

The silver complexes, like the palladium complexes, have different molar absorption coefficients at the absorption maximum (λ_{max}), compositions (reactant : metal ratio in the complex), solubilities, and other characteristics depending on the reaction conditions. In neutral and weakly acid solutions, palladium and silver form readily 1 : 1 complexes with azorhodanines. Saturation is then attained in the presence of a 2–3-fold excess of the reagent.

Among the reagents of the azorhodanine series, those which exist predominantly in the form of the diketo-tautomers in acid and neutral media are best, for example SCPAR, carboxysulfophenolazorhodanine **1d**, and *o*-phenolazorhodanine **1g**. Reagents which contain comparable amounts of diketo- and thiol forms in weakly acid media, for example sulfonitrophenolazorhodanine **1c** and picramineazorhodanine **1e**, are less sensitive. According to quantum-chemical studies, the reactions of silver with benzeneazorhodanines containing electron-donating substituents in the benzene ring should be characterised by a high sensitivity. The presence of a hydroxy-group enhances the contrasting properties of the reaction as a result of the hydroxyazoquinone–hydrazone tautomeric transition. In strongly acid media, the reactions of Ag and Pd as well as those of Rh, Ir, Ru, and Pd proceed over a period of time and in the presence of a large excess of the reagent. The sensitivity of the reactions in strongly acid media is higher than in

neutral and weakly alkaline solutions (pH 7–9). In terms of selectivity, the colour reactions of silver and palladium supplement one another. In strongly acid media, the selectivity of the determination in relation to nonferrous metals is higher and in relation to platinum metals is lower than in weakly acid and neutral solutions (pH 1–6).

5-Azothiorhodanines enter into colour reactions with gold, platinum, and palladium in 1–6 M HCl. The colour changes from red to blue-violet; $\varepsilon = (2-5) \times 10^4$. Silver interacts with 5-azothiorhodanines at pH 1.5, the sensitivity of the reactions being low.

5-Azothiorhodanines and 5-azothiopropiorhodanines do not react with rhodium and iridium, whereas thiopropiorhodanine-based azo-compounds enter into highly sensitive colour reactions with Pt, Pd, Au, and Ag in acid and strongly acid media; the colour changes from yellow to red. The presence of HCl has a negative influence on the reactions of gold and platinum. For platinum and gold, the optimum acid mixture comprises H_3PO_4 (H_2SO_4) and CH_3COOH. For platinum, the rate of reaction and the yield of the complexes increase in the presence of reductants.[16, 17]

For silver, it is possible to identify two regions of interaction with azothiopropiorhodanines: neutral (pH 5–9, $\Delta\lambda = 30$ nm, $\varepsilon = 2.0 \times 10^4$) and acid ($CH_3COOH - H_3PO_4$ mixture, $\Delta\lambda =$ 75 nm, $\varepsilon = 5.3 \times 10^4$) media. The formation of a coloured silver compound in strongly acid media was first noted for azorhodanines. The interaction of silver with azothiopropiorhodanines has a series of characteristic features compared with azorhodanines. In the case of azothio propiorhodanines, the most sensitive colour reaction with silver takes place in a $CH_3COOH - H_3PO_4$ acid mixture, while in the case of azorhodanines the addition of even insignificant amounts of CH_3COOH masks the reaction with silver, which can be accounted for by the greater stability of the silver complexes of azothiopropiorhodanines. The reaction of silver with azothiopropiorhodanines takes place in the presence of a 2–5-fold excess of the reagent, while that with azorhodanines requires a 20–50-fold excess of the reagent for saturation. Among the characteristic features of the reactions of silver with azothiopropiorhodanines, one should include also their high selectivity in relation to copper and other nonferrous metals, which is of great practical interest.

Tyrodine **9a** proved to be a promising reagent for lead.[20, 69–71] Lead(II) interacts with tyrodine, forming a violet complex. The colour reaction develops over a period of 20–30 min. An increase in the temperature of the reaction mixture and changes in pH and in the reagent concentration do not lead to an increase in the rate of reaction. The curve for the time dependence of the optical density $A = f(\tau)$ is characterised by an induction period of 15–20 min, after which the reaction goes to completion in 1–2 min. It has been noted that the presence of up to 2% of the lead complex of tyrodine accelerates the reaction so much that the induction period is eliminated. An autocatalytic mechanism of the colour reaction between lead and tyrodine has been proposed and can be described as follows in general terms.[70]

The first stage — the formation of a simple lead salt PbR involving the sulfo-group which is ionised under these conditions — is not accompanied by a colour change. This reaction is rapid (pH 3–4), the salt formed is sparingly soluble under the reaction conditions, and a weak opalescence of the solutions is observed. The first stage involves the formation of a 1 : 1 complex (PbR) with participation of the hydroxyazothioketone group of the reagent as a result of either an intramolecular rearrangement or interaction with a second molecule of the reagent (which is present in solution in an excess relative to lead). This stage is slow; 2–3 min after its onset, a change in the colour of the solution is observed and the opalescence vanishes. The third stage — the appearance of the final reaction product PbR_2 — is also slow, since both interacting species, PbR and R, are relatively unreactive: lead is partially hydrolysed and the hydroxy-group in the benzene ring of the reagent is undissociated;[16] both species are to a considerable extent hydrated. It has been suggested that the final product PbR_2 actually possesses catalytic activity: in the fourth stage, it dissociates, as a result of which compounds or radicals ($PbR^{\bullet}$ and $R^{\bullet}$) appear and are in the most active form at the instant of their formation (for example, as a result of minimal solvation). In the subsequent rapid reactions

$$PbR + R^{\bullet} \longrightarrow PbR_2^{\bullet}$$

and

$$PbR^{\bullet} + R \longrightarrow PbR_2$$

the number of PbR_2 molecules increases, which is in fact the basis of the catalytic effect. Other mechanisms for the reaction of lead with tyrodine have also been proposed.[70]

From the practical point of view, it is important that the development of the colour reaction between lead and tyrodine is not affected by large amounts of Ni, Co, Fe, Zn, Au, Pt, Rh, Be, Mn, Sn, and Ca; Ag, Hg,and Cu interfere. The high selectivity of the reaction permits the direct determination of lead in a series of systems (for example, in waste waters of the lead industries, anodic and cathodic copper, sulfuric acid) without preliminary separation from the accompanying elements.[20]

A series of quantitative characteristics of the colour reaction of cadmium with tyrodine have been obtained.[72] The colour reaction of cadmium is unaffected by 500–10 000-fold excess amounts of alkali and alkaline earth elements and 10–100-fold excess amounts of heavy metals; Pb, Hg, Ag, and Cu interfere. The influence of copper and mercury may be eliminated with the aid of thiourea. The colour reaction between cadmium and tyrodine has served as the basis of methods for the determination of cadmium in various types of water. Like lead, cadmium forms complexes with Cd : R = 1 : 2 under analytical conditions.[72]

The colour reactions of azo-compounds based on 3-aminorhodanine **5a–f** and substituted 6-aminorhodanine **6a**,**b** with Pt, Pd, Au, and Ag are close to the corresponding reactions of azorhodanines as regards sensitivity, contrasting properties, and rate of development of the colour. On the other hand, like azothiorhodanines and azothiopropiorhodanine, these compounds do not react with rhodium and iridium, which is apparently associated with their instability in strongly acid media on heating, *i.e.* under conditions where the kinetically inert rhodium and iridium complexes react. The azo-compounds based on 3-aminorhodanine, for example *p*-phenolazo-3-aminorhodanine **5d**, are of considerable interest for the determination of monovalent and divalent mercury primarily by virtue of their high selectivity. Mercury interacts with the reagent in strongly acid media at room temperature with formation of a stable raspberry-red complex. Large amounts of Pb, Zn, Bi, Be, Ba, Ca, Mo, Ir, Ru, and Rh do not interfere with the determination; Ag, Au, and Pd do interfere. The reagent has been used in the analysis of biological objects and industrial waters without preliminary separation of mercury from the accompanying elements (in contrast to the widely familiar method for the determination of mercury with the aid of pyridylazoresorcinol).[19]

Derivatives of benzeneazobenzeneazorhodanine **7a–c** enter into colour reactions with noble and heavy metals, but the sensitivity of the reactions is low. In terms of sensitivity, these reactions are inferior to the corresponding reactions with rhodanine-based monoazo-compounds. The colour reactions of azobenzeneazorhodanines proceed in less acid media. This can apparently be accounted for by the characteristic features of the structure of the reagents, namely by the presence of an extended π-electron system. This decreases the acidity required for the protonation of the reagents, which is accompanied by a pronounced deepening of the colour (λ_{max} for the neutral forms of benzeneazobenzeneazorhodanines is 440–480 nm, while that for the protonated forms is 580–620 nm). One of the important features of these reagents is that they enter into highly sensitive and contrasting colour reactions with noble and heavy metals in the presence of surfactants [$c_{surf} <$ CMC (CMC is critical micelle concentration)] and certain organic solvents when the content of the latter is more than 80%–85%.[21–23] Two types of colour

reactions are characteristic of modified derivatives of benzeneazobenzeneazorhodanine. The first type of the interactions of these reagents includes those with Cu, Hg, Ag, Pd, and certain other elements in neutral and alkaline solutions, the reactions being characterised by effective contrasting properties ($\Delta\lambda$ = 250 nm) and a higher sensitivity, the absorption coefficients ε increasing by a factor of 5 – 10. The interactions of the second type are those with Pt, Pd, Rh,and Ru (heavy metals and silver do not enter into reactions of this kind). The reactions proceed at pH 1 – 3 and are characterised by an even more pronounced increase in sensitivity with virtually unchanged contrasting properties. The reactions of Au and Pd with modified SBAPAR **7c** are the most sensitive, the absorption coefficients ε being 3×10^5 and 6×10^5 respectively. The sensitivity of reactions of the second type is greatly superior to that of the most sensitive reactions of noble metals with SCPAR and tyrodine. A high rate of development of the colour in these reactions should also be noted.

The ratio of the reagent to the metal in the complex (molar ratios method) is 2 : 1 in the presence of cetylpyridinium chloride in the case of reactions of the first type. Compounds even more 'saturated' with respect to the reagent are formed by reactions of the second type. The cause of such an increase may be associated both with the increase in the coordination capacity of the metal (for example, by virtue of dehydration on treatment with a surfactant or organic solvent) and with a change in the state of the reagent itself (for example, its aggregation, preceding the formation of the complexes)

Table 2 presents the characteristics of reactions of metal ions with the reagents (including their modified forms). The compounds examined apparently belong to the class of the most promising reagents of the azorhodanine and azo-thiopropiorhodanine series for the determination of noble and heavy metals both in solutions and in the solid phase.[13, 73]

V. Characteristic features of the interaction with acido-complexes of platinum metals

The reactions of sulfate (Pt, Pd, Rh), phosphate (Pt, Pd, Rh, Ir), acetate (Rh), and hydroxonitrate (Pd) complexes have been investigated together with the traditional chloride complexes using sulfochlorophenolazorhodanine and tyrodine as the reagents [1, 4, 8, 9, 53 – 56, 82] (see ‡).

The vast majority of methods for the determination of platinum elements are known to be applicable only to chloride systems. Analysis of other systems involves as a rule an additional stage in which the initial complexes are converted into chloride complexes. On the other hand, from the practical standpoint it is important to investigate the reactivities of acido-complexes of platinum metals based on various oxygen-containing acids (H_2SO_4, $HClO_4$, H_3PO_4, CH_3COOH). These acids are in fact largely employed at various stages in the processing of natural and industrial materials and in refining. Studies of the reactivities of dimeric complexes of platinum elements with a metal – metal bond have acquired special importance. Such compounds have unusual thermodynamic and kinetic characteristics. They are readily aquated and enter into substitution reactions more vigorously than the chlorides. This leads to new possibilities in the analytical chemistry of the platinum elements. In the dimeric complexes,the platinum elements can manifest unusual chemical properties. Many of the difficulties in the development of methods for the photometric determination of platinum metals, for example in the sulfate or phosphate form, are known to be associated with hydrolysis and the formation of unreactive polymeric forms in dilute acid solutions. A characteristic feature of azorhodanines and their analogues consists in their ability to enter into highly sensitive colour reactions with noble metals in strongly acid media, in which readily hydrolysable forms of the platinum elements may retain their reactivity. Simultaneously with the investigation of the colour reactions of acido-complexes of platinum metals, the behaviour of the initial forms of the complexes under the conditions of their colour reactions has been investigated spectrophotometrically. Taking into account the results of such studies, a hypothesis has been put forward concerning the nature of the active forms of the platinum elements and the factors determining their yield. Procedures have also been proposed for the stabilisation (standardisation) of the active forms and in certain cases procedures for the conversion of the initial forms into active ones.[53, 56]

Dimeric platinum(III) phosphate and sulfate complexes as well as their chloride forms give rise to brightly coloured compounds with sulfochlorophenolazorhodanine and tyrodine.[8, 53 – 56] Depending on the nature of the ligand and the oxidation state of the central atom in the initial complex, the conditions, kinetics, sensitivity, and selectivity of the colour reactions are different. Platinum phosphate and sulfate complexes interact with organic reagents in more acid media and a higher kinetic reactivity, compared with platinum(IV) chloride complexes, is characteristic of them. Markedly different effects of reductants on the colour reactions of acido-complexes of platinum have also been observed. Thus the reactions of platinum(IV) chloride complexes with organic reagents are strongly accelerated in the presence of reductants, whereas the influence of the latter on the colour reactions of the phosphates and sulfates is insignificant. The absorption spectra of platinum complexes with organic reagents are independent of the initial form of platinum.

The characteristics (reaction conditions, solubility of the products, behaviour in relation to reductants) of the colour reactions of dimeric platinum sulfate and phosphate complexes are similar. The coloured compounds of platinum sulfate and phosphate with organic reagents are more soluble and more stable on heating than the chloride forms of platinum. In the reactions of the chloride complexes, heating of the solutions even to 40 – 50 °C reduces the yield of the coloured compound, although the rate of reaction increases. Heating of the sulfate and phosphate complexes to 50 – 70 °C shortens the reaction time from 4 h to 30 – 60 min. Regardless of the nature of the ligand in the initial complex, the reaction with the organic reagent is apparently preceded by the stage involving the reduction of platinum(IV) to platinum(II). In the case of platinum(III) sulfate and phosphate complexes, the Pt – Pt bond is initially dissociated with formation of platinum(II) and platinum(IV), after which platinum(IV) is reduced to platinum(II). The reduction of platinum in the sulfate and phosphate complexes is faster than in the platinum(IV) chloride complexes and takes place at lower concentrations of the reductants in solution. One of the causes of the appreciable difference between the reactivities of the acido-complexes of platinum investigated in relation to organic reagents probably consists in the difference between the rates and conditions in the aquation and reduction of the initial forms. Evidently, the similarity of the behaviour of platinum sulfate and phosphate complexes and the characteristics of the colour reactions can be accounted for by the similar structures of such complexes.

The reactions of dimeric platinum sulfate and phosphate complexes are highly sensitive and selective. The complexes exhibit a high kinetic reactivity. All these features make it possible to classify the reactions considered as the most promising for the determination of platinum. Whilst showing equal resistances to the interfering effects of alkaline earth and alkali metals, the

‡ The sulfate complexes of platinum(III) $\{K_5H_3[Pt_4SO_4(HSO_4)_8O_5]\}$, tri- and tetra-valent ruthenium $\{K_2H[Ru_2(O \cdot H_2O)_2(SO_4)_3]\}$, and rhodium(II) $[Cs_4Rh_2(SO_4)_4(H_2O) \cdot 2H_2O)$, the phosphate complexes of platinum(II, IV) $\{K_2(H_3O)_3[Pt_2(PO_4)_3(HPO_4)H_2O]\}$, palladium(II) $\{K_3(H_3O)_3[Pd(P_2O_7)_2] \cdot 2H_2O\}$, rhodium(III) $[Na_3(H_3O)_6Rh(P_2O_7)_3]$, iridium(IV) $\{K_6H_2[Ir_4O_3(H_2PO_4)_{10}(OH)_8]\}$, and tri- and tetra-valent ruthenium $[K_3Ru_2(H_2P_2O_7)_5 \cdot 7H_2O]$, the acetate complexes of rhodium(II) $[Rh_2(CH_3COOH)_4 \cdot 2H_2O]$ and rhodium(III) $[Rh(CH_3COO)_3]$, and the hydroxonitrate complex of palladium(II) $[Pd(NO_3)_2(OH)_2]$ have been obtained by members of the Institute of General and Inorganic Chemistry of the Russian Academy of Sciences.[83 – 91]

selectivity of the sulfate and phosphate complexes with respect to Cu, Fe, and other transition metals as well as Rh and Ir is markedly higher compared with the chloride forms. However, the selectivity with respect to silver and mercury is higher for the chloride forms. On the other hand, from the practical point of view, it is important that conditions have been found under which platinum sulfates and phosphates are stable and retain their reactivity for a long time. The possibility of converting kinetically inert platinum chloride complexes into more reactive ones, for example the phosphate complexes, has also been demonstrated; in this case, the reaction takes place in concentrated H_3PO_4 solutions at 200 °C in the presence of perchloric acid, which decomposes the chlorides, oxidising Cl^- to Cl_2, the aquohydroxo-complexes formed react directly with H_3PO_4.

Palladium(II) sulfate, phosphate, hydroxonitrate, and chloride complexes interact with SCPAR under similar conditions. The spectroscopic characteristics of these complexes are close, but the kinetic reactivity of the sulfates, phosphates, and hydroxonitrates is higher than that of the chlorides. The solubilities of the products of the interaction of the sulfates, phosphates, and hydroxonitrates are higher than those of the corresponding compounds derived from the chlorides.[8, 9, 54, 82]

Iridium sulfate and phosphate complexes are less active in reactions with organic reagents than the chloride complexes. On prolonged heating, iridium in the form of phosphates and sulfates reacts with sulfochlorophenolazorhodanine in strongly acid media. However, these reactions are less sensitive than those involving the chloride complexes.[8, 9]

Tri- and tetra-valent ruthenium sulfate, phosphate, and chloride complexes react with sulfochlorophenolazorhodanine to form coloured compounds with similar spectrophotometric characteristics. The reactions of ruthenium sulfate and phosphate with the reagent are preceded by a stage involving the conversion of the initial forms of ruthenium into the chloride form, which has been identified as $[Ru_2OCl_{10}]^{4-}$ on the basis of absorption spectra. Regardless of the nature of the ligand and the oxidation state of ruthenium in the initial complex, the aquochlororuthenium(III) complex apparently reacts with the organic reagent. The conditions of the colour reaction (a mixture of HCl with CH_3COOH) and the reducing properties of the reagent ensure the conversion of the initial forms of ruthenium into the active form.[53, 56]

In the presence of organic solvents, for example CH_3COOH, the formation of the chloride form from the initial phosphate and sulfate forms is possible in more dilute HCl solutions, for example in 0.5–2 M solutions instead of 5–7 M solutions. In the presence of organic solvents, the degree of hydrolysis of the chloride form apparently diminishes; under these conditions, the organic solvent is a stabilising additive. Furthermore, in the presence of organic solvents, the formation of the active form — the aquochlororuthenium(III) complex — and the substitution for the organic ligand take place more readily than in the case of large amounts of HCl, which entails an increase in the sensitivity of the reaction. Acido-complexes of ruthenium do not enter into colour reactions with sulfochlorophenolazorhodanine in sulfuric and phosphoric acid solutions, which is due to the formation of unreactive hydrolysed forms under these conditions. The interaction of ruthenium with sulfochlorophenolazorhodanine results in the formation of 1:2 complexes. Under the conditions of its interaction with ruthenium, the reagent is in a neutral form[16] and apparently behaves as a monodentate ligand, ruthenium being coordinated to the reagent *via* the thioxo-group of rhodanine.

Regardless of the nature of the ligand and the oxidation state of the central atom in the initial rhodium complexes — rhodium(II) and rhodium(III) sulfates, phosphates, and acetates and rhodium(III) chlorides — coloured compounds with $\lambda_{max} = 510$ nm are formed in the reactions with SCPAR. Similar dependences of the yields of the reaction products on the nature and concentration of the acids and the reagent are observed for the above rhodium complexes. It has been suggested that the nature of the reactive form of rhodium in the reactions with SCPAR is the same for all the initial forms of di- and tri-valent rhodium. There are significant differences in the kinetics and sensitivities of the reactions. The dimeric rhodium(II) acetate and sulfate complexes are more reactive in the ligand substitution reaction than, for example, rhodium(III) chlorides and acetates; the highest reactivity has been noted for the dimeric acetate complex.

The rate of formation of the coloured rhodium(II) acetate complex of SCPAR is unusually high. The reaction develops at room temperature over a period of 10–20 min and is characterised by a fairly high sensitivity. The high kinetic reactivity of the dimeric rhodium(II) complexes compared with the corresponding rhodium(III) complexes is due to their ability to form 'more readily' the labile aquo-complexes, with participation of which many processes, including ligand substitution reactions, take place faster.

In the case of the rhodium(III) sulfate, phosphate, and chloride complexes, one may postulate that one of the intermediate stages of the overall complex formation reaction between rhodium and SCPAR is the conversion of the initial forms into the more reactive (dimeric acetate or acetate-sulfate) rhodium(II) complexes. This is confirmed by the fact that the conditions of the colour reactions of acido-complexes of rhodium with SCPAR (mixture of 7 M H_2SO_4 and 6 M CH_3COOH, heating to 60–70 °C, excess of the reducing agent) are virtually identical with those in the preparative synthesis of these complexes.[4, 8, 9]

The study of the state of solutions of rhodium acetate and sulfate complexes has shown that under certain conditions they retain their reactivity in relation to SCPAR for a fairly long time. The high kinetic reactivity of the dimeric rhodium complexes [in the first place, rhodium(II) acetate] as well as the high sensitivity of their reactions with SCPAR are properties which may serve as the basis for the creation of new high-speed methods for the determination of rhodium *via* reactions of its dimeric complexes.

VI. Applications

1. Photometry

One of the main fields in which azorhodanines and azothiopropiorhodanines are used is photometry. The distinctive features and advantages of azorhodanines as photometric reagents are as follows.

Firstly, the high sensitivity of the determination of the elements, primarily the platinum metals, and, secondly, the interaction with metal ions over a wide pH range. These properties are due to the presence of several functional-analytical groups in the reagent molecules. For example, there are three regions corresponding to the interaction of silver with SCPAR — pH 2–6 and 7–10 and 1–6 M H_2SO_4, which makes it possible to employ in practice the 'optimum' region of the interaction, depending on the composition and the content of the object analysed. Thus, in the determination of silver with the aid of SCPAR, for example at pH 5–7, the presence of the remaining platinum group elements (except palladium) is permissible, whereas the determination of silver in strongly acid media (for example, in 6 M H_2SO_4) permits the presence of a much greater excess of nonferrous and heavy metals.

Thirdly, the reactivity of the reagents in relation to surfactants and certain organic solvents. Under certain conditions, this leads to the formation of modified forms of the reagents, the colour reactions of which with platinum and other metals are characterised by an unusually high sensitivity [$\varepsilon = (100-600) \times 10^3$].

Fourthly, the interaction with platinum metals in the form of various acido-complexes (chlorides, phosphates, sulfates, and acetates). Such interaction is due to the fact that azorhodanines and azothiopropiorhodanines react with platinum metals in strongly acid media, where the presence of stabilising additives (CH_3COOH, HCOOH, metal salts) is permissible. All these features hinder the hydrolysis of the platinum metals, *i.e.* hinder the formation of their unreactive forms.

Fifthly, the possibility of analysing solutions containing both individual forms of platinum metals and their sum. For example, ruthenium is determined in chloride and sulfate solutions, which are used for its preparation in the course of the complex processing of copper–nickel ores. The conditions in the colour reaction of ruthenium with SCPAR (mixture of HCl with CH_3COOH) (Table 2) and the reducing properties of the reagent ensure a fairly rapid conversion of the initial forms of ruthenium into the reactive form — ruthenium(III) chloride.

Sixthly, the high selectivity of the determination. Despite the fact that azorhodanines and azothiopropiorhodanines are group reagents, a high selectivity of the determination is attained by virtue of different spectroscopic characteristics of the colour reactions with the elements (sensitivity and contrasting properties of the reactions), reaction conditions (nature and concentration of the acids, pH), reaction kinetics, the stability of the complexes formed, and, in the case of noble metals, also the different reactivities of their initial forms.

Highly sensitive methods have been developed for the determination of Pt, Pd, Rh, Ir, Ru (in the form of various acido-complexes), Au, and Ag with sulfochlorophenolazorhodanine, Pt, Pd, Au, Ag, Pb, Cd, and Cu with tyrodine, Pd, Pt, Ru, Rh,and Cu with sulfobenzeneazorhodanine derivatives, and Hg and Cu with *p*-phenolazo-3-aminorhodanine, which have found applications in the analysis of various natural and industrial objects.[1, 2, 4–11, 13–23, 50–56, 58, 69, 72, 74, 76, 77, 82, 92–100]

2. Differential photometry

The problem of creating direct differential-photometric (DP) methods for the determination of noble metals which are no less accurate than gravimetric or titrimetric methods (or approach them in accuracy) but are greatly superior to the latter in the speed of the determination has been successfully solved by virtue of the application of azorhodanines and tyrodine. The success has been due to the ready solubility of both the reagents themselves and of their complexes with noble metals, the possibility of the direct determination of the noble metals and a series of accompanying elements in natural and industrial objects, the possibility of using various acido-complexes as the initial form in reactions with the reagent, the fairly high kinetic reactivity of some of these complexes (phosphates, sulfates, acetates), and, in the case of Pt, Rh, and Ir chloride complexes, the possibility of activation, for example with ascorbic acid or copper salts. In the differential measuring procedure, the fundamental light absorption law holds over a wide range of concentrations of the noble metal. The DF methods developed are universal and, when combined with the photometric version, make it possible to determine 0.2–250 μg ml^{-1} of the noble metal. High-speed DF methods are used in the analysis of alloys and composite materials for the direct determination of silver (Ag–Cu, 10%–90% Ag), platinum (Pt–Rh, Pt–Ir, 10%–20% Pt), and ruthenium [lead ruthenite, bismuth ruthenite, 30% Ru; residue remaining after the combustion of the waste from the manufacture of materials for the electronic industry containing Pb and Bi (ash), 50% Ru] and also in the analysis of other objects.[24, 58, 74, 77]

3. Sorption-photometric methods

The methods in which azorhodanines are used both for determination and detection, on the one hand, and for the separation and concentration of reagents, on the other, merit special attention. Such are the electrophoretic and chromatographic (on paper and in a thin layer of sorbent) methods as well as methods based on the use of immobilised reagents. Their principal advantages are simplicity, clarity, and high speed of execution (primarily at the level of qualitative and semiquantitative visual determinations — test methods) and the possibility of combining separation (including the procedure based on the specific effect of the reagent) and concentration from large volumes under static or dynamic conditions.

a. Chromatographic and electrophoretic method

Conditions have been found and limits have been established for the detection of toxic heavy metals such as Cu, Pb, Zn, Fe, Ni, Cd, and Hg (the organic forms are methyl-, propyl-, and phenylmercury, while the inorganic forms are Hg^+ and Hg^{2+}) on a thin layer of sorbent (sorbfil, silufol) with the aid of azorhodanine derivatives — SCPAR and PATAR.

The sensitivity of the visual determination is 0.1–0.5 μg, and for Cu 0.01 μg, of the element in the zone. The possibility of the semiquantitative estimation of the content of both individual toxic elements and their sum has been demonstrated. The selectivity of the detection is achieved as a result of the specificity of the reagents, variation of the colour reaction conditions in a thin layer (nature of the acid, pH), and selection of the separation conditions on the chromatograph.

Conditions have been developed for the separation of various forms of mercury — organic (phenyl-, methyl-, and propylmercury) and inorganic (Hg^+, Hg^{2+}).

At the same time, when SCPAR is used in an ammoniacal medium as the mobile phase, it is possible to separate methylmercury ($R_f = 0.9$) and propylmercury ($R_f = 0.45$) from phenylmercury ($R_f = 0.0$) and inorganic mercury ($R_f = 0.0$) in the form of their coloured complexes with the reagent. The separation of organic and inorganic forms of mercury and their separation from other heavy metals with subsequent detection by means of SCPAR have also been achieved using other chromatographic systems. When chromatograms are sprayed with azorhodanines, red zones appear against the yellow background of the sorbent which is due to the formation of complexes of different forms of mercury with the reagent. The colour in the zones develops over a period of 1–5 min and is maintained for between 2 h and several days. The methods for the determination of toxic elements in a thin layer of sorbents have been tested on food products.[12]

Procedures have been devised for the development of chromatographic and electrophoretic zones of both individual noble metals (except osmium) and their sum in the form of various acido-complexes. The sensitivity of the visual detection is 0.5–0.01 μg of the element in the zone. Together with high sensitivity and stability (as a function of time) of the colour, the advantage of SCPAR as the developer over other reagents consists in the fact that SCPAR develops zones corresponding to different acido-forms of the noble metal. Methods have been proposed for the electrophoretic and paper and thin-layer chromatographic separation with subsequent detection of the noble metal (in the form of chloride complexes) by means of SCPAR in the Pd–Ir, Pd–Rh, Ir–Rh, Pt–Pd–Au, Pd–Pt–Ir, Pd–Pt–Rh, Pd–Au, and Pt–Rh systems. These methods have found applications in the analysis of alloys.[101–102]

The electrophoretic mobilities of noble metals in the form of coloured compounds with azorhodanines in buffer solutions based on formic, acetic, and oxalic acids (pH 1.5–1.7), acetic and boric acids (pH 2), and pyridine and oxalic acid (pH 5.9) have been investigated. The electrophoretic characteristics have been determined. A clear-cut separation of the zones is observed in the case of Pd–Ag, Pt–Ag, and Pd–Au in the form of their complexes with SCPAR and other reagents.[103]

b. Sorption-photometric methods based on the use of immobilised reagents

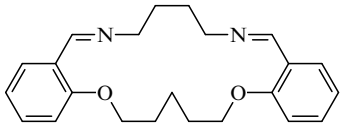
The prospects for the analytical application of the colour reactions of azorhodanines in the solid phase have been demonstrated.[13, 73] Azorhodanines immobilised on a polymer matrix (for example, on a polyamide caprone membrane, a polyacrylonitrile fibre filled with finely disperse KU-2 cation exchanger, and a fabric with phosphate groups) retain their reactivity in relation to noble and heavy metals over a wide pH range (1–10), the reactions being fairly rapid. The similarity of the spectroscopic characteristics of the reactions of azorhodanines in solution and in the sorbent phase has been noted.

High-speed and sensitive methods for the determination of Pt, Pd, Au, Ag, Cu, and Hg with a 1–3 μg ml^{-1} detection limit have been developed with the aid of azorhodanines and azothiopropiorhodanines immobilised on polymer supports.[22,23] A microporous polyamide material (a caprone membrane) or a polyacrylonitrile fibre filled with a finely-disperse cation exchanger (KU-2) have been used as supports. The supports are employed in the form of discs 0.8, 1, and 2 cm in diameter and with a mass of 2–10 mg. The reagents are immobilised by immersing the support disc in 10^{-5}–10^{-6} M solutions of the reagents in a weakly acid medium (pH 2–5) for 15–30 min. Two versions of the determination have been proposed — static and dynamic. In the first case, the coloured discs (photometric elements) are lowered into a flask containing the sample (the preliminary preparation of the sample is carried out — acidification and introduction of additives activating the colour reaction and giving rise to a high rate of response) and are kept there for 5–60 min at 20–50 °C. In the second case, the coloured discs are placed in the cell of an optical sensor analyser or a vacuum pump is employed. The colour change on the discs is estimated visually (test methods) or from the change in the diffuse reflection coefficients. A high sensitivity of the determination is attained both as a result of the employment of qualitative reagents and the possibility of accumulating the element analysed from dilute solutions on the coloured support disc. The selectivity is ensured by the specificity of the immobilised forms of the reagents, the sorption conditions, and the kinetic differences between the colour reactions on the polymer matrix.

A sorption-photometric method for the determination of silver in natural waters with a detection limit of 5 μg $litre^{-1}$ in accordance with the 'sorbent–metal–reagent' scheme has been developed. It involves the sorption of silver on discs made of polyacrylonitrile fibre filled with KU-2 cation exchanger and subsequent detection of silver in the sorbent phase with the aid of rhodazol Kh (compound **1f**) at 490 nm.[23]

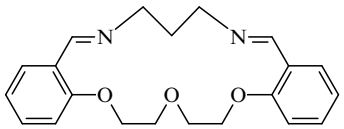
4. Extraction-photometric methods

The extraction-photometric method for the determination of silver (the 'two reagents' method) is based on the ability of silver to form mixed coloured compounds with azorhodanines or azothiopropiorhodanines and certain macrocyclic compounds (MCC) of the type



10

12,13-dibenzo-1,15-diaza-5,11-dioxacyclononadeca-1,14-diene



11

12,13-dibenzo-1,15-diaza-5,8,11-trioxacyclonondeca-1,14-diene

The MCC are used initially for the selective extraction of silver in the form of ionic associated species [Ag-MCC] Pi (Pi = picrate). Then tyrodine, for example, is added to the organic layer. It interacts with the associated species to form mixed coloured compounds (reagent–Ag-MCC) characterised by an unusually high sensitivity; $\varepsilon = (4-9) \times 10^5$. With the aid of the 'two reagents' method, it has been possible to reduce by more than an order of magnitude the detection limit for silver and also to increase the selectivity of the determination relative to Au, Pd, Pb, and Hg (Table 3).[57,58] The method has been used in the determination of silver in drinking water. A somewhat greater complexity of this method compared with the usual photometric version must be included among its disadvantages.

Table 3. Photometric determination of silver with tyrodine by the direct method and by the 'two reagents' (MCC–tyrodine) method.

Characteristics of method	Direct determination with tyrodine [a]	'Two reagents' method, determination in extracts	
		see [b]	see [c]
Range of concentrations of compounds determined /μg ml^{-1}	0.2–2.4	0.01–0.10	0.02–0.40
Detection limit /μg ml^{-1}	0.04	0.015	0.008
ε (λ_{max}/nm)	5×10^4 (540)	4.5×10^5 (550)	9×10^5 (580)
Selectivity factor			
Zn	5×10^3	1×10^4	1×10^4
Co	1×10^3	1×10^4	7×10^4
Pb	50	–	1×10^4
Hg	1	200	200
Pd	1	1×10^3	100
Au	1	500	–
Cu	5×10^3	500	3×10^3
Cl	1	25	25

[a] In 1 M H_3PO_4 + 10 M CH_3COOH solution.[17] [b] Tyrodine–MCS (compound **10**) in dichloroethane.[78] [c] Tyrodine–MCC (compound **11**) in a chloroform–triphenylphosphine mixture.[57]

In order to increase the selectivity of the determination of silver with SCPAR in an inorganic raw material, silver was extracted (in the form of its complex with the reagent) with cyclohexanone (in the presence of tributyl phosphate) and photometric measurements on the coloured organic layer was subsequently carried out.[58]

5. Automatic analytical schemes

A version of the flow-injection analysis (FIA) has been used with the aid of SCPAR for the spectrophotometric determination of noble metals.[104,105] The difficulty of devising such methods arises from the kinetic inertness of noble metal complexes in reactions with the organic reagent.

In order to investigate the conditions under which the colour reactions of Au and Ag take place, a two-channel flow system was employed. Best results in the determination of silver were obtained with the following parameters of the FIA system: microvolume of solution containing the metal to be determined $V_0 = 200$ μl; length of thermostated reaction coil $l = 30$ cm; flow rate of the support (dilute acid solution) with the metal to be determined $v_1 = 2.8$ ml min^{-1}; flow rate of reagent solution $v_2 = 1.2$ ml min^{-1}. The range of silver contents which can be determined is 0.3–4.5 mg $litre^{-1}$. The speed of the analysis is 180 determinations per hour. In the case of the slower reaction involving gold chloride complexes, the peak height is a maximum at $V_0 = 200$–300 μl, $v_1 = 1.2$ ml min^{-1}, $v_2 = 0.8$ ml min^{-1}, and $l = 60$ cm. The range of gold contents which can be determined is 2–19 mg $litre^{-1}$. The speed of the analysis is 90 determinations per hour. Comparison of the conditions in the colour reactions of Au and Ag with SCPAR in the usual photometric version and in the FIA version demonstrates an appreciably lower optimum acid concentration in the latter case, which is necessary to ensure a higher rate of reaction and this is in its turn important for obtaining the narrowest and highest peaks and also attaining a higher number of determinations per unit time.

The flow-injection method for the determination of palladium with SCPAR at pH 5 is characterised by a speed of analysis of 120 determinations per hour.[105] The high speed of analysis in this case

is due primarily to the high rate of interaction of palladium with SCPAR in weakly acid media. The necessary selectivity of the method is achieved with the aid of masking substances. The range of concentration which can be determined is 0.045 – 30 mg litre^{-1}. Thus a high number of determinations of noble metals per unit time is attained in FIA systems without loss of sensitivity and without narrowing the range of contents which can be determined compared with the static version employing the same reagent — SCPAR.

Continuous flow analysis (CFA) also belongs to the class of high-speed automatic analytical methods.[106] A photometric method has been proposed for the determination of silver with SCPAR in the presence of noniogenic surfactants (Triton-100 X).[107] The introduction of the surfactant into the system stabilises the hydrodynamic flow parameters (ensures the stability of the rate and uniformity of the flow) and improves the solubility of the reagent, which has a positive effect on the reproducibility of the results. The selectivity of the determination of silver relative to Pb, Co, Ni, Cu, and Zn also increases under these conditions. The principal characteristics of the method are as follows: range of silver contents which can be determined $(0.4-0.5)\times10^{-5}$ M; relative standard deviation 0.05; Triton-100 X content 0.3% – 0.03%. The determination is carried out in 0.1 M HNO_3.

6. Other methods

The kinetic determination of rhenium is based on the catalytic effect of tetravalent rhenium ions on the reduction of benzeneazobenzeneazorhodanine **7a** by tin(II) in an alkaline medium (1.5 – 2.5 M NaOH) and on the time variation of the optical density of the reagent solution. The calibration plot is linear in the range 0.01 – 0.1 μg of rhenium in 1 ml. The determination of 0.02 μg of rhenium in 1 ml is not interfered with by Mo, W, Ca, and Cu. The method has been used for the high-speed determination of the rhenium content in specimens of cupriferous sandstone.[79 – 81]

In the concentration and separation of noble metals with chelating sorbents based on rhodanine, azorhodanine, and azothiopropiorhodanine, one uses, for example, cellulose, styrene – divinylbenzene copolymers, and sephadexes as the matrix. Polymeric compounds interact under approximately the same conditions as the monomers and the selectivity is also similar. The concentration and separation methods based on chelating sorbents have found extensive application in the analysis of ores, industrial solutions, and natural waters.[108 – 115]

VII. Conclusion

Using azorhodanines and azothiopropiorhodanines as the reagents, it has been possible for the first time to approach the problem of the direct and high-speed determination of noble metals in a form other than the chlorides and to achieve a sensitivity of the determination which is unusually high for analytical reagents ($\varepsilon \simeq 10^6$). There are diverse applications of azorhodanines and azothiopropiorhodanines, including their modified and immobilised forms, in inorganic analysis — in photometry, differential photometry, sorption photometry (primarily in methods where the reagent is used simultaneously for the concentration, extraction, separation, testing, and determination, including procedures employing sensitive photometric cells), in extraction photometry (including the 'two reagents' method), and in chromatographic and electrophoretic analytical methods. The likely usefulness of azorhodanines and azothiopropiorhodanines in automatic analytical schemes (FIA, CFA) has been demonstrated. Other applications of the reagents, including their use as intermediates in the synthesis of chelating sorbents for the concentration and separation of the elements and in kinetic analytical methods, have been noted. The methods developed using azorhodanines and azothiopropiorhodanines cover a wide range of noble and heavy metal concentrations which can be determined — $1\times10^{-3}-2\times10^{2}$ μg ml^{-1}. Reagents such as sulfochlorophenolazorhodanine, tyrodine, *p*-aminophenol-3-aminorhodanine, rhodazol Kh, and sulfo-derivatives of rhodanine and benzeneazobenzeneazorhodanine have found the greatest practical applications.

The unique properties of the reagents and, in the first place, the universality and effectiveness of their analytical activity are in many respects responsible for the interest of investigators in their further study and wider employment in inorganic chemical analysis.

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