Russian Chemical Reviews **75** (3) 255 – 266 (2006) © 2006 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2006v075n03ABEH003610

Pyrocatechol Violet in spectrophotometric and novel optical methods

V M Ivanov, G A Kochelayeva

Contents

I.	Introduction	255
II.	Chemical and analytical characteristics of Pyrocatechol Violet	256
III.	Pyrocatechol Violet as a complexometric indicator	258
IV.	Pyrocatechol Violet as a reagent in optical methods	258
V.	Conclusion	264

Abstract. The published data on chemical and analytical characteristics and the use of binary and ternary Pyrocatechol Violet complexes in spectrophotometric and novel optical methods of analysis are generalised. New promising trends are considered including studies of chromaticity characteristics of complexes of this reagent with various metal ions formed in the presence of cationic surfactants on the surface of anion-exchange resins or neutral sorbents aimed at increasing the sensitivity of determinations and developing new, more efficient test scales and optical sensors. The bibliography includes 105 references.

I. Introduction

The development of methods and techniques that combine high sensitivity and high selectivity with rapidity of analysis, availability of instruments and low cost is a topical task in analytical chemistry. This is achieved, in particular, through combination of preconcentration of tested compounds with new sampling techniques and most advanced methods of analysis. Mixed-origin specimens including environmental subjects supplement traditional analytical (inorganic or organic) subjects. By virtue of rapidity of analysis and possibility of direct visualisation of the tested subjects, spectroscopic molecular absorption methods are in continuous development resulting in appearance of new versions of the determination, novel or modified reagents and combination of several approaches (*e.g.*, hybrid and combinatory methods of analysis). To relatively new procedures one can relate diffuse reflectance spectroscopy, solid-phase spectrophotometry, chromaticity measurement and diverse test methods. The latter are worthy of note in view of simplicity, availability and relatively low cost at reasonably high precision. These methods are especially suitable for express analysis of a broad range of organic and inorganic substances. Chemical test methods are usually based on well-known reagents and analytical reactions where colour change plays the role of an analytical signal. The reagents for test methods should possess high selectivities and high sensitivities in determination of metal ions or various compounds, the abilities to form stable complexes or analytical forms, possibilities to be immobilised on solid supports and ensure sufficiently high contrast of reactions.

Basic and polyhydroxytriphenylmethane dyes are the two main classes that are widely employed as analytical reagents. The reagents of the former class contain alkyl- or arylamino groups in the phenyl substituents and are usually employed in extractive-photometric procedures. An ionic pair of a negatively charged tested component and the protonated form of the reagent can be extracted by weakly polar organic solvents; however, the reagent itself is also partially extracted. The contrast range in such reactions does not usually exceed 10 – 20 nm; the reactions are carried out in acidic media with very strict acidity control (the range of optimum pH is very narrow), however the sensitivity of the determination is rather high [the molar extinction coefficient (ε) is of the order of 10^5].

The reagents of the latter class contain hydroxy groups in the phenyl substituents. Two hydroxy groups in the *ortho*-position (pyrocatechol) form a functional-analytical group in the reagent, which can be involved in complexation with the formation of chelate complexes. The contrast range of such reactions, especially with involvement of additional approaches, can exceed 200 nm; the values of molar extinction coefficients are of the order of 10^5, the optimum acidity range is of the order of several units of pH, while the selectivity of the reaction can be changed upon introduction of masking substances. The reagents of the second class include Pyrocatechol Violet (3,3′,4′-trihydroxyfuchsin-2″-sulfonic acid, pyrocatecholsulfonephthalein, PCV), a popular reagent for photometric determination of some metal ions and an indicator for complexometric studies. Its applications in novel optical methods, solid-phase spectrophotometry and chromaticity present certain interest. Complexes with PCV usually have bright colours; their formation results in marked bathochromic shifts and is often highly selective. Thus, this reagent is suitable for different test methods, since the latter often include preconcentration in the form of a coloured complex.

This review generalises the published data on chemical and analytical characteristics of Pyrocatechol Violet and its applications in analytical chemistry. Special attention is given to the use of this reagent in modern optical methods, such as diffuse reflectance spectroscopy, solid-phase spectrophotometry, chromaticity measurement, as well as in test methods. This type of a review is missing, while the information sources are either dispersed or hardly accessible.

V M Ivanov, G A Kochelayeva Department of Chemistry, M V Lomonosov Moscow State University, Leninskie Gory, 119992 Moscow, Russian Federation. Fax (7-495) 939 02 83, tel. (7-495) 939 22 77

Received 15 November 2005
Uspekhi Khimii **75** (3) 283 – 296 (2006); translated by R L Birnova

II. Chemical and analytical characteristics of Pyrocatechol Violet

1. Protolytic equilibria in solutions

The PCV molecule contains a pyrocatechol and an *o*-hydroxycarbonyl groups as well as a sulfo group in the third phenyl substituent and exists in different ionic forms depending on the acidity of the solution (Scheme 1).[1]

The theoretical and experimental values of wavelengths of the absorption band maxima (λ_{max}) of different forms of PCV are listed in Table 1. It is noteworthy that the band of the doubly ionised form could be identified only after the concentration of the reagent was increased to 8×10^{-4} mol litre^{-1} (pH 13.0), while the analysis of alkaline solutions of PCV could be performed only after addition of 30 vol.% of acetone to suppress side reactions.[1]

Table 1. Theoretical and experimental values of λ_{max} for different PCV forms.[1]

Form of PCV	Existence conditions	λ_{max} /nm	
		theory	experiment
I (H_3R^-)	pH 1–6	450	450
II (H_2R^{2-})	pH > 7	591	600
III(HR^{3-})	pH > 9	646	650
IV(HR^{3-})	pH > 9	656	650
V(R^{4-})	0.5 mol litre^{-1} 40% NaOH	691	690
VI (H_5R^+)	0.5 mol litre^{-1} H_2SO_4 (conc.)	548	546

The hydroxy group of the Pyrocatechol fragment is ionised the first (ionisation of the SO_3H group is not taken into consideration), which results in a bathochromic shift of the long-wave absorption band. The appearance of the doubly ionised forms III and IV at pH > 9 with similar values of λ_{max} is equiprobable; however, with consideration of possible existence of an intramolecular hydrogen bond, the form IV is more likely. The triply ionised form V appears in strongly alkaline media.

Table 2. Dissociation constants of PCV ($c = 4 \times 10^{-5}$ mol litre^{-1}, $l = 1$ cm, $n = 5$, $P = 0.95$).[1]

Dissociation step	λ_{max} /nm [a]	K	pK
$H_3R^- \rightleftharpoons H_2R^{2-}$	600	$(3.4 \pm 2.5) \times 10^{-10}$	9.48
$H_2R^{2-} \rightleftharpoons HR^{3-}$	650	$(3.7 \pm 2.2) \times 10^{-12}$	11.43
$HR^{3-} \rightleftharpoons R^{4-}$	690	$(2.9 \pm 2.1) \times 10^{-14}$	13.53

[a] λ_{max} is related to more strongly ionised forms (right part of the equations).

The dissociation constants of the hydroxy groups are listed in Table 2. It has to be noted, however, that these data are not in full accord with those reported in Ref. 2 (pK_{a1} = 7.82, pK_{a2} = 9.76, pK_{a3} = 11.73).

Chelate-forming chromophoric organic reagents of the triphenylmethane series are Brønsted and Lewis bases. Therefore, studies of their complexation with metal ions should take into account the possible competition between the proton and the metal ion for the reagent. Partial protonation of analytically active groups of the polydentate ligand does not prevent its complexation with metal ions, but the protonation of the donor atom of the functional analytical group often makes this process impossible.

Hence, the reactivities of polydentate reagents of the triphenylmethane series with respect to metal ions in acidic media are largely determined by the formation of the protonated forms.

$$H_4R + H^+ \rightleftharpoons H_5R^+. \quad (1)$$

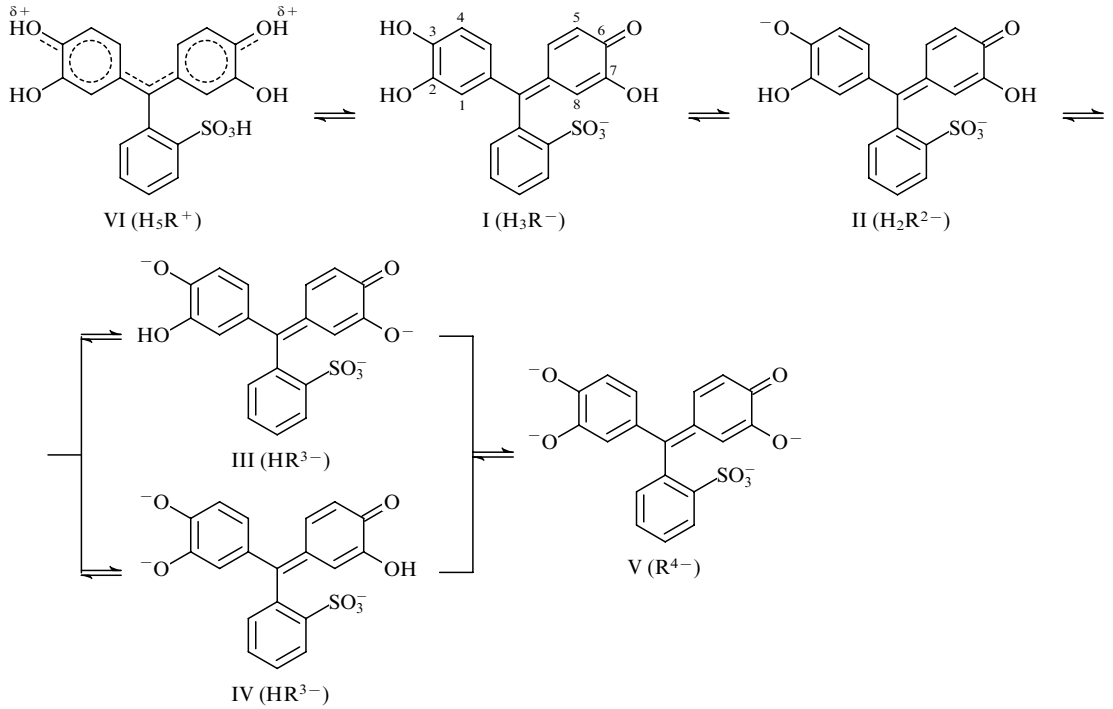
The attachment of the proton to the donor oxygen atom at pH 1 is a characteristic feature of PCV.

2. Effects of surfactants on acid-base properties of Pyrocatechol Violet

The acid-base properties of PCV are influenced by ionic strength, composition of the solution, the presence and the nature of organic co-solvents as well as the nature and concentration of surfactants. These factors determine also the optical characteristics of the reagents and complexes and stabilities of the latter.

Three types of effects were found to be responsible for enhanced sensitivities and selectivities of reactions in metal ion–

Scheme 1



reagent–surfactant systems and protolytic properties of the triphenylmethane reagents,[3,4] such as Phenol Red, Cresol Red, *m*-Cresol Purple, Xylenol Blue, Thymol Blue, Bromophenol Red, Chlorophenol Red, Bromophenol Blue, Bromochlorophenol Blue, Bromocresol Purple, Bromothymol Blue, Bromocresol Green and Pyrocatechol Violet, containing different *ortho*-substituents relative to the phenolic OH group.

One of the effects is related to the increase in the number of coordinated ligands in the analytical forms. The second is associated with the activation by a cationic surfactant (CS), which enables complexation in more acidic media due to deprotonation of the heteroatom and formation of stable associates:

$$LOH \rightleftharpoons LO^- + H^+,$$
$$LO^- + CS^+ \overset{K_a}{\rightleftharpoons} LO^- - CS^+,$$

where LOH is the reagent and K_a is the association constant. In the presence of CS, determination of the dissociation constant (K_{dis}) is impossible due to competitive formation of the ionic associate. The absorption spectra of the reagents, in the presence of CS, contain additional bands of associates, therefore it is the association constant that is determined photometrically. It is usually shifted to a more acidic region as compared with pK for the dissociation of the corresponding acid group that is involved in the formation of the associate. Therefore, the complexation of such associates takes place in more acidic media in comparison with the corresponding ionic forms of the reagents. This effect, *i.e.*, the apparent pH shift of the dissociation of acid groups, should be distinguished from true changes in the properties of acid groups of the reagents induced, as a rule, by non-ionic surfactants. The reasons for this phenomenon are as yet little understood.

The third effect is connected with multisite interactions of polydentate ligands involving both chelating and auxochromic groups in the presence of CS. For example, the number of CS cations [*e.g.*, cetylpyridinium (CP)] that add to PCV is increased in the presence of metal ions, which is only possible where a proton of one of the auxochromic groups of PCV (most probably, the OH group at position 3, see Scheme 1) is replaced by a CP cation with formation of a chelate associate.

The pronounced effect of deprotonation of the auxochromic group at position 3 on the π-electron system of the reagent[5] underlies the increase in the contrast of reactions in the presence of surfactants.

The higher the solution acidity the less pronounced the effect of deprotonation of the donor heteroatoms of the reagents and the greater the amount of CS required for the shift of the reaction equilibrium (1) to the left.[4] It is possible to determine the acidity threshold below which no deprotonation takes place even at maximum possible concentration of CP that is much above the critical micelle concentration (CMC). For PCV, this value was equal to 4.5 mol litre^{-1} of H_2SO_4; in 1% H_2SO_4, the deprotonation pK shift was 0.8. Analysis of this effect at CP concentrations from 10^{-5} to 10^{-2} mol litre^{-1} showed that the deprotonation at CP concentrations far below CMC was typical of all reagents containing sulfo groups.

If the reagent contains no sulfo groups, deprotonation occurs at [CP] $\geqslant$ CMC. At concentrations below CMC, the deprotonation is related with the formation of ionic associates involving sulfo groups. The formation of neutral associates of ionised forms of the reagents and CP cations was established by amperometry. Such associates are much more hydrophobic than the hydrated reagent ions. Therefore, the protonation of hydrophobic associates with CS under the action of H_3O^+ species is hindered. The formation of ionic associates diminishes with a decrease in the solution acidity and an increase in CS concentration up to CMC, since dissociation of sulfo groups is suppressed and sorption begins to predominate.

In the presence of charged CS micelles, deprotonation of polydentate organic reagents obeys the Hartley rule[4] and is reduced to primary sorption of negatively charged ions or neutral species on the surface of positively charged CS micelles. In this case, the deprotonation is of sorption character and is described by the Langmuir saturation isotherm. Similar to formation of hydrophobic associates, this process is accompanied by a shift of the equilibrium (1) to the left, which is consistent with the viewpoint commonly accepted in colloid chemistry. Therefore, the deprotonation of reagents in the presence of CS takes place in both aqueous and micellar phases. The pK values for the deprotonation of PCV in the presence of different concentrations of cetylpyridinium chloride are given below:[4]

c_{CP} /mol litre^{-1}	0	2×10^{-5}	4×10^{-5}	4×10^{-4}	1.2×10^{-3}
pK	0.86	0.78	0.54	0.03	0.02

The addition of CS with the length of the hydrocarbon chain $C_{12}-C_{16}$ to reagents of the triphenylmethane series at concentrations far below CMC ($10^{-6}-10^{-4}$ mol litre^{-1}) in a pH range corresponding to complete dissociation results in a pronounced (by 5–20 nm) bathochromic shift of the absorption band of H_2R^{2-}. The effect of CS on the absorption spectra of the reagents in which only the sulfo groups dissociated was less apparent and was accompanied by a small hypsochromic shift of the absorption band.

Electronic and ^{1}H NMR spectroscopic studies of the effect of CP or cetyltrimethylammonium (CTMA) revealed[6] that the appearance of a new band was due to the formation of reaction products of PCV with surfactants in a 1 : 2 ratio. In more acidic media, where the sulfo group dissociated, the ratio of the components was 1 : 1, as followed from the results of elemental analysis of solid products. As the length of the non-polar radical increasees, the associates become more stable, since counterions are bound by both electrostatic and hydrophobic interactions.

From the practical viewpoint, the shifts or redistribution of absorption band intensities in the spectra of triphenylmethane dyes upon interactions of their anionic forms with polymeric cationic flocculants [*e.g.*, poly(diallyldimethylammonium) chloride] with formation of non-extractable ionic associates can be employed in spectrophotometric determination of microgram quantities of flocculants in aqueous solutions; the use of the addition method is recommended to minimise the effects of admixtures.[7]

The concentration of a surfactant strongly affects the solubility of ionic associates. Its 1.5–3-fold increase in comparison with the stoichiometric ratio of the associate components prevents formation of a solid phase consisting of aggregated species of the associate. This results from dispersion of the associates upon attachment of several additional surfactant cations owing to hydrophobic interactions. The charged ionic associates containing overstoichiometric surfactant ions are sometimes referred to as mixed micelles. The effects of added inorganic salts on the ionic associates of sulfophthaleins and CS have been studied.[6] The nature of a strong electrolyte anion is important. If the electrolyte anion interacts with CS to form its own ion pair CS^+-An^- ($An^- = NO_3^-$, Br^-, I^- or ClO_4^-), the CS–reagent associate is destroyed under the competitive action of An^-. The addition of salts with anions that weakly react with CS brings about abnormal effects of ionic strength: at a concentration of anions in a solution as high as 0.1–0.5 mol litre^{-1}, the associates are either not destroyed at all or the decrease in their concentration is much less than is expected for compounds with an ionic type of bonds.

Two approaches to modification of organic reagents by surfactants can be noted, *viz.*, preparation of ionic associates and solubilisation in micelles. This allows conversion of common organic reagents into new in principle, more efficient compounds possessing quite different analytical properties. The first route is typical of ionogenic surfactants and reagents that dissociate in aqueous solutions. The formation of the corresponding ionic associates can be predicted. The second route is largely known for non-ionic surfactants; it is still little studied and is virtually unpredictable.

Despite such a complex behaviour of PCV in solutions with different pH, this reagent easily modifies organic or inorganic supports, which makes rather promising the application of its kinetically labile complexes in test methods. The absorption bands of aqueous solutions of H_3R^-, H_2R^{2-} and HR^{3-} correspond to the bands in the diffuse reflectance spectra of the same forms.[8] However, the absorption band of H_3R^- adsorbed on the anion-exchange resin AV-17 in the diffuse reflectance spectrum of the PCV sorbate was shifted towards longer wavelengths by 20 nm in comparison with the band characteristic of aqueous solutions of this form. The sorption of the H_3R^- form on AV-17 occurs at pH 1–4; at higher pH values, dissociation of the hydroxy groups takes place. The spectral characteristics of the dissociated form H_2R^{2-} are changed thereupon. The $F = (1-R)^2/2R$ *vs* pH curve (R is the diffuse reflectance coefficient) displayed a minimum at pH 6.5 due to the superposition of the absorption spectra of H_3R^- and H_2R^{2-}.[8,9] The sorption of the doubly charged form of PCV is weaker in comparison with the singly charged form, apparently due to delocalisation of the charge generated upon deprotonation of the OH group. It is of note that PCV sorption is irreversible: the reagent is only partly desorbed in strongly acidic solutions and is not desorbed at all in strongly alkaline solutions.

III. Pyrocatechol Violet as a complexometric indicator

The use of PCV as a complexometric indicator was studied in the presence and in the absence of the cetyltrimethylammonium ion.[10] It is commonly known that the sensitivity and the contrast of the colour reaction are crucial in the choice of an indicator for complexometric titration. Besides, the complexes formed must be highly stable with respect to exogenous substances (*e.g.*, buffer components), but less stable than the metal complex with EDTA. Titration should be carried out at the lowest possible values of pH where the logarithm of the conditional stability constant of the complexonate is $\geqslant 7$ to increase selectivity. In fairly acidic media (pH 1–2), PCV forms coloured complexes with some metal ions; however, its reactions with many metals proceed effectively only in weakly acidic media (pH 5–6). Only metal ions that do not form stable complexes with fluoride ions can be used as titrants for reverse titration in the presence of fluorides; thus, Sc, Th, Zr, Ti(IV), Al and REE salts cannot be used. Chelates of many metals that form unstable fluoride complexes possess fairly high conditional stability constants in the presence of fluorides; however, coloured PCV complexes with these metals are stable in the presence of fluorides not at all pH values. At high pH values where the metal–PCV complexes possess high conditional stability constants they are stable in the presence of fluorides, but are destroyed at low pH values where the conditional stability constants are low. As is known, pH has little effect on the stabilities of fluoride complexes but strongly affects the stabilities of metal complexes with triphenylmethane dyes (including PCV). In many cases, the use of an $NH_4F-H_3BO_3$ mixture instead of NH_4F enables efficient titration even at low pH values, since the concentration of free fluoride ions in the solution decreases drastically due to formation of the complex ion BF_4^-. The metals that can be determined by complexometric titration with PCV in the absence and in the presence of cetyltrimethylammonium [10] are listed in Table 3; the use of ternary complexes makes the titration more sensitive in a broader range of contrast of colour change than with PCV alone.

At present, further development of complexometric titration with PCV takes place. It was proposed to fix the titration endpoint automatically by monitoring the changes in chromaticity characteristics, such as L, A and B (tristimulus coordinates in the *CIELAB* system), ΔE, W and G (total colour difference, whiteness and yellowness indices, respectively) and ΔS (colour saturation difference):

$$\Delta S = S_o - S_{rs},$$

Table 3. Conditions for complexometric titration of metals with PCV in the absence and in the presence of cetyltrimethylammonium.

Metal	In the absence of CTMA			In the presence of CTMA	
	pH	buffer solution, supplementary conditions	colour change	pH	colour change
Bi(III)	2–3	HNO_3	blue–yellow	2	blue–red–yellow
Cd(II)	10	ammonia	–	–	–
Co(II)	9.3	"	–	–	–
Ni(II)	8–9.3	"	greenish-blue–red-violet	–	–
Cu(II)	5–6.5	acetate	blue–yellow	6	blue–green–yellow
Fe(III)	5–6	pyridinium acetate	blue–red-violet	3	blue–red
Ga(III)	3–3.8	acetate	blue–yellow	3	blue–yellow
In(III)	5	hot acetate	blue–yellow	6	yellow–green
Mg(II)	10	ammonia	–	–	–
Zn(II)	10	"	–	–	–
Mn(II)	9.3	ammonia + NH_2OH	greenish-blue–red-violet	–	–
Sc(III)	–	–	–	6	blue–yellow
Pb(II)	5.5	urotropine	blue–yellow	6	yellow–green
Th(IV)	2.5–3.5	HNO_3, 40 °C	red–yellow	–	–

where S_o and S_{rs} are the colour saturations of the tested and reference samples, respectively.[11] Methods have been developed for determination of Zr(IV) (Ref. 12) (where PCV is used together with other indicators), Cu(II) (Ref. 13) and Ni(II).[14] A solution of the opposite problem, *i.e.*, determination of aminopolycarboxylic acids, such as nitrilotriacetic acid and EDTA, in natural waters, is also possible.[15] These acids induce a bathochromic shift of the optical density maximum (580 nm) of a red coloured bismuth complex with PCV, which allows measurements of their concentrations in the range from 0.02 to 1.2 mmol litre^{-1}; other chelating reagents are masked with yttrium; the interference due to ions is suppressed by oxalic, citric and acetic acids.

IV. Pyrocatechol Violet as a reagent in optical methods

1. Binary Pyrocatechol Violet complexes with metal ions

PCV complexes with some metal ions have been investigated since the middle of the 20th century and described in numerous publications. However, in the majority of cases the complexation was studied in a narrow range of pH values. The spectrophotometric characteristics of these complexes are listed in Table 4.

As can be seen from Tables 1 and 4, the bathochromic shift of the absorption band in the complexation of PCV with the majority of metal ions listed exceeds 100 nm; the reason for the hypsochromic shift in a neutral medium for aluminium, gallium and indium remains obscure.[20] The molar extinction coefficients of copper, zinc, cadmium, scandium and vanadium complexes are small.

The complexation of PCV with aluminium was studied in most detail; this reagent was used for spectrophotometric determination of this metal in sea and underground waters as well as in industrial wastes (2–500 μg litre^{-1}, pH 6.1, urotropin buffer,

Table 4. Spectrophotometric characteristics of binary metal complexes with PCV.

Metal	λ_{max} /nm	pH_{opt} (see [a])	$10^{-4}\varepsilon$ (log β)	Ref.
Cu(II)	580	6	0.54	10
	630	5	− (8.42)	16
Zn(II)	600 (pH 6.5 – 8.0)	7.5	0.61	17 – 19
Cd(II)	630 (pH 7.0 – 10.0)	9.5	0.77	17, 18
Ni(II)	−	−	−	18
Ag(I)	−	−	−	18
Al	580	6	7.75	10
	575 – 580	6.5 – 7.2	6.3 (13.81)	20
	610 – 620	5	2.5	20
Ga	580	5	3.95	10
	575 – 580	6.0 – 6.5	6.4 (17.11)	20
	615 – 620	4	2.6	20
In	580	6	2.46	10
	575 – 580	7.0 – 7.8	5.9 (7.54)	20
Sc	600	6	0.98	10
Ti(IV)	570 (without H_2O_2)	6	1.88	10
	590 (with H_2O_2)	6	1.48	10
Zr	550 (pH 1.5)	1.5	2.25	10, 21
	620 (pH 2 – 6)	5	−	10
Bi	550 (pH 1.5 – 2.5)	2	2.26	10
	600 (pH 5 – 6)	6	−	10
V(V)	550 – 555	6	0.54	10
V(IV)	555	6	1.0	10
Mo(VI)	555	1.3	1.39	10
Mo(V)	555	1.3	1.36	10
W(VI)	560	1	2.24	10
Fe(III)	605	6	6.27	10
Fe(II)	605	6	5.6	10
Pb(II)	570	6	1.0	10
	585	6	1.83	10

[a] pH of the maximum complexation.

λ_{max} = 580 nm). It was shown [20] that PCV forms complexes with aluminium with the stoichiometry (*i.e.*, the metal : reagent ratio) from 3 : 1 to 1 : 5, gallium (from 2 : 1 to 1 : 5) and indium (from 3 : 1 to 1 : 1) as true solutions in several narrow intervals of pH values. In the case of indium, the formation of 2 : 3 complexes, which represent mixtures of 1 : 1 and 1 : 2 complexes, was possible with insufficiently pure PCV. The equilibrium in the reaction of Al(III) with PCV in aqueous solutions was studied. [20, 22 – 24]

The coordination of PCV involves both quinonoid and *ortho*-dihydroxy fragments. At pH < 4.5, Al(III) ions, like $Ga(OH)^{2+}$ ions,[23, 24] displace one proton from each of two reagent molecules, since the metal : PCV ratio in the complexes is 1 : 2; higher pH values favour the formation of complexes with different ionic forms of PCV. In the intermediate range of pH, the coordination in the complexes involves both groups. The construction of the distribution diagram of complexes *vs* pH demonstrated that stoichiometric (1 : 2) complexes predominate at pH 5.6 – 6.5; this can be utilised in spectrophotometric determination of gallium and aluminium in natural waters. Computer simulation of conditions for the determination of aluminium ions revealed that in the given range of pH and in the presence of small excess of PCV the measurement error due to the formation of colloidal gibbsite species is minimum. A procedure for flow-injection spectrophotometric determination of total reactive aluminium in natural waters and other objects was developed.[25] It was found [26] that at pH 6.2 the rate of the reaction of aluminium with PCV strongly depended on the presence of competing ligands, such as oxalate, malonate, fluoride, salicylate, citrate and humic acids; the equilibration time was 10 min.

The mechanism and thermodynamic and kinetic characteristics of the reaction of indium with PCV were established by the temperature-jump method with the use of laser emitters.[27] Spectrophotometric measurements showed the predominant formation of $(InH_3R)^{2+}$ and $(InH_2R)^{+}$ species at $[H^+] >$ 0.015 mol litre^{-1} and of $(In_2R)^{2+}$ species at $[H^+] <$ 0.015 mol litre^{-1}. Two relaxation effects were observed. Fast relaxation was associated with the reactions:

$$In^{3+} + H_3R^- \rightleftharpoons (InH_3R)^{2+},$$

$$InOH^{2+} + H_3R^- \rightleftharpoons (InH_2R)^{+} + H_2O,$$

while slow relaxation was associated with the formation of $(In_2R)^{2+}$. The electronic absorption spectra of gallium – PCV complexes in the absence and in the presence of electrolytes were studied.[28] It was found that the light absorption by a solution depends on the nature of the anion and the cation of the electrolyte.

On the whole, the utilisation of PCV – metal binary complex formation for analytical purposes is limited due to low reaction selectivity, narrow range of optimum pH values and, sometimes, by low molar extinction coefficients. Several approaches aimed at eliminating these drawbacks were proposed. One of them consists of a search for a third component of the complexes the introduction of which into the reaction system might significantly improve the spectrophotometric characteristics of the latter and increase the selectivity of the determination (see Section IV).

The second approach consists of preliminary separation of the tested element by extraction [29] or sorption [30 – 32] on appropriate supports with subsequent re-extraction or desorption and determination in aqueous or organic phases using PCV. Alternatively, it is complexes with PCV that are extracted [33, 34] or absorbed [31, 32, 35 – 37] with subsequent determination of metals, as a rule, by spectrophotometric,[29 – 31, 33, 34] atomic absorption [32, 35 – 37] or atomic emission [32] methods. Thus tin(IV) was extracted with tris(2-ethyl)hexyl phosphate in toluene;[29] the linearity range of the calibration curve (CC) was 10 – 100 μg ml^{-1}, the detection limit was 0.4 μg ml^{-1}. PCV complexes with Ga, Al, In [33] and Zr [34] were extracted with solutions of caproic (HL) and propionic (HA) acids in chloroform (Table 5). The linearity range of CC for gallium and aluminium determinations was 0.1 – 1.7 μg ml^{-1}; 100-fold concentrations of indium, 5-fold concentrations of bismuth and 10-fold concentrations of copper did not interfere with the determinations. It is noteworthy that PCV itself is extracted only by caproic acid, the extraction constant (K_{ex}) being equal to $(6.7 \pm 1.8) \times 10^3$.

The following schemes for the formation of extracted compounds were proposed [the subscripts (a) and (o) designate the aqueous and organic phases, respectively]:
for PCV (H_3R^-)

$$H_3R^-_{(a)} + NH^+_{4\,(a)} + 4\,HL_{(o)} \longrightarrow NH_4H_3R \cdot 4\,HL_{(o)},$$

Table 5. Extraction of PCV – metal complexes.

Metal	λ_{max} /nm	pH_{opt}	$10^{-4}\varepsilon$	K_{ex}	Extractant (M : PCV ratio within the complex)
Al(III)	585	6.5 – 7.2	3.7	$(1.8 \pm 0.1) \times 10^{11}$	propionic acid (1 : 2)
Ga(III)	585	6.2 – 6.5	2.5	$(1.4 \pm 0.3) \times 10^4$	caproic – propionic acid mixture (1 : 1)
Zr(IV)	600	6.2 – 6.5	2.6	4.3 ± 0.5	caproic – propionic acid mixture (1 : 1)

for Ga(III)

$$Ga^{3+}_{(a)} + H_3R^-_{(a)} + NH^+_{4\,(a)} + n\,HL_{(o)} + m\,HA_{(o)} \longrightarrow$$
$$\longrightarrow Ga(NH_4H_3R)LA\cdot(m-1)HA\cdot(n-1)HL_{(o)} + 3\,H^+_{(a)},$$

for Al(III)

$$Al^{3+}_{(a)} + H_3R^-_{(a)} + NH^+_{4\,(a)} + m\,HA_{(o)} \longrightarrow$$
$$\longrightarrow Al(NH_4H_3R)A\cdot(m-1)HA_{(o)} + 3\,H^+_{(a)},$$

for Zr(IV)

$$ZrO^{2+}_{(a)} + H_3R^-_{(a)} + NH^+_{4\,(a)} + n\,HL_{(o)} + m\,HA_{(o)} \longrightarrow$$
$$\longrightarrow ZrO(NH_4H_3R)LA\cdot(m-1)HA\cdot(n-1)HR_{(o)} + 2\,H^+_{(a)}.$$

Preconcentration of lead in its determination in atmospheric air and construction materials was performed using Polyorgs VII as the sorbent;[30] the sorption time was 10 min and desorption was performed with 0.1 M acetic acid. Tin was determined in zinc ingots using the anion-exchange resin Dowex 2×4;[31,32] this was combusted and the ash was dissolved in nitric acid.

Direct sorption of metal–PCV complexes was carried out on the anion-exchange resins Dowex 2×4 [31,32] or XAD-2 (for determination of Zn, Cd, Pb and Ni).[35] A procedure for preconcentration in the determination of trace amounts of Cu, Mn, Cd, Pb, Ni and Cr in potable water was developed,[36] which consisted of sorption of complexes with PCV on a column with an anion-exchange resin at pH 4–8 and elution with 1 M nitric acid in acetone; the detection limits for Cd and Cr were < 0.1 and 1 μg litre^{-1}, respectively. A possibility of preconcentration of Cu, Ni and Zn on a PCV-modified cation-exchange resin with subsequent regeneration of the resin at pH 12 or with 3 M KCl was investigated.[37]

2. Interactions of Pyrocatechol Violet with anions

Reactions of this type are documented.[38–40] Procedures were developed for spectrophotometric determination of anions based on oxidation of PCV with halogens. The latter oxidise PCV whereupon its colour fades. Thus for BrO_3^- the conditional $\varepsilon = 3.7\times10^4$, $\lambda_{max} = 557$ nm, the linearity range of CC is 0.1–1.3 μg ml^{-1} (Ref. 38); the anion : PCV stoichiometric ratios for I^- and Br^- are 1 : 5 and 1 : 3, respectively; the detection limit for iodide ions is 0.0006 μg ml^{-1} (Ref. 38); for ClO_2^-, the ClO_2^- : PCV ratio is 1 : 2; chloride, nitrate, sulfate, phosphate, carbonate, perchlorate and arsenate ions are not interfering, but the bromide ion interferes with the reaction course;[39] a method for determination of oxalic acid in food substances, which is based on enhancement of PCV oxidation by dichromate, has been described.[40]

3. Mixed-ligand complexes and ionic associates

As mentioned above, the use of two-component complexes of PCV with metal ions for analytical purposes often faces problems. Mixed-ligand complexes and ionic associates hold more promise for spectrophotometric determinations, since they are more stable, better extracted and demonstrate larger bathochromic shifts; in some cases, the selectivities are higher. Thus a ternary zirconium complex with PCV and EDTA with a component ratio Zr : PCV : EDTA = 3 : 2 : 3 was described [41] as early as 1968 and a method for determination of zirconium was developed. Since 1962, yttrium has been determined in the presence of some rare-earth elements (Pr, Nd, Ce, La) [42] using a red coloured boron–pyrocatechol complex (BPCC) with a component ratio Y : BPCC = 1 : 1; the linearity range of CC is 0.9–4.5 μg ml^{-1} for yttrium; $\varepsilon = 1.85\times10^4$ (590 nm) and 1.90×10^4 (607 nm). Ce(IV) and La(III) ions also react with BPCC, but the complexes formed are less stable. The interfering effect of lanthanum was eliminated by addition of boric acid, that of cerium, of hydrogen peroxide. Of substantial interest for further investigations are synergistic effects in the formation of ion–metal associates with PCV and Rhodamine 6G or Rhodamine B (Table 6). [43–45]

Table 6. Some characteristics of metal complexes with PCV in the presence of Rhodamine 6G.

Metal	λ_{max} /nm	pH_{opt}	$10^{-4}\varepsilon$	Linearity range of CC /μg ml^{-1}	Subject of analysis	Ref.
Al(III)	580	6.5	6.8	0–0.28	gramineal plants	43
Ti(IV)	560	5.0	7.6	0.08–0.48	alloys	45
Sn(II) [a]	560	5.0	11.8	0–0.6	canned fruits, steel samples	44

[a] In this case, as a complex with PCV and Rhodamine B.

The complexation of PCV with titanium(IV) was studied in the presence of diantipyrylmethane (DAM).[46] It is known [10] that aluminium and copper ions interfere with determination of titanium with PCV (see Table 4). The addition of DAM to the reaction system enables determination of titanium in the presence of a 300-fold (with respect to titanium) excess of aluminium and a 150-fold excess of copper. The formation of the Ti–PCV–DAM complex was characterised by a high range of contrast ($\lambda_{max} = 610$ nm, pH_{opt} 1.4–2.4, $\varepsilon = 2.00\times10^4$); the Ti : PCV : DAM ratio was 1 : 2 : 2; the linearity range of CC was 0.2–1.9 μg ml^{-1}; the stability constant of the complex was $(4.00\pm0.09)\times10^{19}$. Titanium reacted with PCV and DAM according to the following scheme:

$$Ti(OH)_i^{4-i} + 2\,H_3R^- + 2\,DAM \longrightarrow$$
$$\longrightarrow [Ti(OH)_i(H_{3-n}R)_2(DAM)_2]^{4-i-2-2n} + 2n\,H^+.$$

It was demonstrated that the role of a coordinating ion is played by $Ti(OH)^{3+}$, which displaces one proton from each PCV molecule (*i.e.*, $i = 1$, $n = 1$). DAM is bound to two OH groups of PCV through the carbonyl oxygen. A tentative structure of the complex formed was proposed.[46]

Heterocyclic bases (HetB), *e.g.*, quinine,[47] 2,2′-bipyridine [48] and 1,10-phenanthroline, were used as third components in mixed-ligand complexes of PCV with metals.[49–51] Compounds formed were insoluble or poorly soluble in water; the addition of gelatin brought about their stabilisation. A gallium complex with PCV and quinine was formed in a very broad pH range ($5 < pH_{opt} < 10$); the component ratio for the Ga : PCV : quinine complex was 1 : 2 : 1, $\lambda_{max} = 680$ nm, the linearity range of CC was $(0.2–2.0)\times10^{-5}$ mol litre^{-1}; this could be used for the determination of both gallium and quinine.[47] 2,2′-Bipyridine [48] (pH_{opt} 3–3.5, Ge : PCV : 2,2′-bipyridine = 1 : 2 : 3, λ_{max} = 610 nm) was used as a third component in the germanium complex with PCV; the solubility product was $(1.04\pm0.02)\times10^{-32}$; $\varepsilon = (3.08\pm0.25)\times10^4$. In this case, aminate-type compounds $[Ge(OH)_i(H_{3-n}R)_2\cdot(HetB)_3]^{4-i-2-2n}$ are formed characteristic of reactions with amines as bases.

In the presence of 1,10-phenanthroline (Phen), the aluminium–PCV complex is formed at pH_{opt} 6.15; $\lambda_{max} = 590$ nm; the detection limit for aluminium is 20 μg litre^{-1}. A procedure for determination of total concentrations of monomeric aluminium in natural waters and soil extracts has been developed.[49]

Vanadyl complexes with PCV and 1,10-phenanthroline [50] or cetylpyridinium bromide (CP-Br) [51] were investigated and the possibility of their extraction was examined. The main characteristics of the complexes formed in aqueous and organic media are listed in Table 7. EPR studies revealed that the complex contained V(IV). The following complexation equation was proposed:[50]

$$VO(OH)_i^{2-i} + p\,H_3R^- + q\,Phen \longrightarrow$$
$$\longrightarrow [VO(OH)_i(H_{3-n}R)_p(Phen)_q] + pn\,H^+.$$

It was found that the character of formation of ionic associates in the presence of CP-Br strongly depends on pH. In acidic media,

Table 7. Some characteristics of vanadium – PCV complexes.

Compound	λ_{max} /nm	pH_{opt}	$10^{-4}\varepsilon$	M : PCV : L ratio [a]	Additional information
PCV	450	2.8 – 3.6	–	–	aqueous medium
	450, 610	6.0			
V – PCV	550 – 560	–	–	–	the same
V – PCV – CP-Br	680	3.0 – 3.6	2.58	1 : 2 : 2	$\log\beta = 29.73$
	550, 680	5.0 – 6.4	2.41	1 : 2 : 2	$\log\beta = 28.36$ aqueous medium
	550	6.0 – 6.4	2.48	1 : 2 : 4	$\log\beta = 33.97$ chloroform (extractant)
V – PCV – Phen	550 – 560	2.8 – 3.0	1.39	1 : 2 : 2 (see [b])	aqueous medium
				1 : 1 : 1 (see [c])	non-extractable

[a] L is CP-Br or Phen. [b] The V : PCV > 1 : 15 and V : Phen > 1 : 30 ratios in solution. [c] The V : PCV < 1 : 15 and V : Phen < 1 : 30 ratios in solution.

as with PCV – Phen associates, cetylpyridinium binds to the SO_3^- group of PCV, as can be judged from the similarity of their absorption spectra. In aqueous (pH 6.4) and organic media, PCV reacts with CP-Br differently. Although under the given conditions the PCV molecule exists in a singly ionised form (H_3R^-), the hydroxy group of the pyrocatechol residue is in a pre-ionisation state. Loosening of the O – H bond occurs under the action of cetylpyridinium, which enables substitution of the cetylpyridinium cation for the hydrogen of the hydroxy group. This group favours additional delocalisation of π-electrons of PCV, resulting in a pronounced bathochromic shift of the absorption band of PCV. In the organic phase, the second CP-Br molecule is bound to the sulfo group of the reagent, owing to which the extraction of the ionic associate PCV-CP is possible.

The extractability of the complexes can also be enhanced by addition of guanidine (GU) [52] or diphenylguanidine (DPG) [17, 39, 53 – 56] to the metal – PCV reaction system (Table 8). Spectrophotometric and IR-spectroscopic studies as well as quantum-chemical calculations revealed that metal ions displace one proton from each PCV molecule in the formation of ternary complexes with GU or DPG; the coordination of the metal occurs with the *o*-hydroxyquinone group of PCV. The PCV polyassociates are destroyed under the action of GU and DPG, which, acting as bases, block the free sulfo and hydroxy groups. It is noteworthy that GU is a more efficient partner for ions with smaller ionic radii, while DPG is more suitable for extraction of ions with larger ionic radii in reactions with the same triphenylmethane dye; the differences between the properties of individual elements are eliminated upon addition of surfactants. The following complexation reactions have been proposed for aluminium,[53] tin [55] and bismuth [56] (Sol is a solvent):

$$Al^{3+}_{(a)} + 3\,DPG-H\cdot(H_3R^-)_{(o)} \rightleftharpoons$$
$$\rightleftharpoons [Al(H_2R^{2-})_3(DPG-H)_3]_{(o)} + 3[H^+]_{(a)},$$
$$Sn(OH)^{4-i}_{i(a)} + 2\,H_mR^-_{(a)} \rightleftharpoons$$
$$\rightleftharpoons [Sn(OH)^{4-i}_i(H_{m-1}R)_2]^{n-2}_{(a)} + 2\,H^+_{(a)},$$
$$[Sn(OH)^{4-i}_i(H_{m-1}R)_2]^{n-2}_{(a)} + HetB_{(a)} + q\,Sol_{(o)} \rightleftharpoons$$
$$\rightleftharpoons [Sn(OH)^{4-i}_i(H_{m-1}R)^{n-2}_2HetB]\cdot q\,Sol_{(o)},$$
$$Bi(OH)^+_{2(a)} + (H_{3-n}R)^{-n}_{(a)} \rightleftharpoons$$
$$\rightleftharpoons [Bi(OH)_2(H_{3-n}R)]^{-(n+1)}_{(a)} + (n+1)\,H^+_{(a)},$$
$$[Bi(OH)_2(H_{3-n}R)]^{-(n+1)}_{(a)} + 2\,HetB_{(o)} + (n+1)\,H^+_{(a)} \rightleftharpoons$$
$$\rightleftharpoons \{HetB_{2n}\}[Bi(OH)_2(H_{3-n}R)]_{(o)} + 2n\,H^+_{(a)}.$$

Mixed-ligand complexes of metals with triphenylmethane dyes (including PCV) and quarternary ammonium salts (QAS) hold a special place. Their advantages include high molecular mass, pronounced basic properties and the fact that they do not form complexes directly with metals. This determines their more unambiguous reactions and rules out competitive effects of other cations. Mixed-ligand complexes of PCV with iron [57] or molybdenum [58] and dialkylbenzylmethylammonium chloride were obtained as long ago as 1968 – 1970. The methods for determination of metals (Groups 3 – 14 of the Periodic Table) based on the use of heteroligand complexes with triphenylmethane dyes and QAS are known (Tables 9 and 10). The formation of these

Table 8. Extraction of metal – PCV complexes in the presence of guanidine and diphenylguanidine.

Metal	λ_{max} /nm	pH_{opt}	$10^{-4}\varepsilon$	M : PCV : DPG ratio	Extractant, additional information	Ref.
Al(III) [a]	600	–	4.4	1 : 2 : 4	aqueous medium	52
	605	11.5	5.6	1 : 2	organic medium	52
	610	6.5	7.6	1 : 2		
Al(III)	590	5.3 – 5.5	5.6	1 : 3 : 3	isobutanol, lower threshold of tested concentrations 0.03 μg ml^{-1} (for extract)	53
Ga(III) [a]	610	11.5	7.0	1 : 2	organic medium	52
Ga(III)	600	5.2	10.7	1 : 3 : 3 or 1 : 3 : 6	the same	52
Zn(II)	620	8.0	0.77	1 : 1 : 2	n-butanol	17
Cd(II)	580	9.0	0.9	1 : 1 : 2	"	17
Ti(IV)	560	6.0	6.6	1 : 4 : 4	chloroform, $\log\beta_4 = 10.38$	54
Sn(IV)	600	4 – 5	6.7	1 : 1 : 1	n-butanol and isobutanol, linearity range of CC 0.025 – 0.25 μg ml^{-1} (for extract)	55
Bi(III)	630	4 – 8	2.6	1 : 1 : 2	n-butanol, linearity range of CC 0.5 – 5.0 μg ml^{-1} (for extract)	56

[a] In these cases, as complexes with guanidine; in other cases, as complexes with diphenylguanidine.

complexes is accompanied by pronounced bathochromic shifts; however, the absorption maxima are usually shifted hypsochromically with an increase in triphenylmethane dyes concentration. This accounts for different λ_{max} values for a mixed-ligand complex of the same element reported by different authors. Contrary to the common opinion that the formation of mixed-ligand complexes is maximum at lower pH values than that of homoligand complexes, the complexation with triphenylmethane dyes and QAS occurs at nearly the same pH values, the number of coordinated triphenylmethane dye molecules in mixed-ligand complexes being larger.[67]

The number of coordinated QAS ions is often not given, only the metal : PCV ratios are determined. But even if this number is indicated, it is most likely approximate. The determination of the metal : QAS ratio requires preparation of a panel of solutions containing different concentrations of QAS, while solutions with low concentrations of QAS are usually turbid; therefore, experimental determination of the component ratios cannot be exact. It is known that physicochemical properties of compounds (including solubility) change upon formation of complexes with various ligands. For the compounds under consideration, in the formation of mixed-ligand complexes their solubilities first decrease and then increase. This can be explained by the stepwise complexation, *viz*., the formation of a less soluble mixed-ligand complex with a smaller number of coordinated ions of the second ligand is followed by the formation of a more soluble complex with a larger number of coordinated ions. One can draw an analogy between mixed-ligand metal complexes with triphenylmethane dyes and QAS, on the one hand, and some metal complexes with inorganic ligands (hydroxide, halide, cyanide ions, *etc*.), on the other hand, where the formation of metal hydroxide, halide or cyanide residues is followed by their dissolution with a further increase in the ligand concentration. The effect of micelle formation of QAS on the state of PCV, in particular, on the degree of its dissociation, was discussed above. The properties of mixed-ligand complexes depend, to a certain extent, on the nature of QAS as can be evidenced from the differences in the λ_{max} values and molar extinction coefficients (see Tables 9 and 10); this can also be explained by different effects of QAS on the dissociation of triphenylmethane dyes. Physicochemical analysis showed [67] that mixed-ligand complexes have permanent compositions due to formation of ionic associates. A positively charged ion or a QAS micelle is bound to a negatively charged metal – PCV complex by electrostatic forces, which brings about changes in the conjugation chains and absorption spectra. Then the ammonium salt of the anionic complex is dispersed in the excess of the surfactant and, contrary to binary PCV – metal complexes, can be extracted by organic solvents. However, virtually no increase in the sensitivity occurs, although the selectivity of metal determination can some-

Table 9. Spectrophotometric characteristics of metal – PCV complexes in the presence of various quarternary ammonium salts.

Metal	λ_{max} /nm	pH_{opt}	$10^{-4}\varepsilon$	Ratio M : PCV : QAS	QAS, additional information	Ref.
Fe(III)	–	–	–	1 : 2 or 1 : 3 (see [a])	benzyltetradecyldimethylammonium chloride	57
Mo(VI)	560	0.25 – 0.6 M HCl	–	1 : 2 (see [a])	dialkylbenzylmethylammonium chloride, extraction with $CHCl_3$; interfering Sn(IV), W, not interfering Zr, Zn, Co, Ni, Cu, Al, Fe(III), Cr(III), Th, Ti, V(V), U(VI)	58
	590	–	18	1 : 1 : 1	dodecylpyridine, room temperature, slow reaction; interfering Al, Th, Zr, Bi	59
	718	–	120	1 : 1 : 1 : 2 (HA)	dodecylpyridine – hydroxylamine (HA), not interfering 5-fold excesses of Al, Th, Zr	
	718	–	120	1 : 1 : 1 : 2 (HA)	dodecylpyridine – HA, linearity range of CC 0.8 – 100 μg ml^{-1}	60
Sn(IV)	591	3.6 (aqueous phase)	7.3	1 : 2 : 2	tridodecylethylammonium bromide; extraction with benzene, xylene, CCl_4, $CHCl_3$, n-butyl acetate, isobutyl methyl ketone, n-butanol	61
	–	–	–	–	triethylenediamino-bis(*N*,*N*′-decyloxycarbonylmethyl ammonium) diiodide; ethylene-1,2-bis(piperidinoyl-*N*-decyl-oxycarbonylmethylammonium) dibromide	62
Zr(IV)	610	1.6 – 3.6	–	1 : 1 : 4	triethylenediamino-bis(*N*,*N*′-decyloxycarbonylmethylammonium) diiodide, extraction with $CHCl_3$	63
	620	1.5	–	1 : 2 : 4	ethylene-1,2-bis(piperidinoyl-*N*-decyloxy carbonyl methyl-ammonium) dibromide, aqueous solution	
Al(III) [b]	585	6.3 – 7.8	4.5	1 : 2 : 3	benzyldimethylphenylammonium chloride	64
	587	6.3 – 7.4	6.2	1 : 2 : 5	decylpyridinium iodide	
	592	6.4 – 7.8	6.0	1 : 2 : 3	pentadecylpyridinium iodide	

[a] The M : PCV ratios are indicated for these cases; [b] data from n-butanol extraction.

Table 10. Spectrophotometric characteristics of metal – PCV complexes in the presence of cetyltrimethylammonium or cetylpyridinium halides.

Metal	In the presence of cetyltrimethylammonium halide				In the presence of cetylpyridinium halide				
	λ_{max} /nm	pH_{opt}	$10^{-4}\varepsilon$	ref.	λ_{max} /nm	pH_{opt}	$10^{-4}\varepsilon$ ($\log\beta$)	M : PCV : QAS ratio	ref.
Be(II)	–	–	–	–	680	8.0	1.5	1 : 1 : 5	65
Co(II)	–	–	–	–	720	10.0	1.1	1 : 1 : 5	65
Cu(II)	650	6	–	10	720	7.0	1.8	1 : 1 : 5	65
	720	–	2.83	10					
	660	6 – 7	5.0	66					

Table 10 (continued).

Metal	In the presence of cetyltrimethylammonium halide				In the presence of cetylpyridinium halide				
	λ_{max} /nm	pH_{opt}	$10^{-4}\varepsilon$	ref.	λ_{max} /nm	pH_{opt}	$10^{-4}\varepsilon$ ($\log\beta$)	M : PCV : QAS ratio	ref.
Zn(II)	–	–	–	–	690	9.0	1.3	1 : 1 : 5	65
Cd(II)	–	–	–	–	710	10.0	1.2	1 : 1 : 5	65
Fe(II)	620	5	4.3	10	–	–	–	–	–
	640	6	–	10					
Fe(III)	630	5	4.37	10	–	–	–	–	–
	630	5.0 – 6.0	5.3	66					
Pd(II)	760	6	6.1	10	700	8.0	1.7	1 : 1 : 5	65
	540	4	–	10					
	580	5	–	10					
	650	6	3.43	10					
	675	5.0 – 6.2	2.4	66					
Al(III)	570	9.7 – 10.2	5.3	67	700	5.0	1.7	1 : 1 : 5	65
	685	6	4.8	10	595	7.4 – 10.0	6.5	1 : 2 : 5	64
	670	6.0 – 7.3	7.3	68				(n-butanol)	
	670	9.7 – 10.2	5.3	52	590	7.5 – 8.0	6.5	1 : 2 : 5	69
								(n-butanol)	
Ga(III)	545	2.4 – 3.2	–	10	680	6.0 – 6.5	5.30	1 : 2 : 2	70
	625	4 – 6	–	10			(31.83)	(aqueous medium)	
	680	–	2.3	10	595	6.8 – 7.8	7.10	1 : 2 : 4	70
	675	7.0 – 7.5	6.2	68			(43.62)	(n-butanol)	
In(III)	675	6	3.65	10	680	6.0 – 6.5	4.75	1 : 2 : 2	70
	680	5.6 – 7.2	7.6	68				(aqueous medium)	
					595	6.8 – 7.8	5.60	1 : 2 : 4	70
							(43.64)	(n-butanol)	
Sc(III)	600	6	0.98	10	–	–	–	–	–
	665	6.8 – 7.1	6.9	68					
La(III)	–	–	–	–	673	8.27	4.3	1 : 2 : 3	71
Th(IV)	665	7.0 – 7.4	4.6	68	–	–	–	–	–
U(VI)	660	5.5 – 6.0	3.5	67	–	–	–	–	–
Cr(III)	650	–	6.2	72	–	–	–	–	–
Bi(III)	550	2	–	10	680	5.0	1.0	1 : 1 : 5	65
	600	6	2.42	10					
	600	4.3 – 5.4	2.9	66					
Ti(IV)	580	6	2.30	10	745	2.0	7.5	1 : 1 : 4	65
	730	3.2	7.4	73	730	–	7.8	1 : 2 : 3	74
					569	6.2	5.5	1 : 3 : 2 : 2 (EDTA)	75
Zr(IV)	540	1.5	1.09	10	700	6.0	1.3	1 : 1 : 5	65
Ge(IV)	–	–	–	–	680	1 M HCl	7.0	1 : 1 : 4	65
Sn(IV)	660	2.5	9.6	67	670	4.0	7.8	1 : 1 : 2	65
	662	2.2	9.5	76					
	660	see [a]	9.54	77					
V(IV)	680	6	–	10	–	–	–	–	–
	690	5	–	10					
	750	4	2.6	10					
	680	4.8 – 5.5	3.7	66					
V(V)	685	4	2.33	10	–	–	–	–	–
	660	6	–	10					
Nb(V)	–	–	–	–	570	0.8 – 1.6	5.3	1 : 4	67
Ta(V)	–	–	–	–	610	–	–	–	67
Mo(VI)	660	4.0 – 6.0	4.7	66	–	–	–	1 : 2 : 2	78
	680	see [b]	4	79					
	638	–	–	80					
Mo(V)	590	1		10	–	–	–	–	–
	680	5 – 6	4.2	10					
Mo(VI)	590	1.1	–	10	670	2.0	8.2	1 : 1 : 5	65
	680	5	4.3	10					
	670	6	–	10					
	640	3.0 – 4.0	1.8	9					
W(VI)	635	1	–	10	670	1.0	6.4	1 : 1 : 2	65
	650	5	4.0	10	670	1 – 1.5	–	1 : 1 : 2	67
	640	6	–	10	–	–	–	1 : 1 : 2	81
	650	2.7 – 4.6	4.4	66					

[a] 0.75 M HCl; [b] acetate buffer.

times be slightly increased through the adequate choice of a solvent.

4. The use of mixed-ligand Pyrocatechol Violet – metal complexes in the analysis of miscellaneous objects

Methods for determination of tungsten,[65,81] chromium,[72] titanium [65,73,74] and molybdenum [80] in steels, of lanthanum in silver alloys,[71] of gallium in GaAs – GaSb films,[70] of tin in bronzes [65] and aluminium ingots [79] as well as in metals and various biological objects [82] are developed. The use of PCV complexes in the analysis of pharmaceutical substances is promising as well, *e.g.*, for determination of fluoxetine and fluvoxamine,[83] imipramine [84] and chloropromixine hydrochloride.[85] Aminoglycoside antibiotics [86] react with PCV and aluminium at pH 3.0 to yield mixed-ligand complexes with the stoichiometry Al : PCV : antibiotic = 1 : 1 : 3 (monomycin and canamycin) and 1 : 1 : 4 (streptomycin and gentamycin); the linearity range of CC is 0.02 – 50 μg per ml of a biological fluid. These determinations can be carried out in the presence of 10^4-fold excesses of tetracyclines, penicillins, amino acids, novocaine and nitrates. Of particular interest are methods for determination of proteins based on their interactions with PCV in the presence of Triton X-100 (pH 1.4 – 2.0) [87] (the linearity range of CC for bovine serum albumin or human blood serum content is up to 8.0 and 9.0 mg litre^{-1}, respectively) or in the presence of tin(IV);[88] the latter allows determination of down to 200 μg of albumin in 10 ml of biological fluids.

5. Novel optical methods

The concentration of a tested element or a compound in natural and biological objects is usually insufficient for its spectrophotometric measurement. As stated above, the introduction of a third component and preparation of a mixed-ligand complex is a way to enhance their chemical and analytical characteristics. An alternative approach to the increase in sensitivity of determinations is a search for novel methods of analysis and their optimisation. Rapid analyses performed under field conditions demand elaboration of easy-to-use novel versions of optical methods based on solid-phase spectrophotometry, which combines preconcentration of a complex on an appropriate sorbent with spectrophotometric determinations.

Sorption of PCV – gallium complexes in the presence of quinine on the cation-exchange resin KU-2 with subsequent solid-phase spectrophotometric analysis was studied as long ago as 1973;[47] sorption of 14 metals except for alkali metals and calcium complexes on silica gel impregnated with a PCV – Aliquat 336 mixture was demonstrated in 1994.[89] It is possible to determine metals by solid-phase spectrophotometry, which includes sorption of binary aluminium PCV complexes [90] on AV-17 or Amberlite IRA-458-Cl (pH 3 – 7) and of tungsten [91] and molybdenum [92] PCV complexes on Sephadex QAE-A-25 (the detection limit was 2 – 8 ng ml^{-1}).

Other promising methods for the solution of this problem include diffuse reflectance spectroscopy (DRS) [93] and chromaticity measurement.[9,11,94] The latter can be regarded as a next stage in the development of DRS (particularly, with regard to colour characteristics). This opens up new opportunities for improvement of the sensitivity of determination and development of simple rapid test methods.[95,96] Of special interest are procedures and techniques, which combine detection of an element owing to formation of coloured compounds, their preconcentration on various supports and determination in the sorbent phase without desorption, *e.g.*, by DRS, or semi-quantitative colorimetric determinations based on special scales built with the use of reference samples. Both methods are complementary: DRS allows investigation of chemical and analytical properties of sorbates, while colorimetry ensures rapid and inexpensive semi-quantitative production tests.

Thus a DRS procedure for determination of molybdenum(VI) (pH 1.5 – 3.5) and tungsten(VI) (pH 1 – 3) was developed, which includes sorption on a chemically modified silica S-80 containing propionamidoxime and propionohydroxamic acid [97] or propylamine [98] residues with subsequent treatment with PCV.[97,98] Complexation in aqueous solutions and on the surface of adsorbents occurred under identical conditions, but the spectral characteristics of the complexes differed considerably. As it was mentioned, the complexation mechanism and chemical and analytical characteristics of the complexes can change depending on the chemical nature of surfactants, whereas the properties of the 'metal – chromophoric reagent – sorbent' system were very similar to those of metal – chromophoric reagent – CS complexes. The complexation can thus be represented as follows. In the sorption step, MoO_4^{2-} and WO_4^{2-} form ionic associates with the protonated amino groups of the sorbent. Subsequent treatment of the latter with PCV yields PCV complexes with metal ions, which bind to the sorbent surface. The formation of ionic-associative bonds between the functional groups of PCV that are not involved in the coordination to the metal ion and the protonated amino groups of the sorbent results in more rigid structures of complexes. This brings about delocalisation of π-electrons and a shift of the absorption maximum towards the longer wavelength region [*e.g.*, λ_{max} for aqueous solutions of PCV at pH 1 – 5 is 480 nm, λ_{max} for aqueous solutions of molybdenum – PCV complexes at pH 2 – 5 is 560 nm, λ_{max} for the sorbent was 660 (Ref. 97) or 610 nm,[98] *i.e.* the bathochromic shift was 130 – 180 nm]. A similar effect was observed in the sorption of the molybdenum(VI) – PCV complex on the anion-exchange resin AV-17.[8] Assuming that the effect of anion-exchange resins is similar to that of CS, it was expected [9] that the sorptive effect would be enhanced after addition of a surfactant (CTMA). However, because of the competition [9] between the anion-exchange resin and CTMA, the AV-17 resin had to be replaced by a neutral sorbent (Silochrome S-120). The bathochromic shift thereupon amounted to 230 nm, while the sensitivity of the determination increased owing to the use of chromaticity characteristics. These results were used for the development of novel test methods [9] and fibre-optical sensors based on PCV. In a recently developed iron-specific fibre-optical sensor in which Sephadex DEAE is used as a sorbent and PCV, as an immobilised indicator,[99] the formation of a metal complex is accompanied by changes in the diffuse reflectance spectra at 460 nm.

V. Conclusion

As can be seen from the literature data, Pyrocatechol Violet is a valuable analytical tool and a popular reagent for classical (as a metal indicator in complexonometry) and physicochemical (optical) methods of analysis. High reactivity of PCV is determined by its functional and analytical groups. The complexation of PCV involving these groups yields mixed-ligand compounds; this process can be controlled by introducing additional reagents or changing the solution acidity. The presence of a sulfo group favours the formation of ionic associates with cationogenic surfactants, whereas the non-compensated charge of binary complexes favours the formation of mixed-ligand complexes some of which are extracted by organic solvents.

Chromaticity offers new opportunities, especially in combination with sorption (sorption chromaticity) and diffuse reflectance spectroscopy. Being a representative of the triphenylmethane group and a close analogue of Pyrogallol Red (PGR), Pyrocatechol Violet is a conformationally active compound. Large molar extinction coefficients of ionic forms of both reagents and very high molar coefficients of chromaticity functions of PGR [100,101] suggest high perspectiveness of PCV chromaticity, especially of its sorption chromaticity version. As regards specific characteristics, PCV complexes share many common features with PGR complexes with molybdenum,[102] copper and titanium,[103] tungsten and vanadium(V),[104] tin(IV) and aluminium [105] as well as other metal ions. Determination of chromaticity characteristics of molecular and ionic forms of PCV will permit one to rationalise the choice of complexation conditions aimed at

the development of new optical methods for determination of various ions. Taking into account the discrepancy between literature data, it seems interesting to specify the values of dissociation constants of PCV using the chromaticity method. An objective confirmation of high practical utility of PCV as an analytical tool for advanced optical measurements can be derived from the values of molar coefficients of chromaticity functions of soluble complexes and sorbates.

Studies of chromaticity characteristics of PCV – metal complexes on the surface of anion-exchange resins and neutral sorbents in the presence of CS aimed at increasing the sensitivity of determinations and development of new, more efficient test scales and optical sensors is the most promising approach to their further application.

This review has been written with the financial support of the Russian Foundation for Basic Research (Project No. 05-03-32337).

References

1. R K Chernova, L I Kharlamova, K I Gur'ev, I S Sergeeva *Zh. Anal. Khim.* **30** 1065 (1975) [a]
2. O Ryba, Y Cifka, M Malat, V Suk *Collect. Czech. Chem. Commun.* **21** 349 (1956)
3. R K Chernova, S N Shtykov, G M Beloliptseva, L K Sukhova, V G Amelin, E G Kulapina *Zh. Anal. Khim.* **39** 1019 (1984) [a]
4. S B Savvin, R K Chernova, I V Lobacheva, G M Beloliptseva *Zh. Anal. Khim.* **36** 1471 (1981) [a]
5. R K Chernova, in *Organicheskie Reagenty v Analize* (Organic Reagents in Analysis) No. 3 (5) (Saratov: Saratov State University, 1979) p. 3
6. S B Savvin, R K Chernova, S N Shtykov *Poverkhnostno-aktivnye Veshchestva* (Surfactants) (Moscow: Nauka, 1991)
7. T V Antonova, V I Vershinin, Yu M Dedkov *Zh. Anal. Khim.* **60** 278 (2005) [a]
8. Yu A Barbalat, V M Ivanov, T V Polenova, N V Fedorova *Vestn. Mosk. Univ., Ser. 2: Khim.* **39** 174 (1998) [b]
9. V M Ivanov, G A Kochelayeva *Zh. Anal. Khim.* **58** 38 (2003) [a]
10. V N Tikhonov, T Ya Stepanova *Zh. Anal. Khim.* **34** 426 (1979) [a]
11. D Judd, G Wyszecki *Color in Business, Science, and Industry* (New York: Wiley, 1975)
12. K M M K Prasad, P Vijayalekshmi, C K Sastri *Analyst (Cambridge, UK)* **119** 2817 (1994)
13. K M M K Prasad, S Raheem *Microchim. Acta* **112** 63 (1993)
14. S Raheem, K M M K Prasad *Talanta* **40** 1809 (1993)
15. T K Wanke *Kernforschungszent. Karlsruhe, Ber., KfK* 1994 KfK 5266; *Chem. Abstr.* **121** 262989 (1994)
16. O P Rathore, S C Larale *Asian J. Chem.* **8** 435 (1996); *Chem. Abstr.* **125** 237011 (1996)
17. E E Beschetnova, L G Anisimova, O A Tataev, E Ya Mel'nikova *Zh. Anal. Khim.* **33** 1205 (1979) [a]
18. P Upadhya, M Singh, R Vimal, R Nayan *J. Indian Chem. Soc.* **74** 367(1997)
19. N M Bezhaeva, in *Sbornik Nauchnykh Soobshchenii Kafedry Khimii DGU* (Collection of Scientific Communications of the Chair of Chemistry of the Dagestan State University) (Makhachkala: Dagestan State University, 1973) No. 8, p. 52
20. V N Tikhonov, V V Bakhtina *Zh. Anal. Khim.* **39** 2126 (1984) [a]
21. I Yu Chupina, S Yu Baranenkova, O M Klimenko, in *Uspekhi Khimii i Khimicheskoi Tekhnologii (Sbornik Nauchnykh Trudov 17 Mezhdunarodnoi Konferentsii Molodykh Uchenykh po Khimii i Khimicheskoi Tekhnologii 'MKKhT-2003')* [Progress in Chemistry and Chemical Technology (Collection of Scientific Works of 17th International Conference of Young Scientists on Chemistry and Chemical Technology)] (Moscow: Mendeleev University of Chemical Technology of Russia, 2003) Vol. 17, p. 20
22. S L Simpson, S Sjöberg, J R Kiptai *J. Chem. Soc., Dalton Trans.* 1799 (1995)
23. V I Kornev, V A Valyaeva, R G Kileev, S A Mokhnachev, in *Ural'skaya Konferentsiya po Sovremennym Metodam Analiza i Issledovaniya Khimicheskogo Sostava Materialov Metallurgii, Mashinostroeniya, Ob'ektov Okruzhayushchei Sredy (Tezisy Dokladov), Ustinov, 1985* [Urals Conference on Modern Methods of Analysis and Investigation of Chemical Structure of Materials of Metallurgy and Mechanical Engineering and Environmental Objects (Abstracts of Reports), Ustinov, 1985] p. 264
24. V I Kornev, in *Ural'skaya Konferentsiya po Sovremennym Metodam Analiza i Issledovaniya Khimicheskogo Sostava Materialov Metallurgii, Mashinostroeniya, Ob'ektov Okruzhayushchei Sredy (Tezisy Dokladov), Ustinov, 1985* [Urals Conference on Modern Methods of Analysis and Investigation of Chemical Structure of Materials of Metallurgy and Mechanical Engineering and Environmental Objects (Abstracts of Reports), Ustinov, 1985] p. 265
25. S L Simpson, J R Kiptai, H S N Nilsson, S Sjöberg *Anal. Chim. Acta* **359** 329 (1998)
26. J R Kramer, J Gleed, K Gracey *Anal. Chim. Acta* **284** 599 (1993)
27. A Ricciu, F Secco, M Venturini, B Gracia, J M Leal *J. Phys. Chem. A* **104** 7036 (2000)
28. A Dmitrova, in *Nauchnye Trudy Plovdivskogo Universitetata. Khimiya* (Proceedings of Plovdiv University. Chemistry) (Plovdiv: Plovdiv University, 1988) Vol. 26, p. 159
29. J S Gaugh, M Shinde *Mikrochim. Acta* **124** 124 (1996)
30. A S Resnyanskaya, in *Kontsentrirovanie v Analiticheskoi Khimii. (Materialy Mezhdunarodnoi Nauchnoi Konferentsii), Astrakhan', 2001* [Preconcentration in Analytical Chemistry (Proceeding of International Scientific Conference), Astrakhan', 2001] p. 29
31. Z Moldovan, L Vladescu *Main Group Met. Chem.* **21** 553 (1998); *Chem. Abstr.* **129** 269623 (1998)
32. Z Moldovan, L Vladescu *Anal. Chim. Acta* **338** 231 (1997)
33. L L Kolomiets, O V Lysenko, I V Pyatnitskii *Zh. Anal. Khim.* **43** 1773 (1988) [a]
34. I V Pyatnitskii, L L Kolomiets, O V Lysenko, M G Sobko *Zh. Anal. Khim.* **45** 56 (1990) [a]
35. R Saxena, A K Singh *Anal. Chim. Acta* **340** 285 (1997)
36. I Narin, M Soylak, L Elci, M Doğan *Talanta* **52** 1041 (2000)
37. R Tica, C Bucur, V Dalbea, M Giubelan *Bull. Transilvania Univ. Brasov. Ser. B* (3) 41 (1996); *Chem. Abstr.* **130** 172328 (1999)
38. Y Sun *Ningxia Danxue Xuebao. Ziran Kexue Ban.* **17** (2) 46 (1996); *Ref. Zh. Khim.* 11G132 (1997)
39. A T Pilipenko, M M Tananaiko *Zh. Anal. Khim.* **28** 745 (1973) [a]
40. A A Ensafi, M Emadi *Anal. Lett.* **37** 321 (2004)
41. V F Luk'yanov, E M Knyazeva *Zh. Anal. Khim.* **23** 536 (1968) [a]
42. A I Busev, V G Tiptsova, V M Ivanov *Rukovodstvo po Analiticheskoi Khimii Redkikh Elementov* (Guide on Analytical Chemistry of Rare Elements) (Moscow: Khimiya, 1978)
43. W Liu, W Ma, R Yu *Guangpuxue Yu Cuangpu Fenxi* **19** 760 (1999); *Chem. Abstr.* **132** 193388 (2000)
44. W Liu, W Ma, B Qian, M Zhang *Guangpuxue Yu Guangpu Fenxi* **19** 765 (1999); *Chem. Abstr.* **132** 160536 (2000)
45. W Liu, W Ma *Yejin Fenxi* **19** 41 (1999); *Chem. Abstr.* **131** 27184 (1999)
46. L I Ganago, L A Mosina *Zh. Anal. Khim.* **35** 672 (1980) [a]
47. M I Shtokalo, L V Livadko *Zh. Anal. Khim.* **28** 484 (1973) [a]
48. L I Ganago, I A Semenovich *Zh. Anal. Khim.* **29** 1964 (1974) [a]
49. J M Samaritan, J D Wehr, A Buccafuri, M Sahn *Int. J. Environ. Anal. Chem.* **50** 175 (1993)
50. L I Ganago, L N Bukhteeva *Zh. Anal. Khim.* **32** 1537 (1977) [a]
51. L N Bukhteeva, L I Ganago *Zh. Anal. Khim.* **41** 2013 (1986) [a]
52. D G Gambarov, E L Glushchenko, A R Abramov, Z L Asadova, A K Talybova *Zh. Neorg. Khim.* **36** 1494 (1991) [c]
53. M M Tananaiko, O P Vdovenko, V M Zatsarevnyi *Zh. Anal. Khim.* **29** 1724 (1974) [a]
54. R Yu Yuryavichyus, I K Blazhis, Ch A Valyukyavichyus *Zh. Anal. Khim.* **30** 708 (1975) [a]
55. N L Shestidesyatnaya, L I Kotelyanskaya, M I Yanik *Zh. Anal. Khim.* **31** 67 (1976) [a]

56. N L Shestidesyatnaya, N M Milyaeva, L I Kotelyanskaya *Zh. Anal. Khim.* **30** 522 (1975) [a]
57. H Kohara, N Ishibashi, A Yoshida *Bunseki Kagaku* **17** 616 (1968); *Chem. Abstr.* **69** 70549 (1968)
58. H Kohara, N Ishibashi, K Abe *Bunseki Kagaku* **19** 48 (1970); *Chem. Abstr.* **73** 72788 (1970)
59. Z Chen *Fenxi Shiyanshi* **17** (6) 20 (1998); *Chem. Abstr.* **130** 158107 (1999)
60. Z Chen, X Chen *Yankuang Ceshi* **18** (1) 50 (1999); *Chem. Abstr.* **131** 193398 (1999)
61. Y Shijo *Nippon Kagaku Kaishi* 1658 (1974); *Chem. Abstr.* **82** 35407 (1975)
62. N K Kofanova, *Reaktsii Kompleksoobrazovaniya Olova s Pirokatekhinovym Fioletovym i Bischetvertichnymi Ammonievymi Solyami, Kommunarsk, 1991* (Complexation Reactions of Tin with Pyrocatechol Violet and Bisquaternary Ammonium Salts, Kommunarsk, 1991); article deposited at the Ukr. NIINTI 24.07.91, No 1073-Uk.91; *Ref. Zh. Khim.* 23G17 DEP (1991)
63. N K Kofanova, *Reaktsii Kompleksoobrazovaniya Tsirkoniya s Pirokatekhinovym Fioletovym i Bischetvertichnymi Ammonievymi Solyami, Kommunarsk, 1991* (Complexation Reactions of Zirconium with Pyrocatechol Violet and Bisquaternary Ammonium Salts, Kommunarsk, 1991); article deposited at the Ukr. NIINTI 24.07.91, No. 1072-Uk.91; *Ref. Zh. Khim.* 21V46 DEP (1991)
64. M M Tananaiko, O P Vdovenko *Zh. Anal. Khim.* **32** 1121 (1977) [a]
65. R K Chernova, L N Kharlamova, V V Belousova, E G Kulapina, E G Cumina *Zh. Anal. Khim.* **33** 858 (1978) [a]
66. V N Tikhonov, A M Mikhailova, I A Myasnikova, V I Vanyurkina *Zh. Anal. Khim.* **38** 216 (1983) [a]
67. V N Tikhonov *Zh. Anal. Khim.* **32** 1435 (1977) [a]
68. V N Tikhonov, O K Pavlova *Zh. Anal. Khim.* **37** 1809 (1982) [a]
69. M M Tananaiko, O P Vdovenko *Zh. Anal. Khim.* **30** 1095 (1975) [a]
70. L I Ganago, N N Ishchenko *Zh. Anal. Khim.* **37** 1636 (1982) [a]
71. S Xiong, M Yang, Z Gao *Ningxia Daxue Xuebao. Ziran Kexue Ban.* **16** (3) 48 (1995); *Ref. Zh. Khim.* 17G103 (1996)
72. L Zheng, J Wang, X Shen, Q Jiao *Yejin Fenxi* **13** (5) 23 (1993); *Chem. Abstr.* **122** 70841 (1995)
73. M Yang, C Xiong, S Zhang, F Li *Ningxia Daxue Xuebao. Ziran Kehue Ban.* **17 (**2) 49 (1996); *Ref. Zh. Khim.* 11G121 (1997)
74. G Lin, J Kuang, C Shu, H Han *Yejin Fenxi* **15** (1) 23 (1995); *Chem. Abstr.* **123** 187251 (1995)
75. G-Y Yu, X-R Dai *Guangpu Shiyanshi* **17** 337 (2000); *Chem. Abstr.* **133** 129298 (2000)
76. R M Dagnall, T S West, P Young *Analyst (Cambridge, UK)* **92** 27 (1967)
77. B Zhao, P Nan *Yejin Fenxi* **19** (3) 55 (1999); *Chem. Abstr.* **131** 138524 (1999)
78. R A Guketlova, L A Alakaeva *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **37** (10 – 12) 129 (1994)
79. A C Basak, K C Ghosh, A R Paul, L P Pandey, S Bhattacharjee *Met. Mater. Processes* **7** 211 (1995)
80. T Zhang, S Fan, L Yan *Lihua Jianyan. Huaxue Fence* **30** (1) 31 (1994); *Chem. Abstr.* **122** 229541 (1995)
81. R K Chernova, L N Kharlamova, V V Belousova *Zh. Anal. Khim.* **32** 2197 (1977) [a]
82. H B Corbin *Anal. Chem.* **45** 534 (1973)
83. B Starczewska, A Jasinska, B Biatous *Pharmazie* **58** 245 (2003)
84. J Karpinska, B Starczewska *Pharmazie* **54** 41 (1999)
85. B Starczewska, J Karpinska *J. Trace Microprobe Techn.* **20** 317 (2002)
86. N M Alykov *Zh. Anal. Khim.* **39** 1425 (1984) [a]
87. X Cong, Z-X Guo, X-X Wang, X-X Shen *Anal. Chim. Acta* **444** 205 (2001)
88. Y Fujita, I Mori, T Matsuo *Bunseki Kagaku* **44** 733 (1995); *Chem. Abstr.* **123** 334075 (1995)
89. R Kocjian, M Garbacka *Talanta* **41** 131 (1994)
90. N V Nelyubina, G N Shraiban, in *VI Konferentsiya 'Analitika Sibiri i Dal'nego Vostoka-2000' (Tezisy Dokladov), Novosibirsk, 2000* [The VIth Conference 'Analytical Chemistry of Siberia and the Far East-2000' (Abstracts of Reports), Novosibirsk, 2000] p. 343
91. M I Pascual-Reguera, A Molina-Diaz, M C Pacheco-Castillo, M C Anquita-Fernandez, M L F de Cordova, L F Capitan-Vallvey *Mikrochim. Acta* **112** 225 (1994)
92. A Molina-Diaz, M I Pascual-Reguera, E Linan-Veganzones, M L F de Cordova, L F Capitan-Vallvey *Talanta* **43** 185 (1996)
93. V K Runov, V V Tropina *Zh. Anal. Khim.* **51** 71 (1996) [a]
94. V M Ivanov, O V Kuznetsova *Usp. Khim.*, **70** 411 (2001) [*Russ. Chem. Rev.* **70** 357 (2001)]
95. Yu A Zolotov, V M Ivanov, V G Amelin *Khimicheskie Test-metody Analiza* (Chemical Test-Methods of Analysis) (Moscow: Editorial URSS, 2002)
96. V G Amelin *Zh. Anal. Khim.* **55** 902 (2000) [a]
97. I B Yuferova, T I Tikhomirova, V I Fadeeva *Zh. Anal. Khim.* **44** 1068 (1989) [a]
98. Do Van Thang, V I Fadeeva, T I Tikhomirova *Vestn. Mosk. Univ., Ser. 2: Khim.* **32** 38 (1991) [b]
99. J Lu *Anal. Lett.* **27** 2431 (1994)
100. V M Ivanov, A M Mamedova *Vestn. Mosk. Univ., Ser. 2: Khim.* **43** 167 (2002) [b]
101. V M Ivanov, A M Mamedova *Vestn. Mosk. Univ., Ser. 2: Khim.* **43** 291 (2002) [b]
102. V M Ivanov, A M Mamedova, S A Akhmedov *Vestn. Mosk. Univ., Ser. 2: Khim.* **44** 253 (2003) [b]
103. A M Mamedova, V M Ivanov, S A Akhmedov *Vestn. Mosk. Univ., Ser. 2: Khim.* **44** 304 (2003) [b]
104. A M Mamedova, V M Ivanov, S A Akhmedov *Vestn. Mosk. Univ., Ser. 2: Khim.* **45** 117 (2004) [b]
105. A M Mamedova, V M Ivanov, A P Korotych, S A Akhmedov *Vestn. Mosk. Univ., Ser. 2: Khim.* **45** 316 (2004) [b]

[a] — *J. Anal. Chem. (Engl. Transl.)*
[b] — *Moscow Univ. Bull. (Engl. Transl.)*
[c] — *Russ. J. Inorg. Chem. (Engl. Transl.)*