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Chemical chromaticity: potential of the method, application areas and future prospects

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Abstract. Data on the application of the chromaticity method in chemical analysis and in various branches of industry are surveyed. The potential of the method is demonstrated and the prospects of its further development are discussed. The bibliography includes 196 references.

I. Introduction

Chromaticity is a science that deals with methods for colour measurement and its quantitative characterisation. The chromaticity method involving calculation of colour characteristics from the available spectral parameters of a test sample makes it possible to both differentiate between spectrally similar compounds and obtain additional information about them. In view of this, researchers are interested in the informative potential of the method, its field of application and limitations.

A great number of studies on the elaboration of visual detection systems and image processing have been published to date; most of these are comprehensive specialised monographs that mostly deal with the traditional methods for colour measurement and data processing.[1–5] However, so far this perfect mathematical apparatus has been little employed in analytical chemistry, although there are a number of computerised spectroscopic analytical procedures that use colour measuring systems.[4]

The appearance of a characteristic colour upon a chemical reaction is normally used in qualitative analysis for the detection of elements. It is well known that our vision is very sensitive to small absolute light intensity and distinguishes hues rather well. Not only can an eye compare two radiations but it can also determine which one is more (or less) intense. Colorimetric systems are designed and perfected for the quantitative evaluation of radiation. For some time, their practical use was hindered by the complexity of the hardware required. The need for determination of the compositions of complex dye mixtures used in the textile industry has served as an impetus for the development of the chromaticity method. The solution of this problem has made it possible not only to develop compact light-measuring instruments but also to create a mathematical apparatus for the calculation of concentration dependences from the colour changes in the test samples.

There are two basic methods for colour measurement which differ in the calculation procedure: one is based on the spectral composition of radiation and the other is based on the number of individual colours in a mixture resulting in the colour to be determined. According to this classification, all colorimetric instruments and procedures for the calculation of chromaticity coordinates can arbitrarily be divided into two types, depending on the quantity to be measured:

1. The chromaticity coordinates are calculated from the known spectral composition of radiation from a test compound (absorption and reflectance spectra, *etc*.). This method is believed to be the most accurate.[6]

2. The measured general function of colour addition (which in many cases corresponds to the sensitivities of photocells) is used to determine directly the chromaticity coordinates of the required component. The development of this method is hampered due to the difficulty of manufacturing photocells with the required spectral sensitivities.

The measurement inaccuracy of a colorimetric instrument is predicted as a function of the principle of its operation.[7–10]

Chromaticity measurements are successfully used in spectrophotometric titration,[11–13] as well as for characterisation of the forms in which indicators exist.[14–17] Chromaticity measurements are even more promising in chemical analysis in the absence or with minor use of instrumentation. Owing to the development of visual-detection express methods, the problem arises of determination of the content of a compound from the overall change in the colour of a test sample (the so-called test-methods); this problem can only be solved by chromaticity measurement methods which approximate most exactly the characteristics of human vision.

The methods of objective colour measurement with computer data processing are popular in many branches of industry, *e.g*., in the printing and paint industries,[18,19] textile industry,[20–22] glass industry[23,24] and pharmaceutical industry.[25,26] In addition, colour is an important parameter of the quality of food.[27,28] There are so many application fields of chromaticity measurement methods that they cannot all be listed.

To our knowledge, only one review on the application of the chromaticity method has appeared over the last ten years.[14] However, more than 200 publications on various aspects of the method have been published over the same period. These vast literature data are scattered, which hampers the studies, especially for those scientists who just start working in this field. In view of this, the purpose of our review is to discuss the analytical

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capabilities and practical applications of the chromaticity method and to estimate the major trends and prospects in this field.

II. The main chromaticity characteristics and relationships between them

In essence, spectroscopic methods of analysis involve the detection of optical radiation parameters of a test sample. As a rule, these are the space–time distributions of radiation, its amplitude, frequency, phase, polarisation and coherence ratio. Measurement of the analytical signal is based on changes in these parameters due to interaction of the optical radiation with the object that is analysed (light absorption, reflection, dispersion) and on changes in the characteristics of the object itself upon exposure to light due to photochromism, electrooptical effects, luminescence and other phenomena.[6] The main informative parameters of optical monitoring in analytical chemistry include amplitude-related parameters, such as optical density (A), diffuse reflection coefficient (R), luminescence intensity (I_{lum}), *etc*. Integral characteristics (the total colour differences measured photometrically) are almost never used for this purpose.

According to Grassman's laws,[1] colour determination requires that three parameters be measured independently; two of them characterise the colour and the third one, the intensity. However, these parameters are used extremely seldom in analytical chemistry because of certain specific features of quantitative measurements.

Spectroscopic analysis does not allow direct determination of the chemical composition of a compound. It gives indirect information in the form of a suitable measurable physical quantity, such as optical density, diffuse reflectance, *etc*. An additional independent parameter, such as wavelength or frequency, is introduced in order to describe the spectrum. Chemical analytical techniques are mostly based on the amplitude-related characteristics and the values of these independently measured parameters. A similar approach is used for measurement of chromaticity characteristics.[29]

The mathematical description of colour in colorimetry is based on the experimental fact that each colour can be represented as a mixture (sum) of certain amounts of three linearly independent colours.[2] The basic colours include red (R), green (G) and blue (B), *i.e*., three monochromatic radiations with wavelengths (λ) of 700, 546.1 and 435.8 nm, respectively.[30]

The colour gamut diagram in this system is shown in Fig. 1. The point S_1 corresponds to a colour within the colour gamut, while S_2 corresponds to a colour outside the gamut. It is most convenient to illustrate this representation geometrically. The three basic colours serve as axes in the orthogonal coordinate system, while any colour determined by three chromaticity coordinates is reflected by a vector **S** (see Fig. 1)

$$\mathbf{S} = R\mathbf{R} + G\mathbf{G} + B\mathbf{B}, \qquad (1)$$

where R, G and B are the red, green and blue chromaticity coordinates, respectively; **R**, **G** and **B** are the unit vectors of these colours that are mixed. Connection of the unit basic colour points ($R = 1$, $G = 1$, $B = 1$) with each other gives a triangle located in the unit plane. A remarkable feature of this plane is that the colour vectors having different lengths but the same direction cross it in the same point S, which characterises the colour saturation. In order to establish the position of the point S on the unit plane, the chromaticity coordinates r, g, b are introduced; these are related to the chromaticity coordinates R, G, B as follows:

$$r = \frac{R}{R+G+B}; \quad g = \frac{G}{R+G+B}; \quad b = \frac{B}{R+G+B}. \qquad (2)$$

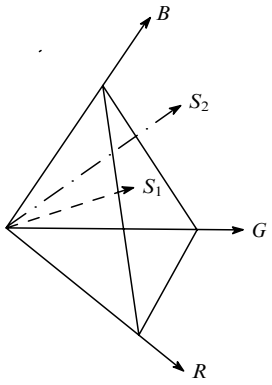


Figure 1. The RGB three-coordinate colour space.[30]

It follows from relationships (2) that $r + g + b = 1$, *i.e*., two chromaticity coordinates are sufficient to determine unambiguously the position of a point on the unit plane.

The colour perception by humans is taken into account based on experiments with colour mixing. In these experiments, one has to equalise visually pure spectral colours of equal intensity (which correspond to monochromatic lights with various wavelengths) with mixtures of the three basic colours produced by an analytical instrument. To make the comparison, pure spectral light and a mixture of the three basic colours are arranged alongside on two halves of the photometric comparison field. Upon equalisation, the amounts of the three basic colours are measured and their ratios to the unit amounts of these colours are determined. The values obtained are the chromaticity coordinates of the colour that is equalised in the selected chromaticity coordinate system. This procedure does not allow equalisation of the majority of pure spectral colours with mixtures of the three basic colours provided by the instrument. In such cases, a certain amount of one of the basic colours is added to the colour to be equalised, *i.e*., the chromaticity coordinate is allowed to be negative. Based on the estimates given by several observers, one calculates the averaged amounts of the three basic colours (specific chromaticity coordinates) which produce a mixture visually indistinguishable from the pure spectral colour. The graphic plots of the basic colour amounts on the wavelength represent the so-called colour addition curves. Based on these curves, one can calculate the fractions of the basic colours required to obtain a mixture visually indistinguishable from a colour with a complex spectral composition. For this purpose, the colour of a complex radiation is represented as a sum of pure spectral colours corresponding to its monochromatic components (with account of their intensities). The possibility of such representation is based on one of Grassman's laws, according to which the chromaticity coordinates of the colour of a mixture are equal to the sums of the corresponding coordinates of all of the colours mixed.

The addition functions are positive for the colours included in the RGB colour gamut. However, if a colour is outside the gamut, the addition functions become negative, which is inconvenient for calculations. In order to overcome this drawback, the International Commission on Illumination (CIE) summarised the known colour properties and formulas for colour variation calculations. As a result, a non-orthogonal three-colour system (XYZ) was created, which describes the spectral properties of a test object as three-dimensional vector coordinates.[2] The integral separation of the light radiation intensity into three components is convenient for correlation with human vision (due to the existence of red-, green- and blue-sensitive fibres in the eye retina).

The XYZ coordinate system is based on the following assumptions:

— the XYZ chromaticity coordinates are always positive for all real colours;

— the Y coordinate defines the colour brightness;

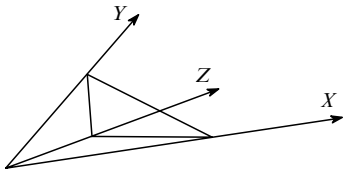


Figure 2. The XYZ three-coordinate colour space.[2]

— the chromaticity coordinates of white equal-energy radiation correspond to the centre of gravity of a triangle located in the unit plane (Fig. 2).

The following relationships are used for conversion from the RGB system of basic colours to the XYZ system:

$$\mathbf{X} = X_R\mathbf{R} + X_G\mathbf{G} + X_B\mathbf{B}, \tag{3}$$

$$\mathbf{Y} = Y_R\mathbf{R} + Y_G\mathbf{G} + Y_B\mathbf{B}, \tag{4}$$

$$\mathbf{Z} = Z_R\mathbf{R} + Z_G\mathbf{G} + Z_B\mathbf{B}, \tag{5}$$

where X_R, X_G, X_B, Y_R, Y_G, Y_B, Z_R, Z_G and Z_B are coordinates of the basic colours in the three-coordinate RGB space. It should be noted that these values have also been standardised. The chromaticity coordinates in the new colour space will have the form

$$x = \frac{X}{X+Y+Z}, \quad y = \frac{Y}{X+Y+Z}, \quad z = \frac{Z}{X+Y+Z}, \quad x+y+z = 1. \tag{6}$$

A unit plane is a right-angled triangle called the chromaticity plot; its vertices are located in the intersection points with the vectors of the basic colours. The vectors of spectral colours cross the unit plane along the pure spectral colour line (Fig. 3), which limits the region of existence of the real colours.

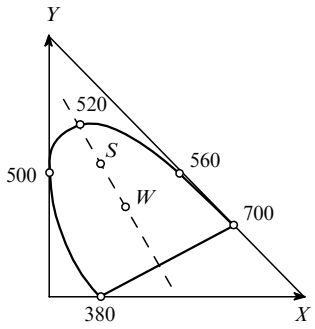


Figure 3. A unit plane in the XYZ system and the line of pure spectral colours (the solid curve).[2]
The S and W points correspond to the chromaticity coordinates of a given colour and white colour. The numbers indicate the irradiation wavelengths (λ /nm).

In addition to the X, Y, Z coordinates, there are other characteristics such as hue [$T(\lambda)$] and colour purity (P), which define unambiguously the radiation chromaticity. Obviously, any real colour can be obtained by additive mixing of white radiation with the appropriate monochromatic radiation. The hue is determined by the intersection point of the straight line which passes through the chromaticity coordinates of a given colour and the white colour (see points S and W in Fig. 3) with the pure spectral colour line (Fig. 4). The colour purity shows the ratio in which the monochromatic and white colours are mixed; the purity of monochromatic radiation is equal to unity and that of white radiation is equal to zero.

It should be noted that the use of the colour plot in the XYZ system (CIE, 1931) meets certain difficulties. For example, some

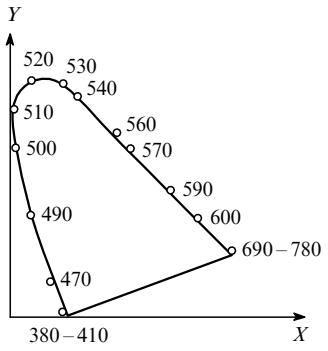


Figure 4. A colour diagram in the XYZ system.[2]
The numbers indicate the irradiation wavelengths (λ /nm).

distances between pairs of points in the plot (see Fig. 4) do not correlate with the visual perception of humans, since the scale of the plot is non-uniform. In addition, it does not give information regarding the colour lightness. The systems considered above provide only a quantitative estimate of the colour, but one cannot estimate visually the difference between two colours using these systems, since the distances between points in the colour space do not correspond to a difference reliably visible by eye. Several attempts have been undertaken to create such an equicontrast space where the distance between two points would correlate with visible colour variation. However, none of these attempts have been successful to date. The International Commission on Illumination has proposed several quasi-equal contrast systems of this kind; *CIELAB* (1976) is most popular of these systems. The L, A, B coordinates in this system are related to the X, Y, Z coordinates by the following relationships:

$$L = 116\,(Y/Y_W)^{1/3} - 16, \tag{7}$$

$$A = 500\,(X/X_W)^{1/3} - (Y/Y_W)^{1/3}, \tag{8}$$

$$B = 200\,(Y/Y_W)^{1/3} - (Z/Z_W)^{1/3}, \tag{9}$$

where L is lightness; A and B are the chromaticity coordinates (A is used for the red-green axis; B, for the yellow-blue axis); X_W, Y_W, Z_W are the coordinates of the white colour in the XYZ system; the axes A and B lie in a plane perpendicular to the L axis (Fig. 5).

The distance between two points in the three-coordinate LAB colour space characterises the total colour difference (ΔE) calculated using the formula

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta A)^2 + (\Delta B)^2}. \tag{10}$$

The hue (T) and saturation (S) are determined by the following relationships:

$$S^2 = A^2 + B^2, \qquad T = \operatorname{arctg}(B/A). \tag{11}$$

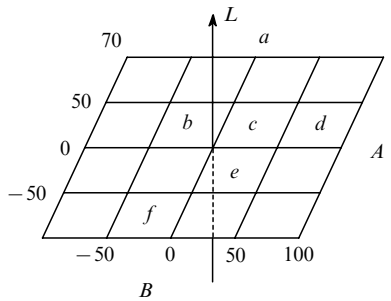


Figure 5. The LAB three-coordinate colour space. The white (a), green (b), grey (c), yellow (d), purple (e) and blue (f) regions.[30]

The yellowness (G) and whiteness (W) are expressed by the equations

$$G = \frac{100(1.28X - 1.06Z)}{Y}, \quad W = 100 - \Delta E. \tag{12}$$

The *CIELAB* colour space is most suitable for calculations, since equal distances between the points corresponding to different colours in any part of this coordinate system correlate with visual perception, enabling one to introduce a convenient measure for the quantitative determination of colour differences. In practice, the chromaticity coordinates in the *XYZ* and *CIELAB* systems and the colour characteristics of the objects of interest are obtained, *e.g.*, from the diffusion reflectance spectrum, as follows:

$$X = k \sum_{\lambda} S(\lambda)\bar{x}(\lambda)R(\lambda)\Delta\lambda, \tag{13}$$

$$Y = k \sum_{\lambda} S(\lambda)\bar{y}(\lambda)R(\lambda)\Delta\lambda, \tag{14}$$

$$Z = k \sum_{\lambda} S(\lambda)\bar{z}(\lambda)R(\lambda)\Delta\lambda, \tag{15}$$

where k is the normalising coefficient; $S(\lambda)$ is the radiation spectral density from one of the standard light sources A, C or D_{65} in relative units; $\bar{x}$, $\bar{y}$ and $\bar{z}$ are the colour addition functions; $R(\lambda)$ is the measured diffuse reflection coefficient. For self-luminous objects:

$$k = \frac{100}{\sum_{\lambda} S(\lambda)\bar{y}(\lambda)\Delta\lambda}.$$

Upon introduction of the factor k, the chromaticity coordinates for non-self-luminous objects are expressed in the scale where $Y = 100$.

Thus, chromaticity characteristics are more informative than the spectral ones, although they cannot be used without analysis of diffuse reflection spectra. The use of chromaticity characteristics in analytical chemistry expands the possibilities of studying processes that occur in test samples. The colorimetric instruments and calculation methods created for this purpose make it possible to detect colour changes and to use colour measurements for the analysis of objects.[31–33]

III. The theoretical aspects of the chemical chromaticity method

The most common task in the broad range of analyses carried out with the use of chromaticity involves the determination of metal ions. It is easy to understand that the essence of the method requires that the metals be transformed into coloured compounds, in most cases into complexes with organic ligands. These compounds can be analysed both in solution and in solid state (in the form of sorbates); in the latter case, the detection limit can be lowered by pre-concentration. Metals are mostly transformed into coloured compounds using the classical organic reagents employed in conventional spectrophotometry. Chromaticity studies on the properties of these organic reagents (optical and chromaticity parameters, *etc.*) is an important but insufficiently studied stage in the development of analytical procedures.

1. Studies of the state of organic reagents in solution and in the sorbent phase

Studies of the properties of organic reagents are important for expanding the analytical capabilities of chromaticity.[34] In view of this, the optical and chromaticity characteristics of Arsenazo III in solution and in the adsorbed state on an AV-17 anion-exchange resin have been studied. The chromaticity functions (CF) of Arsenazo III, namely the chromaticity coordinates x, y, z in the *XYZ* system, lightness (L), chromaticity coordinates A, B in the *CIELAB* system, colour saturation (S), yellowness (G), hue (T), as well as colour differences with respect to saturation (ΔS), lightness (ΔL) and tint (ΔT), were measured relative to a white colour standard with a diffuse reflection coefficient R equal to 0.98. It is assumed for an absolutely white body that $R = 1$, $W = 100$, and both ΔE and G equal zero. The functions R, W, L, X, Y, Z should be lower and ΔE should be higher for coloured compounds that absorb and reflect light simultaneously; these differences are the more significant the more intense the coloration of compounds. In agreement with this, the values of the functions R, W, L, X, Y, Z for sorbates, the coloration of which is more intense than that of solutions due to concentration, are lower, namely, they vary from 20 to 40 (for R in the range 0.2–0.4), whereas for solutions they vary from 80 to 70 (for R in the range 0.8–0.7). Of the CF, the yellowness provides the most abundant colour information. For an absolutely white body, $G = 0$; for yellow and red bodies, $G > 0$, while for green and blue ones, $G < 0$. The inflexion points in the plots (Fig. 6) correspond to regions of transition between the forms. Changes in the magnitude and sign of G in the inflexion points can indicate the state of the organic reagent in the test medium. In Arsenazo III solutions at pH < 5, the yellowness becomes positive as they contain H_8R molecules and ions such as H_7R^- (pH < 2), H_6R^{2-}, H_4R^{4-} (pH ≈ 4.6), which are red. At pH > 9.6, the yellowness is negative (−10), since the blue ions (HR^{7-} and R^{8-}) dominate in the solution. On the contrary, the G values are positive and rather high (from 40 to 120) for all sorbates and reach a maximum (120) at pH 12. It was inferred from these data that only the red ions, most likely the single-charged H_7R^- ions, are sorbed on the anion-exchange resin. Sorption of two- and multicharged ions is hampered or impossible due to steric hindrance. Ivanov *et al.*[34] suggested the use of molar CF coefficients (the ratio of the signal of a given CF to the concentration of the complexing agent expressed in mol litre^{-1}) which increase in the series: $R < G < B < L$, $X < S$, $A < W < \Delta E < Z < Y$. It was also found that the molar CF coefficients are 1.5–2.5 orders higher than the molar absorption coefficients (ε). This suggests that the

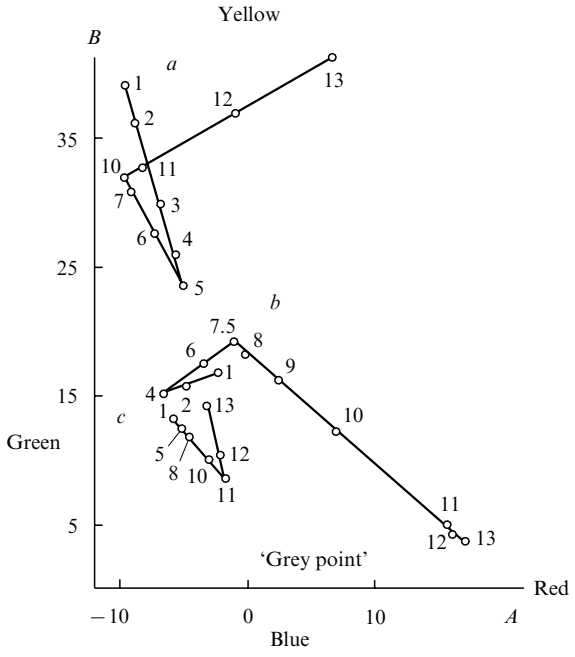


Figure 6. Changes in the A and B chromaticity coordinates (*CIELAB*) of 4-(2-pyridylazo)resorcinol (PAR) (*a*), 4-(2-thiazolylazo)resorcinol (TAR) (*b*) and 1-(2-pyridylazo)-2-naphthol (PAN) (*c*) solutions as functions of the medium acidity.[41]
Solution concentrations ($10^5 c$ /mol litre^{-1}): (*a*) 5, (*b*) 1.5, (*c*) 2.5. Acetone concentration (vol.%): (*a*) 0, (*b*) 10, (*c*) 20; the ionic strength (I) equals 0.1. The numbers indicate the pH of the solutions.

use of CF is promising for an increase in the sensitivity of determinations.

2. Studies of acid – base properties of reagents

In the majority of studies, spectrophotometric methods are used to determine the dissociation constants of organic reagents. In these methods, dependences of optical density on the solution pH are obtained and then processed graphically or by semi- or bilogarithmic computational methods. A correct choice of wavelengths is very important when measuring the optical density. They normally correspond to the maxima of light absorption by various ionic and molecular forms of the reagents. The situation becomes more complicated if the positions of the maxima differ insignificantly and especially if tautomeric equilibria exist and are imposed on the dissociation equilibria.

Changes in the properties of the equilibrium states of a reagent can be recorded using the chromaticity coordinates of the *CIELAB* equicontrast chromaticity system.[30] These values provide data on the integral distribution of light absorption in an equilibrium system tested in a broad range of wavelengths (380 – 720 nm). This allows one to avoid inaccuracies associated with a wrong choice of the range of the reagent absorption spectrum where the measurements are carried out. Thus, the reliability of the results obtained increases considerably.

Two methods exist for the determination of the equilibrium constants (pK_a).

1. Colour saturation (S) is plotted *versus* the solution pH at various reagent concentrations, then pK_a is determined graphically or calculated using the equation

$$pK_a = pH_1 + \frac{(pH_2 - pH_1)(\Delta S_1' - \Delta S_1)}{(\Delta S_2 - \Delta S_2') + (\Delta S_1' - \Delta S_1)}, \qquad (16)$$

where pH_1 and pH_2 are pH values around the assumed pK value; ΔS_1, ΔS_2, $\Delta S_1'$ and $\Delta S_2'$ are the changes in saturation depending on whether the equilibrium is shifted from alkaline to acid or from acid to alkaline medium, respectively.[35]

2. Differential plots of the reagent colour on the medium acidity are used:

$$SCD = \frac{\Delta S}{\Delta pH},$$

where the *SCD* (specific colour discrimination) parameter characterises the change in the colour saturation upon a change in pH.

The latter method is more accurate and has proved itself well in titrimetric methods.[36–39] Its application in complexonometric titration is discussed in detail elsewhere.[30,40] Of considerable interest was the use of the differential method for the determination of dissociation constants in spectroscopic analytical methods (diffuse reflection spectroscopy, solid-phase spectrophotometry). Heterocyclic azo compounds, namely, PAN, PAR and TAR, have been chosen,[41] since these are well studied as metallochromic indicators.

a. Determination of dissociation constants in solutions

It is known that PAR, TAR and PAN can exist in three main forms, *viz*., protonated at the nitrogen atom, neutral (molecular) and anionic (formed due to dissociation of the hydroxy groups) depending on the medium acidity.[42]

The variations of the chromaticity coordinates A and B (*CIELAB*) of model solutions of PAR, TAR and PAN at various pH values are shown in Fig. 6. It follows from the general character of these dependences that there are discrete pH values where the colour changes proportionally to the content of the form in which the reagent exists in the solution, and the differential plots of the colour of PAR, TAR and PAN *versus* the medium acidity should contain maxima corresponding to the pK values of the reagents. Differential curves of this type are usually analysed using the *SCD* parameter.[43,44] Morozko *et al*.[41] made calculations based on the numerical values of colour saturation. The dissociation constants found by the graphical method were found to be close to those obtained by the method of isosbestic points (Table 1).

Table 1. Dissociation constants of PAR, TAR and PAN in water – acetone solutions determined by chromaticity method and the method of isosbestic points ($I = 0.1$).

Reagent	Acetone concentration (vol.%)	Constant	pK_i obtained by	
			chromaticity method [a]	method of isosbestic points
PAR	0 [b]	pK_{NH}	2.7 ± 0.1	2.55 ± 0.15 (see [42])
	0 [b]	$pK_{p\text{-OH}}$	5.3 ± 0.2	5.47 ± 0.09 (see [45])
	0 [b]	$pK_{o\text{-OH}}$	11.5 ± 0.2	11.36 ± 0.08 (see [46])
TAR	10	pK_{NH}	1.0 ± 0.2	–
	10	$pK_{p\text{-OH}}$	5.8 ± 0.2	5.9 (see [47])
	10	$pK_{o\text{-OH}}$	9.5 ± 0.2	9.4 (see [48])
	20	pK_{NH}	1.0 ± 0.1	–
	20	$pK_{p\text{-OH}}$	6.3 ± 0.1	6.15 ± 0.22 (see [49])
	20	$pK_{o\text{-OH}}$	9.8 ± 0.2	9.68 ± 0.19 (see [49])
	40	pK_{NH}	0.8 ± 0.2	–
	40	$pK_{p\text{-OH}}$	7.1 ± 0.2	7.33 ± 0.17 (see [45])
	40	$pK_{o\text{-OH}}$	12.1 ± 0.2	12.32 ± 0.18 (see [45])
PAN	10	pK_{NH}	2.1 ± 0.2	2.32 ± 0.04 (see [50])
	10	pK_{OH}	11.9 ± 0.2	12.0 ± 0.03 (see [50])
	20	pK_{NH}	1.9 ± 0.2	1.90 ± 0.03 (see [51])
	20	pK_{OH}	12.0 ± 0.2	12.22 ± 0.05 (see [51])
	40	pK_{NH}	1.7 ± 0.2	2.09 ± 0.08 (see [52])
	40	pK_{OH}	12.2 ± 0.2	12.63 ± 0.06 (see [52])

[a] Reported data;[41] [b] measurements in water.

In a number of studies on acid – base equilibria in solutions of heterocyclic azo compounds,[53,54] it was noted that the region of existence of the reactive molecular form of an organic reagent expands with a decrease in the dielectric constant (ε) of the medium. This statement has been checked by the chromaticity method for model water – acetone solutions of PAN, PAR and TAR.[41] Figure 7 shows these dependences for TAR. The character of changes in the pK_{NH} and pK_{OH} constants makes it possible to conclude that as the content of the organic solvent increases, the reaction occurs in a more acidic medium (pK_{NH} decreases with a decrease in ε), whereas the stability of the complex increases (pK_{OH} increases with a decrease in ε).

The effect of the solvent on the pK_{NH} and pK_{OH} values for TAR was demonstrated by measuring the half-widths of *SCD* peaks (Table 2). The narrower the peak the closer the pK value

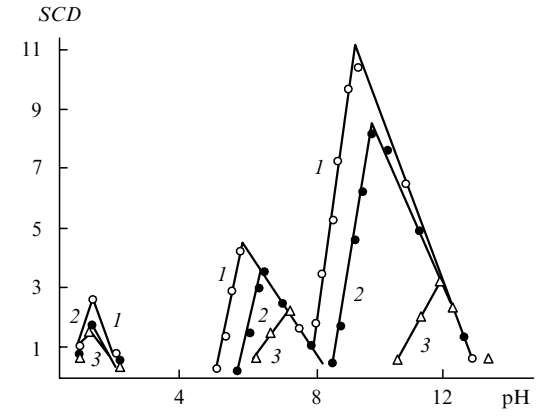


Figure 7. Variation of *SCD* of a TAR solution ($c = 10^{-5}$ mol litre^{-1}) as a function of acetone concentration and pH.[41] Acetone concentration (vol.%): (*1*) 10, (*2*) 20, (*3*) 40.

Table 2. Peak half-widths *SCD* ($\Delta p_{0.5}H_i$) as a function of acetone concentration.[41]

Parameter	$\Delta p_{0.5}H_i$ at acetone concentrations (vol.%)		
	10	20	40
$\Delta p_{0.5}H_{NH}$	0.4 ± 0.1	1.2 ± 0.2	0.3 ± 0.1
$\Delta p_{0.5}H_{p\text{-OH}}$	1.0 ± 0.2	1.2 ± 0.2	0.5 ± 0.2
$\Delta p_{0.5}H_{o\text{-OH}}$	1.2 ± 0.2	1.3 ± 0.2	0.6 ± 0.2

found graphically to that found by calculation. The results obtained suggest a sharper colour change of the reagent forms existing in solution upon both the variation of the medium acidity and the increase in the content of the polar solvent.

b. Determination of dissociation constants in the sorbent phase

The chromaticity approach to the determination of the state of organic reagents has been well proved for solutions.[55, 56] On the other hand, studies of protolytic reactions of these organic compounds on sorbent surfaces are no less important for investigation of the properties of the modified sorbents. First, protolytic equilibria characterise the reactivities of compounds, because this type of reaction is restricted to a larger extent than, *e.g.*, complexation processes. Hence, the data obtained allow one to estimate rather reliably the reactivities of different functional groups of the sorbent and of the organic compound immobilised thereon. In addition, the knowledge of the acid–base properties of reagents is necessary for the quantitative description of the stability of complexes on sorbent surfaces.

The state of TAR in the phases of silica (Silochrom C-120) and an anion-exchange resin with styrene–divinylbenzene matrix (AV-17 × 8) was studied[41] by diffuse reflectance spectroscopy (DRS) and by solid-phase spectrophotometry (SPS). The TAR dissociation constants have been found using the graphical and chromaticity calculation methods based on Fig. 8: the values of pK_{NH}, $pK_{p\text{-OH}}$ and $pK_{o\text{-OH}}$ were 1.5 ± 0.2, 6.6 ± 0.2 and 10.8 ± 0.2 for Silochrom C-120 and 1.0 ± 0.2, 5.7 ± 0.2 and 9.4 ± 0.2 for the anion-exchange resin AV-17 × 8, respectively.

Let us note that the above values of the TAR dissociation constants on AV-17 × 8 are close to those obtained for solutions. For TAR sorbed on silica, the dissociation equilibrium is shifted to the more alkaline region in comparison with solutions. This can probably be explained by specific interactions in the sorbate–sorbent system and by destruction of the silica skeleton (at pH > 10)[57] and possible dissociation of silicic acid ($pK_1 = 9.9$, $pK_2 = 11.8$, $pK_3 = 13.7$).[58]

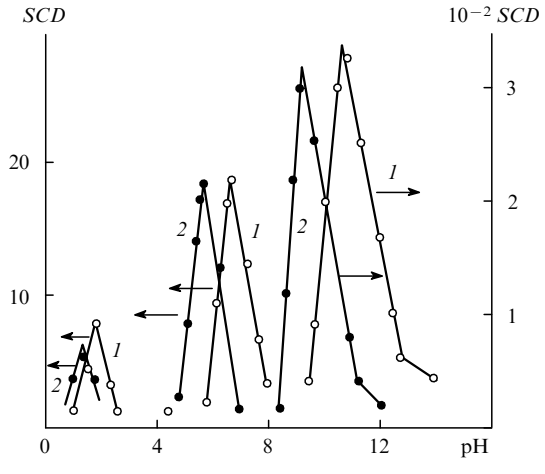


Figure 8. Variation of *SCD* of modified sorbents as a function of medium acidity.[41]
Systems: (*1*) SG–TAR, $c = 20$ μmol g^{-1} (DRS method); (*2*) AV-17 × 8–TAR, $c = 10$ μmol g^{-1} (SPS method). Sorbent fractions 200–350 μm.

It can be concluded that the quantitative description of equilibrium in the sorbent phase is a much more complicated task which usually involves a number of simplifications and assumptions that cannot be verified strictly. In spite of this, studies of equilibria on solid phase surfaces by the chromaticity method not only facilitate experimental procedures but are also of undoubted interest for researchers, as complex-forming sorbents are widely used in analytical chemistry.

3. Increasing the sensitivity of determination of metal ions

It is important to know the chromaticity parameters of complexes in order to expand the determination capabilities of chromaticity methods for elements. The use of chromaticity coordinates can increase both the determination selectivity and its sensitivity, as CF vary over broader limits than optical density or the diffuse reflectance coefficient.

Complexation of a series of transition metals, *viz.*, Cu^{II}, Zn^{II}, Ni^{II}, Mn^{II}, Fe^{III}, Cr^{III}, Co^{II}, Co^{III}, with PAN immobilised on silica gel (SG–PAN) was studied.[59, 60] It was found that the chromaticity coordinates of the SG–PAN surface in the air-dry state are strictly constant, *viz.*, $A = 77.0 \pm 0.5$ and $B = 34.0 \pm 0.5$. Basically, the chromaticity coordinates should remain constant. However, since various masking substances (for example, sodium thiosulfate for masking copper and sodium fluoride for masking iron) were added and the medium acidity was changed during the experiments, the initial chromaticity coordinates of SG–PAN changed also. These changes were particularly pronounced in the case of Mn^{II} and Cr^{III}, because the determination was carried out at pH 10.0, *i.e.*, near the critical acidity of the sorbent (pH 11.0) where it undergoes decomposition (depolymerisation). Owing to cleavage of hydrogen bonds and desorption of PAN, the chromaticity coordinates in the reference experiment are close to the 'grey point'. An increase in the absolute content of a metal ion in the solution changes the chromaticity coordinates of the complex proportionally and linearly; the saturation point of SG–PAN remains virtually constant. This means that the saturation point can serve as an individual characteristic for the detection of elements in solution. This point is usually determined using such parameters as the hue and saturation. In this case, the hue allows one to judge to which primary colour the given colour corresponds. For example, the hue of zinc is 625 nm, *i.e.*, a red colour. Saturation shows to what degree the hue is expressed in the given colour. The higher the saturation the brighter the colour of a complex adsorbed by SG–PAN.

The optimum conditions for the complexation of rare-earth metal (REM) ions, *viz.*, La, Nd, Sm, Tb, Dy, Ho, Er, Yb, with PAR were determined.[61] For all of the complexes, correlation equations for the dependence of CF on the REM concentration in the range of 0.4–2.0 μg ml^{-1} were obtained. As an example, Fig. 9 presents such dependences for erbium pyridylazoresorcinate; for the other REM studied, similar dependences were observed. It was shown that of all CF studied, the chromaticity coordinate A, the yellowness (G) and the hue (T) have the maximum magnitudes; the use of these quantities allows one to increase the determination sensitivity 35–50-fold in comparison with the sensitivity that can be achieved by spectrophotometry. Unfortunately, no correlations between the optical (such as molar absorption coefficients) or chromaticity characteristics and the properties of metal ions (for example, ionic radii) could be found.[61]

Later,[62] the features of complexation of some REM with organic reagents of various classes were studied. In particular, the complexation of lanthanum, terbium and erbium with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PAAP) was studied with and without cationic (dodecyltrimethylammonium bromide), anionic (sodium dodecylsulfate) and non-ionic (OP-7) surfactants at various concentrations of organic solvents. The majority of CF depend linearly on the element concentration in

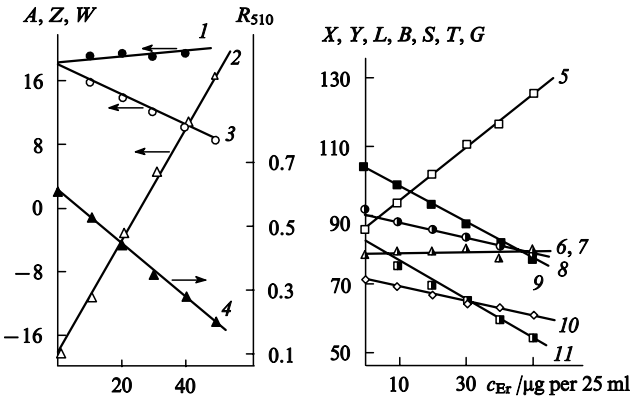


Figure 9. Dependence of the colour functions of erbium 4-(2-pyridylazo)resorcinate on the erbium concentration:[61]
(*1*) whiteness (*W*), (*2*) the chromaticity coordinate *A* in the *CIELAB* system, (*3*) the chromaticity coordinate *X* in the *XYZ* system, (*4*) diffuse reflectance coefficient at $\lambda = 510$ nm (R_{510}), (*5*) yellowness (*G*) (*6*) the chromaticity coordinate *B* in the *CIELAB* system, (*7*) saturation (*S*), (*8*) the *L* coordinate in the *CIELAB* system, (*9*) hue (*T*), (*10*) the *X* coordinate and (*11*) the *Y* coordinate in the *XYZ* system.

solution. However, for some functions, *e.g.*, for *T*, *Z*, *A* and *W*, this proportionality is violated, though the reasons for these anomalies are as yet unclear. The molar absorption coefficients were compared to the molar CF coefficients of the complexes under optimal complexation conditions. The *G*, *S* and *B* values were found to be the most sensitive characteristics. For complexes of lanthanum, erbium and terbium, the molar CF coefficients decrease in the series $G > S > B > W > Y > X > Z > L$, $B > G > S > Y > A > W > X > L$ and $B > S > W > Y > A > X > L$, respectively.

It was also shown that the use of CF provides an essential increase in the sensitivity of REM determination, *viz.*, by a factor of 25 – 100 in comparison with photometric methods (*cf.* Ref. 61).

Similar studies were carried out for complexes of erbium with Arsenazo I, Arsenazo III and Chlorophosphonazo III.[63] The molar CF coefficients for these complexes decrease in the series $G > B > Y > X > Z > L > W > A$ for Arsenazo I, $T > A > S > G > W > X > B > Y > L$ for Arsenazo III and $T > G > S > A > W > B > Y > X$ for Chlorophosphonazo III.

A study on the dependence of colour functions on the optical path length showed that all of them, except hue, change proportionally with the increase in the optical path, but the proportionality coefficient does not correlate with the molar coefficients of these functions. In addition, the sign of the change in a CF does not always coincide with the sign of its molar coefficient. These anomalies are explained [63] by the existence of complex non-linear relationships between the CF. Thus, the CF should be measured at the same layer thicknesses rather than be referred to 1 cm, as is common in photometry according to the Bouguer – Lambert – Beer law.[64] The main chemical-analytical characteristics of complexes in solutions used for the determination of metals by the chromaticity method are listed in Table 3.

A study of indium complexation with PAR,[66] PAN [67] and 5-Br-PAAP [68,69] showed that the CF depend linearly on the In content in the same concentration range (0.07 – 0.53 μg ml^{-1}) as in a study by the DRS method.

Eriochrome cyanine R (ECR) was used for the determination of trace amounts of aluminium [70–72] and beryllium [73,74] by DRS and chromaticity methods. Study on the effect of the sorbent nature on the sorption of complexes showed that the sorption ability of aluminium complexes increases in the following series of sorbents: AV-17 × 8 < silica gel < Chromaton-N-Super < cellulose. The sensitivity and reproducibility are better for colour functions than for the diffuse reflectance coefficient. The sensitivity of functions in the aluminium determination decreases in the series $G > Y > L > B > W > S > A > R$ for Chromaton-N-Super and $G > Y > B > L > S > W > A > R$ for cellulose.

Table 3. Chemical and analytical parameters of complexes in solutions in metal determination by chromaticity ($c_{min} = 0.1$ mg litre^{-1}).

Reagent	Element	pH	CP [a] range /mg litre^{-1}	Ref.
PAR	La	8.1 – 8.9	0.4 – 2.0	61
	Nd	8.0 – 9.0	0.4 – 2.0	61
	Sm	8.3 – 9.1	0.4 – 2.0	61
	Tb	8.0 – 8.6	0.4 – 2.0	61
	Dy	8.0 – 9.0	0.4 – 2.0	61
	Ho	8.5 – 9.1	0.4 – 2.0	61
	Er	8.0 – 9.5	0.4 – 2.0	61
	Yb	7.0 – 8.0	0.4 – 2.0	61
Arsenazo I	Er	6.0 – 8.5	0.4 – 2.4	63
Arsenazo III	Er	2.5 – 4.5	0.4 – 1.6	63
Chlorophosphonazo III	Er [b]	2.0 – 5.0	0.025 – 0.800	63
Lumogallion	Mo^{VI}	2.0 – 3.5	0.23 – 0.90	65
Magnezone	Mo	2.0 – 4.9	0.23 – 0.90	65

[a] CP is the linear region of the calibrating plot; [b] $c_{min} = 0.01$ mg litre^{-1}.

Beryllium interferes in the determination of aluminium; however, the beryllium – ECR complex is not sorbed by cellulose, which allows selective determination of aluminium in the presence of beryllium. The detection limit for aluminium with cellulose as the sorbent was found to be 0.004 mg litre^{-1}. The procedures developed were used for the determination of aluminium in natural water and in sodium acetate.

The complexation of nickel with dimethylglyoxime (DMG) and benzyldioxime (BD) was studied.[75] The complexes obtained were sorbed on silica gel. It was found that the optical and chromaticity characteristics form the following series in terms of determination sensitivity for nickel: $R < S < A < L < Y$ for SG – BD – Ni and $R < L \approx S < A < Y \approx T$ for SG – DMG – Ni.

Thus, the diffuse reflectance coefficient is the least sensitive colour function of coloured immobilised nickel complexes. The highest error of nickel determination is observed if the chromaticity coordinate *A* and saturation are used. The sorption of nickel complexes with DMG and BD on microcrystalline cellulose (MCC) was also studied.[76] It was found that the sensitivity of the CF increased as follows: $R < B < G < L < S < T < A < W = \Delta E < Y$ for MCC – DMG – Ni and $R < B < S < L < T < A < W = \Delta E < G < Y$ for MCC – BD – Ni.

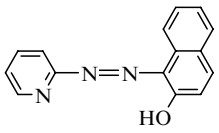
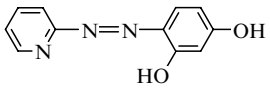
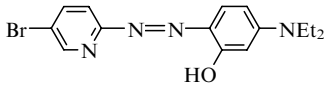
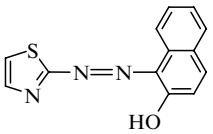
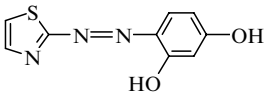
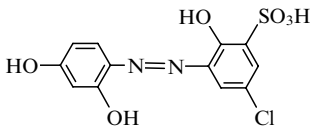
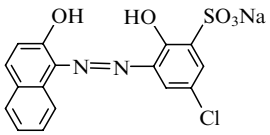
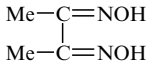
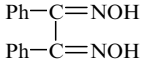
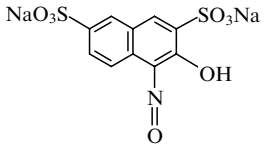
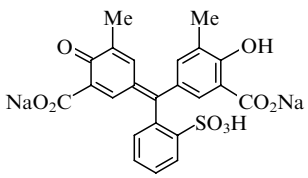
One can see that if MCC is used, a greater number of the CF depend linearly on the nickel concentration and the order in the sensitivity series changes. Simultaneously, the detection limit becomes lower.

The CF of molybdenum(VI) complexes with *o*,*o*′-dihydroxyazo compounds [lumogallion (LG) and IREA Magnezon (MG)] and with heterocyclic azo compounds (PAR, 5-Br-PAAP) in the presence or in the absence of a third component (hydroxylamine) were determined.[65] In all cases, the three-component systems are not inferior, and in most cases superior, to two-component systems with respect to optical characteristics.

Microquantities of Co^{II}, Ni^{II}, Fe^{II} and Fe^{III} in the form of complexes with nitroso-R-salt (NRS) were determined by measurement of chromaticity coordinates of a membrane filter after concentration of metal complexes on it; the detection limits were 0.1 – 0.4 μg.[77] This reagent was also used to find conditions for the separate determination of Fe^{II} and Fe^{III} ions (see Ref. 78). The chemical and analytical characteristics of adsorbed metal complexes determined by the chromaticity method are listed in Table 4.

Three-coordinate chromaticity was used in a study of the behaviour of the $Fe(bipy)_2(CN)_2$ complex (where bipy indicates bipyridyl) in 17 different organic solvents.[81] The chromaticity

Table 4. Conditions for the determination of metal ions in a sorbent phase by chromaticity.

Reagent	Reagent structure	Element	Sorbent	pH	c_{min} /mg litre^{-1}	CP range /mg litre^{-1}	Ref.
PAN		Co^{II}	SG-120	3.0 – 5.0	0.04	0.5 – 5.0	59
		Co^{III}	"	3.0 – 5.0	0.01	0.03 – 0.30	79
		Cu^{II}	"	5.0 – 8.0	1.0	0.5 – 5.0	60
		Cr^{VI}	"	2.5 – 4.5	0.1	5.0 – 50.0	60
		Fe^{III}	"	5.0 – 6.5	0.3	10.0 – 100.0	60
		In^{III}	"	4.5 – 4.8	0.04	0.2 – 0.6	67
		Mn^{II}	"	5.0 – 7.5	0.05	5.0 – 50.0	60
		Ni^{II}	"	6.0 – 9.0	0.03	0.5 – 5.0	60
		Pd^{II}	"	3.0 – 4.5	0.02	0.06 – 1.60	79
		Zn^{II}	"	7.5 – 10.0	0.03	5.0 – 50.0	60
PAR		Co^{III}	"	0.5 – 1.0	0.02	0.06 – 1.00	79
		In^{III}	"	4.8 – 5.2	0.01	0.04 – 0.30	66
		Mo^{VI}	"	4.7 – 5.8	0.03	0.1 – 0.9	65
		Mo^{VI}	AV-17	4.6 – 6.1	0.3	0.95 – 3.80	65
		Pd^{II}	SG-120	0.5 – 3.0	0.1	0.3 – 2.0	79
5-Br-PAAP		In^{III} (see [a])	"	3.8 – 5.2	0.0003	0.008 – 0.600	68
		In^{III}	"	3.5 – 5.0	0.002	0.008 – 0.640	69
		Mo^{VI}	"	5.0 – 6.0	0.04	0.05 – 0.19	65
TAN [b]		Co^{III}	"	4.0 – 6.0	0.02	0.06 – 1.00	79
		Pd^{II}	"	3.0 – 4.5	0.1	0.3 – 2.0	79
TAR		Co^{II}	"	4.0 – 8.0	0.005	0.05 – 1.00	80
		Co^{III}	"	0.6 – 1.5	0.006	0.05 – 1.00	79
		Cu^{II}	"	6.5 – 8.5	0.005	0.05 – 1.00	80
		Ni^{II}	"	5.2 – 6.8	0.005	0.05 – 1.00	80
		Pd^{II}	"	0.5 – 2.0	0.04	0.13 – 1.60	79
		Zn^{II}	"	5.6 – 7.4	0.01	0.15 – 5.00	80
LG		Mo^{VI}	AV-17	2.0 – 3.5	0.1	0.23 – 0.90	65
MG		Mo^{VI}	"	2.0 – 4.9	0.1	0.23 – 0.90	65
DMG		Ni^{II}	MCC	9.5 – 10.5	0.2	0.7 – 2.5	76
		Ni^{II}	SG-120	9.5 – 10.5	0.6	0.6 – 3.3	75
BD		Ni^{II} (see [c])	"	7.8 – 8.8	0.3	0.3 – 1.3	75
		Ni^{II}	MCC	8.5 – 10.0	0.1	0.3 – 1.3	76
NRS		Co^{II}	membrane	–	0.1	0.3 – 3.0	77
		Fe^{II}	"	–	0.3	1.0 – 10.0	77
		Fe^{III}	"	–	0.4	1.5 – 20.0	77
		Ni^{II}	"	–	0.2	0.5 – 5.0	77
ECR		Al^{III} (see [c])	MCC	5.9 – 6.2	0.004	0.004 – 0.040	76

[a] Indium oxide was used as the subject of the study; [b] 1-(2-thiazolylazo)-2-naphtol; [c] natural water was used as the subject of the study.

coordinates allow one to compare all spectral changes occurring in a system on going from one solvent to another. In particular, the hue was used as the basic characteristic. Equations relating the T values with the acceptor numbers of the solvents (AN), the Dimroth–Reichardt parameter (Et) and the Kosover parameter (z) were found:

$$AN = (-29.15 \pm 3.68) + (0.20 \pm 0.01)T, \quad (17)$$

$$T = (151.66 \pm 8.79) + (4.71 \pm 0.30)\,AN, \quad (18)$$

$$T = (73.29 \pm 58.24) + (75.55 \pm 1.22)Et, \quad (19)$$

$$T = (167.02 \pm 55.89) + (6.15 \pm 0.77)\,z. \quad (20)$$

The results obtained make it possible to predict the acid–base properties of solvents based on the hue.

Thus, the chromaticity method provides a considerable increase in the determination sensitivity of microquantities of metals, especially if pre-concentration is used. In view of this, it would be of interest to survey the chromaticity characteristics of complexes used in analytical chemistry, first of all, in photometry. Based on this systematisation, one could try to find regularities of the effect of the reagent structure on chromaticity functions (as has already been made in photometry [42]) in order to select the most valuable organic reagents and hence to develop new determination procedures. In our opinion, this task is made much easier owing to the fact that, with rare exceptions, the optimum complexation conditions found by optical methods (including DRS) coincide with the optimum conditions for chromaticity analysis.

4. Increasing the determination selectivity of metal ions

Photometric methods are promising for the determination of mixtures of elements which form complexes with the same reagent either under different conditions (pH, temperature) or with different positions of their light absorption maxima. In the latter case, derivative spectrometry or two-wave spectrometry is used. Sometimes, this lowers the detection limit;[82] the latter can also be lowered by pre-concentration of complexes, including coloured compounds, on various sorbents or by changing the method for signal recording (for example, DRS). The greatest effect is usually achieved by a combination of analytical procedures with selection of the method for signal recording. However, selective signal recording is still an issue of topical interest.

On the other hand, the chromaticity method makes it possible to increase the determination selectivity of metal ions. For example, the chromaticity method enables separate determination of microquantities of copper and zinc in water after concentration by sorption on SG–PAN.[83] The equations for the calculation of the content of metal ions are derived using vector addition of the analytical signals

$$\Delta A_\Sigma = \sqrt{\sum_i \Delta A_i^2}\,, \quad (21)$$

where ΔA_i is the colour difference with respect to lightness (ΔL), saturation (ΔS) or shading (ΔE). This set of fourth-order equations is solved by the decahotomy method using the SVI.LAB program created by Morozko and Ivanov,[83] which allows determination of no more than two metals based on the total change in the chromaticity coordinates of a sample. Quite satisfactory results were obtained; however, determination of copper and zinc should be carried out in separate aliquots of the test solution.

In a development of this approach, the possibility of separate determination of cobalt and palladium in mixtures after concentration by chromaticity analysis with subsequent calculation of the amounts of these metals using the equations by Ivanov *et al.*[79] was studied. Cobalt and palladium were chosen due to the anomaly of the colours of their complexes with PAN (green to bluish-green) in comparison with complexes of other elements (reddish-violet) rather than by the similarity of their chemical and analytical properties, and also because they can be used to demonstrate the advantages of chromaticity as an analytical method.

Due to the closeness of the absorption (reflection) maxima of both complexes, cobalt and palladium cannot be determined separately by the DRS method because of overlap of the signals. Therefore, the effect of the sorption conditions on their chromaticity characteristics was studied.

Heterocyclic azo compounds immobilised on silica form green complexes with cobalt and palladium which differ in hue (yellowish-green and bluish-green, respectively). Recording of the colour change *versus* the content of metal ions in a solution with the use of the chromaticity coordinates A and B provides the possibility of using these differences for the separate determination of the ions in a mixture by measuring the signal at one wavelength. For example, Fig. 10 shows such dependences for complexes adsorbed on SG–PAN. If the absolute content of a metal ion in the solution (and, hence, in the sorbate) increases, the chromaticity coordinates of the sorbate surface change proportionally; the saturation point of the sorbate with respect to each metal does not change upon further increase in concentration of the corresponding ion in the solution.

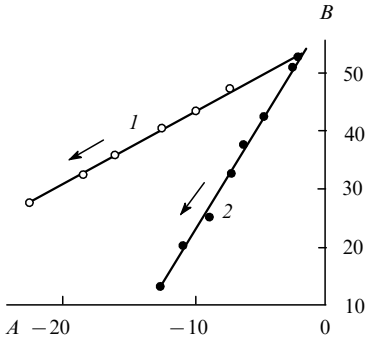


Figure 10. Effect of cobalt (*1*) and palladium (*2*) concentration on the chromaticity coordinates A and B of sorbates on SG–PAN at pH 3.[79] The arrows show the increasing metal concentration.

The equations derived for the change in the chromaticity coordinates of the sample (Table 5) are used to find conditions for separate determination of metal ions in solutions. It was suggested to use the signal separation factor (α) as a measure of completeness of separation; it is calculated using the following equations:

$$\begin{aligned} &\alpha = |\operatorname{arctg} K_{M_1} - \operatorname{arctg} K_{M_2}|, \\ &\text{if } |\operatorname{arctg} K_{M_1} - \operatorname{arctg} K_{M_2}| < 90^\circ; \\ &\alpha = 180^\circ - |\operatorname{arctg} K_{M_1} - \operatorname{arctg} K_{M_2}|, \\ &\text{if } |\operatorname{arctg} K_{M_1} - \operatorname{arctg} K_{M_2}| \geqslant 90^\circ, \end{aligned} \quad (22)$$

where K_{M_1} and K_{M_2} are the slopes of plots of the chromaticity coordinates A and B of the sorbent on the concentration of metal ions M_1 and M_2, respectively.

The magnitude of α is affected by the error of determination of the analytical signal (chromaticity coordinates). It was found experimentally for the Spectroton colorimeter that separate determination of two metals is satisfactory for $\alpha \geqslant 25^\circ$.

For all of the sorbents studied, dependences of the chromaticity coordinates A and B on the content of cobalt and palladium in solution were obtained and the following signal separation factors were found:

Sorbent	SG–PAN	SG–PAR	SG–TAN	SG–TAR
α	27°	21°	20°	15°

Table 5. Chromaticity coordinates of cobalt(III) and palladium(II) complexes on the sorbent surface.

Ion	Reagent	Equation of the sorbent colour change	Range of the sorbent colour change,[a] $(A_i, B_i)-(A_j, B_j)$	Saturation point /μg of ion
Co^{III}	TAR	$B = (28 \pm 0.1)A + (28.3 \pm 0.7)$	(7.0, 48.0)–(−7.5, 8.0)	10.97
	TAN	$B = (1.8 \pm 0.05)A + (29.5 \pm 0.4)$	(−0.5, 28.5)–(−14.0, 4.0)	18.00
	PAR	$B = (4.7 \pm 0.1)A + (19.6 \pm 0.3)$	(1.3, 25.5)–(−2.5, 8.0)	8.40
	PAN	$B = (3.9 \pm 0.05)A + (62.3 \pm 0.2)$	(−2.5, 52.5)–(−12.5, 13.0)	18.00
Pd^{II}	TAR	$B = (1.15 \pm 0.05)A + (38.5 \pm 0.5)$	(7.0, 48.0)–(−18.0, 11.0)	21.10
	TAN	$B = (1.1 \pm 0.1)A + (30.1 \pm 0.6)$	(−0.5, 28.5)–(−19.0, 9.0)	21.00
	PAR	$B = (1.5 \pm 0.1)A + (23.7 \pm 0.1)$	(1.3, 25.5)–(−10.0, 8.5)	13.10
	PAN	$B = (1.2 \pm 0.05)A + (55.6 \pm 0.2)$	(−2.5, 52.5)–(−14.0, 4.0)	35.60

[a] Saturation was used as the reference experiment.

It was concluded on the basis of the data obtained that the separation factor increases on going from thiazole azo compounds to pyridine ones and from resorcinol to naphthol. Only SG–PAN complies with the criterion of satisfactory separation ($\alpha \geqslant 25^\circ$). So this sorbent was chosen for the concentration of cobalt and palladium followed by their determination by the chromaticity method.

The concentrations were calculated using the following set of equations:

$$\Delta L_\Sigma^2 = (a_{11} + b_{11}x_1)^2 + (a_{12} + b_{12}x_2)^2,$$
$$\Delta S_\Sigma^2 = (a_{21} + b_{21}x_1)^2 + (a_{22} + b_{22}x_2)^2, \quad (23)$$

where ΔL_Σ and ΔS_Σ are the lightness and saturation, respectively, for the sum of the two metals; a_{ij} and b_{ij} $(i, j = 1, 2)$ are the factors of the calibration plot for the dependence of the chromaticity coordinates A and B on the metal ion concentrations (see Table 5); x_1 and x_2 are the unknown concentrations of the cobalt and palladium ions, respectively.

This fourth-order set of equations has four different parameters (four x_1 and x_2 pairs) which, in the general, case satisfy the solution. The sets of equations were solved on a personal computer using the Newton method. The amounts of cobalt and palladium (in 20 ml of solution) were varied from 0.5 to 5.0 μg and from 2.0 to 20.0 μg, respectively. Satisfactory results of separate determination of these metals in model mixtures were obtained; they were close to the data of analysis by the DRS method on the SG–TAR sorbent.

Of the greatest interest is the possibility of increasing the selectivity in the determination of metal ions which form reddish-violet complexes, since it is impossible to determine individual metals in a mixture in this spectral region by other methods (DRS, SPS) without masking or separation. TAR was selected as the reagent.[80] The possibility of separate determination was studied for copper, nickel and zinc in the presence of iron and cobalt. The optimum conditions for the sorption of these metals are indicated in Table 4.

The detectability of colour changes depending on the content of metal ions in solution with the use of chromaticity coordinates A and B implies that it is possible to carry out separate determination of ions in two- and three-component mixtures. Figure 11 shows such dependences for sorbates of complexes on SG–TAR. The data obtained were processed by the least-squares method.

Based on the calibration plots for the dependences of the chromaticity coordinates A and B on the content of copper, nickel, zinc and cobalt, the following signal separation factors were found:

M_1-M_2	Cu–Zn	Cu–Ni	Zn–Ni
α	23°	13°	37°

One can see that the nickel–zinc pair satisfies the criterion of separate determination. It should be noted that copper interferes in the simultaneous separate determination of nickel and zinc,

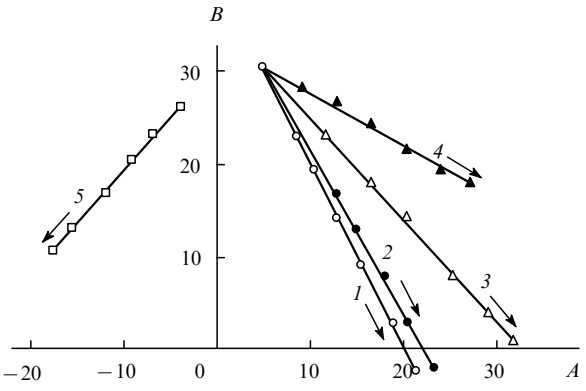


Figure 11. Dependence of the chromaticity coordinates A and B of sorbates on SG–TAR on the content of cobalt(II) (*1*), nickel (*2*), copper (*3*), zinc (*4*) at pH 7.0 and cobalt(III) (*5*) at pH 2.0.[80]
The arrows show the increasing metal concentration.

therefore it is masked with sodium thiosulfate. The ΔL and ΔS values obtained were used to calculate nickel and zinc concentrations using the set of Eqns (23).

Separate determinations of nickel and zinc in the presence of copper and cobalt were carried out similarly, except that the concentrations were calculated using a modified set of equations:

$$\Delta L_\Sigma^2 = (a_{11} + b_{11}x_1)^2 + (a_{12} + b_{12}x_2)^2 + d_1,$$
$$\Delta S_\Sigma^2 = (a_{21} + b_{21}x_1)^2 + (a_{22} + b_{22}x_2)^2 + d_2, \quad (24)$$

where x_1 and x_2 are the unknown concentrations of nickel and zinc ions, respectively; d_1 and d_2 are constants describing the contribution of cobalt to the set of equations.

The contribution of cobalt was estimated by determining its content at $\lambda = 610$ nm. The procedures described above were used to determine nickel, zinc and cobalt in a standard soil sample SP-3.

The above version of chromaticity analysis allows separate determination of 0.03–0.30 μg ml^{-1} cobalt and 0.013–0.130 μg ml^{-1} palladium, as well as 0.05–1.00 μg ml^{-1} nickel and 0.15–5.00 μg ml^{-1} zinc. The advantages of chromaticity for increasing the selectivity of determination of metal ions in two-, three- and four-component mixtures have been shown.

IV. Practical applications of the chromaticity method

1. Application of the chromaticity method in chemical analysis

Let us dwell on the most interesting practical applications of chromaticity. At present, the test procedures are becoming more and more popular. A test metal ion is usually identified by the colour of a complex it forms with a test reagent.[84] In the case of

acid – base indicators, the colour change upon decrease or increase in the medium pH is recorded. General-purpose test paper (pH 1 – 10) or reactive test papers used for qualitative and semi-quantitative analysis can serve as obvious examples.[84, 85] A colour change of the paper (sorbent) after a reaction indicates the presence of the ion in question in the test solution. Only the colour change is usually observed while the laws of this process are not recorded.

Construction of calibration test scales for the visual determination using the known dependence of the total colour difference (ΔE) on the content of the test element allows minimisation of inaccuracy of a test technique and quantitative description of not only the intensity but also of the colour change. Since one colour discrimination threshold corresponds to one ΔE unit in the equicontrast colorimetric system (*CIELAB*), the concentrations of the test element are chosen in accordance with a certain ΔE step to be determined most precisely by a human eye.

Even before the equicontrast *CIELAB* system had been developed, it was noticed that the difference in intensity of luminous fluxes is felt reliably if they differ by approximately 10% (see Ref. 6). The total colour difference is measured in the range of 0 – 100 arbitrary units, hence 10% corresponds to a step of $\Delta E = 10$. If colour is to be recognised from the surface of a reactive paper (sorbent) by a human, it is recommended to create test scales with $\Delta E \geqslant 10$ (see Ref. 86).

If a test sample loses its own colour or discolours due to the analytical reaction and the colour of the test sample support is close to white (for example, in the case of silica), the test scale should better be constructed using the inverse quantity, *viz*., the whiteness of the test sample, $W = 100 - \Delta E$ (see Ref. 68).

The dependence of the variation of the W and ΔE parameters of a test sample on the content of the test microelement has the shape of a logarithmic curve.[59] Thus, for a constant step $\Delta E = 10$ the concentration of a given microelement in a test sample changes in a geometrical progression, which is often suggested for the construction of a visual test scale.[87] In this case, the total colour difference of 10 arbitrary units between the original test sample (E_0) and a test sample following reaction of the microelement to be tested (E) is considered as the lowest determination threshold: $E - E_0 = 10$ (or $W - W_0 = 10$).

It was shown convincingly that the use of heterocyclic azo compounds immobilised on various sorbents makes it possible to achieve low detection limits in sorption-spectroscopic analyses in combination with high sensitivity and good reproducibility of results. In some cases, selective express techniques for the determination of microelements can be created using such reagents.

According to the general ideology of test methods for the environmental control, three basic rules were used as a guide in the development of sorption-spectroscopic procedures.[86]

1. The identification and determination of microelements in the environmental objects should be carried out quickly. This is achieved by comparing the indicator test sample with a standard scale.

2. It is necessary to provide the documentation of the test or the possibility of performing post-instrumental chemical analysis, which is realistic only for stable test samples.

3. The reactions should be contrasting.

The chromaticity method allows one to create an equicontrast chromaticity test scale well discernible by the human's eye. Based on the functional relationship between ΔE and the content of a test element in an object with a colour difference threshold $\Delta E \geqslant 10$, it is possible to construct a calibration test scale with a minimum error. Therefore, the descriptions of sorption-spectroscopic determination procedures involve the $\ln(\Delta E) = f(c)$ dependences in a mathematically processed form.

The non-selective colour difference parameter based on lightness (ΔL) is applicable for the post-instrumental determination of the content of a microelement in a test sample, provided that the chemical reactions which can be used for the sorption-spectroscopic analysis occur selectively and the reaction products are extracted quantitatively. The latter can be predicted to a certain extent based on the regularities of the sorption extraction of reagents by sorbent surfaces that we have studied.

The potential of the chromaticity method with the use of chromaticity coordinates is demonstrated in this study (Ref. 86) for the development of selective sorption-spectroscopic procedures for the separate simultaneous determination of cobalt(III) and palladium(II), copper(II) and zinc(II) using TAR immobilised on silica gel (SG – TAR). The capacity of the sorbent with respect to the reagent determined from saturation curves for metals was 20 μmol g^{-1} (see Refs 79, 80).

An advantage of the sorption version of testing is that it allows one to change the sensitivity of determination of a microelement by varying the sample volume, which is impossible if reagent test papers are used.

When a coloured compound formed and the sorbent sedimented, its colour was compared with the standard calibration colour scale for microelement determination, using the step $\Delta E = 10$ for making the test scale. The sorbates for the test scale were placed in test tubes with a diameter of 4 mm. The test scale obtained in this way is stable for at least five years.

2. Application of the chromaticity method in other fields of science and industry

a. Food chemistry

The greatest number of studies deal with the use of the chromaticity method for monitoring the production of foodstuffs, quality of cultures grown and in wine-making.

The effect of the growth conditions (greenhouse or open air) of hot pepper on its chromaticity characteristics[88] showed that the amount of pigments in pepper grown in a greenhouse can be predicted using the chromaticity coordinates A and B and the ratio A/B. For pepper grown in the open air, a similar correlation is observed for the values L and A/L.

The *CIELAB* system was used to estimate the quality of tomatoes,[89] tinned mushrooms[90] and potato chips.[91] It was found that the angle between the coordinates A and B depends on the colour of vegetables. A similar correlation with the L coordinate is not always observed. In particular, a study on the darkening of cut-off lettuce *versus* time[92] did not show such a dependence.

The *XYZ* chromaticity system can be used to classify honeys[93] and to estimate the natural sweetener from the cactus tree.[94] In this case, some other characteristics (viscosity, glucose content, *etc*.) were used along with the chromaticity coordinates. The chromaticity coordinates were also used to monitor production of sausages,[95, 96] in particular, to study the effect of the content of soybean proteins on the colour characteristics of the product.[95]

The three-coordinate colour system was used to study the first phase of milk turning[97, 98] and to estimate the colour of milk prepared from powder.[99] A theory allowing the preparation of emulsions with certain colour characteristics has been developed.[100] In this case, the chromaticity coordinates are calculated from the diffuse reflectance coefficient (R). The theoretical calculations are in good correlation with the experimental results. The variations of the chromaticity characteristics of soybean milk during the grinding of soy beans have also been studied.[101]

The chromaticity systems *CIEXYZ*, *CIELUV* and *CIELAB* were successfully employed for the characterisation of anthocyans isolated from red grapes,[28, 102] raspberry[103] and strawberry.[104] The effect of an atmosphere enriched with carbon dioxide on the decomposition of strawberry after harvesting was studied.[104]

Two hundred and twenty four model solutions of cyanine copigmented with rutin were studied. The procedure is based on measurements of the total colour difference and the copigment : pigment ratio. The strongest effect is reached at pH 3 – 5 and low copigment : pigment ratio (1 : 1).[105] The chromaticity system *CIELAB* is the best to describe the colour changes observable by a human eye.

The kinetics of colour changes in apples, bananas, beets and potatoes in the course of drying (convective and vacuum drying at 50, 70 and 90 °C) was studied.[106]

The effect of pasteurisation on the chromaticity characteristics of grapefruit juice [107] and pear juice [108] was studied. It was shown that the strongest changes are observed for the saturation and the chromaticity coordinate *B*, in particular, this allows one to monitor the decrease in the content of vitamin C and the discoloration of orange juice during storage at 4–24 °C (Ref. 109).

Two reviews are devoted to the spectrophotometry of wines.[110, 111] It was noted that the *CIELAB* chromaticity system is most promising as it allows one to create any colour scales, quickly compare the results of different operators in various flow points and is advantageous as it requires simple equipment. For port as an example, the effects of temperature, pH, sugar content and time on the colour characteristics of wines was studied.[111, 112] A simpler method for the calculation of the chromaticity coordinates of white, red and pink wines and brandy [27, 33] based on the measurement of the reflectance signal at three fixed wavelengths (440, 540 and 610 nm) was suggested. The method was tested for 690 wine samples.

The effect of pH and content of anthocyans on the chromaticity characteristics of a number of wines was studied.[113–117] Satisfactory correlations were found between the degree of ionisation of anthocyans and the wavelength of absorption maximum (λ_{max}) and between the degree of ionisation of anthocyans and the colour intensity.[114] It was noted that a decrease in the medium acidity increases the colour intensity and the degree of ionisation of anthocyans.[113]

The effect of pretreatment of red table wine with sulfur dioxide on their colour, phenolic composition and quality was studied.[118] It was shown that wines untreated with SO_2 darken faster than the treated wines.

b. Textile industry

The chromaticity method is used for the selection of colours in the dyeing of natural and synthetic fibres, for the control of fading of coloured cloths and fibres and for monitoring the formation of brown spots on paper-based materials.

The observed colours are produced by subtractive and additive methods. In subtractive synthesis, colour appears due to selective absorption of a portion of radiation from a light beam falling on an object. This occurs upon successive passage of a light beam through a series of differently coloured media (for example, colour films) or upon passage of light through a solution containing several dyes. Subtractive synthesis is the basis of the modern methods of colour photography, cinematography and three-colour printing. Required colours of materials formed by several dyes are obtained using this method.

The subtractive synthesis method makes it possible to blend various colours by using triads of dyes whose colours correspond to three linearly independent colours in various ratios. The painting compounds most suitable for these purposes have yellow, light-blue and purple colours. A particularly wide scale is obtained in the case where these are 'ideal' colours. A characteristic feature of the spectra of such dyes is that radiation of each of the three spectral zones is either absorbed completely or transmitted completely. The dyes that have such spectra are ideal for various processes of colour reproduction and allow one to blend virtually any colour.

If real dyestuffs are used, their transmission spectra are characterised by the absence of complete transmission in any of the zones, and the palette of the colours obtained becomes narrower and reproduction of high-purity colour is impossible. Therefore, a number of studies was devoted to the development of dyes the properties of which approached those of ideal dyes.

Several regression models for the optimal selection of dyes for various fibres have been developed.[20, 22, 119, 120]

Three 9-phenylxanthene derivatives were synthesised and used for dyeing polyacrylonitrile and polyamide cloths. All of the products were subjected to chromaticity characterisation.[121] Aqueous extracts of black tea were used for dyeing cotton and jute fibres.[21] The fibre colours were monitored using the *CIELAB* system.

The effect of the solvent system $CCl_3COOH-CH_2Cl_2$ on the ability of cotton yarn to undergo dyeing was studied. The chromaticity characteristics of dyes were studied by varying the concentration and duration of treatment of yarn with the solvent.[122]

A number of natural dyes were used for the colouring of synthetic fibres (polyester, nylon, acrylic and acetate fibre).[123] It was noted that the fibre colour saturation increased with the increase in the treatment temperature and this effect is especially strong in the case of nylon fibres.

The dependence of the chromaticity characteristics of nylon fibres on the conditions of its heating was studied.[124] The temperature was varied from 150 to 180 °C; the time was varied from 2 to 10 h.

The resistance of 15 dyes for cotton fibres and their mixtures to fading was studied.[125] The samples were irradiated with a xenon arc lamp. It was shown that the fibres dyed with a combination of dyes always faded less than the samples dyed with just one dye.

The effect of pH of the starting cochineal solution on the chromaticity characteristics of fibres was studied.[126] The pH values were set using solutions of hydrochloric, sulfuric, nitric and phosphoric acids. It was found that the chromaticity coordinate *B* decreases with the increase in pH of the starting solution; in addition, the coordinates *L*, *A*, *B* decrease regularly on storing the solutions from 1 to 21 days. This effect was most pronounced if phosphoric acid was used for setting the pH.

New synthetic polyoxyalkylene–polyurethane water-repellent fibres were obtained.[127] Polarising fibres from poly(vinyl alcohol) which possess constant light absorption in the visible region were described.[128] Such fibres can be used for making liquid-crystal displays and polarising screens.

The so-called fluorescent (or optical) whiteners are known, *i.e.*, compounds that absorb radiation with wavelengths of 340–400 nm and transform it into radiation with wavelengths of 415–466 nm (in the visible region of the spectrum). Depending on the wavelength of the absorbed light, fluorescence of different colours is observed, *viz.*, violet (the fluorescence maximum is observed at 415–429 nm), dark blue (at 430–440 nm) and light-blue (at 466 nm). The most popular optical whiteners have light-blue fluorescence (radiation with wavelengths of 400–500 nm). Unlike optical whiteners, fluorescent dyes absorb light in the visible spectrum region, like ordinary dyes. As a consequence of fluorescence of dyes, their brightness increases. Optical whiteners are used like ordinary dyes and are often referred to as white dyes.

White paper, cellulose and other cloths and fibres partially absorb light in the shortwave part of the spectrum and thus become yellowish. If optical whiteners are applied on such yellowed objects, the former radiate light with wavelengths of 400–500 nm and hence compensate for the absorbed part of visible light and complement the spectrum of the reflected light. As a result, the degree of whiteness of the objects increases, *i.e.*, an optical (fluorescent) whitening effect is observed. Optical whiteners are widely used for whitening natural and synthetic materials (cotton, wool, viscose, hair, silk, cellulose acetates, polyamides, polyurethanes, polyacrylonitrile, polypropylene, polyester), paper, plastics, for improvement of colour of dyed cloths, *etc.* The *CIELAB* system was used to study the reasons for the appearance of brown spots on materials based on paper (ancient books, paintings).

Optical whiteners are added to washing powders and compositions for dry cleaning. They should have good light resistance, resistance against acids and bases, oxidants and reducing agents and should not form complexes with metals. Bleaching with such substances is similar to dyeing with direct and acid dyes: cellulose fibres are treated with suitable optical whiteners in neutral or weakly alkaline media, while polyamide fibre, silk and wool are

treated in weakly acidic media. Dispersion whiteners are used for polyester and acetate fibres, and cationic whiteners, for polyacrylonitrile fibres.

The synthesis and properties of some unsubstituted triazinylstilbenes as fluorescent whitening agents were described.[129] The spectral and thermal characteristics, the whitening effect for cotton and the chromaticity coordinates were determined. Fluorescent dyes based on naphthalene-1,8-dicarboxylic anhydride suitable for the dyeing of polyamide fibres and epoxy resins were synthesised. The relationship between the dye structure and the colour characteristics was discussed.[130]

The effect of fluorescent additives on the colour saturation of fibres was studied.[131] For this purpose, a cotton fibre was dyed using eight dye types with five various saturation levels. The fibres obtained were treated with two types of fluorescent additives. It was shown that the addition of fluorescent compounds increased the saturation of red and dark blue hued fibres and decreased that of yellow hued fibres.

The total colour difference was used to characterise a coated antibacterial polyester fibre.[132]

A new composition based on esters was suggested for dry cleaning of cotton cloths.[133] The efficiency of laundry disks in the removal of spots from cotton and polyester fibres with the use of detergents in the absence of water was studied.[134] It was shown using chromaticity characteristics that these detergents are not superior to the compounds used for 'wet cleaning'.

c. Geochemistry and mineralogy

The *CIELAB* system allows one to distinguish the hues of precious stones (the alexandrite effect).[135] Depending on the hue, precious stones can be grouped as follows: type 1 — alexandrite, fluorite, spinel, tourmaline; type 2 — glass; type 3 — sapphire; type 4 — garnet. Such functions as lightness and saturation can be used for documentary characterisation of the differences observed.

The microscopy and photometry of ores over the period of 1890–1998 was reviewed.[136] In particular, it was emphasised that identification of ore materials includes plotting of chromaticity diagrams as an obligatory stage.

The chromaticity characteristics of a rare sulfide deposit with the composition Cu_5FeS_6 were obtained.[137]

The chromaticity coordinates ware applied to determine the nature of the colour of the Mozambiquean beryls. It was found that the green colour appears due to the presence of chromium ions in the aluminium crystal lattice, while the purple colour is due to the presence of manganese ions.[138]

A method for non-destructive determination of metal corrosion products with the use of the chromaticity characteristics of the *CIELAB* system was suggested.[139] Studies of alloys based on copper, zinc and aluminium showed that an increase in the content of zinc and aluminium first increases the lightness and yellowness to a certain value and then decreases these values.[140, 141] The results obtained have enabled the creation of differently coloured alloys, *viz*., copperish-red, goldish-yellow, brown, purple and, finally, silverish-grey.

The colour characteristics have been utilised for the description of protective and decorative coatings from chromium and titanium[142–144] and for painted steel panels.[145]

d. Production of glasses and ceramics

The chromaticity characteristics were used to control the colour range of glasses[146–149] and ceramics.[150–152] Twenty five antique glass samples were studied. It was shown that the three fragment types, *i.e*., bluish-green, light-blue and yellowish-green, result from the combinations $Fe^{II}-Fe^{III}$, $Fe^{II}-Co^{II}$ and $Fe^{II}-FeS$, respectively.[148] It was suggested to make grey and bronze glasses[149] by using combinations of such additives as Co_3O_4, Nd_2O_3 and V_2O_5, MnO_2, Er_2O_3. The resulting glass colour was monitored using chromaticity characteristics.

A series of studies was devoted to the effect of temperature–time modes on the synthesis of pigments.[23, 150–153] It was found that the heat treatment temperature is the most important factor determining the colour of the pigments obtained. An optimal temperature should hinder the formation of colourless or weakly coloured compounds. The formation of significant amount of a glassy phase resulting in dissolution of coloured crystal phases is also undesirable.[23, 150–152]

A procedure for the preparation of ceramics by coprecipitation of hydroxides was suggested. The particle sizes of the resulting polymeric hydroxides are comparable to those of colloid species. Such compounds can be transformed into ceramics of a certain colour at lower temperatures compared to those employed in the oxide technology.[152]

A study on the effect of temperature on the colour stability of series of differently coloured ceramic samples showed that the yellowish-brown ceramics are most unstable.[24]

e. Pharmacology and fabrication of cosmetics

In the pharmaceutical industry, chromaticity is used as a reliable method to control the production of dental compositions, to check the uniformity of coatings on pills, *etc*. For example, the hue of silver-containing alloys was made similar to the colour of human tooth enamel by adding cerium dioxide, which discolours silver, to the alloys. The addition of 0.1% CeO_2 causes an essential (threefold) discoloration of the alloys without any loss of strength.[25]

The relationship between the colour of dental cement and paste was studied using chromaticity characteristics.[154] Metal ceramics for tooth crowns were created and characterised by chromaticity.[155, 156]

The value of total colour difference was utilised to control the uniformity of coatings on pills.[157]

The absorption and diffuse reflection spectra of structural isomers of riboflavin tetrabutyrates were obtained.[26] The specific feature of these compounds is that their colour characteristics in the solid state differ depending on the type of the structural isomer, whereas in solution, all of the spectra are identical. This is explained by intramolecular reactions occurring in the solid phase, which result in hydrogen bond formation. The chromaticity method allows one to distinguish one isomer from another.

Tinted powders for correction of face colour were created; they consist of micas covered with granular metal oxides (titanium, iron and their mixtures) and have definite values of the chromaticity coordinates.[158] Studies of the reaction of Methylene Blue with natural white mica and with synthetic sodium-type mica[159] showed that Methylene Blue reacts with both types of mica on heating in the absence of a solvent; as a result, the chromaticity coordinates change strongly (the purple colour changes to light-blue). The resulting compounds are water-insoluble due to immobilisation of Methylene Blue on mica.

Chromaticity characteristics were used to compare a number of sunscreens.[160]

f. Electronic industry, preparation of colour coatings, radio-engineering and photo-engineering

A series of studies dealt with the development of light-emitting diodes.[161–168] It was found that green sources provide a long life of electron-beam tubes and improve the radiating characteristics.[163] A chromaticity-based method for the correction of the electron-beam tube characteristics was developed.[164]

It was suggested to use bathocuproin[161] and triphenyl amine derivatives[169] as blocking layers for organic light-emitting diodes. The diodes were characterised by the chromaticity coordinates X and Y; it was proven on this basis that the source has pure red, dark blue or green radiation.[170–172]

New sources for three-coordinate chromaticity[173] containing red and green reverse lenses were created. Sources based on polymers and oligomers[174] cover a broad spectral range, *viz*., from dark blue through white to green. A series of powder radiation sources were synthesised.[175–178] The effect of the content of Sm^{III} (see Ref. 179), Zn^{II} (see Ref. 180) and Tm^{III} (see

Ref. 181) added to fluorescent powders on the chromaticity characteristics of irradiation was studied.

Resins based on an aromatic polyester with improved colour characteristics were created;[182, 183] the advantages of copolymers of *N*-vinylcarbazole and *N*-phenyl-2-(2-thienyl-5-vinyl)-5-(2′-thienyl)pyrrole were shown.[184]

The synthesis of new copolymers containing electron- and hole-conducting elements (oxadiazole and carbazole, respectively) and an irradiator (naphthalimide) was reported.[185] Their luminescence spectra were studied and the chromaticity coordinates were calculated.

A new process for obtaining a photographic image consisting of an absorbing dye and a sensitive dye was created; the dyes were selected in such a manner that their λ_{max} values were equal. This made it possible to improve the image characteristics in the red spectral region.[186] A uniform image in the blue spectral region was obtained using silver halide grains (95 mol.% AgCl).[187] A material containing photosensitive microcapsules that included fuchsine was used to form the purple layer of the photographic image.[188]

Coatings for steel sheets resistant against changes in weather conditions were developed;[189] they can be suitable for roofs, cars, doors and mechanisms. A mixture of yellow pigments for traffic signs with good reflection properties has been developed.[190] The theory and practice of colour measurement for powder coatings were covered in a review [18] which provided recommendations on controlling the colour of these coatings. A method for the creation of coloured powders by mixing dry powders was suggested.[191] Blending the required powder colour is simplified by plotting the colour diagrams.[192]

A computer-aided method for blending the colour of paints was reported.[193] The panels are coated with various mixtures of a colour and white paints; the reflection signal is measured, and the chromaticity coordinates are calculated. The values obtained are compared with those in a standard database. Such a technique simplifies the colour blending and increases its accuracy.

The optical properties of paint coatings formed on a surface depend on the nature of the pigment and the film-forming agent, on the volume concentration of the pigment and on the surface geometry.[19] The changes in the spectral composition of the light reflected by samples upon increase in their brightness due to application of a polymeric layer were estimated by changes in the optical characteristics in the *CIELAB* system (L, S, T, ΔE). Upon application of the first layer 10–20 μm thick, a sharp decrease in reflection coefficients and increase in lightness are observed; further increase in the layer thickness affects these characteristics only slightly. For light-blue and light-green coatings, the hue decreases continuously with the increase in the layer thickness: the colour vector turns clockwise. The hue of orange samples remains unchanged. This results from the fact that light dispersion is stronger in the short-wave spectral region.

V. Conclusion

Over many years, the progress in colour-measuring systems was restrained by the low technological level. Therefore, simultaneously with development of the equicontrast colorimetric system (*CIELAB*) by the International Commission on Illumination, colorimetric instruments and calculation methods were created which made it possible to record colour and use colour measurements in the analysis. Today, the chromaticity method, especially combined with computer programs for processing spectral data, has become widely popular in polygraphy and in the paint, textile, glass, pharmaceutical and food industries and in a number of other branches of industry.

One can hope that the chromaticity method will be used more widely in analytical chemistry, especially in the cases where the analytical signal is directly related to the colour of the compound to be determined, for example, in the approximate evaluation of the content of a compound from the colour intensity. Test methods, which basically do not require complicated instruments, are promising for fast batch analysis. The use of chromaticity systems which approach as much as possible the colour characteristics of human vision should favour the development of express analysis methods.

In our opinion, chromaticity will also be used more widely in spectroscopic analysis, since the use of optical radiation as the information carrier seems to be undoubtedly promising.

Along with broadening of the scope of the method, one should note two important directions of its development. First, these are studies devoted to the methodology and metrology of the chromaticity processing of spectra, as well as development of the theoretical basis. Publications on this topic have already appeared.[194–196] Second, broadening of the scope of chromaticity can serve as an impetus for improvement of the available instruments and development of new ones and for the creation of databases and software.

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[e] — *Inorg. Mater. (Engl. Transl.)*