

Features of moisture determination in organic solvents by *RGB*-type chromogenic sensor based on color modulation of Co^{2+}

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We proposed a novel and simple *RGB*-type chromogenic signalling system based on color modulation of Co^{2+} , for safety moisture determination in organic solvents. Cation exchanger KU-2-8 was used as a solid carrier of CoCl_2 . The color parameter R was shown undergo the greatest change over time, so it was chosen as an analytical signal. The obtained data confirm that changes in color coordinates depend only on the concentration of water in organic solvents, and do not depend on their nature. Grinding of the colored cation exchanger to a powdery state contributed to a significant decrease of the response time of the sensor and an increase of the sensitivity of the sensor by raising the intensity of the analytical signal. This makes it also promising for controlling the humidity of gases. The dependence of R on the water content for a chromophore probe in the form of powdered cationite KU-2-8 impregnated with cobalt (II) chlorides described by the 1st order exponential dependence with the correlation coefficient close to 1.

Keywords: Cobalt (II) chloride, organic solvents, moisture sensor, water content, digital *RGB* colorimetry.

Для безопасного определения влажности органических растворителей предложена новая и простая хромогенная сигнальная система *RGB*-типа, основанная на цветовой модуляции Co^{2+} . Катионит КУ-2-8 использовался в качестве твердого носителя CoCl_2 . Показано, что параметр цвета R претерпевает наибольшие изменения во времени, поэтому он был выбран в качестве аналитического сигнала. Полученные данные подтверждают, что изменения цветовых координат зависят только от концентрации воды в органических растворителях и не зависят от их природы. Измельчение до порошкообразного состояния окрашенного катионита способствовало значительному уменьшению времени отклика датчика и повышению его чувствительности за счет повышения интенсивности аналитического сигнала, что делало сенсор пригодным также для контроля влажности газов. Зависимость R от содержания воды при использовании хромофорного зонда в виде пропитанного хлоридом кобальта (II) порошкообразного катионита КУ-2-8 описывается экспоненциальной зависимостью 1-го порядка с коэффициентом корреляции, близким к 1.

Особливості визначення вологості органічних розчинників за допомогою хромогенного сенсора *RGB*-типу на основі колірної модуляції Co^{2+} . С.В.Химченко, Т.А.Бланк.

Для безпечного визначення вологості органічних розчинників запропоновано нову і просту хромогенну сигнальну систему *RGB*-типу, що базується на колірній модуляції Co^{2+} . Катионіт КУ-2-8 використовувався в якості твердого носія CoCl_2 . Показано, що параметр кольору R зазнає найбільших змін у часі, тому він був обраний в якості аналитичного сигналу. Отримані дані підтверджують, що зміни колірних координат залежать тільки від концентрації води в органічних розчинниках і не залежать від їх

природи. Подрібнення до порошкоподібного стану обробленого катіоніту сприяло значному зменшенню часу відгуку датчика і підвищенню його чутливості за рахунок підвищення інтенсивності аналітичного сигналу, що робило сенсор придатним також для контролю вологості газів. Залежність R від вмісту води при використанні хромофорного зонду у вигляді просоченого хлоридом кобальту (II) порошкоподібного катіоніту КУ-2-8 описується експоненційною залежністю 1-го порядку з коефіцієнтом кореляції, близьким до 1.

1. Introduction

Determination and quantification of water content, which is usually a permanent and often undesirable impurity in all chemical reagents, is very important in the manufacture of various functional materials, as even trace amounts of water can dramatically affect their physical, chemical, mechanical and technological properties [1–4]. In most cases, methods for controlling the water content include the step of extracting it from the analyzed material with a suitable organic solvent and then determining the moisture content of this solvent [3]. Therefore a simple, fast, and reliable chemical analysis method for water content of organic solvents is essential not only for chemical industries producing dry solvents and moisture-sensitive chemicals [5–8], but also for obtaining functional materials. Various methods such as Karl Fischer titration, gas chromatography, near-infrared (NIR) spectroscopy, Fourier Transform infrared (FTIR) spectroscopy, refractometric method, microwave accelerated Dean-Stark method, fluorescence spectroscopy and time-gated fluorescence spectroscopy have been employed for monitoring of water content in organic solvents and matrices [9]. However, these methods have limitations such as requirement for skilled personnel, specialized equipment and incapability of performing continuous monitoring [7, 10]. Therefore, low-cost, rapid, simple, and sensitive alternative methods for the determination of trace amounts of water in organic solvents are a very appealing goal [6]. Although there are various types of sensors for detection of water vapour present in gas phases, relatively few sensing systems suitable for probing water in organic solvents have been reported, either because the sensitivity is not high or because the organic solvents interfere with the sensing process [11]. At present, two types of methods for water content determination are fast growing: the electrochemical sensors and the optical sensors, which are widely used because of their respective advantages [12]. Optical techniques based on colorimetric or fluorescence changes, possess advantages such as simple, cost-effective and sensitive [13].

Colorimetric detection is a simple and convenient method compared to the other traditional and fluorescent methods. Colorimetric moisture sensor expresses a color change in the presence of moisture which could be detected even by the naked eye [14]. Unlike optical spectroscopic methods, in particular, spectrophotometry or diffuse reflectance spectroscopy, digital colorimetry does not give data on the spectral characteristics of colored substances, but characterizes their color using several color coordinates [15]. Digital colorimeters often use an *RGB* system based on additive mixing of three primary colors (red, green, and blue). All the *RGB* system parameters are selective and depend on the concentration of the colored compound, which allows analyzing the mixture of these compounds [16]. Despite the fact that the *RGB* model is used for field applications for detection and quantification of sweeteners or sugars, toxic industrial chemicals or toxic gases, mycotoxins, the presence of explosives in water, water vapor, air and soil [17], but only a single paper [18] devoted to the *RGB* model combined with image sensor for detection of water contents in organic solvents, has been published so far.

There exist many reports on the development of optical sensing systems employing various functional dye molecules for determination of water content in organic solvents [11, 18–26]. But on the other hand, most of the known colorimetric moisture detecting probes are expensive, not reversible, demonstrate slower response time, need multistep synthesis and less sensitive [14]. Cobalt chloride (II) is an inexpensive and available chemical compound which is produced industrially and needs no additional purification or preparation. Although it is widely used as a moisture indicator in the composition of silica gel and for the production of indicator paper for atmospheric humidity control there is no information about its application as a chromophore probe in moisture sensors.

Herein, we proposed a simple *RGB*-type chromogenic signalling system based on color modulation of CoCl_2 , for safety moisture determination in organic solvents by example isopropanol.

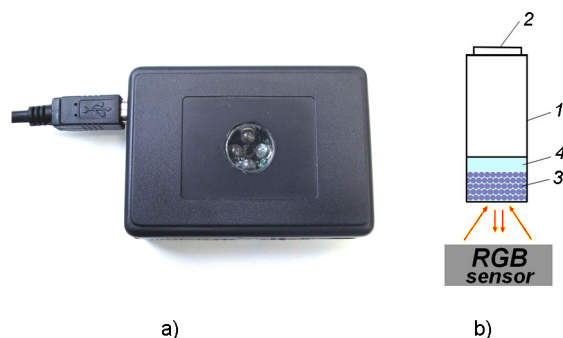


Fig. 1. a) RGB sensor; b) Measuring cell scheme: 1 — glass container; 2 — plastic cap; 3 — chromophore probe; 4 — organic solvent.

2. Experimental section

All the chemicals and solvents were of analytical reagent grade, and used without further purification, unless otherwise specified. Isopropanol (HPLC) from Sigma-Aldrich was dried with activated 4 Å molecular sieves prior being used. Working solutions of organic solvents with different moisture were freshly prepared before each measurement from dried organic solvents by the addition of relevant volumes of water. Ultra pure water from a Human P.Nix Power II System (Human Corporation, Korea) with 18.3 MΩ·cm was used throughout the work. Water contents in the prepared samples were determined by the Karl Fisher method. All the measurements were performed at room temperature (25°C) and atmospheric pressure. Cobalt (II) chloride was synthesized under laboratory conditions by an exchange reaction and purified by means of double recrystallization from an aqueous solution with subsequent drying for 8 h. in a drying oven (150–160°C). A cation exchanger KU-2-8 (GOST 20298-74) in the form of granules and powder was used as a solid carrier of CoCl_2 . Powdered cation exchanger was obtained by grinding the granules in a mechanical mortar Retsch RM200 (Germany) for 10 min. with subsequent sifting on a sieve with an opening size of 0.2 mm. The cation exchanger was soaked in an aqueous solution of CoCl_2 and dried at 150°C in a drying oven for 8 h. As the chromogenic probe in the container is easily regenerated by drying for 5–6 h, it can be used repeatedly.

The colorimetric measurements of the RGB coordinates were carried out in an optical cell, a vial for chromatography (with the dimensions 12×32 mm² and a volume of 2 mL) with a Snap Ring™ neck. The vial

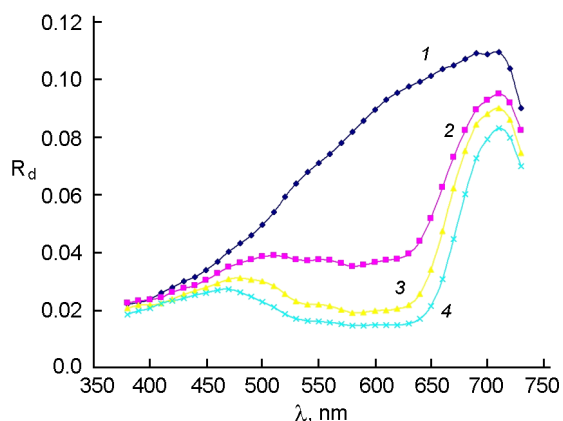


Fig. 2. Diffuse reflectance spectra of untreated and impregnated by CoCl_2 cation exchanger KU-2-8 in the form of granules (CoCl_2 concentration in 1 g of cation exchanger is: 1 — 0 mg, 2 — 1 mg, 3 — 2 mg, 4 — 4 mg, respectively).

containing the sample was covered with a plastic cap. The optical cell was connected with a portable digital colorimeter developed by Analytical Optochemotronics Lab at Kharkiv National University of Radioelectronics [16, 27] (Fig. 1) and equipped with the specially designed software "Colorimeter". The average values (in ADC units) of brightness of the channels R , G , B were displayed in the program window of the digital colorimeter software.

To prepare the optical cell of the sensor the treated cation exchanger carrier was placed into a vial and dried at a temperature of $130 \pm 5^\circ\text{C}$. During the analysis an aliquot of the organic solvent was introduced into the optical cell with a prepared chromophore probe to measure the brightness of the color coordinates of the system. The digital colorimeter was preliminarily calibrated on a white standard which, MgO powder introduced into an optical cell together with an organic solvent.

3. Results and discussion

To determine the spectral characteristics of the chromophore, there was measured the diffuse reflectance spectra of the granules of the untreated and impregnated KU-2-8 cation exchange resin with CoCl_2 solution with a different contents of Co^{2+} ions (Fig. 2). As seen from the above spectra, the reflection maximum is located in the red region of the visible spectrum ($\lambda = 720$ nm) which corresponds to the brightness of the R channel when measuring the color in the RGB system.

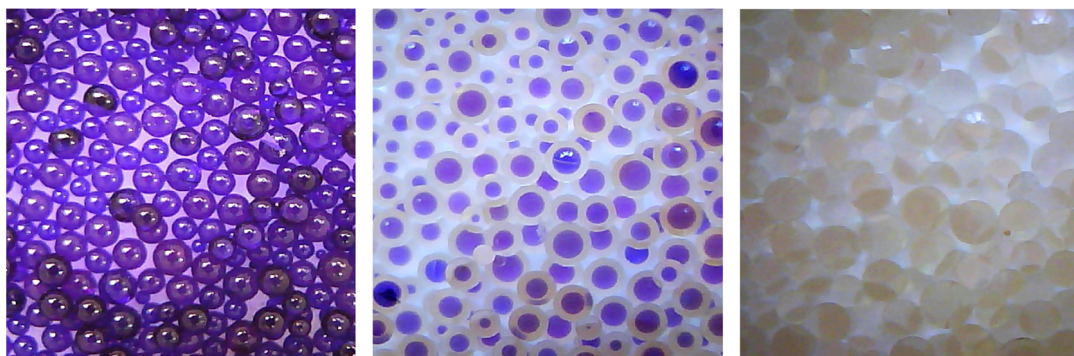


Fig. 3. Change in time of color of granules of cation exchanger KU-2-8 in an organic solvent containing water.

When determining the moisture content of 4 samples of different organic solvents using an *RGB* sensor based on treated Co^{2+} KU-2-8, it was also confirmed that the color parameter R undergoes the greatest change over time. Therefore, it was chosen as an analytical signal.

The water capacity of the chromophore probe depends on the content of cobalt (II) ions in the cation exchanger. Therefore, it was necessary to determine the optimal concentration of cobalt (II) chloride for the treatment of ion exchange resin. The content of cobalt (II) chloride in the cation exchanger should exceed the water content when analyzing wet organic solvents. That is, the cation exchanger with a higher content of cobalt (II) chloride will have higher capacity by water. It should be noted that the color background for the color indication is the color of the cation exchanger, which almost coincides in color with the hydrated form of Co^{2+} ions (Fig. 3). Therefore, with an increase in the moisture content of the analyzed sample, there is observed a color transition caused by a decrease in the blue component of the color (as the ions hydrate in the cationite matrix), and the background color is developing through a series of mixed colors. That is why when the color parameter is used as an analytical signal, its changes are noticeable at less painted matrix i. e. a chromophore probe with a lower content of Co^{2+} is more sensitive to water than the one with a higher content of Co^{2+} . The kinetic dependences of the color parameter R of a sensor system based on a chromophore probe of cation exchanger KU-2-8 with different contents of Co^{2+} also confirms this fact (Fig. 4). The content of Co^{2+} in the cation exchanger equal to 4 mg/g ions corresponds to its maximum total exchange capacity (ac-

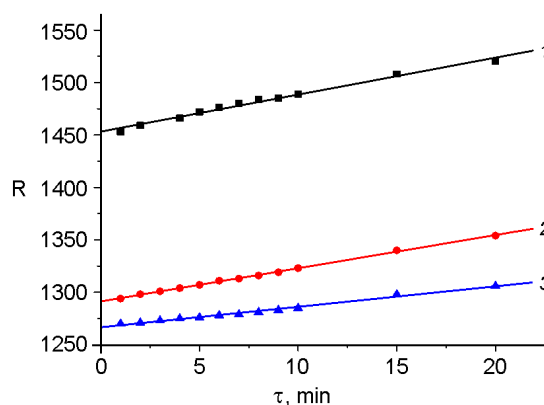


Fig. 4. Kinetic dependences of the color parameter R of chromophore probe KU-2-8 granular cation exchange resin with a content of Co^{2+} 1 (1), 2 (2) and 4 (3) mg/g, respectively when analyzing of ethanol with a water content of 6.3 % (by weight).

ording to the technical characteristics). The content of Co^{2+} equal to 1 mg/g is clearly insufficient for determination of large contents of water, since complete hydration and discoloration of the chromophore occurs before all the water from the organic solvents will react. Therefore, for subsequent experiments, a cation-based chromophore probe was used, in which the Co^{2+} content was 2 mg/g.

It is found that the rate of change in brightness (the tangent of the angle of the slope of the calibration dependence) increases with the rise of the water content in the sample (Fig. 5). The obtained data also confirm that the changes in the color coordinates depend only on the concentration of water in the studied solvents, and are independent of their nature. Moreover, as seen from Fig. 5, the response remains stable during more than 50 min. The water con-

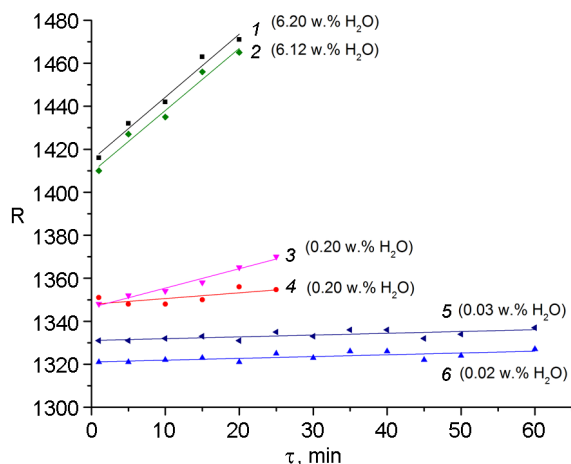


Fig. 5. The time dependence of the color coordinates R (in the RGB system) of granulated cation exchanger KU-2-8 treated with cobalt (II) chloride in ethanol (1), iso-propanol (2, 3, 5) ethyl acetate (4), methanol (6) with different water content.

tent of the investigated organic solvents can be determined from the concentration dependences of $\text{tg } \alpha$. But when analyzing solvents with high moisture, there is a danger of exceeding the water capacity of the probe. Therefore, it is expedient to carry out the measurements within a fixed period of time sufficient to observe a change in color but when yet not all the amount of water has already reacted with Co^{2+} . Such a kinetic determination of water content in the range of 0.2–100 % takes 5–20 min, or about 30 min if the water content is less than 0.2 % (Fig. 5).

Since Co^{2+} is distributed throughout the volume of the cation exchanger, water molecules first react with it on the surface and in the neighbouring layers of the solid carrier granules, and only after a while penetrate into the deeper layers (Fig. 3). Consequently, the response time of the RGB -type chromogenic sensor based on color modulation of Co^{2+} can be shortened by reducing the time necessary for penetration of water molecules into the inner volume of the colored granules by decreasing the size of the granules.

It was found that the colored cation exchanger grinding to a powdery state with a particle size of not exceeding 0.2 mm contributed to a significant decrease of the sensor response time. Moreover, it allowed to increase the sensitivity of the sensor by raising the intensity of the analytical signal, as the powder is less transparent than the granules. As seen from Fig. 6, the pow-

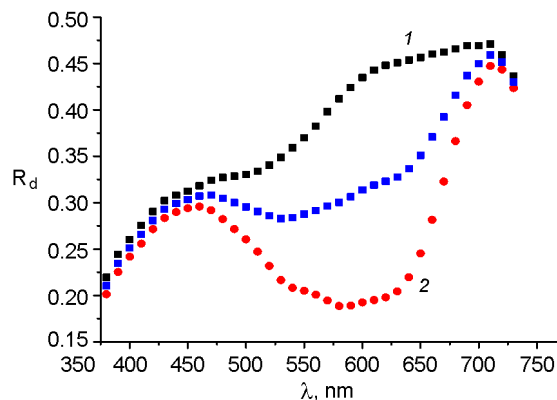


Fig. 6. Diffuse reflectance spectra of powdered cation exchanger KU-2-8, impregnated with cobalt (II) chloride (2 mg of CoCl_2 per 1 g of cation exchanger), when stored in air (1) and after drying for 3 h at 130°C (2).

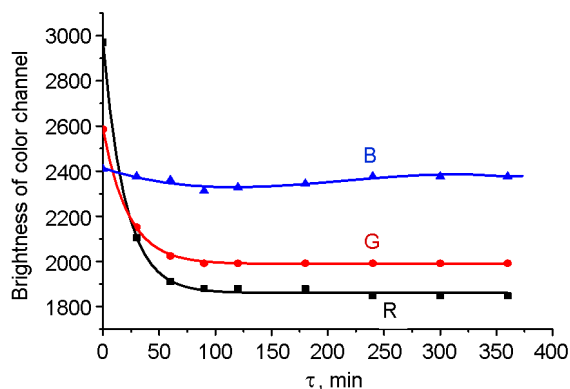


Fig. 7. Kinetics of drying powdered cation exchanger KU-2-8, impregnated with cobalt (II) chloride at a temperature of 130–135°C.

der chromophore probe is so sensitive that even the water vapors in the air change his diffuse reflection spectra. In this case, in order to prevent the systematic errors in the analysis, such a probe should be dried directly before measurements, or stored in a dried state in a desiccator containing a suitable desiccant. In addition, the powder has a higher homogeneity and a bulk mass, due to which it is possible to miniaturize the optical cell of the sensor and in 5 times, reduction in chromophore probe mass and regeneration time (Fig. 7). As found in our study the chromophore probe of the RGB sensor can be used at least 10 times after regeneration in the optical cell.

The study of applicability of the developed RGB -type sensor based on powdered cation exchanger treated with cobalt (II) ions for determination of moisture of real organic solvents was carried out during the analysis of the samples of isopropanol with

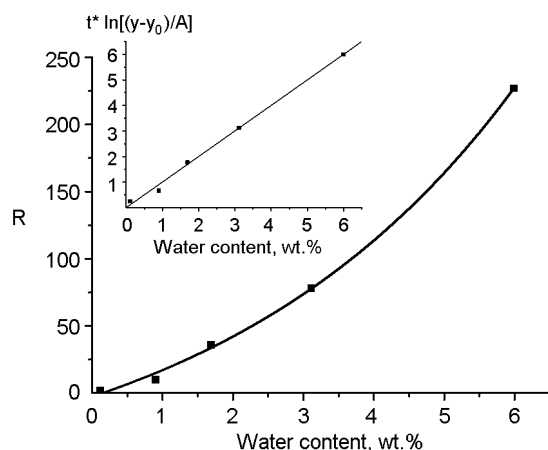


Fig. 8. Concentration dependence of the color parameter R and its linearized form $\{C(\text{wt.}\%) = 4.28 \cdot \ln[(R - 77.65)/75.07]\}$ of a chromogenic probe which is powdered cation exchanger KU-2-8 treated by cobalt (II) chloride, for isopropanol ($n = 5$).

water content ranging between 0.1 and 6.0 wt.%. As established in this study, to obtain a stable analytical signal, 10 min is enough that is 2 times less than the corresponding characteristic of an unmilled cation exchanger. The concentration dependences of the color coordinates R , G , B are usually nonlinear and often described by exponential curves [28, 29]. The dependence of R on the water content for a chromophore probe in the form of powdered cationite KU-2-8 impregnated with cobalt (II) chloride is described by the 1st order exponential dependence with the correlation coefficient close to 1 (Fig. 8). After carrying out logarithmic transformations, we obtain a linear dependence in the coordinates: $[t \cdot \ln[(y - y_0)/A] - C]$ of water, where t , A and y_0 are the parameters of exponential dependence (Fig. 8); $y = R$, the mean value of the analytical signal for the corresponding water content.

4. Conclusions

A novel and simple RGB-type chromogenic signalling system based on color modulation of CoCl_2 with cation exchanger KU-2-8 as a solid carrier, for safety moisture determination of organic solvents was designed. The color parameter R was shown to undergo the greatest change over time and so it was chosen as an analytical signal. Using the analyses of four different organic solvents with the proposed sensor as an example, it was demonstrated that changes in color coordinates depend only on the concen-

tration of water in the studied solvents, and do not depend on their nature. Grinding of the colored cation exchanger to a powdery state contributed to a significant decrease of the response time of the sensor and an increase of the sensitivity of the sensor by raising the intensity of the analytical signal. The dependence of R on the water content for a chromophore probe in the form of powdered cationite KU-2-8 impregnated with cobalt (II) chloride is described by the 1st order exponential dependence with the correlation coefficient close to 1. This sensor is suitable to control both the water content of organic solvents and the humidity of gases.

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