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Determination of Neodymium Diphthalocyanine and its Utilization in Qualitative and Quantitative Evaluation of Synthetic Products

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A simple spectrophotometric method in the VIS range is proposed for the quantitative determination of neodymium diphthalocyanine both in raw synthetic products and purified material. The method is based on absorbance measurements in DMF solutions of the tested samples at four different wavelengths, *i.e.* 500, 633, 671 and 800 nm. The diphthalocyanine content is calculated from the calibration graph obtained in the form of a linear regression equation.

Przedstawiono prostą metodę spektrofotometryczną, w zakresie VIS, ilościowego oznaczania diftalocyjaniny neodymu, zarówno w surowych produktach reakcji syntezy jak i oczyszczonym materiale. Polega ona na pomiarach absorbancji badanych próbek w roztworze DMF przy czterech różnych długościach fal, tj. 500, 633, 671 i 800 nm. Zawartość diftalocyjaniny oblicza się z krzywej kalibracyjnej, przedstawionej w postaci równania liniowego.

Spectroscopic methods have proved to have a great value in studying metal complexes of phthalocyanine. Absorption spectra of neodymium diphthalocyanine in the VIS range were first obtained in the early sixties and since then consequently studied by Kirin and Moskalev [1–7].

In contrary to typical monophthalocyanine spectra, characterized by one, very strong absorption peak, those recorded for the neodymium complex of phthalocyanine revealed two very intensive bands in the VIS range at *ca.* 630 and 670 nm [1,3,6]. Thus, a hypothesis has been set forth assuming the existence of a phthalocyanine complex compound with two coordination centers of a formula Nd_2pc_3 [2,3,5,6]. That particular molecule has been suggested to be composed of two ionic

species, namely $[Ndpc_2]^-$ and $[Ndpc]^+$ (pc – phthalocyanine ligand, $C_{32}H_{16}N_8^{2-}$). A complex of that composition was suggested to be the main solid product in the synthesis of neodymium diphthalocyanine. This form is also present when dissolved in polar organic solvents, such as (*N*,*N*-dimethylformamide (DMF).

A different opinion was presented by MacKay *et al.* [10], however, they conclude that a binuclear complex is also possible.

Both ionic components can be relatively easily separated from each other, either by column or paper electrochromatography [2]. In DMF a blue solution is obtained first and subsequently a green one. To the blue compound a formula $NdHpc_2$ was assigned, while to the green one – NdXpc, where X was a monovalent anion, *e.g.*, CH_3COO^- or Cl^- [2,11].

The "blue" form has proved to be very stable in organic solvent solutions, whereas the "green" one decomposed relatively easy with formation of a metal-free phthalocyanine precipitate. Thus, only the "blue" neodymium diphthalocyanine may be considered to be of any practical use.

The individual character of the VIS spectra, particularly the distribution of maximum absorption peaks of either component gives the possibility to use spectrophotometric methods for analytical purposes. Methods involving metal determination in the tested sample are usually very troublesome and time-consuming. Particularly, if one cannot use such techniques like atomic spectroscopy or X-ray fluorescence diffractometry. Moreover, these methods are restricted only to pure phthalocyanines. One may not apply them to examine raw reaction products since they normally contain the metal combined also in other forms beside the phthalocyanine complex. In this paper a very simple method is proposed for an immediate determination of neodymium diphthalocyanine in a studied material. It involves only very small quantities of the tested sample and standard laboratory equipment.

EXPERIMENTAL

Reagents and apparatus

N,*N*-dimethylformamide (DMF), pure, twice distilled. Silica gel for column chromatography, 70–230 mesh (Merck).

Spectrophotometer Specol 11 with digital readout (C.Zeiss, Jena), standard analytical quartz cuvette (thickness of absorbing medium 1.001 cm). Glass column for chromatography (h = 450 mm, d = 18 mm).

Preparation and purification of the raw synthetic product were performed according to methods described elsewhere [2,3]. Some residual impurities have been sublimed off at 300°C in vacuum (*ca.* 100 Pa). The blue and green components have been separated on the chromatographic column.

Absorption spectra of DMF solutions in the VIS range, both of the individual components as well as their mixture are shown in Fig. 1.

The solutions of either component obey the Beer–Walter's law and their mixture satisfies the absorbance additivity rule [12].

For the analytical calibration graph of $NdHpc_2$ (blue component) solutions in DMF have been prepared, within the concentration range from 1.0×10^{-6} to 1.8×10^{-5} g ml^{-1}. That low analytical concentrations resulted from the measuring range of the spectrophotometer used, due to the relative high absorptivity of neodymium diphthalocyanine in DMF solution. A linear regression equation for the relation between absorbance (A) at 633 nm and concentration (c) of $NdHpc_2$ in DMF solution has been calculated by the least squares method:

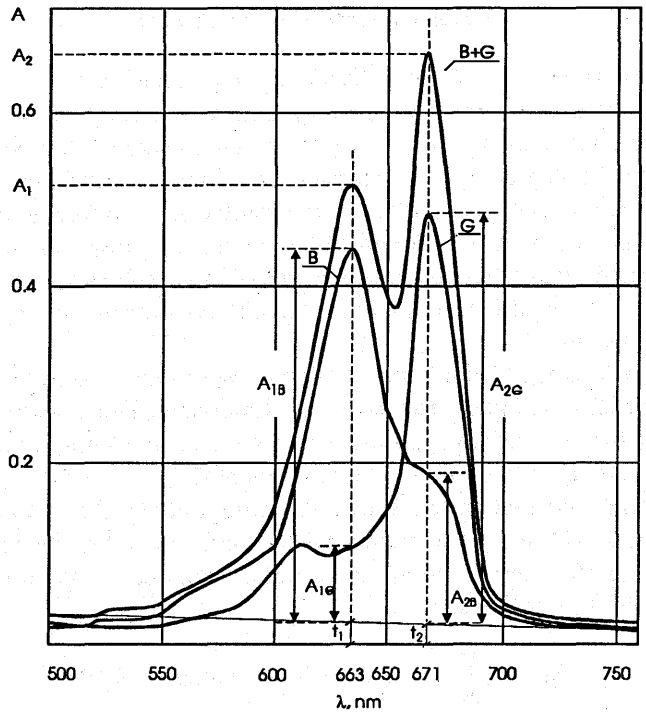

Figure 1. Absorption spectra of the B (blue) and G (green) forms of neodymium diphthalocyanine and their mixture in DMF solutions

$$A = 9.98\times10^{4}c + 2.7\times10^{-3} \quad (1)$$

where c is given in g ml^{-1}. Correlation coefficient for this equation is 0.99.

The developed method was checked on a series of DMF solutions containing a mixture of blue (B) and green (G) components and the results are shown in Table 1.

Table 1. Absorbance of DMF solutions of $NdHpc_2$ (B – blue form) and mixtures of B (blue) and G (green) forms of neodymium diphthalocyanine in DMF

No.	1	2	3	4	5	6	7	8	9	10
$c_B\times10^6$	2.0	8.0	16.0	2.0	6.0	8.0	12.0	14.0	x	2 x
A_1	0.20	0.81	1.62	0.42	0.79	0.97	1.32	1.49	0.70	1.39
A_2	0.07	0.28	0.55	1.42	1.21	1.10	0.88	0.78	0.85	1.72
A_{500}	0.01	0.02	0.05	0.02	0.03	0.03	0.04	0.04	0.12	0.18
A_{800}	0.00	0.01	0.04	0.01	0.02	0.02	0.03	0.03	0.03	0.05
t_1	0.01	0.02	0.05	0.02	0.03	0.03	0.04	0.04	0.08	0.12
t_2	0.00	0.01	0.04	0.01	0.02	0.02	0.03	0.03	0.07	0.11
A_{1B}	0.19	0.79	1.58	0.21	0.62	0.83	1.22	1.42	0.54	1.10
$c_{B,a}\times10^6$	1.9	7.9	15.8	2.1	6.2	8.3	12.2	14.2	5.4	11.0
δ	5.0	1.2	1.2	5.0	3.3	3.8	1.7	1.4	–	–

c_B – concentration of the B component (blue) in the tested solution (calculated from the known concentration of a standard solution), g ml^{-1}.
$c_{B,a}$ – concentration of the B component in the analyzed solution, determined from equations (9) and (1), g ml^{-1}.
δ – relative error of the determination.

RESULTS AND DISCUSSION

The absorption spectra of the individual components as well as their mixtures have proved that the wavelength of absorption maxima (λ_{max}) as well as the general character of the spectra do not depend on the compound concentration. Also, extracts of neodymium diphthalocyanine obtained from raw synthetic products revealed identical λ_{max} values, independent on the concentration. Maximum absorption peaks have been found at λ values 633 and 671 nm (Fig. 1). However, spectra of either component include also other absorption bands of lower intensity. One can recognize them in Fig. 1 either as inflections or distinct peaks, position of which does not depend on their concentration.

In a mixture of B and G components, their individual spectra overlap and the peak intensities (A values) include a share of either component. Thus, to use the absorbance measurements for analytical purposes, it is necessary to eliminate the effect of the spectrum of component G upon that of component B.

It has been found that for each of these components, the ratio of absorbance at λ = 633 and 671 nm is a characteristic constant value independent of the concentration of the compound in the solution studied. This might be defined according to Fig. 1 as follows:

$$K_B = \frac{A_{1B}}{A_{2B}} \qquad \text{for the "blue" component (B)} \tag{2}$$

and

$$K_G = \frac{A_{1G}}{A_{2G}} \qquad \text{for the "green" component (G)} \tag{3}$$

These factors were found for the particular components separated on the chromatographic column and have the following values:

$K_B = 3.00$ for the pure B component

and

$K_G = 0.14$ for the pure G component

Since DMF solutions of these species obey both the Beer–Walter's absorption law as well as the absorbance additivity rule, it follows from Fig. 1, that

$$A_1 = A_{1B} + A_{1G} + t_1 \tag{4}$$

$$A_2 = A_{2B} + A_{2G} + t_2 \tag{5}$$

where A_1 and A_2 are absorbances of the tested sample at 633 and 671 nm, respectively. A_{1B} and A_{1G} represent contributions of component B and G, respectively, at λ = 633 nm, whereas A_{2B} and A_{2G} are "shares" at λ = 671 nm. The background absorbance at the analytical wavelengths λ = 633 and 671 nm is characterized by t_1 and t_2, respectively.

The background absorbance can be determined by the base line method [12]. In this case, for calculation, λ = 500 and λ = 800 nm have been chosen as wavelengths at which the absorbance curve reaches its minimum values. Thus, the background absorbance may be expressed in the form of following equations:

$$t_1 = A_{800} + 0.56(A_{500} - A_{800}) \quad (6)$$

$$t_2 = A_{800} + 0.43(A_{500} - A_{800}) \quad (7)$$

where A_{500} and A_{800} are absorbance records taken at $\lambda = 500$ and 800 nm, respectively.

From equations (2)–(5) one may obtain:

$$A_{1B} = \frac{A_1 - K_G(A_2 - t_2) - t_1}{1 - K_G/K_B} \quad (8)$$

Introducing the values found for K_B and K_G gives:

$$A_{1B} = \frac{A_1 - 0.14(A_2 - t_2) - t_1}{0.95} \quad (9)$$

By substituting A in eq. (1) by A_{1B} from eq. (9) the concentration of the B component in the tested specimen may be determined.

This method refers only to the blue complex, $NdHpc_2$. Since the green component appeared to be very unstable it could not be isolated from DMF extracts and purified in the way the blue one was. So, it was not possible to develop a parallel analytical procedure for the green complex.

Table 1 shows some results obtained according to the presented method when applied to solutions containing $NdHpc_2$. Samples 1–3 represent the pure B (blue) component, while 4–8 are mixtures of B and G compounds. Samples 9 and 10 represent a crude product of the synthesis of neodymium diphthalocyanine.

A comparison of results obtained according to the proposed method ($c_{B,a}$) with the values (c_B) known from the amount of $NdHpc_2$ dissolved in the tested solution, has proved a good agreement between them. The relative error of the method decreases along with the increase of the contents of the analyzed component. It has to be emphasized, however, that solutions used in the tests have to be prepared very thoroughly, particularly in the range of low concentrations, otherwise this may lead to considerable errors. For best analytical results, the tested solutions should be characterized by absorbance values *ca.* 1.0–1.5 (for the analytical wavelengths).

The relative error values, given in Table 1, result both from the assumed accuracy of absorbance measurements (± 0.01) and sample preparation ($\pm 1.0 \times 10^{-7}$ g ml^{-1}). In particular the latter factor may strongly affect the analytical results due to the very high absorptivity of $NdHpc_2$ in DMF.

The principal advantage of the method proposed here is its simplicity and the fact, that tests can be easy performed in almost any laboratory. DMF used as solvent does not absorb in the VIS range. Moreover, unlike in other solvents tried, $NdHpc_2$ is readily dissolved in DMF.

A considerable value of the molar absorptivity $\varepsilon = 1.2 \times 10^5$ l mol^{-1} cm^{-1} allows that very small quantities of specimens may be used in analytical tests.

Conclusions

The presented analytical method allows the determination of $NdHpc_2$ in a mixture containing both the "blue" and "green" modifications of neodymium diphthalocyanine in DMF solutions.

Results have shown that the error of the method varies between 1.2 and 5.0%, depending on the concentration of $NdHpc_2$ in the tested solution. To reduce the error of the method, absorbance measurements should be performed within a concentration range allowing absorbances of *ca.* 1.0–1.5.

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