

Coulometric determination of organic compounds. IV.

Determination of aminophenoxazonium dyes by titanometric coulometry

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Conditions have been found for the determination of aminophenoxazonium dyes by titanometric coulometry at constant current using a glossy platinum electrode to generate Ti(III) ions; the point of equivalency was recorded potentiometrically. The suitable carrier electrolyte for the determination was composed of 0.4 M-TiCl₄, 0.7 M-HCl, and 2.0 M-H₂SO₄. In this electrolyte, higher amounts of the dyes studied than 200 µg in 50—100 ml could be determined at a constant current of 0.5 and 1.0 mA, respectively.

Были найдены условия для кулонометрическо-титанометрического определения аминифеноксазиновых красителей при постоянном токе и использовании блестящего платинового электрода для генерации ионов Ti(III) и при потенциометрическом определении точки эквиваленции. Подходящий фоновый электролит для определений имеет состав 0,4 М-TiCl₄, 0,7 М-HCl и 2,0 М-H₂SO₄, в котором можно определить большие количества исследованных красителей чем 200 µг в объеме 50—100 мл при постоянном токе 0,5 и 1,0 мА.

In the previous work [1] conditions were found for the determination of phenoxazones by titanometric coulometry. The present communication deals with the determination of aminophenoxazonium dyes: 9-dimethylaminobenzo[*a*]phenoxazonium chloride (*I*, Meldolas Blue), 5-amino-9-diethylaminobenzo[*a*]phenoxazonium sulfate (*II*, Nile Blue A), 5-(3-methylphenylamino)-9-dimethylaminobenzo[*a*]phenoxazonium chloride (*III*), 5-(1-naphthylamino)-9-dimethylaminobenzo[*a*]phenoxazonium chloride (*IV*), 5-(3-carboxyphenylamino)-9-dimethylaminobenzo[*a*]phenoxazonium chloride (*V*), and 5-(4-chlorophenylamino)-9-dimethylaminobenzo[*a*]phenoxazonium chloride (*VI*) by constant-current coulometry. The Ti(III) ions, which reduced the dyes to leuco compounds, were generated on the generating platinum electrode immersed into the carrier electrolyte in the electrolytic vessel. The results of determinations are summarized in Table 1 and the course of reduction is illustrated with the compound *I* (Scheme 1).

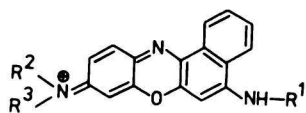
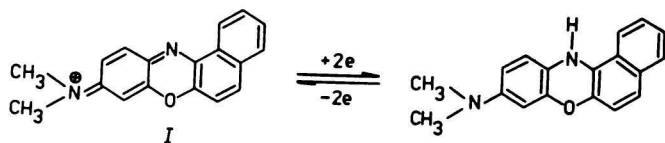
During the determination of Meldolas Blue (*I*), the red-violet colour of the oxidized form turned colourless due to reduction. The determination was carried

Table 1

Determination of phenoxazonium dyes by titanometric coulometry

Compound	Current μA	Given μg	Found ^a μg	Δ^a μg	δ^a %
I	1.0	372	380	2.6	+2.2
I	0.5	248	252	1.4	+1.6
II	1.0	810	815	4.0	+0.6
II	0.5	580	583	2.0	+0.5
III	1.0	618	611	4.7	-1.1
III	0.5	618	606	1.4	-2.0
IV	0.5	402	407	3.1	+1.2
IV	0.5	814	810	2.9	-0.5
V	0.5	540	545	2.7	+0.9
V	0.5	810	814	3.1	+0.5
VI	0.5	483	475	3.2	-1.6

a) Average value of 5 to 7 determinations; Δ — deviation from the average of all values found; δ — relative deviation from the real given value.



	R ¹	R ² , R ³
II	H	C ₂ H ₅
III	3-MePh	CH ₃
IV	naphthyl	CH ₃
V	3-HOOCPh	CH ₃
VI	4-ClPh	CH ₃

Scheme 1

out at two current values. More precise determination was obtained at lower generating current (0.5 mA). Determination of lower amounts than 120 μg of the compound *I* was considerably inaccurate. Somewhat higher results were obtained due to the presence of reducible impurities in the dye. Also the nitrogen content determined was by 0.7% higher than the theoretical value.

Very good results were obtained at the determination of *II*. The method could be utilized also for the determination of nitrogen in Nile Blue A.

The green-blue solution of *III* was gradually decolorized by reduction with the Ti(III) ion. Also this determination showed that at the current of 0.5 mA more precise and correct results were obtained. Though the relative error of the determination at the current of 0.5 mA was higher than at 1.0 mA, the deviation from the average of all values obtained was at 1.0 mA high. Determinations of further compounds were carried out only at the generating current of 0.5 mA.

The original azure colour of the solution containing the oxidized form of *IV* turned gradually light-green then pale-yellow during the determination. In this case also the effect of the amount of the compound to be determined on the accuracy and correctness was followed. Determination of twofold amount of *IV* gave more precise and correct results. In this case, using a current of the same intensity at both determinations, the time of the analysis was doubled and consequently, the relative error at time reading was lower. Determination of lower amounts of *IV* than 0.2 mg did not give satisfactory results.

At the determination of *V* the blue colour of the analyzed solution turned green and then pale-yellow. Analysis of higher amount (810 μg) did not give better results and the average relative error was 0.5%.

During the determination of *VI* the deep-blue analyzed solution turned green and then light-yellow. The compound was probably contaminated with a nonreducible portion which did not contain nitrogen because the amount of nitrogen found (elemental analysis) was by 1.1% lower than would correspond to theoretical value. Determination of lower amounts than 0.25 mg did not give reproducible results.

The results of the determinations of *I*—*VI* proved that pure aminophenoxazonium dyes could be determined by the above-discussed method. This method, however, cannot be applied for the determination of dyes in mixtures. Also other reducible admixtures in the sample can alter the results. For practical determination it is important to work at the highest current efficiency of Ti(III) generation which depends first of all on the constitution of the carrier electrolyte, current density, material and state of the surface of the generating electrode. It was found that the accuracy of determination was considerably affected by the method of purification of the platinum electrode. The most suitable method was proved to be the anode-cathode polarization (+2 and -2 V) in 0.05 M- H_2SO_4 by switching over the current in 20 s intervals so that the end of purification be at -2 V.

It was shown that the solutions of compounds had to be freshly prepared for the analysis because by staying their composition changed. An inert atmosphere was also necessary because the reduced forms of phenoxazine dyes were promptly oxidized by atmospheric oxygen to the original dyes.

Considerable attention was devoted to carrier electrolyte. The electrolyte composed of 0.3 M-TiCl₄ and 8.0 M-HCl was suitable as to achieving current efficiency, however, when bubbling with argon, the evolved hydrogen chloride contaminated the environment. The electrolyte [2] composed of 0.3 M-Ti(IV) and 6.5 M-H₂SO₄, which was prepared by dissolving TiO₂ in concentrated sulfuric acid, was proved to be unsuitable because of the increased redox potential of the Ti(IV)—Ti(III) system [3] in sulfuric acid. The electrolyte containing 0.4 M-TiCl₄, 0.7 M-HCl, and 5.0 M-H₂SO₄ was unsuitable probably for the same reason.

The electrolyte composed of 0.4 M-TiCl₄, 0.7 M-HCl, and 2.0 M-H₂SO₄ was proved to be most suitable for the determination of aminophenoxazine dyes.

Experimental

The investigated dyes were prepared in laboratory scale [4, 5], Nile Blue A was a product of Lachema, Brno. The compounds were after recrystallization from ethanol purified by repeated extraction with ether. Their purity was checked by thin-layer chromatography on alumina Reanal (activity grade II according to Brockmann) in the system benzene—ethanol (8:2) for 50 min. Prior to chromatography, alumina was inactivated with 5% (by weight) concentrated hydrochloric acid. Paper chromatography was performed on a Whatman No. 1 paper in the system butanol—acetic acid—water (4:1:5) for 16 h. Elemental analysis was carried out on a Perkin—Elmer Elemental Analyzer, Model 240. Ti(IV) chloride was a product of BHD-Chemicals Ltd.

Stock solutions of dyes were prepared by dissolving the sample in a small amount of ethanol and filling up with distilled water in a volumetric flask.

The stock solution of the carrier electrolyte was prepared in the following way [6]. Water was added to 200 ml of Ti(IV) chloride under continuous stirring till the vigorous hydrolysis was over. Then the formed solution was filled up with water to 500 ml. The solution prepared in this way was approximately 4.0 M-TiCl₄ (theoretical 3.65 M) and 7.4 M-HCl.

The carrier electrolyte was prepared by 10-fold dilution of the stock solution of TiCl₄ with water and addition of sulfuric acid so that its concentration was 2.0 M; 0.1 M-HCl served as auxiliary electrolyte.

Equipments

A new source of stabilized current was constructed for this work [7]. The intensity of the current passing through the generating electrode was measured with the accuracy of 0.2 mA using an ML 20 instrument provided with a shunt (Metra, Blansko).

The electrolytic vessel, where the cathode and anode parts were separated with a sintered glass S3, was H-shaped [8].

A platinum plate electrode (OP-600, Radelkis, Budapest; 0.5×1.0 cm of 1.0 cm² total area) and a common plate electrode (0.9×0.4 cm of 0.72 cm² total area) served as generating electrodes. The auxiliary electrode was a platinum plate electrode (ETP 3) of 0.56 cm² total area. The potentiometric indication electrode was a common platinum plate electrode of 0.48 cm² total area. Saturated calomel electrode with a graphite closure served as the reference electrode. The analyzed solutions were stirred electromagnetically with a plastic-coated stirrer at maximum intensity. The time of individual determinations was measured by an electric stop-watch TS 1 (Elektročas, Prague) which was connected with the current source by the aid of an auxiliary electron relay RP 90A (ZPA, Trutnov) and thus the current and the stop-watch were turned on simultaneously. The potentiometric indication system consisted of one pair of electrodes immersed into the analyzed solution, voltage divider, and a compensation recorder. A voltage divider of 1:1000 with a resistance of 48 M Ω and 47 k Ω and a recorder EZ 2 (Laboratorní přístroje, Prague) with disconnected polarographic filter were used. Argon (3N5, oxygen content 9 p.p.m.) was used as inert gas which was introduced into the electrolytic vessel by two glass tubes. The first one, narrowed into a capillary, was dipped into the electrolyte while the other one was placed approximately 1 cm below the lid. The shorter tube was provided with a glass valve which enabled to introduce the stream of the gas either into or above the solution. The electrolytic vessel was covered with a teflon lid provided with bores. The lid served simultaneously as a holder of the electrodes. The amount of the inert gas was regulated by a reducing valve on the steel bottle. The scheme of connection was according to [8]. The apparatus for the galvanostatic-coulometric determination was checked by a model determination of As(III) internally generated with bromine with potentiometric indication. At all determinations the distribution of electrodes was as follows: generating electrode—indication electrode—calomel reference electrode in the direction of stirring.

Working procedure

The auxiliary electrolyte was added into the anode part while the carrier electrolyte as well as the aliquot portion of the analyzed solution was added into the cathode part of the electrolytic vessel. The solutions were bubbled with a stream of argon for 5 min. During analysis the solution was stirred at maximum intensity and argon was introduced above the analyzed solution. Ti(III) was generated at a current of 0.5 and 1.0 mA.

The shapes of potentiometric curves were affected by different parameters of the recorder EZ 2, namely, by the range (500—1000 mV with voltage divider), sensitivity (5, 6), and chart speed (5—20 mm min⁻¹).

The first titration served as pretitration. The point of equivalency was read from the further potentiometric curve and then a series of determinations was carried out up to the point of equivalency always in the same carrier electrolyte.

To prevent diffusion of chlorine from the auxiliary electrolyte through sintered glass into the analyzed solution, the evolved chlorine was removed by a stream of argon meantime the individual determinations.

The electrodes were not purified meanwhile the individual determinations in one series.

Before further determinations the platinum electrodes were purified by rinsing with distilled water, immersing into nitric acid (1:1), electrochemical polarization in 0.1 M-H₂SO₄ and finally by thorough rinsing with distilled water.

The reference calomel electrode with a graphite closure was rinsed with distilled water, wiped with filter paper and the graphite closure was now and then mechanically purified with a steel wire.

References

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