

PHOTOLYTIC REACTION OF IODIDE WITH DI- μ -HYDROXO-BIS(DIPHENANTHROLINOFERRIC) CHLORIDE

Josef NOVÁK, Pavel VYHLÍDKA and Marie FLAŠAROVÁ

*Institute of Physics,
Czechoslovak Academy of Sciences, 180 40 Prague 8*

Received July 22nd, 1984

The reaction of di- μ -hydroxo-bis(diphenanthrolinoferric) chloride with iodide in aqueous solutions at pH 3.0 to 6.5 under the action of light radiation at wavelengths shorter than 590 nm was studied. A procedure is suggested for the quantitative determination of iodide in concentrations of 0.7–9.4 $\mu\text{mol l}^{-1}$, based on the evaluation of the slope of the time dependence of absorbance at 530 nm.

The determination of iodide in low concentrations is a topical problem. Photometric methods of determination have been reviewed by Malát¹ and by Babko and Pili-penko², kinetic procedures have been reported by Yatsimirskii³ and Kopanica and Stará⁴. The pulse polarographic determination of iodide was the concern of Vyhlídka⁵.

Di- μ -hydroxo-bis(diphenanthrolinoferric) chloride (*I*), which has been used for the photometric determination of cobalt and uranium^{6,7}, becomes a strong oxidant on the irradiation by short-wavelength light radiation; this has been employed for the oxidation of α -hydroxy acids⁸, cerium(III) salts⁹, and hypophosphites and phosphites¹⁰.

The aim of the present work was to examine the possibility of making use of the oxidative effect of *I*, during its UV irradiation, for the photometric determination of iodide.

EXPERIMENTAL

Chemicals and Apparatus

Di- μ -hydroxo-bis(diphenanthrolinoferric) chloride in aqueous solution was prepared by dissolving 125 mg of $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ and 200 mg of 1,10-phenanthroline hydrochloride in water in a 50 ml volumetric flask and diluting to volume with water.

Buffer solutions of pH 3.6–5.6 were prepared by mixing 0.2M acetic acid with 0.2M sodium acetate.

Aqueous solution of potassium iodide was prepared by dissolving 26.16 mg of the chemical in water in a 100 ml volumetric flask and diluting to the mark. One ml of solution contained 0.2 mg of I^- .

The radiation source, a 500 W high-pressure mercury discharge tube (radiation power 1.34 mW cm^{-2}), was placed 18 cm from the level of the exposed solution¹¹.

The photometric measurements were carried out on a Pulfrich photometer with an Elpho device (Carl Zeiss, Jena) equipped with a 530 nm filter and C type cells 5 cm path length. The pH was measured on an OP-208 digital pH-meter equipped with a glass electrode (Radelkis, Budapest).

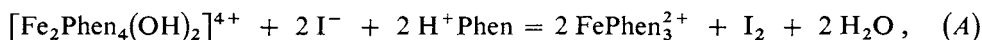
Procedure

Sample containing 0–50 μg of iodide, 5 ml of buffer solution of pH 4, and 2 ml of solution of *I* are added successively to a 50 ml volumetric flask, diluted to the mark with water, and homogenized. The absorbance of the solution is measured in a 5 cm cell at 530 nm. Then the solution is exposed to UV radiation for 10 min in 2 min intervals, the absorbance is plotted in dependence on time, and the slope of the resulting straight line is evaluated. This is performed for solutions of known iodide concentrations and a calibration plot of slope *vs* iodide concentration is constructed. This graph is used for the determination of the iodide concentration in sample.

RESULTS AND DISCUSSION

Iodide ions reduce *I* only reluctantly in sodium acetate-buffered solutions under normal conditions (20–25°C, ordinary room illumination). The reduction is complete in 36–20 h according to the acidity in the pH 1–6 region.

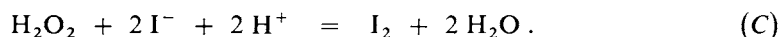
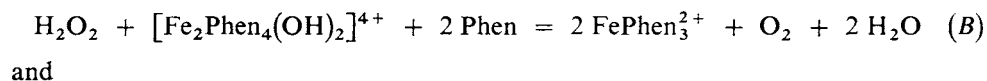
At pH 4–6, iodide is oxidized according to the reaction



where Phen stands for 1,10-phenanthroline.

This reaction is accelerated considerably if the system is exposed to UV radiation. The dependences of absorbance on the exposure time, for various concentrations of iodide, are shown in Fig. 1, the dependence of the slope ($\text{tg } \alpha$) on the iodide concentration is plotted in Fig. 2. The pH-dependences of absorbance are plotted for unexposed (curve 1) and exposed (curve 2) solutions in Fig. 3; curve 3 pertains to iodide solution exposed for 5 min to conventional room illumination.

Fig. 1 shows that the reduction of *I* and thereby also the development of the colour of ferroin is slowed down in the presence of iodide. The reaction mechanism appears to be more intricate than as represented by equation (A). The UV irradiation leads to the formation of hydrogen peroxide, as evidenced by the evolution of oxygen; the peroxide formation rate is constant under a constant radiation flux. Hydrogen peroxide then reacts with *I* and iodide according to the equations



In the absence of iodide, all the peroxide is used up for the reduction of I according to reaction (B), whereas reaction (C) also contributes if iodide is present, whereby the concentration of hydrogen peroxide is additionally lowered. The ratio of the resulting products in reaction (A) is thus also altered. This is responsible for the slowing down of the ferroin absorbance increase for exposed systems containing iodide.

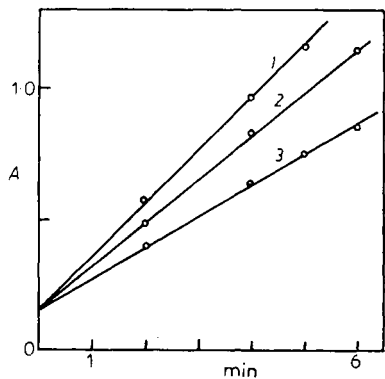


FIG. 1

Change in the absorbance of di- μ -hydroxo-bis(diphenanthrolineferric) chloride solution ($c = 92 \mu\text{mol l}^{-1}$) in the presence of iodide in dependence on the exposure time. $V = 50 \text{ ml}$, $t = 23^\circ\text{C}$, $\lambda = 530 \text{ nm}$, path length 5 cm, radiation source 18 cm above the level. Iodide added (μg): 1 0, 2 25, 3 50

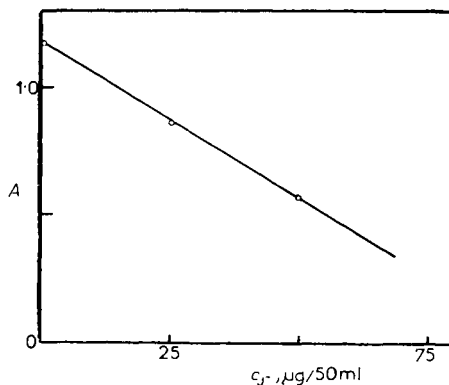
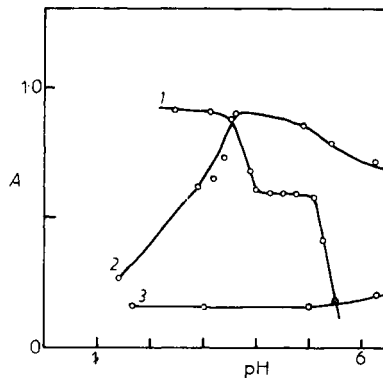


FIG. 2

Dependence of the slope of the straight lines ($\text{tg } \alpha = A$) on the concentration of iodide. Experimental conditions as in Fig. 1

FIG. 3

Dependence of absorbance of ferroin formed by reaction of di- μ -hydroxo-bis(diphenanthrolineferric) chloride (I) with iodide ions on pH of solution. $c_I = 92 \mu\text{mol l}^{-1}$, $c_{I^-} = 7.88 \mu\text{mol l}^{-1}$, 10^{-2} M acetate buffer. 1 solution stored in the dark for 24 h, 2 solution exposed to UV radiation for 300 s, 3 solution measured after 5 min under conventional illumination



It is of importance from the analytical point of view that the increase in the absorbance of the irradiated solution in dependence on the time of exposure is linear (Fig. 1), as is the dependence of the slope on the iodide concentration over the region of $c_{I^-} = 0.7-9.4 \mu\text{mol l}^{-1}$ (Fig. 2). Ten replicate determinations were performed for a solution of pure potassium iodide of $c = 6.3 \mu\text{mol l}^{-1}$, i.e., $40 \mu\text{g I}^-/50 \text{ ml}$, and the relative error of determination was $\pm 6.4\%$.

The method suggested can be applied to the determination of iodide in pure solutions, in solutions of alkali halides, or in samples where the procedure of pyrohydrolytic separation of iodide from a solid phase¹² has been used. Ions of Mn^{2+} , Cr^{3+} , Ce^{3+} (ref.⁹), and hypophosphite and phosphite¹⁰ interfere.

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Translated by P. Adámek.