

OPTIMIZATION OF KINETIC DETERMINATION OF IODATE BY METHYL ORANGE OXIDATION IN THE PRESENCE OF HYDRAZINE

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Instead of the fixed time method the difference in induction periods of decolorization of a blank solution and a sample solution has been suggested as analytical signal for iodate ion determination by Landolt reaction of methyl orange with potassium bromate in the presence of hydrazine. Optimal conditions are: 0.024 M H₂SO₄, 2·10⁻⁶ M methyl orange, (5–6)·10⁻⁵ M KBrO₃, 1·10⁻⁵ N₂H₄. Calibration curve is linear in (0.06–2.4) µg/mL range, reproducibility error is less than 2.7%, relative error of determination is less than 3.3 %, for aqueous solution analysis.

Keywords: kinetic analysis, photometric analysis, iodate, Landolt reaction, induction period, methyl orange, bromate, hydrazine.

Introduction

The important role of iodine in human nutrition is stressed by the World Health Organization, as estimated 2 billion people, including 285 million school-age children, are iodine deficient [1]. Iodine exists in a variety of forms reflecting either the environment in which it is found. For example, the total iodine content of seawater (approximately 50–60 µg/L) is believed to be composed of iodate (30–60 µg/L of I) and iodine–iodide (0–20 µg/L) with perhaps a few µg/L of organically bound iodine [2]. The bioavailability of organic iodine, especially associated with macromolecules, is low, whereas I⁻ and IO₃⁻ have high bioavailability [3]. For example, determination of iodate in salt samples is of considerable importance as the amount of iodate in the salt samples may vary with environmental conditions, the nature of transport, packing conditions, and cooking methods. The same is true about iodate content in aqueous solutions [4].

There are various analytical methods for determination of iodate in natural waters and iodized salt samples. Chromatographic systems coupled with various detectors became the basic tool in many analytical laboratories. Routine analysis of iodine compounds can be carried out by means of gas chromatography and high performance liquid chromatography. Analysis of inorganic iodine species in waters is mainly carried out with the use of ion chromatography or chromatography-mass spectrometry [5–8]. Most of the techniques are complex and involve sophisticated instruments and complex procedures.

Spectrophotometric analysis continues to be one of the most widely used analytical techniques available. Thus, in seawater the iodine species of interest are first converted to iodate. Then the iodate is reacted with acid and excess iodide to give iodonium ions, [I₃]⁺, which are detected spectrophotometrically at 350 nm [2]. Some researchers reported that the spectrophotometric methods for the determination of IO₃⁻ are based on its reaction with the excess I⁻ to liberate I₂ which forms triiodide; its absorbance is measured at 349 nm [9]. Iodine species like iodide, iodine, iodate, and periodate can be determined by a sensitive spectrophotometric method that involves the oxidation of hydroxylamine to nitrite with iodate under acidic condition. The formed nitrite is determined based on the diazo coupling reaction. The method obeys Beer's law in the concentration range 1–15 µg of iodate in an overall aqueous volume of 10 mL at 545 nm and the color is stable for 3h [10]. Some authors recommend using separation methods, such as liquid-phase microextraction [11]. A sensitive spectrophotometric method for determination of multiple iodine species, such as iodide, iodine, iodate and periodate has been described, involving oxidation of iodide to ICl₂⁻ in the presence of iodate and chloride in an acidic medium. The formed ICl₂⁻ bleaches the dye methylred. The decrease in the intensity of the colour of the dye is measured at 520 nm. Beer's law is obeyed in the concentration range 0–3.5 µg of iodide in an overall volume of 10 mL [12].

It is possible to enhance the selectivity of spectrophotometric determination, using kinetic methods, in which the analytical signals are differentiated by the difference between the rates of reactions. Using the same reaction with iodide in acidic media it is possible to determine periodate-bromate and iodate-bromate mixtures simultaneously, by the H-point standard addition method [13]. Kinetic spectrophotometric methods, which are based on the reaction found by Sandell and Kolthoff, set the foundation for

the development of different methods for the determination of iodine in environmental samples (mostly water). Kinetic determination of iodate is based upon its catalytic influence upon the reaction between ammonium cerium sulphate and arsenious acid; as iodide and iodine catalyze the same process, it is possible to determine iodate after extraction of iodide-iodine into chloroform as an ion pair with the tetraphenylarsonium cation [14]. It has been shown that during determination of iodate with starch-iodide the intermediate triiodide ion is produced in consecutive reactions, with the products absorbing at 291, 354 and 585 nm; in the reaction time of 180 s the widest linear range (0.05–1.0 $\mu\text{g/mL}$) and the lowest detection limit is found at 354 nm. The authors have suggested simultaneous kinetic determination of iodate and periodate, based on consecutive reactions [15, 16].

Using organic dyes, it is possible to increase the sensitivity of kinetic photometric determination and carry out the measurement in the visual light. For example, a sensitive kinetic-spectrophotometric method has been developed for rapid determination of trace quantities of iodate. The method is based on the accelerating effect of iodate on the reaction of bromate and hydrochloric acid, with the product of the reaction decolorizing methyl orange. It goes very fast in acidic medium, but the presence of hydrazine conveniently slows it. The reaction is monitored by measuring the decrease of absorbance at 525 nm. Fixed time method (at 150 s) has been used, the concentration range for iodate is (0.03–1.2) $\mu\text{g/mL}$ [17]. The method for the simultaneous determination of iodate and periodate is based on their reaction with pyrogallol red in sulfuric acid medium. The decrease in absorbance of pyrogallol red is measured at 470 nm, the kinetic data is processed by principle component artificial neural network. The constructed model is able to predict the concentration in the range of 0.1–15.0 and 0.1–17.0 $\mu\text{g/mL}$ for iodate and periodate, respectively [18]. In another method the reaction between iodate, excess iodide, and acid has been used, and the iodine liberated is allowed to react with variamine blue dye in the presence of sodium acetate to yield a violet-colored species. The absorbance values are recorded at 550 nm in the intervals of 30 s till 30 min. The fixed time of 5 min has been chosen for measurement (time of equilibration is 20 min). The calibration curve is linear in the concentration range of 2–30 μg of iodate in a final equilibration volume of 10 mL [19].

The chemical system, described in [17], has attracted our attention. The fixed time method is simple, of course, and does not require any special calculations, but the time of measurement in a system that has not reached equilibrium should be very carefully kept, as well as the determination conditions. An example of this is the necessity to equilibrate all the reactant solutions at 30 ± 0.1 °C before beginning of the reaction [17]. The chemical process itself is identifiable as one of Landolt reactions, and there are various possibilities of getting information from them, such as induction period measurement, tangent method, and various differential curves [20].

The present paper studies the possibilities of iodate kinetic determination using the induction period of Landolt reaction of methyl orange with potassium bromate in the presence of hydrazine and optimization of conditions for analysis of iodate in aqueous acidic medium.

Experimental

A standard solution of iodate ion 1000 $\mu\text{g/mL}$ was prepared by dissolving 0.3100 g of analytical-grade reagent potassium iodate KIO_3 in distilled water and diluting to the mark in a 250-mL volumetric flask. Working solutions were prepared daily by precise diluting in distilled water.

A stock solution of hydrazine 0.020 M was prepared by dissolving 0.5248 g of analytical grade reagent $\text{N}_2\text{H}_4 \cdot 2\text{H}_2\text{O}$ in distilled water and diluting to the mark in a 250-mL volumetric flask. Working solutions were prepared daily by precise diluting in distilled water.

A stock solution of potassium bromate 0.100 M was prepared by dissolving 1.670 g of analytical grade reagent KBrO_3 in distilled water and diluting to the mark in a 100-mL volumetric flask. Working solutions were prepared daily by precise diluting in distilled water.

A solution of sodium chloride 2.0 M was prepared by dissolving 11.686 g of analytical grade reagent NaCl in distilled water and diluting to the mark in a 100-mL volumetric flask.

A solution of methyl orange $3.05 \cdot 10^{-4}$ M was prepared by dissolving 0.010 g of $\text{C}_{14}\text{H}_{14}\text{N}_3\text{SO}_3\text{Na}$ in distilled water and diluting to the mark in a 100-mL volumetric flask.

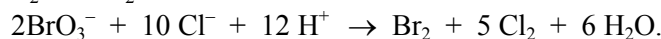
Sulfuric acid solutions 2.0 M and 0.22 M were prepared by appropriate dilution of the concentrated acid H_2SO_4 .

The procedure of iodate determination was as following: a suitable aliquot of a working solution, in the range 2–240 μg of iodate, was transferred into a 100-mL volumetric flask containing 25 mL of

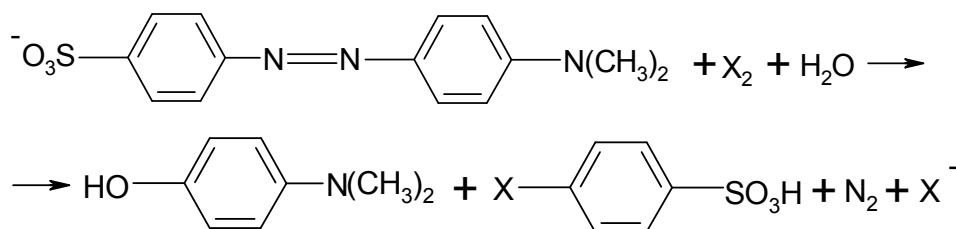
$3.90 \cdot 10^{-5}$ M hydrazine solution, 11 mL of 0.22 M sulfuric acid solution and 28 mL of 2 M NaCl solution. Then 8 mL of $2.44 \cdot 10^{-5}$ M methyl orange solution was added, and the solution was diluted to approximately 80–85 mL with distilled water, 10 mL of $5.11 \cdot 10^{-4}$ M KBrO₃ solution was added, and the solution was diluted to the mark with distilled water. (The parameters belong to the optimized procedure, during the investigation itself concentrations were changed in a wide range, though the order of addition was maintained.) A portion of the solution was transferred into a 1 cm glass cell, the absorbance change in time was measured in reference to distilled water at wavelength 490 nm, with the use of photocolorimeter KFK-2MP, each 20 seconds beginning with diluting to the mark. Then the induction period was calculated, it was assumed to be the point of intersection of two linear parts of a kinetic curve, calculated with the use of the least-squares procedure. The blank solution, containing all the reagents except iodate ion, was submitted to the same procedure.

Results and Discussion

In acidic media in the presence of potassium bromate methyl orange is decolorized by reason of its oxidation. The oxidizing agents are the products of the reaction of bromate ion with the added excess of chloride ions, that is, Cl₂ and Br₂:



The produced chlorine and bromine react with methyl orange and decolorize it:



(X = Cl; Br)

The more acidic the medium, the faster the decolorizing goes, it becomes more difficult to monitor the rate of colour change, which is the basis of kinetic determination. Though if some amount of hydrazine N₂H₄ is added to the solution, the reaction slows down. The inhibiting influence of hydrazine is explained by its reaction with Cl₂ and Br₂, hence, it is a Landolt reactant:



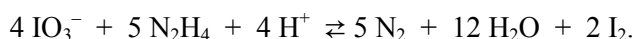
The Landolt process can be described as follows:

(1) slow reaction: A + B → P,

(2) fast reaction: P + L → Y.

As the second reaction is much faster, than the first one, its product (P) can be detected only when the “Landolt reactant” (L) is completely consumed as the result of the second reaction. The colour change in the system is observed only after a certain induction period, which provides a possibility to determine the catalyst concentration by the duration of the induction period, and after it ends, the reaction (decolorization, in this case) becomes noticeable.

Thus, the method, based on the Landolt effect, is considered a variation of the fixed concentration method. Usually it is used to determine the concentration of the Landolt reactant itself, and our data also indicate that hydrazine concentration significantly slows down the decolorization (Fig. 1). The greater is the amount of N₂H₄ in a solution, the greater is the induction period of this Landolt reaction. At a very small concentration no induction period is observed. However, in the presence of iodate, even in microquantities, the reaction rate increases. The reason is that iodate ion reacts with hydrazine:



It is interesting to note that the change in iodate concentration has a different impact upon the usual ways of representation of the reaction rate, such as the slope ratio of the linear part of a kinetic curve (tangent) and its induction period. Experimental investigations has shown that the kinetic curve slope angle changes but little, whereas the dissimilarity of the induction periods is obvious and can be expressed in proportion to concentration, as shown on Fig. 2.

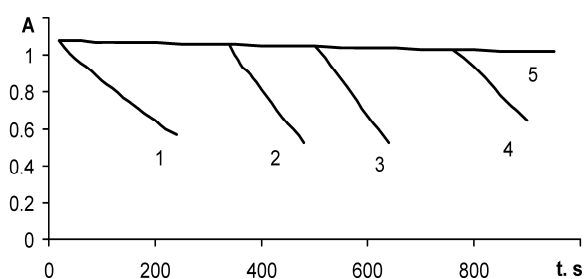


Fig. 1. Absorbance-time plots for the Landolt reaction of methyl orange with bromate in the presence of hydrazine $C(\text{MO}) = 3.05 \cdot 10^{-5}$ M; $C(\text{H}_2\text{SO}_4) = 0.2$ M; $C(\text{KBrO}_3) = 2.4 \cdot 10^{-4}$ M; $C(\text{IO}_3^-) = 0.6$ $\mu\text{g/mL}$; $C(\text{NaCl}) = 0.56$ M; $\lambda = 490$ nm; $l = 1$ cm; $C(\text{N}_2\text{H}_4)$: 1 – $4.68 \cdot 10^{-6}$ M; 2 – $2.65 \cdot 10^{-5}$ M; 3 – $3.28 \cdot 10^{-5}$ M; 4 – $4.52 \cdot 10^{-5}$ M; 5 – $7.49 \cdot 10^{-5}$ M

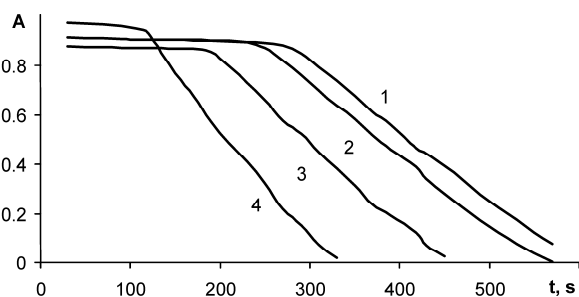


Fig. 2. Absorbance-time plots for the Landolt reaction of methyl orange with bromate in the presence of hydrazine and iodate $C(\text{MO}) = 3.05 \cdot 10^{-5}$ M; $C(\text{H}_2\text{SO}_4) = 0.2$ M; $C(\text{N}_2\text{H}_4) = 1.56 \cdot 10^{-5}$ M; $C(\text{KBrO}_3) = 2.4 \cdot 10^{-4}$ M; $C(\text{NaCl}) = 0.56$ M; $\lambda = 490$ nm; $l = 1$ cm; $C(\text{IO}_3^-)$: 1 – 0; 2 – 0.03 $\mu\text{g/mL}$; 3 – 0.6 $\mu\text{g/mL}$; 4 – 1.2 $\mu\text{g/mL}$

As in the presence of hydrazine at zero concentration of iodate an induction period (of greater duration) also exists on the kinetic curve, during investigation of optimal conditions for the reaction the difference between the induction periods of the reaction in the blank solution and iodate-containing solutions (Δt_{ind}) has been chosen as the analytical signal – if the reaction accelerates, the induction period decreases and the difference increases. The absolute value of absorbance does not play any role.

With increasing concentration of KBrO_3 the induction period decreases: thus, at $1.92 \cdot 10^{-5}$ M it is equal to 810 s, while at $2.50 \cdot 10^{-4}$ M it equals 50 s at the same iodate concentration 0.6 $\mu\text{g/mL}$; in the absence of iodate the induction period also decreases from 939 s to 55 s. The greatest difference corresponds to KBrO_3 concentration $5.76 \cdot 10^{-5}$ M (Fig. 3). At greater concentrations the values of the analytical signal fluctuate to a little degree near the zero line, which can perhaps be explained by nonoptimal conditions.

This is observed at quite high acidity chosen in [17], where the determination is carried out by the fixed time method. Optimizing the conditions of the Landolt reaction in order to use the induction period as the analytical signal, we have come to the conclusion that the sulfuric acid concentration should be decreased: the greater its concentration, the smaller is the induction period, therefore, the possibility to change its duration as the consequence of iodate ion presence also diminishes.

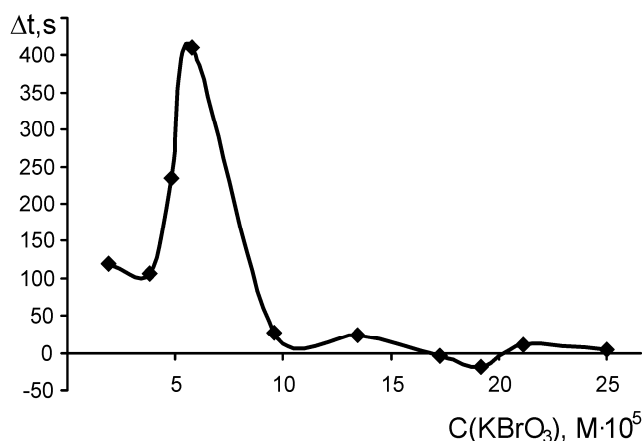


Fig. 3. Effect of potassium bromate concentration on the difference of induction periods. $C(\text{MO}) = 3.05 \cdot 10^{-5}$ M; $C(\text{H}_2\text{SO}_4) = 0.2$ M; $C(\text{NaCl}) = 0.56$ M; $C(\text{N}_2\text{H}_4) = 1.56 \cdot 10^{-5}$ M; $C(\text{IO}_3^-) = 0.6$ $\mu\text{g/mL}$; $\lambda = 490$ nm; $l = 1$ cm

At the chosen KBrO_3 concentration the study has been conducted into the influence of H_2SO_4 concentration upon the difference of the induction periods of the blank solution and the iodate-containing solution. The negative values of the difference in the ascending branch of the curve indicate that at too low concentrations of sulfuric acid the influence of iodate ion upon the reaction rate is more apparent than the acidity influence. The data are plotted on Fig. 4. The graph shows that the optimal concentration of sulfuric acid is equal to 0.024 M in the solution prepared for photometric measurement.

Under lower acidity other optimal concentrations of reagents change also, specifically, the concentration of hydrazine, which serves as an inhibitor to the reaction, and the induction period is the function of hydrazine concentration at that (Fig. 1). After conducting the experiment at chosen conditions according to the procedure described above, the plot on Fig. 5 has been obtained.

Two peaks of reaction acceleration can be observed on this curve (at the values of hydrazine concentration $3.90 \cdot 10^{-6}$ M and $8.74 \cdot 10^{-6}$ M, both are lower than the optimal value in more acidic medium [17]). The Landolt reaction of methyl orange with potassium bromate is sequential: hydrazine consumes

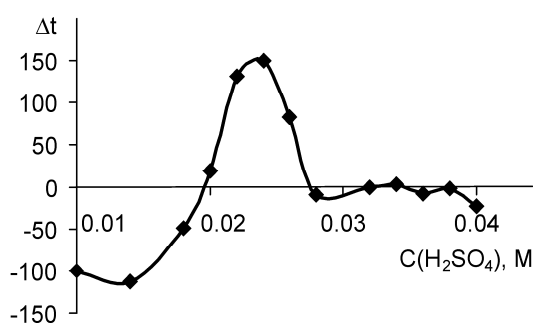


Fig. 4. Effect of sulfuric acid concentration on the difference of induction periods. $C(\text{MO}) = 3.05 \cdot 10^{-5} \text{ M}$; $C(\text{N}_2\text{H}_4) = 1.56 \cdot 10^{-5} \text{ M}$; $C(\text{NaCl}) = 0.56 \text{ M}$; $C(\text{KBrO}_3) = 5.76 \cdot 10^{-5} \text{ M}$; $C(\text{IO}_3^-) = 0.6 \mu\text{g/mL}$; $\lambda = 490 \text{ nm}$; $l = 1 \text{ cm}$

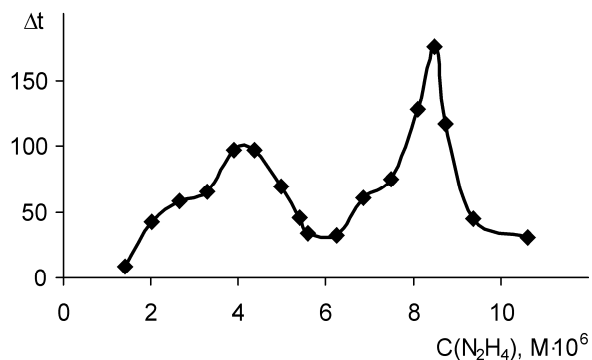


Fig. 5. Effect of hydrazine concentration on the difference of induction periods. $C(\text{MO}) = 3.05 \cdot 10^{-5} \text{ M}$; $C(\text{H}_2\text{SO}_4) = 0.024 \text{ M}$; $C(\text{NaCl}) = 0.56 \text{ M}$; $C(\text{KBrO}_3) = 5.76 \cdot 10^{-5} \text{ M}$; $C(\text{IO}_3^-) = 0.6 \mu\text{g/mL}$; $\lambda = 490 \text{ nm}$; $l = 1 \text{ cm}$

the product of the indicator reaction, iodate uses up hydrazine – as this takes place, the duration of the induction period is determined by the rates of both processes separately. Apparently, as the conditions change, either the rate of one process prevails, or the rate of the other. We have chosen the second peak for further experiments: though it is narrower, the analytical signal is almost twice as high.

Paradoxically, the influence of the dye (methyl orange) concentration manifests itself, the graphs are plotted on Fig. 6. Comparing the induction periods of decolorizing for the iodate-containing solution and the blank solution, it can be seen that up to a certain limit (approximately $3 \cdot 10^{-6} \text{ M}$ of the dye) the pattern is as usual, that is, iodate accelerates the reaction. However, after this the induction periods cease to differ, specifically in the concentration area $3.05 \cdot 10^{-5} \text{ M}$, chosen for the fixed time method. In our experiments methyl orange concentration $2 \cdot 10^{-6} \text{ M}$ has been adopted. Certainly, decreasing concentration of the dye affects the absolute value of absorbance: it decreases (from 1.0 to 0.8), though it still stays within the optimal interval, in which the error of absorbance measurement is minimal. The analytical signal is not affected at all: both the horizontal part of the kinetic curve and the descending branch contain enough points for finding the induction period as the point of intersection.

At the chosen optimal conditions the calibration graph has been plotted, it is shown on Fig. 7. The linearity interval is twice as wide compared to the fixed time method [17], up to $2.4 \mu\text{g/mL}$ of iodate ion in solution. At higher iodate concentration the induction period of the Landolt reaction decreases to values less than 50 s, in consequence there are too few points on the horizontal linear part of the kinetic curve, and the calculation of the intersection point with the use of the least-squares method is made too difficult. The calibration graph for iodate determination, treated by the least-squares method, corresponds to the linear regression equation $Y = (7.5 \pm 7.8) + (68.7 \pm 5.7) X$, with correlation coefficient 0.997.

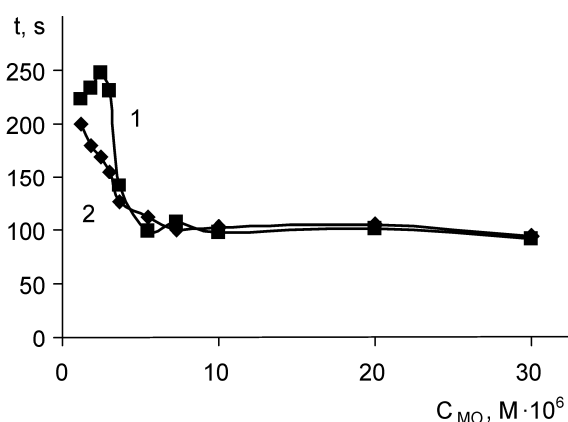


Fig. 6. Effect of methyl orange concentration on the induction period of blank and iodate-containing solutions. $C(\text{N}_2\text{H}_4) = 9.6 \cdot 10^{-6} \text{ M}$; $C(\text{H}_2\text{SO}_4) = 0.024 \text{ M}$; $C(\text{NaCl}) = 0.56 \text{ M}$; $C(\text{KBrO}_3) = 5.76 \cdot 10^{-5} \text{ M}$; $C(\text{IO}_3^-) = 0.6 \mu\text{g/mL}$; $\lambda = 490 \text{ nm}$; $l = 1 \text{ cm}$ $C(\text{IO}_3^-)$: 1 – 0; 2 – $0.6 \mu\text{g/mL}$

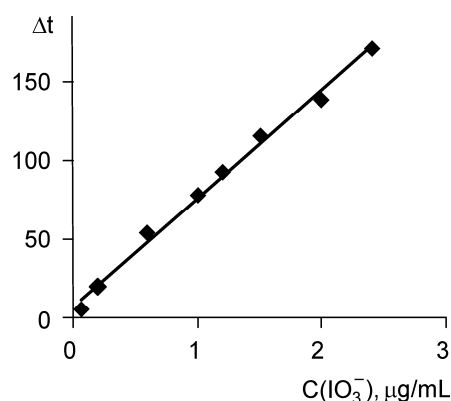


Fig. 7. Effect of iodate ion concentration in the photometric system on the difference of induction periods. $C(\text{MO}) = 1.95 \cdot 10^{-6} \text{ M}$; $C(\text{N}_2\text{H}_4) = 9.6 \cdot 10^{-6} \text{ M}$; $C(\text{KBrO}_3) = 5.76 \cdot 10^{-5} \text{ M}$; $C(\text{NaCl}) = 0.56 \text{ M}$; $C(\text{H}_2\text{SO}_4) = 0.024 \text{ M}$; $\lambda = 490 \text{ nm}$; $l = 1 \text{ cm}$

In order to evaluate the metrological characteristics of iodate ion determination by the suggested method we placed the known amounts of the standard solution of iodate into 100-mL volumetric flasks (in 6 replicate aliquots), added the necessary reagents according to the experimental procedure above, measured the absorbance change in time in 20-second intervals, calculated the induction periods as the point of intersection of linear parts of the kinetic curve got with the use of the least-squares method. The blank solution, containing all the reagents except iodate ion, was submitted to the same procedure. After calculation of the difference of induction periods we found the iodate ion concentration in the analyzed solution using the linear regression equation above.

Evaluation of metrological characteristics has been carried out on the basis of conventional statistical criteria. The results are shown in Table 1.

Evaluation of iodate determination errors ($P = 0.95$, $t_{p,f} = 2.57$)

Table 1

Δt , s	X_i , $\mu\text{g/mL}$	\bar{X}	S	ΔC	$(\Delta C/C)100\%$	$\delta, \%$
present in sample: $C(\text{IO}_3^-) = 0.6 \mu\text{g/mL}$						
47.9; 46.7; 48.7; 46.9; 47.4; 46.0	0.59; 0.57; 0.60; 0.57; 0.58; 0.56	0.58	0.0148	0.0156	2.7%	-3.3%
present in sample: $C(\text{IO}_3^-) = 1.2 \mu\text{g/mL}$						
90.5; 90.0; 91.3; 90.7; 92.1; 91.1	1.21; 1.20; 1.22; 1.21; 1.23; 1.22	1.215	0.0105	0.011	0.91%	+1.3%

According to Table 1, the reproducibility of the results of iodate determination is expressed by the relative error 2.7 % for the lowest concentration, while the relative error of accuracy proves to be -3.3 %. Increasing iodate concentration, we get both metrological characteristics appropriately smaller, namely 0.91 % and +1.3 %, respectively. The metrological parameters are consistent with determination of iodate ion by fixed time method (for 10 replicate samples with concentration 0.5 $\mu\text{g/mL}$ $RSD = 1.15\%$, $\delta = 1.60\%$, and for 1.0 $\mu\text{g/mL}$ $RSD = 0.92\%$, $\delta = 1.20\%$ [17]), and, in fact, with any other optimized photometrical method.

Conclusion

1. Application for iodate ion determination of the induction period of Landolt reaction of methyl orange with potassium bromate as the analytical signal, independent of the absorbance absolute value, has made it possible to stabilize the results compared to the fixed time method, described earlier; among other factors, it is no longer necessary to equilibrate the whole set of reactant solutions in a thermostat at $30 \pm 0.1 \text{ }^\circ\text{C}$ before beginning of the reaction.

2. The optimal conditions of determination are: the concentration of methyl orange is $2 \cdot 10^{-6} \text{ M}$, potassium bromate is $(5-6) \cdot 10^{-5} \text{ M}$, hydrazine is $1 \cdot 10^{-5} \text{ M}$, sulfuric acid is 0.024 M; all of them are smaller than those used earlier.

3. The metrological characteristics of iodate ion determination are as follows: calibration curve is linear in (0.06–2.4) $\mu\text{g/mL}$ range, twice as much as in fixed time method, reproducibility error is less than 2.7%, relative error of determination is less than 3.3 %.

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ОПТИМИЗАЦИЯ КИНЕТИЧЕСКОГО ОПРЕДЕЛЕНИЯ ИОДАТА ПУТЕМ ОКИСЛЕНИЯ МЕТИЛОРАНЖА В ПРИСУТСТВИИ ГИДРАЗИНА

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Вместо метода фиксированного времени было предложено использовать разность индукционных периодов обесцвечивания холостого опыта и исследуемого раствора в качестве аналитического сигнала для определения иодат-иона реакцией Ландольта метилоранжа с броматом калия в присутствии гидразина. Оптимальные условия: 0,024 М H_2SO_4 , $2 \cdot 10^{-6}$ М метилоранжа, $(5-6) \cdot 10^{-5}$ М KBrO_3 , $1 \cdot 10^{-5}$ N_2H_4 . Градуировочный график линеен в интервале (0,06–2,4) мкг/мл, погрешность сходимости менее 2,7 %, относительная ошибка определения менее 3,3 % при анализе водных растворов.

Ключевые слова: кинетический анализ, фотометрический анализ, иодат, реакция Ландольта, индукционный период, метилоранж, бромат, гидразин.

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