Краткие сообщения

APPLICATION OF METHYL ORANGE OXIDATION IN THE PRESENCE OF HYDRAZINE TO KINETIC DETERMINATION OF PERIODATE ION

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It is possible to apply the induction period of Landolt reaction of methyl orange with potassium bromate in the presence of hydrazine to determination of periodate ion. Optimal conditions are: 0.030 M HCl, 10 μg/mL methyl orange, 1.6·10–4 M KBrO3, 3·10–5 M N2H4. Calibration curve is linear (0.06–0.9) μg/mL periodate ion range, reproducibility error is 2.6%, relative error is 4.6%.

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

Introduction

Though iodine in natural waters is predominantly found in the iodide or iodate form, other forms of iodine species include periodate, hypoiodite, and several organic iodine compounds [1]. The concentration limits are in microgram area: 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]. It is possible to determine periodate along with iodate, using their oxidizing action upon the same reactants at different conditions. Thus, periodate, iodate and bromate enter the reaction with iodide ion at different pH values, with absorbance measured at 345 nm [3]. Selective oxidation of Alizarin Navy Blue permits flow-through spectrofluorimetric detection at 516 nm [4]. There is a possibility of iodate and periodate determination by different kinetic behaviours of the analytes, such as their consecutive reactions with iodide-starch system at 291, 354 and 585 nm [5]; 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 [6]. 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, in the reaction with pyrogallol red at 470 nm, the kinetic data for iodate and periodate determination is processed by principle component artificial neural network [7]. By analogy with using methyl orange decolorization for kinetic-spectrophotometric determination of iodate [8], the authors applied the procedure to determination of periodate by the fixed time method at 150 s, equilibrating all the reactants at the temperature (30 ± 0.1) °C [9].

Previously we suggested the way of kinetic determination of iodate using the induction period of Landolt reaction of methyl orange with potassium bromate in the presence of hydrazine [10]. In the present brief report we study the possibility of periodate determination and its optimal conditions.

Experimental

A standard solution of periodate ion $4.30 \cdot 10^{-3}$ M was prepared by dissolving 0.2301 g of analytical-grade reagent sodium periodate $NaIO_4$ 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 $N_2H_4 \cdot 2H_2O$ 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 methyl orange 100 μg/mL was prepared by dissolving 0.010 g of $C_{14}H_{14}N_3SO_3Na$ in distilled water and diluting to the mark in a 100-mL volumetric flask.

Hydrochloric acid solution 3.2 M and 0.3 M were prepared by appropriate dilution of the concentrated acid HCl (ρ = 1.17 g/mL).

The procedure of periodate determination was as following: a suitable aliquot of a working solution, in the range 5–150 μg periodate, was transferred into a 100-mL volumetric flask already containing 9.5 mL of $3\cdot10^{-5}$ M hydrazine solution and 9.5 mL of 0.304 M hydrochloric acid solution. Then 10 mL of 100 μg/mL methyl orange solution was added, and the solution was diluted with distilled water to approximately 80–85 mL, then 8.5 mL of $1.9\cdot10^{-3}$ M $KBrO_3$ 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 found, 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 periodate ion, was submitted to the same procedure.

Results and Discussion

When methyl orange is oxidized by bromate ion, its decolorization slows in the presence of hydrazine (Landolt reactant), and the induction period lengthens. However, in the presence of iodate, even in microquantities, the reaction rate increases, depending on the concentration of iodate. The reason is that iodate ion reacts with hydrazine:

$$4\ IO_3^- + 5\ N_2H_4 + 4\ H^+ \rightleftarrows 5\ N_2 + 12\ H_2O + 2\ I_2.$$

Periodate ion can enter a similar reaction in acidic medium:

$$4\ IO_4^- + 7\ N_2H_4 + 4\ H^+ \rightleftarrows 7\ N_2 + 16\ H_2O + 2\ I_2.$$

The kinetic curves at various concentrations of periodate are shown on Fig. 1.

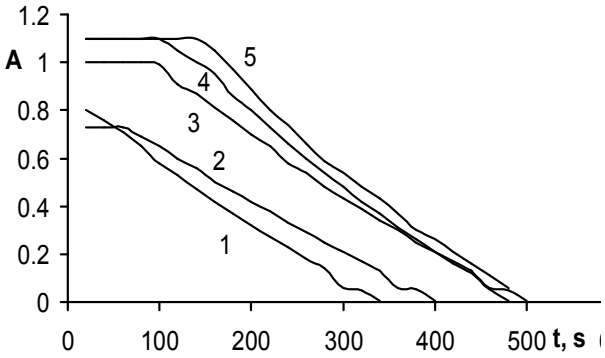

Fig. 1. Absorbance-time plots for the Landolt reaction of methyl orange with bromate in the presence of hydrazine and periodate: C(MO) = 10 μg/mL; $C(N_2H_4)$ = 0.5 μg/mL; C(HCl) = 0.32 M; $C(KBrO_3) = 1.92\cdot10^{-4}$ M; λ = 490 nm; *l* = 1 cm; $C(IO_4^-)$: 1 – 0; 2 – $3\cdot10^{-7}$ M; 3 – $2.8\cdot10^{-6}$ M; 4 – $3.7\cdot10^{-6}$ M; 5 – $7\cdot10^{-6}$ M

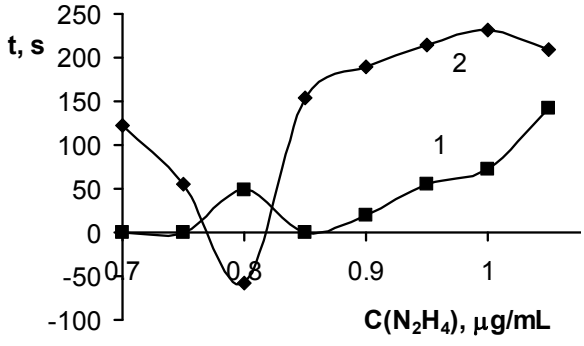

Fig. 2. Effect of hydrazine concentration on the induction periods of the blank (1) and periodate-containing (2) solutions: C(MO) = 10 μg/mL; C(HCl) = 0.03 M; $C(KBrO_3) = 1.92\cdot10^{-4}$ M; λ = 490 nm; *l* = 1 cm; $C(IO_4^-)$: 1 – 0; 2 – $7\cdot10^{-6}$ M

As with iodate, the induction period of Landolt reaction depends on periodate concentration. We have checked other possibilities of getting an analytical signal from the obtained kinetic curves (absorbance value, tangent method, differential curve), but they change less with periodate concentration than the induction period.

The more acidic the medium, the faster the decolorization goes. At HCl concentrations greater than 0.028 M the induction period of the blank zeroes, while being still in the easily measurable range of 138–210 s for the solution containing $7\cdot10^{-6}$ M of periodate ion. We have chosen 0.03 M HCl as the optimal concentration. For comparison, iodate can be determined in the range (0.02–0.028) M H_2SO_4, with optimum at 0.024 M [10], which shows the possibility of measuring the ions in the same solution at different conditions.

The concentration of hydrazine, on the contrary, increases the induction periods of the blank and periodate-containing solutions. The dependences are shown on Fig. 2. The optimal concentration, used henceforth, has been found to be 0.95 μg/mL ($3 \cdot 10^{-5}$ M), twice as much as in [9].

Other studied conditions include the concentration of methyl orange (Fig. 3) and potassium bromate (Fig. 4).

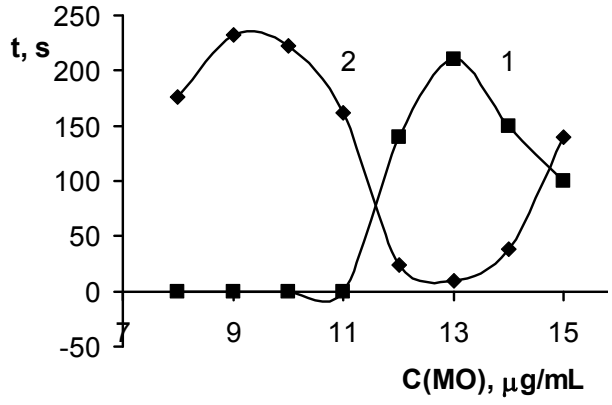

Fig. 3. Effect of methyl orange concentration on the induction periods of the blank (1) and periodate-containing (2) solutions: $C(N_2H_4)$ = 0.95 μg/mL; C(HCl) = 0.03 M; C(KBrO3) = $1.92 \cdot 10^{-4}$ M; λ = 490 nm; l = 1 cm; C(IO4–): 1 – 0; 2 – $7 \cdot 10^{-6}$ M

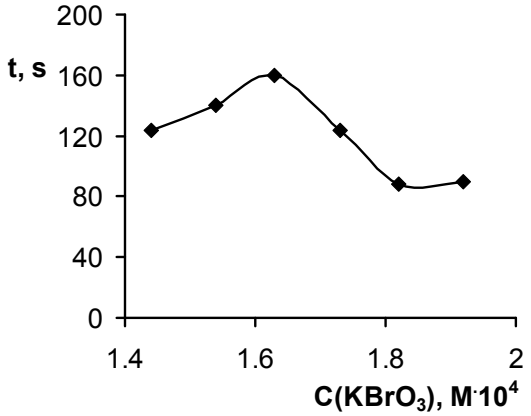

Fig. 4. Effect of potassium bromate concentration on the induction period of the periodate-containing solution: C(MO) = 10 μg/mL; $C(N_2H_4)$ = 0.95 μg/mL; C(HCl) = 0.03 M; $C(IO^{4-}) = 7 \cdot 10^{-6}$ M; λ = 490 nm; l = 1 cm

Under lower acidity and higher hydrazine concentration the induction periods of Landolt reaction without periodate decrease to zero (except when methyl orange is higher than optimal). The optimal concentration of methyl orange is 9.5 μg/mL (but 10 μg/mL can be used), and for potassium bromate it equals $1.62 \cdot 10^{-4}$ M.

At the chosen optimal conditions the calibration graph has been plotted. The linearity interval is narrower compared to the fixed time method [9], (0.06– 0.9) μg/mL of periodate ion in the solution prepared for photometric measurement. The linear part of the calibration curve, treated by the least-squares method, corresponds to the linear regression equation $Y = (-0.02 \pm 5) + (177.6 \pm 9.2)\ X$, with correlation coefficient 0.998.

Evaluation of metrological characteristics has been carried out on the basis of conventional statistical criteria. The known amounts of the standard solution of periodate (to the concentration 0.62 μg/mL) have been placed into 100-mL volumetric flask in 6 replicate aliquots, then the procedure described above has been applied to them. The points of intersection of linear parts of kinetic curves, got with the use of the least-squares method, have been assumed to represent induction periods, as for the points of the calibration curve. The results are shown in Table 1.

Table 1

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

t, s	X_i, μg/mL	$\bar{X}$	S	ΔC	(ΔC/C)100%	δ,%
present in sample: $C(IO_4^-) = 0.62$ μg/mL						
118.8; 112.1; 112.4; 114.7; 116.0; 115.2	0.669; 0.633; 0.631 0.646; 0.653; 0.649	0.65	0.015	0.016	2.6%	4.6%

According to the table data, the reproducibility of the results of periodate determination is expressed by the relative error 2.6%, while the relative error of accuracy proves to be 4.6%.

Conclusion

1. It is possible to apply measurement of the induction period of Landolt reaction of methyl orange with potassium bromate in the presence of hydrazine to determination of periodate ion, instead of the fixed time method at 150 s with previous equilibrating of all the reagents at 30±0.1 ºC.

2. The optimal conditions: concentration of methyl orange is 10 μg/mL, potassium bromate is $1.6 \cdot 10^{-4}$ M, hydrazine is $3 \cdot 10^{-5}$ M, hydrochloric acid is 0.03 M.

3. The metrological characteristics of periodate ion determination are as follows: calibration curve is linear in (0.06–0.9) μg/mL range, reproducibility error is 2.6%, and relative error is 4.6%.

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ПРИМЕНЕНИЕ ОКИСЛЕНИЯ МЕТИЛОРАНЖА В ПРИСУТСТВИИ ГИДРАЗИНА К КИНЕТИЧЕСКОМУ ОПРЕДЕЛЕНИЮ ПЕРИОДАТ-ИОНА

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Возможно применение индукционного периода реакции Ландольта метилоранжа с броматом калия в присутствии гидразина к определению периодат-иона. Оптимальные условия: HCl 0,03 М, метилоранж 10 мкг/мл, $KBrO_3$ $1{,}6\cdot10^{-4}$ М, N_2H_4 $3\cdot10^{-5}$ М. Градуировочный график линеен в диапазоне (0,06–0,9) мкг/мл периодат-иона, погрешность сходимости 2,6 %, относительная погрешность 4,6 %.

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

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