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ARTICLES

Kinetic-Spectrophotometric Determination of Trace Quantities of Thiocyanate Based on Its Landolt Effect on the Reaction of Bromate with Hydrochloric Acid[1]

Tayyebeh Madrakian, Akram Esmaeili, and Azizeh Abdolmaleki

Department of Chemistry, Faculty of Sciences, Bu-Ali Sina University, Hamadan, Iran

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Abstract—A new method for the rapid and sensitive determination of trace quantities of thiocyanate based on its Landolt effect on the bromate-hydrochloric acid reaction was developed. The induction period of the reaction is proportional to the SCN^- concentration. The decolorization of methyl orange by the reaction products was used to monitor the reaction spectrophotometrically at 525 nm. We were able to determine thiocyanate in the range 2×10^{-7}–4×10^{-5} M by this method. The relative standard deviation for 10 determinations of 1.5×10^{-6} M thiocyanate ion is 0.19% and the detection limit of the method was 7.00×10^{-8} M. The method was applied to the determination of thiocyanate in human blood serum and of saliva samples with satisfactory results.

INTRODUCTION

Digestion of certain types of food (particularly vegetables of the cabbage family) produces thiocyanate in the human organism. It is also generated by the metabolic degradation of the compounds in tobacco smoke that contain cyanide; this is the main source of thiocyanate in the human body. Thiocyanate is also administered as a drug in the treatment of thyroid conditions. In addition, higher concentrations of thiocyanate in the human body lead to vertigo-induced unconsciousness. Therefore, quantification of thiocyanate is of medical interest and is also an indicator for distinguishing between smokers and non-smokers [1–3].

Several methods for the determination of thiocyanate have been reported. These include the potentiometric [4], the amperometric [5, 6], ion-selective electrodes [7, 8], gas chromatography [9, 10], and the spectrophotometric [1, 11–13] and kinetic methods [14–16].

Unfortunately, most of these are laborious to perform and involve the use of harmful reagents. Also, because some of them require more expensive instruments, they cannot be easily popularized.

Landolt reactions have frequently been employed for analytical purposes because of their operational and instrumental simplicity and high sensitivity [17]. In this paper, we describe the development of a new method for the determination of thiocyanate, based on its "Landolt effect" on the reaction of bromate with hydrochloric acid. The reaction was monitored spectrophotometrically at the maximum wavelength of methyl orange (525 nm) while measuring the change in the absorbance over time.

[1] This article was submitted by the authours in English.

EXPERIMENTAL

Reagents

All reagents used were of analytical reagent grade, and solutions were prepared in triply distilled water. A 1000 mg/mL stock solution of thiocyanate was prepared by dissolving 0.1673 g potassium thiocyanate (Merck) in triply distilled water and diluting to the mark with water in a 100 mL volumetric flask. A 0.1 M potassium bromate solution was prepared by dissolving 1.770 g of $KBrO_3$ (Merck) in water and diluting to 100 mL in a volumetric flask. A solution of 100 mg/L methyl orange was prepared by dissolving 0.010 g methyl orange (Merck) in water and diluting to 100 mL with water. A hydrochloric acid solution was prepared by the appropriate dilution of concentrated hydrochloric acid (Merck).

Apparatus

A Shimadzu UV-265 UV–Visible spectrophotometer was used for the recording of absorbance-time graphs at fixed wavelength.

Procedure

The Landolt reaction was followed spectrophotometrically by monitoring the change in absorbance at 525 nm. An aliquot of sample solution containing 2×10^{-6}–7×10^{-5} M thiocyanate was transferred into a 10 mL volumetric flask. Then 1.0 mL of 2.8 M HCl was added, followed by 1.0 mL of 100 mg/L methyl orange solution. The solution was diluted to ca. 9 mL with water, and 0.7 mL of 0.013 M bromate solution was

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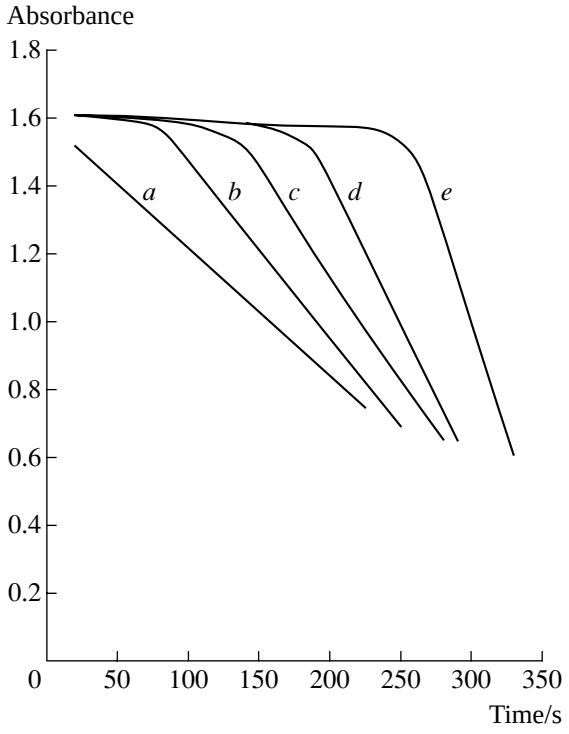

Fig. 1. Change in absorbance of 10 mg/L methyl orange solution over time in the presence of 9×10^{-4} M bromate, 0.28 M HCl and (*a*) 0.00; (*b*) 3×10^{-6}; (*c*) 1.2×10^{-6}; (*d*) 2.2×10^{-5}; (*e*) 3.7×10^{-5} M thiocyanate.

added and diluted to the mark with water. A portion of the solution was transferred to a 1-cm glass cell within 20 s for measurement of the variation in absorbance over time.

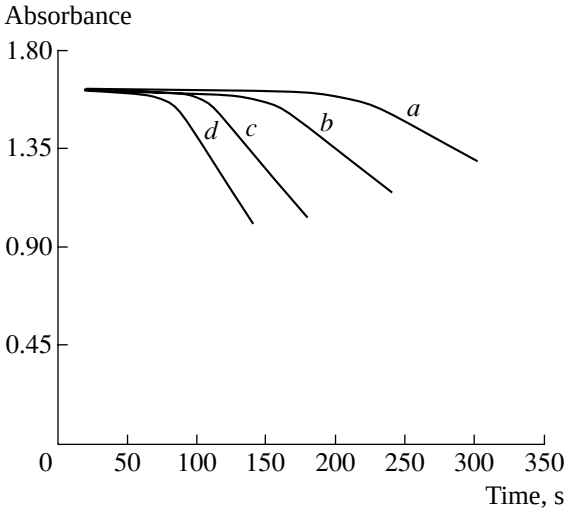

Fig. 2. Change in absorbance of 10 mg/L methyl orange solution with time in the presence of 9×10^{-4} M bromate, 1.23×10^{-5} M SCN^- and (*a*) 0.21; (*b*) 0.25; (*c*) 0.28; (*d*) 0.30 M HCl.

RESULTS AND DISCUSSION

Thiocyanate As a "Landolt Reagent"

In Landolt processes [18], a slow reaction is linked to a fast one by the reaction product of the former. The Landolt effect may be shown as follows:

$$A + B \xrightarrow{k_1} P, \quad (1)$$

$$P + L \xrightarrow{k_2} Y, \quad (2)$$

where $k_2 > k_1$. Since the second reaction is faster than the first, its product (P) can only be detected once L (the "Landolt reagent") has disappeared completely as a result of the second reaction.

The reaction of bromate with the chloride ions takes place in acidic media to produce Cl_2 and Br_2:

$$2BrO_3^- + 10Cl^- + 12H^+ \longrightarrow Br_2 + 5Cl_2 + 6H_2O. \quad (3)$$

The produced Cl_2 and Br_2 react with methyl orange and decolorize it [19]. Thiocyanate is a Landolt reagent in the reaction of bromate because the presence of thiocyanate in the solution causes the consumption of the produced Cl_2 and Br_2, and their reaction with thiocyanate is much faster than their reaction with methyl orange [20–22].

Figure 1 shows the graph of absorbance change over time for different concentrations of thiocyanate concentration, caused by the increase in the induction period of the reaction. A graph of the induction period versus thiocyanate concentration was linear over a certain range of thiocyanate concentration.

The induction period was measured mathematically from the regression equations of the linear parts of the

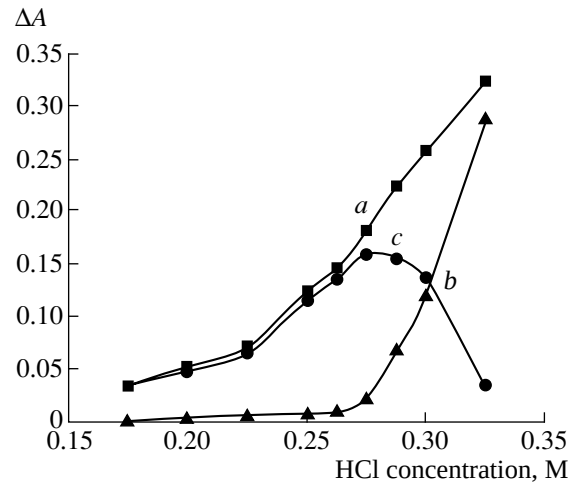

Fig. 3. Absorbance change for (*a*) blank and (*b*) sample reaction and (*c*) their difference as a function of HCl concentration condition: bromate, 9×10^{-4} M; thiocyanate, 1.2×10^{-5} M; methyl orange, 10 mg/L; t = 60 s.

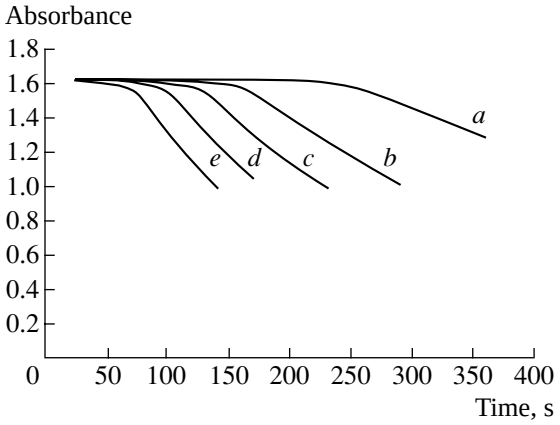

Fig. 4. Change in absorbance of 10 mg/L methyl orange solution over time in the presence of 0.28 M HCl, 1×10^{-5} M thiocyanate and (*a*) 5×10^{-4}; (*b*) 6×10^{-4}; (*c*) 7×10^{-4}; (*d*) 9×10^{-4}; (*e*) 11×10^{-4} M bromate.

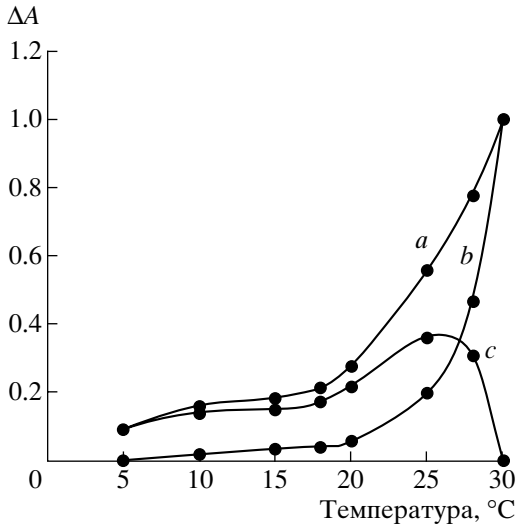

Fig. 5. Absorbance change for (*a*) blank and (*b*) sample reaction and (*c*) their difference as a function of temperature condition: bromate, 9×10^{-4} M, HCl, 0.28 M; thiocyanate, 1.2×10^{-5} M; methyl orange, 10 mg/L; t = 60 s.

absorbance-time graph. The regression equation for the first linear part of the graph is:

$$A = a_1 + b_1 t. \quad (4)$$

For the second linear part, it is

$$A = a_2 + b_2 t. \quad (5)$$

Equating [TCF1][TCF2]equations (4) and (5), the induction period is calculated as:

$$t_{ip} = (a_1 + a_2)/(b_1 - b_2). \quad (6)$$

Effect of Variables

Various experimental parameters were studied in order to obtain an optimized system. These parameters were optimized by setting all parameters constant, and optimized one at a time.

The effect of hydrochloric acid concentration was studied in the range 0.18–0.33 M. As Fig. 2 shows that an increase in HCl concentration caused a decrease in the induction period and an increase in the slope of the absorbance change after initiation of the methyl orange reaction. In order to find the optimum concentration of hydrochloric acid, the absorbance change for the blank reaction (the reaction in the absence of thiocyanate) and the sample reaction (the reaction in the presence of thiocyanate) at a fixed time of 60 s was measured as a function of HC1 concentration. The results are shown in Fig. 3. The difference between the absorbance change for the blank reaction and sample reaction shows a maximum at 0.28 M HC1. Therefore, a final concentration of 0.28 M acid was selected as optimum.

The effect of bromate concentration was also studied. Fig. 4 shows that an increase in bromate concentration caused a decrease in the induction period and an increase in the rate of the absorbance change after the initiation of the reaction. It was also observed that the calibration range differed according to the concentration of bromate and, hence, the concentration of bromate was selected on this basis (Table 1).

The effect of methyl orange concentration on both sample and blank reactions was studied in the range of 5–15 mg/L. The results showed that methyl orange concentration in the investigated range had no effect on the sample or blank reaction. Therefore, a concentration of 10 mg/L methyl orange was used for routine work.

The effect of temperature on the blank and sample reactions was studied in the range 5–30°C. The results are shown in Fig. 5. As the figure shows, the difference between the absorbance change for blank and sample reactions shows a maximum at 25°C. Therefore, 25°C was selected as the optimum temperature.

Table 1. Linear regression parameters of calibration data for different concentrations of bromate

$[BrO_3^-]$ (M)	Slope (s M^{-1})	Intercept (s)	Correlation coefficient	Calibration range (M)	Detection limit (M)
5.0×10^{-4}	3×10^6	36.8	0.9981	3.7×10^{-6}–4.4×10^{-5}	2.2×10^{-6}
1.4×10^{-4}	3×10^7	52.8	0.9993	2.2×10^{-7}–7.4×10^{-6}	7.0×10^{-8}

Table 2. Accuracy and precision of proposed method

SCN^- taken (M)	Relative error (%)	RSD, %
1.5×10^{-6}	0.15	2
7.4×10^{-7}	–1.1	3

Table 3. Tolerance limit for diverse ions on the determination of 1.2×10^{-5} M thiocyanate

Ion	Tolerance limit ratio
Ca^{2+}, Cl^-, Cd^{2+}, NO_3^-, Fe^{2+}, $H_2PO_4^-$, Na^+, SO_4^{2-}, CN^-, Hg^{2+}, ClO_3^-, Mn^{2+}, SO_3^{2-}, Pb^{2+}, $C_2O_4^{2-}$, NH_4^+,	100
Al^{3+}, Mg^{2+}, Ni^{2+}, Zn^{2+}	50
Fe^{3+}	20
I^-, Cr^{3+}, Cu^{2+}	5

Table 4. Determination of thiocyanate in real samples

Sample	Thiocyanate found, mg/L	
	proposed method	reported method
Nonsmoker saliva	51.98	51.62
Smoker saliva	170.23	172.25
Nonsmoker blood	2.91	2.94
Smoker blood	9.56	9.73

Ionic strength had no effect on the rate of both reactions up to 0.3 M; this is an advantage in the determination of thiocyanate in real samples.

Analytical Parameters

Calibration graphs were obtained under the optimum conditions described above for different concentrations of bromate (Table 1). The limit of detection (defined as $c_l = 3S_b/m$ [17], where c_l, S_b and m are the limit of detection, standard deviation of the blank signal and slope of the calibration graph, respectively) was also a function of bromate concentration (Table 1). For a final bromate concentration of 1.4×10^{-4} M, the limit of detection was 7.0×10^{-8} M.

To evaluate the accuracy and precision of the method, a series of independent standard samples was used. The results are shown in Table 2.

Selectivity

Under the chosen experimental conditions, the effect of various cations and anions on the reaction of 1.2×10^{-5} M thiocyanate was tested to study the selectivity of the proposed method. The results are summarized in Table 3. The tolerance limit was defined as the concentration of added ion causing less than ±3% relative error. Most of the cations and anions did not interfere, even when present in 100-fold excess over thiocyanate. Among the investigated ions, Cu^{2+}, Cr^{3+}, and I^- interfered.

Application

The method was applied to the determination of thiocyanate in blood serum and in saliva samples from smokers and non-smokers.

The saliva samples were collected and centrifuged for 5 min. These solutions were analyzed after appropriate dilution. The results are given in Table 4. The results are in good agreement with those given by the reported method in [1].

The blood samples were treated with 10% trichloroacetic acid after centrifugation for 30 min. and the filtrate was analyzed. Table 4 shows the results. As can be seen, there is good agreement between the results and those given by the standard method in [23].

The proposed method was compared with the some of the existing methods reported for the determination of thiocyanate. The results are given in Table 5. These

Table 5. Comparison between the proposed method and some other methods

Analytical method	Linear range (M)	Limit of detection (M)	Ref.
Kinetic spectrophotometry	8.6×10^{-7}–1.9×10^{-5}	4.3×10^{-7}	16
Kinetic spectrophotometry	3.5×10^{-7}–3.5×10^{-6}	2.7×10^{-7}	14
SIA spectrophotometry	3.5×10^{-5}–2.6×10^{-3}	1.9×10^{-5}	24
Spectrophotometry	5.6×10^{-7}–5.2×10^{-5}	–	25
Proposed	2.2×10^{-7}–4.4×10^{-5}	7.0×10^{-8}	–

results indicate that the proposed method provides a lower limit of detection and a wider dynamic range than the existing methods.

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