

*Chemistry*

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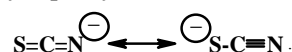
SPECTROPHOTOMETRIC DETERMINATION OF THE THIOCYANATE IONS USING THIONINE BASIC ORGANIC DYE

The optimized conditions for measuring thiocyanate by extracting through formation of ion pair with thionine basic dye (Lauth's violet) have been determined by means of spectrophotometric method. Thionine was extracted at the presence of thiocyanate and has absorption spectrum at the 600 nm wavelength. The increase in the intensity of absorption takes place, because of thionine and thiocyanate ionic associate (ion pair) formation and transfer to the organic phase (extraction). In this investigation all parameters were kept constant except the one to be optimized. The optimal conditions for the determination of thiocyanate ion by means of thionine are the following: solvent – methylisobutyl keton; [thionine] –  $1,566 \cdot 10^{-4}$  mol/l; medium acidity – pH 6–7; temperature –  $30^{\circ}\text{C}$ ; ionic strength – 0,0; extraction process duration – 240 s.

**Introduction.** Thiocyanate or so called rhodanyde is the  $[\text{SCN}]^{-}$  anion. Common compounds include colorless salts potassium and sodium thiocyanates. Organic compounds containing the functional group SCN are also called thiocyanates [1–3]. Thiocyanate is analogous to the cyanate ion ( $[\text{OCN}]^{-}$ ), where oxygen is replaced by sulphur.  $[\text{SCN}]^{-}$  is one of the pseudohalides, due to the similarity of its reactions to that of halide ions. Thiocyanate is produced by the reaction of elemental sulfur or thiosulfate with cyanide:



The latter reaction is catalyzed by the enzyme sulfotransferase known as rhodanase and may be relevant to detoxification of cyanides. Thiocyanate shares its negative charge approximately equally between sulfur and nitrogen atoms:



Potassium, sodium and ammonium thiocyanates are important salts of the thiocyanate anion, one of the pseudohalides. The compound has a low melting point relative to the most other inorganic salts. Thiocyanates have wide application in different branches of industry: mining, agricultural toxins etc. [4]. Dilute aqueous KSCN is occasionally used for moderately realistic blood effects in cinema and theater. It can be painted onto a surface or kept as a colorless solution.

When it contacts with ferric chloride solution ( $\text{FeCl}_3$ ), the product of the reaction is a blood red. Thus, this chemical is often used to create the effect of “stigmata” [5]. Because both solutions are colorless, they can be placed separately on each hand. When the hands are brought into contact, the solutions react and the effect looks remarkably like stigmata.

**Experimental Method.** Thionine can be extracted at the presence of thiocyanate, because of ionic associate (ion pair) formation. It has maximum absorbance at the 600 nm wavelength. The increase in organic phase absorption at this wavelength is appropriate to thiocyanate ion amount.

The base of the work is the measurement of organic phase absorption extracted in 600 nm wavelength. In order to perform the experiment and to reach the optimized conditions for effective parameter in measuring thiocyanate, we should examine the absorption value for the sample and blank solutions. The quantity used for the optimization was the absorption difference for the sample and blank solutions.

*The method of work is as follows.* Firstly all the solutions were put in the thermostat, in order to make the blank and sample solutions. In a 10 ml balloon 1 ml of the considered buffer (pH 1–7) and the specific volumes of thionin and thiocyanate with the concentration 10  $\mu\text{g/ml}$  is added, and then we transfer it to the separating funnel. Then 10 ml pure solvent was added and stirred it for 4 min, and then organic phase was isolated and the absorption level was examined at 600 nm.

For the blank solution the same procedure was used, with the difference that thiocyanate was not added. In order to ensure accuracy each measurement was repeated for 5 times. Measured parameters were: the kind of solvent, dye concentration, pH value, ionic strength, temperature and the process duration. During the measurement all the parameters were kept fixed, and only the parameter to be optimized was changed, and at last absorption difference for blank and sample ( $A_s - A_b$ ) in 4 min after the beginning was measured.

### Results Discussion.

**1. The effect of solvent.** In order to choose suitable solvent several organic solvents such as chloroform, carbon tetrachloride, toluene, dichloromethane, isobutanol, methylisobutyl ketone, acetone, methanol, ethanol, acetonitrile were studied. When methylisobutyl ketone was used, the maximal absorption was measured, that is the maximal extraction took place. Consequently, the suitable solvent is methylisobutyl ketone (Tab. 1).

Table 1

*The effect of solvent*

Solvent	Chloroform	Carbon tetrachloride	Toluene	Dichloromethane	Isobutanol	Methylisobutyl ketone	Acetone	Methanol	Ethanol	Acetonitrile
$\Delta A = A_s - A_b$	0,010	0,008	0,003	0,017	0,010	0,059	0,012	0,013	0,003	0,006

**2. The survey of thionine effect.** The effect of thionine concentration was studied in the range of  $0,384 \cdot 10^{-4}$ – $1,705 \cdot 10^{-4}$  mol/l and considering the results,

the concentration  $1,566 \cdot 10^{-4}$  mol/l of thionine as the optimized one was chosen (Tab. 2).

Table 2

*A survey of thionine concentration effect*

[thionine] $\times 10^5$ , mol/l	0,348	1,04	1,74	2,43	3,13	3,83	4,52	5,22	5,92	6,61	7,31	8,00	8,70
$\Delta A = A_s - A_b$	0,042	0,051	0,063	0,071	0,079	0,089	0,101	0,111	0,123	0,132	0,143	0,157	0,167

[thionine] $\times 10^5$ , mol/l	9,40	10,09	10,79	11,48	12,18	12,88	13,57	14,27	14,96	15,66	16,36	17,05
$\Delta A = A_s - A_b$	0,181	0,193	0,208	0,218	0,232	0,241	0,256	0,273	0,284	0,299	0,301	0,300

**3. The survey of pH effect.** The effect of pH on the absorption using the buffers pH (1–7) was studied. The results showed that the most suitable pH, at which the maximal differences in absorption were observed, correspond to pH 6–7 (Tab. 3).

Table 3

*The survey of pH effect*

pH value	1	2	3	4	5	6	7
$\Delta A = A_s - A_b$	0,020	0,081	0,131	0,155	0,211	0,260	0,255

**4. A survey of ionic strength.** In the survey of ionic strength potassium chloride solution was used. The results showed: with the increase of ionic strength of the reaction media the sensitivity is decreased (Tab. 4).

Table 4

*The survey of ionic strength*

Ionic strength	0,00	0,05	0,10	0,15	0,20	0,25
$\Delta A = A_s - A_b$	0,243	0,121	0,103	0,072	0,047	0,029

**5. The effect of temperature.** The reaction in the temperature range of 5–55<sup>o</sup>C was studied. All the solutions before using were placed in the thermostat at proper temperature. Then the results show that the maximum sensitivity happens at 30<sup>o</sup>C.

**6. The effect of time.** In order to examine the extraction time effect all the optimized conditions reached in the previous phases were used. The blank and sample absorption in 30–360 s time after the beginning of the reaction was studied.

Table 5

## The effect of time

$t, s$	30	60	90	120	150	180	210	240	270	300	330	360
$\Delta A = A_s - A_b$	0,215	0,230	0,241	0,255	0,261	0,275	0,287	0,301	0,299	0,298	0,300	0,299

Until 240 s the difference in absorption in blank and sample increased (Tab. 5). As a result, the time of 240 s was chosen as the optimized time.

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## ՄՈՂԱՍՄԱԴՄԵՆՆԻ ՄՈԱՌԵՖԴՈՍ

ԹԻՈՑԻԱՆԱՏ-ԻՈՆԻ ՍՊԵԿՏՐԱԼՈՒՄԱՉԱՓԱԿԱՆ ՈՐՈՇՈՒՄԸ  
ՀԻՄՆԱՅԻՆ ՕՐԳԱՆԱԿԱՆ ՆԵՐԿԱՆՅՈՒԹ ԹԻՈՆԻՆԻ ԿԻՐԱՌՄԱՍԲ

## Ա մ փ ո փ ու մ

Հաստատվել են թիոնին հիմնային ներկայության հետ իոնական ասոցիատի առաջացման միջոցով թիոցիանատ իոնի լուծահանման սպեկտրալուսաչափական որոշման օպտիմալ պայմանները: Թիոնինը լուծահանվում է թիոցիանատ-իոնի ներկայությամբ, որն ունի կլանման շերտ սպեկտրի տեսանելի մարզում 600 նմ ալիքի տակ: Կլանման մեծացումը տեղի է ունենում թիոնինի և թիոցիանատ-իոնի միջև իոնական ասոցիատի (իոնական զույգի) առաջացման և վերջինիս օրգանական ֆազ լուծահանման հետևանքով: Հետազոտության ընթացքում բոլոր պարամետրերը հաստատուն են պահպանվել, բացի մեկից, որը ենթակվել է օպտիմալացման: Թիոնինի կիրառմամբ թիոցիանատի որոշման օպտիմալ պայմաններն են. լուծիչը՝ մեթիլիզոբութիլկետոն; [թիոնին]= $1,566 \cdot 10^{-4}$  մոլ/լ; միջավայրի թթվությունը՝ pH 6–7; ջերմաստիճանը՝ 30°C; իոնական ուժը՝ 0,0; լուծահանման գործընթացի տևողությունը՝ 240 ս:

МОХАММАДМЕХДИ МОАРЕФДОСТ

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ТИОЦИАНАТ-ИОНОВ  
С ПОМОЩЬЮ ОРГАНИЧЕСКОГО ОСНОВНОГО КРАСИТЕЛЯ  
ТИОНИНА

Резюме

Определены оптимальные условия для экстракционно-спектрофотометрического определения тиоцианат-иона посредством образования ионного ассоциата с основным органическим красителем тионином. Тионин экстрагируется в присутствии тиоцианат-иона, который имеет полосу поглощения в видимой области спектра при длине волны 600 нм. Увеличение поглощения имеет место вследствие образования ионного ассоциата (ионной пары) между тионином и тиоцианат-ионом и переноса последнего в органическую фазу. В ходе исследования все параметры поддерживались постоянными, кроме одного, который подвергался оптимизации. Оптимальные условия для определения тиоцианат-иона при помощи тионина следующие: растворитель-экстрагент – метилизобутилкетон; [тионин]= $1,566 \cdot 10^{-4}$  моль/л, кислотность среды – pH 6–7; температура – 30<sup>0</sup>C; ионная сила – 0,0; продолжительность экстракции – 240 с.