

## Utilization of Iodine in the Spectrophotometric Determination of Azide and Thiocyanate Anions in Acetonitrile

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A simple, rapid, accurate and highly sensitive spectrophotometric method for the determination of azide thiocyanate anions in acetonitrile (MeCN) medium is described. The method is based on the formation of yellow colour complexes,  $I_2N_3^-$  and  $I_2SCN^-$ , by the reaction of  $N_3^-$  and  $SCN^-$  anion with iodine in MeCN. Beer's law is obeyed within the concentration range 1.5–21.2 and 0.5–24  $\mu\text{g/mL}$  of  $N_3^-$  and  $SCN^-$  respectively. A spectrophotometric method has been developed for the titration of azide and thiocyanate anions with iodine in MeCN. The concentration ranges as evaluated by the direct titration are 1.68–22 and 0.58–25.2  $\mu\text{g/mL}$  for  $N_3^-$  and  $SCN^-$ , respectively. The molar absorptivity, Sandell sensitivity, relative standard deviation and recovery percent are evaluated. The formation constants ( $\log K_f$ ) of the  $I_2SCN^-$  and  $I_2N_3^-$  complexes have been evaluated spectro photometrically at  $25 \pm 0.1^\circ\text{C}$  as  $6.60 \pm 0.02$  and  $6.02 \pm 0.03$ , respectively. Iodide and bromide anions interfere in the determination of thiocyanate and azide anions, transition metals and chloride anion interfere in the determination of thiocyanate and azide, respectively, when present in any percentage.

### INTRODUCTION

Methods based on the spectrophotometric determination of thiocyanate using dye cation<sup>1</sup>, metal cation<sup>2</sup>, mercurimetric indicator<sup>3</sup> and oxidation agent<sup>4</sup> have been reported. Potentiometric titration using ion-selective electrodes has been applied in the analysis of thiocyanate anion<sup>5</sup>. Potentiometric and coulometric determination of thiocyanate by oxidimetric titration have been used<sup>6, 7</sup>. Various amperometric titrations<sup>8</sup>, polarographic analyses<sup>9</sup>, cathodic stripping voltammetric analyses<sup>10</sup>, gas chromatographic<sup>11</sup>, liquid eluent ion-chromatographic<sup>12</sup>, high-performance liquid chromatographic<sup>13</sup>, flame atomic absorption spectrometric<sup>14</sup> and kinetic fluorophotometric<sup>15</sup> procedures for the determination of thiocyanate anion have been reported.

Several methods have been used for the determination of azide anion. These include potentiometry using ion-selective electrode<sup>16</sup>, voltammetry<sup>17</sup>, amperometry<sup>18</sup>, polarography<sup>19</sup>, high-performance liquid chromatography<sup>20</sup>, gas chromatography<sup>21</sup> and spectrophotometry<sup>22</sup>.

The aim of this work was to find new spectrophotometric methods that are

simple, time-saving and accurate for the micro-determination of thiocyanate and azide ions in non-aqueous solvents.

## EXPERIMENTAL

A spectrophotometer model UV-240 with graphic printer PR-1 using 0.1 cm quartz cells was used for all spectral measurements and a circulating water bath model TB-85 connected to thermo-spacer in the spectrophotometer was used to maintain constant temperature at  $25.0 \pm 0.1$  °C (Shimadzu Instruments Co., Japan). 10 mm quartz cells were used for the iodine spectrum.

Iodine, potassium thiocyanate and sodium azide were reagent grade, acetonitrile (MeCN) was for HPLC use. Iodine was purified twice by sublimation.  $1 \times 10^{-2}$  mol dm<sup>-3</sup> solution of iodine was freshly prepared in acetonitrile.  $2 \times 10^{-2}$  mol dm<sup>-3</sup> solutions of KSCN and NaN<sub>3</sub> were prepared by dissolving appropriate weight of the reagent in 100 mL acetonitrile. The solutions are stable for at least one week at room temperature.

### General Procedure

*Standard curve method:* Volumes ranging from 12.0–550 µL (0.02 M) of SCN<sup>-</sup> or N<sub>3</sub><sup>-</sup> anions and 1250 µL of 0.01 M iodine were transferred to a 25 mL measuring flask and made up to the mark with acetonitrile. The absorbance of the yellow complex was measured instantaneously at 300 nm for iodine-thiocyanate complex and 292 and 360 nm for iodine-azide complex against a reagent blank. The concentration was calculated from a calibration curve prepared in the same manner. The complexes are stable for at least two days at room temperature.

*Spectral titration method:* A volume containing 14.5–630 µg of SCN<sup>-</sup> or 42–550 µg of N<sub>3</sub><sup>-</sup> anions was transferred to a 25 mL volumetric flask and made up to the mark with acetonitrile. The contents of the volumetric flask were transferred to a titration cell. 0.01 mol dm<sup>-3</sup> iodine solution was added progressively from a microburette. Reaction of SCN<sup>-</sup> or N<sub>3</sub><sup>-</sup> anions was followed by recording the disappearance of the UV-spectrum of the anions and the emergence of new peaks, resulting from the formation of the iodine-thiocyanate or -azide complex, after each addition of the reagent solution. A graph of absorbance vs. the volume of added titrant was constructed and the end-point determined.

## RESULTS AND DISCUSSION

The reaction of iodine with thiocyanate and azide anions in acetonitrile medium results in the formation of an intense yellow coloured product which exhibits an absorption maximum at 300 nm for iodine-thiocyanate complex and 292, 360 nm for iodine-azide complex as shown in Fig. 1. This spectrum is similar to that obtained by the reaction of iodine with iodide anion in acetonitrile, dimethylformamide and dimethylsulfoxide media<sup>23</sup>. The I<sub>2</sub>SCN<sup>-</sup> and I<sub>2</sub>N<sub>3</sub><sup>-</sup> complexes in the solvent used were formed in the ratio [I<sub>2</sub>] : [SCN<sup>-</sup>] or [I<sub>2</sub>] : [N<sub>3</sub><sup>-</sup>] = 1 : 1. There was no other complexes formed in MeCN. The most

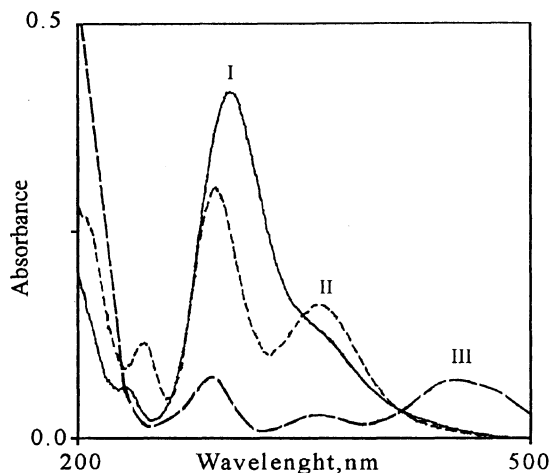


Fig. 1. Absorption spectra of:  $\text{SCN}^-$  (I),  $\text{N}_3^-$  (II) complexes with iodine and iodine (III) in MeCN. Concentration of thiocyanate, azide and iodine =  $1 \times 10^{-4}$  M

important spectral characteristics of the reaction of iodine with thiocyanate and azide anions investigated are presented in Table-1.

TABLE-1  
SPECTRAL CHARACTERISTICS AND QUANTITATIVE PARAMETERS OF THE COLOURED REACTION PRODUCTS OF THIOCYANATE AND AZIDE WITH IODINE IN MeCN

Parameters	$\text{SCN}^-$	$\text{N}_3^-$	
Wavelength (nm)	300	292	360
Molar absorptivity, $\text{L mol}^{-1} \text{cm}^{-1}$	$4.75 \times 10^4$	$3.36 \times 10^4$	$1.64 \times 10^4$
Beer's law limit, $\mu\text{g mL}^{-1}$	0.50–24		1.5–21.2
Sandell sensitivity, $\mu\text{g cm}^{-2}$	0.0024		0.0025
Regression equation*			
Intercept (b)	0.009	0.095	0.058
Slope (m)	0.082	0.068	0.036
Correlation coefficient (r)	0.999	0.998	0.998
Range of error, %	$\pm 0.670$	$\pm 0.83$	$\pm 0.89$
Ringbom optimum concentration range, $\mu\text{g mL}^{-1}$	1.4–20.0		2.6–18.0

\*A = mc + b where c is the concentration in  $\mu\text{g mL}^{-1}$ .

The coloured species may be formed through  $\pi$ -electron donation, regarding the thiocyanate or azide as a donor and the iodine as acceptor, to form charge-transfer complex.

## Quantification

A linear correlation was found between absorbance and concentration in the ranges given in Table-1. The correlation coefficient, intercept and slope values for the calibration data of thiocyanate and azide are calculated using the least-squares method. Beer's law plots can also be used for calculation of the applicable concentration ranges.

The mean molar absorptivity ( $\epsilon$ ) and Sandell sensitivity ( $S$ ) of the resulting coloured products as calculated from Beer's law are presented in Table-1. For more accurate results, Ringbom optimum concentration ranges were evaluated, as shown in Table-1. In order to determine the accuracy and precision of the method, the recommended procedure was applied. The standard deviations, relative standard deviations, the standard analytical errors and 95% confidence limits of the different amounts tested were determined from the calibration curve, as recorded in Table-2.

TABLE-2  
EVALUATION OF ACCURACY AND PRECISION OF THE PROPOSED METHOD

Anion	$\mu\text{g mL}^{-1}$			Recovery %	RSD %	Standard error	Confidence limits
	Taken	Found*	S.D.				
$\text{SCN}^-$	1.20	1.19	0.02	99.16	1.68	0.009	$1.19 \pm 0.025$
	2.40	2.41	0.03	100.14	1.24	0.013	$2.41 \pm 0.037$
	4.00	4.02	0.02	100.50	0.49	0.009	$4.02 \pm 0.025$
	5.80	5.80	0.04	100.00	0.69	0.018	$5.80 \pm 0.049$
	10.00	10.01	0.06	100.10	0.60	0.027	$10.01 \pm 0.074$
	14.00	13.97	0.08	99.78	0.57	0.036	$13.97 \pm 0.099$
	20.00	19.96	0.07	99.80	0.35	0.031	$19.96 \pm 0.087$
$\text{N}_3^-$	2.00	1.96	0.04	98.00	2.04	0.018	$1.96 \pm 0.049$
	4.00	3.98	0.05	99.50	1.25	0.022	$3.98 \pm 0.062$
	6.00	6.05	0.07	100.83	1.15	0.031	$6.05 \pm 0.087$
	8.00	8.02	0.04	100.25	0.49	0.018	$8.02 \pm 0.049$
	10.00	10.00	0.06	100.00	0.60	0.027	$10.00 \pm 0.074$
	14.00	14.04	0.08	100.28	0.57	0.036	$14.04 \pm 0.099$
	18.00	17.98	0.07	99.88	0.39	0.031	$17.98 \pm 0.087$

\*Average of five determinations

## Titration

Acetonitrile solutions of thiocyanate and azide anions have been titrated spectrophotometrically by acetonitrile solutions of iodine. In the titration of thiocyanate, peak for the thiocyanate anions at 234 nm disappears gradually with iodine added. At the same time, the peak resulting from the formation of  $\text{I}_2\text{SCN}^-$  complex grows gradually at 300 nm. Finally, absorbance peak reaches a constant value and remains unchanged with addition excess of iodine. Titration

of azide anions by iodine in MeCN is similar to that found for thiocyanate anions, where the peaks resulting from the formation of  $I_2N_3^-$  complex appear at 292 and 360 nm gradually until constant absorbance is reached. The absorbance value at  $\lambda_{max}$  vs. the volume of added iodine was constructed and the end-point determined.

The results show one well-defined inflection point in the titration curves, corresponding to the expected end-point for  $I_2SCN^-$  and  $I_2N_3^-$  formation in MeCN. There was no point of inflection corresponding to  $I_4SCN^-$  and  $I_4N_3^-$  formation.

Representative titration curves are shown in Figure 2. Two straight lines are obtained intersecting at the end-point, the first branch ascending sharply; the increase of absorbance is attributed to the formation of yellow  $I_2SCN^-$  and  $I_2N_3^-$  complexes in the solution as a result of the reaction. After the end-point, the titration curves indicate a constant absorbance, curve (I), or a slow increase, curve (II), despite the excess of the reagent.

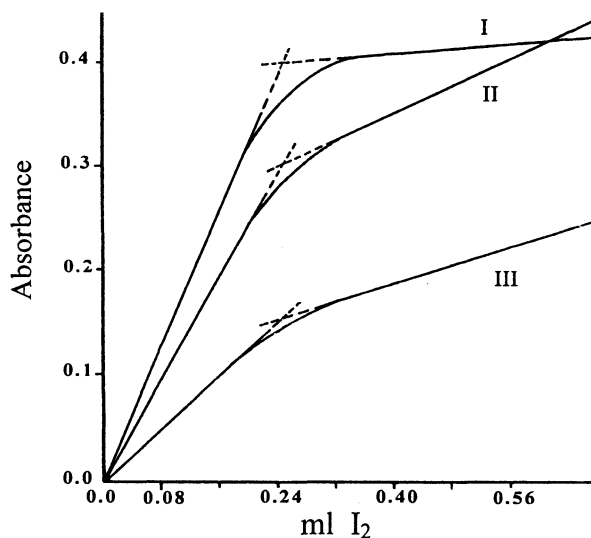


Fig. 2. Spectrophotometric titration curves of 25 mL  $1 \times 10^{-4}$  M of  $SCN^-$  (I) at 300 nm and  $N_3^-$  (II, III) at 292 and 360 nm, resp., vs. 0.01 M  $I_2$  solution in MeCN.

The results from the spectrophotometric titration are summarized in Table-3 and show that good recoveries and standard deviations were obtained. The optimum concentration ranges for determination of thiocyanate and azide anions were in the range 0.58–25.2 and 1.68–22  $\mu\text{g/mL}$ , respectively, at which sharp inflections were obtained.

TABLE-3  
SPECTROPHOTOMETRIC TITRATION OF THIOCYANATE AND AZIDE ANIONS  
USING IODINE IN MeCN

SCN <sup>-</sup>				N <sub>3</sub> <sup>-</sup>			
Taken (µg/mL)	Found* (µg/mL)	Recovery (%)	S.D. (µg/mL)	Taken (µg/mL)	Found* (µg/mL)	Recovery (%)	S.D. (µg/mL)
0.58	0.56	96.55	0.01	1.68	1.63	97.02	0.02
1.74	1.73	99.42	0.02	2.50	2.47	98.80	0.03
2.90	2.89	99.65	0.04	3.40	3.39	99.70	0.07
5.80	5.82	100.34	0.07	4.20	4.23	100.71	0.06
8.70	8.71	100.11	0.06	6.30	6.28	99.68	0.05
11.60	11.60	100.00	0.04	8.40	8.39	99.88	0.04
14.50	14.52	100.13	0.05	10.50	10.50	100.00	0.09
17.40	17.40	100.00	0.06	12.60	12.61	100.08	0.08
20.30	20.31	100.04	0.07	16.80	16.79	99.94	0.07
25.20	25.18	99.92	0.05	22.00	22.00	100.00	0.06

\*Average of five determinations.

### Formation Constant

The formation constants ( $\log K_f$ ) of the  $I_2SCN^-$  and  $I_2N_3^-$  complexes have been calculated spectrophotometrically in MeCN at  $25 \pm 0.1^\circ C$  as  $6.60 \pm 0.02$  and  $6.02 \pm 0.03$ , respectively. The equation for this calculation is used from our earlier work<sup>23</sup>. The stabilities of these complexes in MeCN are very much greater than those in the water<sup>24, 25</sup>.

### Interferences

No interferences were observed in the determination of thiocyanate anion with iodine in acetonitrile from the presence of  $Cl^-$ ,  $SO_4^{2-}$ ,  $CN^-$ ,  $NO_3^-$  and  $N_3^-$  anions when present in 10-fold molar excess, whereas  $I^-$ ,  $Br^-$  and transition metals interfered when present in any percent. Also there was no interferences from  $SO_4^{2-}$ ,  $NO_3^-$  and  $CN^-$  on the determination of  $N_3^-$  with iodine, whereas  $I^-$ ,  $Br^-$  and  $Cl^-$  interfered when present in any percentage.

### Conclusion

The proposed methods are simpler, less time consuming, direct, wider range of determination and higher sensitivity and molar absorptivity than methods in aqueous solutions<sup>1-4, 22</sup>. It is clear that iodine is highly superior compared with other reagents, with very rapid formation of the chromophores in MeCN and very high stability of colour.

The titration method is better than standard curve method in the determination of  $SCN^-$  and  $N_3^-$  anions with iodine due to the wider range and faster assays of determination.

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