Spectrophotometric flow injection determination of thiocyanate

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A spectrophotometric flow injection procedure is described for the determination of thiocyanate in aqueous medium over the range of 0.005-1.800 μg/ml. The effect of reagent concentration, reagent flow rates, sample volume, length of the reaction coil and temperature are reported. The limit of detection is 0.62 ng/ml of thiocyanate. Thiocyanate can be determined at a rate of 40 ± 5 samples/h. The relative standard deviation for ten replicate analysis of 0.060 μg/ml of thiocyanate is 1.3%. The system has been applied for the determination of thiocyanate in water, synthetic sample, and biological fluids.

Thiocyanate is the product of detoxication process of cyanide, usually present in low concentration in biological fluids. Determination of thiocyanate in serum, urine or saliva have consequently been used for monitoring exposure to hydrogen cyanide from tobacco smoke[1-3], fire atmosphere[4] and some vegetables that contain cyanogenic glycosides.

Several methods have been reported for the determination of thiocyanate in water and biological fluids[5-7]. Catalytic methods have also been reported for determining of thiocyanate[8-10]. But these methods suffer from problems like interfering ions, high limits of detection, long reaction time, etc.

Flow injection analysis (FIA) has found wide acceptance as a routine laboratory tool[11] due to its simplicity, low cost, and reliability. The present note describes an FIA-based spectrophotometric method for the determination of thiocyanate in water and urine.

Experimental

All the solutions were prepared in doubly distilled water. All reagents were of AR grade.

Stock thiocyanate solution (1000 μg/ml) was prepared by dissolving 0.396 g of dried NaSCN (E Merck) in EDTA solution (1×10^{-3} M). Sodium azide solution (3.00 M) was prepared by dis-

solving 19.503 g NaN$_3$ (E Merck) in 100 ml distilled water. I$_3^-$ solution (0.0100 M) was prepared by dissolving 0.2540 g of I$_2$ (E Merck) in KI solution (4.50 g KI/100 ml) in a 100-ml volumetric flask.

The flow injection system used for the analysis has been described earlier[12].

Recommended procedure

Sodium azide solution and buffer solution (phosphoric acid, phosphate), (Fig. 1, R$_2$), iodine solution (Fig. 1, R$_3$) and water (Fig. 1, R$_1$), previously thermostated at 25°C, were pumped through a peristaltic pump at a rate of 30 ml/h. At joint S, an aliquot (300 μl) of the thiocyanate solution was injected into the correspondence carrier solution, which was pumped continuously. The decrease in absorbance signal was recorded and the peak height was measured. The concentration of thiocyanate was obtained by comparison with a calibration graph plotted with standard solutions. For general purposes (0.005-0.500 μg/ml of thiocyanate), the following optimum condition are recommended : sodium azide, 0.40 M; iodine solution 1.75×10^{-4} M; pH 5.0; length of the mixing coil, 300 cm; flow rate for each solutions, 30 ml/h; sample injection volume, 300 μg/ml; λ_{max} 349 nm, and temperature of 25°C. For higher concentration of thiocyanate (0.500-1.300 μg/ml), the above conditions with 0.20 M sodium azide solution, and for thiocyanate, concentration of 1.300-1.800 μg/ml, 0.05 M sodium azide solution were used.

Results and discussion

Preliminary tests were performed with 0.100 μg/ml of thiocyanate. The effect of reagent concentration, temperature and other variables were studied to give the best sensitivity.

The effects of reagent concentration and temperature was studied with a pump flow rate of 30 ml/h for each of the reagents. Sample volume of
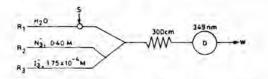

Fig. 1—Schematic diagram of the flow injection system

Table 1—Determination of thiocyanate in real samples

Sample	SCN⁻ added (μg/ml)	SCN⁻ found (μg/ml)		RSD% (n = 10)
		Proposed method	Ref. 6	
S^{2-*}, SO_3^{2-*}	0.250	0.255	—	1,8
$Cu(II)^*, Ag(I)^*$	0.500	0.491	—	1.7
Sewage water	—	0.230	0.220	2.5
Sewage water	0.500	0.721	0.720	2.1
River water	—	0.052	0.05	2.5
River water	0.250	0.300	0.310	2.0
Urine	—	2.25	2.24	2.2
Urine	0.50	2.74	2.70	2.0

*1000 μg/ml was used.

250 μl, and reaction mixing coil length of 240 cm were used.

The effect of pH on the peak heights was studied with 1.50×10^{-4} M iodine solution and 0.40 M azide at buffer solutions with pH varying between 1 and 10. Results show that the peak heights increased with increase of pH between 1.0 and 5.0, but at higher pH values, peak height decreased. This indicates that, in the absence of thiocyanate, the reaction takes place rapidly at basic media. A pH of 5.0 was chosen as an optimum value.

The effect of azide concentration (0.080-0.60 M) on the peak height was studied at pH 5.0 with 1.5×10^{-4} M iodine solution. The results show that by increasing azide concentration up to 0.40 M, peak height increased. Sodium azide concentration of 0.40 M was chosen as optimum concentration for further studies.

The effect of iodine concentration (6.0-17×10^{-5} M) was investigated with 0.40 M sodium azide at pH 5.0. The peak height increased with increasing concentration of iodine solution. Higher concentration of iodine ($> 17 \times 10^{-5}$ M) can not be used due to the molar absorptivity. From the results, 1.75×10^{-4} M iodine solution was selected as the optimum conentration.

The effect of temperature on the peak height and thus sensitivity was studied in the temperature range of 5-50°C at the optimum conditions discussed above. With increasing temperature from 10-50°C, the peak height decreased. Further studies were carried out at 25°C as the cell used was not thermostated.

The sensitivity of the thiocyanate determination largely depends on the flow rate of the reagents and tube length of the reaction coil. The peak heights increased as the flow rate decreased, whereas peak broadening and tailing were observed with low flow rates. This effect is due to increased dispersion of the sample zone leading to unfavourable sampling rate. For practical purposes flow rate was maintained at 30 ml/h for each of the three reagents system. Increasing the length of the reaction coil from 40-350 cm increased the peak height, because the longer residence time of the sample zone allowed greater reaction. However peak broadening and tailing were observed with long reaction coils. Thus a reaction coil of 300 cm was selected for the study.

The effect of the sample volume was investigated. The sensitivity increased with increasing sample volume from 250-500 μl, while sample volume > 300 μl led to peak broadening and tailing. So 300 μl was chosen as optimum sample volume for the present work.

Interference study

The effect of interfering ions which generally accompany thiocyanate have been studied at the optimum conditions given above for 0.100 μg/ml thicyanate. Ba(II), Ca(II), Mg(II), Na⁺, K⁺, Mn(II), Sr(II), La(III), Mn(II), Ni(II), Al(III), Zn(II), NH_4^+, Cd(II), Cl⁻, I⁻, Br⁻, ClO_4^-, ClO_3^-, $C_2O_4^{2-}$, BO_3^{2-}, CO_3^{2-}, SO_4^{2-}, NO_3^-, F⁻, acetate and tartrate were tolerated up to 10000 μg/ml; Bi(III), Co(II) and Cr(III) were tolerated up to 1000 μg/ml; Fe(III), Ce(III), Hg(II), Ag(I) and Cu(II) were tolerated up to 50 μg/ml; S^{2-}, SO_3^{2-} and $S_2O_5^{2-}$ were tolerat-

ed up to 5 μg/ml. The interference may be either due to the formation of a precipitate with azide [e.g. Ag(I)] or with iodine [such as Cu(II)] or because the interfering ions behave similar to thiocyanate (such as S^{2-}).

For the removal of S^{2-} and SO_3^{2-}, the sample was placed in a flask and 10 ml of 0.02 M HCl was added from a separatory funnel. Nitrogen gas was evolved through the reaction flask for 15 min and NaOH solution (5 ml of 0.02 M) was added to the flask. The thiocyanate content was then determined by the recommended procedure (Table 1).

Determination of thiocyanate in real samples

Natural water, biological fluids, and synthetic samples free from suspended matter were tested for thiocyanate. Sewage water and urine were initially filtered through filter paper (Whatman No. 1). The sample (10 ml) was passed through a cation exchanger resin (strongly acidic, Na^+-form). Distilled water was used as the eluent and the thiocyanate concentration was determined by the

proposed method. The results are given in Table 1.

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