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Thin-layer chromatographic separation, colorimetric determination and recovery of thiocyanate from photogenic waste, river and sea waters

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Abstract

TLC was used to study the retention behaviour of some inorganic anions (SCN^- , NO_2^- , MnO_4^- , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MoO_4^{2-} , $\text{Mo}_7\text{O}_{24}^{6-}$, $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$) and metal ions (Fe^{3+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Hg^{2+} , UO_2^{2+} , VO^{2+} , Ag^+ , Mn^{2+} and Bi^{3+}) on cellulose, Kieselguhr and their mixtures. Mixed solvent systems containing 0.1 M NH_4OH and CH_3COCH_3 were used as eluents. SCN^- separated from other ions was determined by spectrophotometry at 460 nm using acidic FeCl_3 solution as chromogenic reagent. Beer's law was followed up to 11.84 ppm of SCN^- . The proposed TLC-colorimetric method was applied to fortified samples of photogenic waste, river and seawaters.

Keywords: Water analysis; Environmental analysis; Thiocyanate; Inorganic anions; Inorganic cations

1. Introduction

Identification, separation and quantification of SCN^- is important due to its application in photography, catalysis, agri-chemicals, rust-inhibition and dyeing–printing of textiles [1]. At high acidities, thiocyanate produces cyanides in the presence of oxidants and thus causes lethal damage to aquatic life when SCN^- containing waste is discharged into rivers. Numerous methods [2–8] have been developed for analysing SCN^- and CN^- but most of them were not applied to polluted water and effluents. A spectrophotometric method based on the colour reaction of Fe^{3+} with SCN^- has been used

for the quantification of SCN^- but it suffers from cationic, anionic and phenolic interferences. An extensive literature survey on the quantitative determination of SCN^- (1981–1992) with respect to the techniques used, shows that out of twenty research papers published, only one dealt with spectrophotometry.

Thin-layer chromatography (TLC) has been a widely used technique for the separation of SCN^- [9–12]. The literature survey [13] shows that out of forty research papers published so far on TLC of SCN^- , none examined the separation of SCN^- from complexing cations (Ag^+ , Fe^{3+} , Co^{2+} , Cu^{2+} etc.). This paper reports a reliable TLC-colorimetric method for the determination of SCN^- in the presence of cationic and anionic impurities. The proposed meth-

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od is applicable to the determination of SCN^- in photogenic waste, river water and seawater.

2. Experimental

2.1. Apparatus

TLC applicator (Toshniwal, India); 20×3.5 cm glass plates, 24×6 cm jars, spectrophotometer (Elico, India, Ultra Spec. Model CL-54) and pH meter (Elico, India, Model LI-10T) were used.

2.2. Test solutions

Aqueous solutions (1.0%, w/v) of following were used.

1. Potassium salts of $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, MnO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$
2. Sodium salts of NO_2^- and MoO_4^{2-}
3. Ammonium salts of SCN^- and $\text{Mo}_7\text{O}_{24}^{6-}$
4. Nitrates of Ag^+ , Bi^{3+} , UO_2^{2+} and Zn^{2+}
5. Chlorides of Fe^{3+} and Hg^{2+}
6. Sulphates of Cu^{2+} , VO^{2+} , Co^{2+} and Mn^{2+}

2.3. Chemicals

Ammonium thiocyanate (Merck, India), ferric chloride and ammonia solution (Qualigens), acetone, cellulose microcrystalline and Kieselguhr G (CDH, India) were used. All other chemicals were of analytical reagent grade.

2.4. Detection reagents

To locate the spots of analyte ions, the reagents used were:

1. 0.3% Diphenylamine in 4 M H_2SO_4 for NO_2^- , MnO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$
2. 8.0% FeCl_3 in 2 M HCl for SCN^- , $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$
3. 0.5% Pyrogallol in methanol for MoO_4^{2-} and $\text{Mo}_7\text{O}_{24}^{6-}$
4. 1.0% $\text{K}_4\text{Fe}(\text{CN})_6$ in water for Fe^{3+} , Cu^{2+} , VO^{2+} and UO_2^{2+}
5. 1.0% Dimethylglyoxime in ethanol for Co^{2+}
6. 1.0% Dithizone in benzene for Zn^{2+} and Cd^{2+}

7. Saturated H_2S in water for Ag^+ , Hg^{2+} and Bi^{3+}

2.5. Stationary phases

Plain cellulose microcrystalline (S_1), Kieselguhr G (S_5) and their mixtures in 4:1 (S_2), 3:2 (S_3) and 1:1 (S_4) ratio were used as adsorbent materials.

2.6. Mobile phases

Mixtures of 0.1 M NH_4OH and CH_3COCH_3 in 1:9 (M_1), 3:7 (M_2), 5:5 (M_3), 7:3 (M_4) and 9:1 (M_5) ratios were used as solvent systems.

2.7. Preparation of chromatoplates

Cellulose, Kieselguhr G or their mixture was slurried with double distilled water in 1:3 and the resultant slurry (without additional binder) was applied onto glass plates with the aid of an applicator to give a layer of 0.25-mm thickness. Plates were dried at room temperature, activated at $100 \pm 2^\circ\text{C}$ and then stored in a desiccating chamber until use.

2.8. Preparation of fortified samples

Four samples of SCN^- solutions (5.09–12.92 mM) were prepared in seawater (collected from Anjuna Beach, Goa). Similarly, spiked river water (Ganga, Rajghat) and photogenic waste (Aligarh) were prepared to examine the recovery of SCN^- .

2.9. Procedure

The entire methodology was carried out as follows

2.9.1. Chromatography of inorganic ions

To study the retention behaviour of some inorganic ions, 0.01 ml of the test solution was spotted onto the TLC plate, air dried and then developed with M_1 – M_5 up to 10 cm. The plate was air dried, analyte ions were detected as colored spots and then identified on the basis of their R_f values. For mutual separations, an aliquot (0.02 ml) of binary or 0.03 ml of ternary mixture of analytes was loaded onto the plate and the chromatography was performed. In order to examine the effect of sample pH on the separation of SCN^- , various mixtures of test solu-

tions were brought to the required pH values (3.0–12.25) by adding either glacial acetic acid or NaOH solution. The effects of amines (2-nitroaniline, β -naphthylamine and diphenylamine) and phenols (phenol, resorcinol and pyrogallol) were examined on the detection and separation of SCN^- by mixing 1% alcoholic solution of additive with binary/ternary mixture containing SCN^- .

2.9.2. Colorimetry of thiocyanate

For quantitative determination of SCN^- by TLC-colorimetry, 0.1 ml of standard ammonium thiocyanate (2.55–25.48 mM SCN^-) was spotted onto the plate (S_2) along with foreign ions and developed with M_1 . A pilot plate was simultaneously run. SCN^- containing portion of adsorbent from the working plate was scraped off and SCN^- was extracted with 10 ml of distilled water followed by washing of the adsorbent with 2 ml of water. Thus, the total volume of solution was kept to 12 ml in each case. To the filtrate, 0.5 ml of chromogenic reagent solution (8.0% ferric chloride in 2 M HCl) was added, absorbance was measured at 460 nm and the absorbance was plotted against the concentration (ppm) of SCN^- solution to sketch the standard calibration curve which was used to determine the concentration of SCN^- in a water sample with preliminary separation from accompanying inorganic ions.

2.9.3. Recovery from fortified samples

For the recovery of SCN^- from spiked waste (photogenic) and water (river and sea) samples, 0.1 ml of the solution was spotted onto TLC plate (chromatographic system; S_2, M_1) and the chromatocolorimetry was performed in the similar manner as that for standards. The loaded and recovered amounts of SCN^- were compared and the relative standard deviation (%), relative error and percentage recovery were calculated.

3. Results and discussion

3.1. Qualitative studies

Inorganic ions were chromatographed on plain and mixed adsorbents containing cellulose and/or Kiesel-

guhr (S_1 – S_5) using mixtures of 0.1 M NH_4OH and CH_3COCH_3 in various ratios as mobile phases (M_1 – M_5). The results of this study are summarized in Tables 1 and 2. The effect of proportional composition of mobile phase on the hR_F values of inorganic anions is examined and the results are reported in Table 1 where only plain adsorbents (S_1 and S_5) were used. Cations were also chromatographed with these chromatographic systems, cations remain at the point of application. However, some metal ions yield occasional tailed spots. To achieve difference in migration of anions, S_1 and S_5 were mixed together to get a set of adsorbents (S_2 – S_4) on which the anions were chromatographed using M_1 as mobile phase. The hR_F values of anions are enlisted in Table 2. Out of three mixed adsorbents, cellulose–Kieselguhr (4:1, S_2) is selected because it provides sufficient difference in hR_F values of SCN^- and others. It also provides compact spots because increasing Kieselguhr proportion results in the tailing of spots. Hence, the combination of S_2 and M_1 is the best chromatographic system which is utilized for the selective separation of SCN^- from all ions studied. These ions strongly interfere in the colorimetric

Table 1
Effect of mobile phase composition on the mobility of inorganic ions^a

Anion	Stationary phase	hR_F values achieved with				
		M_1	M_2	M_3	M_4	M_5
SCN^-	S_1	49	91	91	93	95
	S_5	85	90	90	90	92
NO_2^-	S_1	21	76	82	91	93
	S_5	88	89	90	90	93
MnO_4^-	S_1	0	0	0	0	0
	S_5	0	0	0	0	0
$\text{Fe}(\text{CN})_6^{3-}$	S_1	6	54	89	92	95
	S_5	83	90	90	92	93
$\text{Fe}(\text{CN})_6^{4-}$	S_1	0	6	78	90	96
	S_5	8	17	80	91	93
CrO_4^{2-}	S_1	10	23	70	90	95
	S_5	41	91	91	93	94
$\text{Cr}_2\text{O}_7^{2-}$	S_1	8	20	78	88	92
	S_5	43	89	90	90	94
MoO_4^{2-}	S_1	9	24	83	90	93
	S_5	36	88	90	91	96
$\text{Mo}_7\text{O}_{24}^{6-}$	S_1	12	30	80	92	92
	S_5	38	90	91	95	95

^a Metal ions remain at the point of application in all of the above mentioned chromatographic systems.

Table 2
Effect of stationary phase composition (cellulose/Kieselguhr proportion) on the mobility of inorganic ions^a when developed with M₁

Anion studied	<i>hR_F</i> values achieved on				
	S ₁	S ₂	S ₃	S ₄	S ₅
SCN ⁻	49	79	80	85	85
NO ₂ ⁻	21	21	32	86	88
MnO ₄ ⁻	0	0	0	0	0
Fe(CN) ₃ ³⁻	6	6	7	12	83
Fe(CN) ₆ ⁴⁻	0	0	0	0	0
CrO ₄ ²⁻	10	20	24	28	41 ^b
Cr ₂ O ₇ ²⁻	8	19	19	25	43
MoO ₄ ²⁻	9	11	17	21	36 ^b
Mo ₇ O ₂₄ ⁶⁻	12	15	15	23	38

^a All metal ions studied remain at the point of application (*hR_F* = 0.0).

^b Tailed spots (*hR_L* - *hR_T* > 30).

method of SCN⁻ quantification due to the formation of coloured complexes either with SCN⁻ or Fe³⁺ [14]. For Ag⁺-SCN⁻ separation, the white precipitate of AgSCN formed on mixing of both ions was dissolved in NH₃ solution and the clear solution was spotted on the TLC plate. Fe³⁺-SCN⁻ separation is of great importance, especially when SCN⁻ is to be determined colorimetrically by using FeCl₃ as chromogenic reagent.

For this separation, 1.0% aqueous NaF solution was added to red coloured complex to decolourize it.

FeF₃, a more stable complex was formed and SCN⁻ became free and was detected on TLC plate. In the Co²⁺-SCN⁻ separation, Co²⁺ could not be detected. In general, for metal ion-SCN⁻ separation, the amount of SCN⁻ was taken *x* times more than that of metal ion (*x* is the number of unit charges present on the metal ion). Effects of sample pH, phenols and amines on the detection of SCN⁻ have been examined and SCN⁻ was clearly detected in all cases. The *R_F* value of SCN⁻ remained unchanged over the pH range (3.0–12.25) of sample solution. No change in the mobility of SCN⁻ was noticed on being chromatographed in the presence of amines and phenols.

3.2. Quantitative studies

The proposed TLC system (S₂, M₁) was coupled to the spectrophotometry of SCN⁻ using Fe³⁺-SCN⁻ colour reaction in an acidic (2 M HCl) medium. The complex absorbs incident radiation of 460 nm and follows the Beer's law up to 11.48 ppm. The optical density (*A*) plotted against the concentration (ppm) of SCN⁻ is an average of *A*₁ (of SCN⁻ after separation from NO₂⁻), *A*₂ (from CrO₄²⁻) and *A*₃ (from Fe(CN)₆³⁻). The R.S.D. varies from 2.124–0.442%.

To test the applicability, the proposed TLC-colorimetric method was applied to the fortified

Table 3
Recovery of SCN⁻ from fortified environmental samples

Sample (pH)	Amount of SCN ⁻ loaded (μg)	Amount of SCN ⁻ recovered (μg)	Relative recovery (%)	Relative standard deviation (%)
<i>Photogenic waste</i> (9.4)	29.60	30.19	102.00	9.38
	44.40	45.48	102.44	5.60
	59.20	60.64	102.44	5.42
	74.00	76.46	103.32	10.70
<i>River water</i> (8.2)	29.60	28.12	94.99	9.91
	44.40	42.62	96.00	7.83
	59.20	57.22	96.66	7.09
	74.00	73.03	98.69	5.63
<i>Sea water</i> (8.0)	29.60	27.38	92.50	9.91
	44.40	41.64	93.78	7.57
	59.20	56.23	94.99	6.59
	74.00	71.53	96.66	5.45

samples of photogenic waste, river water and sea water. The results are summarized in Table 3. This table shows that the relative recoveries of SCN^- are almost the same.

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