# Direct & Indirect Titrimetric Determinations of Thiocyanate Ion in Metal Salts & Complexes with Dichloramine-T & Some Further Applications of Chloramine-T

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**Simple and accurate direct and indirect titration (visual and potentiometric) methods for the determination of thiocyanate ion in metal salts and complexes with chloramine-T and dichloramine-T in the presence of sodium acetate and KBr have been developed. The oxidation involves an eight-electron process. A method for determining cyanide and thiocyanate ions in mixtures is also described.**

THE methods reported so far for the determination of thiocyanate include the use of hypohalite[1], bromine[2], iodine[3], iodate[4] and $H_2O_2$ (ref. 5). These involve mostly back titration procedures and have a number of experimental restrictions. Although the reaction of chloramine-T with $CNS^-$ ion has been mentioned in literature[6-9] detailed studies are lacking.

The present communication reports a simple method for estimating thiocyanate ion in metal salts and complexes by (i) a direct titration with chloramine-T (CAT) or dichloramine-T (DCT) in the presence of KBr, with a visual or potentiometric end-point and (ii) a back titration procedure. An eight-electron change is observed under these conditions.

Triply distilled water was used for preparing aqueous solutions. AR grade KCNS (E. Merck) was dried at 150° and its purity checked[4]. Metal thiocyanates, NaCNS, $Cd(CNS)_2$, $Zn(CNS)_2$, $Ni(CNS)_2.0{\cdot}5H_2O$, $Ba(CNS)_2.2H_2O$, $Pb(CNS)_2$, $UO_2(CNS)_2.3H_2O$ and complexes $K_4Pb(CNS)_6$, $K_2Zn(CNS)_4.4H_2O$, $K_2Cd(CNS)_4.2H_2O$, $K_4Ni(CNS)_6.4H_2O$ and $KUO_2(CNS)_3.2H_2O$ were prepared by standard methods and recrystallized from aqueous solution and their purity checked by elemental analyses. Solutions of the compounds (~2 mg/ml) in water or dilute acetic acid (only lead compounds) were prepared. Preparation of standard CAT and DCT solutions are described in earlier communications[10-12]. Approximately 1*N* KBr and 20% sodium acetate solutions were prepared. A Bajaj potentiometer with a platinum indicator electrode and a reference calomel electrode were used for potentiometric titrations.

*Direct titration: Method* (1) — A direct titration of thiocyanate (salt or complex) with CAT or DCT was found practicable in the presence of sodium acetate and KBr (and acetic acid in titrations with CAT). Sodium acetate was found to catalyse the oxidation.

To aliquots of thiocyanate solution were added sodium acetate solution (5 ml), KBr solution (10 ml) and $CCl_4$ (1 ml) [glacial acetic acid (5 ml) in titrations with CAT]. The solution was titrated with CAT or DCT with stirring till the appearance of a faint yellow colour in $CCl_4$ layer. Blank correction was found to be about 0·05 ml of 0·1*N* oxidant. Potentiometric titration was also carried out for the determination of the end-point. A large potential jump of ~300-500 mV was noticed for the addition of 0·1 ml of 0·1*N* oxidant at the end-point.

*Method* (2) — In this method the reductant solution was added to a known volume of the oxidant containing KBr and $CCl_4$ (and glacial acetic acid in the case of CAT). The end-point was noted visually as well as potentiometrically (potential jump of ~300-500 mV at the end-point).

*Back titration method* — The *p*H of the thiocyanate solution was adjusted to any value between 1 and 6. Aliquots of the solution were added to a known volume (~50% excess) of 0·1*N* CAT in an iodine flask and set aside for about 20 min in case of metal salts and only for 5 min with thiocyanate complexes, shaking occasionally. Sulphuric acid (10 ml, 2*N*) and potassium iodide solution (20%, 10 ml) were added and the reaction mixture titrated with 0·1*N* sodium thiosulphate. A blank was run with the same volume of CAT solution.

Similar titration procedure was adopted with 0·1*N* DCT in water or dil. acetic acid.

The eight-electron stoichiometry observed in direct titration is shown in Eqs. (1-3), assuming *in situ* liberation of bromine from KBr by the oxidants.

$$RNClNa + 2Br^- + 2H^+ \rightarrow RNH_2 + Na^+ + Cl^- + Br_2 \quad ...(1)$$

$$RNCl_2 + 4Br^- + 2H^+ \rightarrow RNH_2 + 2Cl^- + 2Br_2 \quad ...(2)$$

where $R = p\text{-}CH_3C_6H_4SO_2$.

$$CNS^- + 4Br_2 + 4H_2O \rightarrow SO_4^{2-} + CNBr + 8H^+ + 7Br^- \quad ...(3)$$

Bromine cyanide formed could be quantitatively estimated by the iodometric method[13].

The stoichiometry observed in the back titration is indicated by Eq. (4).

$$CNS^- + 4RNClNa \text{ (or } 2RNCl_2) + 5H_2O \rightarrow SO_4^{2-} + 2H^+ + CNO^- + 4RNH_2 \text{ (or } 2RNH_2) + 4Na^+ \text{ (or } 4H^+) + 4Cl^- \quad ...(4)$$

The presence of $CNO^-$ ion in the reaction products was detected by spot tests[14,15]. The sulphonamide was detected by paper chromatography[12].

The results of analysis given in Table 1 show the range of amounts of thiocyanate employed and the per cent error in the recovery. Each range covers the amounts present in 8-10 different aliquots of the compound. For comparison the results obtained by the argentometric method[16] are also included in Table 1. It is seen that the maximum error encountered in the present method is about 0·5%.

Common anions such as sulphate, phosphate, nitrate and perchlorate and fluoride do not interfere but iodide ion interferes in direct titration and bromide ion in the back titration and $N_2H_4$ and cyanide ion interfere in both the titrations.

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TABLE 1 — TITRIMETRIC DETERMINATION OF THIOCYANATE WITH CAT AND DCT

| Compound | Range studied (mg) | Error (%) (method-1) Visual | Error (%) (method-1) Potentiometric | Back titration | $AgNO_3$ method[16] | Range studied (mg) | Error (%) (method-2) Visual | Error (%) (method-2) Potentiometric |
|---|---|---|---|---|---|---|---|---|
| | | | TITRATION WITH CAT | | | | | |
| KCNS | 1·02-102 38 | 0·00-0·49 | 0·00-0·49 | 0·00-0·24 | 0·00-0·59 | 1·39-111·12 | 0·00-0·50 | 0·00-0·36 |
| NaCNS | 1·88-112·69 | 0·07-0·53 | 0·02-0·53 | 0·04-0·53 | 0·00-0·27 | 1·13-113·40 | 0·00-0·40 | 0·00-0·40 |
| $Cd(CNS)_2$ | 1·80-108·00 | 0·00-0·55 | 0·00-0·56 | 0·13-0·55 | 0·00-0·60 | 1·60-127·84 | 0·00-0·25 | 0·00-0·31 |
| $Ni(CNS)_2.0·5H_2O$ | 0·93-92·75 | 0·00-0·37 | 0·00-0·54 | 0·00-0·54 | 0·00-0·39 | 1·02-102·00 | 0·00-0·49 | 0·00-0·53 |
| $Pb(CNS)_2$ | 2·00-100·16 | 0·00-0·50 | 0 00-0·55 | 0·00-0·50 | 0·00-0·50 | 1·13-112·98 | 0·00-0·49 | 0·15-0·44 |
| $Zn(CNS)_2$ | 1·56-120·74 | 0·00-0·51 | 0·00-0·32 | 0·03-0·32 | 0·00-0·58 | 1·27-126·90 | 0·02-0·47 | 0·00-0·39 |
| $Ba(CNS)_2.2H_2O$ | 1·00-100·00 | 0·00-0·50 | 0·00-0·31 | 0·00-0·60 | 0·00-0·60 | 1·03-103·44 | 0·00-0·48 | 0·00-0·39 |
| $UO_2(CNS)_2.3H_2O$ | 2·41-120·72 | 0·00-0·25 | 0·00-0·58 | 0·00-0·48 | 0·41-1·03 | 1·36-135·69 | 0·00-0·52 | 0·00-0·52 |
| $K_2Zn(CNS)_4.4H_2O$ | 1·07-128·42 | 0·00-0·56 | 0·00-0·37 | 0·00-0·35 | 0·47-1·17 | 1·38-110·48 | 0·00-0·36 | 0·00-0·43 |
| $K_2Cd(CNS)_4.2H_2O$ | 2·03-101·55 | 0·00-0·49 | 0·07-0·49 | 0·00-0·49 | 0·00-1·08 | 2·83-113·12 | 0·17-0·53 | 0·00-0·35 |
| $K_4Ni(CNS)_6.4H_6O$ | 2·04-101·80 | 0·25-0·49 | 0·25-0·49 | 0·20-0·49 | 0·00-1·19 | 2·62-104·80 | 0·13-0·53 | 0·06-0·46 |
| $K_4Pb(CNS)_6$ | 2·03-101·35 | 0·10-0·50 | 0·20-0·50 | 0·00-0·50 | 0·28-0·74 | 1·46-116·96 | 0·00-0·48 | 0·00-0·55 |
| $KUO_2(CNS)_3.2H_2O$ | 2·01-100·50 | 0·00-0·32 | 0·06-0·50 | 0·00-0·40 | 0·00-1·00 | 1·07-106·70 | 0·00-0·33 | 0·00-0·47 |
| | | | TITRATION WITH DCT | | | | | |
| KCNS | 1·02-102·38 | 0·00-0·49 | 0·00-0·20 | 0·00-0·49 | 0·00-0·59 | 1·25-100·00 | 0·00-0·48 | 0·00-0·40 |
| NaCNS | 1·88-112·69 | 0·09-0·53 | 0·07-0·53 | 0·05-0·53 | 0·00-0·27 | 1·25-124·50 | 0·00-0·40 | 0·00-0·48 |
| $Cd(CNS)_2$ | 1·80-108·00 | 0·00-0·44 | 0·00-0·44 | 0·11-0·55 | 0·00-0·60 | 1·76-122·85 | 0·00-0·51 | 0·00-0·52 |
| $Ni(CNS)_2.0·5H_2O$ | 0·93-92·75 | 0·00-0·54 | 0·00-0·54 | 0·00-0·54 | 0·00-0·39 | 1·22-122·00 | 0·00-0·41 | 0·00-0·33 |
| $Pb(CNS)_2$ | 2·00-100·16 | 0·00-0·50 | 0·00-0·50 | 0·00-0·50 | 0·00-0·50 | 0·99-118·41 | 0·10-0·51 | 0·00-0·28 |
| $Zn(CNS)_2$ | 1·56-124·74 | 0·00-0·42 | 0·00-0·58 | 0·00-0·51 | 0·00-0·58 | 1·39-111·52 | 0·11-0·43 | 0·14-0·39 |
| $Ba(CNS)_2.2H_2O$ | 1·00-100·00 | 0·00-0·60 | 0·00-0·50 | 0·00-0·60 | 0·00-0·60 | 1·86-111·75 | 0·00-0·40 | 0·00-0·54 |
| $UO_2(CNS)_2.3H_2O$ | 2·41-120·72 | 0·02-0·50 | 0·00-0·58 | 0·00-0·46 | 0·41-1·03 | 1·45-115·70 | 0·00-0·35 | 0·00-0·35 |
| $K_2Zn(CNS)_4.4H_2O$ | 1·07-128·42 | 0·00-0·47 | 0·00-0·47 | 0·00-0·40 | 0·47-1·17 | 1·47-117·68 | 0·00-0·41 | 0·00-0·34 |
| $K_2Cd(CNS)_4.2H_2O$ | 2·03-101·55 | 0·02-0·49 | 0·10-0·49 | 0·00-0·37 | 0·00-1·08 | 1·49-119·44 | 0·00-0·35 | 0·00-0·49 |
| $K_4Ni(CNS)_6.4H_2O$ | 1·02-101·80 | 0·00-0·49 | 0·00-0·41 | 0·00-0.49 | 0·00-1·19 | 1·41-112·80 | 0·00-0·43 | 0·00-0·43 |
| $K_4Pb(CNS)_6$ | 2·03-101·35 | 0·00-0·54 | 0·00-0·50 | 0·00-0·49 | 0·28-0·74 | 1·54-123·52 | 0·00-0·51 | 0·00-0·39 |
| $KUO_2(CNS)_3.2H_2O$ | 2·01-100·50 | 0·20-0·51 | 0·00-0·50 | 0·00-0·50 | 0·00-1·00 | 2·25-112·65 | 0·09-0·44 | 0·00-0·44 |

TABLE 2 — DIRECT TITRIMETRIC DETERMINATION OF THIOCYANATE AND CYANIDE IONS IN MIXTURES, WITH CHLORAMINE-T AND DICHLORAMINE-T

| Visual end-point | | | | Potentiometric end-point | | | |
|---|---|---|---|---|---|---|---|
| Taken (mg) | | Found (mg) | | Taken (mg) | | Found (mg) | |
| $CNS^-$ | $CN^-$ | $CNS^-$ | $CN^-$ | $CNS^-$ | $CN^-$ | $CNS^-$ | $CN^-$ |
| | | | TITRATION WITH CAT | | | | |
| 0·92 | 0·92 | 0·92 | 0·92 | 0·92 | 0·92 | 0·92 | 0·92 |
| 2·29 | 2·29 | 2·30 | 2·30 | 2·30 | 2·30 | 2·29 | 2·31 |
| 4·58 | 4·58 | 4·58 | 4·62 | 4·60 | 4·60 | 4·58 | 4·62 |
| 9·20 | 9·20 | 9·20 | 9·17 | 9·20 | 9·20 | 9·16 | 9·24 |
| 18·30 | 18·30 | 18·40 | 18·35 | 18·40 | 18·40 | 18·36 | 18·41 |
| 36·70 | 36·70 | 36·80 | 36·69 | 36·80 | 36·80 | 36·87 | 36·57 |
| 73·40 | 73·40 | 73·45 | 73·64 | 73·60 | 73·60 | 73·52 | 73·52 |
| 92·20 | 92·20 | 92·06 | 91·61 | 92·00 | 92·00 | 91·99 | 91·74 |
| | | | TITRATION WITH DCT | | | | |
| 0·97 | 0·97 | 0·97 | 0·97 | 0·97 | 0·97 | 0·97 | 0·97 |
| 2·44 | 2·44 | 2·42 | 2·44 | 2·42 | 2·42 | 2·43 | 2·42 |
| 4·86 | 4·86 | 4·84 | 4·87 | 4·84 | 4·84 | 4·86 | 4·84 |
| 9·70 | 9·70 | 9·67 | 9·75 | 9·70 | 9·70 | 9·71 | 9·68 |
| 19·45 | 19·45 | 19·42 | 19·36 | 19·40 | 19·40 | 19·39 | 19·43 |
| 38·88 | 38·88 | 38·92 | 39·59 | 38·90 | 38·90 | 38·85 | 38·72 |
| 77·80 | 77·80 | 77·62 | 77·58 | 77·60 | 77·60 | 77·55 | 77·72 |
| 96·80 | 96·80 | 97·19 | 96·68 | 97·00 | 97·00 | 97·04 | 96·95 |

*Estimation of thiocyanate and cyanide ions in a mixture* — Since cyanide ion undergoes a two-electron change[12,17] with CAT or DCT, an aliquot of the oxidant solution ($V_1$ ml) of normality $N$ was titrated against a mixture of cyanide and thiocyanate ions ($V_1$ ml) as in method-2. An aliquot ($V$ ml) of the mixture was then taken and the cyanide ion precipitated out as zinc cyanide by adding 0·5$M$ zinc sulphate. Thiocyanate in the filtrate was determined by method-1 ($V_2$ ml). The amounts of $CNS^-$ ($x$, mg) and $CN^-$ ($y$, mg) in the reaction mixture are given by: $x = 7·26NV_2$ and

$y=13N\ (V_1-V_2)$. Some typical results are given in Table 2.

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**References**

1. TOMICEK, O. & JESEK, M., *Colln Czech. chem. Commun.*, **10** (1938), 353.
2. TREADWELL, F. P. & MAYR, C., *Z. anorg. Chem.*, **92** (1915), 127.
3. RUPP, E. & SOHIED, A., *Ber. dt. chem. Ges.*, **35** (1902), 2191; *Arch. Pharm.*, **243** (1907), 460.
4. HAMMOCK, E. W., BEAVON, D. & SWIFT, E. H., *Analyt. Chem.*, **21** (1949), 970.
5. WILSON, I. R. & HARRIS, G. M., *J. Am. chem. Soc.*, **82** (1960), 4515.
6. SINGH, B. & SOOD, K. C., *Anal. chim. Acta*, **13** (1955), 301.
7. RAO, V. R. S. & MURTHY, A. R. V., *Curr. Sci.*, **30** (1961), 176.
8. KOMAROVSKY, A. S., FILANOVA, W. F. & KORENMAN, I. M., *Z. analyt. Chem.*, **96** (1934), 321.
9. BISHOP, E. & JENNINGS, V. J., *Talanta*, **9** (1962), 581.
10. MORRIS, J. C., SALAZAR, J. A. & WINEMAN, M. A., *J. Am. chem. Soc.*, **70** (1948), 2036.
11. JACOB, T. J. & NAIR, C. G. R., *Talanta*, **19** (1972), 347.
12. MAHADEVAPPA, D. S. & GOWDA, B. T., *Talanta*, **23** (1976), 601.
13 SCHULEK, E., *Z. analyt. Chem.*, **62** (1923), 337.
14. FEIGL, F., *Spot tests in inorganic analysis* (Elsevier, Amsterdam), 1958, 285.
15. WERNER, E. A., *J. chem. Soc.*, **123** (1923), 2577.
16. VOGEL, A. I., *A textbook of quantitative inorganic analysis* (Longmans, Green, London), 1961, 264.
17. GOWDA, B. T. & MAHADEVAPPA, D. S., *Talanta*, **24** (1977), 325.