

Coulometric Bromometric Titration of Free and Coordinately Linked Cyanides

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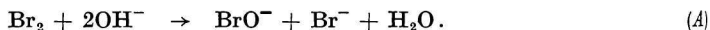
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The conditions of coulometric bromometric determination of cyanides in weak alkaline medium of the borate buffer solution are described. It is possible to titrate free cyanides and the cyanides linked coordinately in $\text{Cr}(\text{CN})_6^{3-}$ and $\text{Cr}(\text{CN})_5\text{NO}^{3-}$. The equivalence point of titration is indicated biamperometrically. The presence of air oxygen influences the results of free cyanide determination. The reaction scheme is discussed on the basis of different results obtained in bromometric oxidation of cyanides and cyanide complexes.

The determinations were performed in the concentration range from 94.8 to 2020 μg of KCN. The accuracy of determination corresponding to 95% probability is expressed for 2020, 776, and 94.8 μg of KCN by the reliability interval of ± 10.1 , ± 7.5 , and ± 1.3 μg of KCN, respectively.

The coulometric bromometric titration of cyanide is especially suitable for the determination of cyanides in the presence of chlorides and bromides. Chlorides do not interfere even if the ratio Cl^-/CN^- has the value of 2.7×10^4 . Bromides do not interfere provided that the ratio Br^-/CN^- does not exceed the value of 5.9×10^4 .

The electrolytic development of bromine proceeds quantitatively under different conditions. Bromine formed at the anode in basic solutions undergoes disproportionation according to the equation



If the pH of solution is too high the disproportionation may lead to the formation of bromate which often reacts with reduction agent differently in comparison with hypobromite. In such solutions the results of coulometric titration are not quantitative.

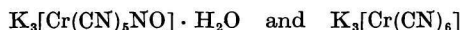
Arcand and *Swift* [1] used the titration with bromine coulometrically generated in weak alkaline medium for the determination of ammonia. *Agasjan* and co-workers [2] studied thoroughly the conditions of the development of BrO^- on platinum electrodes. Using the current-potential curves they found that the current efficiency of hypobromite generation was nearly 100% at current densities of 0.5 to 5 mA cm^{-2} in the hydrocarbonate buffer solutions with pH ranging from 8.3 to 11.0, the concentration of KBr being 0.8–1.6 M. If the current density decreases from 1.0 to 0.5 mA cm^{-2} , the current efficiency increases and approaches 100%. These results are in agreement with the studies [3, 4], in which the borate buffer solutions with pH 8.9 and pH 8.6 were used while the concentration of KBr was 0.84 M or 1.00 M.

Tomíček and *Filipovič* [5] performed determination of cyanides with nascent hypobromite by potentiometric titration in weakly alkaline medium. They used calcium hypochlorite as titration agent and titrated solution contained a considerable excess of KBr. Hypobromite as a titration solution was not used because of its instability. The above authors found that a part of cyanides was oxidized by air oxygen if the titration was carried out slowly.

In the present paper the difficulties arising from the instability of hypohalogenite titration solution are overcome by constant current electrolytic generation of hypobromite directly in the titrated solution. The equivalence point is indicated biamprometrically.

Experimental

The chemicals used were anal. grade except the complex compounds



which were prepared and several times purified according to [6, 7], respectively. Their purity was confirmed by polarographic analysis in agreement with the papers [8, 9] as well as spectrophotometrically according to [6]. Anal. grade potassium cyanide was purified according to [10].

Argon, purified by washing in acidic solution of $CrSO_4$, was employed as an inert gas. $CrSO_4$ was regenerated by zinc amalgam.

Recording spectrophotometer UV-VIS Spekord (Zeiss, Jena) was used for spectrophotometric measurements.

Equipment for coulometric titrations

A high-voltage supply of direct current, type TR 9102 (Orion, Budapest) in series with a slide-wire rheostat (maximum resistance 46,800 ohms), milliamperemeter, and electrolytic vessel was used as an amperostat. The electrolytic current was switched on and off by a relay which simultaneously controlled the electric stop-watch (EAW, GDR — scale division 0.01 s/graduation mark). If the current did not flow through the electrolytic vessel, it was carried by means of a relay through an equivalent resistor the value of which (100—500 ohms) was adjusted to the value of resistance of the vessel. The shape of the vessel and arrangement of electrodes were taken from [11]. The working electrode was an anode made of platinum foil having the geometric surface of 26.1 cm². For small generating currents (5.6—6 mA) a smaller working electrode with geometric surface of 16 cm² was applied. The auxiliary electrode was a mercury electrode with a saturated solution of Na_2SO_4 separated from the solution under investigation by two sintered glasses. The salt bridge between the two sintered glasses contained 0.5 M solution of Na_2SO_4 which was daily exchanged. The overall electric resistance of generation circuit was 300 ohms. Biamprometric indication of equivalence point was performed by means of two platinum electrodes which were polarized with d.c. voltage of 150 mV. The indication current was read on the mirror galvanometer DG 20 (Metra, Blansko). The solution in the vessel was stirred by means of an electromagnetic stirrer with teflon propeller.

Working procedure

The starting solution for electrolytic generation of titration agent was prepared by dissolving 10 g of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and 500 g of KBr in distilled water and diluting to the volume of 1 litre. 10 ml of this solution and 40 ml of water were pipetted into the vessel. The pH of the ground electrolyte thus prepared was 8.9. After preliminary titration, 5 ml of the solution containing the investigated substance in known concentration was added.

For working in inert atmosphere the stock solution of sample was prepared by dissolving the weighed substance in water bubbled with argon. The pipetted volume of sample was transferred into the vessel from which oxygen was removed by bubbling argon through the ground electrolyte. Argon was conveyed over the solution in the volumetric flask as well as in coulometric vessel to prevent the decrease of cyanide concentration.

The generating current flowed through the vessel in the intervals of 5–10 seconds, in the proximity of equivalence point in the intervals of 3–5 seconds (at the titration of the smallest amounts in 0.5 sec intervals). The indication current was always read at the same time after switching off the generating current (20–25 sec).

A preliminary titration and a titration series of three successive additions of the investigated sample was usually carried out without exchanging the solution in coulometric vessel. Then the electrodes and vessel were washed with distilled water, the working electrode dipped into HNO_3 (1 : 1) and rinsed with water. For further titrations a new ground electrolyte was used.

The accuracy of results was statistically evaluated by means of the reliability interval with 95% probability [12].

Results and Discussion*Titration of free cyanides*

The coulometric bromometric titration of cyanides in weak alkaline medium proceeds in agreement with [5] according to the equation



so that two equivalents of agent are consumed for one mole of CN^- .

Table 1
Results of the coulometric titration of cyanides

KCN added [μg]	KCN found, average value [μg]	Absolute error of average value [μg]	Relative error of average value [%]	Generating current [mA]	Number of determina- tions	Reliability interval [μg]
2020 ^a	2036	+16	+0.8	19.00	6	2036 ± 10.1
776 ^a	783	+ 7	+0.9	11.50	9	783 ± 7.5
776 ^b	766	-10	-1.3	11.50	6	766 ± 13.6
94.8 ^a	95.3	+ 0.5	+0.5	5.60	6	95.3 ± 1.3
94.8 ^{a,c}	96.1	+ 1.3	+1.4	5.60	5	96.1 ± 1.2

a — titration in inert atmosphere,

b — titration in the presence of air oxygen,

c — titration in the presence of chlorides; ground electrolyte consisted of 10 ml of the mixture containing $\text{KBr}-\text{Na}_2\text{B}_4\text{O}_7$, 10 ml of 4 M-NaCl, and 30 ml of H_2O .

The results presented in Table 1 show that the oxidation of cyanides with air oxygen is effective to small extent at about pH 9. In this case the amount found by analysis is a little smaller than the real amount of cyanides analyzed (negative error -1.3%). On the other hand, a small positive error occurs provided the titration is performed in inert atmosphere. In this case, the error is caused by the fact that the current efficiency does not fully reach 100% . A similar error was stated in the paper [3] for the titration of ammonium with hypobromite generated from the same ground electrolyte. The value of this error was $+1.0\%$.

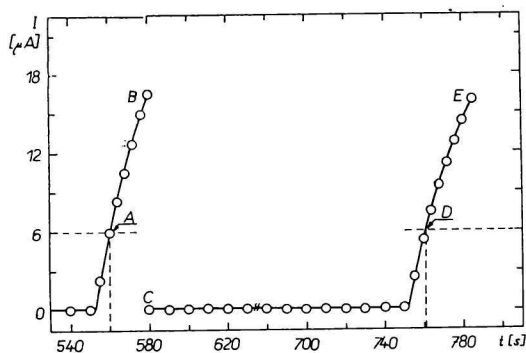


Fig. 1. The time dependence of indication current for the coulometric bromometric titration of cyanides.

A — end point of the preceding titration; AB — excess of titration agent at the preceding titration; BC — addition of 5 ml of the sample containing $766 \mu g$ KCN; CDE — titration of the sample; D — titration end point.

The course of the titration can be seen in Fig. 1 which gives the time dependence of indication current. The increase of current after reaching the equivalence point is not linear as stated earlier [1, 3, 4]. To avoid the non-linear extrapolation necessary to find the equivalence point, the time reading at a suitably selected constant value of indication current (according to the amount of titrated substance) was applied. The titration end point was thus established by using the interpolation between the points on the ascending branch of current. In accordance with *Christian et al.* [4] we found that the ascending branch of indication current did not have the same course at preliminary titration as it had at subsequent titrations. This fact leads to different results for the titration of the first sample. To prevent this error we added a few drops of sample to the ground electrolyte before titration.

Przybyłowicz and *Rogers* [13] have described other method for the coulometric determination of CN^- in which cyanides react with a mercury salt generated electrolytically. Our method of coulometric determination of cyanides is advantageous in comparison with mercurimetric provided it is necessary to determine very small concentrations of cyanides (10^{-4} – 10^{-5} M) in the presence of great excess of Br^- or Cl^- . Chlorides do not interfere at the 0.73 M concentration, *i.e.* up to the ratio Cl^-/CN^- of 2.7×10^4 . Bromides do not interfere even at the 1.55 M concentration (instead of 10 ml of the KBr and $Na_2B_4O_7$ mixture 20 ml was pipetted) what corresponds to the maximum ratio Br^-/CN^- of 5.9×10^4 .

Titration of coordinately linked cyanides

Within the scope of systematic study of the electrochemical properties of transition metal cyanide complexes [17] we tried to perform a coulometric titration of complexes $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ and $\text{Cr}(\text{CN})_6^{3-}$. The shape of titration curve is analogous to that obtained for the titration of CN^- (Fig. 1). The titration results are given in Table 2. The high

Table 2

Results of the coulometric titration of $\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]$ and $\text{K}_3[\text{Cr}(\text{CN})_6]$

$\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]$ added [μmole]	$\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]$ found, average value [μval]	Generating current [mA]	Number of determina- tions	$\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]$ [val/mole]	Reliability interval [val/mole]
1.370 ^a	18.19	11.50	6	13.28	13.28 ± 0.10
1.370 ^b	18.12	11.50	9	13.23	13.23 ± 0.10
0.254 ^a	3.39	6.00	6	13.35	13.35 ± 0.26
$\text{K}_3[\text{Cr}(\text{CN})_6]$ added [μmole]	$\text{K}_3[\text{Cr}(\text{CN})_6]$ found, average value [μval]	Generating current [mA]	Number of determina- tions	$\text{K}_3[\text{Cr}(\text{CN})_6]$ [val/mole]	Reliability interval [val/mole]
1.400 ^a	18.02	11.50	9	12.87	12.87 ± 0.04

a — titration in inert atmosphere,

b — titration in the presence of air oxygen.

number of equivalents necessary for the oxidation of complexes at bromometric titration in weak alkaline medium indicates that these complexes undergo a total oxidation and decomposition. It follows from Table 2 that the presence of air oxygen does not influence the determination.

After a few series of titration determinations of $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ and $\text{Cr}(\text{CN})_6^{3-}$ with a non-cleaned platinum working electrode we observed that it was covered with a gold-brown deposit of the substance which was insoluble in water but soluble in sufficiently concentrated solutions of nitric acid. The formation of yellow, brown or even black precipitate of polymeric cyanogen on electrode was observed by several authors during the electrolysis of cyanide solutions. *Schmidt* and *Meinert* [14] considered this substance to be azulmic acid whereas according to *Hittorf* (cited in [14]) it was paracyanogen.

We assumed that the complex ion would undergo a total oxidation in the course of titration of $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ and would give 17 electrons under formation of CNO^- , CrO_4^{2-} and NO_3^- which are the compounds with the highest degree of oxidation derived from the ligands and central atom. We found, however, that nitrites did not appreciably react with hypobromite at pH 8.9. The biamperometric indication current increased from the very beginning of coulometric titration and continuous rise of the current did not stop even if a multiple excess of hypobromite was generated. The reaction of nitrite with hypobromite in weak alkaline medium is very slow [15] and it is practically ineffective at the common rate of coulometric titration so that the NO ligand is oxidized only

to NO_2^- . The formation of chromate was proved by the spectrophotometric investigation of the titrated solution at the wave length of 375 nm [16].

It is evident from Table 2 that the number of equivalents necessary for the oxidation of molar amounts of $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ and $\text{Cr}(\text{CN})_6^{3-}$ is not integer. With the final oxidation products CrO_4^{2-} , CNO^- , and NO_2^- the value val/mole should be 15 for both above complexes. The values experimentally found are 13.28 ± 0.10 val/mole for $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ and 12.87 ± 0.04 val/mole for $\text{Cr}(\text{CN})_6^{3-}$ (under equal conditions of titration).

This disagreement may be explained by the formation of the mentioned polymeric cyanogen compound on the generating platinum electrode. This by-product causes the decrease in the number of electrons exchanged per one mole of CN^- to a value less than 2. From the result obtained with the oxidation of $\text{Cr}(\text{CN})_6^{3-}$ it is possible to calculate the empiric number of electrons necessary to the oxidation of one cyanide ion

$$\frac{12.87 - 3}{6} = 1.65 \text{ val/mole } \text{CN}^- \quad (C)$$

If the value thus calculated is substituted in the oxidation balance of $\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]$, we obtain

$$5 \times 1.65 + 3 + 2 = 13.25 \text{ val/mole } \text{Cr}(\text{CN})_5\text{NO}^{3-}. \quad (D)$$

This is in good agreement with the value of 13.28 val/mole $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ found experimentally. The good agreement of results indicates that the weight ratio of both oxidation products of linked cyanide (CNO^- and polymeric cyanogen) is equal for the bromometric titration of the investigated chromium complexes.

In contrast to the bromometric oxidation of $\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]$ and $\text{K}_3[\text{Cr}(\text{CN})_6]$ the formation of the deposit of polymeric cyanogen was not observed during the titration of cyanides. This fact as well as the integer number of equivalents consumed per mole in the oxidation of cyanides gives evidence of a fact that the mechanism of bromometric oxidation is different for cyanides and for cyanide complexes of chromium.

Cyanides coordinately linked in $\text{Cr}(\text{CN})_6^{3-}$ and $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ are not oxidized with hypobromite after preceding dissociation. That follows from the fact that they are oxidized in a different way when compared to free cyanides. A high stability constant and substitution inertia of these cyanides disprove this mode of oxidation (in the pH range, in which the titrations were carried out, both these substances are stable).

Probably the first step in the reaction is the oxidation of the whole complex ion (for $\text{Cr}(\text{CN})_5\text{NO}^{3-}$ the existence of the oxidation degree $\text{Cr}(\text{CN})_5\text{NO}^{2-}$ was proved electrochemically [18]). This step is succeeded by a consecution of substitution and redox reactions which provide the final products CrO_4^{2-} , CNO^- , NO_2^- and polymeric cyanogen compound.

The complicated oxidation mechanism of $\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]$ and $\text{K}_3[\text{Cr}(\text{CN})_6]$ causes that bromometric titration proceeds with non-integer number of equivalents per mole. In spite of that high reproducibility and high value of equivalent enables us to analyze very low concentrations (lower than determined polarographically) of these complexes if titration conditions are fulfilled. It is necessary, however, to substitute the molecular weight, divided by the number of electrons found empirically for the equivalent weight in the Faraday law.

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