

## POTENTIOMETRIC DETERMINATION OF CYANIDE IN EFFLUENTS HAVING HIGH CONCENTRATION OF CHLORIDE

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### ABSTRACT

The estimation of cyanide is generally done by titrimetry, colorimetry and polarography but each method has its own limitations. Argentometric titration method is not satisfactory at low cyanide concentration at ppm levels. Distillation and colorimetry method is accurate but time consuming. Presence of large quantities of chloride does not permit the use of ion selective electrodes. Other methods available are Double Pulse Polarography and Atomic Absorption Spectroscopy. They involve sophisticated costly instruments and are difficult as far as small scale industries are concerned. It has been observed that potentiometric titration method can be more easily adopted with fair accuracy even at ppm levels. The most important advantage is that the estimations can be done at fast rate and does not require much of sophisticated instruments or technique. Series of experiments were carried out with varying cyanide concentrations and large excess of chloride ions. Detection limit by this method is 100 ppb and the results agree well with those obtained by the other methods. The results on actual samples and standards are presented in this paper.

**Key words:** Potentiometry, cyanide, effluent treatment

### INTRODUCTION

Estimation of cyanide in effluents has been a problem whenever several samples are to be analysed. The most commonly adopted methods are distillation and volumetry or colorimetry [1]. Normally in effluent treatment processes, the analysis involves determination of very low concentrations of cyanide. In such cases, simple volumetry or colorimetry methods are proved to be less reliable. Polarography, fast scan double pulse polarography [2] and atomic absorption spectra [3] methods have been found to be very accurate and reliable but they involve sophisticated costly instruments. Ion selective electrodes for determination of cyanide are reported to be unsuitable in presence of chloride ions. Potentiometric titrations using ion selective electrode as indicator electrode has been reported to give accurate results even at 0.3 ppm cyanide in a  $10^3$  excess of chloride concentration [4]. In this case, there is a possibility of the poisoning of the ion selective electrode. Determination of cyanide by potentiometric titration method using platinum as indicator electrode is attempted in this paper.

### EXPERIMENTAL

The estimations were carried out using silver nitrate as titrant. A platinum wire of 1 mm dia has been used as the indicator electrode, and SCE as reference electrode.

A cyanide stock solution was prepared by dissolving 1.178 gm of NaCN in 25 ml of 1 N NaOH and diluted to 250 ml (2500 ppm cyanide). From this stock, 12 standards were prepared viz. 250, 200, 150, 100, 50, 20, 10, 5, 2, 1, 0.5 and 0.1 ppm by dilution. The titrations were carried out against standard  $\text{AgNO}_3$  with appropriate dilutions to match the respective cyanide concentrations. The estimations were made both with and without chloride ions. In the former, the concentration of chloride ions was kept at 3000 ppm (corresponding to 5 gpl NaCl). The experiments were repeated a number of times to check for reproducibility and reliability of the measurements.

Adopting this method, cyanide was estimated in the electrolyte samples drawn after anodic oxidation trials in a packed bed electrolyser.

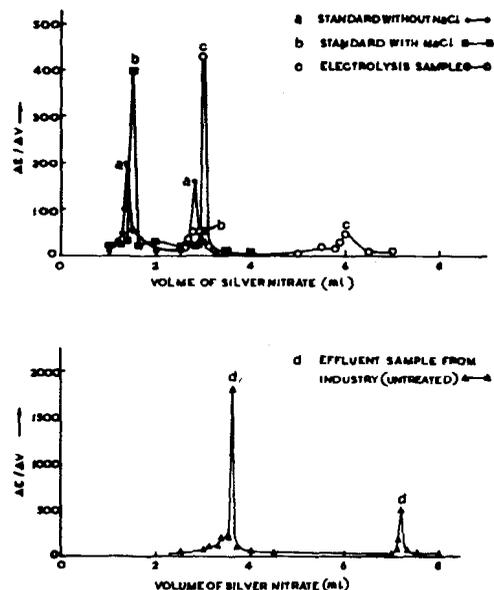


Fig. 1: Potential vs volume of titrant (derivative curves)

### RESULTS AND DISCUSSION

The results are presented in Tables I & II and figs. 1 & 2. Fig. 1 shows a plot of  $\Delta E/\Delta V$  vs  $V$  (the volume of  $\text{AgNO}_3$ ); the curves a & b refer to the standards, whereas c and d are for practical samples. It has been observed that the curve "a" shows two definite peaks in the absence of chloride, and

the volume of the titrant corresponding to second peak refers to complete consumption of cyanide. The first peak corresponds to the formation of dicyanoargentate  $[\text{Ag}(\text{CN})_2]$  whereas the second corresponds to the conversion of this complex ion into insoluble silver cyanide. In presence of excessive chloride ion, the second peak is obscured, as can be seen from curve "b" in fig. 1. In such a case the cyanide concentration is calculated from the first inflection itself multiplied by a factor of 2. The sample from the electrolytic cell contained 3000 ppm of chloride and varying concentration of cyanide with progressive electrolysis. Plot of  $\Delta E/\Delta V$  vs  $V$  as shown in curve c in fig. 1 indicates well-defined single peak, even though there is a small inflection on continuing the titration beyond this point, the second point of inflection has been found to be a bit shifted and the actual cyanide concentration can be calculated from the first peak. The untreated effluent sample received from a plating industry contained zinc and considerable amount of alkali along with 600 ppm chloride. The cyanide concentration was found to be 240 ppm by separate experiment. The derivative curve for the titration of the sample is given in curve "d" in fig. 1, which shows two definite peaks corresponding to the two end points for cyanide. But normally the treated sample may contain chloride anywhere between 2000 and 3000 ppm, in which case the second peak will get completely obscured.

The values for  $\Delta E/\Delta V$  corresponding to the end points while treating different concentrations of CN are summarised in Tables I & II.

Table-I: Results obtained with pure sodium cyanide (200 ppm)

No.	Conc. of cyanide (ppm)	$E_1$ Initial Potential (mV)	$\Delta E/\Delta V$ corresponding to peak I	$\Delta E/\Delta V$ corresponding to peak II
1.	249.98	-240	1800	400
2.	199.98	-230	1800	400
3.	148.30	-210	1600	400
4.	100.02	-210	1400	300
5.	46.69	-180	1000	400
6.	20.04	-160	800	260
7.	10.02	-140	700	260
8.	4.68	-100	600	200
9.	1.97	-60	500	180
10.	0.97	-30	200	160
11.	0.47	0	200	160
12.	0.10	+5	200	160

Table-II: Results obtained with sodium cyanide (200 ppm) and sodium chloride (5000 ppm)

Sl. No.	Conc. of cyanide (ppm)	$E_1$ Initial pot. (mV)	$\Delta E/\Delta V$ mV/ml
1.	249.980	-210	2000
2.	199.980	-210	2000
3.	146.650	-190	1800
4.	100.020	-180	1600
5.	46.690	-160	1200
6.	20.040	-140	1000
7.	10.020	-130	900
8.	1.002	-10	460
9.	0.501	-5	400
10.	0.100	+5	200

The values obtained for the system without NaCl are given in Table I. The value of  $\Delta E/\Delta V$  corresponding to the first peak varies from 200 to 1800 mV/ml depending on the concentrations of cyanide and titrant. Similarly the  $\Delta E/\Delta V$  for the peak 2 varies from 160 to 400 mV/ml. The values for 1 peak in presence of chloride also ranges from 200 to 2000 mV/ml and the second peak has been completely obscured as can be seen from the figure and also from Table II. The initial potential is also more positive when chloride is present in the solution.

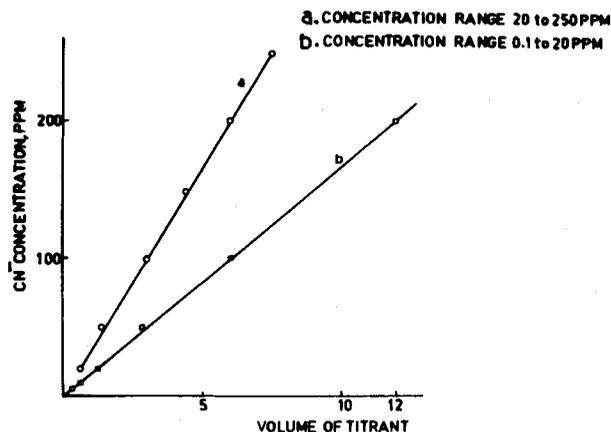


Fig. 2: Actual  $\text{CN}^-$  concentration vs observed volume of titrant

Fig. 2 gives a plot of concentration of cyanide vs volume of titrant required. The curve "a" is a plot corresponding to the concentration range 20 to 250 ppm and curve "b" corresponds to the concentration range 0 to 20 ppm. The straight line passing through origin indicates the linear relationship in the entire concentration range studied, confirming the validity of the method.

## CONCLUSION

It is evident from the foregoing, that the potentiometric titration method can be successfully used for the determination of cyanide in ppm level in presence of large excess of chloride with fair accuracy. At very low levels below 5 ppm, a confirmation by other methods may be desirable.

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