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QUANTITATIVE ANALYSIS OF NICKEL BY A MODIFIED METHOD

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Abstract. Quantitative determination of nickel by back titrating with nickel(II) solution instead of using standard silver nitrate and 10% potassium iodide solutions is as accurate as standard method.

Silver has for many years been determined by the cyanide method.[1] The method is also applied indirectly for the determination of nickel(II). If potassium cyanide solution is added to an ammonical solution of nickel(II) containing silver iodide in suspension, a clear solution is obtained when cyanide is in excess and all the nickel(II) is complexed. The excess of cyanide is determined by adding standard silver nitrate solution until the turbidity reappears. This work describes the determination of nickel(II) merely by adding a slight excess of cyanide ions and then back titrating with nickel(II) solution till a precipitate of hydrated nickel(II) cyanide appears.

Experimental

Analar grade chemicals from Merck, and May and Baker were used. Four samples of nickel(II) solutions were prepared and five titrations were carried out from each sample.

5 ml of the nickel(II) sulphate hexahydrate was taken in a 250-ml conical flask. To this was added 5 ml of saturated ammonium chloride and 2 ml of 6N ammonia solutions. Then from a burette added standard potassium cyanide solution till a clear light yellow solution was obtained. This required 11.50 ml of 0.20N KCN. Now back titrated the excess of cyanide with nickel(II) solution, the turbidity was obtained when 0.80 ml of nickel(II) solution was added.

$$4\ KCN \equiv Ni$$

i.e. 1 ml N-KCN $\equiv$ 0.01468 g Ni $\equiv$ 0.06569 g $NiSO_4.6H_2O$. Therefore, the amount of $NiSO_4.6H_2O$ per 250 ml = 6.512 g. Analytical Results:

	Found	Calculated	Purity %
$NiSO_4.6H_2O$	6.512 g	6.570 g	99.1
$NiSO_4.6H_2O$	5.902 g	5.981 g	98.7
$NiSO_4.7H_2O$	5.343 g	5.401 g	98.9
$NiSO_4.7H_2O$	4.259 g	4.310 g	98.8

%Purity found by standard method[1] 98.9

Discussion

The precipitate obtained by the interaction of Ni^{2+} and $Ni(CN)_4^{2-}$ ions is hydrated nickel(II) cyanide which is formulated as Ni_{aq} $[Ni(CN)_4]$ and not $Ni(CN)_2$. In the system Ni^{2+}—CN^-, Ni_{aq} $[Ni(CN)_4]$ is the only species identified between Ni^{2+} and $[Ni(CN)_4]$. This has been shown by Hume and Kolthoff[2] who found constant solubility product value (1.7×10^{-9}) of hydrated nickel(II) cyanide whether made from Ni_{aq}^{2+} and CN^- or Ni_{aq}^{2+} and $Ni(CN)_4^{2-}$. The presence of two types of nickel in hydrated nickel(II) cyanide $\{Ni_{aq}[Ni(CN)_4]\}$ was further confirmed by tracer technique.[3] From the value of the instability constant (10^{-30}) at 25°C for the $Ni(CN)_4^{2-}$ ion[4] we worked out the suitability of the reaction

$$Ni^{2+} + 4CN^- = Ni(CN)_4^{2-}$$
$$Ni^{2+} + Ni(CN)_4^{\ 2-} = Ni[Ni(CN)_4]$$

in quantitative analysis. Suppose the amount of potassium cyanide solution used in the titration is equivalent to 10 ml of 0.1N Ni_{aq}^{2+} and the volume at the end point is 100 ml. The concentration of the complex ion $Ni(CN)_4^{2-}$ will then be 0.01N. At this point the Ni^{2+} and CN^- ions in solution are due to dissociation of $Ni(CN)_4^{2-}$ ion i.e.,

$$Ni(CN)_4^{2-} \rightleftharpoons Ni^{2+} + 4\ CN^-$$

and the instability constant

$$10^{-30} = [Ni^{2+}]\ [CN^-]^4/[Ni(CN)_4^{2-}] \qquad (1)$$

If $[Ni^{2+}] = x$ then $[CN^-] = 4x$

Substituting these values in equation 1,

$$10^{-30} = [x]\ [4x]^4/[0.01]$$

or $x = \sqrt[5]{3.9 \times 10^{-35}} = 1.31 \times 10^{-7}$

From the solubility product of hydrated nickel(II)-cyanide $\{Ni_{aq}[Ni(CN)_4]\}$ which is 1.7×10^{-9}, the precipitation will occur when

$$[Ni^{2+}] \rangle \frac{1.7 \times 10^{-9}}{[Ni(CN)_4^{2-}]} \rangle \frac{1.7 \times 10^{-9}}{[0.01]} \rangle 1.7\times10^{-7}$$

The difference between the two values of the concentration of Ni^{2+} is very small and the titration error

in the precipitation of hydrated nickel(II) cyanide is negligible. Therefore, we carried out the quantitative determination of nickel by the modified method and compared the results with the standard method. The percentage purity of nickel in the analar grade hydrated nickel sulphate was almost the same as found by the standard method.[1] Our modified method of quantitative determination of nickel is as good as the standard method and the use of standard silver nitrate and 10% potassium iodide solution can be avoided.

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