

جامعة الانبار

كلية : الصيدلة

قسم : الكيمياء الصيدلانية

اسم المادة باللغة العربية: الكيمياء التحليلية

اسم المادة باللغة الإنكليزية: Analytical Chemistry

المرحلة: الأولى

التدريسي: م.م. سحر فائق عبد صالح

عنوان المحاضرة باللغة العربية: الكيمياء التحليلية العملي التجربة السادسة

عنوان المحاضرة باللغة الإنكليزية: Practical Analytical Chemistry (6)

Exp. 6

Determination of Chloride by the Volhard Method

The most important application of the Volhard method is for the indirect determination of chloride. A measured excess silver nitrate solution is added to the chloride sample, and the excess silver ion is determined by back-titration with a standard thiocyanate solution. The requirement of a strongly acid environment represents a distinct advantage for the Volhard titration over other methods for chloride because such ions as carbonate, oxalate, and arsenate (which form slightly soluble silver salts in neutral media) do not interfere.

Silver chloride, in contrast to the other silver halides, is more soluble than silver thiocyanate. As a consequence, the reaction:



cause the end point in the Volhard determination of chloride to fade; an overconsumption of thiocyanate ion and a negative error for the analysis may result. The magnitude of this error is dependent upon the indicator concentration.

Two general methods are employed to avoid the error resulting from the reaction between thiocyanate and silver chloride. The first involves the use of the maximum allowable indicator concentration [about 0.2M iron(III) ion]. The more popular way involves isolation of the precipitated silver chloride before back-titration with the thiocyanate. Filtration, followed by titration of an aliquot of the filtrate, yields excellent results provided the precipitated silver chloride is first briefly digested. The time required for filtration is, of course, a disadvantage. Probably the most widely employed modification is that of Caldwell and Moyer, which consists of coating the silver chloride with nitrobenzene, thereby substantially removing it from contact with the solution. The coating is accomplished by shaking the titration mixture with a few milliliters of the organic liquid like nitrobenzene prior to back-titration.

Silver nitrate reacts with the chloride according to the equation:



The excess silver nitrate (doesn't react) then determined by back-titration with standard potassium thiocyanate solution, and using Fe(III) ions as an indicator.



When all silver ions is reacted, the first excess drop from the thiocyanate reacts with Fe(III) ions forming red complex indicating the end point of the reaction.



Procedure

Weight about 1.5 g from the chloride sample and dissolve it in 250 ml water. Transfer by a pipette 10 ml from the sample solution into a conical flask and add 20 ml silver nitrate 0.1N; silver chloride is precipitate. Add 5-6 drops of HNO₃ 6N and 2 ml nitrobenzene. Close the end of the conical flask and shake thoroughly for few minutes, then leave the mixture to settle down. Add about 2 ml of iron(III) ammonium sulfate (Fe(SO₄)₂NH₄·12H₂O) indicator. Titrate with 0.1N KSCN solution from a buret until the red-brown color of FeSCN²⁺ is permanent, which indicates the end point. Write down the volume of KSCN consumed to find the volume the excess AgNO₃.

no. of the KSCN milliequivalents = no. of the AgNO₃ milliequivalents

$$N_1 \times V_1 = N_2 \times V_2$$

$$0.1 \times (\text{from buret}) = 0.1 \times V_2$$

The volume of the AgNO₃ needed to precipitate the chloride in the sample v₃ = the volume of added AgNO₃ v₁ (which is 20 ml) – V₂.

$$\frac{\text{weight of sample in g} \times 1000}{\text{equivalent weight} \times \text{volume of solution in ml}} = N$$

$$\frac{\text{equivalent weight}}{1000} \times \text{volume} \times N = \text{weight of sample}$$

weight = N × volume × milliequivalent1)

$$\frac{N \times V \times \text{milliequivalent}}{\text{weight of sample}} \times 100 = \text{Cl \%}$$

$$\frac{250/10 \times N(\text{AgNO}_3) \times V (v_3 (\text{AgNO}_3) \times 0.0354)}{100 \times \text{weight of sample (1.5 g)}} = \text{Cl \%}$$

$$\frac{\text{weight of fraction}}{\text{weight of sample}} \times 100 = \% \text{ in the equation numerator equation 1 represent the}$$

.If NaCl is to be calculated we use 0.05845 instead of 0.0354

