

A NOTE ON THE ESTIMATION OF ZINC

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The usual method of estimation of zinc is by its separation as ZnS , dissolving and precipitation as $Zn(NH_4)PO_4$ and weighing as $Zn(NH_4)PO_4$ after drying or as $Zn_2P_2O_7$ after ignition. This lengthy method can be easily replaced if a standard volumetric method, free from the usual drawbacks, can be obtained. The following work was undertaken with a view to normalising the conditions of potassium ferrocyanide titration with a suitable indicator.

For the titration of zinc with potassium ferrocyanide numerous indicators have been suggested, both external and internal, but owing to the necessity of carefully controlled conditions of experiment and also to the colour change being not very distinct, their use is limited. Along with indicators like $FeSO_4$, diphenylamine, uranium nitrate (*J. Amer. Chem. Soc.*, 1927, **49**, 356; *Chemist and Analyst*, 1928, **17**, 14; *Chem. Weekblad.*, **24**, 203), ammonium molybdate (*Giorn. Chem. Ind. Appl.*, 1924, **6**, 234) has been tried and found to be more suitable than others. As the actual experimental results could not be obtained, a detailed study of this indicator has been made.

Factors influencing the end-point in the above titration are : (i) acidity, (ii) temperature, and (iii) presence of ammonium salts.

In cold acid solution the end-point is variable. in strongly acid solution it is not at all detectable. To get a quick end-point, the solution should be kept moderately hot, near about 50 to 60°, and an acid concentration of 5% in the final volume should be maintained. Ammonium chloride also helps in getting a sharp end-point. If it is not present, premature end-point is obtained or otherwise the titration has to be carried out very slowly. The following procedure may be conveniently adopted.

E X P E R I M E N T A L

Dissolve the sample, containing 0.03 g. ZnO in 25 c.c. of HNO_3 or HCl as found convenient. After filtration and washing off the metals like Pb , Sn , Ni , Cu , etc. if any, neutralise with ammonia, using phenolphthalein as indicator, bring the volume to 100 c.c., add 5 c.c. of glacial acetic acid and 10 c.c. of 10% ammonium chloride. Add 0.5 c.c. of 2% of ammonium molybdate solution (aqueous) and titrate with potassium ferrocyanide solution to a chocolate brown end-point. If traces of iron be present, the colour change at the end-point is from azure blue to chocolate brown, but much iron gives variable end-point and should be avoided by removal.

It has been observed that the more dilute the zinc solution, the longer it takes for attaining the equilibrium.

TABLE I

Sample.	Gravimetric.	Volumetric.	Diff.	% Error.
Zinc oxide	80.18%	80.08%	0.10	-0.12
" "	80.12	80.00	0.12	-0.14
" "	80.20	80.11	0.09	-0.11
" "	80.03	79.81	0.22	-0.26
Pigment	32.52	32.48	0.04	-0.12
" "	24.21	24.30	0.11	-0.45
Brass	40.16	40.00	0.16	-0.40
" "	39.80	39.72	0.08	-0.20

The following indicator has been tried with considerable success. The end-point is from blue to colourless. Although an outside indicator yet easy detection of the end-point makes it all the more convenient for use.

Preparation of the Indicator.—Take a 10% solution of ferric chloride, oxidise with a few drops of nitric acid, to ensure all the iron is in the oxidised condition, boil for 5 min., cool, discharge the yellow colour with dropwise addition of phosphoric acid (d, 1'75) and then 1 c.c. of HNO₃ in excess. A filter paper soaked with this solution is an external indicator.

Standardisation of K₃Fe(CN)₆ (34 g. per litre).—Take 50 c.c. of the solution, add 1 c.c. of HCl (1:1) and make up the volume to 100 c.c. Titrate with N/50-KMnO₄ until a drop of the solution no longer gives a blue colour. (A persistent blue ring, the inner zone being colourless, shows the presence of some unoxidised iron in the indicator). Repeat the titration with an addition of 25 c.c. of zinc solution, (2 g. ZnO per 500 c.c.) after neutralising and acidifying in a similar way. The difference between the two titres gives the number of c.c. equivalent to the amount of Zn present in 25 c.c. of the ZnO solution.

Estimation.—Dissolve 0.2 to 0.3 g. of the sample in 25 c.c. HNO₃. Filter and wash and after adjusting the acid concentration to 15% and boiling to remove any nitrous fume, electrolyse with platinum electrodes (6 volts and 0.4 amp.) for an hour. Add 2g. of NH₄Cl, neutralise and precipitate Fe or any other third group metal. Filter and wash, add a few drops of methyl orange and carefully neutralise with HCl and add 1 c.c. in excess. The volume at this time should be near about 100 c.c. Titrate as above. The estimation should be done, as usual, after removal of Sn, Pb, Fe, Ni, and Cu.

TABLE II

Sample.	Gravimetric.	Volumetric.	Diff.	% Error.
Zinc oxide	80.18%	80.00%	0.18	0.22
" "	80.12	80.10	0.10	0.02
" "	80.20	80.17	0.09	0.11
" "	80.03	80.13	0.10	0.12
Pigment	32.50	32.10	0.40	1.25
" "	24.41	24.09	0.32	1.33
" "	20.08	20.10	0.02	0.10
" "	15.56	15.50	0.06	0.38
" "	15.13	15.06	0.07	0.46
Brass	40.16	40.09	0.07	0.17
" "	39.80	39.60	0.20	0.50
" "	40.20	40.16	0.04	0.10
" "	38.86	38.81	0.05	0.12
" "	36.55	36.64	0.09	0.25
" "	41.11	41.09	0.02	0.05
Bronze	4.20	4.18	0.02	0.50
" "	4.16	4.14	0.02	0.50
Bearing metal	12.03	12.00	0.03	0.25
" "	10.54	10.59	0.05	0.48

The above method is very suitable for the estimation of ZnO in pigments and also Zn in non-ferrous metals and the estimations have been done mainly on those two materials.

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