DETERMINATION OF CALCIUM AND MAGNESIUM IN CLINKER, CEMENT & FLY ASH BASED CEMENT BY EDTA WITHOUT USING MASKING REAGENTS

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Abstract: *This method for determination of calcium and magnesium in clinker, ordinary Portland cement and fly ash based Portland pozzolana cement, is unique among the other available methods (such as gravimetric method, titrimetric method by using $KMnO_4$/ EDTA method as per IS:4032- [1].It is very quick method as compared to above. The uniqueness of this method is that it gives accurate results in short interval of time and also avoids use of high temperature muffle furnace.Calcium and magnesium are determined in filtrate after separation of combined ferric oxide and alumina from the sample solution.*

***Key words**: CaO, MgO, Cement, Clinker & EDTA.*

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INTRODUCTION:

Cement including Ordinary Portland cement, Portland Pozzolana cement are used as binding materials of concrete in civil construction industries. There is huge requirement of cement in construction work all over the world. The main ingredient of concrete structure as binder of concrete is cement. The quality of cement as per standard specification is very important for the cement manufacturing industries as well as for the civil construction industries for making solid and long life structure. Cement consists of mainly following constituents.

CHEMICAL COMPOSITION OF ORDINARY PORTLAND CEMENT, (OPC)[2]:

TABLE-1

Sr. No.	Constituents	Range
1	Silica (as SiO_2)	17-25 %
2	Calcium (as CaO)	60-67%
3	Alumina (as Al_2O_3)	3-8 %
4	Iron (as Fe_2O_3)	0.5-6%
5	Magnesia (as MgO)	0.5-4.0 %
6	Oxides of alkalis (Na_2O & K_2O)	0.3-1.2 %
7	Sulphuric Anhydride (as SO_3)	2.0 -3.5 %

Above range of constituents exists in complex compound form.

Sr. No.	Formal Name of Compound	Abbreviated Formula #	Formula	Brogue's Equation for calculating %age of compound
1	Tri Calcium Silicate	C_3S	($3CaO. SiO_2$)	$4.07*CaO-7.60*SiO_2-6.72*Al_2O_3-1.43*Fe_2O_3-2.85*SO_3$
2	Di Calcium Silicate	C_2S	($2CaO.SiO_2$)	$2.87*SiO_2-0.75*C_3S$
3	Tri Calcium Aluminate	C_3A	($3CaO. Al_2O_3$)	$2.65*Al_2O_3-1.69*Fe_2O_3$
4	Tetra Calcium Aluminate Ferrite	C_4AF	($4CaO. Al_2O_3.Fe_2O_3$)	$3.04*Fe_2O_3$

**#**The above symbols are used in cement manufacturing industries.

The main constituent of the cement and clinker is calcium oxide (CaO) which is the major factor for cement quality. It is determined by several analytical techniques. One of the analytical technique to determine calcium oxide is complexometric titration with EDTA. It is

also used to find the total calcium and magnesium content of milk, sea water and various solid materials. It can also be used to determine the total hardness of fresh water provided the solutions used are diluted. The combined concentration of calcium and magnesium ions is thetotal hardness of water.

The method uses a very large molecule called EDTA which forms a complex with calcium and magnesium ions. A blue dye called Eriochrome Black T (EBT) is used as the indicator. This blue dye also forms a complex with the calcium and magnesium ions, changing colour from blue to pink in the process. The dye–metal ion complex is less stable than the EDTA–metal ion complex. For the titration, the sample solution containing the calcium and magnesium ion reacts with an excess of EDTA. The indicator is added and colour changes to blue as all the Ca2+ and Mg2+ ions present are complexed with the EDTA.

The main reaction is:

$$Ca^{2+} + EDTA^{4-} \rightarrow [Ca\text{-}EDTA]^{2-}$$
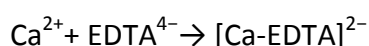
In complexometric titration with EDTA, interferences are mainly caused from cations of iron, aluminium and manganese. Apart from reacting with EDTA, these metals also react irreversevely with indicators. These cations also give rise to colour change in the indicator, making difficult to detect the end point. However, there are standard test methods available to determine calcium oxide and magnesium oxide by EDTA method. But the present study has been carried out to develop a method quicker, accurate and less expensive method.

GLASS APPARATUS REQUIRED:

Pipette (25 ml,10ml & 50ml capacity),burette(10 ml, 25 ml capacity), Volumetric flask (100ml, 250ml, 500ml & 1000ml capacity), Conical flask-100 ml capacity.

CHEMICAL & REAGENTS REQUIRED:

STANDARD EDTA SOLUTION:0.01 M:[3]

Dissolve 1.8612 gm of disodium ethylenediamine tetra acetate dihydrate in 200 ml hot water and make up the volume to 500 ml in calibrated volumetric flask.

BUFFER SOLUTION-pH 10: [4]

Dissolve 70 g of ammonium chloride in 570 ml of ammonium hydroxide (sp gr. 0.90) and make up volume to 1000 ml with distilled water in a calibrated volumetric flask.

STANDARD ZINC SOLUTION:0.01M: [5]

Dissolve accurately weighed 0.6537gm of granulated zinc in minimum quantity of dilute hydrochloric acid (1:1). Make up to mark with distilled water in a calibrated volumetric flask of capacity 1000 ml.

ERICHROME BLACK T- INDICATOR: [6]

Grind 100 mg of indicator with 10 gm of sodium chloride till homogeneous mixture is obtained and store in an airtight container.

PATTON-REEDERS INDICATOR /(P & R) INDICATOR :[7]

[2-hydroxy-1-(2-hydroxy-4 - Sulpho -1-Napthylazo)-3-Napthoic Acid], ($C_{21}H_{14}N_2O_7S$)

Grind 100 mg of indicator with 10 gm of sodium or potassium sulphate till homogeneous mixture is obtained and store in airtight bottle.

METHYLTHYMOLBLUE INDICATOR-MIXTURE:

0.1 gm Methylthymolblue mixed with 10 gm of KNO_3.

STANDARDIZATION OF EDTA- SOLUTION USING STANDARD ZINC SOLUTION:

Take 10 ml of standard zinc solution in conical flask. Add 20 ml buffer solution of pH-10 and warm at 50 to 60°C. Add 50 mg Erichrome Black –T indicator and titrate with 0.01M EDTA till the color changes from red wine to clear pink blue. Note the volume of EDTA used and calculate the molarity of EDTA by using formula,   M1xV1 = M2xV2

Note: Use burette of least count 0.05 ml for accurate results.

TABLE-2

Sr. No.	Molarity of zinc Solution (M1)	Volume of Zinc Solution (V1-ml)	Molarity of EDTA Solution (M2)	Volume of EDTA Solution (V2-ml)	M1 x V1 = M2 x V2 M2 = (M1 x V1) / V2
1	0.01	10	To be determined	9.85	0.01015
2	0.01	10	To be determined	9.90	0.01010
3	0.01	10	To be determined	9.85	0.01015
Average Molarity of EDTA Solution using standard zinc solution:					**0.01013**

STANDARDIZATION OF EDTA- SOLUTION USING CERTIFIED REFERENCE MATERIAL CaCO₃:

Weigh known quantity (W-gm) of the standard $CaCO_3$ traceable to NIST into a 100 ml capacity conical flask and dissolve in 25 ml- distilled water andadd 10 ml of 10 % KOH solution and shake well to adjust pH to highly alkaline range of 12 or slightly more. Add approximately 50 ml of distilled water and 50 mg of solid P & R indicator. Titrate against 0.01 M EDTA solution to a sharp change in colour from wine red to clear blue.

TABLE-3

Purity of $CaCO_3$ [8]	A	=	99.98 %
Equivalent weight of $CaCO_3$	B	=	50.03
Molecular weight of $CaCO_3$	C	=	100.09
Purity Fraction	D	=	Purity/100

TABLE-4

Sr. No.	Weight of $CaCO_3$ Taken (W-gm)	Purity fraction of $CaCO_3$ (D)	Volume of EDTA Consumed (V-ml)	Molecular weight of $CaCO_3$ (C)	Molarity of EDTA Solution (W*D*1000)/(V*C)
I	0.01232	0.9998	12.1	100.09	0.01017
II	0.01626	0.9998	15.9	100.09	0.01021
III	0.01142	0.9998	11.2	100.09	0.01018
Average Molarity of EDTA Solution using standard Calcium Carbonate					0.01019
Final Average Molarity used for Calculation M-EDTA Average of (molarity standardized against Zinc and molarity standardized against Std. Calcium Carbonate) = (0.01013+ 0.01019)/2					0.01016

PREPARATION OF SOLUTION OF CEMENT/CLINKER SAMPLE:

Take approximately0.5 gm of the sample in an evaporating clean dish / clean beaker; moisten with 10 ml of water at room temperature. Care should be taken to avoid any lump formation. Add 5 to 10 ml of HCl and agitate with the help of policeman (glass rod fitted with rubber / glass rod soften at the agitating end by melting), till completely dissolves. Evaporate the solution till complete dryness on a steam bath or hot plate, temperature of the steam bath or hot plate should be adjusted in such a way to avoid any spurting of the sample from dish or beaker. Without heating the residue, further treat it 1:1 HCl and water (20-ml) and digest on the water bath or hot plate. Dilute the volume with equal volume of hot water. Filter through ash less filter paper (Whatman No 40 or its equivalent), wash the

separated silica thoroughly with hot water and reserve the residue.Re evaporate the filtrate to dryness; bake the residue in an oven for one hour at 105 to 110 deg. C. Treat the residue with 20-ml of HCl (1:1) and heat the solution on water bath or on hot plate. Dilute the solution with an equal volume of hot water and catch the silica into the filter paper. Make up the filtrate up to 250 ml in a calibrated volumetric flask. Reserve the filtrate and washings for separation of combinedaluminium and Iron oxide.

SEPARATION OF COMBINED FERRIC OXIDE AND ALUMINA FROM SAMPLE SOLUTION:

From the filtrate reserved above in 250ml volumetric flask, take 50 ml aliquot into a conical flask, add few drops (1-ml of H_2O_2 + 1-ml of HNO_3) and heat to boiling in order to oxidize any ferrous iron to the ferric condition. Treat the boiled solution with (1:1) NH_4OH drop- wise till colour of the solution becomes distinctly yellow and subsequently treat this solution with 0.5 gm of $NH_4S_2O_8$ and pour excess four –five drops NH_4OH until the indicator turns yellow. Boil the solution for further one minute and allow the precipitate to settle for five minutes and filter through Whatman No. 41filter paper and wash with 2 % hot NH_4NO_3.

Transfer precipitate&filter paper to original beaker and dissolve the precipitatewith hot dilute HCL (1:3) and dilute to 100 ml.Re-precipitate the hydroxides and filter the solution.Wash the precipitate with two to 10 ml portion of the hot NH_4NO_3 solution. Combine the filtrate and washings and make up to 250-ml in a calibrated volumetric flask. Reserve the filtrate for determination of CaO and MgO.

(Final Solution:0.5 gm into 250 ml volumetric flask, Aliquot 50 ml and volume make up 250 ml)

DETERMINATION OF CALCIUM BY EDTA-METHOD:

Take 50-ml aliquot of the solution (reserved for determination of CaO & MgO) into a conical flask and add 1 gm of NH_4NO_3+ 20 ml of 10 % KOH and shake well to adjust pH to highly alkaline range of 12 or slightly more. Add approximately 50 ml of distilled water and 50 mg of P&R indicator. Titrate against 0.01 M EDTA solution to a sharp change in colour from wine red to clear blue. Record the volume of EDTA consumed (V-ml).

Calculations: Calculate the percentage of CaO

% CaO= (V-EDTA x 56.08 x M-EDTA x100) / (1000 x Weight of samplein aliquot taken)

Where,

V-ml=   Volume of EDTA solution consumed-ml,

M-EDTA = Molarity of EDTA

DETERMINATION OF MAGNESIUM BY EDTA-METHOD:

Take 50- ml of the solution (reserved for determination of CaO and MgO) add 1-gm of NH_4NO_3 + 20 ml. of buffer solution of pH 10 and 20 ml of NH_4OH. Add 50 mg of methylthymolblue indicator and titrate against 0.01-M EDTA to change colour from light blue to colourless greyor50-mg of EBT indicator and titrate it against standard 0.01-M EDTA solution until the colour changes from pink to light green. This titration gives the sum of the calcium and magnesium oxide present in the sample solution. Titre value of magnesium is obtained by subtracting the titre value of calcium oxide (V-ml) from the total titre valueof (calcium + magnesium oxide), (V1ml).

Calculations:

Calculate the percentage of MgO

Magnesium Oxide (MgO) percent =(V1-V) x 40.32 x M-EDTA x 100 / (1000 x W)

Where,

V1 = Titre value used for total (calcium + magnesium)

V = Titre value used for Calcium

W = Weight of the sample in aliquot.

VALIDATION OF METHOD USING REFERENCE MATERIAL OF KNOWN CHEMICAL COMPOSITION FOR CaO AND MgO:

NAME OF REFERENCE MATERIAL FOR ORDINARY PORTLAND CEMENT(OPC):

Reference Material CRM-1012K-Ordinary Portland Cement Standard [9]

TABLE-5

CHEMICAL COMPOSITION OF CRM-1012K

Sr. No.	Chemical Constituents	% By Mass	Expanded Uncertainty (Coverage Factor k=2)
1	Loss On Ignition	3.56	± 0.02
2	Silica (as SiO_2)	21.27	± 0.06
3	Iron (as Fe_2O_3)	4.14	± 0.02
4	Alumina (as Al_2O_3)	4.51	± 0.05
5	Calcium (as CaO)	61.42	± 0.14
6	Magnesium (as MgO)	1.21	± 0.04
7	Sulphuric Anhydride (SO_3)	2.06	± 0.03
8	Sodium (as Na_2O)	0.22	± 0.003
9	Potassium (as K_2O)	0.46	± 0.006

NAME OF REFERENCE MATERIAL FOR PORTLAND POZZOLANA CEMENT:

Reference Material CRM-1016C- Portland Pozzolana Cement Standard [10]

TABLE-6

CHEMICAL COMPOSITION OF CRM-1016C

Sr. No.	Chemical Constituents	% By Mass	Expanded Uncertainty (Coverage Factor k=2)
1	Loss On Ignition	4.58	± 0.02
2	Silica (as SiO_2)	31.24	± 0.11
3	Iron (as Fe_2O_3)	3.78	± 0.03
4	Alumina (as Al_2O_3)	9.99	± 0.05
5	Calcium (as CaO)	44.89	± 0.12
6	Magnesium (as MgO)	1.13	± 0.04
7	Sulphuric Anhydride (SO_3)	2.18	± 0.03
8	Sodium (as Na_2O)	0.27	± 0.01
9	Potassium (as K_2O)	0.60	± 0.01

EXPERIMENT CARRIED OUT:

TABLE-7

Sample Name	Sr. No.	Weight of sample taken (gm)	Volume make Up (ml)	Aliquot taken for R_2O_3 Separation(ml)	Volume make from the filtrate of R_2O_3 (ml)	Aliquot taken for testing of CaO & MgO(ml)	weight of Final aliquot(sample in aliquot)(gm)	EDTA Used for CaO Titration(V-ml)	EDTA Used for MgO Titration(V1-ml)	% CaO = (V*M*56.08*100)/(wt. of aliquot*1000)	% MgO = (V1-V)*M*40.32*100)/(wt. of aliquot*1000)
ORDINARY PORTLAND CEMENT	1	0.5034	250	50	250	50	0.020136	21.7	22.3	61.40	1.22
	2	0.5031	250	50	250	50	0.020124	21.7	22.3	61.44	1.22
	3	0.5012	250	50	250	50	0.020048	21.6	22.2	61.39	1.23
	Average analytical results of Calcium Oxide (CaO) and Magnesium Oxide (MgO) %									61.41	1.22
PORTLAND POZZOLANA	1	0.5018	250	50	250	50	0.020072	15.8	16.4	44.85	1.22
	2	0.5042	250	50	250	50	0.020168	15.9	16.4	44.92	1.02
	3	0.5024	250	50	250	50	0.020096	15.8	16.4	44.80	1.22
	Average analytical results of Calcium Oxide (CaO) and Magnesium Oxide (MgO) %									44.86	1.15

(PRIMARY DATA ON ACTUAL ANALYSIS BASIS) [11]

TABLE-8

COMPARISON OF ANALYTICAL VALUES WITH KNOWN VALUES OFCRM

Analyte		CRM-1012K (Ordinary Portland Cement)			CRM-1016C (Portland Pozzolana Cement)		
		Analytical Results by experiment	CRM Value	Remarks	Analytical Results by experiment	CRM Value	Remarks
Calcium (as CaO)	I	61.40		Average analytical value of CaO is within the specified limit of CRM.	44.85		Average analytical value of CaO is within the specified limit of CRM.
	II	61.44			44.92		
	III	61.39			44.80		
Average Value		61.41	61.42 ± 0.14		44.86	44.89 ± 0.12	
Magnesium (as MgO)	I	1.22		Average analytical value of MgO is within the specified limit of CRM.	1.22		Average analytical value of MgO is within the specified limit of CRM.
	II	1.22			1.02		
	III	1.23			1.22		
Average Value		1.22	1.21 ± 0.04		1.15	1.13 ± 0.04	

CONCLUSION:

The above test procedure for determination of Calcium Oxide (CaO) and Magnesium Oxide (MgO) has been used for determination of known values of two Certified Reference Materials (CRM). The analytical results by experiments have been found within the specified tolerance of the known values.

REFERENCE:

1. IS 4032-1985

2. Safari Books Online (Chemical Composition of Portland Cement)

3. Clause 4.1.15 of IS 4032-1985

4. Clause 4.1.13 of IS 4032-1985

5. Clause 4.1.14 of IS 4032-1985

6. Clause 4.1.16 of IS 4032-1985

7. Clause 4.1.18 of IS 4032-1985

8. Certified Reference Material (CRM) traceable to NIST of CaCO3

9. Certificate of Analysis for Ordinary Portland Cement (OPC) Standard (CRM-1012 K)

10. Certificate of Analysis for Portland Pozzolana Cement (PPC) Standard (CRM-1016 C)

11. Primary Analytical Data for OPC and PPC.