NCB RAPID EDTA METHODS FOR ESTIMATION OF MAJOR CONSTITUENTS IN CEMENT

A Monograph

MS-12-87

NATIONAL COUNCIL FOR CEMENT AND BUILDING MATERIALS

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PREFACE

Chemical analysis is required in cement manufacture for evaluating the quality of raw materials, raw meal and finished products and for effecting quality control. As the traditional practices in chemical analysis were time consuming some time resulting in inadequate data for proper evaluation, the Cement Research Institute (CRI) of NCB developed rapid complexometric (EDTA) methods of estimation of major constituents in cement; these methods ensured accuracy and reproducibility while saving time and cost in testing. Most of the cement plants in India today follow these methods.

These methods were published as a monograph in 1979 (MS-6-79) and widely circulated to cement plants and concerned laboratories. The Centre for Continuing Education (CCE) of NCB also conducted training courses and contact programmes for analysts and chemists from cement plants and laboratories. The feedback confirmed the advantages complexometric methods have.

In view of the importance of these methods to the cement industry, NCB has been all along monitoring and improving the efficacy of the technique and the present monograph also incorporates improvements in presentation on the basis of the feedback from the users. It is hoped that it would prove handy guide to chemists and analysts working in cement plants and other laboratories.

New Delhi
01 November 1986

H C Visvesvaraya
Chairman and Director-General

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NCB RAPID EDTA METHODS FOR ESTIMATION OF MAJOR CONSTITUENTS IN CEMENT

1. INTRODUCTION

1.1 National Council for Cement and Building Materials (NCB) has developed rapid complexometric (EDTA) methods of analysis after thorough investigations and critical testing of the methods for their precision and accuracy. The data thus obtained have been statistically evaluated and the results are presented in Appendix A (Tables 1-4). The maximum deviation from the true value obtained by the NCB rapid EDTA methods of analysis for Fe_2O_3, Al_2O_3, CaO, and MgO is of the order of $\pm$ 0·15, $\pm$ 0·15, $\pm$ 0·2, $\pm$ 0·2 respectively. The average mean deviations from the true values have been calculated to be 0·06 for Fe_2O_3 and Al_2O_3 and 0·08 for CaO and MgO. It is evident, therefore, that these methods are capable of giving a high degree of precision and accuracy. Above all, these methods offer an alternative to those prescribed in IS: 4032-1968* for the determination of these elements.

1.2 This monograph gives the procedures for the rapid estimation of major constituents in ordinary, rapid hardening and low-heat portland cement, by EDTA methods as standardized by NCB.

2. SAMPLING

2.1 The samples of cement shall be drawn as per the requirements of IS: 3535-1966†.

3. REAGENTS

3.1 Unless specified otherwise, pure chemicals of analytical reagent grade shall be employed in all tests. Distilled water conforming to IS: 1070-1960‡ shall be used where the use of water as a reagent is intended.

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* Methods of chemical analysis of hydraulic cements.

† Methods of sampling hydraulic cements.

‡ Water, distilled quality.

3.2 The following reagents are required for the purposes of these methods of estimation :

a) *Acetic Acid*—glacial.

b) *Sulphuric Acid*—1·3 (by volume).

c) *Hydrochloric Acid*—1:1 (by volume).

d) *Phosphoric Acid*—1·3 (by volume).

e) *Nitric Acid*—sp gr 1·42

f) *Sulphosalicylic Acid*—solid.

g) *Ammonium Hydroxide*—1:1, 1:6 (by volume).

h) *Sodium Hydroxide Solution*—4 N (approximately). Dissolve 80 g sodium hydroxide in 500-ml volumetric flask. Make up to the mark with distilled water.

j) *Potassium Periodate.*

k) *Glycerol*—1:1 (by volume).

m) *Triethanolamine*—1:1 (by volume).

n) *Diethylamine*—liquid.

p) *Ammonium Acetate* - 50 per cent solution. Weigh 50 g of ammonium acetate and make up the volume to 100 ml with distilled water.

q) *Thymol Blue*—0·1 per cent solution in ethyl alcohol.

r) *Bismuth Nitrate Solution*—Weigh about 5 g of bismuth nitrate pentahydrate, $Bi(NO_3)_3 . 5H_2O$ in a 500-ml dry beaker. Add 25 ml acetic acid. Stir and dilute with about 40 ml water. Filter and transfer the solution to one litre volumetric flask and make up the volume to the mark with distilled water.

s) *Buffer Solution pH 10*—Dissolve 70 g ammonium chloride in 570 ml of ammonium hydroxide (sp gr 0·92) and make up to one litre with distilled water.

t) *Standard Zinc Solution*—0·01M. Weigh accurately 0.6537 g analytical reagent grade granulated zinc and dissolve it in the minimum quantity of dilute hydrochloric acid (1:1). Make up to the mark with distilled water in one litre flask.

u) *Standard EDTA Solution*—0·01M. Dissolve 3·7224 g of disodium ethylenediamine tetra acetate dihydrate in 400 ml hot water and make up the volume in one litre flask. Take 10 ml of standard

zinc solution in an Erlenmeyer flask. Add buffer solution of *p*H 10 and warm to 50°-60°C. Add 50 mg Eriochrome Black-T indicator and titrate with EDTA till the colour changes from wine red to clear blue. Note the volume (V) of EDTA used.

$$\text{Molarity of EDTA} = \frac{0{\cdot}01 \times 10}{V}$$

Adjust the molarity to 0·01 M if required.

v) *Eriochrome Black-T*—Grind 100 mg of indicator with 10 g of sodium chloride. Store in airtight polythene bottle.

w) *Xylenol Orange*—Grind 1 g of indicator with 100 g potassium nitrate and store in an airtight bottle.

x) *Patton and Reeder Indicator*—Grind 100 mg of the indicator with 10 g of sodium or potassium sulphate until a homogeneous mixture is obtained. Store in an airtight bottle

y) *Thymol Phthalexone Indicator*—Grind 100 mg of thymol phthalexone indicator with 10 g of potassium nitrate. Store it in an airtight container.

3.3 Use of Filter Papers—In the present methods, Whatman filter papers have been prescribed; however, any other suitable brand of filter papers with equivalent porosity may be used.

4. REPRODUCIBILITY OF RESULTS

4.1 Blank determinations shall be made on the reagents for each constituent in the cement and the corrections shall be applied where necessary. In all cases check determinations shall be made and repeated if satisfactory checks are not obtained. The reproducibility of the results shall be within the accuracies mentioned in **1.1.**

5. PREPARATION OF THE SAMPLE SOLUTION

5.1 Weigh accurately into a 250-ml beaker about 0 5 g of the sample which has been previously dried at 105°C for one hour. Moisten with water and add 10 ml hydrochloric acid (1:1) to it. Heat to boil to ensure complete decomposition Wash the walls of the beaker with distilled water and evaporate to dryness on a steam-bath. Bake for one hour in an oven at 105°C and add 10 ml (1:1) HCI. Heat and filter immediately through Whatman filter paper 40. Preserve the filtrate. Fuse the residue left after hydroflourization of silica with sodium or potassium per sulphate and dissolve in hydrochloric acid. Add thus solution to filtrate. Then cool and dilute the solution to 250 ml in a standard volumetric flask.

6. DETERMINATION OF FERRIC OXIDE

6.1 Measure out 25 ml of the acid solution of the sample (*see* **5.1**) and add very dilute ammonium hydroxide (1:6) till turbidity appears. Clear the turbidity with a minimum amount of dilute hydrochloric acid (1:3) and add a few drops in excess to adjust the *p*H to 1-1·5. Shake well. Then add 100 mg of sulphosalicylic acid and titrate with 0·01 M EDTA solution carefully to a colourless or pale yellow solution.

6.2 Calculations

1 ml of 0·01 M EDTA = 0·7985 mg of Fe_2O_3

$$\text{Iron Oxide } (Fe_2O_3) \text{ Per cent by weight} = \frac{0{\cdot}7985 \times V}{W}$$

where, V = volume of EDTA used, and

W = weight of the sample in g.

7. DETERMINATION OF ALUMINA

7.1 Measure out 25 ml of the acid solution of the sample as prepared under **5.1** and titrate iron at *p*H 1·5 with EDTA using sulphosalicylic acid as indicator as given under **6.1**. Add 15 ml standard EDTA solution. Add 1 ml of phosphoric acid (1:3), 5 ml of sulphuric acid (1:3) and one drop of thymol blue into the titration flask. Add ammonium acetate solution by stirring until the colour changes from red to yellow. Add 25 ml ammonium acetate in excess to attain a *p*H of about 6. Heat the solution to boiling for one minute and then cool. Add 0·5 g solid xylenol orange indicator and bismuth nitrate solution slowly with stirring until the colour of the solution changes from yellow to red. Add 2 to 3 ml of bismuth nitrate solution in excess. Titrate with EDTA to a sharp yellow end point.

7.2 Calculations

$$V_1 = V_2 - V_3 - (V_4 E)$$

where

V_1 = volume of EDTA for alumina,

V_2 = total volume of EDTA used in the titration,

V_3 = volume of EDTA used for iron (**6.1**),

V_4 = total volume of bismuth nitrate solution used in the titration, and

*E = equivalence of 1 ml of bismuth nitrate solution

1 ml of 0·01 M EDTA = 0·5098 mg of Al_2O_3

Aluminium Oxide (Al_2O_3) per cent by weight

$$= \frac{0{\cdot}5098 \times V_1}{W}$$

W = weight of the sample in g.

8. DETERMINATION OF CALCIUM OXIDE

8.1 Measure 10 ml of silica-free acid solution of the sample (*see* **5.1**) into a 250-ml conical flask. Add 5 ml of 1:1 glycerol with constant stirring and then 5 ml of diethylamine To this, add 10 ml of 4N NaOH solution and shake well to adjust *p*H to highly alkaline range of 12 or slightly more. Add approximately 50 ml of distilled water and 50 mg of solid Patton and Reeder's indicator. Titrate against 0·01 M EDTA solution. The end point of the titration is reached when one drop of EDTA produces a sharp change in colour from wine red to clear blue.

8.2 In the presence of high manganese (Mn_2O_3), the procedure is slightly modified as under : Measure 10 ml of silica-free acid solution of the sample into a 250-ml conical flask. Add 2-3 drops of nitric acid followed by 50 mg of potassium periodate. Keep the flask on water-bath till a pink colour develops. Shake and allow to cool to room temperature. Add 5 ml of 1:1 glycerol with constant stirring and then 5 ml of diethylamine. Add 3-4 pellets of NaOH and shake well to adjust the *p*H to 12 or slightly more. Add approximately 50 ml of distilled water and 100 mg of solid Patton and Reeder's indicator and titrate against 0·01 M EDTA solution. The end point of the titration is reached when one to two drops of EDTA produce a sharp change in colour from violet to blue.

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* Equivalence of bismuth nitrate solution is obtained as follows :
Transfer 100 ml of bismuth nitrate solution to a 500-ml flask and dilute with about 100 ml water. Add a few drops of thymol blue solution and ammonium acetate solution until the colour changes from red to yellow. Add xylenol orange indicator and titrate with 0·01 M EDTA until the colour changes from red to yellow.

The equivalence E (ml of 0·01 M EDTA) of 1 ml of bismuth nitrate solution is $E = \frac{V}{100}$ where V is the volume in ml of EDTA solution.

8.3 Calculations

1 ml of 0·01 M EDTA = 0·5608 mg of CaO

$$\text{Calcium Oxide (CaO) per cent by weight} = \frac{0{\cdot}05608 \times 25 \times V}{W}$$

where

V = volume of EDTA used and

W = weight of the sample in g.

9. DETERMINATION OF MAGNESIUM OXIDE

9.1 Measure out another aliquot of 10 ml of silica-free acid solution of the sample (*see* **5.1**). Add 5 ml of 1:1 triethanolamine with constant shaking and 20 ml of buffer solution of *p*H 10. Add 50m g of the solid thymol phthalexone indicator followed by approximately 50 ml of distilled water. Titrate it against standard EDTA solution until the colour changes from blue to clear pink. This titration gives the sum of calcium and magnesium present in the solution. Titre value of magnesium is obtained by subtracting the titre value of calcium from the total titre value.

9.2 Calculations

1 ml of 0·01 M EDTA = 0·4032 mg of MgO

$$\text{Magnesium Oxide (MgO) per cent by weight} = \frac{0{\cdot}04032 \times 25 \times V_1 - V)}{W}$$

where

V_1 = volume of EDTA used in this titration.

V = volume of EDTA used in CaO determination, and

M = weight of the sample in g.

APPENDIX A

ANALYTICAL DATA ON MAJOR CONSTITUENTS OF CEMENT DETERMINED BY NCB EDTA METHODS AND STATISTICAL EVALUATION OF THE DATA

TABLE 1

ESTIMATION OF IRON IN NBS-SRM CEMENT SAMPLES BY NCB RAPID EDTA METHOD AND STATISTICAL EVALUATION OF THE RESULTS

	NBS-1011			NBS-1013			NBS-1014		
	True Value %	*Observed Value* %	*Deviation from True Value*	*True Value* %	*Observed Value* %	*Deviation from True Value*	*True Value* %	*Observed Value* %	*Deviation from True Value*
	2·07	2·07	0·00	3·07	2·97	−0·10	2·50	2·48	−0·02
		2·02	−0·05		3·10	+0·03		2·60	+0·10
		1·99	−0·08		3·05	−0·02		2·58	+0·08
		2·09	+0·02		3·15	+0·08		2·40	−0·10
		2·15	+0·08		3·17	+0·10		2·50	0·00
		2·21	+0·14		3·06	−0·01		2·36	−0·14
		2·03	−0·04		3·20	+0·13		2·63	+0·13
		2·20	+0·13		2·99	−0·08		2·42	−0·08
		2·08	+0·01		3·09	+0·02		2·52	+0·02
		2·06	−0·01		3·06	−0·01		2·37	−0·13
		2·07	0·00		3·19	+0·12		2·51	+0·01
		2·06	−0·01		2·96	−0·11		2·64	+0·14
		1·97	−0·10		3·07	0·00		2·47	−0·03
		2·17	+0·10		2·94	−0·13		2·50	0.00
		2·05	−0·02		3·08	+0·01		2·49	−0·01
No of observations		15					15		15
Maximum value		2·21					3·20		2·64
Minimum value		1·97					2·94		2·36
Mean value		2·08					3·07		2·49
Mean deviation		0·05					0·06		0·06
Standard deviation (10^{-2})		7·2					8·2		8·9

TABLE 2

ESTIMATION OF ALUMINA IN NBS-SRM CEMENT SAMPLES BY NCB RAPID EDTA METHOD AND STATISTICAL EVALUATION OF THE RESULTS

NBS-1011			NBS-1013			NBS-1014		
True Value %	*Observed Value* %	*Deviation from True Value*	*True Value* %	*Observed Value* %	*Deviation from True Value*	*True Value* %	*Observed Value* %	*Deviation from True Value*
5·38	5·40	+0·02	3·30	3·32	+0·02	6·38	6·39	+0·01
	5·36	−0·02		3·38	+0·08		6·36	−0·02
	5·38	0·00		3·29	−0·01		6·46	+0·08
	5·39	+0·01		3·28	−0·02		6·38	0·00
	5·39	+0·01		3·40	+0·10		6·37	−0·01
	5·29	−0·09		3·26	−0·04		6·50	+0·12
	5·45	+0·07		3·16	+0·14		6·48	+0·10
	5·48	+0·10		3·31	+0·01		6·38	0·00
	5·37	−0·01		3·28	−0·02		6·39	+0·01
	5·23	−0·15		3·17	−0·13		6·29	−0·09
	5·24	−0·14		3·30	0·00		6·24	−0·14
	5·37	−0·01		3·32	+0·02		6·37	−0·01
	5·28	−0·10		3·43	+0·13		6·38	0·00
	5·52	+0·14		3.44	+0·14		6·28	−0·10
	5·50	+0·12		3·20	− 0·10		6·23	−0·15
Number of observations	15			15			15	
Maximum value	5·52			3·44			6·50	
Minimum value	5·23			3·16			6·23	
Mean value	5·37			3·30			6·37	
Mean deviation	0·07			0·06			0·06	
Standard deviation (10^{-2})	8·9			8·6			8·8	

TABLE 3

ESTIMATION OF CALCIUM OXIDE IN NBS-SRM CEMENT SAMPLES BY NCB RAPID EDTA METHOD AND STATISTICAL EVALUATION OF THE RESULTS

	NBS-1011			NBS-1013			NBS-1014		
	True Value %	*Observed Value* %	*Deviation from True Talue*	*True Value* %	*Observed Value* %	*Deviation from Mean Value*	*True Value* %	*Observed Value* %	*Deviation from True Value*
	66·60	66·58	−0·02	64·34	64·35	+0·01	63·36	63·34	−0·02
		66·51	−0.09		64·17	−0·17		63·20	−0·16
		66·68	+0·08		64·44	+0·10		63·33	−0·03
		66·70	+0·10		64·27	−0·07		63·50	+0·14
		66·43	−0·17		64·50	+0·16		63·18	−0·18
		66·76	+0·16		64·16	−0·18		63·44	+0·08
		66·42	−0·18		64·31	−0·03		63·26	−0·10
		66·78	+0·18		64·52	+0·18		63·35	−0·01
		66·62	+0·02		64·40	+0·06		63·28	−0·08
		66·50	−0·10		64·34	0·00		63·36	−0·00
		66·61	+0 01		64 30	−0·04		63·46	+0·10
		66·60	−0.00		64·35	+0·01		63·36	0·00
		66·52	−0·08		64·24	−0·10		63·35	−0·01
		66·61	+0·01		64·37	+0·03		63·54	+0·18
		66·59	−0·01		64·33	−0·01		63·34	−0·02
No of observations		15			15			15	
Maximum value		66·78			64·52			63·54	
Minimum value		66·42			64·16			63·18	
Mean value		66·59			64·33			63·35	
Mean deviation		0·08			0·08			0·07	
Standard deviation (10^{-2})		10·6			10·2			10·0	

TABLE 4

ESTIMATION OF MAGNESIUM OXIDE IN NBS-SRM CEMENT SAMPLES BY NCB RAPID EDTA METHOD AND STATISTICAL EVALUATION OF THE RESULTS

NBS-1011			NBS-1013			NBS-1014		
True Value %	*Observed Value* %	*Deviation from True Value*	*True Value* %	*Observed Value* %	*Deviation from True Value*	*True Value* %	*Observed Value* %	*Deviation from True Value*
1 12	1·09	−0·03	1·39	1·38	−0·01	2·80	2·79	−0·01
	1·30	+0·18		1·22	−0·17		2·63	−0·17
	1·03	−0·09		1·57	+0·18		2·71	−0·09
	1·22	+0·10		1·41	+ 0·02		2·98	+0·18
	1·11	−0·01		1·23	− 0·16		2·84	+0·04
	1·20	+0·08		1·39	0·00		2·62	−0·18
	1·12	0·00		1·49	+0·10		2·78	−0·02
	1·29	+0·17		1·31	−0·08		2·76	−0·04
	1·02	−0·10		1·56	+0·17		2·81	+0·01
	1·15	+0·03		1·29	−0·10		2·80	0·00
	0·96	−0·16		1·38	−0·01		2·97	+0·17
	1·11	−0·01		1·46	+0·07		2·90	+0·10
	0·94	− 0·18		1·36	−0·03		2·89	+0·09
	1·13	+0·01		1·40	+0·01		2·82	−0·02
	1·14	+0·02		1·40	+0·01		2·70	+0·10
No of observations	15			15			25	
Maximum value	1·30			1·57			2·98	
Minimum value	0·94			1·22			2·62	
Mean value	1·12			1·39			2·80	
Mean deviation	0·08			0·07			0·08	
Standard deviation (10^{-2})	10·6			10·3			10·8	


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