NCB RAPID EDTA METHODS FOR ESTIMATION OF MAJOR CONSTITUENTS IN LIMESTONE

A Monograph
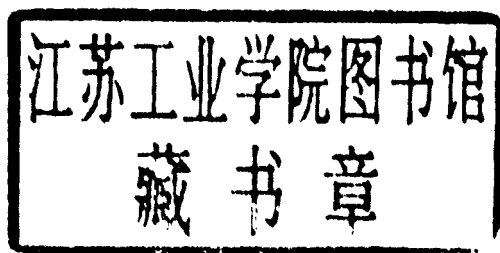
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PREFACE

Chemical analysis is employed in Cement Industry for evaluating the quality of raw materials, exercising manufacturing controls and controlling the quality of cement produced. The conventional gravimetric and volumetric methods generally used in most cement plants in India are laborious and time consuming. As compared to these, complexometric (EDTA) methods are simple, fast and easy to operate. The scope of applying these methods for the estimation of major oxides present in limestone, was therefore, taken up by NCB for investigation as far back as 1967.

After a long laboratory trials and feed back of plant experiences, and wide acceptance, the methods were published as a monograph in 1979 (MS-4-79) and more widely circulated to cement plants and concerned laboratories. NCB also organised training courses and contact training programmes, where chemists from cement plants and laboratories participated. The feedback testifies that the complexometric methods have been found very useful for controlling effectively the process and quality of the product. Consequently most of the cement plants in India have adopted these methods.

This monograph gives the practical details of the methods and it is hoped that it would be quite useful to working analysts and chemists in cement plants and other laboratories and pave the way for still more rapid and modern methods.

New Delhi
22 October 1986

H C Visvesvaraya
Chairman and Director-General

C O N T E N T S

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A Monograph

1. INTRODUCTION

1.1 The scope of applying complexometric (EDTA) methods for the analysis of limestone seemed to remain unexplored. Since the methods were potentially useful in cement manufacture and quality control, studies were undertaken in NCB to develop and standardize them for the rapid and accurate determination of Fe_2O_3, Al_2O_3, CaO and MgO in limestone. The results of these investigations have been presented in Appendix A (Tables 1-4)

1.2 The data obtained have been statistically evaluated and the values for the various statistical functions also presented in the above tables. The maximum deviations from the true values obtained by the NCB rapid EDTA methods as applied to NBS-SRM limestones are of the order of $\pm$ 0·15 for iron and aluminium, and $\pm$ 0·2 for calcium and magnesium. The average mean deviations from the true values are 0·06, 0·05, 0·09 and 0·08 for Fe_2O_3, Al_2O_3, CaO and MgO respectively. This indicates that the methods are highly precise and accurate. The methods have also been applied to the determination of these constituents in commercial samples of limestones and the data statistically evaluated.

1.3 In view of their suitability for the quantitative estimation of Fe_2O_3, Al_2O_3, CaO and MgO in limestone, these methods can be alternative to the methods of analysis of these constituents given in IS : 1760-1962*. This monograph covers the rapid EDTA methods of estimation of major constituents in limestone as standardized in NCB.

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* Methods of chemical analysis of limestone, dolomite and allied materials.

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2. SAMPLING

2.1 Laboratory Sample—The sample shall be drawn and prepared in accordance with IS : 2109-1962*, since a truly representative and homogeneous sample is essential.

2.2 Test Sample—Grind 5 to 10 g of the laboratory sample to pass through IS Sieve 15 (100 mesh). Dry to constant weight at 105° ± 2°C and use it for the purpose of chemical analysis.

3. REAGENTS

3.1 For the purposes of the methods given in the monograph, analytical grade reagents should be used, unless otherwise specified. If distilled water is required to be used as a reagent, it should conform to IS : 1070-1962†.

3.2 Use of Filter Papers—Relative numbers of Whatman filter paper or any other suitable brand of filter paper of corresponding porosity may be used.

4. PREPARATION OF THE SAMPLE SOLUTION

4.1 Take about 0˙7g of the sample of limestone in a platinum crucible and add 5 times its weight fusion mixture (Na_2CO_3 and K_2CO_3 in equimolecular quantities). Heat the material on low flame in a burner and then at 1000°C in a muffle furnace for 30 minutes. Extract in 40 ml HCl (1 : 1) and evaporate on a steam-bath. Bake for 30 minutes at 105°C in an oven and add 15 ml (1:1) HCl. Filter through Whatman 40, wash the residue left 5-6 times with hot water and estimate silica after hydrofluorization. Fuse the residue with sodium or potassium persulphate and dissolve it in hydrochloric acid. Add this to the filterate, cool and dilute the solution to 250 ml mark in a standard volumetric flask.

5. DETERMINATION OF FERRIC OXIDE

5.1 Outline of the Method—A suitable aliquot of the silica-free acid solution of the sample is titrated against standard EDTA solution at *p*H

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* Methods of sampling limestone, dolomite and allied materials.

† Water, distilled quality (revised).

1 to 1˙5 using sulphosalicylic acid as indicator to a colourless or pale yellow solution.

5.2 Reagents

a) *Sulphosalicylic Acid*—Solid

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

c) *Hydrochloric Acid*—1:3 (by volume).

d) *Eriochrome Black-T*—Grind 100 mg of Eriochrome Black-T with 10 g of sodium chloride (solid powder).

e) *Standard Zinc Solution* (0˙01)—Dissolve 0˙6537 g of zinc powder in minimum quantity of dilute HCl (1:1) and make up to the mark in a one litre flask.

f) *Standard EDTA Solution*—0˙01M. Dissolve 3˙7224 g of di-sodium ethylenediamine tetraacetate dihydrate in 400 ml of hot water and make up to the volume in one-litre flask. Take 10 ml of standard zinc solution in an Erlenmeyer flask, add buffer solution of pH 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.

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

Adjust the molarity to 0˙01 M if required.

5.3 Procedure

Measure out 25 ml of silica-free acid solution of the sample as prepared under **4.1** and add very dilute ammonium hydroxide (1:6) till turbidity appears. Clear the turbidity with the minimum amount of dilute hydrochloric acid (1:3) and add a few drops in excess to adjust the pH to 1-1˙5. Shake well. Then add 100 mg of sulphosalicylic acid and titrate with 0˙01M EDTA solution carefully to a colourless or pale yellow from dark violet colour.

5.4 Calculations

1 ml of 0˙01M EDTA = 0˙7985 ml of Fe_2O_3

Iron oxide (Fe_2O_3), per cent by weight $= \dfrac{0˙7985 \times V}{W}$

where V = volume of EDTA used, and
W = weight of the sample in g.

6. DETERMINATION OF ALUMINA

6.1 Outline of the Method—In a suitable aliquot of the silica-free acid solution, iron is first titrated at pH 1'5. Then, a known volume of EDTA is added and the pH of the solution raised with ammonium acetate. Thereafter, bismuth nitrate solution is added in excess which is back-titrated with EDTA to a sharp yellow colour.

6.2 Reagents

a) *Sulphosalicylic Acid*—Solid.

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

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

d) *Thymol Blue*—0'1 percent solution in ethyl alcohol.

e) *Ammonium Acetate*—50 percent solution. Weigh 50 g of ammonium acetate and make up the volume to 100 ml with distilled water.

f) *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.

g) *Bismuth Nitrate Solution*—Weigh about 5 g of bismuth nitrate pentahydrate, Bi $(NO_3)_3$. $5H_2O$ in a 250-ml beaker. Add 25ml of acetic acid. Stir and dilute with about 40 ml water. Filter and transfer the solution to one-litre volumetric flask and dilute it to the mark with distilled water.

h) *Ammonium Hydroxide*—Sp gr 0'92, 1:6 (by volume).

j) *Acetic Acid*—Glacial.

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k) *Phosphoric Acid*—1:3 (by volume).

m) *Sulphuric Acid*—1:3 (by volume).

n) *Hydrochloric Acid*—1:1, 1:3 (by volume).

p) *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.

q) *Standard EDTA Solution*=0'01M. As per 5.2 (d)

6.3 Procedure

Take 25 ml aliquot of the silica-free acid solution in a titration flask and complex the iron as described in 5.3 adding the same volume of 0'01 M EDTA solution as in the determination of Fe_2O_3. Then add 15 ml standard EDTA solution followed by one ml of phosphoric acid (1:3), 5 ml of sulphuric acid (1:3) and one drop of thymol blue. Add ammonium acetate solution with stirring until the colour changes from red to yellow. Add 25 ml ammonium acetate in excess to obtain a pH of ~ 6. Heat the solution to boiling for one minute and then cool. Add 50 mg of 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.

6.4 Calculations

$V = V_1 - V_2 - (V_3R)$

Where V = volume of EDTA for alumina,

V_1 = total volume of EDTA used in the titration,

V_2 = volume of EDTA used for iron,

V_3 = total volume of bismuth nitrate solution used in the titration, and

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*R=equivalence of 1 ml of bismuth nitrate solution.

1 ml of 0'01 M EDTA = 0'5098 mg Al$_2$O$_3$

Aluminium oxide (Al$_2$O$_3$), per cent by weight $= \dfrac{0'5098 \times V}{W}$

where W=weight of the sample in g.

7. DETERMINATION OF CALCIUM OXIDE

7.1 Outline of the Method —A suitable aliquot of the silica-free acid solution is directly titrated against standard EDTA using Patton and Reeder's indicator at *p*H 12 or slightly more. The colour change from wine-red to clear blue indicates the end point.

7.2 Reagents

  a) *Patton and Reeder's 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.

  b) *Sodium Hydroxide Solution* – 4 N. Dissolve 80 g of sodium hydroxide in a 500-ml volumetric flask. Make up to the mark with distilled water.

  c) *Glycerol*—1:1 (by volume).

  d) *Triethanolamine*—Liquid.

  e) *Standard EDTA Solution* 0'01M. As per **5.2** (d)

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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 EDTA until the colour changes from red to yellow. The equivalence (ml of EDTA) of one ml of bismuth nitrate solution is :

$$R = \frac{N}{100}$$

where N is the volume in ml of EDTA solution.

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f) *Nitric Acid*

g) *Potassium Periodate*

7.3 Procedure

7.3.1 Measure 25 ml of silica-free acid solution of the sample in a 250·ml conical flask. Add 5 ml of 1:1 glycerol with constant stirring and 2 ml of triethanolamine. To this, add 10 ml of 4 N NaOH and shake well to adjust the *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 0·01M EDTA solution till one drop of EDTA produces a sharp change in colour from wine-red to clear blue.

7.3.2 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.

7.4 Calculations

1 ml of 0·01 M EDTA = 0·5608 mg CaO

Calcium oxide (CaO), per cent by weight = $\dfrac{0\cdot5608 \times V}{W}$

where V = volume of EDTA used, and

W = weight of the sample.

8. DETERMINATION OF MAGNESIUM OXIDE

8.1 Outline of the Method − A suitable aliquot of the silica-free acid solution of the sample is titrated at *p*H of 10 against standard EDTA

solution using triethanolamine for overcoming interference due to iron and aluminium and with thymol phthalexone as indicator. The titre value gives the sum of calcium and magnesium present in the solution from which the value corresponding to magnesium is obtained by subtracting that of calcium.

8.2 Reagents

a) *Triethanolamine*—1:1 (by volume).

b) *Buffer Solution pH 10*—As per 6.2 (f).

c) *Thymol Phthalexone Indicator*—1'0 per cent. Grind 100 mg of thymol phthalexone indicator with 10 g of potassium nitrate. Store it in an airtight container.

d) *Standard EDTA Solution*—As per 5.2 (d).

8.3 Procedure—Measure out 25 ml of silica-free acid solution of the sample and add to it 5 ml of 1:1 triethanolamine with constant shaking and 20 ml of buffer solution of pH 10. Add 50 mg of the solid thymol phthalexone indicator followed by approximately 50 ml of distilled water. Titrate against standard EDTA solution until the colour changes from blue to clear pink.

8.4 Calculations

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

Magnesium oxide (MgO) by weight $= \dfrac{0'4032 \times (V_1 - V)}{W}$

where V_1 = volume of EDTA used in this titration,

   N = volume of EDTA used in CaO determination, and

   W = weight of the sample in g.

APPENDIX A

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

TABLE 1

ESTIMATION OF FERRIC OXIDE IN NBS-SRM AND COMMERCIAL LIMESTONE SAMPLES AND STATISTICAL EVALUATION OF THE RESULTS

NBS-SRM 1b			COMMERCIAL SAMPLE A			COMMERCIAL SAMPLE B		
True Value %	Observed Value %	Deviation from True Value	Mean Value %	Observed Value %	Deviation from Mean Value	Mean Value %	Observed Value %	Deviation from Mean Value
0·75	0·64	- 0·11	0·75	0·66	−0·09	2·00	1·92	- 0·08
	0·78	+0·03		0·80	+0·05		1·97	- 0·03
	0·75	0·00		0·78	+0·03		2·00	0·00
	0·65	−0·10		0·73	−0·02		2·04	+0·04
	0·69	- 0·06		0·78	+0·03		2·11	+0·11
	0·90	+0·15		0·61	− 0·14		2·05	+0·05
	0·79	+0·04		0·72	− 0·03		1·88	−0·12
	0·83	+0·08		0·67	- 0·08		1·91	−0·09
	0·78	+0·03		0·86	+0·11		2·12	+0·12
	0·77	+0·02		0·86	+0·11		2·09	+0·09
	0·62	−0·13		0·75	0·00		2·01	+0·01

(Contd.)

TABLE 1 (Contd.)

	NBS-SRM 1 b			COMMERCIAL SAMPLE A			COMMERCIAL SAMPLE B	
True Value %	Observed Value %	Deviation from True Value	Mean Value %	Observed Value %	Deviation from Mean Value	Mean Value %	Observed Value %	Deviation from Mean Value
	0·74	−0·01		0·88	+0·13		2·03	+0·03
	0·73	−0·02		0·76	+0·01		2·11	+0·11
	0·57	−0·18		0·77	+0·02		1·86	−0·14
	0·60	−0·15		0·62	−0·13		2·01	+0·01
	0·88	+0·13		0·70	−0·05		1·90	−0·10
	0·85	+0·10		0·75	0·00		1·95	−0·05
	0·59	−0·16		0·79	+0·04		2·00	0·00
	0·78	+0·03		0·66	−0·09		2·02	+0·02
	0·63	−0·12		0·74	−0·01		2·14	+0·14
	0·65	−0·10		0·89	−0·14		1·99	−0·01
	0·77	+0·02		0·69	−0·06		1·98	−0·02
	0·74	−0·01		0·81	+0·06		2·08	+0·08
	0·75	−0·00		0·76	+0·01		2·02	+0·02
	0·79	+0·04		0·77	+0·02		1·99	+0·01

Number of Observations	25			25			25	
Maximum Value	0·90			0·89			2·14	
Minimum Value	0·57			0·61			1·86	
Mean Value	0·75			0·75			2·00	
Mean Deviation	0·07			0·06			·06	
Standard Deviation	9×10^{-2}			$7·5 \times 10^{-2}$			$·6 \times 10^{-2}$	

TABLE 2

ESTIMATION OF ALUMINIUM OXIDE IN NBS-SRM AND COMMERCIAL LIME SAMPLES AND STATISTICAL EVALUATION OF THE RESULTS

	NBS-SRM 1b			COMMERCIAL SAMPLE A			COMMERCIAL SAMPLE B		
True Value %	Observed Value %	Deviation from True Value		Mean Value %	Observed Value %	Deviation from Mean Value	Mean Value %	Observed Value %	Deviation from Mean Value
1·12	1·10	−0·02		0·31	0·36	+0·05	1·34	1·24	−0·10
	1·07	−0·05			0·31	0·00		1·31	−0·03
	1·02	−0·10			0·40	+0·09		1·34	0·00
	1·13	+0·01			0·21	−0·10		1·37	+0·03
	1·26	+0·14			0·22	−0·09		1·22	−0·12
	1·22	+0·10			0·31	0·00		1·26	−0·08
	1·14	+0·02			0·37	+0·06		1·23	−0·11
	1·15	+0·03			0·44	+0·13		1·30	−0·04
	0·98	−0·14			0·32	+0·01		1·34	0·00
	1·09	−0·03			0·29	−0·02		1·44	+0·10
	1·22	+0·10			0·18	−0·13		1·42	+0·08
	1·02	−0·10			0·34	+0·03		1·35	+0·01
	1·27	+0·15			0·35	+0·04		1·25	−0·09
	1·26	+0·14			0·32	+0·01		1·32	−0·02
	1·12	0·00			0·46	+0·15		1·47	+0·13
	1·13	×0·01			0·31	0·00		1·43	+0·09
	1·15	+0·03			0·20	−0·11		1·35	+0·01

(Contd.)

TABLE 2 (Contd.)

	NBS-SRM 1b		COMMERCIAL SAMPLE A			COMMERCIAL SAMPLE B		
True Value %	Observed Value %	Deviation from True Value	Mean Value %	Observed Value %	Deviation from Mean Value	Mean Value %	Observed Value %	Deviation from Mean Value
	1·12	0·00		0·28	−0·03		1·36	+0·02
	1·09	−0·03		0·29	−0·02		1·44	+0·10
	1·04	−0·08		0·41	+0·10		1·28	−0·06
	1·09	−0·03		0·18	−0·13		1·33	−0·01
	0·97	−0·15		0·30	−0·01		1·46	+0·12
	1·06	−0·06		0·32	+0·01		1·36	+0·02
	1·12	0·00		0·27	−0·04		1·33	−0·01
	1·11	−0·01		0·33	+0·02		1·34	0·00
Number of Observations	25			25			25	
Maximum Value	1·27			0·46			1·47	
Minimum Value	0·97			0·18			1·22	
Mean Value	1·12			0·31			1·34	
Mean Deviation	0·06			0·05			0·05	
Standard Deviation	$8·2 \times 10^{-2}$			$7·4 \times 10^{-2}$			$7·2 \times 10^{-2}$	

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