

## A New Digestion and Chemical Separation Technique for Rapid and Highly Reproducible Determination of Major Elements in Limestone Sample

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Analysis of varying grades of limestone samples were performed and a simple, rapid and sensitive method has been developed for all grades of limestone sample. The interference of silica and other metal oxides on the determination of limestone sample is studied. The method is found to be consistent and the results are very much comparable with the existing procedure. The results are in good agreement with the certified values of the reference standard samples. The novelty in the present study is fusion of the sample is avoided totally from high calcium content samples down to low grade limestone samples. Hence the method is very much suitable for analysis of sample spectrophotometrically.

**Key Words:** Limestone, Rock analysis, Loss on ignition.

### INTRODUCTION

Limestone is a very common sedimentary rock composed of at least 50 % calcium carbonate, with varying percentage of impurities present. In general, the term limestone is applied only to those rocks in which the carbonate fraction exceeds the non-carbonate constituents. Commercial limestone rocks generally consists of over 90 % calcium carbonate and normally the term limestone is used for the rocks in which the carbonate fraction is composed of calcite or areonite<sup>1</sup>. Limestone finds application in the process of minimizing industrial emission where the fresh limestone is calcined to lime (CaO) which then react with CO<sub>2</sub>, SO<sub>x</sub> (x = 2 and 3), H<sub>2</sub>S and NH<sub>3</sub> and the reaction depends upon the nature of the limestone<sup>2-5</sup>. It is a well known fact that the high pure limestone is used as a raw material in cement industries.

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It is known that the major element present in limestone is calcium and the determination of calcium in presence of magnesium was done by conventional gravimetric oxalate procedure<sup>6</sup>, chelometric titration with EDTA<sup>7,8</sup>, thermometric precipitation titration<sup>9</sup>. Calcium and magnesium in limestone samples are also determined by enthalpimetric flow-injection technique, from their substitution reaction with EDTA<sup>10</sup>. Various fusion methods are applied to break the sample with a variety of fusing agent which include sodium carbonate, lithium metaborate, lithium tetraborate and a combination of oxalic acid, lithium tetraborate and lithium carbonate<sup>11-13</sup>.

Microwave digestion techniques are also being used for the digestion of carbonate samples<sup>14</sup>. Complete analysis of limestone samples are also being carried out using wet conventional analytical techniques<sup>15</sup>. The elemental composition and major element present in limestone were determined using proton induced X-ray emission (PIXE) and proton induced  $\gamma$ -ray emission (PIGME)<sup>16</sup>. Recently limestone samples are analyzed for major and trace element composition X-ray fluorescence spectrometrically using the fusion mixture  $\text{La}_2\text{O}_3$ ,  $\text{LiB}_4\text{O}_7$  and  $\text{Li}_2\text{O}$ <sup>17,18</sup>.

In general, the methodology adopted for the analysis of limestone samples varies in line with the presence of carbonates and also depends upon other constituents mainly silica. An idea about the carbonate content of the given limestone sample can be indirectly determined from the loss on ignition values (loss on ignition values can be determined by keeping the sample at 900 °C in a muffle furnace for 1 h). During calcination,  $\text{CO}_2$  present in the sample as carbonates gets evolved completely from the sample and from the loss in weight, the quantity of carbonate present in the sample may be understood. The type of analysis followed for various grades of limestone is decided at this stage. In the present work, a new method has been proposed for the analysis of limestone samples using only acid digestion technique and also the stages to be followed in the analysis of samples for varying grade of limestone is also recommended.

## EXPERIMENTAL

All reagents used are of analytical reagent grade. Out of 100's of limestone samples analyzed for the past 5 years, samples are selectively chosen to meet present requirements. Samples showing loss on ignition (LOI) values from 10 to 43 % are selectively chosen for development of the new procedure. The samples are collected from various places of southern Tamil Nadu, India.

The sample is finely ground to 100 mesh size and kept in the muffle furnace and the temperature is slowly raised to 550 °C to decompose the organic compounds (calcination of limestone starts from 600 °C onwards<sup>19</sup>) and to remove the traces of moisture present in the sample. The sample is

then cooled in a desiccator and *ca.* 1 g of the above sample is accurately weighed in a platinum crucible and kept in a muffle furnace at 900 °C for 1 h, cooled in a desiccator and weighed. The loss on ignition value is calculated from the difference in weight. This loss in weight is attributed to the complete decomposition of the carbonate present in the sample. In the proposed procedure, the calcinated sample is placed in a 250 mL beaker containing 75 mL of 6 M HCl and kept over the hot plate, keeping the beaker closed with a watch glass. The sample is leached out from the platinum crucible and the crucible is thoroughly washed with distilled water and the washings are collected in the same beaker. The solution is allowed to digest for 1 h and then filtered through Whatmann 42 filter paper. The filtrates are collected in a 250 mL standard flask (solution 1). The filter paper containing the residue is kept in a pre-weighed platinum crucible, air dried for 5 to 10 min and then ignited in a muffle furnace at 900 °C. The dried residue is weighed and the difference in weight gives the acid insolubles ( $X_1$ ). About 10 mL of HF is added to the residue and hydrofluorised by keeping the platinum crucible containing the mixture over the hot plate and baked to dryness. The crucible is kept in a muffle furnace at 900 °C for 2 to 3 min. The crucible is cooled and weighed and the decrease in weight ( $X_2$ ) is recorded. The remaining residue is leached out with minimum amount of 6 M HCl in a 250 mL beaker and the solution is baked to dryness. Then about 10 mL of conc.  $H_2SO_4$  is added and fumed over hot plate at low heat by covering the beaker with watch glass. Then the watch glass is removed and the heat is increased and the solution is allowed to dry. The baked mass is digested with 6 M HCl for about 1 h, filtered through Whatmann 42 filter paper and the filtrates are combined with solution 1 and made up to 250 mL (main solution A). The filter paper is ignited, cooled and weighed ( $X_3$ ).  $X_2 + X_3$  gives total silica content present in the sample. The calcium and magnesium and other metal oxides are determined quantitatively either spectrophotometrically or by following conventional techniques. The main solution A may be directly fed into AAS after giving necessary dilution correction and the individual metal oxides can be quantitatively determined.

## RESULTS AND DISCUSSION

In the present investigation, about 40 limestone samples of varying degrees of carbonate content are chosen for analysis. The results are found to be in good agreement with the reported procedure. In the proposed method, fusion of the sample with fusing agents such as sodium carbonate, lithium borate is avoided but only acid attack is used to digest the sample completely. The major hindering radical, silica is removed by hydrofluorization. The remaining other metal oxide and silica present in combined state are attacked by sulphuric acid.

From the results of the complete analysis of various samples with wide range of LOI values, it has been proposed that the analysis of limestone samples may be carried out with the following three stages. Calcination and digestion with 6 M HCl, filtration, ignition forms the first stage of the analysis. Hydrofluorization of the residue and digestion of remaining dried mass with 6 M HCl forms the second stage. Evaporating the acid to dryness and further sulphuric acid attack on the residue, baking to dryness, digestion with 6 M HCl, filtration and ignition forms the third stage.

In this work, it has been suggested that the number of stages required to be followed in the analysis depends upon the LOI value of the sample.

In the case of high grade limestone samples having 95 % or above (more than 42 % LOI) total carbonates, the attack and digestion of the sample completed in the first stage itself. During calcination, the carbonates lose the entire carbon dioxide and become their respective oxides. Since in these samples, silica and other metal oxides are present in smaller quantities and mostly in their free state and only a part of their oxides will be in their combined state, the acid digestion of the calcinated sample itself breaks the oxides. The  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  gets dissolved and goes into the solution and the silica which is left free is filtered off. Since silica is completely removed at this stage itself, the other metal oxides can easily be determined spectrophotometrically or conventionally and the results are found to be in good agreement with the reported procedure<sup>20</sup>.

For those samples having total carbonates 90-95 % (40-42 % LOI), here also the first stage of analysis is quite enough for extracting calcium, magnesium and other metal oxides. Silica,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  are present in slight excess when compared to 95 % grade. Though in this case the ratio of free metal oxides to combined metal oxides is slightly lesser than the earlier case, the acid digestion of the sample itself can break the individual metal oxides and the insolubles obtained in this stage are mostly of silica with less than 0.15 to 0.25 % of other metal oxides. From the results, it had been concluded that the quantitative determination of prime metal oxide in limestone sample *viz.*, CaO has not been affected and thorough analysis of the results indicates that there is no need to go to the second stage of analysis for these samples.

For those samples containing 80 to 90 % carbonate (35 to 39 % LOI), the ignited residue in the first stage is hydrofluorised and the remaining mass is acid digested. By the combined attack of hydrofluorisation and acid digestion, the silica and other metal oxides get separated from one another and hence their individual determination can easily be carried out. As expected, the combined silicates are found to be high which warrants the sample to proceed to the second stage of analysis.

In the case of low grade limestone (less than 35 % of LOI), the insolubles obtained in the first stage of analysis have lower values of the ratio of free metal oxides to combined metal oxides. The ratio decreases as we go down from 34 % LOI to 20 % and hence the analysis has to be carried out up to the third stage. During the first stage, the free metal oxides and some combined metal oxides goes into the solution. The remaining silica and other combined metal oxides are hydrofluorised in the second stage wherein the free silica present in the sample is converted into tetra fluoride, a volatile compound, which get driven off. The combined metal silicates are also attacked by HF which then converts them into their hexafluoride. These fluorides will be present in the solution. As the solution is baked to dryness in the second stage the hexafluorides and other combined metal oxides will be present as residue, which warrants breaking into their respective metal oxide. This is accomplished in the third stage. During this stage sulphuric acid is used as an attacking agent and the metal ions get separated out and goes into the solution facilitating the individual metal determination.

It has been concluded that for samples having less than 20 % loss on ignition value the results of individual metal oxides obtained from the proposed method varies widely with respect to known procedure.

All the reference standards show good recovery of the individual metal oxides. For the sample Nos. 3, 4 and 5 the recovery of silica was found to be more than 100 %. This may be attributed to the poor breaking of metal silicates into their individual metal oxides which might have contributed to the increase in silica value. The other metal oxide values for the above samples are found to be less than the IP value which supports the view that the metal silicates are not completely broken (Table-1).

TABLE-1  
PERCENTAGE RECOVERY OF METAL OXIDES USING  
SULFURIC ACID EXTRACTION

S. No.	Metal oxide	Certified values/IP	Sulfuric acid extraction	
			Content	Recovery (%)
GV	Silica	18.61	18.54	99.62
SVG	Silica	13.12	13.09	99.77
JVG	Silica	1.82	1.805	99.17
1	Silica	0.42	0.415	98.80
2	Silica	20.53	20.42	99.46
3	Silica	28.71	29.15	101.53
4	Silica	37.22	38.09	102.33
5	Silica	45.85	48.13	104.97

S. No.	Metal oxide	Certified values/IP	Sulfuric acid extraction	
			Content	Recovery (%)
GV	Fe <sub>2</sub> O <sub>3</sub>	0.68	0.675	99.26
SVG	Fe <sub>2</sub> O <sub>3</sub>	0.72	0.714	99.16
JVG	Fe <sub>2</sub> O <sub>3</sub>	0.38	0.375	98.68
1	Fe <sub>2</sub> O <sub>3</sub>	0.63	0.622	98.73
2	Fe <sub>2</sub> O <sub>3</sub>	0.27	0.266	98.51
3	Fe <sub>2</sub> O <sub>3</sub>	1.59	1.580	99.37
4	Fe <sub>2</sub> O <sub>3</sub>	1.00	0.985	98.50
5	Fe <sub>2</sub> O <sub>3</sub>	1.81	1.780	98.34
GV	Al <sub>2</sub> O <sub>3</sub>	4.82	4.76	98.76
SVG	Al <sub>2</sub> O <sub>3</sub>	2.62	2.59	98.85
JVG	Al <sub>2</sub> O <sub>3</sub>	1.94	1.92	98.97
1	Al <sub>2</sub> O <sub>3</sub>	1.76	1.74	98.86
2	Al <sub>2</sub> O <sub>3</sub>	4.00	3.94	99.00
3	Al <sub>2</sub> O <sub>3</sub>	8.24	8.16	99.03
4	Al <sub>2</sub> O <sub>3</sub>	10.24	10.08	98.44
5	Al <sub>2</sub> O <sub>3</sub>	12.14	11.79	97.12

P.M = Proposed Method; I.P= Internationally followed procedure; GV, SVG, JVG = In-house Reference Standards.

The salient feature of the proposed procedure is that the sample attack is only with acids and not any fusion procedure is adopted at any stage of the proposed method. Hence, it is very convenient to determine the individual metal oxides spectrometrically. The problem most frequently faced by the analyst in the fusion technique is the much higher salt content present in the solution. Hence while going for spectrometrical analysis, dilution of the solution is required to minimize the salt content but in the proposed method no such problem will occur and the solution need not be diluted.

TABLE-2  
REPRODUCIBILITY OF VALUES OBTAINED BY  
THE PROPOSED METHOD

S. No.	SVG	Sample A	Sample B	Sample C
1(SiO <sub>2</sub> )	13.12	33.38	12.11	1.92
2	13.16	33.46	12.09	1.88
3	13.20	33.52	12.35	1.98
4	13.18	33.28	12.16	1.79
5	13.24	33.24	12.02	2.01
6	13.16	33.32	12.04	1.95
7	13.32	33.44	12.05	1.91
8	13.02	33.39	11.98	1.88
Mean	13.18	33.38	12.10	1.920
S.D	0.087	0.095	0.115	0.068

S. No.	SVG	Sample A	Sample B	Sample C
1( $\text{Fe}_2\text{O}_3$ )	0.72	0.34	0.33	0.41
2	0.76	0.36	0.39	0.48
3	0.66	0.29	0.28	0.42
4	0.64	0.37	0.42	0.39
5	0.78	0.33	0.26	0.36
6	0.81	0.40	0.36	0.47
7	0.70	0.26	0.29	0.35
8	0.68	0.28	0.33	0.47
Mean	0.72	0.33	0.33	0.42
S.D.	0.060	0.049	0.055	0.051
1( $\text{Al}_2\text{O}_3$ )	2.62	2.81	6.85	2.64
2	2.68	2.91	6.94	2.62
3	2.72	2.85	6.80	2.72
4	2.54	2.74	6.89	2.58
5	2.55	2.75	6.79	2.66
6	2.65	2.82	6.86	2.59
7	2.70	2.79	6.92	2.70
8	2.64	2.85	6.84	2.65
Mean	2.63	2.82	6.86	2.65
S.D.	0.072	0.056	0.056	0.049
1( $\text{CaO}$ )	45.02	25.74	44.84	50.47
2	45.12	25.84	44.94	50.55
3	45.24	25.82	44.88	50.42
4	44.88	25.68	44.78	50.38
5	44.96	25.64	44.72	50.58
6	45.05	25.76	44.89	50.52
7	45.08	25.72	44.88	50.49
8	45.14	25.70	44.79	50.42
Mean	45.06	25.74	44.84	50.48
S.D.	0.111	0.067	0.072	0.069
S.No.	SVG	S10	S20	S26
1( $\text{MgO}$ )	0.45	6.99	0.36	2.93
2	0.48	7.12	0.38	2.99
3	0.38	7.08	0.42	2.88
4	0.46	7.06	0.32	2.90
5	0.48	6.96	0.30	2.82
6	0.41	6.94	0.35	2.88
7	0.36	7.02	0.34	2.95
8	0.49	7.05	0.41	2.79
Mean	0.44	7.03	0.36	2.89
S.D.	0.049	0.062	0.042	0.066

## Conclusion

The proposed method is simple, economic and precise with higher accuracy. Moreover, the reproducibility of the results is comparable with the existing methods. Since no fusion of the sample is required, the proposed method is better than the existing method. The dilution error in the proposed method is very minimum. This method is applicable to wide range of limestone samples.

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