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Estimation of dolomite mineral in limestone by infra-red spectroscopy

Dolomite, $\text{CaMg}(\text{CO}_3)_2$, occurring as an impurity in limestone mineral has been observed to be the major contributor to the ultimate MgO content of cement clinker. Further, the recent investigation [1] on the high magnesia clinker up to at least 10% MgO makes it necessary to assess the mineral forms in which MgO occurs in limestone. As such the detection and estimation of dolomite

in limestone is important. Earlier infra-red study [2] was limited to the estimation of calcite using the 975 cm^{-1} band. However, this band is not unique since other carbonates (dolomite, etc) contribute to it and in general the band is split. In this communication, we are reporting an infra-red spectral technique for rapid estimation of dolomite and the results of the analysis have been compared with other existing techniques.

The infra-red spectra of calcite and dolomite are characterized by bands at 711 and 727 cm^{-1} ,

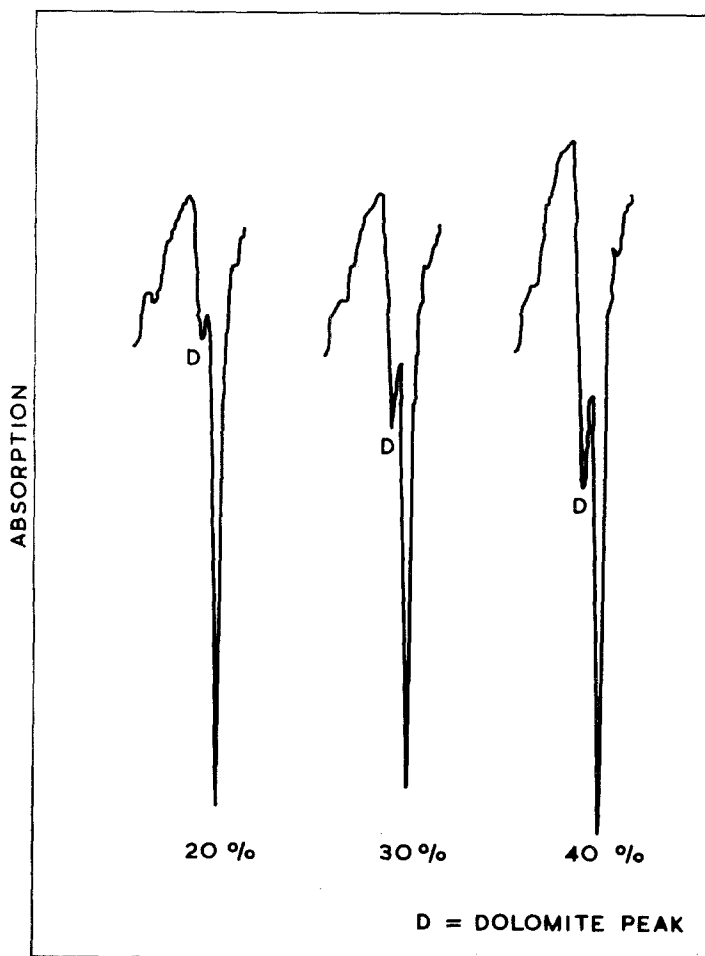


Figure 1 Infra-red spectra of standard mixes.

TABLE I Chemical analysis of standard mix components

Constituents	Limestone	Dolomitic rock
SiO ₂	4.92	1.20
Fe ₂ O ₃	0.75	0.28
Al ₂ O ₃	1.12	0.19
TiO ₂	0.046	0.02
MnO	0.20	0.03
CaO	50.90	30.10
SrO	0.14	0.01
MgO	0.36	21.30
Na ₂ O	0.04	0.01
K ₂ O	0.25	0.12
P ₂ O ₅	0.08	0.01
CO ₂	40.40	46.60
LOI	41.1	46.70

respectively. These bands appear unperturbed and sharp with varying intensity depending on the concentration of these minerals (Fig. 1). A Perkin-Elmer 621 spectrometer using standard settings

was used for carrying out the present work. The carbonate rocks (a dolomite stone and a pure limestone) were chosen to prepare the standard mixes (Table I). The standards were found from X-ray diffraction study to be free from each other, i.e. no dolomite in the pure limestone and no calcite in the dolomite stone, the actual dolomite content in which was 97.46% (recalculated from the chemical analysis). A satisfactory homogeneous mixing of the standards was carried out in a Perkin-Elmer vertical tube vibrator. 3 mg standard mix or unknown sample was mixed with 250 mg of spectral grade KBr for making pellets for infra-red studies. Both absolute intensity (dolomite peak intensity at 727 cm⁻¹) and relative intensity (ratio of the intensities dolomite/calcite bands) of the standard mixed were plotted against concentration of dolomite. The regressed lines obtained are shown in Figs. 2 and 3.

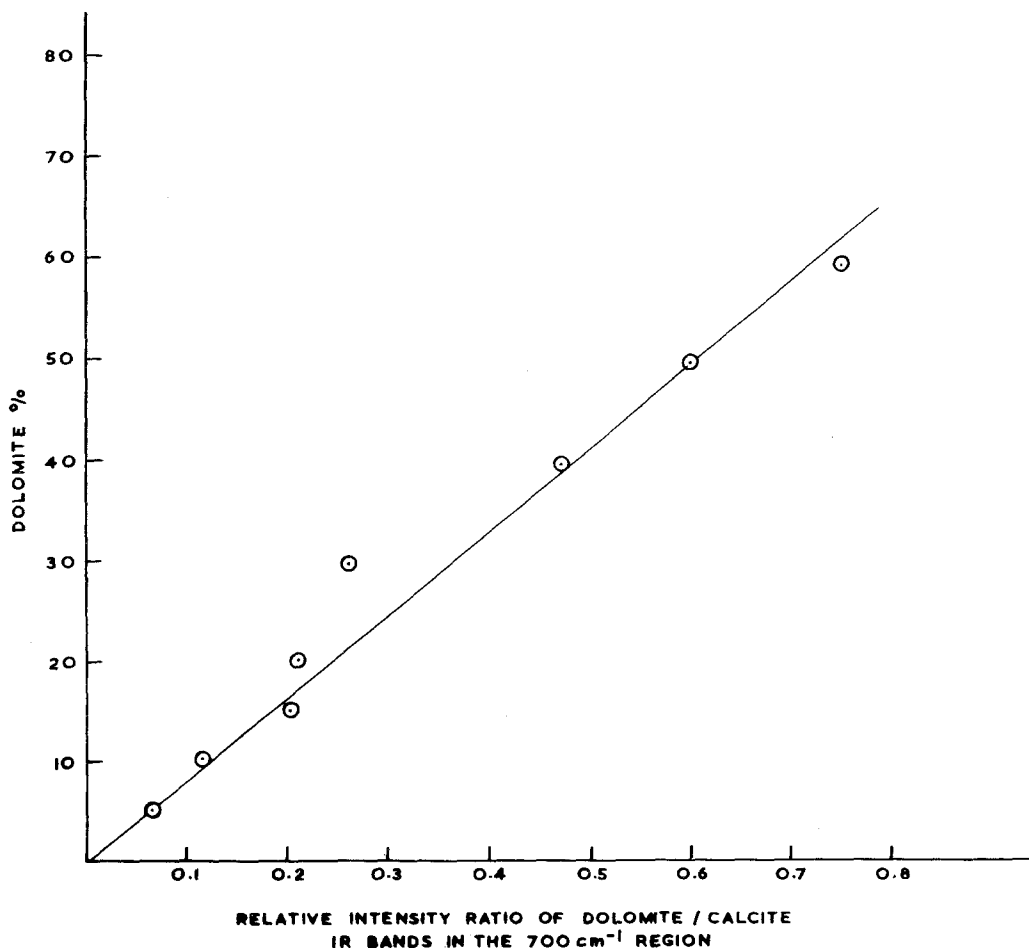


Figure 2 Infra-red calibration curve based on the absolute intensity of dolomite band.

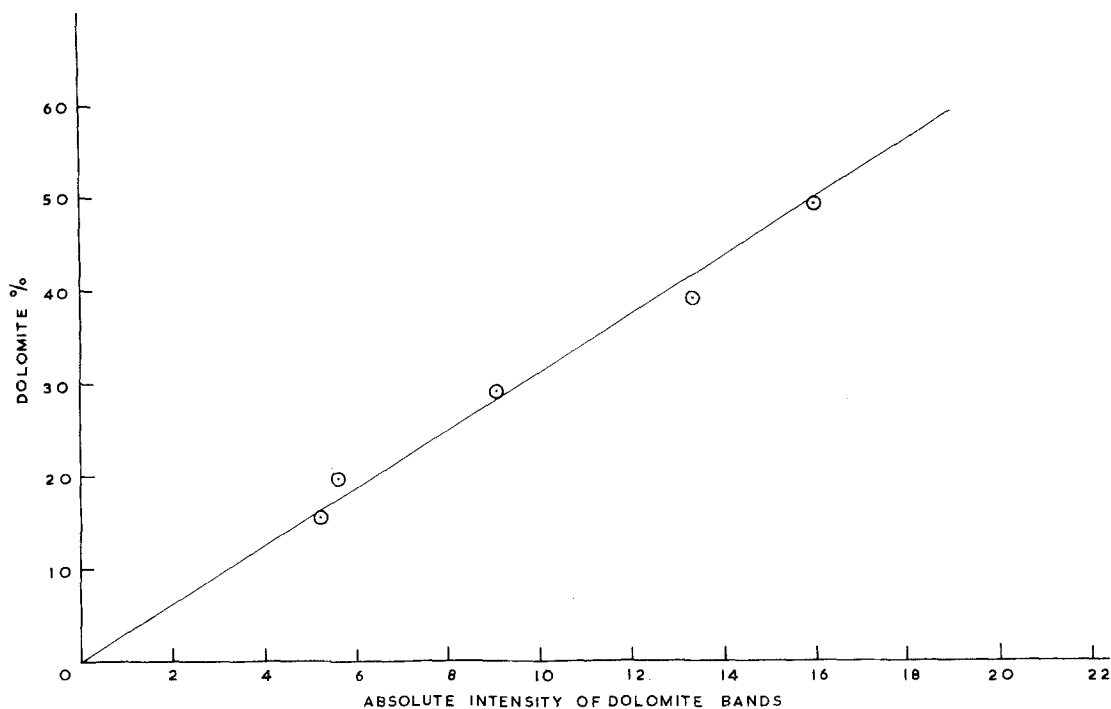


Figure 3 Infra-red calibration curve based on relative intensity ratio of dolomite/calcite bands.

The results of analysis of two limestone samples ($L_1 = 43.93\% \text{ CaO}$ and $16.79\% \text{ SiO}_2$; $L_2 = 54.15\% \text{ CaO}$ and $1.60\% \text{ SiO}_2$; to each of which, 30% by weight of dolomite standard sample was added) are presented in Table II. The relative intensity method gives some kind of a measure of impurities (here SiO_2 in L_1). The higher value of dolomite content (33.50%) in L_1 is caused by the lower calcite content as evident from the high percentage of compensating SiO_2 . The results of three unknown samples are presented in Table III and are verified by DTA and chemical analysis. It is to be noted that the results obtained by infra-red spectrometric method are the mean values of

TABLE II Comparative analysis of limestones by absolute and relative intensity* methods

Absolute intensity method

Samples	Infra-red absorption intensity at 727 cm^{-1}	Actual dolomite content (%)	Determined dolomite content (%)	Difference obtained in dolomite percentage
Mix L1	8.4	29.25	27.25	2.00
Mix L2	9.2	29.25	28.50	0.75

Relative intensity method

Samples	Relative intensity ratio of 727 and 711 cm^{-1} bands	Actual dolomite content (%)	Determined dolomite content (%)	Difference obtained (%)
Mix L1	0.41	29.25	33.50	4.25
Mix L2	0.34	29.25	28.25	1.00

*Measured in arbitrary units.

TABLE III Analysis of unknown limestones*

Sample no.	Chemically determined		Dolomite percentage recalculated from MgO%	Dolomite content determined by	
	CaO	MgO		Infra-red spectra	Thermal
RS 727	41.10	10.17	46.43	42.5	41.4
BMLS 8	34.63	5.0	22.88	20.5	17.5
RM 353	49.65	3.43	15.78	14.8	15.8

*Absolute intensity method

TABLE IV Reproducibility of result by the absolute intensity* method

Sample no.	Absolute intensity of 717 cm ⁻¹ dolomite band	Mean	Standard deviation	Coeff. of variation	Standard deviation for the mean	Coeff. of variation for the mean values
L 1-1	8.5 8.2 8.6	8.43	0.16	1.9%		
L 1-2	8.0 8.2 8.4	8.20	0.17	2.1%	0.11	1.33%
L 1-3	8.3 8.2 8.2	8.23	0.05	0.61%		

*Measured in arbitrary units

DTA and chemical analysis. The experimental error of the method has been calculated by running three separate mixes of two samples (70% L₁ + 30% reference dolomite stone) and is presented in Table IV.

The conclusions are, therefore,

(1) the infra-red spectroscopic method of quantitative estimation of dolomite-containing limestones is direct and dependable. It takes about 30 min to analyse a sample, the results of which compare favourably with thermal and X-ray methods;

(2) the relative intensity method is useful for a check of other impurities (SiO₂, etc) besides being complementary to the absolute intensity method;

(3) only a conventional infra-red spectrometer is required for this analysis and the range studied (800 to 700 cm⁻¹) is free from atmospheric interference;

(4) the estimation of calcite can also be carried out simultaneously.

Acknowledgement

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