Determination of Calcium Carbonate in Limestone by Attenuated Total Reflectance Fourier Transform Infrared Spectrometry

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Attenuated total reflectance Fourier transform infrared (ATR/FT-IR) spectrometry was applied to the determination of calcium carbonate in limestone. Both of the simple and multiple linear regression methods have been investigated. The correlation coefficient was found to be increased to 0.985 when the multiple linear regression analyses using the absorbance values at all of the wavelengths were applied. The standard deviation of calibration for 37 samples by this method was 0.601. In order to test the applicability of the multiple linear regression method to routine analyses of limestones, 31 samples collected from the various mines distributed in Korea were analyzed by chemical and ATR/FT-IR methods. The range of CaCO₃ concentrations of the tested samples were 86—97%. The standard error of prediction (SEP) was found to be 0.294 when the absorbance values at all of the three wavelengths were used, whereas the SEP values were 1.340, 1.072 and 0.961 for the wavenumbers of 711, 1406 and 875 cm⁻¹, respectively. The results indicate that the ATR/FT-IR method can be applied to the routine determination of CaCO₃ in limestone by mid-infrared spectroscopy. The present method required virtually no pretreatment procedure and thus took less time comparing with the conventional wet chemical methods.

Keywords Attenuated total reflectance Fourier transform infrared spectrometry, calcium carbonate, multiple linear regression method

Limestone is a sedimentary rock whose major component is calcium carbonate (CaCO₃). It is one of the most widely used material in the inorganic material industry such as cement, plaster, glasses and ceramics.¹ The estimated limestone deposits in Korea is about 40 billion tons. Currently, limestone is produced in Korea mainly from the limestone plateau in the Ongcheon-Taebaegsan zone located in the southeastern part of the Korean peninsular and the Cambrian and Ordovician rocks in this zone are well exposed.² The limestone produced in Korea contains about 90% of CaCO₃ and minor components such as SiO₂, Al₂O₃, and Fe₂O₃.³

The analysis of rocks and minerals takes in a diverse range of techniques employing a wide variety of physical phenomena.⁴ The traditional systematic scheme of rock analysis is mainly gravimetric and based on separating the constituents of a sample into four groups of elements, each group being precipitated from the rock solution successively. Silica is at first separated by dehydrating silicic acid H₂SiO₃ to insoluble SiO₂, accompanying elements are dissolved off in dilute acid solution. The so-called R₂O₃ group of elements, comprising Fe₂O₃, Al₂O₃, TiO₂ and P₂O₅, is precipitated as hydroxides when an acidic solution from which silica has been removed is neutralized with ammonia. Calcium and strontium are then precipitated as insoluble oxalates and magnesium and manganese are precipitated as insoluble phosphates. Determinations by this method can be carried out after extensive chemical manipulations designed to isolate quantitatively individual compounds. The classical method is recently being replaced by the variety of instrumental methods such as atomic absorption spectrometry, X-ray fluorescence spectrometry, inductively coupled plasma-atomic emission spectrometry, inductively coupled-mass spectrometry and neutron activation method.⁵ However, these analytical methods are too time-consuming in the sample pretreatment or cost high to determine one specific compound for the strategic geochemical prospecting. In order to grade limestone, the content of CaCO₃ is the most important parameter.

In the present paper, the development of an analytical procedure using attenuated total reflectance
(ATR) Fourier transform infrared (FT-IR) spectrometry is described for the determination of CaCO₃ in limestone. For 37 limestone samples collected from various limestone deposits in Korea, chemical analyses were carried out for the determination of CaCO₃. The relationships between the contents obtained by the chemical method and the absorbances at three wavenumbers obtained by ATR/FT-IR were used for calibration. The best equation obtained by multiple linear regression was used to predict the contents of CaCO₃ in 31 samples used for a validation set.

**Experimental**

**Apparatus**

The FT-IR spectra were recorded at room temperature with a Mattson (Madison, WI, USA) Galaxy 7020A FT-IR spectrometry with a deuterated triglycine sulfate (DTGS) detector using a high efficiency air-cooled infrared ceramic emitter (ICE) for light source. The ATR spectra were obtained using a Spectra-Tech (Stamford, CT, USA) baseline HATR combination kit (Part Number, 0001-1) incorporating a ZnSe crystal (reflections at 45°). The software used were First (Mattson) and Minitab Release 8.2.

**Reagents**

CaCO₃, HCl, HNO₃, HClO₄, H₂SO₄, HF, KCN and triethanolamine were obtained from Sigma Chemical Co. (St. Louis, MO, USA) and used without any further purification. Ethylenediaminetetraacetic acid (EDTA; disodium salt, dihydrate) was purchased from Sigma Chemical Co. and used after recrystallization. All of the aqueous solutions were prepared with deionized water purified using a Millipore Milli Q water system (Bedford, MA, USA).

**Chemical analysis**

Two different schemes (gravimetric and volumetric) for the determination of CaCO₃ by wet chemical methods were used. The gravimetric method described in the following is a part of the whole procedure used for the routine analytical services to determine 13 constituents in rocks for the samples requested by several mine clients. For the gravimetric analysis, 1 g of sample powder was fused with 3 g of anhydrous sodium carbonate in a platinum crucible at temperatures increasing from 700 to 1200 °C and the melt was then disintegrated with water after cooling. The aqueous mixture was dissolved in hydrochloric acid and evaporated to dryness until all hydrochloric acid fumes had been expelled, and the residue after evaporation was then attacked with hydrochloric acid solution. After silica residue was filtered off, the mixed oxides (R₂O₃ group) was recovered from the combined filtrates and washings by adding ammonia to a hot solution acidified with hydrochloric acid until it became just alkaline. The hydroxide precipitate was then filtered from the slightly alkaline solution and the filtrate was reserved for the determination of Ca. The precipitate after filtration was re-precipitated with ammonia a second time and the filtrate was again combined with the first filtrate. The combined filtrates was made just alkaline and heated to boiling. Hot ammonium oxalate solution was then added. The calcium oxalate precipitate was re-dissolved in hydrochloric acid and then re-precipitated with ammonium oxalate under controlled conditions in order to remove possible co-precipitated elements. The final calcium oxalate precipitate was decomposed at 500 °C in a muffle furnace and weighed as calcium carbonate.

For the volumetric analysis, 0.5 g of sample was digested with a mixture of HF (12 mL), H₂SO₄ (2.5 mL) and HNO₃ (0.6 mL) on a steam bath overnight in a covered Teflon beaker. The residue was transferred to a Vycor beaker using the minimum quantity of water, and reheated on a hot plate until SO₃ fumes were emitted. Four drops of HClO₄-HNO₃ mixture (1:1) were then added and the samples reheated until strong fumes were evolved. After cooling, water (225 mL), concentrated HNO₃ (5 mL) and hydrazine sulphate (1 mL) were added and the solution boiled. After cooling the solution, potassium cyanide and triethanolamine was added and made up to a final volume of 500 mL. Calcium carbonate was determined by EDTA titration in a strongly alkaline solution, using NN as an indicator, of 25 mL aliquots of this solution.

**ATR/FT-IR measurements**

Samples were pulverized in a jaw crusher and grinded in an agate grinder. The grinding vessel was cleaned between samples by grinding a quartz sample followed by a flush with ethanol. The grinding period was controlled to have the grain size of about 20 μm. The grinded sample was introduced to the trough sampling plate. The power press was placed on top of the powder and screwed the pressure device in to ensure intimate contact between the crystal and the powder. Spectra were recorded in a single beam mode between 4000 and 650 cm⁻¹ in 1 cm⁻¹ increments. In order to achieve a satisfactory signal-to-noise ratio, 50 interferogram scans at a spectral resolution of 4 cm⁻¹ were averaged. All analyte spectra were recorded as differences from the background spectra frequently obtained with the empty sampling plate to minimize baseline drift. Three measurements were performed for each sample.
Results and Discussion

ATR/FT-IR spectroscopy of CaCO₃

Figure 1 shows the ATR/FT-IR spectrum (a) and the transmission spectrum (b) of CaCO₃ in KBr matrix over the wavenumber range of 650-4000 cm⁻¹. The contents of CaCO₃ are 40 % (w/w) and 4 % (w/w) for ATR spectrum and transmission spectrum, respectively. Three well-shaped bands for carbonate are observed at 1406 cm⁻¹ (asymmetric stretching), 875 cm⁻¹ (out-of-plane bending) and 711 cm⁻¹ (in-plane bending) in the ATR spectrum. In contrast, in the transmission spectrum the bands of 1406 and 875 cm⁻¹ are overscaled and several other characteristic bands of carbonate are observed in the higher wavenumber region. It should be noted that the ATR spectrum does not exhibit any absorption band over the wavenumber range of 1600-4000 cm⁻¹ in spite of the 10 times higher concentration of CaCO₃ than that used for the transmission spectrum. The result is explained by the decrease of the effective penetration depth with the increase of the evanescent wave of radiation.

Calibration for the determination of CaCO₃

Table 1 shows the results of chemical analyses and absorbances obtained by using ATR/FT-IR method at 711, 875 and 1406 cm⁻¹. The correlation coefficients for the simple linear regression of the relationships between absorbances and concentrations obtained by the chemical analyses were 0.858, 0.942 and 0.945 for the wavenumbers of 711, 1406 and 875 cm⁻¹, respectively. Multiple linear regression analyses were also applied to the data set of the concentration of CaCO₃ obtained by the chemical analyses and three ATR absorbance values for each sample. The correlation coefficients and standard deviations of calibration for different combinations of absorbances used to solve four normal equations are represented in Table 2. When all of the absorbance values at three wavenumbers were used, the highest correlation coefficient was obtained. The solved equation of the regression line for this case is given by:

\[
\text{CaCO}_3(\%) = 77.7 + 50.9X_{711} + 17.1X_{875} + 26.1X_{1406}
\]  

where \(X_{711}, X_{875}, X_{1406}\) are absorbances at 711, 875, 1406 cm⁻¹, respectively. In order to test the applicability of the multiple linear regression method to routine analyses of limestones, 31 samples collected from the various mines distributed in Korea were analyzed.
were analyzed by using wet chemical analysis and ATR methods. The range of CaCO$_3$ concentrations of the tested samples were 86–97%. The standard error of prediction (SEP) was calculated by using equation (2):

$$\text{SEP} = \sqrt{\frac{\sum (\text{IR} - \text{chemical})^2}{n-k-1}}$$

where $n$ is number of samples and $k$ is number of wavenumbers used in calibration.

The SEP value was 0.294 when the absorbance values at all of the three wavelengths were used, whereas those were 1.340, 1.072 and 0.961 for the wavenumbers of 711, 1406 and 875 cm$^{-1}$, respectively. The results indicate that the ATR method can be applied to the routine determination of CaCO$_3$ in limestone by mid-infrared spectroscopy. The present method required virtually no pretreatment procedure and thus took less time comparing with the conventional wet chemical methods. The ATR/FT-IR method is now adopted as a standard operation procedure for the determination of CaCO$_3$ in limestone in this laboratory, where about one hundred limestone samples per month are routinely analyzed for analytical services. The reliability of this method was also validated by comparing the present results with those obtained by using XRF, AAS and ICP-AES.

### Table 2

<table>
<thead>
<tr>
<th>Used wavenumbers (cm$^{-1}$)</th>
<th>$R^b$</th>
<th>$S^c$</th>
<th>SEP$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>711</td>
<td>0.858</td>
<td>1.727</td>
<td>1.340</td>
</tr>
<tr>
<td>1406</td>
<td>0.942</td>
<td>1.134</td>
<td>1.072</td>
</tr>
<tr>
<td>875</td>
<td>0.945</td>
<td>1.102</td>
<td>0.961</td>
</tr>
<tr>
<td>711 875</td>
<td>0.949</td>
<td>1.076</td>
<td>0.942</td>
</tr>
<tr>
<td>875 1406</td>
<td>0.976</td>
<td>0.739</td>
<td>0.735</td>
</tr>
<tr>
<td>711 1406</td>
<td>0.980</td>
<td>0.670</td>
<td>0.485</td>
</tr>
<tr>
<td>711 875 1406</td>
<td>0.985</td>
<td>0.601</td>
<td>0.294</td>
</tr>
</tbody>
</table>

a. Number of samples used is 37. The contents of CaCO$_3$ determined by wet chemical method are in the range of 86–97% and the mean value is 91.65%.

b. Correlation coefficient
c. Standard deviation of calibration ($n=37$)
d. Standard error of prediction for 31 test samples used for validation of the present method.

### References