

Quantitative determination of water in granites by infra-red analysis

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SUMMARY. Two methods using nujol and hexachloro-butadiene mulls are described to analyse the water content of powdered granite samples. The nujol mull analyses were carried out on a Unicam SP 100 spectrometer using the silica content of the rock as an internal standard. The hexachloro-butadiene mull analyses were done by a twin-path Unicam SP 200 spectrometer, using hexachloro-butadiene as the internal standard. The broader and more pronounced V_1 vibrational mode (3450 cm^{-1}) is ratioed to a standard of known composition. Comparisons are also made between absorption due to free water ($V_1 = 3450\text{ cm}^{-1}$) and combined water ($V_3 = 3680\text{ cm}^{-1}$) in aplites, biotite granite, and chlorite schists.

INFRA-RED investigations into the structure of water, ice, and silica gel systems are numerous (Benesi and Jones, 1959; Davis and Litovitz, 1965; Sheppard, 1959; Ockman and Sutherland, 1958). Work on silicate structures and the relation of hydroxyl groups within silicates is also extensive (Lyon, 1967; Stubican and Roy, 1961; Vedder, 1964). Quantitative determinations are limited to different mineral groups, but difficulties occur in relating specific absorption peaks to their correct type of structural bonding. Although the problem of using whole rock powders seem overwhelming, the methods described here are considered reliable and capable of further development.

The usual procedure in quantitative analysis of infra-red absorption spectra is to calculate the area under the absorption peak, which is related to concentration. But in this investigation peak height was considered sufficient to give results comparable with the normal wet chemical methods.

Sample preparation is simple and only small quantities of material are required, less than 0.1 g in all cases. Including the preparation of samples plus analysis time it is possible to complete between five and six analyses an hour. The method has the advantage that water is being determined every time, whereas some other methods are not so specific. The unknown silicate samples are compared directly with standards of accurately known water content. The accuracy of the method obviously depends on the accuracy of the water determination on the standard, and the similarity of the structural position of the water between standard and sample.

Two methods have been used to measure the V_1 and V_3 longitudinal OH-stretching frequencies in silicates, which occur at approximately 3450 and 3680 cm^{-1} . Free OH groups normally give sharp absorption peaks, but the spectrum of water consists of a wide diffuse hump. Free OH groups consist of non-hydrogen-bonded molecules, but

if extensive H-bonding is present the vibrational frequencies are generally lowered. The V_1 and V_3 stretching frequencies without H-bonding produce a narrow spectrum between 3400 and 3700 cm^{-1} . In granites, two sharp absorption peaks occur at 3450 and 3680 cm^{-1} ; the 3450 cm^{-1} is broader than the 3680 cm^{-1} peak and consists of H-bonded and free OH groups. The 3680 cm^{-1} peak is due to combined OH.

Powders for water determinations are ground to pass 250 B.S.S. mesh and dried at 110–20 °C for at least 24 hours. This particle size was chosen because the samples analysed were used for X-ray fluorescence analysis also. The bulk of the grains average about 20 μm .¹ Ideally particle size should be below 3 μm , i.e. the wavelength of the V_1 , V_3 vibrational modes.

TABLE I. Comparison of wet-chemical analyses and infra-red H_2O determinations

Method	JWA 50	JWA 60/1	JWA 76	JWA 88	JWA 123	JWA 133	JWA 152	JWA 154/3	JWA 195	JWA 242	PH 8	PH 19	AGP 15
Penfield (modified)	—	—	1.02	—	1.43	—	—	—	0.76	{ 0.56 0.57 }	0.65	{ 2.11 2.10 2.38 2.30 }	0.57
Loss on ignition	{ 0.84 0.98 }	{ 0.47 0.44 }	{ 0.81 0.87 }	{ 1.69 0.59 }	{ 1.07 1.07 }	{ 0.68 0.65 }	{ 0.71 0.72 }	{ 0.51 0.53 }	—	—	—	—	{ 1.00 0.86 0.86 }
Infra-red SiO_2 internal standard	{ 0.85 0.95 }	{ 0.64 0.76 }	{ 0.57 0.84 }	{ 0.76 0.70 }	{ 1.10 1.01 }	{ 0.68 0.74 }	{ 0.70 0.74 }	{ 1.00 0.98 }	—	—	—	—	—
Infra-red H.C.B. internal standard	0.87	0.67	{ 0.92 0.80 1.02 0.88 0.92 }	0.59	1.08	0.65	0.74	0.61	0.69	0.84	0.74	1.90	0.90

In table I, the results of wet-chemically analysed rocks are compared with those obtained by infra-red spectroscopy.

Silica internal standard method

From Beer's Law, the following equation may be derived

$$\% \text{H}_2\text{O}/\% \text{SiO}_2 = K \log I_1/\log I_2,$$

where I_1 is the intensity of the OH absorption band, I_2 the intensity of the 800 cm^{-1} or 1100 cm^{-1} Si–O band, and K a constant that can be determined by running a standardized sample. From one instrument scan it is possible to obtain two determinations by measuring the absorption of the OH vibrational mode at 3450 cm^{-1} and relating it to both Si–O vibrational modes, using percentage silica as an internal standard.

The powdered samples are mixed with nujol, the mull mounted between KBr windows, and the sample scanned on a Unicam SP 100 spectrometer between 650 and 4000 cm^{-1} (fig. 1). The Si–O vibrational modes are resolved from nearby absorption peaks due to nujol at 725, 775, 975, and 1150 cm^{-1} .

¹ 1 μm (micrometre) = 1 μ (micron).

Hexachloro-butadiene internal standard method

Samples are mixed with hexachloro-butadiene (H.C.B.) and mounted between KBr discs. The method is simpler and quicker than the previous one. Using the twin-path Unicam SP 200 scanning times are reduced, as the area of interest lies between 2000 and 4000 cm^{-1} only (figs. 1 and 2). There are several absorption peaks due to H.C.B. in the 2000–4000 cm^{-1} region and one which occurs at 2800 cm^{-1} is used as an internal standard, the amount of H.C.B. being constant for each analysis.

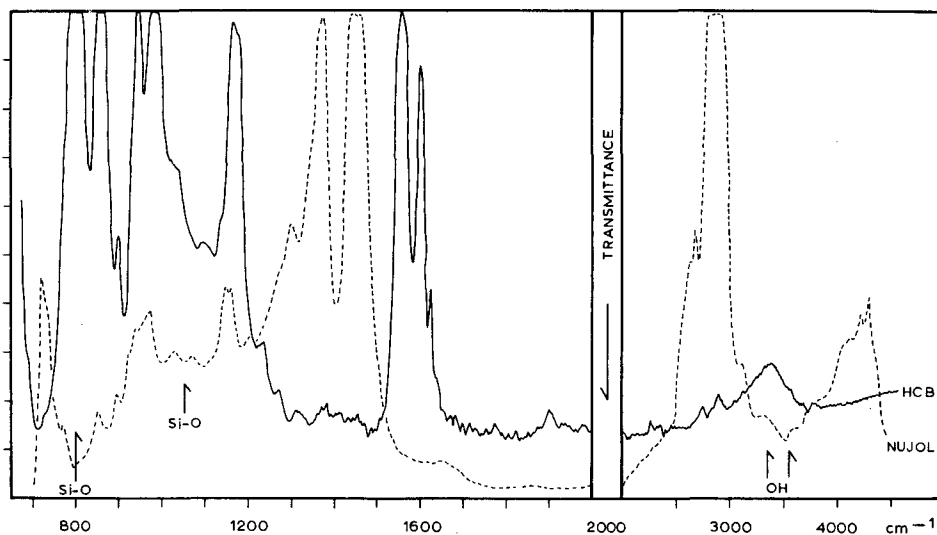


FIG. 1. Comparison of nujol and hexachloro-butadiene mulls, showing positions of OH and Si-O vibrational modes.

The ratio of sample to medium should be large so that the absorption peaks due to the H.C.B. mull are low. The absorption of the OH stretching frequencies should lie between 40 and 90 % to obtain maximum sensitivity. For granites, 0.0800 ± 0.0004 g of sample are weighed out directly on to the KBr window and 0.06 ml of H.C.B. added from a syringe in two stages to facilitate complete mixing. A 0.065-mm thick spacer is used to retain the mullied sample between the windows. With a twin-path instrument, the sample is placed in one beam and the other beam attenuated by means of a shutter, thus zeroing the instrument.

The absorption of the unknown sample is compared against the standard sample, which is run at the start of each session. A control sample is analysed as well.

For rocks that contain more than 2 % water the absorption peak exceeds 90 %, therefore the amount of sample should be lowered, and only 0.0200 ± 0.0004 g of powder and 0.03 ml of H.C.B. are required. A 0.035-mm thick spacer is used between the KBr discs.

Relation of the OH stretching frequencies to mineralogical composition

The peak due to the OH vibrational modes is a compound one consisting of the interference of two closely overlapping absorption bands (fig. 2A). The two peaks generally occur at approximately 3450 and 3680 cm^{-1} on scans obtained with the SP 200. The two peaks when developed independently from each other are usually

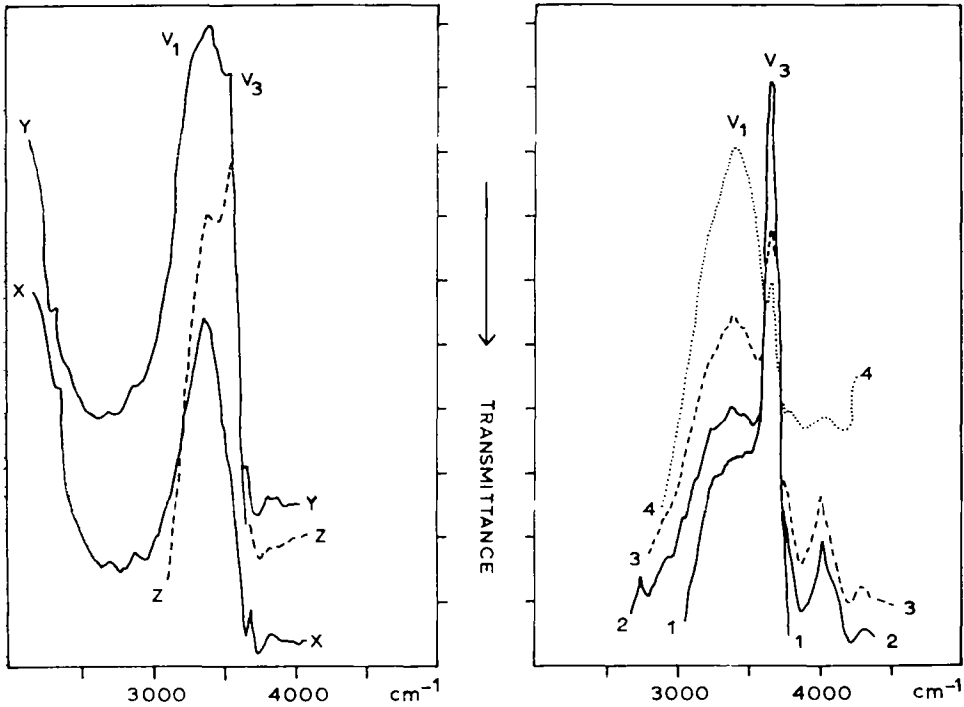


FIG. 2. A (left). Peak shape variation, X = aplite, Y = biotite granite, Z = chlorite schist. B (right). Variation of peak shape in magnesium hydroxide by addition of water; trace 1, dried at 110 °C, trace 2 after standing 10 min in air, trace 3 after addition of water vapour, trace 4 after addition of water.

sharp and correspond to the V_1 and V_3 vibrational modes. The low-frequency side of the V_1 absorption peak is not as sharp as the higher-frequency side of the closely associated V_3 peak. Hydrogen bonded OH will tend to modify the V_1 peak by lowering the frequency and the peak will appear asymmetric (trace Z, fig. 2A). If the V_3 peak is not strong enough to be resolved, which is usually the case, it may form a slight inflection on the higher frequency side of the V_1 (trace Y, fig. 2A).

When the V_1 and V_3 peaks are compared with rock type, the peak profiles can be related to the mineralogy. Aplites and high-silica granites give a low absorption peak due to the low water content, which occurs at 3450 cm^{-1} and corresponds to the V_1 vibrational mode. Granites with fresh biotite usually give the one main absorption

band, which is partially resolved into the V_1 and V_3 stretching frequencies at the top of the band (trace Y, fig. 2A). The V_3 stretching frequency is generally lower, and if peak area is compared, the integrated intensity of the V_3 peak would be lower still due to the narrowness of the profile when compared with the V_1 peak.

Rocks that contain chlorite as the predominant layered mineral give a very prominent V_3 absorption peak, whose peak height is in excess of the V_1 peak. For comparison, trace Z (fig. 2A) is produced by a chlorite–glaucophane–calcite schist that contains about 30 % chlorite. The relationship between the V_1 and V_3 absorption peaks is clearly seen.

The origin of the V_1 and V_3 vibrational modes is related to the mineralogy of the rocks. The V_3 absorption peak is the result of the OH molecules being combined to other atoms in the lattice by covalent or ionic bond forces, i.e. layered lattice minerals (Vedder, 1964), hence the V_3 vibrational mode is a measure of combined water. The V_1 vibrational mode is due to free OH groups attached to hydrogen atoms and is therefore a measure of free water in the rock. The origin of the V_1 and V_3 modes can be checked by examining the spectrum of a compound such as $Mg(OH)_2$, which contains OH groups that are bonded to cations.

Magnesium hydroxide was dried at 110 °C and prepared with H.C.B. in the usual way. Scans between 2000 and 4000 cm^{-1} were completed using various water-content conditions. The results can be seen in fig. 2B. Oven-dried $Mg(OH)_2$ gives a very sharp absorption peak at 3680 cm^{-1} with a broad shoulder on the lower frequency side. As the $Mg(OH)_2$ takes up water the shoulder increases and eventually an absorption peak appears at 3440 cm^{-1} corresponding to the V_1 vibrational mode. The V_3 vibrational mode now appears as a sharp-sided peak on the side of the V_1 peak similar to the absorption peaks from granite samples.

During the investigation of the origin of the V_3 absorption peak a number of schists were examined and the water content calculated using a granite as the reference standard. The infra-red results were too low, but if a schist was used as the standard the results were in reasonable agreement with the wet-chemical figures, hence standards of similar composition are required. In fig. 2A background absorption for granites decreases with increasing frequency, but the background absorption for schists increases. This could be a function of particle shape causing the orientation of chlorite between the KBr windows, hence the need for similarity of standard and unknown.

Conclusions

The results show that the coefficient of variation on the modified Penfield method can be up to 6 %, loss on ignition methods 9 %, and infra-red methods up to 9 % also. This could be improved by reducing the particle size of the samples to about 3 μm ; this will give better control over the mull thickness between the KBr windows. By using a low resolution instrument, absorption of the more pronounced V_1 vibrational mode gives a good estimate of total H_2O present in the rock. The method could be developed further, using peak area instead of peak height, and this would necessitate the use of a higher resolution instrument. Analysis time would be slower but a direct ratio between free and combined water would be possible.

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