DETERMINATION OF WATER IN SILICATE ROCK SAMPLES BY COMBUSTION AND INFRARED ABSORPTION

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An infrared absorption method is described for the determination of water in powdered silicate rock samples. For determination of the total water (H₂OTot), airdried samples were combusted at 1100°C without a flux and the evolved water was passed through an IR cell for the measurement. Essential water (H₂O⁺), was determined in a similar way but from samples dried at 110°C. For determination of non-essential water (H₂O⁻), air-dried samples were heated at 110°C.

Results (H₂Otot, H₂O⁺ and H₂O⁻) for 13 in-house reference rock samples (maximum grain size about 80 mesh) and eight international geological reference samples (maximum grain size about 200 mesh) agreed well with the results obtained by conventional methods, and the results obtained for the international samples compared well with published data. The precision of the IR absorption method is good (relative standard deviation <3 %) if the water content of the sample is more than 0.5 % and poorer if the content is less than 0.5 %. The practical detection limit is about 0.01 % H₂O. The new method is more rapid than the conventional methods.

Key words: chemical analysis, infrared spectroscopy, water, abundance, silicate rocks, samples.

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Introduction

In the total analysis of silicate rocks water cannot be determined by the common instrumental techniques such as atomic absorption, X-ray fluorescence or plasma emission. The determination of water with high accuracy is difficult and the method is often complicated and slow compared with analytical methods for other components. Non-essential water (H_2O^+), or free moisture, is held by surface forces such as adsorption and capillarity and its presence is not essential to the characterization of the sample. It tends to be related more to physical properties and sample treatment (humidity, grain size etc.) than to composition. Normally, the nonessential water is determined as the loss in weight of an air-dried sample after heating at 105— 110°C (Johnson and Maxwell 1981; Jeffery and Hutchison 1983). Essential water (H_2O^+), also known as water of crystallization, bound water or combined water, is present in regular atomic arrangement in the molecular or crystal structure. In many silicate rocks (e.g. basaltic glasses) hydrogen is present mainly in the form of water (Potts 1987). Elemental H occurs in metamorphic rocks and in sedimentary rocks (Jeffery and Hutchison 1983). The hydroxide group (OH), is important in clays (Volborth 1969). The water in fluid inclusions in minerals is non-essential water,

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but in common minerals it is not released from the inclusions by heating at low temperatures (below 110°C). The role and classification of hydrogen and water in silicate rocks and minerals have been discussed in detail by Hillebrand et al. 1953; Mitchell 1961; Baur 1978 and Pyper 1985.

Total water is non-essential water plus essential water (H₂OTot = $H_2O^- + H_2O^+$). The existing methods for the determination of H2OTot and H2O⁺ generally involve the combustion of an air-dried sample and a sample dried at 110°C with or without a flux. Most rocks will release all water without a flux if the combustion temperature is high enough (Skinner et al. 1981; Potts 1987). Some minerals do not release all their water without a flux unless temperatures exceed 1100°C, e.g. talc, topaz, staurolite, chondrodite, titanite, epidote and cordierite (Riley 1958; Maxwell 1968; Potts 1987). A flux is also necessary for mica and for rocks having a fairly high mica content (Kuzuhisa 1979). The evolved water is usually determined by gravimetric, titrimetric, thermal conductivity or infrared spectrometric methods. The classic gravimetric methods, including the Penfield method and its modifications, are slow and require close attention of the analyst during the determination (Penfield 1894; Peck 1964; Maxwell 1968; Donaldson 1973; DeLong and Lyman 1981). Titrimetric methods like the Karl-Fischer titration give fairly good results but are slow (Westrich 1987; Kuzuhisa 1979; Abbey 1979; Turek et al. 1976; Troll and Farzaneh 1978). Thermal conductivity methods (e.g. C-H-N elemental analyzer) are rapid, but the requirement for a 25-mg portion of sample could result in loss of sample representativiness (Skinner et al. 1981; Din and Jones 1978). Direct determination of essential water in a variety of rocks by infrared absorption using O-H stretching vibrations has been demonstrated to be useful when only a small amount of sample (a few milligrammes) is available (Augott and Marchall 1969; Breger and Chandler 1969). A method for the combined determination of water, carbon and sulphur by volatilization and non-dispersive infrared absorptiometry has been described by Bouvier and Abbey (1980), who claim that their procedure is more rapid than most similar methods.

In this study the new RMC -100 moisture analyzer (Leco Corporation) of the Geological Survey of Finland was used to determine the content of water (H₂OTot, H₂O⁺ and H₂O⁻) in 13 in-house reference rock samples (maximum grain size about 80 mesh, Backman and Liukkonen 1990) and eight international geological reference samples (maximum grain size about 200 mesh, Govindaraju 1980; Abbey 1983; Flanagan 1984). The results are compared with results obtained by the Penfield method (H_2Otot , H_2O^+) and the classical gravimetric method (H₂O⁻), and in the case of the international geological reference samples also with published data. The purpose of the study was to develop a rapid and satisfactory method for complete rock analysis.

Experimental

Conventional methods

Non-essential water, H_2O^- , was determined by gravimetric method from the loss in weight of air-dried samples heated at 110°C. The method was as follows: About 0.5 g of powdered sample was accurately weighed and transferred to a clean 30-ml platinum crucible. The crucible and contained sample were weighed, after which the crucible was placed in an oven and heated at 110°C for at least 2 hr. The crucible was transferred to a desiccator and allowed to cool for 30 min before weighing. Heating, cooling and weighing were repeated until no further loss in weight occurred.

The total water, H2Otot, and the essential water, H_2O^+ , were determined by the modified Penfield method (Danielsson and Saikkonen 1985; Maxwell 1968). The method was as follows: 0.5 g of air-dried powdered sample or sample dried at 110°C and 1 g of lead oxide were weighed and transferred into the sample bulb at the end



Fig. 1. RMC-100 rapid moisture analyzer.

of a Penfield tube. The water collection bulbs of the Penfield tube were wrapped with cold wet paper. The sample bulb was heated over a Bunsen burner for about 20 min, while the water evolved condensed into the collection bulbs. The Penfield tube with the contained water was weighed, after which the tube was dried and weighed. The weight difference is the content of the total water or essential water, depending on whether the sample was air-dried or dried at 110°C.

Infrared absorption method

Description of apparatus

The RMC-100 is a microprocessor-based instrument (Fig.1) for determining the non-essential, essential and total water in rock samples and in a variety of other materials. For measurement of the non-essential water the sample is loaded into the reaction chamber at the loading temperature. The water, driven from the sample with nitrogen carrier gas, passes through the infrared (IR) cell, where the water absorbs energy at a specific wavelength within the IR spectrum. This wavelength is selectively passed though a filter to an IR sensor where the concentration of water is detected as an energy level. The energy level is then amplified, rectified and converted to a digital signal. The data are sampled twice a second, linear corrections are made and the data are integrated to find the concentration of the water. The results are displayed as weight percent.

For the measurement of the essential water and the total water, the high-power ramping furnace heats to a preset high temperature driving the essential water or the total water from the sample. The concentrations of the essential and total water are calculated in the same manner as the

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concentration of the non-essential water. When analysis is done in the rapid mode the loading temperature can be set to a maximum of 500°C and the high temperature up to 1200°C. This optimizes sample throughput.

Two types of plots can be selected for the automatic print out of results. Moisture loss plots show percentage moisture of the sample on the vertical axis and time in seconds on the horizontal axis. A temperature line indicates temperature in respect to time. Intensity plots show the concentration of water in the IR cell in computer counts on the vertical axis, time on the horizontal axis and the temperature line in respect to time.

The electronic balance is interfaced with the instrument. Ceramic crucible boats (model 781-335) are used to hold the samples. The recommended carrier gas is 99 % pure nitrogen.

Procedure used

The RMC-100 instrument was operated as specified in the manufacturer's manual. The instrument was calibrated on the basis of several determinations of the geological reference samples: BHVO-1 Basalt, G-2 Granite, SDC-1 Mica Schist, PCC-1 Peridotite and UB-N Serpentine (Abbey 1983). Air-dried powdered samples were used for the determination of H₂O- and H₂OTot and samples dried at 110°C for the determination of H₂O⁺. Both H₂OTot and H_2O^+ were measured in the rapid mode where the loading temperature was 500°C. Briefly the procedure was as follows: About 0.5 g of the powdered, air-dried sample or sample dried at 110oC was accurately weighed into a clean dry ceramic crucible boat, with the powder spread evenly over the bottom of the boat. The boat was then slid into the reaction chamber (temperature 110°C or 500°C) using the sample puller. The free moisture, H₂O⁻, was driven off at 110°C and passed with nitrogen gas through the IR cell. In the rapid mode used for the measurement of combined and total water, the temperature was

quickly raised from 500°C to 1100°C, and the water driven from the sample with nitrogen gas was again passed through the IR cell. The result was displayed as weight percent. The print out was taken in the long format and with data shown in the form of intensity plots.

Results and discussion

Precision and accuracy

The contents of the total, essential and nonessential water in thirteen in-house rock samples were determined by infrared absorption method. The total water was also determined by the modified Penfield method, and the free moisture by the gravimetric method. The results are shown in Tables 1 and 3. In addition, eight international geological reference samples were analyzed by the same methods. These results, along with the published results, are shown in Table 2. The precision of the infrared absorption method was evaluated from the results of 3-20 determinations of the in-house and international reference samples (Tables 1-3). The coefficients of variation (CV), followed reasonably well the general trend of small coefficients for samples with high concentrations and large coefficients for samples with low concentrations of the constituents.

The precision of the Penfield method and the gravimetric method was calculated from the results of 2—13 analyses of the in-house and international reference samples (Tables 1—3). The coefficients of variation were of the same magnitude as for the infrared method.

The values of replicate blank analysis obtained by combusting 20 empty, dry crucible boats were as follows: 17 times 0.000 %, twice 0.001 % and once 0.006 % H₂O. The mean was 0.0004 % H₂O, and the standard deviation (s) was 0.0014 % H₂O. The detection limit, defined as 3 times the standard deviation (3s) of the blank value, was 0.004 % H₂O. The practical detection limit using a sample weight of 0.5 g was approximately 0.01 % H₂O.

Table 1. Comparison of total water (H₂OTot) and essential water (H₂O⁺) determinations for in-house reference rock samples by the infrared absorption method and by the modified Penfield method. N = number of replicate determinations, CV = coefficient of variation.

Sample		Infrared absorption method				Penfield method			
		$H_2OTot \ \%$	Ν	CV %	$H_2O^+ 0/0*$	H ₂ OTot %	Ν	CV %	H ₂ O+ %**
RS	11 Gabbro	1.63	15	2.0	1.52	1.55	7	2.6	1.51
RS	31 Rapakivi								
	granite	0.62	10	2.4	0.47	0.50	7	5.1	0,47
RS	51 Quartzite	0.27	10	4.8	0.24	0.26	1	_	0.26
RS	61 Trondjemite	0.50	7	2.9	0.42	0.54	1		0.54
RS	71 Diabase	0.88	8	1.4	0.70	0.83	2	8.5	0.70
RS	81 Granite	0.45	8	2.2	0.35	0.48	1		0.44
RS	91 Phyllite	3.94	10	0.5	3.65	3.94	2	0.2	3.75
RS	101 Diorite	0.71	8	1.0	0.57	0.70	3	11.0	.61
RS	121 Peridotitic								
	komatiite	7.58	10	1.4	7.30	7.21	7	1.0	7.04
RS	131 Basaltic								
	komatiite	6.24	10	1.0	6.08	6.62	6	1.4	6.53
RS	211 Serpentinite	13.76	15	1.6	13.04	13.46	7	1.0	12.70
RS	212 Serpentinite	13.73	6	0.9	13.02	13.22	2	0.1	12.51

* N = 3-4 and the coefficients of variation, CV, are approximately same as in the data for H₂OTot by IR absorption method.

** Calculated: $H_2OTot - H_2O^- = H_2O^+$ (see Table 3).

The results (H_2OTot , H_2O^+ and H_2O^-) determined by the IR absorption method and by the conventional methods were in good agreement (Tables 1—3). The IR absorption method gave good results for most of the international geological samples relative to published values, but too low values for the samples MA-N and ES-681—1 (Table 2). The information obtained from the intensity plots showed that the temperature, 1100°C, was high enough for all samples in this study.

General remarks

The fine grinding of minerals and rocks may lead to either an increase or a decrease in total water content. An increase is the result of the subdivision of grains and development of a greater

Table 2. H_2O^+ content in weight percent for some international geological reference samples determined by infrared absorption method (this study) and by the modified Penfield method (earlier at the Geological Survey of Finland). n = number of determinations during three days, N = number of replicate determinations, CV = coefficient of variation. D = Danielsson and Saikkonen 1985, G = Govindaraju 1980, A = Abbey 1979, Ab = Abbey 1983.

Sample	Infrared absorption method			Modified Penfield method			Liter.val.	
Sample		H ₂ O+ %	n	CV %	H ₂ O+ %	N	CV %	H_2O^+ %
BIR-1	Icelandic basalt	0.09	3	8	0.06 D	6	9	0.09 D
W-2	Centerville diabase	0.59	3	3	0.58 D	6	4	0.55 D
DNC-1	Diabase	0.76	3	2	0.60 D	6	4	0.73 D
MA-N	Granite	0.92	3	4	0.93 G	1		1.08 G
AN-G	Anorthosite	0.63	3	4	0.61 G	1		0.61 G
BE-N	Basalt	2.25	3	3	2.14 G	1		2.25 G
MRG-1	Gabbro	0.98	3	3	1.07 A	1		0.98 A
ES-681-1	Iron ore	9.93	3	3	9.92	10	2	10.4 Ab

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Sample		Sampling site	Infrared absorption	Gravimetric method		
			$H_2O- \% \pm sd$	N	H_2O- % ± sd	N
RS 1	Gabbro	Hyvinkää	0.03 ± 0.01	20	0.04 + 0.01	7
RS 31	Rapakivi				_	
	granite	Uhlu	0.03 ± 0.02	3	0.03 + 0.01	2
RS 51	Quartzite	Nilsiä	0.00 ± 0.01	3	0.00 ± 0.01	2
RS 61	Trondjemite	Uusikaupunki	0.01 ± 0.01	3	0.01 ± 0.01	2
RS 71	Diabase	Kuivanen	0.13 ± 0.03	3	0.13 ± 0.03	2
RS 81	Granite	Kuru	0.04 ± 0.02	3	0.04 + 0.02	2
RS 91	Phyllite	Karunki	0.30 ± 0.04	3	0.23 ± 0.06	2
RS 101	Diorite	Huopana	0.10 ± 0.03	3	0.05 ± 0.01	2
RS 111	Granite	Väkkärä	0.05 ± 0.02	3	0.03 ± 0.01	2
RS 121	Peridotitic					-
	komatite	Moskuvaara	0.33 ± 0.03	10	0.17 ± 0.02	7
RS 131	Basaltic					,
	komatite	Sattasvaara	0.17 ± 0.03	10	0.09 ± 0.01	6
RS 211	Serpentinite	Luikonlahti	0.78 ± 0.05	10	0.76 ± 0.06	7
RS 212	2 Serpentinite	Luikonlahti	0.66 ± 0.04	3	0.71 ± 0.07	2

Table 3. Comparison of free moisture (H_2O^-) determinations for in-house reference samples made by the infrared absorption method and by the gravimetric method. N = number of determinations, $H_2O^- \% \pm sd = mean\% \pm standard$ deviation.

surface area upon which water can be adsorbed or otherwise held. A decrease is mostly due to decomposition caused by local heating or it may also occur through the evaporation of water of fluid inclusions when grinding exposes them (Hillebrand et al. 1953; Maxwell 1968). Heating at 110°C will drive off most of the non-essential water, although temperatures considerably above this are necessary on occasion. The division into »minus» and »plus» water is partially an arbitrary one, but the determination of the nonessential water is important in providing the petrologist with a means for reducing analyses to a common dry-weight basis.

The infrared absorption method described has several advantages. Once the RMC-100 instrument is set up and has stabilized, the operation is simple and unvarying. The method is also rapid. In the rapid mode, determinations of H_2OTot and H_2O^+ in most samples can be completed in five to ten minutes. Forty determinations of H_2OTot or H_2O^+ can be made by an

analyst during one working day, compared with 15 determinations with the Penfield method. Alternatively 30 determinations of $H_2OTot =$ $(H_2O^- + H_2O^+)$ can be made daily, compared with 10 determinations with the conventional methods. Sample calibration is required and standards such as in-house reference samples need to be analyzed periodically to confirm accuracy and proper operation of the instrument. The method is suitable for determining water in silicate rocks at level 0.01 to 13 % if the sample weight is 0.5 g. Although a sample size of 0.5 g was used in this work, sizes down to 0.100 g are suitable for materials with high water content and sizes up to 2.000 g for materials with low water content.

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