



Quantitative hydrogen analysis in minerals based on a semi-empirical approach

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ABSTRACT

Hydrogen normally occurs as hydroxyl ions related to defects at specific crystallographic sites in the structures, and is normally characterized by infrared spectroscopy (FTIR). For quantification purposes the FTIR technique has proven to be less precise since calibrations against independent methods are needed. Hydrogen analysis by the NMP technique can solve many of the problems, due to the low detection limit, high lateral resolution, insignificant matrix effects and possibility to discriminate surface-adsorbed water. The technique has been shown to work both on thin samples and on thicker geological samples.

To avoid disturbance from surface contamination the hydrogen is analyzed inside semi-thick geological samples. The technique used is an elastic recoil technique where both the incident projectile (proton) and the recoiled hydrogen are detected in coincidence in a segmented detector. Both the traditional annular system with the detector divided in two halves and the new double-sided silicon strip detector (DSSSD) has been used.

In this work we present an upgraded version of the technique, studying two sets of mineral standards combined with pre-sample charge normalization. To improve the processing time of data we suggest a very simple semi-empirical approach to be used for data evaluation. The advantages and drawbacks with the approach are discussed and a possible extension of the model is suggested.

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1. Introduction

Hydrogen normally occurs as hydroxyl ions related to defects at specific crystallographic sites in the structures, and is normally characterized by infrared spectroscopy (FTIR). For quantification purposes the FTIR technique has proven to be less precise since calibrations against independent methods are needed. Hydrogen analysis by the NMP technique can solve many of the problems, due to the low detection limit, high lateral resolution, insignificant matrix effects and possibility to discriminate surface-adsorbed water.

To avoid disturbance from surface contamination the hydrogen is analyzed inside semi-thick geological samples. The technique used is an elastic recoil technique where both the incident projectile (proton) and the recoil hydrogen are detected in coincidence with a specially developed surface barrier detector. The technique has been shown to work both on thin samples and on thicker geological samples [1–5].

In this work we present the last step towards a quantitative technique for hydrogen measurement based on a set of mineral

standards and pre-sample charge normalization. We will present characterization of the calibration standard and give examples from analysis of minerals with known hydrogen concentration. We also discuss briefly the upgrade of the detector in the system.

2. Model

The shape of the total energy spectra in transmission mode after a pp scattering is influenced by a number of effects, both physical and analytical. The energy loss compared to the original beam energy depend both on the thickness of the sample, where in the sample the interaction took place and the scattering angles of the particles [6]. This implies that a thicker sample will show a broader distribution shifted towards lower energies. In this distribution the highest total energy comes from collisions on the detector side of the sample, the mid-part of the distribution comes from the interior of the sample and the low-energy part from the backside of the sample. For determination of the hydrogen concentration the mid-part is that of highest interest since this part will not suffer from any surface contamination. For samples in the range 2–20 μm the variation in stopping power, $-dE/dx \approx \frac{\text{const}}{E^2}$, will influence the spectral shape and for a homogeneous sample a decrease in coincidence counts per energy bin with decreasing energy will be seen. Other effects that also influence the spectral shape is the

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detector resolution and different analytical cuts done in the evaluation process. For the approach taken in this paper it has been assumed that the two last effects will be the same for data collected at one run. This is of course an approximation and effects due to multiple scattering will influence samples of different thicknesses in different ways [7] but is partly taken care of by using a set of standards with different thicknesses as discussed later. This implies that differences in energy distribution between samples with different composition and thickness will be caused by different stopping power and the difference in intensity depends on the hydrogen concentration.

In earlier work [4] it has been noted that a large portion of the energy distribution has an exponential or close to exponential behavior and this has been the basis for the idea of parameterization of the inner part of the energy spectra.

$$N(E) = N_0 \cdot e^{E/\lambda} \quad (1)$$

In this formula $N(E)$ is the intensity observed at energy E in the relevant interval, λ is the slope and to first approximation sample independent and finally N_0 is a measure of the hydrogen concentration in the sample. In a more refined model one can introduce a weak dependence in N_0 of E_0 (maximum energy after sample) but in the simplest approach treated in this paper N_0 is kept constant over the data range.

The idea is then to determine the free parameter λ and N_0 from a set of standards with different thickness but with the same hydrogen concentration. The relative concentration in the measured (unknown) sample is then deduced from the ratio:

$$R_{\text{concentration}} = \frac{N_{\text{sample}}(E)}{N_{\text{standard}}(E)} = \frac{N_0^{\text{sample}} \cdot e^{E/\lambda}}{N_0^{\text{standard}} \cdot e^{E/\lambda}} = \frac{N_0^{\text{sample}}}{N_0^{\text{standard}}} \quad (2)$$

The parameterization of data with an exponential function is of course not necessary and an alternative way, used by Wegdén [3] could be a polynomial fit. The essential part for the approach taken in this paper is that the experimental distribution should be described with a simple set of parameters were only one couples to the hydrogen concentration in the sample.

3. Experimental

The two experiments were performed at the sub-micron beam line at the Lund Ion Beam Analysis Facility (LIBAF). The facility is built around a single-ended 3 MV NEC 3UH accelerator and the beam line has a split quadrupole design for optimal focusing power. The system is described in detail in references [8–10]. In the first experiment a 2.5 MeV proton beam was sent into the sample in 0° angle to the sample normal and in the second the energy was increased to 2.9 MeV. In both experiments the hydrogen was measured by elastic scattering in transmission geometry with coincidence criteria, i.e. both the projectile and the target atom were detected. The hydrogen detection systems were designed with respect to the scattering process of a projectile colliding elastically with a target of equal mass, in this case a proton colliding with a hydrogen nucleus. The two identical collision products are always sent out in 90° relative to each other according to the laws of conservation of energy and momentum. If the recoiled proton and the scattered proton are detected in time coincidence, it is possible to distinguish random events or events from collisions with other nuclei, from the true hydrogen events. Charge measurement for data normalization was done with a pre-sample beam deflector [11], allowing sample independent charge measurement.

3.1. Detector setup one

This detector, specially designed for hydrogen coincidence measurement is an annular surface barrier detector divided into two

insulated halves positioned in the forward direction, i.e. on the exit side of the sample seen from the beam direction. The two halves are read out separately. The detector is manufactured by Ortec and has an active area of 4120 mm^2 with a hole-diameter of 12 mm, placed at a distance relative to the sample so that the angular interval between 35 and 75 degrees was covered, but only 45 ± 10 was used for hydrogen analysis. The nominal resolution is 25 keV and the depletion depth 300 μm . Details of the setup can be found in [12]. From this system, three parameters are extracted for each event, the two energies and the relative time between the two signals. These parameters are then used to produce a background suppressed total energy spectra to be used for the hydrogen profiling analysis.

3.2. Detector setup two

The successful installation of a double-sided silicon strip detector for backscattering analysis at the LIBAF [13] inspired us to also test it in the forward direction. This detector is an annular detector with 64 radial strips on the front side and 32 rings at the backside. With the overlap this results in a system corresponding to 2048 closely packed detectors, placed at a distance relative to the sample so that the angular interval between 40 and 65 degrees was covered. The detector-set up for hydrogen analysis are described in detail elsewhere [14].

The big advantage compared with the previously used two-sectioned detector is that the measurement not only gives the energy and time for the two particles, but also the space coordinates are recorded. This implies that in the off-line analysis, hard conditions on reaction plane and opening angle can be applied minimizing and controlling the background. A small temporarily drawback of this detector is that it can not yet be incorporated in the present scanning microprobe data acquisition system, but data have to be acquired with a VME test system. This implies that there is no position information in this data set, which would have been important due to the inhomogeneity in the standard samples.

3.3. Calibration samples

A natural muscovite sample (mica) was used as calibration standard. The choice of mica standard was governed by the relative ease to prepare thin mica specimens without a grinding process, due to the perfect cleavage. The hydroxyl ions in the mica structure are also strongly bound with a high thermal stability [15] and show limited concentration variation [16].

The muscovite sample (NRM#23069) was analyzed by electron microprobe technique, which resulted in the structural formula $\text{Na}_{0.06}\text{K}_{0.91}\text{Fe}_{0.14}\text{Al}_{2.79}\text{Si}_{3.09}\text{O}_{10}(\text{OH})_{1.85}\text{F}_{0.15}$. The OH content was calculated by stoichiometry assuming that only F and Cl will

Table 1

Measured elemental concentration the in muscovite sample measured with an electron microprobe. The concentrations marked with an * are calculated from stoichiometry.

Element	wt.%	Compound	wt.%
Na	0.35	Na ₂ O	0.48
Al	18.56	Al ₂ O ₃	35.33
Si	21.39	SiO ₂	46.11
K	8.75	K ₂ O	10.62
Mn	0.03	MnO	0.03
Fe	1.98	FeO	2.57
F	0.71	F	0.72
O*	43.36	H ₂ O*	4.13
H*	0.48		
		Sum	100

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