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# Quantitative determination of mineral content of geological samples by X-ray diffraction

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## Abstract

Geological samples from the Nevada Test Site are being analyzed for mineral composition by a rapid, routine X-ray powder diffraction procedure based on the external-standard intensity ratio method. The automated procedure uses X-ray diffraction to analyze each sample for the 12 minerals commonly found at the Nevada Test Site—quartz, montmorillonite, illite, clinoptilolite, cristobalite, feldspars, calcite, dolomite, hornblende, kaolinite, muscovite, biotite, and volcanic glass. The amount (wt.%) of a given mineral component present in the sample is determined by the ratio of the highest integrated intensity peak for the mineral to the highest integrated intensity peak for quartz, together with a constant for the mineral obtained from a calibration curve. The technique is accurate to ±7.0 wt.% of the total sample. The minimum amount of each of these minerals detectable by XRD has been determined, thus placing lower limits on the technique.

## Introduction

For a number of years Lawrence Livermore National Laboratory (LLNL) has used X-ray diffraction (XRD) for semi-quantitative analysis of the mineral composition of samples of Tertiary volcanic tuffs and Tertiary-Quaternary alluvium from the Nevada Test Site (NTS). The samples are made up of a limited suite of minerals, probably no more than 20. Amorphous glass and some 12 of these minerals are commonly found (quartz, montmorillonite, illite, clinoptilolite, cristobalite, feldspars, calcite, dolomite, hornblende, kaolinite, muscovite, biotite), but most of the samples contain only five to ten phases.

The "semi-quantitative" method used at LLNL was rather loosely defined. Some minerals were quantified by reporting that the XRD intensity was similar to previously run known compositions, while others were quantified by simply describing their XRD intensities as high, moderate, or low. This method was often inconsistent, and could actually be misleading. To improve accuracy, we looked for a technique to allow rapid, routine quantification of all minerals present in these samples. It was imperative that the technique be able to handle several hundred samples a year, and the quantification be accomplished in a timely fashion.

Many XRD quantification methods exist and are commonly used. The basic principle is that weight fractions can be calculated by knowing the XRD intensities, mass-absorption coefficients, densities, and constants. Some of these methods are: unknown/pure, spiking/dilution, internal-standard (all described in Klug and Alexander, 1954), standardless (Zevin, 1977), external standard (Copeland and Bragg, 1958), and matrix flushing (Chung, 1974). Unfortunately, none of these methods met our need to rapidly quantify five to ten minerals in a sample at one time.

We found, however, that the external-standard intensity ratio technique (Goehner, 1982) did meet our needs for rapid quantification of multicomponent systems. It is a modification of the external-standard method of Copeland and Bragg (1958); instead of using an external standard, it uses as its standard a component mineral that is common to each sample. This allows summation of all components in the sample to equal 100 wt.%. Quartz is the common component, since it has been found in every NTS sample tested by LLNL to date. The highest integrated intensity peak of each mineral to be quantified is used with the highest integrated intensity peak of quartz to calculate a ratio, and these ratios are used with predetermined constants to calculate the weight fraction of each mineral.

## Calculations involved

The external-standard intensity ratio technique uses the following calculations:

$$\frac{x_{\text{mineral}}}{x_{\text{quartz}}} = K \frac{I_{\text{mineral}}}{I_{\text{quartz}}}, \tag{1}$$

where

$x_{\text{mineral}}$ = weight of mineral,
$x_{\text{quartz}}$ = weight of quartz,
$K$ = slope of calibration curve for mineral,
$I_{\text{mineral}}$ = integrated intensity of highest peak of mineral XRD pattern,
$I_{\text{quartz}}$ = integrated intensity of highest peak of quartz XRD pattern.

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When these weight fractions are summed to equal 1.0, the mineral composition of the sample is calculated:

$$\sum_{k=1}^{n} x_k = 1.0, \tag{2}$$

where

$n$ = number of components in sample,
$x_k$ = weight fraction of mineral k.

### Experimental preparation

All X-ray scans were run utilizing a Philips Norelco generator equipped with a Cu X-ray tube and Ni filter, and a Philips Norelco goniometer. Operating conditions were 45 keV and 30 mA, with a theta compensating slit, and 1° receiving slit. The XRD scans cover 2–45° $2\theta$, automatically stepping 0.04° $2\theta$ every four seconds; scan positions and intensities are electronically recorded on a floppy disc at each step (Wallace et al., 1980). Good counting statistics are obtained from the step size and counting time. Total scan duration is 73 minutes. The scan length obtains much useful data for the mineral suite in a reasonable amount of time. The highest intensity peak of each mineral in question falls within the scan length. Other peaks of these minerals also fall within this length, ensuring positive identification of all minerals present. A quartz standard was used daily to ensure accuracy of the diffraction unit.

It was necessary to determine the optimal particle size that would yield high quality X-ray data but not require excessive sample preparation, since handling of many samples is likely and excessive preparation time is not permitted. For reproducible, high quality XRD data particle size must be small, within the range of 5–60 $\mu$m. It is well known that grinding can cause a wide range of particle sizes (Klug and Alexander, 1954; Tatlock, 1966). Also, minerals in a multicomponent system may grind inconsistently, and upon sieving the sample may become unrepresentative. Multicomponent samples of known compositions were crushed in a shatter-box grinder and various size fractions were X-rayed and analyzed. The data showed the size fraction $>35 < 45$ $\mu$m to be the most accurately represented. Repeated tests showed mineral quantities as known, and no mineral was selectively chosen or eliminated. The $>35 < 45$ $\mu$m size fraction was chosen to work with since it yielded reproducible, high quality XRD data and would not require excessive sample preparation.

Sample preparation to establish and test the external-standard intensity ratio technique required each mineral (purchased in a pure form) to be broken into approximately one-quarter inch pieces and ground in a shatter-box grinder. The samples were then seived for the $>35 < 45$ micron fraction. Mixing of this size fraction of the minerals was performed after grinding. This allowed very accurate control over sample composition, a feature necessary for establishing and testing a new quantification procedure. The powdered samples were then backpacked into standard aluminum holders to be X-rayed.

### Applying the method

Constants were calculated from calibration curves for each of the 12 minerals and glass commonly found in NTS samples. Standards were made of various compositions of each mineral with quartz; these standards were X-rayed, and the weight ratios $x_{quartz}/x_{mineral}$ were plotted against the ratios of the highest integrated peak of quartz (100 peak = $d$ spacing of 3.34Å) and the highest intensity peak of each mineral, $I_{quartz}/I_{mineral}$. A calibration curve (line) for each mineral was calculated by a linear least-squares fit of the data (at least eighteen data points), and the slope of the line was taken as the K constant for that mineral. These constants are listed in Table 1.

### Accuracy and sensitivity determinations

Sixteen samples of various compositions of the minerals listed in Table 1 were prepared, X-rayed, and quantified using equations (1) and (2), to determine the accuracy of the external-standard intensity ratio technique. The samples were prepared to be representative of geologic environments found at NTS. They contained from three to 11 mineral components. The errors in quantifying each mineral in a sample and the maximum error for each sample are given in Table 2, and the error distribution is shown in Figure 1. The average error of 0.0 wt.% was expected, since we knew the calculated values could deviate above or below the known value. The standard deviation is 2.89 wt.%, and the maximum error is ±7.0 wt.%.

Table 2 shows that the external-standard intensity ratio technique has an accuracy of ±7.0 wt.%. This accuracy has not been tested by other methods because funding has not existed for this. Also, it is difficult to check the accuracy of this method by other methods (IR, spectroscopy, fluorescence, etc.) because most are not mineral specific, but rather determine elemental content, which can vary widely with the varying mineral contents of NTS samples. The most logical type of testing would be modal analysis, which may be difficult since these samples rarely exist as a whole rock, but rather as cutting or sidewall samples from drill holes. One quick statistical test has been done to compare $CO_2$ measurements routinely made on NTS samples to $CO_2$ measurements of these same samples calculated from XRD determined calcite and dolomite contents. The two data sets have overlapping distributions—measured

Table 1. *K* constants for the 13 minerals commonly found in Nevada Test Site samples

| | | | |
|---|---|---|---|
| Quartz | 1.0000 | Dolomite | 0.3528 |
| Montmorillonite | 22.0412 | Glass | 36.8405 |
| Illite | 30.2904 | Hornblende | 2.7698 |
| Clinoptilolite | 9.7432 | Kaolinite | 10.5970 |
| Cristobalite | 1.2940 | Muscovite | 1.9180 |
| Feldspars | 1.2774 | Biotite | 0.4304 |
| Calcite | 0.6544 | | |

Table 2. Error in quantifying known sample contents using the external standard intensity ratio technique*

| Sample No. | Error (wt%) Q | MO | IL | CC | CR | FS | CA | DO | GL | HO | KA | MU | BO | Maximum error |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | +4 | -2 | -- | -- | -- | +1 | -3 | -- | -- | -- | -- | -- | -- | 4 |
| 2 | +4 | +2 | -- | -- | -- | -4 | -1 | -- | -- | -- | -- | -- | -- | 4 |
| 3 | +2 | -3 | -1 | -7 | -- | +5 | +3 | +3 | -- | -- | -1 | -- | -- | 7 |
| 4 | +4 | -2 | -- | -1 | -- | +2 | -- | 0 | -- | -1 | -- | -2 | -- | 4 |
| 5 | +4 | -4 | +7 | -3 | -- | +2 | -- | 0 | -- | -2 | -2 | +2 | -4 | 7 |
| 6 | +4 | -3 | 0 | 0 |  | +3 | -- | +1 | -- | -2 | -3 | -- | -- | 4 |
| 7 | +6 | -- | -- | -7 | -- | -- | -- | -- | -- | -1 | +1 | +1 | -- | 7 |
| 8 | +7 | -- | -2 | -- | -- | +3 | -2 | -4 | -- | -- | 0 | -3 | -- | 7 |
| 9 | -1 | 0 | -- | +1 | -- | +4 | +1 | 0 | -- | -2 | 0 | -- | -3 | 4 |
| 10 | +6 | -7 | +3 | -5 | -- | +3 | -- | -- | -- | -- | -- | -- | -- | 7 |
| 11 | 0 | -- | -- | -- | -- | +4 | -- | -- | -4 | -- | -- | -- | -- | 4 |
| 12 | +2 | -1 | -- | -- | -- | -1 | -- | -1 | -- | -- | -- | -- | -- | 2 |
| 13 | 0 | -- | -- | -1 | -- | +4 | -- | -- | -2 | -- | -- | -- | -- | 4 |
| 14 | 0 | +3 | -- | -2 | +2 | -2 | -- | -- | -- | -- | -- | -- | -- | 3 |
| 15 | +3 | -- | -3 | -- | -2 | 0 | 0 | -1 | -- | -1 | +3 | -- | -- | 3 |
| 16 | +2 | -- | -- | -- | 0 | -2 | -- | -- | -1 | -- | -- | -- | -- | 2 |

Mean error = 0.0 wt% Standard deviation = 2.89 wt% Number (population) = 95

*Mineral symbols defined as follows:

Q = quartz
MO = montmorillonite
IL = illite
CC = clinoptilolite
CR = cristobalite
FS = feldspars
CA = calcite
DO = dolomite
GL = glass
HO = hornblende
KA = kaolinite
MU = muscovite
BO = biotite

$CO_2 = 0.86 \pm 1.26$ wt.%, and calculated $CO_2 = 1.11 \pm 2.08$ wt.%. Linear regression of these data indicates that at a 95% confidence interval the calculated $CO_2$ contents can predict measured $CO_2$ contents 73% of the time. This tests only two minerals, and the data set is not large ($n = 104$), but it indicates that the external-standard intensity ratio technique is an accurate method for quantifying mineral content of samples.

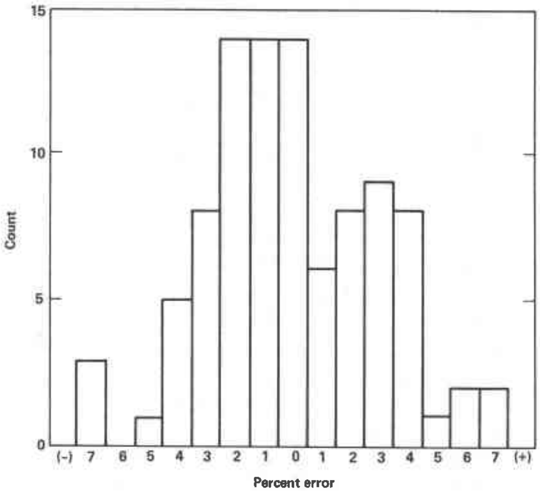

Fig. 1. Error distribution in quantifying the mineral content of 16 prepared samples using the external-standard intensity ratio technique ($n = 95$). The samples were representative of various geologic environments found at NTS.

It was important to determine the minimum amount of each mineral in a multicomponent sample that could be detected by XRD, thus placing lower limits on the quantification procedure based on what could actually be observed in XRD data. Samples with small amounts of the various mineral components were prepared to determine the minimum amounts the analyst could positively identify in the XRD pattern. These minimum amounts are listed in Table 3.

With the exception of glass, all minerals can be accurately identified below 10 wt.%, and some as low as 0.5 wt.%. The minimum detectable amount of glass is 40 wt.%. The XRD pattern of volcanic glass is a wide hump extending from approximately 19° to 36° $2\theta$. Small amounts of glass are difficult to distinguish from normal or abnormal background levels. Information on geologic setting or hand-sample observations could help indicate if much glass is present. For example, knowing that the sample came from a vitrophyre would indicate high glass content, while presence of clays and zeolites would probably indicate low to negligible amounts of glass. It is possible that other

Table 3. Minimum amounts of the 13 minerals detectable by XRD (wt.%)

| | | | |
|---|---|---|---|
| Quartz | 0.5 | Dolomite | 0.5 |
| Montmorillonite | 5.0 | Glass | 40.0 |
| Illite | 7.0 | Hornblende | 2.0 |
| Clinoptilolite | 5.0 | Kaolinite | 5.0 |
| Cristobalite | 1.0 | Muscovite | 3.0 |
| Feldspars | 2.0 | Biotite | 5.0 |
| Calcite | 0.5 | | |

methods may detect smaller amounts of glass present in samples.

Figure 2 shows a schematic of the procedure used at LLNL to routinely quantify minerals in NTS samples by means of the external-standard intensity ratio technique. The computer code QUANTS stores the K constants and calculates mineral contents by accessing a file consisting of drill hole identification, sample information, and ratios of the highest intensity peak of each mineral present and the highest intensity peak of quartz—the same two peaks of the sample that were used for calculating the K constant of the standard. It is important to note that occasionally some peaks will be composed of more than one mineral (namely illite, muscovite, and biotite) and will need to be mathematically deconvoluted.

## Discussion

There are several important advantages to the external-standard intensity ratio technique as a quantification method. The sample need be X-rayed only once, and for a short time (73 minutes). Because the intensities are used as ratios and are obtained from one short scan, many XRD problems are minimized (Goehner, 1982). These include changes in barometric pressure, machine factors (keV and mA drift), long-term drift of the X-ray tube (aging), matching of mass-absorption coefficients, sample problems such as compactness of powder and sample transparency, and alignment problems such as sample positioning in the goniometer circle and slight goniometer alignment changes.

Several XRD problems not minimized with this technique, and which the user needs to be concerned with, are particle statistics, preferred orientation, micro-absorption, and extinction (Goehner, 1982).

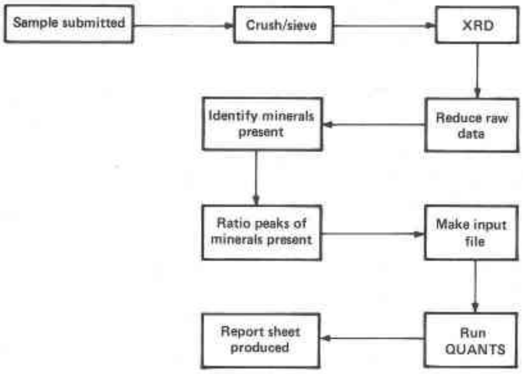

Fig. 2. Procedure used by LLNL for quantifying the mineral content of NTS geological samples.

Quartz was chosen as the common mineral because it has been present in all NTS samples in some amount. But even if quartz is not present in a sample, a known amount of it can be added, and then the calculated sample composition can be corrected to account for the added quartz. Also, new minerals can be added to the quantification process at any time by simply determining a K constant and incorporating it into equation (2).

It should be noted that feldspars from NTS samples show chemical variation, as could be expected in almost any geologic environment. Constants for these feldspars can also be expected to vary. Initial tests show that this variation in constants to be small, and may cause 2% error in the calculated feldspar quantity. Future work may determine constants for a wide range of feldspars, which will more accurately quantify the content of samples.

Although the external-standard intensity ratio method has been devised to quantify a specific set of minerals found in NTS samples, it can easily be made applicable to other areas or minerals suites. There are two basic requirements to this method—a common mineral must always be used, and constants must be known for each component in the mineral suite. The common mineral may be chosen in several ways. It may be a mineral always (or usually) occurring in the mineral suite, and if the chosen common mineral is not present in a sample it may be added to the sample. It is also possible to choose a phase never found in the mineral suite, and add it to all samples (and adaptation of the internal-standard method). Adding a phase would require addition of a known amount of "common mineral", and normalizing the calculated mineral quantities. It is always possible and relatively simple to calculate K constants for new minerals, thus establishing or expanding mineral suites desired.

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