

## **Quantitative mineralogical analysis of granitoid rocks: a comparison of X-ray and optical techniques**

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### **Abstract**

Five igneous rock specimens from the Peninsular Ranges batholith of southern California have been analyzed for mineral content in a comparative study by X-ray diffraction (reference intensity technique) and optical polarizing microscopy. The X-ray method utilizes aerosol suspension of pulverized rock samples, followed by collection and analysis on glass fiber filters by powder X-ray diffractometry. Under some conditions, a standard well mount may be used for sample preparation, eliminating the need for sample transparency and matrix corrections. Optical analysis consists of standard identification procedures using polarized light followed by point counting. Excellent agreement between the two methods is observed for quantities of the major components for all rocks except an olivine gabbro. Discrepancies in the gabbro analyses are primarily due to sample inhomogeneities as well as the use of calculated reference intensity constants for the several solid solution minerals occurring in this sample. Where both experimental reference intensity constants and sample measurements are obtained using the aerosol suspension technique for sample preparation, relatively high accuracy and relatively rapid data collection may be achieved with the X-ray method.

### **Introduction and background**

Quantitative analysis by X-ray diffraction methods has received increasing attention in recent years (see the review by Alexander, 1977). Nevertheless, problems associated with preferred orientation, extinction, and micro-absorption have still limited the application of X-ray diffraction quantitative analysis to relatively inaccurate or semi-quantitative results. Point counting by microscopy still remains the basic and most widely used technique for direct mineralogical analysis of rock materials where particle size is above the 10  $\mu\text{m}$  diameter level. However, many X-ray diffraction studies using specialized calibration techniques have been described in the literature and include examples such as that of Parker (1978) for analysis of analcite in pumice, Bidjin and Lahodny-Sare (1976) for a study of kaolinite and boehmite in bauxite samples,

the calcite study of Garish and Friedman (1973), and the clay mineral work of Cody and Thompson (1976). Additional specialized techniques such as those described by Henslee and Guerra (1977) using PVC membranes and Leroux and Powers (1970) for films deposited on silver membrane filters, were designed for analysis of free  $\text{SiO}_2$  materials. Many additional specialized studies of these types exist but cannot be enumerated here.

In recent years, a general X-ray diffraction technique has emerged, known as the reference intensity method (RIM), which permits quantitative multi-component analysis of crystalline materials without the requirement for preparation of calibration curves, and more recently without the need for the adding of an internal standard to the sample. Formulation of the RIM process was given by Chung (1974a, 1974b, 1975) and was applied to compounds used in paint pigments, such as  $\text{PbO}$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$ ,

*etc.*, with the compounds reduced to a fine powder and mounted in accordance with the National Bureau of Standards' technique (NBS Monograph 25, 1971). The technique as applied to these compounds proved highly successful, primarily due to the use of reference intensity constants determined for the same specific batches of compounds that were used in the "unknown" mixtures. Most of the early work used an introduced compound, such as  $\text{Al}_2\text{O}_3$  as the reference material, but the latest study (Chung, 1975) made use of one of the compounds in the unknown mixture as the arbitrary reference. This, of course, was made possible by the previous knowledge of the reference intensity constants for all components of the sample so that transformation of the reference base was possible.

In response to a need for characterization of compounds in the atmosphere, a comprehensive study was undertaken by one of us (BLD) to develop a quantitative analysis technique for ambient aerosols. In this case, analysis was made directly on the collecting filter media, usually a high-volume glass fiber filter or one of the membrane filters such as Teflon or Nucleopore. The unique filter method of sample preparation was shown by Davis and Cho (1977) to eliminate preferred orientation in calcite aerosols, and it has been presumed that preferred orientation of other inequant shaped materials is similarly eliminated or greatly reduced. These studies are further described by Davis (1980), and Davis and Johnson (1982a,b).

Optical techniques for quantitative evaluation of mineral constituents in thin section have long been used by mineralogists and petrologists. It is important in such an analysis, however, to be sure that the volume adjustment of the various species for shape differences is made to the point count data set. This adjustment is vital in order to make a comparison of the traditional optical analytical technique with the recently developed RIM. To avoid making such corrections, we have selected a series of relatively homogeneous even-grained plutonic rocks from the Peninsular Ranges batholith of southern California. Classification of these rocks range from granite through quartz diorite to gabbroic species that have been described previously by Walawender (1976) and Walawender and Smith (1980). Further interest was added to the study by completing the work independently. Data from one laboratory was not examined by the workers of the other laboratory until completion of the experimental work and compilation of the final analytical results. We feel, therefore, that the present results

give a true evaluation of the X-ray technique if one considers the optical results to be the "standard" of comparison. To the authors' knowledge, this study represents the only attempt at a direct and independent verification of the RIM technique since the method was successfully applied by Chung.

#### Brief summary of required X-ray parameters

A complete description of the X-ray theory and methodology is not possible here. These details can be obtained by review of the Institute of Atmospheric Sciences (IAS) literature cited above. Briefly, the raw intensity data can be obtained from digital or strip chart output of any properly maintained powder diffractometer. They should be integrated intensities (at least by "triangular" approximation) and must be corrected to constant volume conditions in cases where the theta-compensator has been employed. The intensities representing the "infinite" thickness condition for such a sample is obtained from the relation

$$I_i^\infty = \frac{I_i^\alpha \mu_H^* \xi}{W_B^H \mu_B^* [1 - e^{-2\mu_H \check{M}_B / W_B^H \sin\theta}]} \quad (1)$$

where  $I_i^\alpha$  is the raw integrated intensity (counts) for component  $i$ ,  $W_B^H$  is the fraction of the sample material in the sample/matrix composite layer,  $\xi$  is the constant volume factor for diffractometers with theta-compensating slit systems,  $\mu_B^*$  is the mass absorption coefficient experimentally determined for the sample material alone,  $\mu_H^*$  is the mass absorption coefficient for the sample/matrix composite,  $\check{M}_B$  is the mass per unit area of sample layer B on the filter substrate, and  $\theta$  is the Bragg diffraction angle. This relation corrects the initial intensities for transparency, matrix absorption, and departure from constant volume conditions (if appropriate).

The mass absorption coefficient of the filter is obtained from the relation

$$\mu_f^* = - \frac{1}{M_f} \ell_n \left( \frac{I_f}{I_0} \right) \quad (2)$$

where  $I_f$  is the beam intensity attenuated by the filter,  $I_0$  is the initial beam intensity,  $\check{M}_f$  is the mass per unit area of the filter substrate, and  $\mu_f^*$  is the mass absorption coefficient of the filter material alone. A similar relation is used to obtain the mass absorption coefficient of the sample;

$$\mu_B^* = - \frac{1}{M_B} \ell_n \left[ \frac{I_{fB}/I_0}{I_f/I_0} \right] \quad (3)$$

where  $I_{FB}$  is the X-ray beam attenuated by both filter and sample material, and other quantities as defined above. This *measured* value of the sample mass absorption coefficient is then compared with a similar quantity calculated from constituent elements, oxides, or mineral components whose mass absorption coefficients are a mass-weighted sum of elemental values tabulated in the *International Tables for X-ray Crystallography* (1968, Vol. 3, Table 3.2.2a). Significant departures of the measured value from the values calculated from the analyses would indicate errors in sample processing, or errors in physical parameters such as the reference intensity constants, or the presence of amorphous components. For plutonic rocks, we can safely eliminate the possibility of amorphous constituents.

Reference intensity constants must be available for each component expected in the analysis. These are intensity ratios  $I_i/I(\text{Al}_2\text{O}_3)$  measured experimentally from mixed equal-weight proportions of the component (i) and a reference standard, which has been Linde A synthetic  $\text{Al}_2\text{O}_3$  in the latest IAS investigations. Reference intensity constants are also available in the JCPDS (Berry, 1970), although we do not recommend their use since the methods of sample preparation are generally not stated and certainly not consistent from source to source. Since the sample in the IAS RIM technique has been suspended and collected on a filter, it is imperative that the reference intensity constants be determined with an identical procedure, which has been the case for all analyses completed by the IAS group.<sup>1</sup>

With these reference intensity constants determined, the final analysis is obtained quickly and simply by use of the equation

$$W_i = \left[ \frac{k_i}{I_i^\infty} \sum_{i=1}^n \left( \frac{I_i^\infty}{k_i} \right) \right]^{-1} \quad (4)$$

where  $W_i$  and  $k_i$  are the weight fraction and reference intensity constant, respectively, of the  $i^{\text{th}}$  component of  $n$  components of the mixture.

In the present analyses, the experimental instrumentation consisted of a Norelco powder diffractometer fitted with theta-compensator and graphite vertical monochromator, operating with  $\text{CuK}\alpha$  radiation at a scan speed of one-half degree per minute.

Mass absorption coefficients were measured with an automatic direct-beam transmissometer constructed in part from components of a Philips small-angle scattering goniometer. In the latter system, the circular filter sample was rotated and translated normal to the X-ray beam to integrate the count over the entire sample for a 20-sec period. The direct beam count was made alternately with the filter count for an identical period. Direct beam strength was approximately  $2 \times 10^4$  counts per second. No less than 10 separate integrated passes were made on each filter and filter/sample composite; the average value for the 10 passes was used in Equation (3).

#### Description of the optical technique

Point count techniques, long used by petrologists, are described by Chayes (1956). The procedure simply consists of fixing a standard thin section into a mechanical stage equipped with a 2-axis micrometer control and translating the thin section in fixed increments across the stage of a petrographic microscope. At each increment, the grain underneath the ocular crosshair was identified and recorded on a point counter device. The final tally of points recorded for each mineral is then equated to a volume percent of that mineral in the thin section.

Our procedure consists of counting an initial 200 points and calculating the appropriate weight percent for each mineral. An additional 100 points ( $i_1$ ) are then determined and added to the initial count. This total ( $200 + i_1$ ), as weight percent, is compared to the initial 200 points. If all the major minerals in the initial count (200) are within 5% of the ( $200 + i_1$ ) subtotal, that addition adds no new information and the ( $200 + i_1$ ) subtotal is considered to approximate the mode of the thin section. If any of the minerals in the ( $200 + i_1$ ) subtotal are not within 5% of those in the initial count, an additional 100 points ( $i_2$ ) are counted and added to the previous subtotal. Using the 5% limit, the ( $200 + i_1 + i_2$ ) subtotal is compared to the ( $200 + i_1$ ) subtotal. The procedure is repeated until the final increment ( $i_n$ ), when added to the previous subtotal, falls within the 5% limit for each major mineral. The final total, converted to volume percent, approximates the mode of the thin section. Although 400 points were generally sufficient for the rock types used in this study, 2 of 10 thin sections required a 500 point total to meet the "diminishing returns" requirement. All thin sections were thus counted to a total of 500 points for consistency. Duplicate thin sections of each rock type were counted and the average values, along

<sup>1</sup>Up-to-date list of the current reference intensity values obtained by the air suspension method may be obtained from the IAS laboratories on request.

with the error factors ( $\pm$  one-half the differences) are listed in Table 1.

### Sample preparation

For the normal RIM procedure, the rock samples are ground in a carbide ball mill to "flour" consistency and the powdered material was suspended in the simplified aerosol suspension device described by Davis (1981a). The vertical flow velocity within the chamber allows approximately 10  $\mu\text{m}$  diameter particles or less to be incorporated into the filter. Best results are obtained when using the Whatman GF/C (37 or 42.5-mm diam) glass fiber filter. The surface is much smoother than that of the heavier "high-volume" type filter and the fine fiber matte aids in creation of random orientation of the trapped particles. No substrate peaks are contributed to the sample spectra, although loadings in excess of 300  $\mu\text{g cm}^{-2}$  are necessary for obtaining adequate peak intensities.

For the present study, mass loadings of 3–8 mg  $\text{cm}^{-2}$  were accumulated on the filter in an even layer by rotation of the Buchner funnel assembly while collecting the aerosol. The diameter of the filter/sample composite is reduced in two stages:

First, a cut to 3.65-cm diameter to eliminate the border areas that have incomplete sample coverage such that an accurate  $\bar{M}_B$  can be measured; and secondly, to obtain a 25-mm diameter disk for mounting in the spinning sample pedestal of the diffractometer.

It is possible to bypass the filter mounting of the sample whenever it is apparent that materials with good cleavages or inequant habit are not present or are only minor components of the sample. Under such conditions, that is, when preferred orientation is not expected to be serious, it is possible to eliminate the corrections by mounting the pulverized rock material in a normal "well" mount. This allows straightforward use of Equation (4) without correcting for sample transparency or matrix absorption.

In the present study, reference intensity constant measurements were made for biotite and hornblende from the diorite samples because the grain size of these components was large enough to allow their separation. These constants were obtained from pulverized component material treated in the same manner as the sample material. Prior to suspension, the mineral components were mixed with

Table 1. Quantitative mineralogic analyses of peninsular ranges batholith rocks by X-ray diffraction and polarizing optical microscopy (weight percent)\*

Component	LQD		MQD		WD-1			WD-2		W-113	
	Optic	X-ray	Optic	X-ray	Optic	X-ray	$W^{\Delta}$	Optic	X-ray	Optic	X-ray
Quartz	22.7	26.1 (2.7)	9.6	8.4 (1.2)	35.8 (1.6)	33.7 (4.0)	37.3	16.3 (0.7)	16.7 (3.0)	-	-
Plagioclase**	60.4-0	55.1-0 (3.2)	57.6-L	57.9-L (5.3)	40.7-0 (0.1)	33.6-0 (2.3)	35.7	64.3-0 (2.5)	66.2-L (4.7)	28.0-B (3.4)	25.2-B (2.4)
Microcline	-	-	-	-	19.0 (0.6)	16.9 (7.1)	24.5	-	-	-	-
Biotite	12.2	14.1 (1.6)	7.0	5.7 (2.2)	3.2 (0.4)	0.4 (0.2)	1.5	13.0 (2.8)	9.0 (3.4)	-	-
Muscovite	-	-	-	-	-	-	6.4 (1.1)	-	-	-	-
Hornblende	2.6	2.7 (0.4)	10.4	13.3 (3.9)	-	-	-	5.4 (1.2)	8.2 (2.6)	23.8 <sup>†</sup> (3.2)	43.0 (8.1)
Diopside	-	-	15.4	13.4 (5.8)	-	-	-	-	-	-	-
Enstatite	-	-	-	-	-	-	-	-	-	22.2 (2.0)	7.4 (1.4)
Augite	-	-	-	-	-	8.3 (4.0)	-	-	-	-	-
Olivine	-	-	-	-	-	-	-	-	-	23.2 <sup>†</sup> (1.4)	22.4 <sup>††</sup> (3.5)
Magnetite	-	-	-	1.3 (0.4)	-	-	0.7 (0.4)	-	-	-	2.1 (0.8)
Sphene	tr	-	-	-	0.1 (0.1)	-	-	-	-	-	-
Apatite	tr	-	-	-	tr	-	-	0.1 (0.1)	-	-	-
Chlorite	2.0	2.0 (0.4)	-	-	0.2 (0.2)	-	1.0	-	-	-	-
Spinel	-	-	-	-	-	-	-	-	-	2.3 (0.3)	-
"Opakes"	-	-	-	-	0.9 (0.2)	-	-	0.9 (0.1)	-	tr	-

\*Numbers in parentheses are  $\pm \frac{1}{2}$  difference in the two optical counts and  $\pm$  variance errors for XRD (Davis, 1981a).

\*\*0 = Oligoclase; L = Labradorite; B = Bytownite ( $\text{An}_{86-90}$  from optic analysis;  $\text{An}_{85}$  from x-ray analysis).

<sup>†</sup>Edenite or pargasite variety.

<sup>††</sup>Fo<sub>78</sub>.

<sup>‡‡</sup>Fo<sub>80</sub>.

<sup>Δ</sup>Sample WD-1 analysis from well mount.

equal proportions of Linde A synthetic  $\text{Al}_2\text{O}_3$  reference standard.

### Sources of uncertainty

Davis (1981) describes a variance error propagation procedure which incorporates the standard deviations of the reference intensity constants, mass absorption coefficients, and other physical parameters using the reduced multivariate error expression for  $n$  uncorrelated variables

$$s^2 = \sum^n \left[ \frac{\partial f(X_1, X_2, \dots, X_n)}{\partial X_i} \cdot s(X_i) \right]^2 \quad (5)$$

where  $s^2$  is the variance propagated from use of Equations (1) and (4) and other expressions (where amorphous components are present) involving the variables  $X_n$  where the  $X$ 's stand for  $k_i$ ,  $\mu_i^*$ , etc., and  $s(X_i)$  represents the estimated standard deviation of each parameter. Standard deviations are not always available, but estimates of them can be obtained by use of range information and from the maximum or minimum error expected. Description and listing of the specific standard deviations for all parameters is beyond the scope of the present discussion. In the absence of amorphous components, the major sources of uncertainty are the reference intensity constants,  $k_i$ , and the mass loading,  $\bar{M}_B$ . The error from the latter source begins to be appreciable only below  $0.05 \text{ mg cm}^{-2}$  and therefore errors from this source should be insignificant for the present study. For those components having only one measured value for  $k_i$  or  $\mu_i^*$ , the arbitrarily assigned value of  $\sigma' = 0.10 X_i$  for the variance error has been used in all calculations. The highest measured relative standard deviation (standard deviation divided by the mean) is 0.57 for magnetite based on analyses of three separate specimens. The variance error process has suggested from past studies that the major components of the analysis (greater than 50 weight percent) will be known to within  $\pm 10\%$  of the stated analyzed amount, whereas minor components (less than 10 wt.%) may have uncertainties as high as 100% or greater.

Unfortunately in the current study, reference constants were not available for all mineral components. The values for diopside, enstatite, augite, and olivine were obtained from calculated absorption and intensity data of Borg and Smith (1969). This introduces additional uncertainty into the final analyses, and in these cases standard deviations of

10% were assigned to the  $k_i$  and  $\mu_i^*$  parameters as in the case where only one measured value is available. We have found that the calculated and measured reference intensity constants agree within reasonable limits, but that large variations in this agreement may occur with different mineral species. The reasons for such disagreement are unknown and obviously suggest the need for additional work in the area of reference intensity constant determination.

The potential sources of uncertainty in the point count method have been considered in detail by many investigators. Only a brief summary will be attempted herein and the reader is directed to Chayes (1956), Solomon (1963), and Frangipane and Schmid (1974). Major sources of uncertainty include:

(1) The average grain size of the rock relative to the traverse increment of the mechanical stage. The former value cannot be determined from a thin section since it represents a random slice through the rock. As such, the maximum and minimum grain sizes can only be approximate. If the traverse increment is greatly different from the average grain size of the rock, a significant bias may be encountered.

(2) Direct conversion of areal proportions to volume proportions. This is dependent on the distribution of grains in the rock, and on the ratio of the grain size of total area of the thin section (Frangipane and Schmid, 1974).

(3) Misidentification of a mineral lying under the ocular crosshair. This error may be insignificant compared to the previous sources of uncertainty (Solomon, 1963)

(4) Apparent enlargement of small grains with high refractive index (Holmes effect; Chayes, 1956).

Reproducibility tests reports by Chayes and Fairbairn (1953) indicate that, for the major minerals in a given thin section, the variation in modes determined by several observers was essentially the same as that reported on replicates from one observer. These results seem to suggest that for granitoid rocks such as those used in this study, the volume percentages of the major minerals could be determined to within approximately 5% of the amount present.

### Results

Table 1 presents the mineralogical analyses for the five Peninsular Ranges rock samples. Values are in weight percent and include estimated uncer-

tainties from the difference measurements in the optical counts and from the variance error routine of the RIM. For sample WD-1, we completed an analysis by the RIM procedure using a standard "well" mount for comparison with results from the filter preparation. This column is marked W in Table 1. Although the major components agree well in quantity with those obtained from the filter sample, the higher biotite component and appearance of chlorite in the well mount results suggest the enhancement of these intensities from phyllosilicate particle orientation in the well mount.

Table 2 presents the physical parameters required for the analysis and includes the source information from which average compositions of the oxides of the mineral components were obtained and used for

oxide reduction. In addition to the X-ray diffraction and polarizing optical analyses, atomic absorption and X-ray fluorescence analyses were available or completed for the samples during the study. Therefore, a direct comparison of the oxide reduction for both optical and X-ray analyses can be made with the elemental analyses (also converted to oxides) obtained from X-ray fluorescence and atomic absorption. These reductions and analyses are given in Table 3.

Table 4 presents the mass absorption coefficient data as measured directly from the loaded filters and as calculated from the optical, X-ray, and chemical analysis procedures.

In first examining Table 1, we note excellent agreement between the values for components of

Table 2. Physical constants required for reference intensity analysis

Component	hkl	$k_i^{\Delta}$	$\mu_i^*$	Composition for Oxide Reduction**
Quartz	101	2.84	34.9	Pure SiO <sub>2</sub>
Oligoclase	†	1.55	38.1	IV; 14; 1-14
Andesine	†	1.65	42.2	IV; 15; 1-14
Labradorite	†	1.68	45.9	IV; 16; 1-14
Bytownite	†	1.71	49.2	IV; 17; 1-15
Microcline	$\bar{2}02 + \bar{2}20$	0.28	41.3	IV; 5; 9-16
Biotite <sup>‡</sup>	001	1.47	88.9	III; 12; 1-7, 9, 11, 12, 14
Biotite	001	2.43	96.5	
Muscovite	002	0.27	45.4	II; 5; 12-15
Hornblende <sup>‡</sup>	110	0.80	77.8	II; 40; 17, 19, 20, 24-27, 29, 36, 38
Hornblende	110	0.67	87.9	
Edenitic Hornblende	--	--	59.1	II; 41; 3
Diopside	$\bar{2}21$	1.05 <sup>††</sup>	68.0	II; 5; 10, 12, 13, 16-24
Enstatite	310	0.84 <sup>††</sup>	45.6	II; 2; 1-5
Augite	$\bar{2}21$	1.14 <sup>††</sup>	78.6	II; 17; 15
Olivine	112	1.29 <sup>††</sup>	63.5	I; 2; 10
Magnetite	311	2.62	232.0	V; 12; 1-3, 5, 6
Chlorite	002	0.46	65.3	III; 25; 1-3, 12-20, 24-30
Spinel	--	--	31.2	V; 11; 1
Sphene	--	--	98.9	I; 12; 2-7

<sup>Δ</sup>Relative to Al<sub>2</sub>O<sub>3</sub>-113 standard (Linde 600 mesh).

\*\*Volume; Table; Sample Number -- Deer *et al.* (1963).

<sup>†</sup>All peaks between  $d=3.19$  and  $d=3.24$  Å are included in the reference intensity constant for the plagioclase feldspars. These include  $\bar{2}02$ ,  $\bar{2}20$ , 040, and 002 for most species [see Goodyear and Duffin (1954), Borg and Smith (1969)].

<sup>‡</sup>Determined from mineral separation of LQD and MQD samples.

<sup>††</sup>Calculated from data of Borg and Smith (1969).

Table 3. Analyses† expressed as oxides (weight percent)

Oxide	LQD			MQD			WD-1			WD-2			WD-113		
	Optic	X-ray	XRF	Optic	X-ray	XRF	Optic	X-ray	XRF	Optic	X-ray	XRF	Optic	X-ray	AAS
SiO <sub>2</sub>	68.0	66.9	68.6	55.1	54.3	52.7	74.7	73.0	72.2	64.1	59.5	56.8	47.3	44.9	43.0
Al <sub>2</sub> O <sub>3</sub>	16.3	16.2	15.7	21.5	19.3	16.2	13.4	13.2	14.6	16.9	21.3	20.2	12.9	11.5	16.5
Na <sub>2</sub> O	5.6	4.7	4.3	4.0	2.8	3.1	3.8	3.2	4.0	5.9	3.1	6.5	1.5	1.0	1.0
K <sub>2</sub> O	1.1	1.2	1.3	0.5	0.8	0.7	3.4	3.4	4.2	1.5	1.1	2.2	0.1	0.4	0.05
CaO	2.7	3.8	4.3	10.2	11.4	8.3	1.7	2.9	2.0	3.2	8.8	4.6	7.6	9.6	13.3
FeO	1.0	3.6	} 3.2*	2.5	4.3	} 10.6*	1.0	1.2	} 1.6*	3.6	3.1	} 5.7*	5.0	10.4	} 8.4 <sup>Δ</sup> *
Fe <sub>2</sub> O <sub>3</sub>	0.7	0.7		1.7	2.2		0.9	0.9		1.7	1.2		0.8	3.4	
MgO	4.0	1.9	1.0	4.6	3.9	3.6	0.4	1.3	0.5	1.7	1.7	2.0	23.5	17.4	17.0 <sup>Δ</sup>
MnO	-	0.04	0.05	-	0.1	0.2	0.01	0.02	0.05	0.6	0.1	0.2	0.1	0.2	-
TiO <sub>2</sub>	-	0.6	0.7	-	0.5	1.2	0.2	0.2	0.3	0.5	0.4	1.1	0.05	0.4	0.3
BaO	-	-	-	-	-	-	0.01	0.05	-	-	0.01	-	-	-	-
SrO	-	-	-	-	-	-	0.2	0.02	-	0.2	0.03	-	0.01	0.01	-
H <sub>2</sub> O (LOI)	0.3	0.6	(0.6)	0.1	0.5	(1.5)	0.3	0.5	-	0.6	0.5	-	0.7	1.0	-

\*Iron expressed as Fe<sub>2</sub>O<sub>3</sub>.

†Reduced from mineral compositions in "Optic" and "X-ray"; independent analyses by x-ray fluorescence spectrometry in "XRF", and by Atomic Absorption Spectroscopy in "AAS".

<sup>Δ</sup>These two values were erroneously interchanged in Table 2 of Walawender (1976) and have been corrected here.

three of the samples. For samples LQD, MQD, and WD-2, the agreement between the optical and X-ray results are well within the difference errors and variance errors listed. This agreement is not only with respect to the numerical values of the mineral types present, but with regard to the specific mineral "sub-species" determined independently by well established optical and X-ray techniques. In the X-ray analysis, trace amounts of sphene, apatite, chlorite, and spinel were not observed primarily because of the extensive coverage of the various

peaks of the plagioclase spectra throughout the scanning interval. In the cases of some of the minor components, the reference intensity used was not the value given in Table 2, which is based on the strongest peak of the pattern, but rather one based on a peak of lesser magnitude, the reference intensity value of which was scaled down from a knowledge of the relative calculated or observed intensities of the pure component spectrum. Magnetite is an example where interference by plagioclase peaks was extensive, and in the case of W-113 correction due to the overlapping plagioclase peak was made based on the calculated intensities given for bytownite by Borg and Smith (1969). In the optical analysis, magnetite, ilmenite, and other metallic oxides or sulphides were simply listed as "opaques".

The computation procedure used in the IAS laboratory (on a CDC Cyber 170) includes reduction of all mineralogical components to oxides based on average compositions of these components obtained from the tabulated analyses given in Deer *et al.* (1963). This results in what may be termed a "probably" oxide analysis. For the oxide reductions of Table 3, no modification of the composition files in the computer was completed as an attempt to adjust for unusual amphibole or pyroxene com-

Table 4. Measured and calculated mass absorption coefficients\*

Sample	Measured	Calculated		Chemical Analysis
		Optical	X-ray	
LQD	43.6	46.3	46.4	45.8
MQD	58.5	56.2	58.8	63.4
WD-1	44.1	41.2	42.9	43.1
WD-2	53.0	49.6	52.0	52.4
W-113	67.2	53.4	72.6	62.2

\*Units of cm<sup>2</sup> gm<sup>-1</sup>, CuK $\alpha$  radiation. Calculated values obtained from elemental mass absorption coefficients.

positions. The file does separate, however, individual feldspar ranges into the six "member" classification commonly used by petrologists and mineralogists. With regard to samples LQD, MQD, and WD-2 discussed above, the comparison of the oxides also shows generally very good agreement. An exception to this is in the somewhat higher iron oxide content of the XRF analysis compared to optic and X-ray oxide reduction values for sample MQD. This anomaly is also reflected in the computed mass absorption data of Table 4. In the case of WD-2, the analysis by X-ray fluorescence shows quite good agreement with the X-ray data and reasonable agreement with the optic data. The higher silica and lower alumina content observed for the optic analysis in WD-2 is the result of classification of the feldspar as oligoclase rather than labradorite. The optic/X-ray discrepancy for this sample with regard to the plagioclase type was resolved by determination of the difference  $2\theta(1\bar{3}1)-2\theta(131)$  and use of the Smith and Yoder (1956) procedure for determination of An content. The An value thus determined for WD-2 is 32% (sodic andesine). With this reassignment the oxide analysis would move closer to that observed by the optical technique and further from agreement with the X-ray fluorescence analysis.

Agreement in the results of optic and X-ray analysis of WD-1 is generally good, with the exception of the assignment of the mica quantities. In these analyses, the  $10\text{\AA}$  spacing, similar for both biotite and muscovite, was used as the reference peak and assignment to a specific mica species is very difficult because of the weak nature of other peaks in the diffraction spectra or their masking by plagioclase. Only slight diffractometer misalignment can cause serious errors in spacing measurement in this region of  $2\theta$  and the lack of suitable internal standards in this region precludes accurate measurement. Therefore it is safer to rely on the optical data in this case. Except for this minor difference, the optic and X-ray data for WD-1 are also in good agreement as demonstrated by the mineralogical comparison and the oxide comparisons.

For samples LQD, MQD, WD-1, and WD-2, the correctness of the optic and X-ray analysis is substantiated by the mass absorption coefficient data of Table 4. Those samples containing the higher proportions of basic constituents are readily apparent in the table. Samples LQD and WD-1 are similar in this respect in their absence of significant "mafic"

constituents, whereas values for MQD and WD-2 indicate moderate iron contents (as also demonstrated in the XRF analyses, Table 3).

More serious discrepancies in analyses are obvious for sample W-113. In this analysis, measured reference intensity constants were not available for enstatite, olivine, and the specific variety of amphibole which is different from the common hornblende parameters presently in use in the RIM computer files. Consequently, the reference intensity constant for the common hornblende was used in the analysis and calculated reference intensity constants for the other two minerals were determined from the data of Borg and Smith (1969). From Table 1, we see that for W-113 the amphibole and orthopyroxene contents represent the major differences in the optic and X-ray results. Although these differences could be the result of uncertainties in the reference intensity constant assignments, it is also possible that sample inhomogeneities are responsible for the observed discrepancies. Large oikocrystic amphiboles, which are common in this rock unit (Walawender, 1976), may not have been incorporated into the thin section slices but were present in the remainder of the block crushed for the X-ray sample. The larger volume of rock used in the X-ray technique could thus be more representative of the actual modal proportions.

### Conclusions

Remarkably good agreement between the traditional optical point count analysis and X-ray diffraction quantitative analysis by means of the reference intensity method is demonstrated in the study of the granitoid rocks of the Peninsular Ranges batholith. The best agreement is noted for those samples for which measured reference intensity constants have been obtained by the aerosol suspension technique, and poorer agreement is observed where such data are not available but reliance was made on calculated data. The reduction of the mineralogical analysis to oxides permits additional comparison between the two methods as well as with standard chemical analytical results. The results of this study suggest to us the need for more widespread use of the RIM procedure in quantitative analysis of rock specimens.

Successful use of the technique ordinarily requires the suspension of pulverized rock material into an aerosol and collection and analysis on special filter substrates. Exceptions to this requirement might be those materials not containing signif-



ificant amounts of micas, carbonates, or other components subject to strong preferred orientation. The filter-sample preparation procedure is very simple and requires no elaborate laboratory apparatus. The X-ray scanning can be accomplished on any powder diffractometer and with the additional X-ray transmission measurements provides a means for analysis of both crystalline and amorphous components. These studies have demonstrated that with the use of good reference intensity constants, uncertainties on the order of only a few percent may be associated with the analyses for even minor components. Much larger errors are possible, however, when analyzing coarse- or uneven-grained rocks and when using calculated reference intensity constants, especially for those minerals showing extensive solid solution properties.

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