A method for quantitative mineralogical analysis by X-ray powder diffraction.

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Summary. A method of quantitative analysis by photometry of X-ray powder diffraction patterns is described. Co-$K\alpha$ radiation is used and absorption difficulties are overcome by using thin diluted specimens containing an internal standard. An arbitrary universal intensity scale has been established and the values for the stronger lines of a number of minerals are given. Within individual patterns these are consistent with published data obtained by counter diffractometry.

X-RAY diffraction has been applied to quantitative determinations, by comparing the intensities of the diffraction maxima from an internal standard with those of the material to be determined. Both photometric (Hellman and Jackson, 1943; Jarvis, Dragsdorf, and Ellis, 1957) and counter diffractometer (Gross and Martin, 1944; Phillippe and White, 1950) methods have been used.

Many of the primary rock minerals were formed at elevated temperatures and pressures, and are not stable when exposed to the various agencies of subaerial weathering. The processes involved in their alteration to form the more stable secondary minerals characteristic of soils comprise a complex mixture of physical and chemical reactions (Keller, 1957), the course and products of which vary with a number of factors, such as the nature of the parent rock, climate, topography, and vegetation. A proper understanding of pedogenesis can only be obtained by quantitative mineralogical analysis of all stages from the parent material, through the weathering rock and subsoil layers to the most highly weathered surface horizons of the soil profiles. It is primarily with this kind of investigation in mind that the method described here has been evolved.

Apparatus and technique. A photographic technique is used with 9 cm. precision powder cameras having double-slit collimation, the slit dimensions being 4·35 × 0·27 mm. The design of the cameras is similar to that described by MacEwan (1949). Co-$K\alpha$ radiation was chosen as it is the most useful for soil minerals in general; it gives fairly large diffraction angles, an important consideration when dealing with large spacings, and, unlike the commonly used Cu-$K\alpha$ radiation, it does not give fluorescent scattering with specimens containing iron. Although Co-$K\alpha$ X-rays are strongly absorbed by dense specimens this effect can be reduced to a negligible minimum by the specimen preparation technique described below. Ilford industrial 'B' X-ray films are used and exposure times are adjusted to give an ideal density maximum of about 0·5 units, although densities up to 0·8 can be used. Film processing conditions are carefully standardized.

The photometer is a Hilger non-recording X-ray microphotometer, which has been converted to a recording unit using a Kipp drum camera. The six-volt supply for the light source of the photometer is obtained from accumulators. The response of the photocell was checked, using Ilford neutral density filters to give a series of standard steps. As the density range varies from film to film the sensitivity of the photometer is adjusted for each run so as to use the full (12 cm.) width of the recording paper. At the end of each run the levels of at least two of the standard steps are recorded on the same chart at the same sensitivity setting, so that the density value can be found for any point on the curve. Fig. 1 shows the photometer tracing from a specimen containing aluminium and hematite in the weight ratio 1:2. The two standard steps have the density values 0·25 and 0·30.

Calibration films were obtained using a rotating lead step-sector, the blackness levels being recorded along with the series of standard steps on the same photometer charts. From these charts the film strip densities were found and plotted against a linear time of exposure scale. This calibration curve was chosen in preference to a logarithmic one as it is more accurate at low density levels. This is especially true for the soft Co-$K\alpha$ radiation, which is appreciably absorbed in the film base between the two emulsions and in the emulsions themselves, so that the inner emulsion layer reaches its critical density level before the outer, and the curve for the combined densities has two discontinuities. Another advantage of using low density levels is that exposure times are reduced. In practice, suitable densities are obtained by giving the same exposure as would be used to get photographs suitable for visual inspection on the faster Ilford 'G' films.

The cylindrical specimens have a diameter of 0·125 mm. and are prepared by rolling the sample, mixed with an internal standard and a little 'Durofix' adhesive as a binder, between two glass plates as described by MacEwan (1949). This small specimen of concentrated material still has appreciable absorption effects, but these are greatly reduced when two parts by weight of powdered gum arabic are mixed with the sample before making the specimen. This dilution by a light amorphous material gives a low and almost constant absorption value to all specimens. Dilution with 66 % by weight of gum corresponds to about 80 % by volume (for samples with the specific gravity of quartz), and this large volume dilution has an incidental advantage in greatly reducing the amount of preferred orientation that occurs on making rolled specimens from samples containing platy or rod-shaped minerals. It is very important that the sample, the standard material, and the gum should be thoroughly mixed together and finely ground. Brindley (1945) considers theoretically the influence of particle size on the diffraction intensities from mixed powders, and shows that for any component it appears at a particle size depending on the absorption coefficient of that component, and that furthermore the effect of particle size on the relative intensities from two components is proportional to the difference between their absorption coefficients. Since the amount of sample material contained in the irradiated part of the specimen in this method is very small—about 0·2 mg.—results will be representative of the whole sample only if sampling errors are avoided.

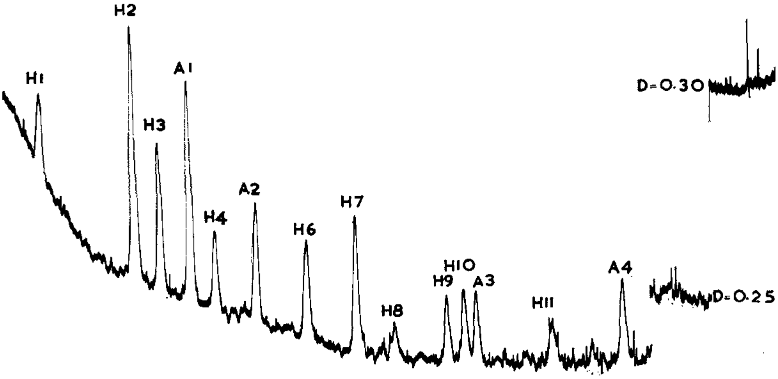

FIG. 1. Photometer record of the diffraction pattern from a mixture of hematite and aluminium in the weight-ratio 1:2. The peaks are numbered to correspond with table I.

Universal intensity scale. In order to make the method applicable to routine determinations, an arbitrary universal scale of intensity has been set up using potassium chloride as the primary internal standard. The value of the 200 reflection has been taken as 1000 and the other powder lines have been given corresponding values obtained from the means of measurements from a number of films from different specimens prepared in the standard way (see table I). Using the same techniques with standard mixtures of potassium chloride and various pure minerals, the intensities of the diffraction lines of these minerals have been put on the same scale.

As potassium chloride is water soluble, very small amounts can be measured accurately by adding the required amount of a dilute solution of the chloride to the sample, which is then dried and reground. This method gives a very intimate mixture. A water-soluble standard, however, has the disadvantage that its particle size tends to increase by recrystallization in the presence of traces of moisture, giving spotty diffraction lines. After the final grinding it is therefore essential to keep the sample and specimen dry. It was found, for example, that when finely ground potassium chloride was added to air-dry montmorillonite spotty lines were obtained, but if the clay was dried at 300° C. before mixing with the salt, the diffraction pattern showed smooth lines. Another difficulty with potassium chloride is the possibility of chemical reactions occurring with the sample. For example, ammonium salts or ammonium-saturated clay minerals will react to give ammonium chloride at the expense of some of the potassium chloride. It was found experimentally that these and similar reactions may occur at room temperatures in the presence of hygroscopic moisture, or on heating oven-dry material to 500–600° C. Since heating to these temperatures is a standard treatment in the identification of some minerals it is important that any internal standard present should be unaffected, so that changes in the relative densities of the diffraction lines can be detected. In practice, therefore, potassium chloride is frequently not the most suitable material to use, but it is a convenient reference against which other possible standards can be calibrated. The actual choice of a standard for any particular determination may depend on a number of considerations such as the position and distribution of the diffraction lines, solubility in water or other liquids, chemical reactivity, hardness, or thermal stability.

The properties of corundum make it a convenient standard in many cases. It has been found useful in the determination of crystalline compounds in dried plant leaves, where its presence helped in the grinding of the soft material. It frequently happens that the amount of material available for analysis is small, and the ideal amount of internal standard necessary may be very small. For these cases a mixture of 10% corundum in powdered gum arabic has been prepared, and small amounts of corundum can be obtained by weighing out suitable amounts of the mixture. Powdered aluminium has also been used as a standard (Brindley and Ridley, 1938).

Most of the internal standards used belong to the cubic system, and have therefore the advantage of giving diffraction patterns with few and intense lines. This means that the chances of line coincidence with the patterns of other materials in mixtures are reduced, and also that, to give lines of suitable density, relatively small amounts of internal standard are necessary.

Table I gives the intensity scale values and interplanar spacings for a number of common minerals and possible standards. The figures are all based on peak-height measurements, which have been found reliable for all well crystallized materials of suitable particle size.

In theory, any two uncontaminated lines, one from the standard and one from the material to be determined, should be sufficient; but it is preferable to measure a few of the strong lines of each pattern. The amount of the unknown is found from the equation:

$$x = 100aI_sI_{xm}/sI_xI_{sm},$$

where x = percentage of unknown, s = weight of sample used, a = weight of internal standard added, I_x = universal scale intensity of line of unknown, I_{xm} = measured intensity of line of unknown, I_s = universal scale intensity of line of standard, and I_{sm} = measured intensity of line of standard.

The accuracy of the method is dependent on a number of variable factors: the number of components in the mixture, the absolute intensity of the diffraction patterns of the components, the level and uniformity of the film background, particle size and shape, &c. In simple mixtures minerals like quartz and hematite can be determined within about 5 % (table II). For minerals with variable chemical composition such as feldspars or chlorites in which the relative intensities of the powder lines vary, errors may arise through the use of the wrong intensity scale values. It may be possible, however, to use the measured intensity values to identify such minerals if data are available for a series of pure members of known composition. Fig. 2 shows the variation in intensity for the strongest line (3·17–3·23 Å.) of four plagioclase feldspars with composition.

For many purposes only an approximate estimate of the composition of mixtures is required and this can be obtained by visual inspection of films. The accuracy of such visual estimations can be greatly improved

TABLE I. Universal Intensity Scale.

	Potassium chloride		*Aluminium*		*Corundum**		*Quartz*		*Calcite*	
	d, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*
1	3·14	1000	2·33	870	3·47	145	4·26	150	3·86	55
2	2·22	655	2·03	430	2·55	225	3·34	895	3·04	695
3	1·82	210	1·43	270	2·38	105	2·46	90	2·49	85
4	1·57	95	1·22	290	2·08	240	2·28	70	2·28	140
5	1·40	230	1·17	90	1·74	130	2·23	40	2·10	120
6	1·28	155	1·01	55	1·60	275	2·12	50	1·91	185
7	1·11	45			1·51	15	1·98	35	1·87	165
8	1·05	110			1·40	80	1·82	130	1·60	65
9	0·99	85			1·37	155	1·67	45	1·52	50
10	0·95	75			1·24	40	1·54	110	1·44	50
11					1·19	15	1·37	115	1·18	35
12							1·26	40	1·15	45

	Hematite		*Goethite*		*Lepidocrocite*		*Gibbsite*		*Kaolinite*	
	d. Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*
1	3·67	145	4·96	80	6·25	660	4·83	620	7·15	120
2	2·69	540	4·17	450	3·28	420	4·35	120	4·45	50†
3	2·51	290	3·36	65	2·79	90	3·30	30	4·35	60†
4	2·20	150	2·68	265	2·47	245	2·45	60	4·17	60†
5	2·07	40	2·56	80	2·08	45	2·38	50	3·57	130
6	1·83	185	2·47	115	1·93	220	2·16	30	2·55	45
7	1·69	265	2·44	355	1·84	65	2·04	40	2·49	40
8	1·59	60	2·23	100	1·73	75	1·99	30	2·37	20
9	1·48	140	2·18	180	1·53	40	1·91	30	2·33	50
10	1·45	145	1·71	195	1·52	90	1·80	25	2·28	30
11	1·31	85	1·55	150	1·49	35	1·75	30	1·66	25
12	1·25	30	1·50	85	1·45	50	1·69	25	1·49	35

	Pennine		*Pennine* 600° *C.*		*Microcline*		*Oligoclase*		*Labradorite*	
	d, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*. Å.	*I*
1	14·5	75	14·2	250	4·22	70	4·19	110	4·05	135
2	7·14	135	7·10	25	3·99	35	3·87	75	3·88	25
3	4·78	105	3·54	25	3·76	40	3·77	115	3·77	120
4	4·60	30	2·81	60	3·68	35	3·20	530	3·66	85
5	3·58	105	2·67	30	3·49	75	2·99	50	3·37	60
6	2·86	35	2·60	15	3·37	65	2·93	115	3·20	480
7	2·59	45	2·55	15	3·25	320	2·85	55	3·01	55
8	2·55	70	2·45	50	3·03	50	2·55	40	2·94	95
9	2·45	50	2·24	20	2·96	90	2·10	35	2.84	50
10	2·38	25	1·88	10	2·91	85	1·83	60	2·53	90
11	1·58	30	1·71	10	2·16	60	1·80	60	1·83	50
12	1·54	65	1·54	30	1·80	65	1·78	55	1·77	60

* These corundum intensities may be too low as the material was prepared by igniting synthetic gibbsite, and complete recrystallization may not have occurred.

† Doubtful values from broad overlapping lines.

if the true relative intensities of the powder lines are known. In general it is usually simple to decide by visual observation whether one powder line on a photograph is stronger or weaker than another, but it is very difficult to say by how much. When the two lines compared have equal intensities the term I_{xm}/I_{sm} in the above equation becomes unity and the

TABLE II. Analysis of synthetic mixtures using aluminium as internal standard, from means of measurements of lines on both sides of one film for each mixture.

	Quartz.	*Hematite.*	*Goethite.*
Weight % in mixtures	33·33	33·33	50·00
Number of powder lines used	5	6	6
Means of determinations %	36·9	34·8	53·2
Standard deviation	1·7	2·1	3·7

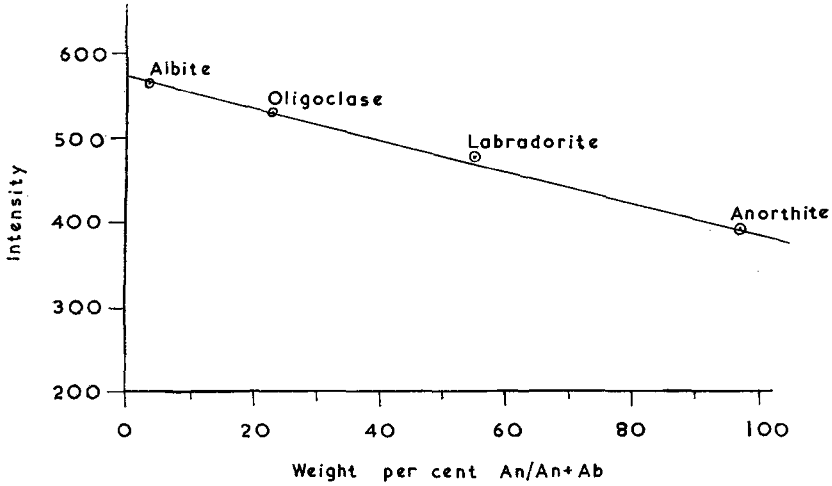

FIG. 2. The variation with composition of the intensities of the strongest lines (3·17 to 3·23 Å.) of plagioclase feldspars.

amount of the unknown can be calculated directly from the universal scale figures. For example, if the amount of quartz in a sample is to be estimated, a mixture can be made of two parts of sample to one of corundum along with six parts of gum arabic. Then, in the powder photograph of a specimen prepared by the standard procedure, by comparing the third corundum line with the third quartz line (as numbered in table I) one can tell if the amount of quartz is greater or less than $(50 \times 105)/90 = 58$ %. Similarly, by comparing the first quartz line with the first corundum line, and the eighth quartz line with the eighth corundum line, values are obtained above or below 48 % or 31 % respectively. There is a danger in the visual method that coincident lines may unwittingly be used, but these can readily be detected on photometer curves as they will give relatively high values compared with the other lines of the same component.

The relative intensities of the diffraction lines of single compounds found by the method described here are consistent with the counter data in the American Society for Testing Materials powder diffraction data cards. Hanawalt, Rinn, and Frevel (1938) also obtained values similar to more recent counter data. Their intensities were obtained by visual comparison of the lines with a series of calibration film strips; and Mo-$K\alpha$ radiation was used so that absorption effects would be small.

The method described here has been widely applied to analyses of clay, silt and sand fractions of soils, rock and mineral specimens, fertilizers, &c., and universal scale intensity data are gradually accumulating. If a universal intensity scale could be generally adopted in the publication of X-ray powder diffraction data, it would be possible to use such information for approximate quantitative analysis, without the necessity of obtaining pure samples and preparing special calibration mixtures.

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