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## Analytical Edition

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### Chemical Analysis by Powder Diffraction

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This paper cites examples of use of the powder diffraction method in the chemical identification of solids, and discusses some of the general difficulties that may be encountered in its use.

In THE past ten years the powder diffraction method has been used to an increasing extent in the chemical identification of solids (4, 5, 9, 12, 13, 16, 24, 26, 30, 34, 46, 47, 59, 60, 62). The utility of the method resides in its ability to detect the state of chemical combination for each crystalline component in a mixture (30). The present paper cites a few typical examples and discusses some of the general difficulties that may be encountered in this physical method of chemical analysis.

Identification of boiler deposits is a general problem that is conveniently handled by the powder method. A particular scale submitted for identification was examined by chemical analysis, by microscopic examination, and by powder diffraction. Table I lists the data ascertained by each method.

The information obtained by the diffraction method is of evident value to the chemist interested in selecting the correct treatment for the removal of scale or in devising methods to diminish scaling. The manner in which the diffraction data are conveniently compared with published powder data is illustrated in Table II.

Other typical problems solved by the diffraction method are: the identification of corrosion products, the constitution of fluxes, the detection of pigments or fillers in plastics or elastomers, the analysis of minerals, the recognition of allotropic modifications, and the study of chemical reactions in the solid state.

As illustrated in Table II, chemical analysis by the powder method consists of matching the diffraction pattern of an unknown material with one or more standard powder patterns. This requires (1) a correct registration and measurement of the diffraction lines and (2) a careful interpretation and evaluation of these data as applied to chemical analysis. The first part of the problem has received considerable attention in the literature and only a few points require enumeration. The second part, however, has not been treated extensively in previous publications and deserves detailed discussion.

#### COMPLICATIONS IN REGISTRATION OF POWDER DIFFRACTION PATTERNS

ABSORPTION EDGES. In view of the fact that most x-ray diffraction work is being done with filtered radiation, characteristic

Table I. Data on Boiler Scale

	Chemical Analysis	Microscopic Analysis	Powder Diffraction Analysis
	%		%
Fe	28.32	Black shiny powder,	~40 Fe <sub>2</sub> O <sub>3</sub>
Ca	22.30	heterogeneous; particles too small for refractive index measurements	~30 CaCO <sub>3</sub> , calcite
S	6.21		~30 CaSO <sub>4</sub>
CO <sub>2</sub> --	22.10		
Ignition loss	15.70		
		Advantages	
		Accurate quantitative data, method of analysis independent of state of aggregation of sample	High sensitivity for detecting minor phases, morphological details readily ascertainable (29)
			Direct identification of compounds, nondestructive method applicable to extremely fine powders

Table II. Powder Diffraction Data on Boiler Scale

Filtered MoK $\alpha$  radiation used to obtain powder diffraction patterns.  $d$  = interplanar spacing measured in Å.  $I$  = peak intensity of a diffraction line as estimated with a direct comparison intensity scale (arbitrary units).  $I/I_1$  = relative intensity of a diffraction line, where  $I_1$  is intensity of strongest line of particular phase in question. Most representative value for  $I_1$  of phase 1 is taken as 33 and is obtained by multiplying intensities of six unambiguous reflections (4.83, 2.95, 2.41, 1.705, 0.967, 0.855 Å) by corresponding relative intensities of Fe<sub>2</sub>O<sub>3</sub> and taking arithmetic mean of computed values of  $I_1$  (36, 55, 37, 22, 25, 20). The average value for the strongest line of phase 2 is 22; for phase 3 it is 38.

Spectroscopic analysis of scale: Fe, Ca, chief constituents; Co, Mo, Cu, Na, 0.001 to 0.01%.

Boiler Scale	Fe <sub>2</sub> O <sub>3</sub>	Phase 1	CaSO <sub>4</sub>	Phase 2	CaCO <sub>3</sub>	Phase 3	
$d$ , Å.	$I$	$d$ , Å.	$I/I_1$	$I/I_1$	$d$ , Å.	$I/I_1$	$I/I_1$
5.80	1	4.85	0.06	0.09	..	..	..
4.83	3	..	..	..	..	..	..
3.87	4	..	..	..	3.89	0.03	(1)
3.49	25	..	..	..	3.49	1.00	1.14
3.03	30	..	..	..	..	..	3.04
2.95	10	2.97	0.28	0.30	..	..	1.00
2.84	15	..	..	..	2.85	0.67	0.68
2.52	75	2.53	1.00	(33)	..	..	..
2.41	6	2.42	0.11	0.18	..	..	..
2.33	8	..	..	..	2.32	0.33	0.36
2.27	10	..	..	..	2.26	0.01	(0.2)
2.21	8	..	..	..	2.20	0.33	0.36
2.08	30	2.10	0.32	(11)	2.08	0.11	(2)
1.99	1	..	..	..	1.99	0.11	(2)
1.91	10	..	..	..	1.93	0.04	(1)
1.865	12.5	..	..	..	1.86	0.27	(6)
1.745	4	..	..	..	1.74	0.20	0.18
1.705	6	1.71	0.16	0.18	..	..	..
1.640	4	..	..	..	1.64	0.27	0.18
1.606	20	1.61	0.64	(21)	1.59	0.03	(1)
1.560	1	..	..	..	1.56	0.05	0.05
1.518	6	..	..	..	1.52	0.07	(2)
1.480	30	1.483	0.80	(26)	1.487	0.08	(2)
1.439	4	..	..	..	..	..	1.439
1.420	1	..	..	..	1.420	0.08	(2)
1.320	2	1.326	0.06	(2)	1.318	0.09	(2)
1.278	6	1.279	0.20	(7)	1.275	0.09	(2)
1.210	2	1.210	0.05	(2)	1.215	0.05	(1)
1.150	2	..	..	..	..	..	1.150
1.120	2	1.121	0.10	0.06	..	..	..
1.090	7	1.092	0.32	0.21	..	..	..
1.047	6	1.049	0.10	(3)	..	..	1.045
1.010	2	..	..	..	..	..	1.011
0.967	4	0.970	0.16	0.12	..	..	..
0.938	2	0.940	0.06	0.06	..	..	..
0.879	2	0.880	0.10	0.06	..	..	..
0.855	4	0.859	0.20	0.12	..	..	..
0.850	1	0.853	0.08	0.03	..	..	..
0.810	1	0.814	0.10	0.03	..	..	..

Table III. Preparation of Powder Specimens

Method of Preparing Powder Specimen	Precautions to Be Observed				
	Abrasion contamination	Mechanical strain	Volatilization	Phase decomposition	
Grinding or filing	Influence of atmosphere ( $H_2O$ , $O_2$ , $CO_2$ , dust.) Grind and load sample in a drying box flushed with purified dry $N_2$ ; or grind sample under dry benzene and load wet powder into a thin-walled glass capillary (31, 63)	Grind hard nonferrous materials in an agate mortar. (Micromicronizer may be useful in the pulverization of abrasives.) Remove metallic iron contamination from steel mortar by magnetic methods	Vacuum-anneal metallic filings at suitable temperature (31)	Grind sample containing sublimable substances in a small closed system or in an equilibrium atmosphere [ $NH_4HCO_3$ , $(NH_4)_2CO_3$ , $NH_4OCO-NH_2$ , $NH_4N_2$ , $NH_4CN$ , $NH_4SH$ , etc.; ammonates or alcoholates may lose $NH_3$ or $ROH$ on grinding]	(Supersaturated solid solutions, quenched alloys, pressure-sensitive substances such as wurtzite or brookite chemical reaction in solid state (14, 68). For alloys a structure-integrating camera of micro design may be adaptable)
Precipitation or crystallization	Coprecipitation or co-crystallization Make qualitative spectroscopic analysis and spot tests on washed precipitate	Oxidation Load precipitate in wet condition—e.g., pyrophoric catalysts such as Raney nickel	Solvation Vacuum-dry washed precipitate	.....	.....
Condensation, electrodeposition, or sputtering	Preferred orientation Check condensed film for preferred orientation of crystallites by taking exposures at various inclinations	Oxidation (Adsorbed $O_2$ , $H_2O$ , etc., on substrate)	.....	.....	.....

Table IV. Powder Diffraction Pattern of Magnesium Oxide

(hkl)	$d_{\text{obs}}$	$d_{\text{calcd.}}$	$(I/I_0)_{\text{obs.}}$	$(I/I_0)_{\text{calcd.}}$
111	2.425	2.428	0.08	0.08
200	2.103	2.103	1.00 (50)	1.00
220	1.487	1.487	0.50 (25)	0.55
311	1.268	1.268	0.04	0.06
222	(1.216)	1.214	0.12 (6B)	0.15
400	(1.053)	1.052	0.04 B	0.06
381	(0.9681)	0.9649	0.01 B	0.03
420 $\alpha_1$	0.9405	0.9405	....	..
420 $\alpha_2$	0.9404	0.9405	....	..
422 $\alpha_1$	0.8583	0.8585	....	..
422 $\alpha_2$	0.8587	0.8585	....	..

Type B1;  $a = 4.206 \pm 0.001 \text{ \AA}$ . (25° ± 3° C.)

EXPOSURE. Filtered MoK $\alpha$  radiation; camera radius, 20.477 ± 0.010 cm., calibrated with spectroscopically pure Mg ( $a = 3.2026 \text{ \AA}$ ,  $c = 5.1998 \text{ \AA}$  at 25° C.); slit dimensions, 0.2 × 5 × 50 mm.; specimen radius, 0.2 mm.; duplex film without intensifying screen.

PREPARATION OF MgO. Sublimed magnesium metal, spectroscopically pure, was dissolved in ≈ 10% HCl (c.p. grade distilled). Magnesium hydroxide was precipitated by dropwise addition of freshly prepared c.p. ammonium hydroxide. The precipitate was washed twice by decantation, followed by filtration and washing. The wet hydroxide was transferred to a clean ignited sillimanite crucible and vacuum-dried over Mg(ClO<sub>4</sub>)<sub>2</sub>. The Mg(OH)<sub>2</sub> was then converted to MgO by heating to 890° C. for 1 hour in an oxygen atmosphere free of carbon dioxide.

CHEMICAL ANALYSIS. % Mg = 60.22 ± 0.05 (pyrophosphate method); calcd. % Mg = 60.32.

SPECTROSCOPIC ANALYSIS FOR IMPURITIES. Si 0.01 to 0.1%, Al 0.005 to 0.05%, B 0.001 to 0.005%, Cu 0.001 to 0.005%.

PARTICLE SIZE DISTRIBUTION. Electron microscope, 200 to 1200 Å; average diameter 650 Å, very uniform; particles are not of regular shape, though crystalline in character; general tendency is for platelike particles ~200 Å thick (see Figure 1).

x-ray absorption manifests itself in four ways: (1) in the silver bromide emulsion ( $AgK_\alpha = 0.4845 \text{ \AA}$ ,  $BrK_\alpha = 0.9181 \text{ \AA}$ ); (2) in the filter (17) ( $ZrK_\alpha = 0.6874 \text{ \AA}$ ,  $NiK_\alpha = 1.484 \text{ \AA}$ ); (3) in the specimen containing elements, the characteristic absorption edges of which fall within the transmitted background radiation; and (4) in the tungsten contamination of the target ( $WL_1 = 1.022 \text{ \AA}$ ) (2). There also exists the possibility that the zinc edge (1.281 Å) may introduce a discontinuity in the response of fluorazure intensifying screens. For powder diffraction work these effects are observed only for the more intense reflections. For example, using a sealed-off Mo tube operated at 35 kv., one finds that the intense (111) reflection of cubic silver iodide produces one spectrum toward the longer wave-length end of AgK $\alpha$  and another corresponding to IK $\alpha$ . In the case of silver phosphate the intense portion of the continuous spectrum from (210) is slightly stronger than the (220) MoK $\alpha$  reflection. For powder patterns the sharpness of the edge of the transmitted spectrum is often blurred; consequently care must be exercised in distinguishing these edges from weak K $\alpha$  reflections.

FLUORESCENCE. Fluorescence excited in the sample by primary K $\alpha$  radiation is readily detected by a general enhancement of the background and a corresponding decline in the prominence of the desired diffraction pattern. Using MoK $\alpha$  radiation for specimens containing yttrium, strontium, rubidium, bromine, or selenium, one obtains relatively weak diffraction patterns with high background. For example, carbon tetrabromide gives an

extremely poor powder pattern with MoK $\alpha$  but a normal intense pattern with CuK $\alpha$ . Specimens containing elements of high atomic number—e.g., gold, mercury, thallium, lead, bismuth—show L-fluorescence with MoK. These fluorescence considerations apply not only to filtered K $\alpha$  radiation but also to crystal-monochromatized x-rays. In the case of filtered x-rays, the distribution of the continuous radiation may noticeably affect fluorescence. Thus if a zirconium oxide screen is placed in front of the film to filter the diffracted MoK radiation, the resultant diffraction pattern from a molybdenum specimen has a background 3.5 times as high as in the case when the filter is placed in front of the slit system. For general routine analysis by powder diffraction, two sources of K $\alpha$  radiation—e.g., MoK $\alpha$  and CuK $\alpha$ —are usually adequate to avoid serious cases of fluorescence.

RESOLUTION. The geometrical factors deciding the resolution of a Debye-Scherrer-Hull pattern are:  $R$ , radius of the camera;  $r$ , radius of the powder specimen;  $h$ , length of the specimen;  $\delta$ , divergence of the impinging x-ray beam; and  $\sigma$ , difference in wave length of the K $\alpha$  doublet. For a fixed camera radius the optimum resolution corresponds to the limiting condition:  $r$ ,  $h$ ,  $\delta$ ,  $\sigma \rightarrow 0$ . In general, however, the hardness of the primary radiation used and the time required for the registration of a good diffraction pattern are the limiting factors in the design of a suitable camera.

The geometrical resolution for a camera of radius  $R$  can be expressed approximately as the sum of  $\delta$ , the divergence of the diffracted beam due to the divergence or convergence of the impinging primary beam, and  $\omega_{r,h}$ , the angular spread of the diffracted beam due to the dimensions of the powder specimen ( $\omega_{r,h} = \frac{2r}{R}$  radian, for parallel x-rays) (8, 32, 41). Accordingly, two powder reflections  $d$  and  $(d + \Delta d)$  will be resolved if

$$(\Theta_{\alpha_2} - \Theta_{\alpha_1})_d < (\Theta_d - \Theta_{d+\Delta d})_a > (\delta + \omega_{r,h})_e$$

where  $\Theta$  is the Bragg angle for the interplanar spacing,  $d$ , and  $\alpha$  denotes the wave length under consideration (33). For example, with MoK $\alpha_1$  radiation the two powder reflections corresponding to 2.260 Å and 2.274 Å will be separated by 3.4', which interval is equal to the MoK $\alpha$  doublet separation,  $(\Theta_{\alpha_2} - \Theta_{\alpha_1})_{2.26}$ . Evidently the use of very narrow slits does not aid greatly in the resolution of a noncubic powder pattern because of the disturbing doublet separation. (The utility and precision of powder diffraction work would be greatly enhanced if an intense source of strictly monochromatic WL $\alpha_1$  could be made available for precision-focusing cameras). Convenient standards for testing and calibrating powder cameras are 200-mesh powders of the following substances: pure fused magnesium oxide, pure crystallized silicon, annealed 99.9% molybdenum metal, c.p. thallous chloride, and indium sesquioxide prepared by the direct oxidation of 99.95% indium metal.

ABSORPTION. The intensity distribution of a powder diffraction line is markedly influenced by absorption in the powder

Table V. Ambiguities Arising from Solid Solution or Isomorphism

Diffraction patterns taken with filtered MoK $\alpha$  radiation.  $d$  = interplanar spacing;  $I/I_1$  = relative intensity

Substance	$d, \text{\AA}$	2.85	2.47	1.74	1.490	1.428	1.134	1.105								
Pb	$I/I_1$	1.00	0.50	0.50	0.50	0.17	0.17	0.17								
85Pb.15Na	$d, \text{\AA}$	2.85	2.47	1.74	1.487	1.424	1.131	1.102								
	$I/I_1$	1.00	0.37	0.20	0.31	0.07	0.07	0.07								
	Examples: In, In-Ag; Mg, Mg-In; Pd, Pd-Ag; Fe, Fe-Cr															
Ag	$d, \text{\AA}$	2.36	2.04	1.445	1.232	1.179	1.022									
	$I/I_1$	1.00	0.53	0.27	0.53	0.05	0.01									
Au	$d, \text{\AA}$	2.35	2.03	1.440	1.227	1.173	1.019									
	$I/I_1$	1.00	0.53	0.33	0.40	0.09	0.03									
	Examples: Co, Ni; Cr, Fe; Pd, Pt; Rh, Ir; Mo, W; Cb, Ta															
CuCl	$d, \text{\AA}$	3.12	2.70	1.91	1.63	1.353	1.240	1.104								
	$I/I_1$	1.00	0.08	0.60	0.30	0.06	0.08	0.06								
$\beta$ -ZnS	$d, \text{\AA}$	3.12	2.69	1.91	1.63	1.353	1.242	1.104								
	$I/I_1$	1.00	0.05	0.75	0.50	0.05	0.18	0.15								
	Examples: NaBr, PbS; NaCl, Ag(Cl, Br); KCN, RbCl; Mg <sub>2</sub> Sn, Mg <sub>2</sub> Pb; Fe <sub>2</sub> O <sub>3</sub> , NiMn <sub>2</sub> O <sub>4</sub> , ZnFe <sub>2</sub> O <sub>4</sub> ; Er <sub>2</sub> O <sub>3</sub> , Y <sub>2</sub> O <sub>3</sub>															
ZnF <sub>2</sub>	$d, \text{\AA}$	3.38	2.60	2.35	2.27	2.10	1.75	1.67	1.56	1.492	1.412					
	$I/I_1$	1.00	0.80	0.06	0.20	0.05	0.80	0.20	0.08	0.11	0.32					
CoF <sub>2</sub>	$d, \text{\AA}$	3.37	2.64	..	2.30	..	1.75	1.67	1.58	1.496	1.420					
	$I/I_1$	1.00	0.86	..	0.29	..	0.86	0.29	0.14	0.14	0.14					
SnO <sub>2</sub>	$d, \text{\AA}$	3.34	2.64	2.36	2.30	2.11	1.75	1.67	1.58	1.492	1.435					
	$I/I_1$	1.00	0.63	0.18	0.03	0.02	0.63	0.10	0.05	0.10	0.10					
(NH <sub>4</sub> ) <sub>2</sub> CrO <sub>4</sub>	$d, \text{\AA}$	5.6	4.80	3.91	3.74	3.65	3.45	3.18	2.94	2.84	2.77	2.32	2.01	1.87		
	$I/I_1$	0.62	1.00	0.35	0.10	0.10	0.40	0.75	0.40	0.20	0.10	0.62	0.15	0.05		
(NH <sub>4</sub> ) <sub>2</sub> SeO <sub>4</sub>	$d, \text{\AA}$	5.5	4.80	3.89	..	..	3.45	3.17	2.95	..	2.75	2.33	1.98	1.87		
	$I/I_1$	0.60	1.00	0.40	..	..	0.40	0.80	0.40	..	0.20	0.40	0.20	0.10		
CoCl <sub>2</sub> .6H <sub>2</sub> O	$d, \text{\AA}$	5.6	4.85	3.52	3.11	2.94	2.73	2.56	2.40	2.20	2.07	2.02	1.98	1.89	1.86	1.81
	$I/I_1$	1.00	1.00	0.31	0.10	0.63	0.50	0.20	0.63	0.50	0.05	0.03	0.31	0.20	0.10	0.03
NiCl <sub>2</sub> .6H <sub>2</sub> O	$d, \text{\AA}$	5.5	4.85	3.53	3.08	2.95	2.70	2.54	2.40	2.18	2.05	2.02	1.97	1.90	1.86	1.81
	$I/I_1$	1.00	1.00	0.50	0.04	0.50	0.30	0.50	0.50	0.06	0.06	0.20	0.20	0.14	0.02	
	Examples: CoSO <sub>4</sub> .H <sub>2</sub> O(?) <sub>2</sub> , ZnSO <sub>4</sub> .H <sub>2</sub> O, NiSO <sub>4</sub> .7H <sub>2</sub> O, ZnSO <sub>4</sub> .7H <sub>2</sub> O Co(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> .6H <sub>2</sub> O, Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> .6H <sub>2</sub> O, Zn(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> .6H <sub>2</sub> O, Cu(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> .6H <sub>2</sub> O															

specimen (48, 49). With an essentially parallel x-ray beam and a suitable combination of absorption coefficient and diameter of the powder rod, the resulting diffraction lines for low values of  $\Theta$  can appear as pseudo-doublets (40). For MoK $\alpha$  radiation and a specimen radius of 0.2 mm., only the denser powders containing elements of high atomic number exhibit this effect—e.g., mercuric bromide, tungsten, bismuth, etc. Dilution with flour or reducing the specimen diameter will overcome this complication. The standard wedge technique used in many laboratories does not lead to pseudo-doublets.

**PREPARATION OF SPECIMEN.** The two most common factors influencing the quality of a powder diffraction pattern are particle size distribution and instability of the sample. The grating limitations of a powder specimen are manifested in the breadths of the resulting diffraction lines (10). Thus materials of colloidal

Table VI. Partial Ambiguities Due to Isomorphism

 $d$  = interplanar spacing;  $I/I_1$  = relative intensity. In the case of mixtures the above differences are more difficult to check

Substance	$d, \text{\AA}$	4.80	3.80	3.40	3.06	2.52	2.40	2.34	2.19	2.10	2.05	1.97	1.91
ZnSO <sub>4</sub> .H <sub>2</sub> O	$I/I_1$	0.64	0.11	1.00	0.40	0.40	0.06	0.11	0.14	0.10	0.05	0.13	0.08
MgSO <sub>4</sub> .H <sub>2</sub> O	$d, \text{\AA}$	4.82	..	3.38	3.07	2.55	2.40	2.33	2.19	2.10	2.05	1.97	1.90
	$I/I_1$	0.40	..	1.00	0.20	0.40	0.05	0.03	0.05	0.04	0.17	0.05	0.05
MgSO <sub>4</sub> .7H <sub>2</sub> O	$d, \text{\AA}$	5.9	5.3	4.50	4.22	3.76	3.41	2.96	2.87	2.74	2.66	2.48	2.38
	$I/I_1$	0.20	0.20	0.08	1.00	0.10	0.12	0.18	0.20	0.08	0.40	0.02	0.05
ZnSO <sub>4</sub> .7H <sub>2</sub> O	$d, \text{\AA}$	..	5.3	4.50	4.20	3.76	3.44	2.99	2.87	2.75	2.66	2.50	2.37
	$I/I_1$	..	0.60	0.16	1.00	0.20	0.30	0.12	0.30	0.10	0.25	0.12	0.08
Co <sub>2</sub> O <sub>4</sub>	$d, \text{\AA}$	4.68	2.86	2.43	2.34	2.02	..	..	1.65	1.56	..	1.432	1.235
	$I/I_1$	0.08	0.20	1.00	0.06	0.13	..	..	0.04	0.25	..	0.30	0.02
ZnAl <sub>2</sub> O <sub>4</sub>	$d, \text{\AA}$	..	2.85	2.44	..	2.02	1.91	1.85	1.65	1.55	1.480	1.431	1.232
	$I/I_1$	..	0.53	1.00	..	0.07	0.07	0.07	0.13	0.33	0.07	0.40	0.07
Mn <sub>2</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	$d, \text{\AA}$	2.89	2.59	2.48	2.36	2.27	2.10	2.04	1.88	1.67	1.60	1.545	1.44
	$I/I_1$	0.30	1.00	0.02	0.20	0.13	0.15	0.05	0.25	0.15	0.30	0.40	0.085
Mg <sub>2</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	$d, \text{\AA}$	2.88	2.58	2.45	2.35	2.26	2.10	2.03	1.87	1.66	1.595	1.54	1.440
	$I/I_1$	0.50	1.00	0.18	0.20	0.20	0.15	0.02	0.25	0.13	0.40	0.63	0.13
(NH <sub>4</sub> )Al(SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O	$d, \text{\AA}$	7.0	5.4	4.97	4.30	4.07	3.67	3.26	3.05	2.95	2.79	2.60	..
	$I/I_1$	0.30	0.60	0.30	0.80	0.60	0.40	1.00	0.30	0.08	0.12	0.12	..
KAl(SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O	$d, \text{\AA}$	7.0	5.4	4.96	4.29	4.05	3.65	3.24	3.03	2.93	2.78	2.58	..
	$I/I_1$	0.04	0.20	0.08	1.00	0.40	0.04	0.40	0.16	0.12	0.20	0.06	..
KCr(SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O	$d, \text{\AA}$	7.0	5.5	4.98	4.31	4.08	3.68	3.26	3.04	..	2.81	2.59	..
	$I/I_1$	0.12	0.16	0.08	1.00	0.30	0.60	0.35	0.30	..	0.12	0.06	..
K <sub>2</sub> CaFe(CN) <sub>6</sub>	$d, \text{\AA}$	6.0	5.1	4.60	3.72	3.64	3.07	2.85	2.57	2.35	2.30	2.13	2.06
	$I/I_1$	0.07	0.30	0.03	0.13	1.00	0.10	0.03	0.42	0.03	0.10	0.07	0.10
K <sub>2</sub> CuF <sub>2</sub> (CN) <sub>6</sub>	$d, \text{\AA}$	..	5.1	..	..	3.63	3.06	2.86	2.57	2.36	2.29	2.13	2.06
	$I/I_1$	..	0.38	..	..	1.00	0.20	0.08	0.75	0.15	0.31	0.25	0.63
As <sub>2</sub> O <sub>3</sub>	$d, \text{\AA}$	6.3	3.18	2.75	2.53	2.24	2.12	1.95	1.66	1.59	1.54	1.438	..
	$I/I_1$	0.56	1.00	0.24	0.32	0.08	0.16	0.24	0.16	0.08	0.16	0.08	..
Sb <sub>2</sub> As <sub>2</sub> O <sub>6</sub>	$d, \text{\AA}$	6.4	3.18	2.75	2.52	2.24	2.11	1.95	1.66	1.58	1.54	1.430	..
	$I/I_1$	0.25	1.00	0.25	0.13	0.02	0.04	0.30	0.30	0.06	0.10	0.07	..

subdivision, such as coprecipitated oxides of the spinel type, specially prepared catalysts, or clays give rather diffuse diffraction patterns that may appear insignificant in the presence of an intense sharply defined pattern. A similar situation is encountered in the field of high polymers. In order to obtain information of greater value in the case of these idiosyncrasies, the use of crystal-monochromatized radiation has been advocated by a number of diffractionists.

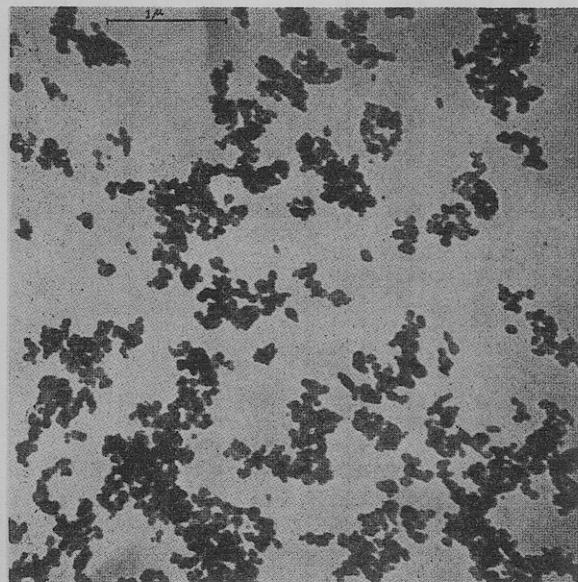


Figure 1. Electron Micrograph of Magnesium Oxide Standard

The problem of the instability of a sample usually can be overcome without serious difficulty (see Table III). Hygroscopic substances are readily powdered in a drying box and loaded into thin-walled glass capillaries that can be sealed easily. Efflorescent materials can be loaded wet (to prevent extreme crystal growth, a little amorphous material, either starch or charcoal, is admixed with the wet powder). In the case of complex organic compounds the existence of two or more allotropic modifications must be kept in mind; thus a material crystallized from a melt may give an entirely different powder pattern than the same substance crystallized from a solution. Other cases of less general occurrence are: allotropic transformation on grinding or filing (wurtzite, brookite, supersaturated solid solutions); photosensitivity ( $\text{BaN}_6 \cdot \text{P}_4$ ); and chemical interaction of the substance with glass capillaries [acid fluorides, such as  $\text{NH}_4\text{HF}_2$  to form  $(\text{NH}_4)_2\text{SiF}_6$ ]. Polystyrene capillaries, developed for the study of acid fluorides, have proved useful for powder diffraction with soft radiation such as  $\text{CuK}\alpha$  and  $\text{FeK}\alpha$ .

#### COMPLICATIONS IN METHOD OF ANALYSIS

Chemical analysis by the Debye-Scherrer-Hull method consists of matching the diffraction pattern of an unknown material with one or more standard powder patterns. When a match is found (see Table II) one infers that compounds  $A, B, C \dots$  are present in the unknown. If  $p$  denotes the powder diffraction data of the unknown material;  $p_r$ , the diffraction data of all the catalogued standard patterns; and  $\Omega'$ , the composite operation of matching the unknown with the standards  $A, B, C \dots$  one may express the mode of analysis symbolically as

$$\Omega'(p, p_r) \supset A, B, C \dots$$

The uniqueness of this inference is not evident and requires further examination.

**VALIDITY OF STANDARD PATTERNS.** It is convenient to consider first the validity of the standard patterns,  $p_r$  (4, 25, 26). From the results of x-ray diffraction analysis it is well recognized that the powder diffraction pattern of a single phase is a function of the particular crystal structure, the elements present, and the crystallite-size distribution of the powder. To be acceptable as a standard each substance should be subjected to a precise analysis to substantiate the assigned chemical formula. The method of preparation of the powder specimen should also be stated. Table IV illustrates a satisfactory presentation of a powder diffraction standard.

On examining the published tabulated powder data (4, 25, 26) one finds the labeled standards usually have not been examined for the correctness of the ascribed chemical formulas. This deficiency was realized when the first 1000 Dow standards were published (25).

The more frequent types of errors are: (1) incorrect degree of hydration [pattern 240 is  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; pattern 338,  $\text{CoSO}_4 \cdot \text{H}_2\text{O}$ ; pattern 623,  $\text{NiF}_2 \cdot 4\text{H}_2\text{O}$ ; pattern 864,  $\text{Na}_2\text{S} \cdot \text{xH}_2\text{O}$ ]; (2) chemical reaction between standard substance and water, oxygen, or carbon dioxide [pattern 193 is mixture of  $\text{CaCO}_3$ ,  $\text{Ca}(\text{OH})_2$ , and graphite (7); pattern 227,  $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$  and  $\text{Ca}(\text{OH})_2$ ; pattern 215, vaterite plus calcite]; and (3) incorrect chemical formula [pattern 13 is  $\text{Al}(\text{OH})_3$ , gibbsite; patterns 68 and 69 are largely  $(\text{Sb}, \text{As})_2\text{O}_3$ ; patterns 132 and 143 are largely  $\text{Bi}(\text{OH})_3$ ; pattern 269 refers to a mixture containing minor amount of hexamethylene tetramine]. Some errors in the diffraction data have been noted—e.g., the most intense line for  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  (pattern 409) is 5.5 Å. (40); the (020) reflection for  $\text{Na}_2\text{SO}_4 \cdot \text{III}$  (pattern 859) should read 4.47 Å.

An examination of the useful compilation of powder data on minerals (26) reveals a similar state of affairs for these tabulated standards:

Pattern 3 (alabandite,  $\text{MnS}$ ) lists in addition to the diffraction data for cubic manganese sulfide the lines 2.83 Å. and 1.995 Å. (probably  $\text{NaCl}$ ). Pattern 23 [bravoite,  $(\text{Fe}, \text{Ni})\text{S}_2$ ] gives the accepted C2 pattern plus the noncubic reflections 3.08, 2.18, 2.04, 1.86, and 1.682 Å. Pattern 35 (chromite,  $\text{FeO}\text{Cr}_2\text{O}_3$ ) does not correspond to the H1 structure for  $\text{FeCr}_2\text{O}_4$ . Pattern 37 (clausenthalite,  $\text{PbSe}$ ) lists an extraneous 2.86 Å. reflection. In pattern 39 (coloradoite,  $\text{HgTe}$ ) the strong (111) reflection is missing and the lines 2.82 Å. and 2.52 Å. appear extraneous, as does the line 2.79 Å. in pattern 95 (magnetite,  $\text{Fe}_3\text{O}_4$ ). Pattern 93 (löllingite,  $\text{FeAs}_2$ ) does not check the published data (53); the specimen used may have been an impure form of arsenopyrite. Pattern 137 (sphalerite,  $\text{ZnS}$ ) checks the B3 structure except line 3.95 Å. Pattern 143 (sylvanite,  $\text{Cu}_3\text{VS}_4$ ) omits the (220) reflection (1.90 Å.) and lists the extraneous lines 5.2, 4.15, 3.70, and 2.84 Å.

For a number of substances the innermost reflections have not been recorded: pattern 9 (argentite,  $\text{Ag}_2\text{S}$ ) should include the line 3.91 Å. (57); pattern 16 (berthierite,  $\text{FeS}\text{Sb}_2\text{S}_3$ ), 8.0, 7.2, 5.7, 5.1 Å.; pattern 66 (gersdorffite,  $\text{NiAsS}$ ), 3.99 Å.; pattern 76 (hauerite,  $\text{MnS}_2$ ), 3.52 Å.; pattern 77 (hausmannite,  $\text{Mn}_3\text{O}_4$ ), 4.92 Å.; pattern 95 (magnetite,  $\text{Fe}_3\text{O}_4$ ), 4.85 Å.; pattern 141 (stibnite,  $\text{Sb}_2\text{S}_3$ ), 8.2 Å. Pseudo-doublets due to absorption are noted in pattern 30 (cerargyrite,  $\text{AgCl}$ ), the (200) reflection; and in pattern 38 (cobaltite,  $\text{CoAsS}$ ), the (220) reflection.

While the experimental inaccuracies discussed can be remedied (the A.S.T.M. has an organization set up to issue new patterns periodically and correct old ones), there remain inherent limitations to the uniqueness of an established standard pattern. Solid solution, isomorphism, or structural similarity can contribute to the ambiguity of a standard pattern (see Tables V, VI, and VII). The absence of solid solution in an identified phase should always be checked by qualitative spectroscopic analysis and spot tests. If solid solution is indicated, a sensitive back-reflection technique is required to measure the  $d$ -shifts between standard and solid solution. Ambiguities attributed to isomorphism (see Tables V

and VI) or structural similarity (Table VII) usually are resolvable by spectroscopic analysis, spot tests, or some simple physical criterion such as solubility in water, melting point, etc. In the identification of multicomponent mixtures the intrinsic limitations illustrated in Tables V to VII become pronounced because of superposition of lines (see Tables II and XI).

The phases present in an unknown may be formed under rather haphazard or 'unequilibrated' conditions conducive to the formation of defect structures (6, 27, 51, 52). The differences between the diffraction pattern of such a defect structure and that of a normal standard may be subtle and escape the notice of the analyst. In general, structural irregularities in crystalline phases may be detected by changes in intensities of the diffraction lines (as compared to an ordered standard), by an increase of diffuse scattering, by the appearance of broad diffraction ghosts (6), by a broadening of one or more types of reflections, and by a change in the small angle scattering. Serious refinements in the normal powder technique, however, are required to gain information of sufficient reliability to justify an evaluation of the type of randomness in a particular phase. In a careful analysis of an unknown, due consideration should be given to the possible presence of defect structures (see Table VIII). The formation of a continuous range of solid solutions of cocrystallized salts is a rather common occurrence.

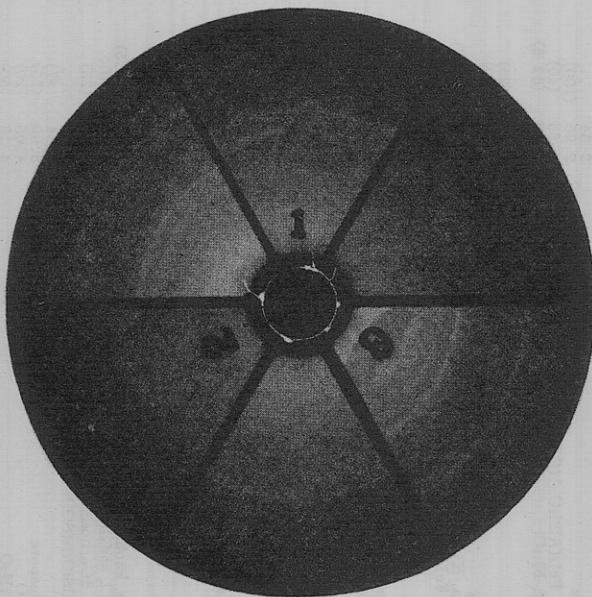


Figure 2. Back-Reflection Patterns

Taken with unfiltered FeK radiation. Specimen-to-film distance, 7.50 cm. Sector 1 refers to a mechanical mixture of 98% KI and 2% KBr; sector 2, same mixture crystallized from water; sector 3, same mixture fused. All samples ground to ~200-mesh powders

Table VII. Ambiguities Arising from Structural Similarities

Substance		<i>d</i> , Å.	1.312	1.91	1.63	1.354	1.242	1.104	1.044	0.958	0.916	1.044
	<i>I/I<sub>1</sub></i>	1.00	..	1.00	0.63	0.18	0.25	0.40	..	0.06	0.13	..
$\beta$ -ZnS	<i>d</i> , Å.	3.12	2.69	1.91	1.63	1.353	1.242	1.104	1.044	0.957	0.913	..
	<i>I/I<sub>1</sub></i>	1.00	0.05	0.75	0.50	0.05	0.18	0.15	0.05	0.03	0.04	..
CuCl	<i>d</i> , Å.	3.12	2.70	1.91	1.63	1.353	1.240	1.104	1.043	..	..	..
	<i>I/I<sub>1</sub></i>	1.00	0.08	0.60	0.30	0.06	0.08	0.06	0.04	..	..	..
CoO	<i>d</i> , Å.	..	2.45	2.12	1.50	1.281	1.227	1.060	0.975	0.951	0.869	0.819
	<i>I/I<sub>1</sub></i>	..	0.67	1.00	1.00	0.40	0.40	0.10	0.10	0.30	0.20	0.07
Cu <sub>2</sub> O	<i>d</i> , Å.	3.00	2.45	2.12	1.51	1.283	1.228	1.065	0.977	0.953	0.869	0.819
	<i>I/I<sub>1</sub></i>	0.03	1.00	0.31	0.44	0.31	0.05	0.03	0.05	0.03	0.03	0.03
FeO	<i>d</i> , Å.	..	2.47	2.14	1.51	1.293	1.238	1.072	0.984	0.959	..	..
	<i>I/I<sub>1</sub></i>	..	0.50	1.00	0.63	0.15	0.08	0.03	0.03	0.05	..	..
CdO	<i>d</i> , Å.	2.70	2.34	1.65	1.412	1.352	1.171	1.075	..	..	..	..
	<i>I/I<sub>1</sub></i>	1.00	1.00	1.00	0.75	0.30	0.15	0.30	..	..	..	..
Ag <sub>2</sub> O	<i>d</i> , Å.	2.72	2.36	1.67	1.422	1.360	1.179	1.082	..	..	..	..
	<i>I/I<sub>1</sub></i>	1.00	0.40	0.24	0.16	0.03	0.01	0.02	..	..	..	..
Al	<i>d</i> , Å.	2.33	2.02	1.43	1.219	1.168	..	..	..	..	..	..
	<i>I/I<sub>1</sub></i>	1.00	0.40	0.30	0.30	0.07	..	..	..	..	..	..
LiF	<i>d</i> , Å.	2.32	2.00	1.42	1.211	1.160	..	..	..	..	..	..
	<i>I/I<sub>1</sub></i>	0.67	1.00	0.23	0.03	0.03	..	..	..	..	..	..
$\alpha$ -Ce	<i>d</i> , Å.	2.97	2.57	1.815	1.55	1.481	1.288	1.179	..	..	..	..
	<i>I/I<sub>1</sub></i>	1.00	0.60	0.40	0.40	0.28	0.12	0.16	..	..	..	..
LiCl	<i>d</i> , Å.	2.96	2.56	1.81	1.55	1.482	1.283	1.178	..	..	..	..
	<i>I/I<sub>1</sub></i>	1.00	1.00	0.60	0.32	0.12	0.05	0.12	..	..	..	..
ThO <sub>2</sub>	<i>d</i> , Å.	3.22	2.80	1.97	1.68	..	1.399	1.280	1.245	1.140	..	..
	<i>I/I<sub>1</sub></i>	1.00	0.38	0.75	0.88	..	0.13	0.38	0.25	0.38	..	..
Ca	<i>d</i> , Å.	3.21	2.80	1.97	1.68	1.61	..	1.28	1.246	1.138	..	..
	<i>I/I<sub>1</sub></i>	1.00	0.30	0.20	0.20	0.10	..	0.05	0.03	0.05	..	..
AgCl	<i>d</i> , Å.	3.20	2.77	1.96	1.67	1.60	1.385	1.270	1.240	1.131	..	..
	<i>I/I<sub>1</sub></i>	0.40	1.00	0.75	0.20	0.25	0.09	0.06	0.20	0.13	..	..

occurrence. Figure 2 illustrates the sensitivity of the back-reflection method for ascertaining this effect.

CLASSIFICATION OF STANDARDS. Up to the present about 2500 patterns have been cataloged at Dow. When one deals with this number of standards the identification of unknowns by the group classification system (24) is adequate, as has been amply demonstrated at Dow during the past ten years. However, it is of theoretical interest to consider what probable limitations may arise when a comparatively larger number of standards is considered. A statistical study of this problem has been made and is presented here purely as a guide to any modified index that might be considered by the diffraction analyst.

To arrive at a tentative answer to the above query it is instructive to examine how the three most intense diffraction lines (reference lines) for each of the catalogued patterns are distributed with respect to interplanar spacing. Figure 3 shows

Table VIII. Defect Structures

Examples	Diffraction Effects	References
Continuous range of solid solutions K(I, Br)	Merging of $K\alpha$ doublet on back-reflections	..
Structures with "Leerstellen" $Fe_{1-x}R$ (R = O, S, Se, Te) $Na_xWO_3$	Occurrence of superstructure lines and anomalous change in lattice constants with $x$	(20-23)
$Mg_{1-x}Al_2O_{4-x}$	Broadening of diffraction lines	..
Pseudomorphism $Mg(OH)_{2(1-x)}O_x$	..	(1, 37)
Randomness in layer structures $CdBr_2$ (Wechselstruktur)	X-ray data can be accounted for on basis of a unit of structure containing a fractional stoichiometric weight	(3, 27, 28, 35, 38, 39, 45)
Micas, clays $nCdCl_2mCd(OH)_2$ , luster carbon	Broadening of diffraction lines, changes in intensities	(27, 28, 38)
Alloy systems with transition structures Al-Cu, Al-Ag, Cu <sub>4</sub> FeNi <sub>3</sub> , AuCu <sub>3</sub>	Broad diffraction ghosts (6)	(6, 11, 19, 36, 55, 56, 61)

**Table IX.** Index to Aluminum-Containing Substances

Below headings 1, 2, 3 are listed respective reference lines and corresponding intensities for substances of second column. Pattern numbers refer to published Dow standards (86). Isomorphism is indicated by a bracket; corresponding structure (16) is stated in column "Pattern". Supplementary index (2, 1, 3, No.) refers to ordered arrangement of second reference line and is used whenever first reference line is obscured by superposition.

No.	Substance	1	2	3	4	Pattern	Reference	2	1	3	4	Pattern	Reference	2	1	3	4	Pattern	Reference	2	1	3	4	Pattern	Reference
1	MnAl <sub>2</sub> O <sub>5</sub>	1.398 (6)	2.49 (3)	2.39 (3)	556 (3)	556	...	1.151	1.99	2.47	2.82	7	1.423	2.47	2.38	24	...	...	...	...	...	...	...	...	
2	Na <sub>0.11</sub> Al <sub>2</sub> O <sub>5</sub>	1.400 (75)	11.8 (40)	1.59 (40)	14 (2B)	1.59 (40)	...	1.166	2.44	2.428	2.86	8	1.428	2.44	2.44	20	...	...	...	...	...	...	...	...	
3	Al <sub>2</sub> O <sub>5</sub>	1.400 (75B)	2.42 (2B)	2.01 (6)	1.430 (6)	2.01 (6)	...	1.180	2.04	2.89	10	1.430	2.44	2.02	21	...	...	...	...	...	...	...	...		
4	Al <sub>2</sub> O <sub>5</sub>	1.421 (8)	2.43 (6)	2.01 (6)	1.430 (6)	2.15 (30)	...	1.417	2.41	2.43	2.00	15	1.431	2.33	2.33	14	...	...	...	...	...	...	...	...	
5	γ-AlOOH, boehmite	1.86 (50)	3.17 (60)	6.15 (60)	1.57 (40)	6.17 (18)	...	1.423	2.43	2.43	2.85	18	1.431	2.44	2.85	19	...	...	...	...	...	...	...	...	
6	NaAlF <sub>6</sub>	1.94 (75)	1.51 (30)	1.57 (30)	813 (18)	813	...	1.455	2.48	1.58	2.48	27	1.445	2.48	2.24	25	...	...	...	...	...	...	...	...	
7	AlNi	2.02 (75)	1.166 (15)	2.82 (15)	B2; 2.82 Å	B2; 2.82 Å	...	1.462	2.49	2.92	2.92	27	1.462	2.49	2.24	25	...	...	...	...	...	...	...	...	
8	AlCo	2.02 (75)	2.08 (62.5)	2.86 (62.5)	B2; 2.86 Å	B2; 2.86 Å	...	1.532	2.64	3.73	3.2	1.881	10.1	4.48	78	...	...	...	...	...	...	...	...		
9	FeAl	2.04 (125)	1.180 (25)	1.445 (15)	403	403	...	1.634	2.65	10.4	3.4	1.52	10.4	2.20	53	...	...	...	...	...	...	...	...		
10	FeAl	2.08 (20)	1.59 (25)	2.89 (15)	402	402	...	1.534	2.68	2.88	29	1.534	2.42	2.84	16	...	...	...	...	...	...	...	...		
11	α-Al <sub>2</sub> O <sub>5</sub>	2.11 (62.5)	2.05 (62.5)	2.55 (15)	11	11	...	1.55	2.59	2.89	30	1.55	2.68	2.96	33	1.55	1.94	2.65	2.75	6	...	...	...		
12	FeAl <sub>2</sub>	2.25 (12)	2.05 (12)	3.00 (25)	404	404	...	1.58	2.65	2.96	33	1.57	2.45	2.45	26	...	...	...	...	...	...	...	...		
13	LiAl	2.33 (100)	2.02 (40)	1.92 (30)	B32; 6.36 Å	B32; 6.36 Å	...	1.59	2.08	2.55	11	1.58	2.48	2.48	26	...	...	...	...	...	...	...	...		
14	Al	2.41 (100)	1.417 (75)	2.00 (62.5)	497	497	...	1.62	2.71	3.03	39	1.59	1.400	11.8	21	...	...	...	...	...	...	...	...		
15	MeAl <sub>2</sub> O <sub>5</sub>	2.42 (125)	2.84 (50)	1.54 (40)	C15; 8.02 Å	C15; 8.02 Å	...	1.64	2.95	3.10	43	1.63	3.99	2.31	66	...	...	...	...	...	...	...	...		
16	CaAl <sub>2</sub>	2.42 (125)	2.84 (50)	1.54 (40)	C15; 8.04 Å	C15; 8.04 Å	...	1.76	2.76	2.11	59	1.64	2.87	2.80	42	...	...	...	...	...	...	...	...		
17	CeAl <sub>2</sub>	2.43 (15)	1.423 (10)	2.32 (5)	C15; 8.04 Å	C15; 8.04 Å	...	1.84	2.60	3.67	31	1.70	2.78	2.25	42	...	...	...	...	...	...	...	...		
18	CuAl <sub>2</sub> O <sub>5</sub>	2.43 (15)	1.423 (10)	2.85 (5)	C15; 8.04 Å	C15; 8.04 Å	...	1.89	2.67	3.78	36	1.70	2.78	2.25	42	...	...	...	...	...	...	...	...		
19	ZnAl <sub>2</sub> O <sub>5</sub>	2.44 (15)	1.423 (10)	1.431 (6)	H1; 8.08 Å	H1; 8.08 Å	...	1.90	2.68	1.55	37	1.78	3.41	2.09	54	...	...	...	...	...	...	...	...		
20	CoAl <sub>2</sub> O <sub>5</sub>	2.44 (60)	2.85 (25)	1.428 (23)	H1; 8.08 Å	H1; 8.08 Å	...	1.92	2.68	3.13	44	1.64	2.78	2.12	55	...	...	...	...	...	...	...	...		
21	FeAl <sub>2</sub> O <sub>5</sub>	2.44 (25)	2.02 (20)	1.430 (20)	H1; 8.10 Å	H1; 8.10 Å	...	1.99	2.55	3.25	48	1.70	2.86	2.16	60	...	...	...	...	...	...	...	...		
22	LaAl <sub>2</sub>	2.46 (62.5)	2.89 (40)	2.36 (30)	C15; 8.16 Å	C15; 8.16 Å	...	2.02	2.33	1.430	14	1.430	2.25	2.82	47	...	...	...	...	...	...	...	...		
23	Al <sub>2</sub> Cl <sub>6</sub>	2.47 (75)	5.8 (40)	2.80 (40)	E2; 3.67 Å	E2; 3.67 Å	...	2.02	2.44	2.02	21	1.92	2.44	2.25	13	...	...	...	...	...	...	...	...		
24	MeAl <sub>2</sub>	2.47 (150)	2.38 (30)	1.423 (30)	H1; 8.16 Å	H1; 8.16 Å	...	2.05	2.44	2.02	20	1.91	2.44	2.25	13	...	...	...	...	...	...	...	...		
25	MgAl <sub>2</sub>	2.48 (150)	2.24 (50)	1.434 (50)	H1; 8.16 Å	H1; 8.16 Å	...	2.08	2.48	2.02	1.445	9	2.01	2.42	3	15	...	...	...	...	...	...	...	...	
26	Fe <sub>2</sub> O <sub>3</sub> ·Cr <sub>2</sub> O <sub>3</sub> ·Al <sub>2</sub> O <sub>5</sub>	2.49 (50)	1.455 (20)	1.55 (17.5)	H1; 8.27 Å	H1; 8.27 Å	...	2.09	2.69	3.41	2.09	1.78	2.01	1.421	23	...	...	...	...	...	...	...	...		
27	MnAl <sub>2</sub> O <sub>5</sub>	2.56 (15)	9.99 (9)	4.47 (8)	(16, 60)	(16, 60)	...	2.09	2.62	2.77	54	1.6	3.29	2.30	51	...	...	...	...	...	...	...	...		
28	Fe <sub>2</sub> O <sub>3</sub> ·Al <sub>2</sub> SiO <sub>5</sub> ·(Al <sub>2</sub> SiO <sub>5</sub> ) <sub>2</sub>	2.58 (100)	1.54 (62.5)	2.88 (50)	S14; 11.51 Å	S14; 11.51 Å	...	2.16	2.53	1.85	60	1.61	3.68	2.61	63	...	...	...	...	...	...	...	...		
29	Fe <sub>2</sub> O <sub>3</sub> ·Mg <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub>	2.59 (100)	1.55 (40)	2.89 (30)	S14; 11.60 Å	S14; 11.60 Å	...	2.20	3.40	2.57	53	1.52	3.50	3.50	57	...	...	...	...	...	...	...	...		
30	MeAl <sub>2</sub> SiO <sub>5</sub>	2.60 (15)	1.84 (30)	3.67 (30)	E2; 3.78 Å	E2; 3.78 Å	...	2.23	5.14	2.48	1.434	25	2.31	4.36	7.46	73	...	...	...	...	...	...	...	...	
31	YAl <sub>2</sub> O <sub>5</sub>	2.64 (100)	1.62 (62.5)	3.73 (30)	H1; 11.37 Å	H1; 11.37 Å	...	2.24	2.48	2.48	2.30	2.29	2.05	2.42	2.84	...	...	...	...	...	...	...	...		
32	AlNd	2.65 (100)	1.55 (62.5)	2.96 (40)	S14; 11.37 Å	S14; 11.37 Å	...	2.24	2.48	2.48	2.30	2.30	2.05	2.32	2.84	...	...	...	...	...	...	...	...		
33	CaAl <sub>2</sub> SiO <sub>5</sub>	2.65 (40)	1.54 (25)	10.4 (15)	(46, 60)	(46, 60)	...	2.24	2.48	2.48	2.30	2.30	2.05	2.32	2.84	...	...	...	...	...	...	...	...		
34	K <sub>2</sub> Na <sub>2</sub> (Mg <sub>2</sub> Fe <sub>2</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>10</sub> ) <sub>2</sub> ·biotite-phlogopite	2.66 (62.5)	7.98 (40)	4.17 (40)	SO <sub>13</sub> ; 82 Å	SO <sub>13</sub> ; 82 Å	...	2.25	2.48	2.48	2.38	2.47	2.01	2.45	2.80	...	...	...	...	...	...	...	...		
35	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> ·(Al <sub>2</sub> SiO <sub>5</sub> ) <sub>2</sub> ·graphite	2.67 (25)	1.89 (25)	3.78 (30)	E2; 3.78 Å	E2; 3.78 Å	...	2.26	2.48	2.48	2.38	2.38	2.01	2.45	2.80	...	...	...	...	...	...	...	...		
36	LaAl <sub>2</sub> O <sub>5</sub>	2.68 (25)	1.90 (6)	1.65 (6)	B3; 5.43 Å	B3; 5.43 Å	...	2.27	2.51	2.51	2.38	2.38	2.01	2.45	2.82	...	...	...	...	...	...	...	...		
37	3Ca <sub>2</sub> O <sub>3</sub> Al <sub>2</sub> O <sub>5</sub>	2.68 (30)	1.92 (20)	4.05 (17.5)	B3; 5.43 Å	B3; 5.43 Å	...	2.28	2.52	3.66 (12.5)	2.01	1.86	2.22	2.46	2.82	...	...	...	...	...	...	...	...		
38	5Ca <sub>2</sub> O <sub>3</sub> Al <sub>2</sub> O <sub>5</sub>	2.71 (30)	1.62 (15)	3.03 (15)	B3; 5.43 Å	B3; 5.43 Å	...	2.29	2.52	3.66 (12.5)	2.01	1.86	2.22	2.46	2.82	...	...	...	...	...	...	...	...		
39	(Na <sub>2</sub> Li <sub>2</sub> AlF <sub>6</sub> ) <sub>n</sub>	2.73 (17.5)	8.7 (15)	3.12 (8)	(46, 60)	(46, 60)	...	2.30	2.55	2.55	2.30	2.30	2.05	2.42	2.84	...	...	...	...	...	...	...	...		
40	(Na <sub>2</sub> Ca <sub>2</sub> N <sub>2</sub> F <sub>6</sub> ) <sub>n</sub>	2.75 (50)	3.08 (8)	2.51 (8)	(46, 60)	(46, 60)	...	2.31	2.55	2.55	2.30	2.30	2.05	2.42	2.84	...	...	...	...	...	...	...	...		
41	(Na <sub>2</sub> Al <sub>2</sub> Ca <sub>2</sub> Fe <sub>2</sub> Al <sub>2</sub> SiO <sub>10</sub> ) <sub>n</sub>	2.75 (25)	3.25 (15)	1.66 (25)	(46, 60)	(46, 60)	...	2.32	2.55	2.55	2.30	2.30	2.05	2.42	2.84	...	...	...	...	...	...	...	...		
42	Al <sub>2</sub> Ca <sub>2</sub> SiO <sub>5</sub>	2.76 (50)	3.26 (15)	5.4 (40)	(46, 60)	(46, 60)	...	2.33	2.56	2.56	2.30	2.30	2.05	2.42	2.84	...	...	...	...	...	...	...	...		
43	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	2.76 (75)	3.29 (15)	2.30 (40)	(46, 60)	(46, 60)	...	2.34	2.57	2.57	2.30	2.30	2.05	2.42	2.84	...	...	...	...	...	...	...	...		
44	AlP <sub>2</sub>	3.02 (50)	4.05 (15)	2.52 (10)	(46, 60)	(46, 60)	...	2.35	2.58	2.58	2.30	2.30	2.05	2.42	2.84	...	...	...	...	...	...	...	...		
45	Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>5</sub> , anorthite	3.20 (50)	4.05 (15)	2.52 (10)	(46, 60)	(46, 60)	...	2.36	2.61	2.61	2.30	2.30	2.05	2.42	2.84	...	...	...	...	...	...	...	...		
46	Al <sub>2</sub> Si <sub>2</sub> Al <sub>2</sub> O <sub>5</sub>	3.42 (75)	2.99 (50)	1.78 (40)	(46, 60)	(46, 60)	...	2.37	2.62	2.62	2.30	2.30	2.05	2.42	2.84	...	...	...	...	...	...	...	...		
47	AlAs <sub>2</sub>	3.42 (75)	2.99 (50)	1.78 (40)	(46, 60)	(46, 60)	...	2.38	2.63	2.63	2.30	2.30	2.05	2.42	2.84	...	...	...	...	...	...	...	...		
48	AlAs <sub>2</sub>	3.46 (75)	2.12 (5)	1.81 (20)	(46, 60)	(46, 60)	...	2.39	2.64	2.64	2.30	2.30	2.05	2.42	2.84	...	...	...	...	...	...	...	...		
49	KAlSi <sub>2</sub> O <sub>5</sub> microcline	3.46 (75)	2.12 (5)	2.14 (20)	(46, 60)	(46, 60)	...	2.40	2.65	2.65	2.30	2.30	2.05	2.42	2.84	...	...	...	...	...	...	...	...		
50	AlCl <sub>3</sub> ·6H <sub>2</sub> O	3.46 (75)	2.30 (40)	2.05 (40																					

No.	Substance	1 A. A.	2 A. A.	3 A. A.	Pattern	Reference	2 A. A.	1 A. A.	3 A. A.	No.
69	KAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	4.29 (50)	4.03 (20)	3.24 (20)	...	4.48 10.1	1.481 78	3.78	2.67	1.89 36
70	TiAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	4.32 (30)	2.80 (20)	5.46 (15)	H4u; 12.21 Å.	...	4.48 12.2	3.98	4.23	3.65 68
71	RbAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	4.34 (40)	2.81 (30)	3.28 (15)	...	4.92	2.68	4.17	2.66	7.98 35
72	CaAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	4.35 (40)	2.83 (30)	5.5 (15)	302	...	5.6	3.42	2.93	5.5 61
73	Ca <sub>2</sub> Si <sub>2</sub> Al <sub>2</sub> O <sub>7</sub> metahalloysite	4.36 (40)	7.46 (20)	2.31 (15)	(46)	...	5.8	2.46	2.80	4.47 50
74	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> ·18H <sub>2</sub> O	4.42 (50)	3.96 (30)	2.48 (20)	...	5.8	3.50	2.65	5.4	3.26 50
75	Al <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O gibbsite	4.43 (40)	4.39 (62.5)	2.45 (40)	J2; 8.90 Å.	...	7.46	3.88	4.43	4.32 70
76	(NH <sub>4</sub> ) <sub>2</sub> AlF <sub>6</sub>	5.14 (50)	2.23 (20)	2.57 (25)	...	7.46	4.36	6.1	5.46	4.35 72
77	AlF <sub>3</sub> <sup>31</sup> /H <sub>2</sub> O	5.50 (50)	3.86 (25)	3.28 (25)	J2; 8.90 Å.	...	7.98	2.66	5.56	3.32 52
78	(OH) <sub>2</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> ·2H <sub>2</sub> O, halloysite	10.1 (40)	4.48 (20)	1.481 (8)	(46)	8.7	2.73	3.12	4.17	3.40 5
79	Bentonite	12.2 (40)	4.48 (20)	3.14 (8)	(46)	9.99	2.56	4.47	2.27	3.62 62
80	(OH) <sub>2</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> ·nH <sub>2</sub> O, montmorillonite	15.2 (40)	4.45 (20)	2.54 (25)	...	11.8	1.400	1.59	2	2.65 62

Table X. Index to Iron-Containing Substances

Below headings 1, 2, 3 are listed respective reference lines and corresponding intensities for substances of second column. Pattern numbers without parenthetical designation refer to published Dow standards (26). Isomorphism is indicated by a bracket; corresponding structure (46) is stated in column "Pattern." Superscripted index (2, 1, 3, No.) refers to ordered arrangement of second reference line and is used whenever first reference line is obscured by superposition.

No.	Substance	1 A. A.	2 A. A.	3 A. A.	Pattern	Reference	2 A. A.	1 A. A.	3 A. A.	No.
1	FeS <sub>2</sub> pyrite	1.63 (62.5)	2.70 (50)	2.42 (30)	443 (23)	...	1.166	2.01	1.428	7
2	{Fe, Ni}S <sub>2</sub>	1.675 (62.5)	2.77 (50)	2.49 (30)	443 (23)	...	1.180	2.04	1.428	7
3	{Fe, Ni}eS <sub>2</sub>	1.77 (62.5)	3.03 (50)	1.95 (30)	433 (110)	...	1.184	2.05	1.450	11
4	Fe <sub>2</sub> Si <sub>2</sub> eS <sub>2</sub>	1.84 (100)	2.37 (62.5)	5.1 (30)	20 (26)	29 (60)	1.196	2.07	1.466	17
5	Ca <sub>2</sub> Fe <sub>2</sub> S <sub>4</sub>	1.93 (100)	3.30 (40)	3.15 (20)	432 (401)	...	1.432	2.44	2.02	24
6	FeSi	2.00 (100)	1.82 (40)	1.93 (20)	401 (403)	...	1.455	2.48	1.58	26
7	$\alpha$ -Fe	2.01 (40)	1.66 (15)	1.428 (6)	403 (402)	...	1.464	2.07	2.39	14
8	FeAl <sub>2</sub>	2.02 (75)	2.08 (50)	1.445 (15)	403 (402)	...	1.468	2.50	1.60	27
9	FeAl	2.04 (125)	1.80 (50)	2.89 (15)	402 (401)	...	1.476	2.51	2.95	11
10	Fe <sub>2</sub> eS	2.04 (100)	1.71 (50)	2.97 (40)	B8 <sup>a</sup> = 3.43 Å.	...	1.476	2.52	1.61	30
11	$\beta$ -Fe(1070° K.)	2.05	1.84	1.450	A2; 2.90 Å.	...	1.481	2.53	1.61	31
12	FeS	2.06 (75)	2.97 (25)	1.450 (25)	442 (442)	...	1.482	2.53	1.61	33
13	$\delta$ -Fe(1700° K.)	2.07	1.96	1.465	A2; 2.93 Å.	...	1.484	2.53	2.97	32
14	(63.13)Fe <sub>2</sub> O <sub>3</sub> ·37Li <sub>2</sub> TiO <sub>5</sub>	2.08	1.64	2.39	(B1); 4.142 Å.	...	1.488	2.54	1.62	34
15	Teniente, 57.7% Fe, 40.8% Ni, 0.5% P	2.09 (40)	2.19 (10)	2.73 (10)	A1; 3.60 Å.	...	1.492	2.55	1.62	37
16	FeNi	2.10 (40)	1.82 (10)	1.61 (10)	417 (417)	...	1.492	2.55	1.63	36
17	$\gamma$ -Fe(1370° K.)	2.11 (62.5)	2.05 (62.5)	2.30 (25)	A1; 3.63 Å.	...	1.497	2.55	1.63	36
18	FeAl <sub>3</sub>	2.14 (40)	1.51 (25)	2.47 (20)	404 (425)	...	1.51	2.14	2.47	19
19	FeO	2.18 (10)	1.88 (4)	1.36 (3)	418 (418)	...	1.51	2.57	1.64	38
20	Fe <sub>2</sub> N	2.23 (17.5)	2.03 (10)	1.92 (10)	429 (429)	...	1.514	2.57	2.88	39
21	Fe <sub>2</sub> P	2.43 (30)	1.87 (17.5)	2.82 (8)	422 (422)	...	1.514	2.58	2.88	40
22	FeAl <sub>2</sub> S	2.43 (20)	2.67 (17.5)	1.81 (8)	93 (93)	...	1.514	2.66	10.4	43
23	Fe <sub>2</sub> Al <sub>2</sub> Sn	2.44 (25)	1.82 (25)	2.33 (20)	H1; 8.10 Å.	...	1.515	2.66	1.97	44
24	FeAl <sub>2</sub> O	2.45 (25)	2.72 (20)	2.02 (20)	H1; 8.10 Å.	...	1.61	2.70	3.00	47
25	(Co, Fe)As <sub>2</sub>	2.48 (50)	1.455 (20)	1.82 (25)	67 (36)	...	1.66	2.53	1.42	48
26	Fe <sub>2</sub> Cr <sub>3</sub> O <sub>8</sub>	2.60 (62.5)	1.468 (62.5)	1.60 (50)	H1; 8.33 Å.	...	1.678	2.37	55	42
27	FeCr <sub>2</sub> O <sub>4</sub>	2.63 (50)	2.84 (50)	2.23 (50)	51 (51)	...	1.71	2.04	2.97	19
28	Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>	2.64 (50)	2.84 (50)	2.62 (50)	51 (51)	...	1.76	2.71	3.45	49
29	Mg <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>	2.65 (50)	2.95 (50)	2.95 (50)	527 (527)	...	1.77	2.70	3.02	63
30	Na <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>	2.62 (50)	1.476 (50)	1.61 (50)	H1; 8.35 Å.	...	1.80	2.08	2.50	63
31	Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>	2.53 (50)	1.481 (40)	1.61 (40)	H1; 8.38 Å.	...	1.81	2.95	1.541	59
32	Zn <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>	2.53 (50)	1.484 (15)	2.97 (12.5)	979 (979)	...	1.81	2.96	1.541	59
33	FeAl <sub>2</sub> (SiO <sub>4</sub> ) <sub>2</sub>	2.53 (62.5)	1.483 (50)	1.61 (40)	426 (426)	...	1.82	2.00	1.183	6
34	(Mg, Fe)Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>2</sub>	2.54 (50)	1.488 (40)	1.62 (40)	H1; 8.42 Å.	...	1.82	2.10	1.218	53
35	(Mg, Fe)Fe <sub>2</sub> O <sub>4</sub>	2.54 (50)	1.492 (30)	1.63 (30)	H1; 8.44 Å.	...	1.82	2.43	2.82	22
36	Fe <sub>2</sub> Al <sub>2</sub> O <sub>5</sub>	2.55 (50)	1.497 (30)	1.63 (30)	H1; 8.47 Å.	...	1.86	3.03	1.59	64
37	(Fe, Zn, Mn)(Fe, Mn)O <sub>4</sub>	2.55 (50)	1.497 (30)	1.62 (30)	H1; 8.50 Å.	...	1.88	2.95	1.59	64
38	MnFe <sub>2</sub> O <sub>4</sub>	2.57 (100)	1.51 (40)	1.64 (40)	H1; 8.51 Å.	...	1.88	3.07	1.601	65
39	FeAl <sub>2</sub> (SiO <sub>4</sub> ) <sub>2</sub>	2.68 (100)	1.54 (62.5)	2.88 (50)	H1; 8.51 Å.	...	1.88	3.22	1.75	67
40	(Mg, Fe)Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>2</sub>	2.59 (100)	2.32 (50)	2.52 (50)	H1; 8.51 Å.	...	1.89	3.11	1.63B	66
41	Fe <sub>2</sub> Sb <sub>2</sub> S <sub>3</sub>	2.69 (100)	3.08 (25)	3.15 (25)	16 (16)	...	1.904	2.75	6.7	53
42	Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>	2.62 (30)	3.08 (17.5)	1.67 (12.5)	161 (161)	...	2.03	2.04	7.4	3.51
43	(Mg, Na)(Mg, Fe)(Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> )(OH) <sub>2</sub> , biotite-phlogopite	2.66 (100)	1.59 (62.5)	1.64 (40)	(46)	...	2.04	2.05	7.4	115
44	Ca <sub>2</sub> (Al, Fe)(Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> )(OH) <sub>2</sub> , phlogopite	2.68 (62.5)	2.08 (25)	2.97 (40)	81 <sub>a</sub> ; 11.39 Å.	...	2.05	2.02	1.445	8
45	Fe <sub>2</sub> Cl <sub>4</sub>	2.69 (40)	2.51 (30)	5.9 (20)	407 (407)	...	2.08	2.08	5.9	45
46	Fe <sub>2</sub> O <sub>3</sub> (SiO <sub>4</sub> ) <sub>2</sub>	2.70 (100)	1.61 (40)	1.84 (25)	423 (423)	...	2.18	2.09	2.09	16
47	Ca <sub>2</sub> Fe <sub>2</sub> (SiO <sub>4</sub> ) <sub>2</sub>	2.70 (100)	1.61 (40)	3.00 (30)	S1 <sub>a</sub> ; 12.02 Å.	...	2.22	2.22	2.92	57.

(Continued on page 216)

Table X (Cont.)

No.	Substance	Pattern	Reference	No.	No.
1	A.	A.	A.	1	2
2	A.	A.	A.	2	3
3	A.	A.	A.	3	4
4	A.	A.	A.	4	5
5	A.	A.	A.	5	6
6	A.	A.	A.	6	7
7	A.	A.	A.	7	8
8	A.	A.	A.	8	9
9	A.	A.	A.	9	10
10	A.	A.	A.	10	11
11	A.	A.	A.	11	12
12	A.	A.	A.	12	13
13	A.	A.	A.	13	14
14	A.	A.	A.	14	15
15	A.	A.	A.	15	16
16	A.	A.	A.	16	17
17	A.	A.	A.	17	18
18	A.	A.	A.	18	19
19	A.	A.	A.	19	20
20	A.	A.	A.	20	21
21	A.	A.	A.	21	22
22	A.	A.	A.	22	23
23	A.	A.	A.	23	24
24	A.	A.	A.	24	25
25	A.	A.	A.	25	26
26	A.	A.	A.	26	27
27	A.	A.	A.	27	28
28	A.	A.	A.	28	29
29	A.	A.	A.	29	30
30	A.	A.	A.	30	31
31	A.	A.	A.	31	32
32	A.	A.	A.	32	33
33	A.	A.	A.	33	34
34	A.	A.	A.	34	35
35	A.	A.	A.	35	36
36	A.	A.	A.	36	37
37	A.	A.	A.	37	38
38	A.	A.	A.	38	39
39	A.	A.	A.	39	40
40	A.	A.	A.	40	41
41	A.	A.	A.	41	42
42	A.	A.	A.	42	43
43	A.	A.	A.	43	44
44	A.	A.	A.	44	45
45	A.	A.	A.	45	46
46	A.	A.	A.	46	47
47	A.	A.	A.	47	48
48	A.	A.	A.	48	49
49	A.	A.	A.	49	50
50	A.	A.	A.	50	51
51	A.	A.	A.	51	52
52	A.	A.	A.	52	53
53	A.	A.	A.	53	54
54	A.	A.	A.	54	55
55	A.	A.	A.	55	56
56	A.	A.	A.	56	57
57	A.	A.	A.	57	58
58	A.	A.	A.	58	59
59	A.	A.	A.	59	60
60	A.	A.	A.	60	61
61	A.	A.	A.	61	62
62	A.	A.	A.	62	63
63	A.	A.	A.	63	64
64	A.	A.	A.	64	65
65	A.	A.	A.	65	66
66	A.	A.	A.	66	67
67	A.	A.	A.	67	68
68	A.	A.	A.	68	69
69	A.	A.	A.	69	70
70	A.	A.	A.	70	71
71	A.	A.	A.	71	72
72	A.	A.	A.	72	73
73	A.	A.	A.	73	74
74	A.	A.	A.	74	75
75	A.	A.	A.	75	76
76	A.	A.	A.	76	77
77	A.	A.	A.	77	78
78	A.	A.	A.	78	79
79	A.	A.	A.	79	80
80	A.	A.	A.	80	81
81	A.	A.	A.	81	82
82	A.	A.	A.	82	83
83	A.	A.	A.	83	84
84	A.	A.	A.	84	85
85	A.	A.	A.	85	86
86	A.	A.	A.	86	87
87	A.	A.	A.	87	88
88	A.	A.	A.	88	89
89	A.	A.	A.	89	90
90	A.	A.	A.	90	91
91	A.	A.	A.	91	92
92	A.	A.	A.	92	93
93	A.	A.	A.	93	94
94	A.	A.	A.	94	95
95	A.	A.	A.	95	96
96	A.	A.	A.	96	97
97	A.	A.	A.	97	98
98	A.	A.	A.	98	99
99	A.	A.	A.	99	100
100	A.	A.	A.	100	101
101	A.	A.	A.	101	102
102	A.	A.	A.	102	103
103	A.	A.	A.	103	104
104	A.	A.	A.	104	105
105	A.	A.	A.	105	106
106	A.	A.	A.	106	107
107	A.	A.	A.	107	108
108	A.	A.	A.	108	109
109	A.	A.	A.	109	110
110	A.	A.	A.	110	111
111	A.	A.	A.	111	112
112	A.	A.	A.	112	113
113	A.	A.	A.	113	114
114	A.	A.	A.	114	115
115	A.	A.	A.	115	116
116	A.	A.	A.	116	117
117	A.	A.	A.	117	118

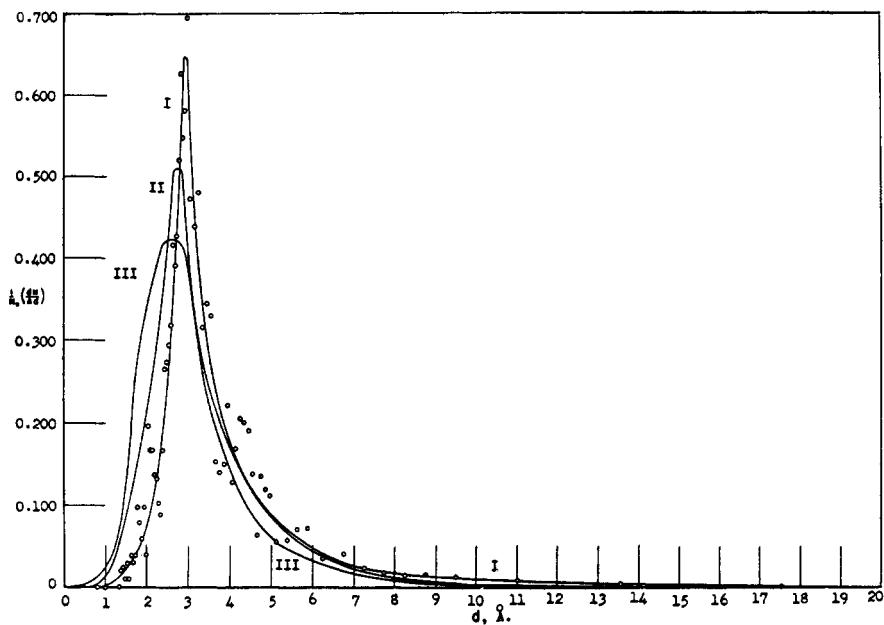


Figure 3. Distribution of Interplanar Spacings of Reference Lines

I refers to distribution of first reference line of various standards with respect to  $d$ , interplanar spacing; II and III pertain to second and third reference lines, respectively.  $N_0$  = total number of cataloged standards = 2100.  $(dN)_{I,d}$  = number of standards having their first reference line located in interval  $(d \pm \frac{\Delta d}{2})$ . For sake of clarity experimental points are shown only for I.

Maxima for I, II, and III occur at  $2.95 \pm .08$ ,  $2.75 \pm .20$ , and  $2.60 \pm .30 \text{ \AA}$ , respectively.  $n$  = number of diffraction lines per pattern;  $4 \leq n \leq 45$ ;  $\bar{n} = 19$ .  $I_r$  = intensity of  $r^{\text{th}}$  reference line;  $2 \leq I_r \leq 212$  based on  $I_1 (\text{NaCl}) = 150$ .  $I_1, I_2, I_3 = 42.3:25.7:20.2$  for MoK $\alpha$  (when corrected for factor  $\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$ , continued ratio is proportional to 26.0:22.0:19.2).  $\nu_1$  expresses probability that  $d_1 > d_2$  or  $d_3$ ;  $\bar{\nu}_1: \bar{\nu}_2: \bar{\nu}_3 = 1.00:50:0.28$ . A bar above a letter signifies an arithmetic average for  $N_0$  standards.

that for most common inorganic substances the reference lines fall within the interval 2.0 to 3.5 Å. Considering the first reference line, one finds 15 patterns listed in the interval 15 to 20 Å. and 74 patterns in the interval 2.95 to 3.00 Å. (of course, the second and third reference lines of a substance materially reduce the number of standards to be considered). In the identification of mixtures, however, a crowding of reference in the relatively narrow interval from 2.6 to 3.0 Å. might necessitate an undue amount of searching to locate the sought standard patterns in a very large collection of standards. The point may be visualized by the diffraction pattern of a binary mixture for which there are six reference lines, the intensities of which may be denoted by  $I_r$  and  $\xi_s$  where  $r, s = 1, 2, 3$ . Assuming (1) that there are no superpositions of lines, (2) that the six most intense reflections are also the six reference lines for the binary mixture, and (3) that  $I_1 \geq I_2 \geq I_3 \geq \xi_1 \geq \xi_2 \geq \xi_3$ ; one may have to exhaust from 1 to 119 possible combinations to find the appropriate set

under aluminum as shown in Table IX. Those substances containing both aluminum and iron would be listed under

Table XI. Powder Diffraction Data

Filtered MoK $\alpha$  used to obtain diffraction patterns.  $d$  = interplanar spacing.  $I$  = peak intensity of a diffraction line.  $I/I_1$  = relative intensity, where  $I_1$  is intensity of strongest line of particular phase in question (values in parentheses refer to calculated intensities). Diffraction pattern of albite, Amelia Court House, Va., was taken with a 0.1-mm. slit to resolve some of the broader reflections.

SPECTROSCOPIC ANALYSIS OF UNKNOWN. Fe, Al, Si, Na chief constituents; minor constituents P 0.1 to 0.5%, K 0.01 to 0.1%, Ca 0.001 to 0.01%.

Unknown		Albite, NaAlSi <sub>3</sub> O <sub>8</sub>	$I/I_1$	Phase I	Goethite, $\alpha$ -FeO.OH	$I/I_1$	Phase II	NaAlSi <sub>3</sub> O <sub>8</sub> , Albite, Amelia Court House, Va.	
$d, \text{\AA.}$	$I$	$d, \text{\AA.}$		$I/I_1$	$d, \text{\AA.}$	$I/I_1$	$I/I_1$	$d, \text{\AA.}$	$I/I_1$
6.5	1	6.4	0.08	0.02				6.4	0.06
5.0	3		.		4.98	0.04	0.09	5.9	0.04
4.20	25		.		4.21	1.00 (25)	0.76	5.5	0.02
4.02	12.5	4.05	0.35	0.28				4.01	0.50 (50)
3.80	3	3.80	0.16	0.07				3.84	0.06
3.67	9B	3.66	0.25	0.20				3.76	0.08
3.38	4		.		3.39	0.12	0.12	3.66	0.40 (40)
3.19	50	3.20	1.00 (50)	1.14				3.50	0.10
2.95	12.5	2.96	0.25	0.28				3.37	0.08
2.69	12.5	2.65	0.02	(1)	2.70	0.36	0.38	3.19	1.00B (100)
2.57	12.5	2.56	0.12	(5)	2.58	0.24	(8)	2.94	0.20B
2.44	30	2.44	0.14	(6)	2.45	0.80	(26)	2.85	0.10
2.37	1		.					2.64	0.04
2.32	2	2.32	0.12	0.05				2.55	0.10
2.25	5		.		2.25	0.12	0.15	2.43	0.10
2.18	6	2.18	0.06	(3)	2.19	0.20	(7)	2.38	0.04
2.10	3B	2.13	0.12	0.07				2.31	0.10B
2.01	4	1.99	0.08	0.09				2.24	0.01
1.90	5B	1.90	0.12	(5)	1.92	0.08	(3)	2.19	0.02
1.81	6B	1.83	0.18	(8)	1.80	0.08	(3)	2.12	0.08
1.72	17.5	1.73	0.08	(4)	1.72	0.86	(12)	2.06	0.06
1.60	4		.		1.60	0.08	0.12	1.98	0.06B
1.56	15	1.58	0.12	(5)	1.56	0.28	(9)	1.89	0.10
1.51	12.5	1.50	0.08	(4)	1.50	0.24	(8)	1.85	0.08
1.455	10	1.460	0.16	(7)	1.455	0.12	(4)	1.82	0.10
1.419	9	1.425	0.16	(7)	1.420	0.04	(1)	1.782	0.08
1.350	4	1.350	0.14	(6)	1.355	0.08	(3)	1.743	0.04
		$(I_1)_1 \approx (44)$				$(I_1)_{11} \approx (33)$			

of reference lines for one component [for an  $n$ -component mixture there are  $3n(3n - 1)(3n - 2) - (n - 1)$  combinations]. In the general case of a binary mixture, allowance must also be made for the following possibilities: (1) the superposition of reference lines, for example, the second reference line of phase A and the third reference line of phase B so that  $I_2 + \xi_3 > I_1$  or  $\xi_1$ ; (2) the superposition of a reference line of phase A and a moderately intense reflection of phase B ( $I_3 + \xi_4 > I_2$ ); and (3) the presence of prominent nonreference lines for phase A, so that  $I_4$  or  $I_4 + n > \xi_2$ . These considerations are general and apply to any scheme of classification.

In case the number of standards exceeds 10,000 to 20,000, the problem may arise as to how to circumvent the probable congestion of reference lines and the multiplicity of trial reference lines for multi-component mixtures. In view of the fact that the great majority of analyses are supplemented or confirmed by qualitative spectroscopic analysis, it may be expedient to reverse the procedure and obtain the spectroscopic data first to facilitate finding the appropriate diffraction standards.

For example, all compounds containing aluminum would be grouped under aluminum as shown in Table IX. Those substances containing both aluminum and iron would be listed under

aluminum and iron—e.g.,  $\text{FeAl}_2\text{O}_4$  is listed in Tables IX and X (there are nine such substances listed). Under the nonmetals—H, C, N, O, F, S, Cl, Se, Br, Te, I—one would list only those compounds which do not contain elements detectable by the conventional arc spectra—i.e., which do not contain any of the following: Li, Be, B, Na, Mg, Al, Si, P, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Pb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Ra, Th, U. Chemical tests are convenient to identify the nonmetals—e.g., the use of aqueous sodium hydroxide and Nessler's reagent to detect ammonium salts. Organic compounds may also be detected in the arc (using copper electrodes) by the 2478.5 Å. emission line of carbon and the cyanogen band. For routine analysis it would be advisable to check the diffraction standards listed under carbon and nitrogen.

The procedure for identifying an unknown by this modification of the triple index system (25) is illustrated by Table XI.

Qualitative spectroscopic analysis of the unknown shows the following chief constituents: iron, aluminum, silicon, sodium. The more prominent diffraction lines of the unknown (column 1, Table XI) are: 4.20, 4.02, 3.19, 2.95, 2.69, 2.57, 2.44, 1.72 Å. Looking under Table X to locate the iron-containing phase(s), one finds  $\alpha\text{-FeO(OH)}$  as a likely component of the unknown. Checking the complete data of standard pattern 424, one establishes the presence of goethite in the mixture. In a like manner Table IX indicates albite,  $\text{NaAlSi}_3\text{O}_8$ , as the second phase of the unknown. The presence of albite also could have been ascertained by looking under the index for sodium or silicon. As all the diffraction lines of the unknown are satisfactorily accounted for, the qualitative compound analysis is considered complete and there is no need to check the diffraction standards listed under carbon, nitrogen, etc.

The extent to which the suggested classification of diffraction standards by elements circumvents the anticipated congestion of reference lines can be estimated by an examination of Tables IX and X in regard to the number of times the average compound is listed under more than one element.

For aluminum (Table IX) there are 18 substances listed only once (under aluminum), 47 substances listed twice (distributed over 23 elements), 11 substances listed three times (distributed over 8 elements), and two substances listed 4 times (distributed over 5 elements). For Table X there are 39 substances indexed only under iron, 60 substances indexed twice (distributed over 23 elements), 13 substances listed three times (distributed over 19 elements), and five minerals listed 4 times (distributed over 11 elements). A calculation of the quotient

$$\frac{\sum n_r}{N \sum n_r}$$

where  $n_r$  = number of substances listed  $r$  times  
 $N$  = total number of elements under which the various substances are indexed

shows that the congestion of references lines has been reduced by a factor of 12.7 for the aluminum compounds and 13.9 for the iron compounds.

However, it appears that the intrinsic advantage of combining spectroscopic information with diffraction data is the natural incorporation of isomorphous groups in the various tables. This combination of empirical standards and structural types into one index should broaden the scope and utility of chemical analysis by powder diffraction.

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