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X-ray determinative tables for minerals

Part I

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First Division

Description of principles and details of determinative methods

I. Introduction

In the beginning of the present century, E. S. Fedorov created a method for the determination of a substance after the forms of its crystals, named by the inventor "The Crystallochemical analysis" (*29*). This method, based on the measurement of the angles between the crystal faces, proved to be an important principial and practical achievment in Crystallography.

In the course of the following years, this method deserving by its essence the proper name of goniometrical diagnosis, was considerably simplified by Fedorov's disciples. At present in Fedorov Institute and in the Central Geological and Prospecting Institute (ZNIGRI) the composition of "Determinative Tables of Crystals" (*2*) is performed, which will make it possible to introduce the goniometrical diagnosis in its new form, on a par with the optical diagnosis, into the every day practice of the crystallographer, chemist, and mineralogist.

The chief advantages of the goniometrical diagnosis are as follow no expence whatever of the substance, a relatively short time necessary for substance identification and an equal simplicity of the diagnosis course, both in cases of simple substances and in cases of extremely complicated chemical compounds.

The main defects of the geniometric method are: the necessity to have a good enough crystal of the unknown substance and the variability of the exterior form of different crystals of the same substance. The second defect in several cases, may make it even impossible to determine a substance by means of the goniometer. This defect is especially felt in the Barker's variant (*16*) of the goniometric diagnosis (*20*, 328, 329), somewhat less in the Fedorov's "Crystallochemical analysis", and its influence is stil lless felt when using the "Determinative tables" mentioned above.

But even in the latter method, there are a priori possible and there will probably occur in future practice such cases, when some crystalline substance will be met with in crystalline form with such external faces, which have never

been observed before in the study of this substance. In these cases such a substance cannot be determined by any goniometrical method.

2. Owing to the variability of the forms of the crystals Fedorov was obliged to try to base his method of determination on another, absolutely constant property of the crystalline substance — on its structure, on which depend all its geometrical properties, the interfacial angles included. In this direction, Fedorov has done all that it is possible to do without the aid of later rapidly developed X-ray investigation of crystals (roentgenometry of crystals).

After the development of the latter, the creation of new determinative methods for crystalline substances, — X-ray (or roentgenometrical) methods became inevitable.

At present three main groups of X-ray methods are applied to the investigation of substance: 1) permeability method, 2) spectroscopic investigation and 3) interference methods.

The first of these groups can be used for diagnostic purposes by the way of determination of the absorption coefficient μ, just as the method of determination of the indices of refraction serves as one of the principles for the optical diagnosis. Hitherto, so far as we know, no systematic work has been performed in this direction.

The second group of methods — X-ray spectroscopy — is the basis of the X-ray spectral analysis. It is applied for qualitative and quantitative determination of several elements, composing a given substance, but for diagnosis or for identification of this substance in the whole it is not used.

For the latter purpose the most suitable would be the group of interference methods.

3. There are possible two principially different ways of application of X-ray interference methods for the determination of crystalline matter.

a) With a preliminary structure determination of any unknown substance.

b) Without such determination directly after the X-ray patterns.

At first sight, the way a) seems to be more well-grounded and much more promising. However, very great, often even insuperable difficulties, arising on the way of structure determination of most substances discard the possibility of such diagnosis on a large scale.

(Let us mention here that recently Donnay, Tunnel and Barth (*27*) have traced the plan of a possible construction of X-ray determinative tables based on a preliminary determination of the crystal structure.)

No difficulties mentioned above exist on the way b).

4. In order to answer the question, which of the interference methods are here to be applied, let us remember, first of all, that for the present moment we dispose of such principal methods as: 1) Powder method; 2) Laue method, 3) Bragg's method, 4) rotation method, 5) Weissenberg-Böhm's method.

The first of these methods differs from the rest by the fact that for the latter it is necessary to have a monocrystal, although of minor, but yet of macroscopic dimensions (1,0—0,1 mm). For fine-grained, cryptocrystalline and almost colloidal substances only the powder (Debye-Scherrer-Hull) method is applicable. In this feature consists its first advantage. The second is that it is the simplest of all by its apparatus, its experimental conditions and by the necessary interpretation of its results; for instance, the sample orientation is of no matter for the pattern obtained by this method.

Thus, there is no doubt that for crystalline matter diagnostic purposes the best applicable, the most practical will be the powder method.

5. The above formulated statement was recognised long ago by many X-ray investigators-mineralogists. Ever since the moment when crystal roentgenometry had appeared, a series of investigations was published, which followed this direction.

First of all we have to say that in the practice of all crustallographic,

mineralogical, chemical, metallographic and other laboratories the *X*-ray method is now used as one of the methods of crystalline matter identification. It is mostly applied in combination with other methods, but sometimes it is used separately too. In most of these cases the powder method is applied.

As examples of such works, we may cite Hull's (*36*) paper on chalcedony, Böhm's (*21*) on hydrates of ferric oxide, Young's (*39*) on "semihydrate", Boldyrev's and Alexeieva's (*1*) on artificial phlogopite, and a great many other. A still greater number of them remains unpublished, being usual diagnostic works. But besides such identification of different minerals, several writers have raised and solved a problem of a larger scale — namely of creating standard powder photographs (etalons) and of compiling special tables for identification (i. e. for determination) of the crystals, within the limits of definite groups. Here to belong: Kerr's work (*40*) concerning the identification of opaque ore minerals, the works of Nagelschmidt (*48*) containing standart powder patterns of clay minerals, of Smitheringale (*60*) — for manganese minerals, of Harrington (*34*) — for crystalline components of portland-cements, of Haraldsen (*32, 33*) — about minerals, connected by paragenesis with serpentine, Waldo (*61*) — for copper ore minerals, etc.

6. About 1930, in connection with the above-mentioned large work of the Fedorov Institute on the goniometrical "Determinative Tables of Crystals" a thought came into our minds to compose the project of *X*-ray (or Roentgenometrical) Determinative Tables for crystalline substances. However, it was clear to us that for the solution of such a problem it was necessary to organise a series of systematic laboratory works in order to obtain standard substances. The enormous bulk of this task forced us to limit it considerably at first.

Thus we decided to begin by composing a systematic identification tables of minerals. Therefore we have occupied ourselves firstly in systematically preparing standard powder patterns and corresponding number tables for minerals. In this direction in the mineralogical X-ray laboratories of three Institutes (Fedorov Institute, Central Geological and Prospecting Institute and All-Union Institute of Economic Mineralogy) there were performed up till now following works: in 1932 — by G. M. Popov (*12*) powder-patterns were obtained for the most important ore minerals of Fe and Mn; in 1935 and 1936 — by G. A. Kovalev (*6, 7*) — for a series of minerals of the classes of elements, sulphides, oxides and partly of other ones; in 1935—36, by V. I. Mikheiev (*9*), and in 1936 by V. N. Dubinina (*5*) — for minerals of the stone casting; in 1936 the last named investigators (*10*) gave data for several minerals of the class of oxides and, finally, in 1936 A. N. Liamina and A. I. Liubimzev (*8*) obtained powder patterns for the oxide and hydroxide class.

7. V. I. Mikheiev (*9*) has made a first attempt to give systematic determinative tables (an index or key for the identification) for those 11 minerals, for which he had obtained standard *X*-ray powder photographs. A similar attempt, and on a considerably larger scale was made by Waldo (*61*) having compiled identification tables for 48 copper ore minerals. Both these works were performed independently of one another.

We have considered this part of Mikheiev's investigation as a first sketch of the *X*-ray determinative tables for minerals. It had to clear up concretely, which a direction must be followed by our further work, and this purpose along with its other purposes was attained. We regard Waldo's work as another attempt or experiment of compilation of the future "Determinative Tables of minerals"

It seems to us that after these preliminary works it is time to expose the general principles and the concrete details on which we base to-day our *X*-ray determinative tables and to give the first fascicle of these tables. This is indeed the purpose of the present paper.

II. Material taken as a basis for the X-ray determinative tables

1. Before speaking of the determinative tables themselves, it is necessary to describe their real basis.

This basis, as was mentioned above, consists in the standard powder patterns of minerals, or — in further generalization of this idea, — in such patterns of all crystalline substances.

2. For the composition of the determinative tables we take all necessary material from two sources: from available literature and from laboratory work especially performed for our purpose.

3. Concerning literary data it is to be noted, that not every X-ray investigation paper, examining some mineral or crystalline matter in general, can give suitable data for our purpose. On the contrary, very many of the most detailed and exast works, even containing a full crystal structure determination include sometime no data precise enough concerning the relative X-ray powder patterns. It was impossible to use this kind of papers for the fulfilment of our task.

Further, many papers where results of the powder-diagram measurements are given, but wherein corrections of these results are either not introduced at all, or are not made in a quite suitable manner, cannot contribute as material for the "Tables" or may be but used conventionally with necessary remarks, and only in the absence of more precise data.

4. Then, what are the requirements that must be satisfied by a powder-pattern and by its treatment in order to be of use in the "Determinative tables"?

a) A powder-pattern must be obtained from a matter of sufficient purity; strictly speaking it is necessary to have a chemical analysis of the recorded substance; but at first time we shall be obliged to use powder-patterns without the corresponding chemical analyses.

b) Further, the treatment of the powder-diagram as final result must give the interplanar distances $\frac{d}{n}$ calculated after Bragg-Wulf's formula:

$$n\lambda = 2d \sin \theta$$

for each line of the powder pattern.

This follows from the necessity to exclude out of the powder-diagram characteristic the influence of the variable conditions of the experiment: the wave length and the diameter of the chamber-D. The final characteristic we adopt $\left(\frac{d}{n}\right)$ depends exclusively on the structure and composition of the given substance.

c) In order that the calculated values $\frac{d}{n}$ schould be precise enough, the experimental errors must be excluded by means of corrections, properly performed. This question is to be discussed below.

d) Time spent for the preparation of the patterns and their treatment by measurement and calculation is to be reduced to a possible minimum. No complication of the experiment or of the calculations (if possible to avoid it) is to be allowed.

Requirements a) and b) need no further comments. The latter two are to be developed as follows:

5. We consider as a most satisfactory procedure for the fulfilment of the condition c), i. e. the correction of values, measured directly on X-ray pattern, their comparison with a standard substance. As such one, we have used NaCl.

As methods of correction we applied 1) Wyckoff-Ott's method (*63, 53*)— records of the mixture of the investigated and the standard matter, and 2) a method analogous to that of Davy (*26*): prparation of a photograph in a cylindric chamber,

divided in the middle by a plate parallel to the bottom: the specimen rod is here combined: in the upper part of the chamber is situated the substance under investigation, in the lower part the standard matter: of the latter the most simple will be a copper wire. One of the records obtained is shown in fig. 3. (p. 10)

The advantage of the first method consists in its greater accuracy and its simple apparatus. The advantages of the second one: 1) in less time expense because here one has to make and to calculate one record instead of two, and 2) in the possibility of approximative determination not of the relative, but the absolute photographic intensity of the lines on the powder diagram.

Both these methods were known long ago (*63, 26*). The best (according to our opinion) procedures of their application are described in a series of our papers (*1*), (*6*), (*9*), (*5*).

The course of correcting is given in the tables forlmularies below, accompanied by suitable explanations.

We point out here that the principle of an approximative determination of the absolute photographic intensity of the lines consists firstly in the visual evaluation of the photographic intensity of the ten strongest lines of the copper record. The following table is then obtained:

№ № of lines	1	2	3	4		6		8	9	10
Indices	111$\bar{3}$	111	200$\bar{3}$	200	200$\bar{3}$	220	311$\bar{3}$	222$\bar{3}$	311	322
Visual intensity	4	9	3	8	4	10	4	2	9	5

It is to note, that the measuring by the photometer gives a considerably different intensity for the same line according to our observations.

After transformation on the ten step scale this "photometric intensity" is obtained in the following table:

Intensity, measured by Moll's photometer	5	10	4				1	1	3	

It is obvious that for lines with greater angles θ photometric measurements give lower intensities than their visual evaluation.

Since visual evaluations in diagnostics, notwithstanding their minor accuracy, have the advantage of rapidity, it is suitable to use the first of these two tables. On the divided pattern (fig. 3) it is easy to evaluate visually the intensity of the lines of a mineral comparing it with the Cu lines.

The details of this method are as yet in a stage of development, and in our present work we have not used them. But in the future this method will be of the greatest importance for the "Determinative Tables"

It is essential that in a divided chamber the conditions of obtaining X-ray photographs of both halves of the rod, i. e. that of the investigated matter, and that of the standard one, — should be the same. If intensities of the li nes are determined even after the 10 step scale visually, and not by the photometer (i. e. rather roughly), we obtain here a quite new and important series of constants for the powder-pattern. Thus it is easy to understand that for diagnostic purposes it is very essential to know whether the given substance under definite conditions of photograph taking gives an intense, or a faint powder-diagram.

6. The condition formulated above as d), namely the possible rapidity and simplicity of experimental and graphical operations, has lead us at first hand to the use of exposure without filter, which needs less time and a more simple ap-

paratus; and at second hand to the compilation of auxiliary tables for calculations of spacing $\frac{d}{n}$ more detailed, than the corresponding parts of the well known international tables (*37*, II, pp. 588 — 608). These our tables shall be published in a short time.

7. We must pay attention to one circumstance more. For a greater resolving power of the powder-diagrams, and for the decrease of voltage as much as possible it is of use to take the photographs with more soft rays, thus — by the Fe-anticathode. Only when Fe-radiation is not suitable (in the investigation of compounds of the elements preceding iron: Mn, Cr, V, Ti, in consequence of a high absorption of FeK radiation and the producing of secondary X-rays, as well as in the preparation of powder-photographs of crystals, which have $\frac{2d}{n} < \lambda_{Fe}$) it is necessary to use other anticathodes: Cu, Mo, etc.

On the other hand, soft rays increase the exposure; this is their disadvantage. However, we found it reasonable to make the most part of our records with the aid of a Fe-anticathode.

8. Other conditions of our experiments are as follows: diameter of the chamber $D = 46$ mm (approxim.), diameter of the rod $d = 0{,}5 — 1{,}0$ mm; $E = 30 — 40$ kV; $I = 8 — 20$ mA. We used in all cases the Hadding's tube.

9. A constructive defect of our chamber did not allow us to obtain lines with $\angle\theta < 12°$ (aproxim.). Further, indeed, this defect is to be removed.

10. In general we have to say, that the experimental material of our determinative tables is obtained and treated in such a manner, that the unknown mineral will be identified, notwithstanding the method used, by another investigator in order to gain analogous data, if only his results are near enough to the true values of $\frac{d}{n}$.

11. As it was mentioned above, many very valuable X-ray investigations of crystals do not contain powder-diagrams and their calculation, and therefore they cannot serve as material for our determinative tables, based on precise powder-pattern data.

This explains the fact that the experimental material now available in literature is quite insufficient for the compilation of more or less complete tables not only for crystalline substances in general, but even for minerals in particular.

In addition to this it is necessary to emphasise that a suitably calculated powder pattern of a given crystalline matter is one of its most important characteristics. A crystalline matter, for which the powder pattern is unknown, is as incompletely studied as, for instance, a matter for which there is unknown its specific gravity.

It follows thereout the necessity of organization of special works for the accumulation of data, which will serve as the basis of complete X-ray determinative tables. It would be of great importance to draw attention of a possibly large number of X-ray laboratories to this study in order to contribute to the preparing and to the publishing of precisely calculated powder-diagrams, as well of those obtained for this special purpose, as those being done in connection with other X-ray investigations.

Above conditions were indicated which such powder patterns as well as their treatment have to fulfil. We consider as being of use to add hereto the forms of tables, which we put in practice in our investigations of this kind.

III. Formularies of tables for detailed powder pattern description

Here we shall give formularies for two series of tables: a) for a pair of patterns — of a pure mineral and of its mixture with NaCl, and b) for one pattern in a divided chamber of a composite rod: mineral above and standard substance (copper wire) — below.

The first series includes 4 formularies, the second — 2 ones.

Table 1

Pure mineral. Distances $2e'$ between the pairs of lines and "observed" glancing angles θ' calculated out of them

Spinel

№№ of lines.	Intensity (relative) I	Distance between lines $2e'$ mm				Maximal deviation $\Delta 2e'$ mm	$\theta' = 90° \frac{2e'_0}{\pi D}$
				3	Average $2e'_0$		
1	2	3	4	5	6	7	8
1	3	20,35	20,35	20,40	20,33	0,05	12°40′
2	2	29,70	29,75	29,75	29,73	0,05	18 31
3	6	32,90	32,85	32,85	32,87	0,05	20 28

Table

Mixture of the mineral with NaCl. Distances between the pairs of lines and "observed" glancing angles θ'', calculated from them

Spinel + NaCl

№№ of lines	Intensity (relative) I	Distance between the lines $2e''$ mm				Maximal deviation $\Delta 2e''$mm	$\theta'' = 90° \frac{2e''_0}{\pi D}$
		1		3	Average $2e_0''$		
9	10	11	12	13	14	15	16
1	2	20,45	20,45	20,50	20,47	0,05	12°45′
I	1	28,95	28,90	28,90	28,92	0,05	18 01
2,II	3	30,25	30,25	30,25	30,25	0,00	18 50
3	3	32,95	32,90	32,85	32,90	0,10	20 29

These formularies represent the first lines of the tables included in V. I. Mikheiev's work (*9*).

1) Distance $2e'$ or $2e''$ between each pair of lines on powder-diagram was measured usually three times and then we took the average $2e_0$. The results of separate measurements are given in columns 3, 4, and 11, 12, 13 of the above formularies.

2) Mesurements of $2e$ in our studies were performed by means of one of the following three methods: a) by direct juxtaposition of a verified ruler with sharp edge to the film, the ruler being divided into 1/2 mm; b) by measurement of the distance $2e$ between the middles of the lines by the aid of a divider, with following juxtaposition of the divider's legs to the same ruler; c) by the aid of a comparator (of the microscope-micrometer) with a precision up to 0,001 mm.

The first two methods give an accuracy sufficient for our purposes. The third one is more precise indeed, but it requires a comparator at hand and much more time.

3) In table 2 are usually present less lines of the mineral, than in table 1. It is desirable to indicate in table 2 the lines of the mineral by the same № as in table 1, though there will be blanks by this reason. The lines of NaCl in table 2 are shown by Roman numerals I, II, III and so on.

4) In order to separate immediately NaCl lines, it is of use to have at hand the table with $\frac{d}{n}$ of the most intense NaCl lines. This table is given below (p. 32).

NaCl powder-diagram Table 2a

Glancing angles θ are calculated from the parameter $a = 5{,}6285$ Å (*37*, II 609).

$\frac{\lambda_{FeK\alpha_1} + \lambda_{Fe\,K\alpha_2}}{2} = 1.934$ Å. $\lambda_{Fe\,K\beta} = 1{,}753$ Å (*37*, II, 586), and from the indices (nh, nk, nl) faces after the formula:

$$\sin\theta = \frac{\lambda}{2a}\sqrt{(nh)^2+(nk)^2+(nl)^2}$$

The intensities are estimated by V. I. Mikheiev (*9*) visually from an especially made powder-pattern

№№ of the lines	Intensity (relative) I	Reflection angles θ theor	Indices of net-planes n, k, l	№№ of the lines	Intensity (relative) I	Reflection angles θ theor	Indices of net-planes n, k, l
	15	19	17		15	19	17
I	–	17°19′	111α	X	4	43°25′	400α
II	4	18 09	200β	XI	2	44 08	420β
III	9	20 06	200α	XII	1	48 30	331α
IV	3	26 08	220β	XIII	2	49 43	422β
V	10	29 05	220α	XIV	10	50 12	420α
VI	2	32 39	222β	XV	10	57 12	422β
VII	1	34 44	311α	XVI	1	61 45	440β
VIII	6	36 31	222α	XVII	2	63 13	511α; 333α
IX	1	38 32	400β	XVIII	4	69 07	600β; 442β

A similar table may be calculated for $\lambda_{CuK\alpha} = 1{,}5393$ and $\lambda_{CuK\beta} = 1{,}38935$ for NaCl (*37*, II, 586), as well as for every standard matter.

Let us pass to table 3 of the first series.

Correction of angles θ of table 1

№№ of lines	Spinel		Spinel + + NaCl		NaCl			$\Delta\theta_{NaCl} = \theta'' - \theta_{NaCl}$	$\Delta\theta''$ after the curve for NaCl	$\theta_0 = \theta'' - \Delta\theta''$	$\Delta\theta' = \theta' - \theta_0$	$\delta\theta'$ after the curve without NaCl	$\theta = \theta' - \delta\theta'$
	I	θ′	I	θ″	hkl	I	θ_{NaCl}						
17	2	8	10	16	17	18	19	20	21	22	23	24	25
1	3	12°40′	2	12°45′	—	—	—	—	54′	11°51′	49′	52′	11°48′
I	—	—	1	18 01	111α	2	17°19′	42′	47′	—	—	—	—
2,II	2	18 31	3	18 50	200β	4	18 09	41	46	18 04	27	46	17 45
3	6	20 28	3	20 29	—	—	—	—	45	19 44	44	44	19 44

The first five columns (17, 2, 8, 10, 16) of table 3 are taken from tables 1 and 2. The following three (17, 18, 19) — from a table for NaCl powder-diagram. Column 20 containing values $\Delta\theta_{NaCl}$ give the difference between the values θ″ for NaCl lines observed on the pattern of the mixture and the theoretical θ_{NaCl} angles of corresponding lines. By reason of the presence of accidental errors in experimental θ values, these differences may also have a random value. For the elimination of such random errors we perform a graphical regulation of the corrections. To this purpose we take the data of column 20, i. e. the values of $\Delta\theta_{NaCl}$ as ordinates on a graphical chart and as abscissas — the corresponding angles θ″ (fig. 1, p. 8). Then on this plot we shall have a series of points (the two left ones correspond to the lines I and II in table 3). Following these points we trace a curve, extrapolating to the left in the domain of small angles.

By the aid of this curve there are then easily found values of corrections $\Delta\theta''$ for all the θ″ angles of table 3. They are contained in column 21. Substracting these values from θ″ we get corrected values θ_0 of glancing angles for mineral's lines present on the film of its mixture with NaCl (column 22). These angles

could be considered as most probable values of true glancing angles if on the mixture film there was not a superposition of several NaCl lines on the lines of the mineral, this superposition removing the latter lines from their true position. Therefore, the final values of θ angles are to be obtained from the powder pattern of the pure mineral, e. of θ′ angles of table 3.

Considering θ_0 angles as probable true angles only somewhere removed by possible superposition (and by random errors), we find corrections $\Delta\theta'$ for θ′ angles with regard to θ_0 (column 23). In order to exclude here also every possibility of haphazard sharp deviations, we perform a graphical regulation of these corrections, the same as we did it for the corrections $\Delta\theta''$ of θ″ angles. I. e. according to angles θ′ as abscissas and to corrections $\Delta\theta'$ as ordinates we trace a correction curve for the pure mineral film (fig. 2, p. 9).

By the aid of this curve we find further the final corrections $\delta\theta'$ of angles θ′ and then — according to the formula $\theta = \theta' - \delta\theta'$ the final glancing angles θ.

It is to note that on the plot of fig. 2 one can see a sharp deviation of one of the points, namely of that corresponding to the superposed lines 2, II of the mixture powder diagram 1 (tables 2 and 3). This deviation depends evidently on the superposition of NaCl lines on the line of the mineral.

Table 4

Calculation $\frac{d}{n}$ Spinel

№№ of lines	Intensity I	θ	$\frac{d_\alpha}{n} = \frac{\lambda_\alpha}{2 \sin \theta}$	$\frac{d_\beta}{n} = \frac{\lambda_\beta}{2 \sin \theta}$	$h\,k\,l$	a
1	2	25	26	27	28	29
1	3	11°48′	4,72	(4,28)	111α	8,17
2	2	17 45	(3,17)	2,88	220β	8,13
3	6	19 44	2,864	(2,596)	220α	8,10

The first three columns of this table are taken from the preceding tables. The following two columns — 26 and 27 — represent the final result of the exposed treatment of a powder pattern. Namely the values $\frac{d_\alpha}{n}$ and $\frac{d_\beta}{n}$ are to be used for our determinative tables.

Both last columns are not obligatory. They contain indices of lattice planes and lattice parameters (i. e. the edge lengths of a unit cell and the angles between them) calculated from corresponding $\frac{d}{n}$. In our work we took indices partly out of literary data and partly we have estimated indices for our powder patterns ourselves. For diagnostic purposes, according to the method we use, the determination of indices is unnecessary. It is useful in the separation of α and β lines, which may be done however in most cases by direct comparison of figures in columns 26 and 27 $\left(\frac{d_\alpha}{n} \text{ and } \frac{d_\beta}{n}\right)$, when the intensities of the corresponding lines are taken in account too.

Fictive values $\frac{d}{n}$ (see table 4) are put here in brackets. In the case of any doubt we use only one first bracket without the second one. Values of a (for polygyric crystals) or of a and c (for crystals belonging to middle syngonies) calculated from quadratic forms give us an idea of the limits of variations of these values obtained from $\frac{d}{n}$ for different lines. These disagreements are a measure of the grade of accuracy of the given $\frac{d}{n}$ for each line of the powder pattern. This is the principal aim of the estimation of indices and of the calculation of a and c, i. e. the aim of both last columns of table 4.

As mentioned above, the second series of tables for the case of a divided chamber photograph (fig. 3, p. 10) consists of 2 tables only. The numeration of the tables shall be continued.

Table 5

The half of the diagram with lines of standard (Cu)
(in a divided chamber)

№№ of lines	Intensity (absolute) I_0	$2e'_{Cu}$				Maxim. deviation $\Delta 2e'_{Cu}$	$\theta'_{Cu} = 90 \frac{2e_{Cu}}{\pi D}$ (observed)	Indices hkl	θ_{Cu} (calculated)	$\Delta\theta'_{Cu} = \theta'_{Cu} - \theta_{Cu}$
		1	2	3	Average $2e_{Cu}$					
1	2	3	4	5	6	7	8	9	10	11

Table 6

The half of the diagram with the mineral's lines
(in a divided chamber)

№№ of lines	Intensity (absolute) I_0	$2e'$				Maxim. deviation $\Delta 2e'$	$\theta' = 90 \frac{2e'_0}{\pi D}$ (observed)	$\delta\theta'$ after the curve	$\theta = \theta' - \delta\theta'$	$\frac{d_\alpha}{n} = \frac{\lambda_\alpha}{2\sin\theta}$	$\frac{d_\beta}{n} = \frac{\lambda_\beta}{2\sin\theta}$	hkl	a, b, c
		1	2	3	Average $2e'_0$								
12	13	14	15	16	17	18	19	20	21	22	23	24	25

These tables are composed in analogy with tables 1, 2, 3, 4. Therefore, after explanations, accompanying those tables, only brief comments are needed.

1) In column 2 and 13 is given the absolute photographic intensity of the lines, determined visually as it was explained above at § 5, chapter II. In tables accompanying this paper, we have not yet used this method, but we intend, after some development of its details, to describe it in a special article, and to apply it in our further work of compilation of the complete X-ray determinative tables.

2) Table 5 is composed after the half of the pattern, with fixed lines of the standard substance. In our chambers, as such a standard substance serves Cu (fig. 3, lower part). The final result of this table is contained in column 11, where are given differences of the angles θ'_{Cu} found for Cu from powder photography, and the theoretical angles θ_{Cu}, calculated for the same net-planes from their indices and from the lattice parameter a_{Cu}.

3) After these deviations we plot a curve analogous to those of figures 1 and 2, by the aid of which we find the corrections $\delta\theta'$ (column 20, table 6), for angles θ' of the crystal under examination.

IV. Principles and details of the composition of the determinative tables

1. Till now we have exposed only the preliminary general notions and informations. In this chapter we shall pass to the main features of our Roentgenometric determinative tables. In the second part of the present paper we give the first essay of this determinative tables for minerals. As yet they do not pretend to be complete; they are destined chiefly for a test of realization of our design and partly — for the practical identification of minerals. In further time we purpose to publish similar tables completed as much as possible by the new data of our laboratories and by all the available tables published by other authors. These must be gradually supplemented.

2. Alike the "Goniometric crystal determinative tables" we are publishing

(2), our "Roentgenometric determinative tables" consist of a key (index) and of descriptions of powder-patterns.

Let us at first consider the descriptions and then — the "key".

3. The powder-diagram description is arranged according to the following plan:

a) № of mineral.

b) Name of mineral.

c) Its chemical formula.

d) Indication of the crystallo-chemical group, if the mineral belongs to such one. This indication is given in form: К. Г. 71 — 77, the letters К and Г meaning "crystallo-chemical group" Thereafter follow №№ of all the minerals belonging to this group. The aim of such an indication is to draw the attention of the investigator to the necessity of comparison of the substance, to which he came in the course of the identification by aid of the determinative tables, with the substances similar by their composition and structure to that found: such a comparison is to be made in order to avoid sometimes possible errors in identification.

e) Deposit of the investigated sample.

f) Chemical analysis.

g) Physical properties.

h) Physico-chemical and chemical properties.

i) Conditions of *X*-ray photograph preparation, namely: 1) anticathode material, 2) presence (or absence) of filter, 3) chamber diameter D, 4) sample diameter d, 5) voltage, 6) current power, 7) exposition, 8) method of corrections. It is to be remembered here once more, that we have used three methods of corrections: 1) by the aid of two patterns (one — of the mixture with NaCl and another — of the pure mineral); 2) after a single pattern of the mixture with NaCl; 3) after a single pattern in a divided chamber (see fig. 3) of a composite rod: mineral above, copper wire below.

j) Syngony and space group of symmetry.

k) Dimensions of a unit cell of the lattice. If the author of these constants is not quoted, it means that they are given after the first author mentioned in literature references below the table.

l) Table of lines; its columns see in the last part of the present work; this table represents an extract from an original paper, cited in the first place in the reference closing each description.

m) Literature reference. The paper indicated here in the first place without brackets has afforded the main part of the material for all the above mentioned data. Papers in brackets have usually served to supply data less essential or even only for comparison. Several papers are mentioned only as bibliographical material containing *X*-ray data for a given mineral, and being not at all used here for our purposes. When the determinative tables will be composed finally, it will be desirable to give at this place a complete bibliography of the *X*-ray investigations of a corresponding mineral. In the present paper we did not intend to give a full bibliography.

4. Moreover, in the present work, too, we have no purpose to collect data on the powder patterns of all minerals for which there had ever been made such photographs up till now.

5. It is necessary to note, that all the descriptions are arranged in our table according to the mineralogical system. We have adopted here the system of the A. K. Boldyrev's (3) Text-book of "Descriptive Mineralogy" and of "The Course of mineralogy" (1936) edited by Boldyrev, Rasumovsky and others.

6. Now let us examine the "key" Its destination is to make possible a systematical search of the mineral corresponding to a powder-pattern of an unknown matter.

The key is to be adopted to the indentification of a pure mineral, as well as to its identification in a mixture with other minerals.

7. The first design of the key was given in V. I. Mikheiev's paper (9).

However, before the publication of this work, there appeared A. V. Waldo's paper (*61*) where was given another more expedient design of such index. In our present work we use the principles which Waldo took as a basis of his key (his first index) arrangement. We complete these principles by a set of essential details which shall be pointed out below.

8. We have already mentioned above that the characteristic of a powder diagram, consisting of a series of $\frac{d}{n}$ and I values of its lines one of the most important diagnostic properties of a crystalline matter. However it is to be noted that even such results of a powder-pattern treatment, devoid of the influence of the wave-length λ, of the chamber diameter D and of the specimen diameter d, are yet dependent on the experiment conditions.

Namely, parallel to the exposure, to the diminishing of the general fogging on the film and parallel to the replacement of the anticathode by that with a smaller 1) the number of the lines, appeared on the pattern, increases, and 2) the intensity of the lines varies. Only $\frac{d}{n}$ of the corresponding lines remains strictly constant for a same substance. The values of I given in the 10-step scale are nearly constant for corresponding lines only on the records of the same sample by the same apparatus and under wholly analogous other experiment conditions: even in such cases one must keep in mind that the visual estimation of the intensity can give errors up to 2 degrees of the ten-degree scale.

For the records of different specimens in various experiment conditions these divergences can be much more considerable. The most influential factors are for instance: the use of filter, great exposure difference, and changes in mineral composition. Only a general course of the change of intensity from line to line is independent of these random factors as much as it is not broken by errors of visual estimation. This course of the intensity change (but not the balls themselves) must be used in the last account in the identification of powder-patterns recorded at very different conditions.

9. At short exposure or at low content of the given crystalline matter in a mixture, the powder-pattern show only the most intense lines of this matter.

Moreover, it is clear that on the photographs made with the aid of anticathodes with a larger wave length (for instance with Fe-anticathode), the lines of small values of $\frac{d}{n}$ cannot appear on the powder-diagram, although they possess a sufficient intensity when photographed by means of other anticathodes (Cu, Mo, W). Their absence at Fe-anticathode use depends on the condition: $\frac{d}{n} \geqslant \frac{\lambda}{2}$ that follows from the Bragg's-Wulf's formula.

10. The above statements lead us to the following general operation for the identification of crystalline substances by means of powder diagrams: after the powder pattern of an unknown matter is made, we must take the most intense line of this pattern and search such a standard powder photograph on which there is present a line with the same value of $\frac{d}{n}$ (in error limits), and with a maximal intensity too.

As there may exist many of such standard powder-diagrams, it is necessary to compare each of them with the powder pattern of the matter investigated, and to find among them that which is identic with the pattern under investigation.

The identification of crystalline substances which compose any mixture by means of powder-diagrams shall be discussed later.

11. The foregoing paragraph shows that the simplest method of key composing would be as follows. One could choose only one line, the most intense one of the powder-diagram of each standard, and arrange the interplanar distances $\frac{d}{n}$ of these lines in the order of decrease, accompaning them by the name of the standard matter and by its number, after which it would be easy to find

a detailed description of the complete powder pattern of the corresponding substance. After such a list (or key) it would be very simple to make the first choice of the matters, that was mentioned in paragraph 10.

However, many circumstances obliged us to complicate the form of the index, depicted above. First of all, on a given powder-diagram there may occur many lines (for instance 3) with the intensity 10. Evidently, in compiling the key we cannot prefer any of them to the other. Therefore such a substance is to be put down into the key three times after $\frac{d}{n}$ of each of its lines with the intensity 10.

12. Then, as the visual estimation of intensity cannot be considered as quite exact, it is possible that the intensity of some line, estimated on the powder pattern as 10, was adopted equal to 9 on the standard powder-diagram of the same substance when the tables were compiled.

We think that after sufficient experience it is impossible to confound intensities evaluated by 10 and 8, and in general those which differ by two degrees (or steps). (The practice of the use of the essay determinative tables here published will show whether the error limits pointed out are sufficient, or not. It is possible that they must be enlarged up to 1 or 2 marks. This would not change the exposed principles of construction of the key.)

It is clear therefore that one must introduce the given substance into the key as many times as many of its lines have the intensity equal to 10 and 9.

As an example of this may serve the mineral hausmannite. Its description is easely found under the № 104. It has two lines with a relative intensity 10, and one line with the intensity 9. Corresponding values $\frac{d}{n}$ for these lines are: 2,73; 2,45; 1,53. After each of these spacings hausmannite is put down into the key asit can be seen when searching these values in its first column.

13. In few cases, when the powder patterns were very faint, we began our evaluations of lines intensity not by the mark 10, but by mark 7, 6, etc.

In such cases the substance was also introduced into the key according to all its lines with two highest marks of intensity.

As an example of such substances in our determinative tables published here, may serve the mineral thorite. The description of its powder pattern can easily be found below under № 48. The most intense lines have following I and $\frac{d}{n}$: 1) 4 and 2,583; 2) 3 and 2,855; 3) 3 and 1,664. After these $\frac{d}{n}$ values it is included three times in the key (see further, the key).

14. A second complication of the key consists in the fact that in all cases we give there $\frac{d}{n}$ of no less then five the most intense lines though with $I < 9$. If a given powder-diagram has more than five lines with intensity 10 and 9, all of them are included too. Thus, for a little number of substances there are given in the key the values of $\frac{d}{n}$ for 6—7 lines. In this addition of lines in the key besides the absolutely necessary one we follow Waldo (*61*) and we do it in order to facilitate and to accelerate the identification. These 5—7 lines represent according to V. I. Mikheiev (in his article *9*) the "characteristic complex" of lines of a given powder pattern. We diminish here only the number of the lines of the "characteristic complex" from 10, as adopted by V. I. Mikheiev, to 5—7.

Let us note that since β-lines are considerably weaker than α-lines, —only the latter (almost without exception) are included in the "characteristic complex" and along with in the key itself. This confirms that it is quite admissible for the diagnosis after our method to prepare the powder-photographs without a filter.

15. The purpose of including in the key of the whole characteristic complex of lines is as follows. As explained in § 9, by the aid of the most intense line on the powder-diagram of an unknown matter, we choose some 5—10 substances

with approximate values of $\frac{d}{n}$. Instead of applying immediately thereafter to the detailed descriptions of powder patterns, one can compare at first the given powder diagram with the characteristic complex of each matter included in the key choosen in the limits of possible error. This comparison allows to reject at once all the substances with powder patterns which differ enough from the given one. After this rejection there will remain only one or very few convenient substances. Thus, the number of detailed descriptions to revise as well as the time of identification will be considerably diminished.

16. Finally the last complication of the key consists in the addition to the name of the substance of its chemical formula. This again facilitates and accelerates the identification, especially in those cases, when we have already some preliminary considerations on the possible composition of the substance under examination as is often the case especially when minerals are identified.

We can conclude thereby the description of the key.

17. Some words are to be said on the differences between our key and the key ("index 2") of A. W. Waldo.

1) We give relative intensities of the lines according to the 10 mark (10 step) scale. Waldo uses sightfully only a 5 mark scale, though in the choice of lines for the key he adopts, moreover, several differences between lines evaluated by a same mark of intensity. He does not give the intensities in his key, but he shows only their order.

2) We put in the key no less than 5 lines, or, in cases explained above, some more. Waldo includes in his key from 2 to 6 lines and thereby sometimes lines of a same intensity are partly included and partly not included. [See (*61*) for instance, linarite, boléite and other.]

3) According to all the lines with intensity 10 and 9 the mineral is entered in our key.

4) Finally we give in our key the chemical composition of the mineral. This is absent in Waldo's key.

18. When we separate in our key substances with $\frac{d}{n}$ of their most intense lines approximate enough to $\frac{d}{n}$ of the powder pattern of the unknown matter, it is of great importance to establish the possible limits of error in estimation of $\frac{d}{n}$ values. In the description of the powder patterns we have almost always given these values with an accuracy up to 0,001 Å except the zone of small angles θ, where the accuracy is mostly 0,01 Å only. In our present work and in former ones we have drawn a comparison of the data for $\frac{d}{n}$ of different writers for the same minerals. This comparison shows that, for crystals of a constant composition, such as CO_3Ca, Fe_2O_3, Fe_3O_4, SiO_2, etc., in case of sufficient experience of the investigator and of careful enough though not especially precise, work — the differences of $\frac{d}{n}$ values, found by different authors for the same lines vary within the limits from 0 for the sharpest lines to 0,02 Å for the less sharp ones, and that they are in general larger for lines with small angles θ and less for lines with greater angles θ.

It may approximatively be admitted that data on $\frac{d}{n}$ values, given in our determinative tables (except those few ones, which are given with two decimals) for the sharper lines of crystals with a constant composition, are estimated with an error less than $^1/_2\%$. For lines where $\frac{d}{n} = 1$ Å it will be 0,005 Å, for lines where $\frac{d}{n} = 10$ Å, — it gives 0,05 Å. However we take the possible error equal to 1%.

Therefore, if a most intense line of the matter under examination has, for instance, an interplanar distance $\frac{d}{n} = 2{,}051$ Å, — when looking for substances

with suitable values of $\frac{d}{n}$ in the first column of our key, one has to choose substances within the interval $\pm 0{,}02051$ Å, i. e. from $\frac{d}{n} = 2{,}072$ Å to $\frac{d}{n} = 2{,}030$ Å.

19. For bad photographs, or for less accurate work, or for minerals of variable composition, these limits must be widened to $1^1/_2$—2 and more per cent. If the investigator knows approximately the grade of accuracy of his work, he may always establish the limits in which he has to search and to separate the substances in the key during the identification.

20. All above said (§ 19) shows that our determinative tables may be applied even in the case of less accurate methods of $\frac{d}{n}$ correction, namely at the preliminary calibration of the chamber by means of a separate photograph of NaCl, and by means of different calculation methods.

21. The above statements are quite sufficient for the understanding of the course of identification of a matter with the aid of the determinative tables we publish.

Now let us turn to concrete examples illustrating the identification process.

V. Examples of identification

We shall examine here two examples: a simple one (identification of a separate mineral) and a more complicate one (determination of minerals in a mixture of them).

We shall presume, therewithal, that nothing is known about the mineral substance to be determined, except its $\frac{d}{n}$ and I table. Practically indeed we know always something more, at least its appearance.

First of all, let us formulate several general rules which are to be followed in the identification procedure.

a) If the given substance in a mixture is present in a quantity large enough for the appearance of its lines on the powder pattern in given experiment conditions, then its lines will appear in order of their intensity. If the exposure is too short or the film is a fogged one, the weakest lines may not appear at all on the film. If any line of the given substance is absent on the powder diagram, none of the weaker lines of this matter can appear. However, it is to be remembered, that the visual evaluation of intensities may give errors to 1—2 and in some cases 3—4 units of the 10-mark scale.

b) On powder diagrams of a mixture in the case of a small content of a mineral, its lines may display a considerably lowered intensity.

c) In mixtures, in consequence of the superposition of lines of one mineral on those of others, the intensities may highly vary not only in their absolute, but also in their relative value.

I Example. Let us suppose that a sufficiently accurately made and suitably calculated powder-diagram has given results, quoted in the first four columns of table 7. We take the first of the most intense lines of the unknown matter. It is the line № 3. For it we have: $\frac{d}{n} = 4{,}168$, $I = 10$. Let us add $\pm 1\%$ to $\frac{d}{n}$. We obtain then such an interval: from 4,210 to 4,126. Now, we look in the key for this interval among the figures of the first (left) column. We find here that in the fixed limits there are contained 3 substances, and we examine them one after another.

1) $\frac{d}{n} = 4{,}194$, $I = 10$. Kaolinite. Its second line has: $\frac{d}{n} = 4{,}464$, $I = 10$. Such a line is absent in the investigated mineral pattern. Kaolinite does not fit.

2) $\frac{d}{n} = 4{,}178$, $I = 10$. Hydrogoethite. Its second line: $\frac{d}{n} = 2{,}450$, $I = 10$. To it corresponds the line № 9 of the unknown substance (within the limits of error

$\pm 1\%$) with the intensity $I = 10$. The third line of hydrogoethite has $\frac{d}{n} = 2{,}690$, $I = 8$. The corresponding line № 6 of the unknown matter has $I = 10$. To the fourth and the fifth lines of hydrogoethite with $\frac{d}{n} = 1{,}719$ and 2,189 and with $I = 8$, and 6 correspond lines № 16 and № 11 with $I = 9$ and 6. Thus all the lines of the characteristic complex of hydrogoethite are fitting well. In order to check definitively this preliminary identification we find by the aid of the № of hydrogoethite (№ 66), written in the right column of the key and following the name of the mineral, a detailed description of its powder pattern. Therefrom we write down (in table 7) $\frac{d_\alpha}{n}$ and I for all its lines without any omission, and look then whether they correspond or not to the same values of the same lines of the unknown mineral. From table 7 we see a doubtless agreement of both powder diagram in $\frac{d}{n}$ and in I. An exception is presented only by 8 faint lines of the unknown mineral having intensities 1, 2, 3; six of them lay among those with

Table 7

Identification of a separate mineral

	Unknown mineral				Hydrogoethite		
	№	I	$\frac{d_\alpha}{n}$	$\frac{d_\beta}{n}$	I	$\frac{d_\alpha}{n}$	Δ
	1	1	4,935	(4,476)	—	—	—
	2	1	(4,607)	4,178	2	(4,613)	+ 0,006
	3	10	4,168	(3,780)	10	4,178	+ 10
	4	1	3,359	(3,042)	3	3,385	+ 26
	5	1	(2,960)	2,685	1	(2,975)	+ 15
	6	10	2,686	2,435	8	2,690	+ 4
	7	3	2,572	(2,333)	3	2,580	+ 8
	8	1	(2,472)	2,241	—	—	—
	9	10	2,435	(2,208)	10	2,450	+ 15
	10	5	2,245	(2,036)	4	2,253	+ 8
	11	6	2,180	(1,977)	6	2,189	+ 9
	12	1	2,004	(1,818)	1	(2,020	+ 16
diffuse	13	2	1,916	(1,778)	1	1,923	+ 7
	14	2	1,896	(1,755)	1	(1,895)	— 1
	15	3	1,797	(1,668)	2	1,832	+ 35
	16	9	1,716	1,556	8	1,719	+ 3
	17	4	1,686	(1,529)	2	1,692	+ 6
	18	2	(1,654)	1,500	1	(1,659	+ 5
	19	4	(1,599	1,450	2	1,603	+ 4
	20	8	1,559	1,414	6	1,564	+ 5
	21	6	1,505	(1,365	4	1,510	+ 5
	22	7	1,450	1,315	4	1,454	+ 4
	23	3	1,419	(1,290)	2	1,423	+ 4
	24	2	1,392	(1,262	2	1,395	+ 3
diffuse	25	4	1,353	(1,229	1	1,362	+ 9
	26	5	1,315	(1,193	2	1,319	+ 4
	—	—	—	—	1	(1,292	—
	27	2	1,264	(1,147	1	1,266	+ 2
	28	2	1,239	1,124	1	(1,246	+ 7
	29	3	1,197	(1,086)	—	—	—
	30	2	1,144	(1,038)	—	—	
	31	5	1,124	(1,020	1	(1,127	+ 3
	32	1	(1,093	(0,991	—	—	
	33	1	(1,065	(0,961	—		
	34	2	(1,050	(0,955		—	
	35	3	(1,022	(0,927	—	—	

About one or two brackets see p. 41.

small $\frac{d}{n}$ (i. e. large glancing angles θ). The presence of these lines in the pattern of the mineral under determination and their absence in the standard pattern is easily explained by the circumstance, that evidently the standard powder pattern is in general fainter than the mineral's one, and the fog at its border parts is denser in comparison with the powder pattern of the mineral to be identified. Then the presence of one supplementary line in the standard pattern (between № 26 and № 27) with the intensity $I = 1$ is not surprising because the lines with $I = 1$ are at the visibility limits and therefore they may be occasionally overlooked by the investigator. Thus, hydrogoethite is quite fitting.

However, the identification cannot be considered as completed, because in the above mentioned interval of the key (from 4,210 to 4,216) one matter is still present: pyrophyllite.

3) $\frac{d}{n} = 4{,}15$, $I = 9$. Pyrophyllite (see p. 50). Its second line: $\frac{d}{n} = 2{,}56$, $I = 10$. The line № 7 of the unknown matter corresponds to this second line after spacing $\left(\frac{d}{n} = 2{,}572\right)$ $(I = 3)$. However its intensity is too weak. Therefore the pyrophyllite should be put aside. For a complete certainty we must consider its following lines. Its third line: $\frac{d}{n} = 2{,}43$, $I = 10$, has a corresponding line № 9 on the powder photograph of the unknown mineral $\left(\frac{d}{n} = 2{,}435, I = 10\right)$. But the fourth line of the pyrophyllite: $\frac{d}{n} = 4{,}45$, $I = 9$ is quite absent on the pattern under determination. Pyrophyllite does not fit. The identification is finished.

The identification process (leaving aside its experimental part) takes here only 15—20 minutes.

The experimental part, when a well arranged apparatus is available, requires from 2 to 25 hours of work in dependance on the experimental conditions and on the investigated substance. At the simultaneous exposure of 5 powder-diagrams the experimental part of the identification of each of them requires approximately $^1/_2$—5 hours. To this it is to be added the calculation treatment of the powder pattern, which needs about 5—20 hours.

II Example. The results are given of a suitable treatment of a powder pattern of an unknown mineral substance, represented in the first 4 columns of table 8. The photograph was made without filter (the Fe-anticathode was used), and therefore there are present both α- and β-lines. Comparing the $\frac{d_\alpha}{n}$ values with those of $\frac{d_\beta}{n}$ and also the corresponding intensities I of different lines, we part them into α and β. At lines produced doubtless by β-radiation only, the values $\frac{d_\alpha}{n}$ are put into simple brackets, for those produced probably by β-rays or by both α- and β-rays, — $\frac{d_\alpha}{n}$ values have only one bracket before them. Likewise for $\frac{d_\beta}{n}$.

I. Let us take the first most intense line. It will be № 7. For it $\frac{d}{n} = 2{,}52$, $I = 10$. By addition of $\pm 1\%$ to $\frac{d}{n}$ we get an interval from 2,545, to 2,495. In the key 12 substances are included in this interval. Let us examine them one by one.

1) $\frac{d}{n} = 2{,}545$, $I = 10$. Acmite. Its 2-d line has $\frac{d}{n} = 3{,}012$, $I = 10$. To it corresponds line № 1 of the mixture powder-diagram $\left(\frac{d}{n} = 3{,}09, I = 1\right)$. In consequence of the weak intensity of the last, there is very little acmite if any and line № 7 is not fully explained by this mineral.

Identification of the mineral components of a mixture

Unknown miner.				Are present						Are absent or present in very small quantity	
				Tenorite		Cuprite		Copper		Wood tin	
№	I	$\frac{d_a}{n}$		I	$\frac{d_a}{n}$	I		I		I	$\frac{d_a}{n}$
1	1	3,09	2,80								
2	1	3,02	2,74			4	3,02				
3	2	2,89	2,62							1	2,89
4	3	(2,79)	2,53								
5	3	(2,72	2,46	4	2,74						
6	2	(2,56)	2,32							(5	2,63)
7	10	2,52	2,29	10	2,53						
8	9	2,46	2,23			10	2,46				
9	10	(2,31	2,10	10	2,32					(4	2,36)
10	½	2,18	1,98								
11	7	2,13	1,93			8	2,13				
12	1	2,08	1,89					9	2,085		
13	1	(2,05)	1,86								
14	1	1,950	1,768	1	1,951					3	1,94
15	1½	1,926	1,745								
16	1½	(1,901	1,716								
17	7	1,858	1,685	8	1,865					1	1,85
18	½	1,811	1,642					8	1,806		
19	½	1,773	1,608							10	1,761
20	2	(1,732)	1,570			2	1,740				
21	5	1,703	1,544	6	1,710						
22	4	(1,654)	1,501								1,672
23	1	1,618	1,460								
24	6	(1,570	1,426	4	1,578					2	1,587
25	2½	(1,548)	1,404							2	1,554
										(1	1,526)
26	10	(1,496	1,356	8	1,501	8	1,506			8	1,497
27	1	1,421	1,319							7	1,435
28 [1]	6	(1,414	1,282	8	1,410					7	1,410
29	6	(1,405	1,274								
30	8	1,371	1,244	8	1,370						
31	2	1,348	1,222			4	1,345			1	1,338
										(4	1,320)
32	3	1,290	1,170	2	1,302						
33	7	1,283	1,164			8	1,282	10	1,276		
34	6	1.260	1,143	6	1,260						
35	4	1,229	1,115			6	1,230				
										(8	1,214)
36	3	1,193	1,082	3	1,193					3	1,183
37	3	1,166	1,058							7	1,153
38	2	1,157	1,049	2	1,155			2	1,041β		
39	1	1,123	1,018	1	1,112					6	1,116
40 [1]	4	1,095	0,993							7	1,090
41	2	1,089	0,970	7	1,082			9	1,089	8	1,079

[1] The lines 28 and 29 join practically together; the lines 40 and 41 represent a close doublet at the very border of the film.

2) $\frac{d}{n} = 2{,}541$, $I = 10$. Magnetite. Its second line: $\frac{d}{n} = 1{,}612$, $I = 9$. To it corresponds the line № 19 of the mixture, having $I = {}^1/_2$. The same conclusion as for acmite.

3) $\frac{d}{n} = 2{,}54$, $I = 10$. Azurite. Its second line has $\frac{d}{n} = 5{,}20$. It is absent in the mixture pattern. Azurite is not fitting (is absent).

4) $\frac{d}{n} = 2{,}534$, $I = 10$. Montmorillonite. The second line: $\frac{d}{n} = 4{,}45$. It is absent in the mixture photograph. Does not fit.

5) $\frac{d}{n} = 2{,}534$, $I = 7$. Arsenolite. Second line $\frac{d}{n} = 3{,}189$. Such a line is absent in the mixture pattern, the mineral is not fitting.

6) Tenorite. Second line $\frac{d}{n} = 2{,}32$, $I = 10$, $\frac{d}{n} = 2{,}53$, $I = 10$. It corresponds to the line № 9 of table 8. The 3-rd line of tenorite, having $\frac{d}{n} = 1{,}865$, $I = 8$, corresponds to line № 17 of table 8. The 4-th and 5-th lines of tenorite, having $\frac{d}{n} = 1{,}501$ and 1,410 and $I = 8$, correspond to the line № 26 and №№ 28—29. Thus all the characteristic complex of the tenorite lines is present in the powder pattern of the mixture examined. To be definitively sure of the presence of tenorite, we look, according to its № 40, put in the key after its name, for a detailed description of its powder-diagram, and we write out all the lines without omission (see columns 5 and 6 of table 8). It is clear therefrom, that all of them without exception are present in the mixture powder pattern. And moreover, not only, $\frac{d}{n}$, but intensities coincide too, except the following two cases: a) the line № 24 of the mixture has $I = 6$, while the corresponding line of tenorite has $I = 4$ only; but that is easily explained by the fact that the line № 24 is not only an α-line, but a β-line of № 28 too;

b) line № 41 of tenorite has $I = 7$, the corresponding line of our mixture has $I = 2$. But we have to note that 1) P. Niggli, who has given this standard line, had used a copper anticathode and therefore in his pattern this line superposes probably № 40, and 2) that we have also both these lines almost undivided and moreover they lay on the very border of the film, where a strict evaluation of intensities is difficult.

Thus tenorite is doubtless present in the mixture.

7) $\frac{d}{n} = 2{,}523$, $I = 10$. Diopside. Its second line: $\frac{d}{n} = 3{,}00$, $I = 10$. To it corresponds the line № 2 of the mixture with intensity = 1. The same remark as for acmite.

8) $\frac{d}{n} = 2{,}523$, $I = 10$. Inyoite. Its second line has $\frac{d}{n} = 2{,}792$, $I = 10$. To it corresponds the line № 4 of the mixture with intensity = 3. Third line: $\frac{d}{n} = 2{,}052$, $I = 9$. To it corresponds line № 13 of the mixture with $I = 1$. Therefore one may remark on inyoite the same as on acmite: it is either absent or it is present in a very small quantity.

9) $\frac{d}{n} = 2{,}51$, $I = 10$. Antlerite. Second line: $\frac{d}{n} = 3{,}85$, $I = 10$. Such line is absent in the mixture powder pattern. Does not fit.

10) $\frac{d}{n} = 2{,}499$, $I = 10$. Chrompicotite. Second line: $\frac{d}{n} = 1{,}592$, $I = 9$. It has no corresponding line in the mixture diagram; does not fit.

11) $\frac{d}{n} = 2{,}497$, $I = 10$. Jadeite. Second line: $\frac{d}{n} = 2{,}938$. Such a line is absent in the mixture pattern. Does not fit.

12) $\frac{d}{n} = 2{,}495$, $I = 10$. Cobaltite. Second line has $\frac{d}{n} = 2{,}278$, $I = 10$. Such a line is absent in the mixture. Does not fit.

Thus the selection after the line № 7 gives the following results:

Doubtless presence — tenorite.

The powder pattern does not contradict the presence of small quantities of acmite, magnetite, diopside, inyoite.

II. Among the remaining unoccupied lines of the mixture let us take the first of the most intense ones. It will be (see table 8) the line № 8. For it $\frac{d}{n} = 2{,}46$, $I = 9$. Adding $\pm 1\%$ to $\frac{d}{n}$, we have such an interval: from 2,485 to 2,435. We open the corresponding pages of the key, and see that within these limits there are included 11 substances. Let us examine them.

1) $\frac{d}{n} = 2{,}48$. Connellite. The second line has $\frac{d}{n} = 2{,}72$, $I = 10$. To it corresponds the line № 5 of the mixture, with $I = 3$. The third line: $\frac{d}{n} = 2{,}27$, $I = 10$. This line is absent in the mixture pattern. Connellite is absent.

2) $\frac{d}{n} = 2{,}477$, $I = 9$, Serpentine. Second line: $\frac{d}{n} = 3{,}656$, $I = 10$. Absent in the mixture. Serpentine is absent.

3) $\frac{d}{n} = 2{,}463$, $I = 8\frac{1}{2}$. Serpentine. Its second line: $\frac{d}{n} = 3{,}695$, $I = 10$. It is absent in the mixture record (table 8). Serpentine does not fit.

4) $\frac{d}{n} = 2{,}46$, $I = 10$. Cuprite. Its second line: $\frac{d}{n} = 2{,}13$, $I = 8$. To that fully corresponds the line № 11 of the mixture. Third line of cuprite: $\frac{d}{n} = 1{,}506$, $I = 10$. With it agrees very well the line № 26 of the mixture. The fourth line of cuprite: $\frac{d}{n} = 1{,}282$, $I = 8$. To it fully corresponds line № 33 of the mixture. Fifth line of cuprite: $\frac{d}{n} = 1{,}230$, $I = 6$. To it corresponds line № 35 of the mixture with a somewhat less intensity $I = 4$. Thus, according to the characteristic complex of the lines cuprite is present in the mixture, and it is there as an essential component. In order to be quite sure of it (as well as during the identification of tenorite), after the cuprite number in the key (№ 41) we find its detailed description and write down into table 8 all the lines without any exception, one by one. The presence of all of them in the mixture pattern proves undoubtedly that cuprite is present in the mixture too.

5) $\frac{d}{n} = 2{,}451$, $I = 9$. Asharite. Its second line: $\frac{d}{n} = 2{,}690$, $I = 10$. Is absent in the mixture. This mineral does not fit.

6) $\frac{d}{n} = 2{,}450$, $I = 10$. Hydrogoethite. The second line $\frac{d}{n} = 4{,}178$, $I = 10$. Absent in the mixture, does not fit.

7) $\frac{d}{n} = 2{,}45$, $I = 10$. Hausmannite. Its second line: $\frac{d}{n} = 2{,}73$, $I = 10$. To it corresponds line № 5 of the mixture with $I = 3$. Its third line: $\frac{d}{n} = 1{,}53$, $I = 9$. It is absent in the mixture. Does not fit.

8) $\frac{d}{n} = 2{,}45$. Wad. The intensity of this strongest line of wad in the standard pattern is equal to 4. The second line of wad has $\frac{d}{n} = 1{,}491$, $I = 4$. To it corresponds the 29-th line of the mixture with $I = 4$. No other lines of standard wad are shown. Therefore the presence of wad in the mixture is possible, but, in consequence of a very small quantity of lines, it cannot be in any way regarded as proved.

9) $\frac{d}{n} = 2{,}441$. Spinel. Second line: $\frac{d}{n} = 1{,}427$, $I = 10$. To it corresponds line № 27 of the mixture, but the intensity of the latter is only 1. It may be only in the case if spinel is present in a very small quantity in the mixture; or one may suppose that the second line corresponds to the line № 28 of the mixture with a difference of $\frac{d}{n} = 0{,}014$ Å and with $I = 6$. Third line: $\frac{d}{n} = 1{,}053$, $I = 10$. This line is beyond the limits of our powder pattern of the mixture. Fourth line: $\frac{d}{n} = 2{,}020$, $I = 9$. To it corresponds line № 13 of the mixture, with intensity $= 1$, yet being occupied by β-line (of № 17) of tenorite. Fifth line: $\frac{d}{n} = 1{,}552$, $I = 9$. It agrees with line № 25 of the mixture with intensity $I = 2^1/_2$, also occupied by β-line (of № 29) of tenorite.

We see that the characteristic line complex of spinel is present on the whole in the mixture powder-diagram, coinciding partly with its faint lines. According to these data the presence of spinel in small quantity seems possible. However, if even spinel is present, its presence does not explain the existence of the strong line № 8 with $I = 9$.

10) $\frac{d}{n} = 2{,}44$, $I = 10$. Penroseite. Its second line: $\frac{d}{n} = 2{,}67$, $I = 10$. Such line is absent in the mixture. Does not fit.

11) $\frac{d}{n} = 2{,}438$, $I = 10$. Hydroboracite. Its second line: $\frac{d}{n} = 1{,}908$, $I = 8$. To it corresponds line № 16 of the mixture with $I = 1^1/_2$. Third line: $\frac{d}{n} = 2{,}210$, $I = 6$. Such a line is absent in the mixture. The possibility of the presence of hydroboracite in small quantity is not excluded, since the absent lines (to begin with the 3-rd one) have a considerably lower intensity than the present ones.

Thus the search in the key for the standard mineral explaining line № 8 of the mixture has lead us to following conclusions:

Doubtless presence: cuprite.

Possible presence of small quantity of wad, spinel, hydroboracite.

III. Examining further the line unoccupied by tenorite and cuprite, we choose again the most intense of them. Such a line is № 40. For it $\frac{d}{n} = 1{,}095$, $I = 4$. Let us add $\pm 1\%$ to $\frac{d}{n}$. Then we get the interval from 1,106 to 1,084. In the key we find in this interval the following 2 substances:

1) $\frac{d}{n} = 1{,}101$. Grossularite. Its second line: $\frac{d}{n} = 2{,}662$, $I = 10$. Such a line is absent in the mixture diagram. Does not fit.

2) $\frac{d}{n} = 1{,}089$. Copper. Its second line: $\frac{d}{n} = 1{,}276$, $I = 10$. To it corresponds line № 33 of the mixture. Third line: $\frac{d}{n} = 2{,}085$, $I = 9$; it agrees with line № 12 of our mixture with the intensity 1. Fourth line of copper $\frac{d}{n} = 1{,}806$, $I = 8$. To it corresponds line № 18 of the mixture with $I = 1/2$. Fifth line of copper: $\frac{d}{n} = 1{,}042$, $I = 5$. It is situated beyond the border of the mixture diagram.

Thus copper is present, but in small amount.

Passing over to the detailed description of copper (№ 1) we see that its powder-pattern, given in the determinative tables has only those five lines. Let us write them down in the appropriate places of table 8.

Thus, copper is present in the mixture in a relatively small amount.

IV. Hereafter there remain unoccupied the following 9 lines of the mixture.

№№	1	3	10	15	16	19	23	27	37
I	1	2		$1^1/_2$	$1^1/_2$	$^1/_2$	1	1	3

Now let us examine the line № 37. Its $\frac{d}{n} = 1{,}166$, $I = 3$. Adding $\pm 1\%$ to $\frac{d}{n}$, we get an interval from 1,178 to 1,154. Within this interval there are no lines at all in the key. This may be explained by several circumstances.

1) By the fact that, thanks to the incompleteness of our determinative tables which are only a preliminary essay of such tables, the mineral giving this line is yet absent in the tables.

2) By the fact that this line does not belong to the lines of the characteristic complex, and is a faint line of a mineral (not yet found by us) the characteristic lines of which have coincided with those of tenorite, cuprite and copper, these lines being occupied before.

In the first case obviously we cannot yet identify at all that mineral which gives such a line. In order to avoid this cause, hindering the identification, it is necessary to compile complete determinative tables.

In the second case one may try to found this mineral examining all the intense lines ($I > 3$) of the mixture powder pattern, besides the already examined № 7 and № 8.

Let us make such an examination of the key by use of line № 9 following № 7 and № 8. For line № 9 we have: $\frac{d}{n} = 2{,}31$, $I = 10$. Adding $\pm 1\%$ to $\frac{d}{n}$, we get the limits from 2,333 to 2,287. Within this interval in the key there are found 4 substances: let us examine them.

1) $\frac{d}{n} = 2{,}33$, $I = 10$. Emplectite and wolfsbergite. Their second line has $\frac{d}{n} = 3{,}22$. $I = 10$. This line is absent in the photograph of the investigated mixture. (The chamber construction permitted the appearing of lines with $\frac{d}{n} \leqslant 5{,}60$ Å). Thus these minerals are absent in our mixture.

2) $\frac{d}{n} = 2{,}32$, $I = 10$. Boleite. Its second line has $\frac{d}{n} = 4{,}40$, $I = 10$. This line is absent in table 8. Boleite is absent.

3) $\frac{d}{n} = 2{,}32$. Tenorite. It was stated above that tenorite is present in the mixture.

4) $\frac{d}{n} = 2{,}29$. Silver jodide. Its second line has $\frac{d}{n} = 3{,}75$. The mixture has no such line. Does not fit.

Thus our search after this line in the key has shown that this line cannot belong to any mineral of those which are included there except tenorite.

Just likewise we can convince ourselves that no other possible mineral may give the lines №№ 11, 17, 21, 22, 24, 26, 28, 29, 30, 33, 34, 35 with intensities higher than 3, i. e. higher than that of line № 37.

This shows us, that line № 37 belongs to some mineral, not yet embraced by our determinative tables in their present "in embryo" state.

V. Operating in the same manner with the remaining 8 lines as we have just done with № 37, we shall easily convince ourselves, that the search after these lines in the key will lead us or to no mineral having an appropriate powder pattern, or it will lead us to such ones, the most intense line of which shall correspond only to one of the weak remaining lines of the mixture, all other lines of this mineral will be absent in the mixture diagram.

Under such conditions the present method may give only a series of minerals, the presence of which is not contradicted by the mixture powder-diagram. A part of such minerals appeared in our investigations for instance in the case, when we have looked for line № 8 (wad, spinel, hydroboracite). Other minerals were similarly found after the remaining faint lines; namely line № 15 ($\frac{d}{n} = 1{,}926$, $I = 1^1/_2$) led us to the possible presence of bornite (its strongest line: $I = 10$, $\frac{d}{n} = 1{,}925$, but several of its lines with $I = 8$ are yet absent in our mixture), of wood tin (its line $I = 10$, $\frac{d}{n} = 1{,}761$ may correspond, though not very well to line № 19 of the mixture, having $\frac{d}{n} = 1{,}773$, $I = {}^1/_2$), and some other.

For the latter mineral we wrote down all the lines in table 8 in order to show how coincidence of $\frac{d}{n}$ even for many lines is insufficient for the statement of presence of a given mineral in the mixture. In table 8 all the lines of the wood tin, corresponding by their $\frac{d}{n}$ (within the limits of error $\pm 1\%$) to any lines of the mixture are put without brackets, while those which do not correspond, are put in brackets. We see, that among the not yet explained 9 lines, three (№№ 19, 27, 37) coincide with the lines of the wood tin; but since their intensities are below 8, and on the other hand the line of this mineral with $\frac{d}{n} = 1{,}214$, $I = 8$, has no corresponding one in the mixture powder-diagram, — the coincidences of all these lines having $I < 8$ have no importance at all for the identification, because these lines of wood tin could not appear in the powder pattern of the mixture. Only the coincidence of a line $I = 10$, $\frac{d}{n} = 1{,}761$, with the line № 19 of the mixture is of importance for us. This leads us to the conclusion, that wood tin is either absolutely absent in the mixture, or is present in such small quantity, that the relative intensity of the lines $I = 10$ is lowered for the mixture to $I = {}^1/_2$.

Thus, by aid of our present determinative tables though far from being complete, we come to the following conclusion.

1) Doubtless present in the given mixture are: tenorite cuprite and copper. The first two minerals are the chief components, and among them tenorite is the prevailing one. Copper is in considerably minor quantity.

2) Not contradicting to the powder pattern there are (in small amounts): acmite, magnetite, diopside, inyoite, wad, spinel, hydroboracite, bornite, wood tin (all of them are not well fitting and are evidently less probable). In the practice of the identification such minerals must be nearly always omitted.

3) There are no less than 7 lines, partly unexplained even by these latter minerals. They belong to minerals, not yet embraced by our preliminary determinative tables.

This example was taken from the practice of one of our laboratories (that of Fedorov Institute). The substance, which was given by prof. P. J. Saldau to V. I. Mikheiev for *X*-ray investigation represented a dark powder in a very small quantity insufficient for chemical analysis. It was known about it, that it was scratched off a metallic object, found in archeological excavations. Having informations of this kind such minerals as acmite, magnetite, diopside, inyoite, spinel and hydroboracite could be rejected at once.

Notwithstanding the fact that this exmaple is not quite solvable by means of the method exposed, we regard as necessary to quote it here in order

1) to show clearly the necessity of complete roentgenometric (X-ray) determinative tables for minerals;

2) to show, that even when operating with complete determinative tables there will occur cases when the mineral present in the mixture will not admit of an unambiguous identification (in recent usual technical conditions of preparing powder diagrams). This depends on the fact that, when the mineral is present in the mixture in very small amounts, very few of its lines (1—2) may appear in the mixture powder pattern. If the greater sensibility of the film for photographing should be attained, and the apparition of more numerous lines of the mineral for the same quantity of the latter should be available (4—5—10 lines), — a definitive, not a conditional, identification of the mineral would be secured.

Indeed, for such mixtures, where all the components are present in considerable quantities, the determination of their mineral components by this method shall be carried out in many cases to the end and without any ambiguity.

VI. Conclusion

All the above said leads us to the following conclusions.

1. The present roentgenometric determinative tables for minerals even in this state, far from being complete, give a considerable help to the identification of minerals.

2. For a suitable development of the method of identification here described, it is necessary to compile full determinative tables, as well by collection of literature data, as by the accumulation of precise data on powder-diagrams of all the known minerals, in recent laboratory works.

3. One may foresee that the identification of monominerals with the aid of the present method will give in most cases satisfactory and unambigous results. Minerals of variable composition will present difficulties, which shall be surmounted along with a more detailed roentgenometric (X-ray) study of different groups of such minerals.

4. In the determination of the mineral composition of mixtures, the essential (after their quantity) components of the mixture are identified with the same convenience and accuracy as separate minerals.

5. Mineral components, present in small amounts, and therefore giving in the powder-pattern of the mixture only 1—2 lines (in the present state of technics of the photograph preparation) cannot yet be identified by means of this method unambigous even when complete determinative tables may be at hand.

6. It may be supposed that further improvements of the technics of preparing powder-diagrams in general will contribute to the accuracy of the method, to the widening of its application, and will remove the defect mentioned in § 5.

7. As every method of identification of substance, the present roentgenographic method here described cannot indeed pretend to eliminate all others. In several cases it is alone to be applied; in others — it is more quickly leading to the aim than any other method; in some more cases it is to be applied together with other methods, completing and precising them; in a fourth group of cases, its application is less rational than that of any other; in a fifth group of cases it may prove to be quite useless.

8. An especially great assistance the present X-ray method of identification may afford, and does afford, for the investigation of minute fraction of different mineral mixtures with grain sizes from 10^{-3} cm to 10^{-6}, when the optical analysis is ineffectual.

9. The main aim of the present work is to gather scattered attempts and methods of identification of minerals, either quite separate or united by any feature in several groups, and to develop these attempts into a single method, appliable to the entire mineral world.

10. This our work we consider as one of the steps towards the creation of complete roentgenometric (X-ray) determinative tables for minerals, and in course of time, for crystalline substances in general.