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THE PETROGRAPHIC MICROSCOPE IN ANALYSIS.¹

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In science, as in business, no line of research or activity is entirely isolated and self contained, free to exist by itself and for itself, but it is related to, and dependent on, other branches of scientific or business endeavor. A discovery in one particular field of investigation is not limited to that field but may have profound bearing on many other fields. Similarly a new method or a new tool devised for a special purpose in one field may serve well other purposes in another field; thus the petrographic microscope which has been developed and used chiefly by geologists can be applied with success to many chemical problems. The purpose of the present paper is to indicate briefly some of these problems and to emphasize the function of the petrographic microscope in their solution.

The petrographic microscope was introduced half a century ago by geologists because chemical and mineralogical methods failed to furnish adequate information regarding the rocks. A chemical analysis gave the bulk chemical composition of a rock but did not indicate how the

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several elements were distributed among the component minerals; chemical analyses of the soluble and the insoluble portions of a rock aided to some extent, but they were not adequate to meet the requirements of petrology. To know a rock thoroughly it was essential to know not only its chemical composition but also its mineral composition and its texture as expressed in the spacial grouping of the mineral components. This knowledge was obtainable only through the aid of the petrographic microscope.

In recent years the effort has been made, especially at this laboratory, to study from the standpoint of experimental geology the conditions of formation of minerals, rocks, and ores. This implies the artificial reproduction of these minerals and rocks and their identification under the petrographic microscope. In such work the time element is a most important factor. Rocks in nature form slowly and the crystals which develop have ample opportunity to grow to a fairly large size. In the laboratory, on the other hand, time is limited, the furnace charges are small, and the resulting crystallized aggregates are very fine grained. This has of necessity led to the development of petrographic microscope methods suitable for the accurate measurement of the optical constants of crystal grains measuring only 0.01 mm. in diameter. With these methods it is now possible to measure readily and with sufficient accuracy the optical constants of a substance in particles so fine that in water they settle at the rate of only 30 cm. an hour, or in air at the rate of 25 cm. a minute. As the diameter of the particles in most materials and powders exceeds 0.01 mm. ($1/2500$ inch), it is evident that this downward extension of the limits, to which petrographic microscope methods can be applied, has greatly increased the range of application and usefulness of the petrographic microscope. Up to the present time, however, such methods have been used in only a few chemical problems, but in each instance they have proved to be a most effective weapon of attack for the solution of difficulties which have heretofore been considered unsurmountable.

In this connection it may be well to emphasize the fundamental difference between the petrographic microscope and the ordinary chemical or biological microscope which has been used by chemists for many decades and which is essentially a magnifier and serves to render visible minute objects and details which would otherwise escape attention. Such objects are recognized by their shape, their size, and their color. In the case of bacteria the differences in their behavior toward certain stains aid in the diagnosis, while in other lines of investigation microchemical reactions serve the same purpose. The petrographic microscope, on the other hand, is not only a magnifier but also, and essentially, an optical instrument of precision for the measurement of the optical constants of substances either in thin plates or in powder form.

To illustrate this difference between the two types of microscopes by an example: Quartz (SiO_2) is a colorless, transparent mineral crystallizing in hexagonal prisms and pyramids of such characteristic shape that this feature alone, when present, is sufficient to establish its identity. If quartz appeared invariably in such well developed crystals, the crystal habit would suffice for its determination and the ordinary microscope would answer the purpose well; and if all substances had different and equally characteristic crystal shapes the crystal-form alone would constitute an adequate basis for distinguishing substances. But this is of course not the case, for we can destroy external crystal form by crushing the crystal into bits. Each fragment of a quartz crystal is still quartz in spite of its irregular form. Under these conditions other properties inherent in quartz itself and not dependent on its outer form must serve for the determination. The chemist naturally turns to chemical composition, melting point, boiling point, solubility, etc., which are constants and are adequate for the identification of the substance if it be available in sufficient quantity and purity for the purpose. In the case of quartz and many other minerals the determination of these properties is, however, difficult and time-consuming, while in many fine-grained mixtures of different substances these properties are not ascertainable. Under these circumstances properties must be selected which can be determined on each crystal fragment, and these are preëminently the optical properties, which serve to distinguish with certainty between different substances, especially crystallized substances.

In a crystal the component atoms are arranged in orderly fashion as the result, during crystallization, of the action of the interatomic forces. These forces are different in different directions and are vectorial and polar in character; they find expression not only in crystal form but also in the vectorial behavior of a crystal toward any external system of forces, as light-wave forces, acting upon it. The physical properties of crystals vary in such definite manner with the direction that these properties and their variations serve as diagnostic features in the determination of crystallized substances. Thus on quartz fragments we can measure with the petrographic microscope the refractive indices for different wave lengths of light, the differences in refractive indices for any given wave length (birefringence), and the character and shape of the optic ellipsoid to which the several optical properties are referable. These data of measurement serve to render the determination of the fragments as quartz practically certain. It may be noted that there are only four optical properties of crystals which are ordinarily measured in determinative work and are expressed as numerical optical constants of a given substance. These are: the principal refractive indices, the principal birefringences, extinction angles, and the optic axial angle. Other optical

properties of diagnostic value, as color, absorption, pleochroism, elongation, optical character, dispersion of the optic axes, etc., are stated in more or less qualitative form.

Of these properties the refractive indices are the most important and fundamental and also the easiest to measure with the petrographic microscope. The refractive index is the ratio of the velocity of light in air to that in the given substance. The fact that different substances have different refractive indices enables us to use the refractive index as a basis for classification. For a given wave length of light a substance which crystallizes in the isometric system has only one refractive index; this index is the same for all directions in the substance and the optical surface of reference is a sphere. In other substances, as those of the hexagonal and tetragonal systems, the optical surface of reference is an ellipsoid of rotation; such crystals have two principal refractive indices. In still other crystals (orthorhombic, monoclinic, triclinic) there are three principal refractive indices and the surface of reference is a triaxial ellipsoid.

In the practical measurement of the refractive indices of the grains in a powder, the particles are immersed in liquids of known refringence and the refractive index of any given grain is compared with that of the enveloping liquid. These grains are more or less lenticular or prismatic in shape and when immersed in a drop of liquid on an object glass and placed on the microscope stage give rise to the phenomena of prismatic refraction. Under conditions of oblique or central illumination these phenomena are easily recognizable; and relative refringence determinations between liquid and mineral grains can be made with an accuracy of ± 0.001 under favorable conditions. This method requires a set of standard refractive liquids. A convenient set is one of mixtures so prepared that the refractive index of each successive liquid is 0.005 higher than that of the liquid preceding it.

The birefringence, another useful constant, is the difference between the principal refractive indices; it signifies a difference in the rate of transmission for plane polarized light waves vibrating along different directions in the crystal and this in turn gives rise to interference phenomena which are of value in determinative work. The strength of the birefringence of a crystal grain is estimated from its interference colors between crossed nicols. In colorless minerals like quartz the scale of interference colors is practically identical with Newton's color scale.

A birefracting mineral becomes alternately light and dark four times during a complete rotation of the microscope stage between crossed nicols. In many crystal sections these positions of darkness or extinction, as they are called, make definite angles with a crystallographic direction such as the trace of a cleavage plane. These are then called extinction angles and are a useful diagnostic feature.

A further important constant is the optic axial angle. Its measurement includes the determination of the angle between the two optic axes or binormals and also the determination of the character of the acute bisectrix, whether α or γ , from which follows by definition the optical character, negative or positive, of the mineral. For most purposes a rough estimate of the size of the optic axial angle is sufficient.

These are the more important of the several optical phenomena which can be readily determined with the petrographic microscope on grains measuring at least 0.01 mm. in diameter. They may be used in the identification of any given substance, especially crystal grains or mixtures of different crystal fragments. In many cases the determination of only two or three of these constants is sufficient to establish the identity of a substance.

If in the field of chemistry the optical properties of all chemical compounds were known, as they are for the rock making minerals, it would be an easy matter for the microscopist to determine any given compound as such even in powder form and in the presence of other compounds. A chemical analysis in the case of mixtures may accomplish little because of the impossibility of separating the different compounds. Methods are available for estimating with the petrographic microscope the relative amounts of the different compounds which are present, and thus to make a fairly good quantitative analysis of a preparation.

In tests for homogeneity the petrographic microscope is especially valuable. By immersing the preparation in a liquid of the refractive index of the main crystal compound this compound practically disappears and any foreign material can then be detected at a glance. Solid solution can also be detected by these methods and in many instances a quantitative measure of the amount of solution in the crystal state can be obtained.

The fact that it is possible to measure accurately the optical properties of minute grains measuring only 0.01 mm. suggests at once many fields in chemistry for the application of petrographic microscope methods. Thus it may serve for the identification of chemical compounds in crystalline aggregates; it is also of value in testing the purity of a preparation, either a chemical precipitate, a drug, or other commercial product, as an abrasive, cleaning powder, tooth powder, baking powder, stones in glass, and a host of other products of similar type; in research work it is useful in the study of the phase relations in two, three, and polycomponent systems. For a given composition the primary phase is determined by chilling the preparation heated to a definite high temperature and examining the quenched product under the microscope. Measurements of the refractive indices of glasses of different composition in a given system enable the observer to trace step by step the change in the composi-

tion of the liquidus as crystallization proceeds and the final eutectic is approached. By thus combining thermal, chemical, and microscopical evidence it is possible to determine the equilibrium relations in poly-component systems with a high degree of accuracy, higher in fact than is possible in metal-component systems (alloys) even though these latter are better suited for thermal study. Without the aid of the petrographic microscope the attempt to ascertain the equilibrium relations in complex silicate systems is hopeless; with its aid each one of the three-component-systems studied in this laboratory has been brought to a successful finish; the degree of accuracy of the results can be ascertained in each case.

Experience has shown that these methods are applicable to the study and identification of all nonmetallic solid substances even though present in individual grains measuring only 0.01 mm. in diameter. It requires, of course, practice to apply these methods most expeditiously. In this respect the petrographic microscope is analogous to the lathe in the machine shop. The lathe in the hands of an instrument maker is a most successful instrument and remarkable results can be accomplished with it; and yet the principles on which it is based are not difficult to grasp. Similarly the petrographic microscope is equally useful in its line and its methods are simple and easy to apply for one who has had the necessary practice. One of the most difficult features of such work is the necessity of thinking in space. The optical properties of crystals vary with the direction and the observer must picture to himself the spacial relations involved if he would understand and take advantage of the phenomena he observes. This means, of course, a certain amount of training on the part of the chemist who would utilize this tool, but the saving of time and expense thereby gained more than compensates for the labor involved. It is fortunate that in most problems the determination of the refractive indices alone suffices for the diagnosis and that the method used for such determination is extremely simple and can be learned in a few hours' time and can be accomplished with the simplest type of petrographic microscope.

To cite a few examples of the application of petrographic microscope methods to chemical problems which have come within my own experience.

Identification of Chemical Compounds.

The Osazones.¹—Of the osazones there are two in the pentose sugars; four in the hexose group; 8 in the heptose, etc. Within each group the identification by chemical means is difficult and in the pentose group it may be uncertain. In view of the many optical constants which can be ascertained, it should be possible easily to distinguish between the differ-

¹ Samples of the pentose and hexose osazones were kindly furnished to the writer by Dr. C. S. Hudson and Dr. La Forge of the U. S. Bureau of Chemistry.

TABLE I.

Name.	Melting point.	Habit.	Elongation.	Optical orientation.	α .	γ .	Birefringence.	Remarks.
<i>Pentosazones</i>								
Xylosazone	160°	needles	+	$c = \gamma$ parallel extinction	1.745	1.860	strong	Characteristic green and yellow interference colors
Arabinosazone	160	long needles	-	$c = \alpha$ parallel extinction	1.765	1.870	strong	Abnormal interference colors
<i>Hexosazones</i>								
Allosazone	175	needles	+	$c = \gamma$	1.740	1.805	strong	Characteristic blue and orange interference colors
Galactosazone	208	needles in radial groups	=	$c : \gamma = 0^\circ$ to a large angle	1.825	1.850	medium	Strong dispersion of bisectrices. No position of extinction in white light. Interference color orange and green
Glucosazone	208	needles in radial groups	=	$c : \alpha = 0^\circ$ to a large angle	1.800	1.835	medium	Abnormal interference colors, green, blue, purple
Gulosazone	168	single needles	+	$c = \gamma$	1.670	1.820	very strong	Blue, green, and yellow interference colors

ent osazones by use of the petrographic microscope, even though only a few milligrams of material be available. The optical properties of the osazones, so far as determined, are listed in Table I; the determination of these suffices for the identification of any one of the pentose or hexose osazones.

A comparison of the properties of the two pentosazones shows that both are strongly birefracting, the arabinose showing abnormal interference colors and negative elongation while xylosazone crystals show characteristic green and yellow interference colors and positive elongation. The difference in the character of elongation of the needles is a diagnostic feature sufficiently characteristic to enable the observer to distinguish between the two pentosazones at a glance on a single needle weighing a small fraction of a milligram.

The hexosazones are likewise readily distinguished by their optical properties. In the case of galactosazone and glucosazone the differences in refractive indices and in character of elongation may be used as diagnostic features. The diagnosis in this case is, however, a little less easy than it is between other osazones. In Table I the refractive indices as listed are only approximately correct, but are adequate for diagnostic purposes. Characteristic for the entire group of osazones is the strong spectral absorption in the violet and blue-violet, and consequent lemon to orange yellow color.

The Alkaloids.¹—The determination of certain alkaloids by chemical methods is not easy and may be exceedingly difficult in the case of mixtures. It is of interest, therefore, to note that their determination by petrographic microscope methods is, so far as can be judged from the writer's limited experience with such substances, a simple matter. It should be possible to prepare a table, similar to the tables used by petrologists for rock minerals, in which the optical properties of all known alkaloids are listed; by the use of such a table the microscopist can ascertain with certainty the different alkaloids present in a crystalline mixture or the degree of purity of a particular alkaloid in the case of a drug preparation. The optical properties, so far as determined, of the several alkaloids examined, are listed in Table II. Several of the alkaloids in the list were soluble in the refractive liquid employed and their refractive indices could not be determined accurately; but the values obtained are of the proper order of magnitude and suffice for diagnostic purposes. In case more exact data are desired a new set of refractive liquids chosen with special reference to the alkaloids is required.

Certain of the alkaloids in Table II are difficult to distinguish by chemical methods, especially if present in mixtures or in small amounts; their

¹ Samples of the alkaloids listed in Table II were kindly furnished to the writer by Dr. C. L. Alsberg, Chief of the U. S. Bureau of Chemistry.

TABLE II.

Name.	Crystal habit.	Elongation.	Optical orientation.	α .	β .	γ .	Birefringence.	$2E$.	Optical character.	Dispersion.	Remarks.
Morphine	needles, prisms	\neq	$c = \beta$	1.580	1.625	1.650	strong	large	—	$2E_r > 2E_v$	Plane of optic axes normal to elongation
Codeine	rounded grains			<1.525		>1.60	very strong	very large	—	weak	Soluble in refractive liquid
Strychnine	prisms	+	$c = \gamma$	1.61	1.68	1.74	very strong	very large	+(?)	noticeable	Well crystallized
Brucine	very fine grained			<1.60		>1.65	strong				Soluble in refractive liquid
Quinidine	fine needles	—	$c = \alpha$	<1.60		>1.65	fairly strong	apparently uniaxial	—		Apparently tetragonal
Quinine	very fine grained			<1.60			medium				Soluble in refractive liquid
Cinchonidine	radial spherulites	+	$c = \gamma$	<1.625		<1.65	medium				Attacked by refractive liquids
Cinchonine	prismatic tabular	+	$c = \gamma$	1.575		1.690	strong	40° to 50°	$-2E_r < 2E_v$		Plane of optic axes normal to elongation
Cocaine	grains			1.49		1.58	strong	very large			Soluble in refractive liquid
Atropine	needles and prisms	\neq	$c = \beta$	1.580		1.60	medium to weak	large	—(?)	noticeable	Plane of optic axes normal to elongation
Caffeine	very fine grained			<1.60		>1.60	strong				
Papaverine	prisms	—	$c = \alpha$	1.625		1.690	strong	large		noticeable	Attacked by refractive liquids

optical properties are so different that a correct diagnosis under the petrographic microscope is relatively easy. In view of the importance of such work, especially in cases where only small quantities are available, it would seem that a thorough study of the whole group of alkaloids from this viewpoint is advisable.

Homogeneity Tests.—As noted above, the testing of the purity of materials can, in many instances, be accomplished best by the petrographic microscope. Thus these methods have been used in the examination and testing of sugars, salt, flours, drugs, photographic developing powders, chemical preparations and precipitates, organic and inorganic, and of many other products.

Analysis of Commercial Products.—There are on the market many preparations, such as baking and cleaning powders, abrasives, paints, fertilizers,¹ cements, etc., which are difficult to test adequately by chemical methods alone and in which a knowledge of the actual composition as revealed by the petrographic microscope may be of assistance. To cite an illustration: in Table III are listed the approximate compositions

TABLE III.

No.	Kind.	Abrasive.		Alkali.		Soap or fat.
		Maximum diameter in mm.	Per cent.	Kind.	Per cent.	
1	Powdered quartz.....	0.3	65	sodium carbonate	25	10
2	Powdered quartz.....	0.25	85	sodium carbonate	5-10	10
3	Crushed quartz.....	0.3	75	sodium carbonate as well crystallized sal-soda	25	..
4	Powdered alkali-feldspar (microcline), some quartz....	0.15	85	10
5	Powdered "pumice"-obsidian, slightly vesicular.....	0.25	80	sodium carbonate	5	10
6	Powdered "pumice"-obsidian similar to 5.....	0.25	40	sodium carbonate	5	10
	Powdered quartz.....	0.25	40			
7	Powdered "pumice"-obsidian similar to 5.....	0.25	40	sodium carbonate	5	10
	Powdered quartz.....	0.25	40			
8	Fine quartz silt, occasionally a larger grain of quartz...	0.25	5	sodium carbonate	20	..
				sodium bicarbonate	65	..

of eight common cleaning powders as ascertained by examination under the petrographic microscope. Many others, including soaps, etc., have been examined but the list is taken as representative of the several types. The total time taken for the examination of the eight samples was about two hours and the results listed are only first approximations sufficient

¹ See W. H. Fry, "Identification of Commercial Fertilizer Materials," U. S. Bureau of Soils, *Bull.* 97 (1914); also *Science*, N. S., 42, 89 (1915).

to establish the general character of the powders. In the table the optical properties of the different components are not listed, nor are certain characteristic features such as quality of crushing and sizing, purity of raw materials, etc. These are important and in case a given powder is to be used for a special purpose they determine in large measure its efficiency.

Study of Equilibria Relations in Physical-Chemical Systems.—In this laboratory petrographic microscope methods are applied primarily to the examination of the phase relations in two, three, and polycomponent systems, especially of silicates. The most detailed system yet solved is the system lime–alumina–silica.¹ In the course of this investigation microscopic examinations of over 5,000 heat treatments were made. The relations in this system are complicated and their elucidation required the combined attack of thermal and microscopic methods. Without the petrographic microscope the system could not have been solved; the solution was, however, of more than academic interest because of the fact that Portland cement clinker occupies a small area in one part of the diagram and the definite mineral composition of Portland cement clinker was unknown. Chemical methods alone were not competent to determine this mineral composition and it was not until after the introduction of petrographic microscope methods specially adapted to the study of fine grained preparations that we could hope for a satisfactory determination of its composition.

At present there is no text-book in which petrographic microscope methods are presented from the standpoint of this paper. Professor Chamot in his recent *Elementary Chemical Microscopy* devotes several chapters to the general description of petrographic microscope methods, but does not discuss them with reference to their applicability to fine grained materials. The writer is at present engaged in the preparation of a pamphlet in which these methods are to be presented in a form acceptable to chemists.

Summary.

In this paper the function of the petrographic microscope as applied to certain classes of problems of a chemical nature is discussed in a general way and its usefulness in such work is emphasized. Attention is directed to the difference between the ordinary microscope which is only a magnifier and the petrographic microscope which in addition serves for the determination of the optical properties of minute crystal grains and plates measuring at least 0.01 mm. in diameter. The several optical properties thus used in diagnostic work are described briefly and the mode of their determination by means of the petrographic microscope is indicated.

¹ G. A. Rankin and F. E. Wright, "The Ternary System CaO–Al₂O₃–SiO₂," *Am. J. Sci.*, [4] 39, 1–79 (1915).

The single fact that it is now possible by means of simple petrographic microscope methods to ascertain the optical constants of minute crystal grains with sufficient accuracy for diagnostic purposes suggests a number of chemical problems in which the petrographic microscope may render useful service; a few such problems are noted above. In some instances, as in Portland cement clinker and in the set cement, the actual mineral composition and the physical-chemical phase relations can be ascertained only by means of petrographic microscope methods.¹

Long experience with the petrographic microscope has convinced the writer that the field of its application is a large one and full of possibilities both from the viewpoint of pure research and of practical application in the technical world; in many instances information can be obtained by means of the petrographic microscope in a few moments which it would take several days to get by the usual methods; this means an appreciable amount of time and of money saved. To know at each step in a process or investigation just what is taking place is essential to effective work and such knowledge is obtainable in many problems only with the aid of the petrographic microscope.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

DENSITY OF RADIO-LEAD FROM PURE NORWEGIAN CLEVEITE.

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Through the kindness of Professor Ellen Gleditsch of the University of Kristiania, we have been so fortunate as to receive a specimen of lead sulfide from carefully selected Norwegian cleveite. According to Dr. Gleditsch, "The Norwegian uraninites are very old and very unaltered. They are found in well developed crystals and occur in connection with the pegmatite dykes in southeastern Norway." The sample in question occurred in cubic crystals near Langesund.

As Hönigschmid has already pointed out,² the properties of radio-lead³ obtained from pure minerals of this sort are far more interesting and significant than those of lead obtained from ordinary uranium ores, which doubtless contain some admixture of ordinary lead. Hönigschmid has shown that the lead from pure cleveite has an atomic weight as low as

¹ G. A. Rankin and F. E. Wright, *Am. J. Sci.*, [4] 39, 1-79 (1915); A. A. Klein and A. J. Phillips, "The Hydration of Portland Cement," U. S. Bureau of Standards, *Bull.* 43 (1915).

² Hönigschmid, *Sitz. Wien. Akad.*, 123, IIa, 20 (1914).

³ The name radio-lead is used provisionally to designate lead which appears to be the result of radioactive transformation.