iodine number of 97 were obtained. Ethyl oleate has an iodine number of 82.

Hence, oleic acid was the chief unsaturated acid; traces of a more unsaturated acid were also present. No palmitoleic acid was found.

## Summary

The ether-soluble phospholipides of *A. sydowi* were found to be a mixture of lecithin and cephalin. From the mycelium 0.4–0.7% of phospholipides was isolated. Glycerophosphoric acid, choline, cholamine and oleic acid were identified as the chief hydrolysis products. Stearic, palmitic, and a more unsaturated acid were also probably present in small amounts.

MADISON, WISCONSIN RECEIVED OCTOBER 17, 1935

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

# An x-Ray Investigation of the Solid Solution Nature of Some Nitrate Contaminated Barium Sulfate Precipitates[1]

BY GEORGE H. WALDEN, JR., AND M. U. COHEN

Almost from the inception of quantitative analysis the contamination of precipitates by foreign substances has been a universal difficulty encountered by analytical chemists. The cause of the phenomenon has been assigned[2] in general to (1) inclusion of the mother liquor in the precipitate mass, (2) adsorption on the crystal faces, both "inner" and "outer," (3) compound formation and (4) solid solution. That such theories have been purely speculative in character is demonstrated by the fact that their application has varied with different workers from the assumption of one such theory to explain all cases of contamination, almost to the assumption of all such theories to explain any particular case.

The resulting confusion in a field as complex as this is easily understood when the experimental evidence is examined. This has been almost entirely confined to analytical studies of precipitate contamination as a function of the medium in which the precipitates have been formed, or even to the purely pragmatic study of the weight relations of contaminated precipitates. It is clear from a survey of the literature that such methods by themselves cannot furnish conclusive evidence for the mechanism of contamination, and that a truly critical evaluation of the various possibilities awaits the development of experimental methods of an entirely different character. It is further desirable that such experimental methods be applicable almost universally, and not limited either to certain precipitates or to certain contaminants. In these respects the method of radioactive indicators, for example, is severely limited. However, a very positive and direct experimental test is available, at least for theories (3) and (4), in the combination of chemical analysis with x-ray diffraction studies.

In the application of this method to precipitate contamination, that which is due to inclusion and adsorption will lead to no observable changes in the diffraction pattern. Compound formation will lead to the formation of a new solid phase which if present in sufficient amount will manifest itself by the appearance of new lines in the diffraction pattern. Finally, the entrance of a contaminant by the process of solid solution will cause a change in the lattice dimensions dependent on the proportion of contaminant present in the precipitate without affecting the lattice symmetry of the latter.

The great power of this method has been recognized in the case of crystals prepared from melts particularly in metallic systems,[3] and the very numerous studies in that field prove beyond question its validity and utility. There has been, however, but very meager application to crystals formed by precipitation from solution. As part of a systematic investigation by Grimm[4] and his students of solid solutions in ionic crystals, Wagner[5] studied the system $BaSO_4$–$KMnO_4$ with the help of the x-ray technique and established its solid solution nature.

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[1] This article is based upon part of a dissertation submitted by M. U. Cohen in partial fulfilment of the requirements for the degree of Doctor of Philosophy under the Faculty of Pure Science of Columbia University, May, 1935. The material was presented at the New York Meeting of the American Chemical Society, April, 1935.

[2] I. M. Kolthoff, *J. Phys. Chem.*, **36**, 860 (1932); *Chem. Weekblad*, **31**, 102 (1934), and following papers.

[3] Westgren, *Trans. Am. Inst. Min. Met. Eng.*, Inst. Metals, p. 13 (1931); Jette, *ibid.*, **111**, 75 (1934).

[4] (a) Grimm, "Handbuch der Physik," **24**, 1096 ff. (1933); (b) Dahlmann, Diss., Wurzburg, 1930; (c) Peters, Diss., Wurzburg, 1930.

[5] Wagner, *Z. physik. Chem.*, **2B**, 27 (1929).

In order to form "mixed crystals," *i. e.*, solid solutions, in such systems, their constituents, Grimm asserts, must possess: (1) identical types of chemical structure, *e. g.*, $BaSO_4$–$KMnO_4$; (2) identical types of crystal structure, *e. g.*, $BaSO_4$ and $KMnO_4$ are both orthorhombic and in the same space group, $V_h^{16}$; (3) nearly identical lattice parameters.

Such requirements may perhaps be valid for the occurrence of complete miscibility, but their force is certainly weak in the case of limited solubility. Thus in metallic systems a necessary condition for complete miscibility is that the components be of identical lattice type. On the other hand, for a limited range of solid solution no such condition is necessary, and as a matter of fact systems which fail to meet this requirement are fully as numerous as those which do comply.[3] While the very different nature of the metallic and the ionic types of bond makes any wide-spread analogy between ionic and metallic systems a very dangerous one, the fact is that in ionic systems also the available evidence[4a] points to the absence of such conditions of isomorphism for limited solid solubility. It is precisely this case, rather than that of complete miscibility, which is of most interest in the problem of precipitate contamination.

It is our aim to study, without regard to the limitations imposed by such rules as those of Grimm, the possible incidence of solid solution of foreign ions in analytical precipitates. As an initial study, the analytically important example has been chosen of barium sulfate precipitated in the presence of nitric acid.

While it has been known for a long time that such precipitates may contain quite large amounts of nitrate, the mode of entrance of this contaminant has been quite unknown, and indeed even the actual amount of nitrate in such precipitates has hardly been investigated.[6] To these facts may be added the additional one that, while the chemical nature and crystal structure of the contaminant are unknown, it is certainly not of the same chemical type as barium sulfate ($MXY_4$), and therefore according to Grimm should not form a solid solution. Further, Wagner reported[5] that barium nitrate did not form solid solutions with barium sulfate, stating that the contaminated crystals showed diffraction patterns identical with those from barium sulfate prepared in other ways.

All of these points total to the sum that the contamination of barium sulfate in the presence of nitric acid is a very interesting case for study, and one likely to prove most illuminating for the interpretation of precipitate contamination in general.

Since the proof or disproof of the existence of solid solution in any system depends entirely on the precision of the x-ray work, it should be emphasized that methods of the highest precision are essential. The greatest variation in the lattice parameters of the precipitates here investigated is about 0.3%, and this would have been overlooked entirely as being within the experimental error, if the usual type of powder camera and method of calculation had been used. The apparatus to be described, when used in conjunction with the method of interpretation developed by one of us,[7] permits the measurement of lattice parameters with a precision of at least 0.01%. This greatly extends the application of the x-ray method into the dilute solid solution range, the region of interest in connection with precipitate contamination.

## Experimental

**x-Ray Apparatus.**—The self-rectifying gas x-ray tube used in this investigation was designed to provide for high asymmetry of the anode–cathode parts to give good rectifying and focusing properties; for efficient cooling of all parts of the tube to give high power dissipation; and for simplicity in construction and assembly.

Fig. 1 shows a longitudinal section through the corners of the tube and a top view with the plate B removed. Cooling water flows through tube b into the annular chamber A and then through the four longitudinal holes t drilled in the corners of the anode block to connect A with the water jacket D. The body of the tube and the 0.01-*mm.* aluminum windows are thus cooled very effectively. These aluminum foil windows are placed on three of the tube faces, the fourth face being occupied by 1.9-cm. flexible metal tubing (American Flexible Metal Hose Co.) which serves to connect the tube with the vacuum pumps. The tube is mounted vertically when used with the focusing cameras described below.

A simple regulator (Fig. 2) holds the tube current very constant. The solenoid is shunted across a tapped resistance placed in series with the primary of the high voltage transformer. An increase in the tube current increases the current in the transformer primary and therefore changes the current in the solenoid, causing the iron armature to rise. The resulting increase in the effective pumping speed of the diffusion pump reduces the gas pressure in the tube, bringing the current back to its original value. On the other hand, a decrease in the

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(6) Weiser and Sherrick, *J. Phys. Chem.*, **23**, 234 (1919).

(7) For the theory of these cameras see M. U. Cohen, *Rev. Sci. Instr.*, **6**, 68 (1935).

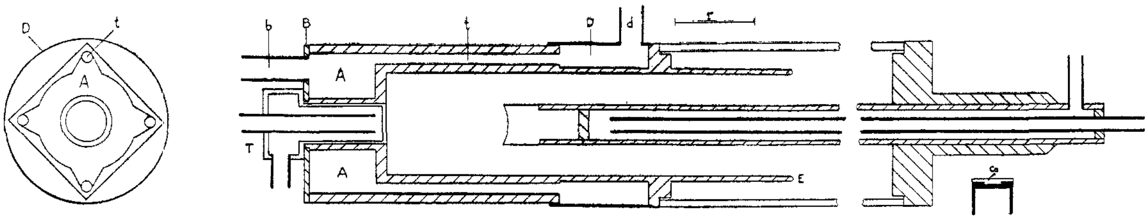

Fig. 1.

tube current lowers the armature, increasing the gas pressure and again restoring the original current. Changes in the equilibrium current are made by varying the proportion of the tapped resistance shunted across the solenoid.

Other supplementary equipment which may be of interest in view of its utility and the inexpensiveness includes a synchronous AC time clock and switch (New Haven), a solenoid-controlled water valve (General Electric No. CR9507-C1B), and a pressure-controlled switch (Detroit Lubricator No. 250) which opens the electrical circuits if the water pressure drops below a safe value. The inclusion of such auxiliary apparatus is invaluable because the operating time of the x-ray equipment may thereby be safely extended to periods when no personal attention is available.

**The Precision Camera.**—The design of the symmetrical focusing powder camera[7] for high angle reflections used in this investigation was conditioned by the difficulties encountered in securing x-ray photograms of barium sulfate powders which could be measured with sufficient precision. These crystals are orthorhombic and have relatively large lattice parameters. The use of long wave length x-rays is therefore indicated; short x-rays will be reflected only from planes so complicated that the intensity of the reflected beam will be very low and not very much greater than that of the general background. As a matter of fact copper radiation ($\lambda \sim 1.5$ Å.) gives very poor films; those taken with chromium are somewhat better; but really satisfactory photograms are secured only when resort is had to the use of calcium metal targets. This is the first extensive use reported of such radiation for powder work.[8]

Since the wave length of the calcium K lines is about 3.3 Å. they are very strongly absorbed and scattered by air. This makes it necessary to use an evacuated camera. The large size of the crystal grains leads to very spotty reflections if the sample is kept stationary during the exposure, and it is desirable therefore to arrange for continuous motion *in vacuo* of the powder under investigation. Constructional details of the camera designed with these points in mind will be evident from the photograph, Fig. 3.

The inner camera rings 6 and 6′ are machined to a diameter equal to that of the case 1 minus twice the film thickness, the latter being held to very close tolerances in the process of manufacture. Only the upper ring 6′ need be removed in loading the film 4. To facilitate this operation the diaphragm system 5, into which is inserted the replaceable lead slit 5′, is also removed. By means of the sector 3′ the sample 2 is pressed against the sample holder 3, the radius of the arc on which it is held being equal to that of the inner rings. The mechanism 9 for oscillating the sample holder operates through a stuffing box 10 and has the advantages that the sample holder is easily removable and that the need for a vacuum-tight central bearing is eliminated. The opening in the case through which the x-rays enter the slit system is covered by a cellophane window. The cover 8 carries a rubber gasket which forms a vacuum-tight seal when the camera is evacuated by a Hyvac pump connected to the outlet 7. The powder is mounted for exposure by dusting it on a sheet of mica on which a thin film of rubber cement has been allowed to set. The photograms obtained are excellent, the lines being very sharp and giving good contrast with the background.

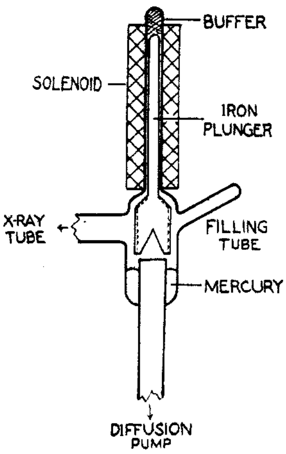

Fig. 2.

A millimeter scale for measuring purposes is printed on the single-coated x-ray film directly under the exposed portion. The original scale which serves as a negative was ruled on a Société Génévoise dividing engine by cutting through the blackened emulsion of a photographic plate. A vernier scale (10 divisions = 9.00 mm.) prepared in a similar way was printed on a photographic plate. Line distances on the photograms are measured by setting the zero of this vernier scale on the center of the line, tenths of a millimeter being given by coincidence of a vernier division with the millimeter scale printed on the film. The precision of such a setting is ±0.1 mm. and the distance between two lines is therefore precise to ±0.2 mm. The precision of the lattice constant determinations is discussed below for the case of the contaminated precipitates.

**Preparation of the Precipitates.**—The contaminated barium sulfate precipitates used in the present research have been prepared by the slow addition of sulfuric–nitric acid solutions to boiling barium nitrate–nitric acid

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(8) By the pressure exerted in a vise a calcium metal disk may be squeezed into good contact with the brass target body, if this is machined as indicated in Fig. 1. Such a target will carry 15 ma. at 40 kv. [*cf.* Haag, *Z. Krist.*, **A86**, 246 (1933), and Kersten and Maas, *Rev. Sci. Instr.*, **4**, 381 (1933)], but for continuous service it is better to use somewhat less power. At 5 ma. and 35 kv. good photograms of the cubic metals are obtainable in thirty minutes. Under these conditions the exposure time for the barium sulfate precipitates is about eight hours. The authors are indebted to Prof. H. T. Beans for pointing out that metallic calcium is sufficiently inert to be used in this way. Single targets have given several hundred hours of service over a period of months.

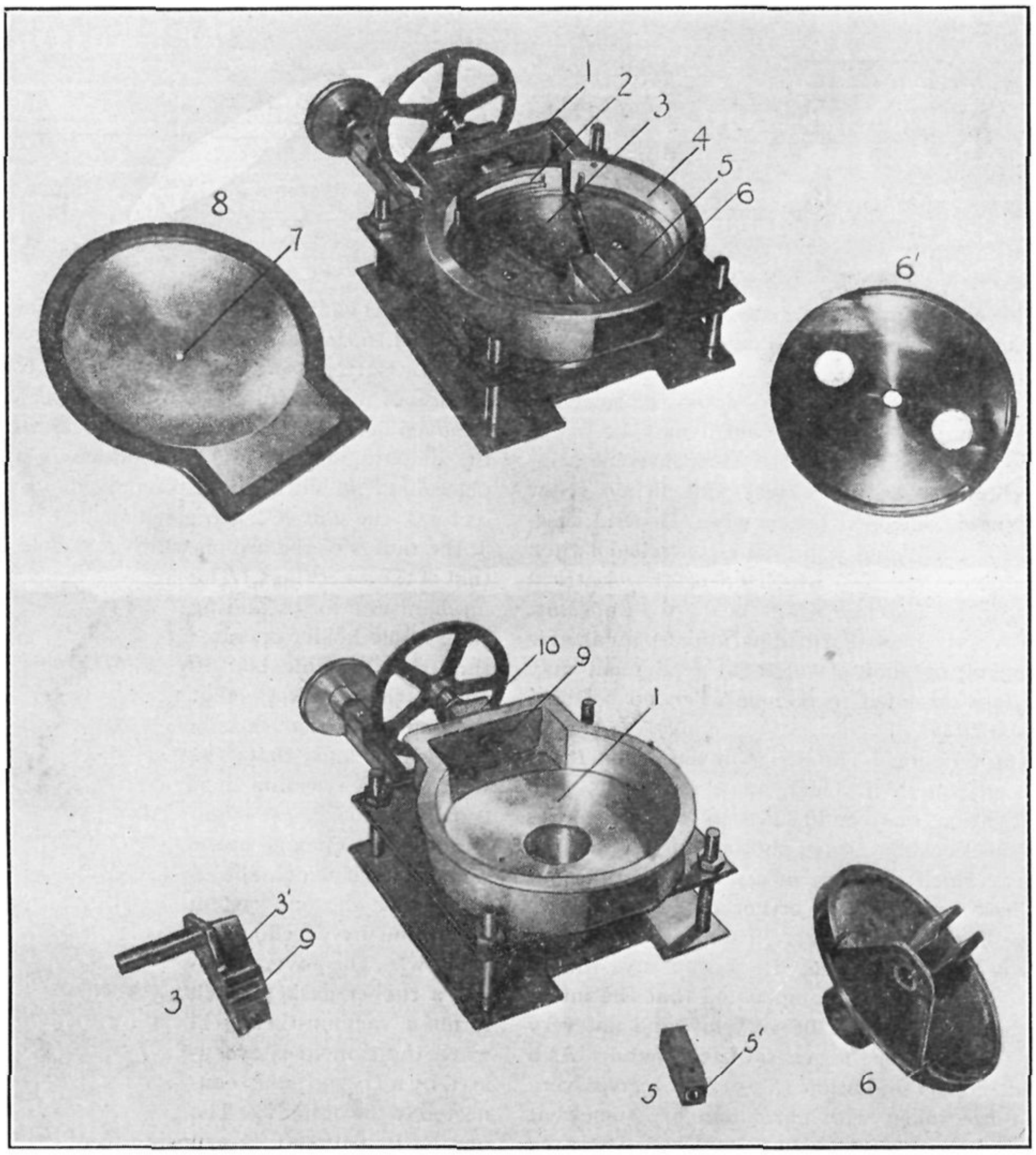

Fig. 3.

solutions with vigorous mechanical stirring. The ratio of sulfuric acid to barium nitrate was so chosen that only one-half of the initial barium ion was precipitated. The concentration of nitric acid in the sulfuric acid solution was adjusted to give the same concentration of nitrate ion as existed in the barium nitrate–nitric acid solution. This arrangement allowed the precipitates to form in the presence of a constant concentration of nitrate ion and a not too greatly varying concentration of barium ion. The precipitates were thoroughly washed by decantation with boiling water until the washings were neutral. They were then collected on a Büchner funnel and after air-drying preserved in glass-stoppered bottles.

Experience with a number of preliminary preparations led us to make the final precipitates in fairly large quantities; these are indicated in Table I. Five-liter flasks were used in the preparations, the sulfuric–nitric acid solutions being added from a separatory funnel drawn down to give a thirty-minute rate of addition. Digestion of the precipitates at the boiling point extended for thirty minutes, after which they were washed six times by decantation with boiling water and several times after transfer to the filter. The total volume of wash water was about four liters.

TABLE I

COMPOSITION OF PRECIPITATING SOLUTIONS

| | Solution A Concn., $M$ | | Solution B Concn., $M$ | | Moles $BaSO_4$ |
|---|---|---|---|---|---|
| Ppt. | $Ba^{++}$ | $NO_3^-$ | $NO_3^-$ | $SO_4^=$ | precipitated |
| 11 | 0.2 | 3.2 | 3.2 | 0.5 | 0.4 |
| 12 | .2 | 1.6 | 1.6 | .5 | .4 |
| 13 | .2 | 0.8 | 0.8 | .5 | .4 |
| 14 | .2 | .4 | .4 | .5 | .4 |
| 15 | .02 | .32 | .32 | .05 | .04 |
| 18 | .02 | .04 | .04 | .05 | .04 |

Total volume A = 4 l. B = 0.8 l.

The precipitates prepared with nitric acid present in solution A were extraordinarily coarse and their crystalline character obvious. On the other hand, precipitates formed with only barium nitrate present in solution A (14 and 18) were much finer and about twice as bulky in the air-dried state as the others. As a matter of fact they took much longer to dry than any of the others, and for analytical purposes No. 14 had to be dried at 110° for a short time. Professor P. F. Kerr of the Department of Mineralogy, Columbia University, reports that microscopic examination shows No. 14 to consist of crystals which are smaller and not as well formed as No. 11, whose crystal grains are quite uniform and perfect. In neither case is there any evidence of the presence of more than one phase.

The standard barium sulfate No. 1, later referred to as "pure" barium sulfate, was prepared by the slow addition of barium chloride to an excess of boiling dilute sulfuric acid. The washed precipitate was treated with 18 *M* sulfuric acid, the excess being fumed off in a platinum crucible. The word "pure" is here used for convenience rather than as a claim.

**Nitrate Analysis.**—The complete analysis of the precipitates offers various difficulties, and the nitrate content alone is here reported. Even this determination is not simple, because of the lack of a completely satisfactory method for small quantities of nitrate, coupled with the insolubility of the substances in question. The method evolved after extensive trials of other schemes depends on the release of the nitrate from the precipitates by metathesis of the barium sulfate with concentrated sodium carbonate–sodium hydroxide solution, followed by determination of the nitrate in the alkaline solution by the Devarda method.[9]

That digestion with boiling sodium carbonate solution is effective in metathesizing barium sulfate to the carbonate has been shown previously.[10] It is evidenced further by the fact that the residue after digestion dissolves practically completely in dilute acid, a faint opalescence being the only sign of incomplete conversion. The solution of the residue also gives a negative ring test for nitrate with diphenylamine.

A sample of about 1 g. was digested in a 300-ml. Kjeldahl flask for one-half to one hour with 150 ml. of a boiling solution containing 12 g. of sodium hydroxide and 30 g. of sodium carbonate. When the contents of the flask were sufficiently cool, 3 g. of Devarda's alloy was introduced, and the mixture warmed gently until the reduction was complete. Distillation of the ammonia was then started and continued until 75–100 ml. of the solution had passed over into a cylindrical separatory funnel in which there was held 25.00 ml. of standard 0.1 *N* hydrochloric acid. At the conclusion of the distillation, the stopcock of the funnel was opened and the distillate run into a 500-ml. flask. The funnel was then washed down, and the contents of the flask titrated with standard 0.1 *N* sodium hydroxide solution. In these titrations brom cresol purple (2 drops of a 0.1% solution in 20% ethanol per 100 ml.) was used. It does not appear to be generally recognized that brom cresol purple is an excellent indicator for this titration; the color change, while fleeting, is so sharp as to be unmistakable.

All apparatus used in the analytical work was calibrated. The hydrochloric acid was standardized against a Bureau of Standards sample of potassium acid phthalate.

The nitrate determinations were made on the air-dried precipitates in all cases but No. 14, as indicated above. This sample, dried for one hour at 110° is numbered 14.2. The results of the determinations are expressed in weight per cent. of nitrate ion, Table II.

TABLE II

NITRATE CONTENT OF THE PRECIPITATES, WT. %

| Ppt. | Determination 1 | Determination 2 | Mean, % |
|---|---|---|---|
| 11 | 4.43 | 4.41 | 4.42 |
| 12 | 4.51 | 4.56 | 4.53 |
| 13 | 4.21 | 4.30 | 4.25 |
| 14.2 | 3.53 | 3.68 | 3.61 |
| 15 | 1.42 | 1.44 | 1.43 |
| 18 | 1.29 | 1.26 | 1.28 |

A very striking feature of these results, and one hardly to be anticipated, is that the nitrate content of the precipitates is practically independent of the nitrate content of the precipitating solutions. An eight-fold variation in the nitrate concentration of the solutions produces in precipitates 11 and 14 (Table I) a change only from 4.42 to 3.61% in nitrate content. Nos. 15 and 18 exhibit a similar phenomenon. To be noted however is the fact that the nitrate content of the precipitates varies with the barium ion concentration; in Nos. 11–14 the solutions were ten times as concentrated as in Nos. 15 and 18 (Table I).

Attempts to extend the range of concentrations for further study will lead in the more dilute region to the use of very large volumes or microanalytical methods; in the more concentrated range the precipitates settle as muds which are difficult to wash and filter, and which give poor x-ray photograms.

**Lattice Constants.**—The lattice constants of the contaminated barium sulfate precipitates have been measured using the precision focusing camera. All the x-ray photograms were taken with calcium K radiation. In most cases every measurable line was used in the computations, but the overlapping of two sets of doublets with varying composition caused these to be neglected in some of the films. At any rate, no fewer than fourteen pairs of lines have been used in any film, and as many as nineteen pairs have been utilized in the case of the pure barium sulfate preparation. A typical set of data is shown in Table III.

One of the authors has derived[7] a very general method for the calculation of lattice constants from x-ray powder photograms whereby account is taken of the inevitable presence of various systematic errors which have hitherto severely

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[9] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929.

[10] Wolesensky, *Ind. Eng. Chem., Anal. Ed.*, **1**, 29 (1929).

TABLE III

$BaSO_4$ No. 1 (T = 26°) Calcium $K\alpha_1 = 3.35169$ Å., $K\alpha_2 = 3.35495$ Å., $K\beta_1 = 3.08343$ Å.

| | $\sin^2 \Theta \longrightarrow K\alpha_1$[a] | | |
|---|---|---|---|
| Plane | Exptl. | Calcd. | $\Delta \times 10^5$ |
| $321\alpha_1\alpha_2$ | 0.75478 | 0.75477 | − 1 |
| $303\alpha_1$ | .81630 | .81639 | + 9 |
| $303\alpha_2$ | .81640 | .81639 | − 1 |
| $230\beta$ | .99550 | .99551 | + 1 |
| $421\beta$ | 1.00552 | 1.00545 | − 7 |
| $114\beta$ | 1.01086 | 1.01090 | + 4 |
| $004\alpha_1$ | .88060 | .88060 | 0 |
| $004\alpha_2$ | .88073 | .88060 | −13 |
| $231\beta$ | 1.05089 | 1.05086 | − 3 |
| $031\alpha_1$ | .90824 | .90819 | − 5 |
| $313\alpha_1$ | .91186 | .91186 | 0 |
| $313\alpha_2$ | .91196 | .91186 | −10 |
| $104\alpha_1$ | .91654 | .91661 | + 7 |
| $104\alpha_2$ | .91662 | .91661 | − 1 |
| $132\beta$ | 1.10914 | 1.10936 | +22 |
| $131\alpha_1$ | .94425 | .94419 | − 6 |
| $131\alpha_2$ | .94434 | .94419 | −15 |
| $501\alpha_1$ | .94859 | .94864 | + 5 |
| $501\alpha_2$ | .94866 | .94864 | − 2 |
| | | Av. dev. | ± 6 |

$a_0 = 8.8625 \pm 0.0002$ Å.
$b_0 = 5.4412 \pm 0.0001$ Å.
$c_0 = 7.1401 \pm 0.0002$ Å.

[a] $\sin^2 \Theta \longrightarrow K\alpha_1 = (\lambda K\alpha_1/\lambda_i)^2 \sin^2 \Theta_i$.

limited the precision obtainable, particularly in non-cubic systems. The complete elimination of systematic errors by this method is very well shown by the random distribution of the difference of experimental and calculated $\sin^2 \Theta$ values given as Δ in Table III, 10 units in Δ representing approximately 0.1 mm. With the complete elimination of systematic error the data may be combined by the method of least squares, thus reducing to a minimum the effect on the lattice parameters of accidental errors of measurement. A very great advantage of this method is the fact that the probable errors as defined in the theory of least squares[11] may also be determined and thus a purely objective statement can be made of the precisions of the derived lattice parameters.

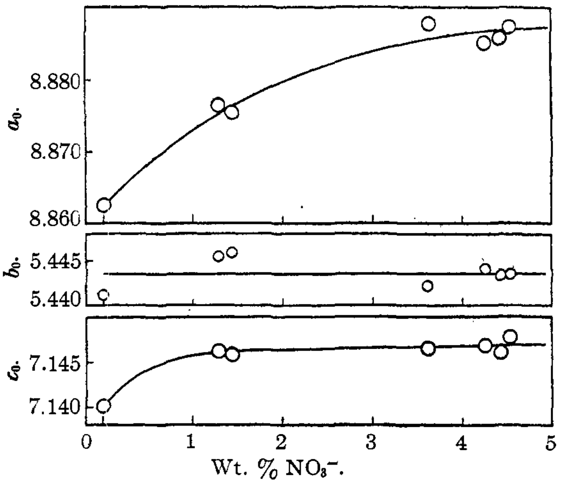

Fig. 4.

The approximate range of the probable errors on the various films is $a_0 = \pm 0.002$–$0.01\%$, $b_0 = \pm 0.002$–$0.004\%$, $c_0 = \pm 0.002$–$0.004\%$. In practically every case values of the lattice parameters obtained from different films of the same precipitate check within the probable errors calculated from the individual films. The parameters reported here are values from the best photograms of the various preparations. However, because of differences in the temperature and perhaps other influencing factors under which the various exposures were made, comparison of the results is probably valid only within 0.01–0.02%.

In Fig. 4, which shows the relation between the lattice parameters and the nitrate content of the crystals, the radius of the circles is equivalent to 0.01%. Table IV gives the numerical values of the parameters.

TABLE IV

LATTICE PARAMETERS OF THE PRECIPITATES (Å.) (23–26°)

| Ppt. | $a_0$ | $b_0$ | $c_0$ |
|---|---|---|---|
| 1 | 8.8625 | 5.4412 | 7.1401 |
| 18 | 8.8763 | 5.4455 | 7.1462 |
| 15 | 8.8753 | 5.4459 | 7.1458 |
| 14 | 8.8876 | 5.4422 | 7.1465 |
| 13 | 8.8849 | 5.4441 | 7.1469 |
| 11 | 8.8856 | 5.4434 | 7.1461 |
| 12 | 8.8871 | 5.4435 | 7.1478 |

Visual comparison of the x-ray photograms has been shown by the experience gained in this work to have semi-quantitative significance. In this way two interesting observations have been made. In the first place, drying the precipitates at 110° produces no visible change in the diffraction pattern. In the second place, when the nitrate content of the precipitates is eliminated by fuming with sulfuric acid, the residues show a pattern and relative spacing identical with that of pure barium sulfate.

## Discussion

In the contaminated barium sulfate precipitates prepared as described in this work, there is no doubt but that the phenomenon of solid solution

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[11] Wright and Hayford, "Adjustment of Observations," D. Van Nostrand Co., New York.

appears. The orderly variation of the lattice spacing with the nitrate content shown in Fig. 4, and the regular change in the volume of the unit cell shown in Fig. 5, are conclusive evidence for the expansion of the fundamental barium sulfate lattice. Such an expansion, it has been pointed out in the introduction, is due to the entrance of foreign ions into the lattice. It cannot conceivably be due to any adsorption or occlusion process known at present. That such mechanisms may account for part of the contamination is of course not ruled out by the present investigation, but even this may be questioned because of the remarkably homogeneous and strain-free character of the precipitates.

It is abundantly clear from the extensive literature of the subject that such essentially *ad hoc* theories as adsorption or occlusion have been of relatively slight value in the problem of precipitate contamination. That this failure is due to the absence of critical and positive experimental evidence for them has already been pointed out.

On the other hand, theories of a more or less *a priori* character, such as the Grimm rules for solid solution formation, have had a tendency to control the direction in which, it was thought, the existence of solid solution might profitably be investigated. As a result, its possible importance in precipitate contamination has been largely neglected. In the precipitates examined in this investigation the entrance of the contaminant as a solid solution emphasizes the fact that such considerations of isomorphism have little bearing for small ranges of solubility, and that therefore solid solution phenomena may play a very large part. The extent and importance of such a mechanism in other cases of precipitate contamination are impossible to predict. The function of the present research has been to show that this question may be decided in certain cases with a high degree of certainty, and by the use of a physical method whose evidence can scarcely be misinterpreted.

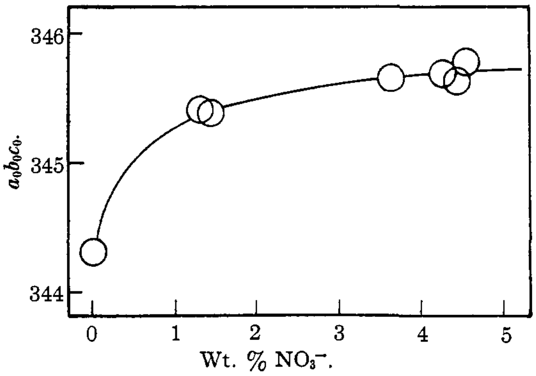

Fig. 5.

## Summary

1. Apparatus is described which when used with a method of calculation previously developed makes it possible to determine the lattice parameters of powdered crystals with a precision of better than 0.01%. A feature of this apparatus is the use of a vacuum focusing camera in conjunction with long wave length x-rays from a calcium metal target.

2. A series of nitrate-contaminated barium sulfate precipitates has been prepared in the absence of all foreign cations except hydrogen ion, and in such a manner as to avoid large changes in the composition of the precipitating media.

3. The nitrate content of these precipitates has been determined by an adaptation of Devarda's method. Their compositions depend primarily on the barium ion concentration of the precipitating solutions, and only to a slight extent on the nitrate ion concentration.

4. The lattice parameters of the precipitates have been determined and correlated with their nitrate content.

5. The evidence indicates that the contaminant enters the barium sulfate lattice with the formation of a solid solution.

6. The role of such solid solution formation in the general problem of precipitate contamination has been discussed.

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