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# Report on

# Storage Batteries

# X-Ray Studies

FR-1392

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON, D.C.

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# ABSTRACT

This report presents the results of the application of X-Ray diffraction methods to the study of lead-acid storage cells. The fundamental chemistry of lead compounds with oxygen and sulfate was established by X-Ray methods. Then these data were used in studying actual storage cells--nature of freshly-pasted plates, formation processes, effects of charge and discharge, etc. It is believed that the work has established the importance of X-Ray methods in research work necessary to the improvement in the life and capacity characteristics of storage batteries.

## AUTHORIZATION

1. This problem was authorized by reference (a). This is a final report on the problem and supersedes the interim reports, references (b) and (c). Other references pertinent to this study are listed as references (d) and (e).

Reference:
(a) BuEng. ltr. SS/S62(7-30-D1) of 7 August 1935.
(b) NRL Report No. P-1254 dated 24 March 1936.
(c) NRL Report No. P-1334 dated 16 December 1936.
(d) G. L. Clark, "Applied X-rays", 2nd Edition.
(e) NRL 1st End. to BuEng. SS/19 dated 2 July 1932.

## STATEMENT OF PROBLEM

2. The object of this work was to study the application of modern X-ray diffraction methods which have proved so fruitful in studying the crystal structure of various materials to the study of lead-acid submarine storage cells.

## KNOWN FACTS BEARING ON THE PROBLEM

3. Studies of lead-acid storage cells by chemical and physical-chemical methods have shown that the mechanism in the generation of electric current by these cells is given by the chemical equation expressing the classical double sulphate theory

$$PbO_2 + Pb + 2H_2SO_4 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O$$

This equation describes merely the initial and final states in the operation of the cells and, given certain physical chemical data, the voltage and the temperature coefficient of voltage of the cells under no load. The capacity and life characteristics of the actual storage cells, which are of such importance in the Navy applications, depend on the physical character of the chemical compounds making up the active material. The active material in lead storage cells is initially made of a paste composed primarily of the several oxides of lead in various proportions. The type of oxides used and their proportions are determined by the several manufacturers by empirical methods; and the optimum characteristics of the individual oxides, such as their particle size, crystal structure, etc., are determined empirically by the manufacturer of the oxides. Since the capacity characteristics of the final battery are so largely determined by the characteristics of the oxides from which it is made, a knowledge of the physical chemistry of these oxides is important for an understanding of and improvement in the action of the storage cells. Another important factor in determining the capacity of the lead storage cell is the process used in initially forming the active material. So far, the forming processes have been developed by purely empirical methods without an adequate appreciation of the physics and chemistry involved.

4. The common chemical methods are inadequate for a study of the battery oxides and of formation methods, the effectiveness of which depends

not alone on the chemical substances which are present but also on the physical structure - the particle size and whether the particles are crystalline or non-crystalline, whether or not the crystals are strained or distorted, etc.

5. Given a properly manufactured storage cell, its capacity and life characteristics depend then on its operation and maintenance. The methods used for charging, the operating temperature, the consistency or variability of the temperature, the type of service, the presence or absence of "sulfation", etc., all affect the capacity and life. The effects of these influences have so far been studied by empirical methods. Chemical methods alone gave little information, while most physical methods, such as microscopic examination, are likewise inadequate to study these effects.

6. Recent research in physics has supplied two powerful research tools for the study of such problems. These are: (a) Electron optical methods, and (b) X-ray diffraction methods. The former have not as yet been developed sufficiently to enable them to be used on storage battery problems. Hence the latter methods were used in this work.

7. The theory and methods of using X-ray diffraction for the study of technical problems are given in detail in reference (d). The theory of X-ray diffraction methods given therein is briefly as follows. When ordinary light of known wave-length falls upon a ruled diffraction grating and the light reflected from it is caused by a suitable optical system to form an image on a photographic plate, the nature of this image gives information concerning the structure of the grating. In an analogous manner, if a monochromatic beam of X-rays impinges on a solid material, the reflected X-rays form on a suitably disposed photographic film a series of images constituting a diffraction pattern the nature of which affords detailed information concerning the structure of the material. The principal types of information thus obtainable are:

(a) Whether a substance is crystalline or non-crystalline. For example, whether the lead in the negative active material of a storage cell is crystalline or amorphous in structure.

(b) The type of structure of a crystal--crystallographic system, space group, unit cell dimensions, etc. For example, the type of structure of the lead oxides used in manufacturing storage cell plates can be determined.

(c) The chemical identity and chemical and crystallographic changes in the material. For example, whether the "pernicious sulfate" in the cell is the same as ordinary lead sulfate.

(d) The size of particles making up a material. Thus, the size of the particles of oxide comprising a newly made positive plate can be determined and the effect of various manufacturing conditions upon this grain size determined.

(e) The internal strain or distortion in the material.

(f) The analysis of the effect of grain growth. For example, the effect of various charging procedures upon the change in the grain growth of the positive and negative plates.

(g) Differentiation between surface and interior structure of a material.

## NARRATIVE OF ORIGINAL WORK DONE AT THIS LABORATORY

8. The first important use of X-ray diffraction methods in the study of submarine storage batteries was made at this Laboratory by Dr. C. S. Barrett and reported in reference (e). Unfortunately, this work could not be carried forward owing to the separation of Dr. Barrett from the staff of this Laboratory. The present work was done by Professor G. L. Clark and Dr. N. C. Schieltz in the laboratory of the Department of Chemistry of the University of Illinois.

## METHODS

### (a) Apparatus

9. Experience with and studies of different types of X-ray diffraction apparatus led to the design and adoption of the circular camera shown schematically in Plate 1a. The common flat plate type of camera proved decidedly unsatisfactory since in this particular work most of the spacings are rather small and consequently only a few lines would be obtained on flat patterns.

10. Copper target X-ray tubes were used. Nickel filters, which are often used to filter out the beta-rays of copper, proved unsatisfactory since they did not completely filter out the stronger beta lines.

11. Numerous studies were made of the best method of holding the samples under investigation in the camera. Glass capillary tubes, commonly used by many workers, proved unsatisfactory; fine glass rods, silk threads, etc., the sample being attached thereto with collodion, similarly were unsatisfactory. The best sample holders proved to be wedges (Plate 2b). The 45° wedge was used to obtain a rather thin sample with a resultant pattern with lines appearing on both sides of the central spot, making measurements more accurate. For other work the 30° wedge was adopted; for heavy materials this gives lines on only one side of the central spot but decidedly better definition with a shorter exposure time.

12. A special 30° wedge was adopted in studying actual storage cell plates. This wedge permitted the use of a solid section of a plate as a sample, thus retaining any orientation or other characteristics which might exist. These wedges gave the combined effect of transmission and reflection which is desirable in general qualitative work. Other apparatus designed and built for the present work comprised a view-box for permitting the comparison of film patterns simultaneously; a measuring instrument which enables measurements to be made with an accuracy of 0.1 mm; and various other sample holders and special devices.

## (b) Materials and Experiments

### I. Lead and its Compounds with Oxygen

#### (a) Lead

13. Lead has a tendency to grow into crystals of such size that only a few large spots appear on the pattern, which makes it useless for comparison. This difficulty was finally overcome by melting the test lead, permitting it to cool almost to freezing, and then suddenly chilling it by quenching in cold water. The specimen was then filed with a clean fine file and screened by means of a 200 mesh screen. Thus finally, after numerous trials, a pattern was obtained with grain size sufficiently small so that it could be used as a standard in examining the negative charged plates. This standard pattern was taken with the 30° wedge and without a nickel filter (Plate 1c). The lines marked (.) are due to the Kα radiation and those not so designated to Kβ.

14. In negative plate studies and in the lead-antimony alloy investigations several additional lines appeared from time to time which could not be accounted for. Finally in one series of studies they appeared in a sufficient number to trace their origin and it was found that they were caused by the characteristic radiation of the "L" series of tungsten, which had plated out on the copper target as the filament of the tube evaporated.

#### (b) Lead monoxide (PbO)

15. Patterns of orthorhombic and tetragonal lead monoxide were made from oxides obtained from the storeroom (Plate 2 a and b). These patterns were to serve as standards of comparison throughout the entire work. X-ray studies later disclosed the presence of a lead carbonate (structure I, and very probably a basic carbonate) in both samples. This compound forms very readily when the oxides are exposed to air and will be discussed further under the treatment of carbonates.

16. Fused Baker's analyzed orthorhombic oxide was submitted by Rensselaer Polytechnic Institute and found to be a mixture of the orthorhombic and tetragonal forms. Distortion effects appeared to be quite evident since some planes were characterized by decidedly fuzzy lines while others remained sharp. This effect was so pronounced that it became difficult to recognize the individual patterns.

17. Yellow and red crystals obtained from hot sodium plumbate solutions during $PbO_2$ preparations were the orthorhombic and tetragonal forms of the monoxide respectively.

18. When 15 g. $PbO_2$, 5 g. NaOH and 20 cc $H_2O$ were heated in a steel bomb overnight at, or above, 360° C., during attempts to prepare Simon's crystalline $PbO_2$, the orthorhombic form was obtained. Over a period of three days and with some grinding the tetragonal form was found to be dominating.

19. Orthorhombic oxide when heated with $H_2O$ at 150-180° for thirteen hours had been completely converted over into the tetragonal form.

20. Tetragonal oxide when boiled for a long time with water changed over to $2PbCO_3.Pb(OH)_2$ (compound II as discussed under carbonates), and a small amount of compound I.

### (c) Minium ($Pb_3O_4$)

21. A pure sample of red lead was obtained from the storeroom and a standard pattern made (Plate 2c). When comparing this pattern with those made from the well defined needle-like crystals obtained by heating 10 g. $PbO_2$ (Mallinckrodt's), 5 g. $PbO_2$ (Merck's), 5 g. NaOH and 20 cc of water, or sodium plumbate and water, especially between 355 to 375° C., it was observed that the patterns from the ground large crystals showed numerous planes that were characterized by diffuse lines. The spacings otherwise agree perfectly (Plate 3a). These patterns show no evidence of the presence of other oxides as $PbO_2$, PbO, etc.

22. The above procedure produces exceptionally good specimens (One quarter inches long and one thirty-second inches in cross-section) for structure determination, which thus far has never been determined. From a preliminary crystallographic analysis of these crystals Dr. T. T. Quirke of the Geology Department of the University of Illinois has obtained the following results:

> These red lead crystals are distinctly prismatic in habit. They are entirely transparent and under polarized light show pleochroism, yellow to red. Extinction is inclined thirteen degrees to the long axis. They have well marked cleavage, prismatic in type, making angles of 120° with one another with conchoidal fracture transverse to the long axis. The crystals belong to the monoclinic system, are characterized by almost square cross-sections and with great length in proportion to their diameter, terminating in a combination of basal pinacoid and dome with a very high angle beta. Some prisms are terminated by a basal pinacoid with a 101 dome and two faces of the 011 dome, making a four-sided pyramidal termination. In other cases the termination is wedge shaped with the domes 011. Still another termination showed basal pinacoid and the dome 011 terminating the prism 110 and the orthopinacoid 100.

### (d) Lead dioxide ($PbO_2$)

23. Due to distortion characteristics found in charged positive plates, more or less extensive efforts were made to produce various lead dioxides with the expectation of reproducing this distorted pattern. The standard pattern was made from a sample of dioxide obtained from the storeroom (Plate 2d).

24. Other samples were prepared according to the following procedures: lead nitrate was treated with sodium hydroxide to give lead hydroxide which was then filtered off and washed. Thereupon it was dissolved in concentrated sodium hydroxide and:

(1) Oxidized with bromine. One pattern was taken with a

sample that was removed immediately from the solution, washed and dried at 105° . Another with a sample that had been left in the solution for 48 hours. Both patterns showed mostly colloidal lead dioxide and some red lead. A second preparation gave almost identical results with the exception of grain size which was considerably larger.

(2) Oxidized with chlorine. The pattern showed a product approaching the standard pattern in particle sizes and possibly containing a very small amount of red lead.

(3) Oxidized with hydrogen peroxide. This gave a product similar to lead dioxide in color but which had the structure of red lead.

25. All three preparations failed to show any signs of distortion and attempts were made to produce such a product by:

(1) Mixing lead dioxide and 5% (by wgt.) sulfuric acid and refluxing for two hours. Some of the dioxide was converted to normal lead sulfate of rather large grain size while the remainder was unmodified. The experiment was repeated with the refluxing time of ten hours giving identical results. It was also modified in that 5% (by wgt.) of 3.682 N sulfuric acid was added to the dioxide and the mixture heated to dryness with low heat. Again the results were identical with the exception of grain size which was smaller. Lead dioxide and sulfuric acid were also mixed in a 50/50 ratio (by wgt.) and heated to dryness with low heat. Results in this case showed that all of the dioxide had been converted to lead sulfate of rather large grain size. The temperature at which this conversion takes place may be of considerable importance in storage battery operation where higher temperatures are involved and further investigations may be advisable.

(2) Adding sufficient sulfuric acid (1.250 gravity) to red lead to completely wet it and then drying it in a vacuum desiccator. The product obtained was dark brown in color (much like the dioxide color) but the results showed a mixture of approximately 60% red lead and 40% lead sulfate. The particle size of the red lead had increased considerably. It may be possible that the smaller particles reacted leaving only the larger ones. The same procedure was repeated with a red lead to acid ratio of 1:2. The filtrate in this case was still acid and the X-ray results showed approximately a 50/50 mixture of lead dioxide and lead sulfate. All evidence of red lead was lacking.

(3) To 10 grams of red lead nitric acid was added in 30 cc of water in the ratios:

| $Pb_3O_4$ | $HNO_3$ |
|---|---|
| 1 | 1 |
| 1 | 2 |
| 1 | 3 |
| 1 | 4 |
| 1 | 8 |

The procedures were run in duplicate and one sample was permitted to stand at room temperature for one hour while the other one was refluxed for the same length of time. After the reaction time had expired, the products were promptly filtered, washed free from lead salts and dried in vacuum over calcium chloride. The results are most conveniently given in table form (Table 1).

26. All of the above preparations failed to show any signs of distortion. Such a product was later successfully prepared in the laboratory by Dr. J. N. Mrgudich. (Patterns of distorted and colloidal $PbO_2$ are shown in Plates 3b and 3c respectively.)

27. Large crystalline lead dioxide. The distortion evidences in positive plate material referred to above and always present in batteries, especially the better brands, are unquestionably related to the internal fine structure of the lead dioxide. On account of the great difference in scattering power between the lead and the oxygen, it has thus far been impossible to determine the complete structure, that is, to identify the exact position of all the atoms, or molecules, in the unit cell from powder patterns. Such information is highly desirable in postulating a working principle for this oxygen deficiency as reported by LeBlanc and Eberius. Rotation patterns are very frequently a great asset in such determinations if single crystals can be found which are sufficiently large and efforts were made to obtain natural crystals of Plattnerite which, however, were quite unsuitable for this type of work. As a last resort large crystalline lead dioxide was to be prepared according to the method of Simon, who, in the estimation of LeBlanc and Eberius was the first person to ever succeed in preparing the dioxide corresponding exactly to the formula $PbO_2$. These efforts, however, remained unrewarded since it was found that Simon's large crystalline material was not tetragonal $PbO_2$. A chemical analysis showed it corresponded to $Pb_2O_3$ and X-ray results gave a distinctively different pattern than that of any known oxide of lead. A preliminary crystallographic examination shows the crystals to be triclinic. In connection with this work another new oxide, $Pb_5O_8$, was also found and identified.

28. When Simon's results appeared ambiguous, that is, the physical properties, but not the formula, agreed with his description, he submitted a sample of his product upon request and it was found that he had used the large clusters of $Pb_2O_3$ crystals for the photomicrographs which he included in his publication, while the X-ray analysis was made on small crystalline material hardly more than a coarse powder. The pattern of this product is distinctly a composite pattern of $PbO_2$ and $Pb_2O_3$ (Plate 3d). The lines of the $Pb_2O_3$, somewhat depressed in intensities, were entirely disregarded in his interpretation.

29. Photomicrographs of these oxides may be of interest at this point (Plate 4). The general description and methods of preparation will be given later under the section, "Other Higher Oxides of Lead."

30. The following procedures employed in attempts to prepare this large crystalline dioxide:

(a) Red lead with nitric acid in water was refluxed for one week. This produced a product with a rather coarse particle size when considering the general behavior of the compound but entirely unsatisfactory for the purpose intended.

(b) Lead dioxide heated with water in a steel at 200° C. for three days. The results in this experiment were negative.

(c) Sodium plumbate heated in water should, according to Simon, produce large crystalline $PbO_2$. However, the product obtained from this procedure was $Pb_2O_3$.

31. The actions of sodium peroxide, sodium hydroxide and hydrogen peroxide on lead dioxide were studied as preliminary bomb experiments. Sodium peroxide with water or hydrogen peroxide readily decomposed lead dioxide to minium. Sodium hydroxide with hydrogen peroxide gave the same results but less rapidly, while hydrogen peroxide alone did not show decomposition.

32. Difference between Merck's and Mallinckrodt's lead dioxide was studied. This study was suggested by the fact that Merck's product (manganese free) failed to give any $Pb_2O_3$while Mallinckrodt's (low manganese) dioxide produced a splendid product. Addition of a very small amount of manganese dioxide to the Merck's product caused it to yield results identical with those obtained from low manganese dioxide. X-ray investigations failed to disclose any difference between the two oxides.

33. Plattnerite was found to have a structure identical to lead oxide prepared from various procedures. The oxygen content upon analysis with the modified Bunsen method was found to be 5.68%.

(e) Other higher oxides of lead

34. The results given in this section were obtained in attempts to duplicate Simon's work in the preparation of the large crystalline lead dioxide which has been discussed above. Since the work is of considerable interest, because it produced several new oxides which in the opinions of other investigators should not exist and because certain catalytic effects seem to be of major importance the different procedures used will be given somewhat in detail.

35. a. The preparation of the large black crystals ($Pb_2O_3$):

(1) By heating lead plumbate, which had been prepared according to the method of Fremy (from filtrate), in a steel bomb at 250° C. for two or three days. This produced in most cases, only $Na_2CO_3.H_2O$ or a mixture of $Na_2CO_3.H_2O$ and $Na_2CO_3$ but not the expected oxide.

(2) From by-product obtained as insoluble precipitate in plumbate preparation (assuming it to be $Na_2PbO_3$):

$$Na_2PbO_3 + H_2O \xrightarrow[\text{(Pressure)}]{\text{Heat}} PbO_2 + 2NaOH$$

(aa) Heating three days at 250-265° gave some red lead, a good crop of the large black crystals and a fine crystalline dark brown to black substance later shown to be a lead sodium oxygen compound.

(bb) A second sample heated at 230-275° for three days gave relatively the same results.

(3) From the constituents of sodium plumbate:

$$PbO_2 + 2NaOH + H_2O\ (20\ cc) \xrightarrow[\text{(Pressure)}]{\text{Heat}} PbO_2$$

(aa) Reagents were mixed in above proportions and heated for three days at range of temperature given above gave very good results; red lead crystals, the large black crystals and the lead sodium compound.

(bb) Three attempts were made using Merck's (manganese-free) $PbO_2$ with 20, 15 and 10 cc of $H_2O$ consecutively, keeping the procedure otherwise identical. The first case gave a good crop of <u>pure red lead</u> (small) crystals, the second not quite so good a yield and the third a reasonable crop again. The second case also produced a rather coarse crystalline material later identified as $Pb_5O_8$ and referred to as "small black crystals", rather similar to octahedral forms and decidedly of twinning or intergrowing nature. All three cases produced this dark brown to bluish black sodium lead compound. No large triclinic ($Pb_2O_3$) crystals were obtained from this oxide. The temperature for these experiments was 260-275° C.

(cc) A mixture of 10 g. $PbO_2$ (unidentified and same as under (1) - the last of the reagent), 5 g. Merck's $PbO_2$, 5 g. NaOH and 20 cc $H_2O$ under identical conditions as used above gave a reasonable yield (not any too well developed) of the large black triclinic crystals; a very good and well developed sample of the smaller $Pb_5O_8$ crystals; some red lead and some lead sodium compound.

(dd) 15 g. Mallinckrodt's $PbO_2$, 5 g. NaOH and 20 cc $H_2O$ for three days at 260-275° gave a good yield (about 50/50) of red lead and the large black crystals with practically no lead sodium compound. It should be noticed that a new bomb (walls not previously oxidized) was used for this experiment, and a large amount of red lead resulted.

(ee) It was observed that Mallinckrodt's $PbO_2$ contained 0.0003% (as max.) manganese while $PbO_2$ obtained from Merck's was manganese free.

Thereupon an experiment was performed using Merck's $PbO_2$ and 0.0003% manganese as $MnO_2$ (see Chem. Ztg., 39, 858-859 (1915), J. Milbauer on "Minimum" for catalytic effects of oxides for the formation of $Pb_3O_4$). Otherwise the conditions of the experiment were kept identical (proportions the same, and three days at 260-275° C.) An exceptionally large crop of well developed large black crystals and a small amount of lead sodium compound.

The same procedure was repeated with 1% Mn as $MnO_2$ and again the same results were obtained although the yield was not nearly so good.

(ff) A mixture of 10 g. Mallinckrodt's $PbO_2$, 5 g. Merck's $PbO_2$, 5 g. NaOH and 20 cc $H_2O$ heated for three days at 260-275° C. and permitted to cool while in solder bath gave a very good crop of well formed large black crystals, a fairly good yield of the small black crystals and some lead sodium compound.

(4) Density: The density as reported by Simon apparently was taken on the powder sample of lead dioxide since he reports 9.604 while the density as determined on the true $Pb_2O_3$ crystals was found to be 9.925 (average of three determinations).

(5) Decomposition by Heat: The crystals are very resistant to decomposition by heat requiring bright red heat. On decomposition a mixture of the tetragonal and orthorhombic forms of lead oxide was found.

(6) Solubility in Acid: Sulfuric and nitric acids show very little, if any, visible effect either at room or boiling temperatures. Cold (con.) hydrochloric acid gradually changes the crystals over to lead chloride over a period of several days, while the other known oxides are usually converted over in a relatively short time.

(7) Crystallographic analysis: In a preliminary examination these elongated crystals were found to be definitely of the triclinic system, the axes a to b to c approximately equal to one to one to five. The angle beta equals 46°, gamma 98°; and alpha 82°. Twins are common with b as the twinning axis and 010 as the composition plane. Common crystal forms are the three pinacoids, the prism 110 but not 110, the dome 011, the dome 101, the dome $\bar{1}01$ and occasionally another prism 130. The crystal has conchoidal fracture and apparently no cleavage, although repeated twinning on the 010 face sometimes simulates cleavage. The luster is brilliantly vitreous; color, jet black.

(8) Chemical Analysis: Due to possible instability the sample was not dried in oven previously. To insure a relatively pure

sample the crystals had been separated by hand with the aid of a 10x hand lens. A sample of red lead (pure crystals) was analyzed simultaneously to obtain some sort of a check on the methods used. For active oxygen the U.S. Bureau of Standards Method was used since it had been shown that the modified Bunsen method was giving results approximately 0.2% low. For lead the sulfate method, using HCl as solvent, was employed on account of its simplicity even if it has a tendency to be somewhat inconsistent.

| | Large Black ($Pb_2O_3$) | | Red Lead ($Pb_3O_4$) | |
|---|---|---|---|---|
| | Actual | Theoret. | Actual | Theoret. |
| Lead | 88.5<br>and<br>88.5 | 89.62% | 89.1% | 90.64% |
| Oxygen active | 3.445<br>and<br>3.46 | 3.46% | 2.32<br>and<br>2.33% | 2.34% |

In attempting to dissolve the crystals for analyses with nitric acid and hydrogen peroxide a very small precipitate remained which was later identified by means of x-rays as $Fe_2O_3$.

36. Hydrated lead sesquioxide ($Pb_2O_3 . 3H_2O$): To serve as a comparison with the above described crystals $Pb_2O_3 . 3H_2O$ was prepared according to the method of Glasstone and x-ray analysis showed the preparation to be truly amorphous as reported by Darbyshire. In the wet state it decomposes with age into lead dioxide and basic carbonate ($2PbCO_3 . Pb(OH)_2$). According to Darbyshire, these wet preparations all give an amorphous x-ray pattern even if the $PbO_2$ content varies from 17% to 57.1% as compared with the theoretical value of 57.7%.

37. Preparation of the small black crystals ($Pb_5O_8$):

(1) A mixture of 15 g. Mallinckrodt's $PbO_2$, 15 g. NaOH and 60 cc $H_2O$ for three days at 260-275° produced a small amount of these small black crystals, a few individual large crystals and mostly the lead sodium compound.

(2) See (3)-(bb), (cc) and (ff) above.

(3) Mixture of 10 g. Mallinckrodt's $Pb_2O$, 5 g. Merck's $PbO_2$ and 20 cc $H_2O$ heated three days at 295-310° C. gave a very good yield of the small black crystals--no large black crystals and some lead sodium compound.

X-ray studies showed them to have an individual structure not possessed by any other known lead oxide. A preliminary interpretation of the pattern would indicate a tetragonal structure where the value of the c axis is very nearly equal to unity.

(4) Chemical analysis: Crystals had been hand sorted and were dried overnight at 105° C.

Using U.S. Bureau of Standards and sulfate methods:

| $Pb_5O_8$ | | Actual | Theoretical |
|---|---|---|---|
| Pb | | 88.6 and 88.7% | 89.0% |
| Active Oxygen | + | 4.03 and 3.975% (Contained some insoluable fibrous material.) | 4.12% |

(5) Density: 9.514 (av. of three determinations).

(6) Stability: These crystals are also appreciably stable to dissolving action ($H_2SO_4$, $HNO_3$ or HCl con.), although not as much as the $Pb_2O_3$ crystals, and to temperature decomposition.

They form at a higher temperature (approximately 300°) than do the $Pb_2O_3$.

(7) Crystallographic analysis: These small crystals seem to vary in habit between a double pyramid and a short prism terminated with double pyramids, apparently of the tetragonal system. The axial ratios make c approximately equal to one. The crystal appears to be tetragonal although not completely measured. Lines on some of the pyramid faces parallel to the base give some indication of its symmetry. Since no measurements have been made on these crystals it apparently is possible that they may be orthorhombic with a very nearly equal to b since certain pyramids terminate in an edge instead of a point. This, however, may be due to distortion.

38. Effect of lower temperatures in the above procedures: Heating the mixture, 10 g. Mallinckrodt's $PbO_2$, 5 g. Merck's $PbO_2$, 5 g. NaOH and 20 cc of water at temperatures lower than 210° C. for three days did not change the $PbO_2$ structure in any manner whatsoever.

39. Temperature ranges at which these different crystals grow: The results of the general procedure (15 g. $PbO_2$ containing some $MnO_2$, 5 g. NaOH and 20 cc of water heated in bomb for three days) as regards temperature may be summarized as:

| Product | Formation Temperature |
|---|---|
| Sodium lead oxygen compound | 225 to 350° C. |
| $Pb_2O_3$ | 240 to 275° C. |
| $Pb_5O_8$ | 270 to 320 °C. |
| $Pb_3O_4$ | 220 to 370° C.<br>(mostly above 350°) |
| PbO | Above 350° |

### (f) Lead Sulfates and Basic Lead Sulfates

#### a. Lead Sulfate

40. Since lead sulfate and probably basic sulfates are some of the primary constituents which we may expect to find in battery plates at the various stages of discharge a careful study of these substances is essential.

1. Normal lead sulfates were prepared by the following procedures:

(a) Lead oxide (tetragonal) in contact with excess sulfuric acid for several days.

(b) Test lead dissolved in dilute nitric acid, cooled and concentrated sulfuric acid added, washed and permitted to dry naturally.

(c) Test lead dissolved in dilute nitric acid, evaporated to dryness, redissolved with acetic acid and dilute (1:1) sulfuric acid added while the solution was boiling hot. The mixture was then heated to dryness, washed and dried at 110° C.

(d) Sample was prepared by and obtained from Dr. J. H. Reedy.

(e) Tetragonal lead oxide was digested with excess (1.280) sulfuric acid for thirty-six hours, heated to dryness, washed and dried.

(f) The above procedure was repeated using concentrated sulfuric acid.

(g) Sample consisted of Baker's Analyzed Lead Sulfate without any further treatment.

All of the above preparations gave the same identical pattern with grain size as the only variation.

41. Basic Lead Sulfates. Since basic lead sulfates are the most logical intermediate compounds that one might expect to find in storage battery plates, they were studied in considerable detail.

42. There seems to be no question in the literature concerning the compositions of the basic sulfates of lead prepared by high temperature methods. The early work of Schenck and Rassbach, in which they studied molten mixtures of PbO and $PbSO_4$ previously described by Berthier and from which they concluded that the three basic sulfates $PbO \cdot PbSO_4$, $2PbO \cdot PbSO_4$ and $3PbO \cdot PbSO_4$ could exist, has been amply confirmed by Reinders, Schenck and Albers, Jaeger and Germs, Schenck and Borkenstein and Schenck.

43. With respect to the compositions of the basic lead sulfates prepared at low temperatures, however, the literature is somewhat indefinite. A brief chronological summary of the more important procedures reported as yielding basic sulfates will serve to illustrate the conflicting opinions of different investigators.

44. In 1899 Frankland postulated that $2PbO \cdot PbSO_4$ and $PbO_2 \cdot 2PbSO_4$ were formed when sulfuric acid was added to a lead oxide consisting of a mixture of litharge and red lead. Toelle later patented a process for preparing $2PbO \cdot PbSO_4$ by the slow addition of sulfuric acid to litharge. In 1893 a patent was granted to Lunge and Lyte for the preparation of basic sulfates of any desired composition by mixing appropriate amounts of lead nitrate and alkaline sodium sulfate solutions. By a very careful study of this reaction, however, Cloutier was able to find only one basic sulfate, $3PbO \cdot PbSO_4$. In 1896 Ganelin prepared $PbO \cdot PbSO_4$ by the treatment of lead sulfate with magnesium oxide and two years later Schulten reported the formation of the same compound by the action of sodium sulfate on a basic lead acetate solution. Following a rather extensive study of basic lead salts, Stromholm published his results concerning the formation of $3PbO \cdot PbSO_4 \cdot H_2O$ when sodium sulfate reacts with freshly precipitated lead hydroxide. In the same paper he discusses the preparation of $PbO \cdot PbSO_4$ by the reaction between lead sulfate and ammonium hydroxide. Pleissner using the latter process reported the same compound. In 1905 a German patent issued to Toelle and vom Hofe described the preparation of $PbO \cdot 2PbSO_4$, $PbO \cdot PbSO_4$ and/or $2PbO \cdot PbSO_4$ by the addition of PbO to moist $PbSO_4$, while a similar British patent issued to Kronen postulates the formation of $2PbO \cdot PbSO_4$. In 1910 Hileman prepared basic sulfates of lead merely by boiling $PbSO_4$ and PbO, the composition of the basic sulfates being predetermined by the amounts of sulfate and oxide used. In 1920 MacInnes, Adler and Joubert in an attempt to explain the fact that their measured acid consumption during storage battery discharge was lower than that demanded by the Gladstone-Tribe equations postulated that basic sulfates of the general form $_xPbO \cdot yPbSO_4$ were formed deep within the plates.

45. All of the above investigations, with the possible exceptions of those of Stromholm and Cloutier, are open to the objection that classical analytic (al) methods cannot as a rule distinguish (a) between a mixture A + B and a chemical compound A·B, nor (b) between a solid solution of A in B or B in A and the chemical compound, nor (c) between an equimolecular mixture of A·4B + A·2B and the single phase A·3B. These objections have already been pointed out by Thevenaz who suggested the use of X-ray diffraction methods since these can readily differentiate between mixtures, solid solutions and true chemical compounds.

46. Briefly outlined, this research consisted in the registration of approximately 200 patterns of basic sulfates prepared by various methods.

The more important procedures employed were as follows:

1. Reaction between sulfuric acid and lead monoxide. General equation = $(x + y)\ PbO + yH_2SO_4 = {}_xPbO \cdot yPbSO_4 + yH_2O$.

   a. Addition of varying amounts of sulfuric acid to moist tetragonal (red) PbO.

   b. Fast and slow additions of varying amounts of sulfuric acid to hot and cold water suspensions of tetragonal and orthorhombic (yellow) PbO.

   c. Allowing orthorhombic PbO to stand in tall glass cylinders under sulfuric acid solutions of various concentrations followed by analysis of samples removed from the centers of various segregated layers of residue.

2. Reaction between various amounts of $PbSO_4$ and PbO (both the tetragonal and orthorhombic modifications) in both hot and cold water suspensions for varying periods of time, covering the range from theoretical $PbO \cdot 2PbSO_4$ to theoretical $10PbO \cdot PbSO_4$. General equation = ${}_xPbO + yPbSO_4 = {}_xPbO \cdot yPbSO_4$.

3. Reaction between alkalies (NaOH and $NH_4OH$) and $PbSO_4$. General reaction = $(x + y)\ PbSO_4 + 2_xNaOH = {}_xPbO \cdot yPbSO_4 + {}_xNa_2SO_4 + {}_xH_2O$.

   a. Slow and fast additions of varying amounts of alkali to hot and cold water suspensions of the sulfate.

   b. Allowing $PbSO_4$ to stand in tall glass cylinders under alkali solutions of various concentrations followed by analysis of samples removed from the centers of various segregated layers of residue whenever such segregations were observed.

47. During and after the registration of the large number of patterns, an extensive statistical analysis of all the X-ray negatives was carried out. An idealized example will serve to illustrate the mechanics of this analysis. Suppose Pattern S, exhibiting 84 lines, has a set of 40 which matches a corresponding set of 40 of the 78 lines of Pattern Y. It follows that Substances X and Y contain at least one common constituent A. Obviously it is impossible from just these two patterns to say that the 40 matched lines are due to but one common constituent (they might arise from 2 or more). In order to differentiate between a single and a mixture of common constituents it is necessary to analyze a large number of other patterns exhibiting the 40 matched lines. If in *all* cases the 40 lines appear simultaneously, *always* have the same relative intensities and *always* have the same characteristics (speckled, indicating large grain size, or smooth, indicating smaller grain size), we can assume with a reasonable degree of assurance that only one common constituent A is present in Substances X and Y and moreover that this component is characterized by the 40 matched lines. Referring again to Pattern X and Y, the lines of X unmatched by any of those of the Y pattern indicate the presence in X of one or more constituents absent in Y and the lines of Y unmatched in the pattern of X are indicative of

one or more constituents in Y absent in X. Statistical investigation again will lead to an evaluation of the number of non-common constituents in X and Y with a determination of the pattern characterizing each constituent.

48. With approximately 200 patterns, the statistical labor involved becomes enormously large, but at the same time it is essential for the identification of the components of mixtures containing unknown amounts of unknown constituents. It is not necessary here to present the data in lengthy and cumbersome tables. The results of the analysis can be summarized best by the statement that all the patterns could be considered as composites of but three primary patterns. The fact that three patterns are necessary to account for all of the observed diffraction effects proves that a minimum of at least three basic sulfates of lead exist and implies (the implication is not proof since only 200 patterns were registered) that only three can exist.

49. It is, of course, possible from the above analysis to calculate the pattern of each theoretically 100 per cent pure basic sulfate. Any preparation then which matches one of these patterns exactly over the entire range of reflections with no evidences whatsoever of extra lines may be considered as being homogeneous and a subsequent chemical analysis of this material or a knowledge of the amounts of reactants required for its preparation may be used to determine the chemical formula of the basic sulfate concerned. Thus, using the X-ray pattern as a criterion of purity and a chemical analysis or synthesis as a criterion of composition, it is theoretically possible to assign definite formulae to each of the three observed basic sulfates.

50. Certain preparations made in the course of the above experimental work gave patterns which corresponded very closely to the three theoretical patterns of the 100 per cent pure basic sulfates. Moreover, it was found possible, using data obtained in the synthesis of each of these preparations, to assign chemical formulae to each of the three possible basic salts.

51. In Plate 5a, pattern 2a is of a substance prepared by boiling a known amount (42.07 gms.) of pure lead oxide with distilled water until the liquid phase was basic, the decanted solution neutralized with sulfuric acid and then boiled again with the residual oxide, the slow addition of acid being continued to complete neutralization. The residue was then filtered, washed, dried and its pattern registered. The total elapsed time required for the neutralization approximated 30 hours and the total amount of 4.46 molar sulfuric acid used was 10.07 cc. The X-ray pattern shows that the material is very nearly a single homogeneous basic sulfate, since it corresponds quite closely to the theoretical pattern of one of the basic sulfates, and the amounts of acid and oxide used for its preparation show that its formula corresponds to $4PbO \cdot PbSO_4$. It might be added here that if the neutralization is carried out carelessly, especially if the endpoints are far overstepped, a mixture of various basic sulfates will result, the X-ray pattern in some cases showing the superimposition of all the theoretical basic sulfates. This same basic sulfate in a practically pure form can be and was obtained by the addition of 25.0 cc of 20 per cent NaOH to a suspension of 23.7 gms. of $PbSO_4$ in boiling hot water and also by the boiling of

a mixture of 20.0 gms. of $PbSO_4$ and 58.5 gms. of PbO for approximately 10 hours. In both of these cases the amounts of reactants correspond to the formula $4PbO \cdot PbSO_4$.

52. Pattern 2b in Plate 5a is of a material prepared by refluxing 17.2 gms. of PbO with 7.8 gms. of $PbSO_4$ for approximately 40 hours. The X-ray pattern indicates homogeneity while the amounts of PbO and $PbSO_4$ used assign a formula $3PbO \cdot PbSO_4$ to the compound formed. This trioxysulfate of lead is probably the most difficult to prepare pure since a definite tendency exists for the reactants to precipitate a mixture of the tetra, the tri, and the dioxy lead sulfates. Moreover, boiling the trioxy form with PbO results in the formation of $4PbO \cdot PbSO_4$ while boiling with $PbSO_4$ precipitates the $2PbO \cdot PbSO_4$ compound. It is possible that the trioxy form is a manifestation of excess PbO incorporated into the $2PbO \cdot PbSO_4$ lattice or, what seems less probable, of excess $PbSO_4$ in the $4PbO \cdot PbSO_4$ lattice along lines described by Strock in his article on defect structures. Pattern 2b is the only one obtained which indicates that the $3PbO \cdot PbSO_4$ compound is not closely related structurally to the $2PbO \cdot PbSO_4$ salt. To this extent, therefore, there is some uncertainty as to the existence of the $3PbO \cdot PbSO_4$ as a separate, distinct structural entity.

53. Pattern 2c in Plate 5a is that of a basic sulfate prepared by the addition with continuous and rapid stirring of 52.2 cc of sulfuric acid (50.11 per cent) to a suspension of 250 gms. of PbO in 1000 cc of water at 25° C., the acid addition being so slow that the mixture never became acidic. The X-ray pattern again indicates homogeneity and close correspondence to the pattern of the theoretically possible third basic sulfate and that amounts of acid and oxide used indicate that the chemical formula of this basic sulfate is $2PbO \cdot PbSO_4$. The 2c material can also be prepared by refluxing appropriate amounts of PbO and $PbSO_4$ for approximately 30 hours.

### (g) Lead Carbonate Studies

54. A pattern obtained from various substances of diverse sources, some of which indicated a possible carbonate compound, prompted these investigations. A series of carbonates were prepared:

a. Thirty grams of tetragonal lead oxide were added to several hundred cc of distilled water in a test tube (approximately 1-1/4" x 10"). The tube was suspended in boiling water and $CO_2$ gas introduced while the mixture was vigorously agitated with a mechanical stirrer. At thirty minute intervals a sample of the mixture was removed by means of a specially constructed pipette. These samples were immediately filtered and dried under vacuum. The X-ray results showed that at the end of two hours a definite compound, which from now on will be referred to as structure I, had formed which then rather suddenly (between 2 and 2-1/2 hours) changed over into a new definite compound, structure II, (later identified as $2PbCO_3 \cdot Pb(OH)_2$), which in turn gradually was transformed into a third compound, structure III, having the same crystal structure as Baker's Analyzed Basic Lead Carbonate. It was also observed that the lead oxide available for this investigation already contained a small amount of structure I, evidently due to exposure to air.

b. The above procedure was repeated with yellow or orthorhombic lead oxide (somewhat larger in grain size than the tetragonal oxide) and identical results were obtained. It should be noted, however, that the reaction time for this oxide was very nearly double that for the tetragonal oxide or:

| Structure | Tetragonal | Orthorhombic |
|---|---|---|
| I | 2 hrs. | 4 hrs. |
| II | 2-1/2 hrs. | 6 hrs. |
| III | 5 hrs. | 12-1/2 hrs. |

Again the oxide available contained a small amount of structure I.

55. Comparisons of the above results with the patterns obtained previous to this work from substances of various other sources and various carbonate preparations gave the following results:

(a) Eagle Picher White Lead (Old Dutch Process)-structure II.

(b) Precipitate from supernatent liquid from $3HNO_3 + Pb_3O_4$ - structure II.

(c) "Pearly" precipitate from supernatent liquid from $9PbO + H_2SO_4$- structure II.

(d) Precipitate from dissolving lead acetate in cold water - structure II.

(e) Sample from Mr. Seabury, tetragonal oxide boiled in water for a long time - structures I and II.

(f) Product leached from a partly discharged negative plate (from pos. plate formation studies) - structure II with several lines unaccounted for.

(g) Lead acetate in water treated with $CO_2$ gas - structures II and III.

(h) Lead nitrate treated with sodium bicarbonate and lead acetate treated with sodium bicarbonate - structure III with several lines mission indicating that Baker's analyzed product was a mixture containing some of structure II.

(i) Excess lead nitrate treated with sodium bicarbonate gave a new unidentified structure.

(j) Excess ammonium carbonate treated with lead nitrate gave the same results as "h".

(k) Lead nitrate treated with sodium carbonate (both solutions hot) - same as Baker's analyzed product or III and several strong lines of II (both solutions cold) - structure II and III.

(l) Lead acetate treated with sodium carbonate - structure III - one line hard to account for.

(m) Lead acetate treated with $CO_2$; the precipitate washed and kept for several days in water made slightly alkaline with $NH_4OH$ (one drop). Same as Baker's analyzed - two extra lines.

(n) Excess lead nitrate treated with sodium carbonate - apparently is a transition from structure II to III. Some of the fuzzy lines are hard to explain otherwise.

(o) Cerussite from the Geology Department - same results as "h" above.

56. A correlation of the above facts, together with the results of a chemical analysis from Mr. Lindgren's laboratory showed that Baker's Analyzed Basic Lead Carbonate was essentially normal lead carbonate and thus gave a solution to this rather complex problem.

57. The compound with structure II is of special interest since it was so readily obtained from such a variety of sources and a definite knowledge concerning its composition was essential at this point. The facts leading to these conclusions may be briefly stated as follows:

(1) Eagle Picher White Lead (Old Dutch Process) is supposedly basic lead carbonate and agrees with structure II.

(2) Cerussite is normal lead carbonate and agrees with structure III.

(3) Baker's Analyzed Basic Lead Carbonate agrees essentially with structure III.

(4) Mr. Lindgren's report gives as average results:

| Structure | No. 1 | No. 2 | No. 3 |
|---|---|---|---|
| PbO | 88.15% | 87.18% | 83.8% |
| $CO_2$ | 10.58% | 11.71% | 16.05% |
| $H_2O$ (by absorption) | 1.82% | 2.26% | 1.59% |
| (by difference) | 1.27% | 1.11% | 0.15% |

(5) The theoretical values for $2PbCO_3 \cdot Pb(OH)_2$ are:

| | |
|---|---|
| PbO | 86.35% |
| $CO_2$ | 11.33% |
| $H_2O$ | 2.32% |

and for $PbCO_3$;

| | |
|---|---|
| PbO | 83.53% |
| $CO_2$ | 16.47% |

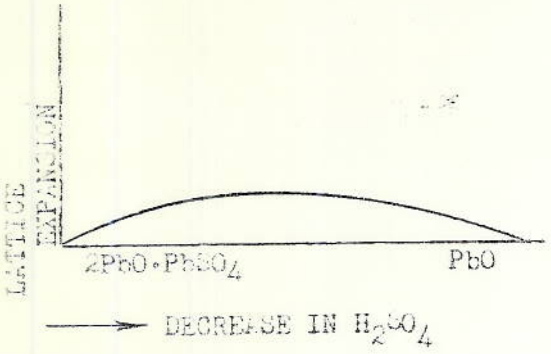
57. Thus the composition of the compound with structure II is in good agreement with the theoretical values for the basic lead carbonate - $2PbCO_3 \cdot Pb(OH)_2$ - and that of III with the values for normal lead carbonate - $PbCO_3$ (Plate 5b).

### (h) Distortion Studies

58. Numerous distorted effects obtained in various cases, especially when there was a question of transformation from one compound to another, or addition or removal of oxygen to an oxide without any observed changes in crystal structure, led to the following preliminary investigations. The two substances were intimately mixed together and enough water was added to make a paste which was then worked with a spatula for thirty minutes. Thereupon the specimen was dried under vacuum prior to the X-ray studies.

59. In all cases new compounds are formed as is shown by the new lines coming into the pattern while at the same time the lattice of the oxide is decidedly distorted before the crystal structure finally changes over. The lines do not disappear uniformly from the pattern and in some cases exhibit considerable fuzziness.

60. From basic sulfate studies it was found that where $H_2SO_4$ had been added in amounts too small to produce a basic sulfate the lattice of the oxide expanded unquestionably beyond any experimental error. This effect can be shown, perhaps best, in graphic form (patterns 196-200).



61. Some variation for line shifting can at times be explained by variation of the sample height which, of course, in all cases is quite small and can readily be checked by a full size drawing of the equipment used. No such variations were possible in these patterns, however,

## II. Studies of Positive Battery Plates

### (a) Commercial Batteries

62. Positive plates from commercial batteries were studied by mounting the powdered active material in the 45° wedge. The following were studied:

a. Material from Prest-O-Lite formed plate gave a pattern identical with that of lead dioxide.

b. Plates from a Prest-O-Lite "mercury" which was completely dead, supposedly due to standing without charging, showed a few large, scattered, white crystals on the surface which were evidently deposited lead sulfate. X-ray results on the surface showed the plates to consist of lead dioxide including a very small amount of large grained material, the spots being too much scattered for absolute identification. The material from the interior gave a similar pattern but without the large grain specks. This would indicate that the positive plate is not readily subject to self discharge. These results were also verified, although not so completely, from studies of other makes of batteries as Firestone, etc.

c. A group from the above battery was charged and then dismounted. Some of the plates were only rinsed in water and then dried on the radiator while the remainder was thoroughly washed in running water (five hours) and dried. All results, both from surface and interior, were very nearly identical with pure lead dioxide indicating that washing for positive plates is not so very important.

d. Material from a Globe Union plate, formed, dismounted and washed several years ago gave a pattern identical with lead dioxide.

e. The third cell of the above "Mercury" battery was charged in reverse order for 97 ampere hours expecting to find the positive plate converted, at least to some extent, to lead. The results, however, showed very coarse lead sulfate on the surface with just an indication of dioxide (the strongest line). Toward the center (light brown regions) finer grained lead sulfate was found, containing considerably more dioxide, while along the grid wires conversion to relatively fine grained lead had taken place. A very small amount of lead sulfate was found in this lead, as well as some lead oxide, no doubt formed from very finely divided active lead during washing. Several of the faint lines also appeared which could not be accounted for.

f. Willard positive material gave the dioxide pattern but in addition showed a distorted structure (fuzzing between first pair of triplet and one weak line considerably heavier than expected). Careful examination of the positive plate material from old batteries near the grid wires shows the formation of a very dark brown scale while between this scale and the grid proper a thin film of a white material is found. X-ray results showed the scale to be a mixture of small grained lead sulfate and what appears to be highly distorted lead dioxide, and the white film to be principally composed of finely divided lead sulfate.

63. In all these preliminary studies evidences of secondary or intermediate compounds, although not any too positive, were nevertheless not entirely lacking.

### (b) Positive Plate Formation Studies

64. For these studies a small storage battery was constructed which

was mounted in an X-ray camera and X-ray patterns were taken during the formation of the battery plates. The dimensions of the battery were calculated so that a plate to electrolyte volume ratio existed in the same proportion as it does in a commercial unit. The charging and cycling rates per unit positive plate area were also kept the same as in industrial practice. The plate under observation was made the center (of three) plates of the battery. (Plates 6a and 7)

## III. Studies of Negative Plates

### (a) Commercial Plates

65. All negative materials were treated and studied in the same manner as were the positive materials:

a. Formed Prest-O-Lite material consisted mostly of very finely divided lead. The pattern also showed a number of foreign lines which agree with the basic sulfate pattern No. 188 ($3PbO \cdot PbSO_4$) as far as spacings and relative intensities are concerned.

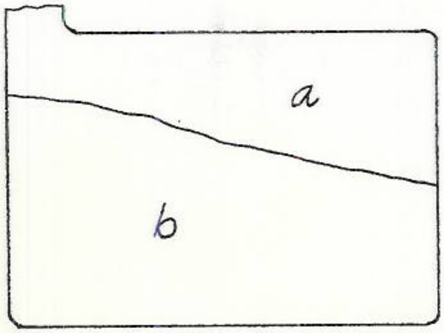
b. A study of "dead" negative material from the "Mercury" battery revealed very coarse grained lead sulfate on the surface. In the interior the particle size was decidedly smaller and a very small amount of lead still existed. This would indicate self discharge in the negative plates, which phenomenon was not observed in the positive plates of the same group.

c. A group from the above battery was charged (152 amp. hrs.) before dismounting it for examination. During drying these plates became somewhat warm due to probably insufficient washing. As soon as this was observed, washing was again continued. The drying was natural in open air. Results showed the surface of the plates to be still mostly lead sulfate, of large grain size, and a small amount of lead. The inside of the plates was primarily lead of comparatively larger grain size and a small amount of normal lead sulfate which appeared reasonably small in grain size. Faint extra unaccounted lines also appeared representing rather long spacings (3-5 Å). Most of these lines were later shown to be due to the characteristic radiation of the X-ray tube.

d. Material from a Globe Union battery formed, dismounted and thoroughly washed several years ago showed about a 50/50 mixture of lead and lead oxide.

e. Negatives from the reversed group, as discussed for positive plates, were studied with the expectation of finding lead dioxide. The outside surface was still lead sulfate containing a very small amount of lead. Direct comparison of patterns would indicate a small change (increase) lattice spacings; actual measurements do show a decrease in film distance of 0.04 cm. for 8 cm. of film distance.

66. External appearance of plates:



(1) brown on surface

(2) hard and gray on surface. Region "a" was mostly lead and the remainder lead sulfate. Region "b" was brown (similar to lead dioxide) in the interior of the plate, but nevertheless showed about a 50/50 mixture of lead and lead sulfate. Signs of dioxide were not found anywhere in the plate. Later work indicated that the charging time was much too short to expect the results anticipated.

### (b) Antimony in Negative Plates

67. According to elementary principles of electrochemistry, antimony would be expected to dissolve from the positive grid into the electrolyte and then to be plated out on the negative plate. This would ultimately cause failure in the positive grid and, more seriously, would cause self discharge of the negative plate.

68. X-ray studies of pure test lead (without any antimony) prepared in the same manner as was used for the standard lead pattern, except that some of the samples were washed in water for 6 hours and then dried under vacuum, showed oxide formation in only the part of the cases where the samples had been washed. Practically all patterns showed numerous additional lines which were finally proved to be due to the individual characteristics of the particular X-ray tube.

69. Next grid metal (8-9% antimony as a rule) was studied. The alloy was filed with a new file, screened through a 200 mesh sieve and the X-ray pattern taken immediately. These patterns were much the same as the general pattern of the lead standard without any noticeable shift in lines.

70. As the X-ray spectroscopic method proved to be not sensitive enough for study of antimony, optical spectrographic methods were used. Spectrographic studies showed antimony to be present in appreciable amounts throughout the entire negative plate; various depths of the plate showed approximately the same proportions of antimony (Plate 6b).

### (c) Negative Plate Formation and Cycling Studies

71. For these investigations the same plan and procedures were followed as had been used for the positive plate studies with the exception that the negative plate was now made the center plate of the battery and the region observed was chosen reasonably close to a grid wire; a suggestion obtained from the positive plate studies (Plate 8).

## IV. Effect of Hot-Cold Cycling on the Sulfation of Battery Plates.

72. Two new (possibly had been slightly used) Delco batteries of serial number 13AA-WB4 were "boosted" before starting these tests; one (No. 1) for hot-cold cycling and the other (No. 2) for a control test at room temperature.

Gravities after charging:

No. 1 Pos. 1.290 Cen. 1.300 Neg. 1.295
No. 2 Pos. 1.295 Cen. 1.295 Neg. 1.298

73. Thereupon the center and negative cells were shorted through small wires (moderate discharge) taking the negative cell down to complete discharge and the center cell to half discharged condition. The following gravities were then observed:

No. 1 Pos. 1.290 Cen. 1.175 Neg. -- 22° C.
No. 2 Pos. 1.285 Cen. 1.175 Neg. -- 22° C.

74. Battery No. 2 was now permitted to stand undisturbed at room temperature for a period of four months. Battery No. 1 was alternated every 48 hours between a steam radiator and a refrigerator at 0° C. The radiator was, of course, of varying temperature but nevertheless above that at which any battery might be stored or subjected to in actual service.

75. Specific gravities were taken at various intervals during this cycling period:

| | Temp. | | Pos. | | Gen. | | Neg. | |
|---|---|---|---|---|---|---|---|---|
| Date | No. 1 | No. 2 | No. 1 | No. 2 | No. 1 | No. 2 | No. 1 | No. 2 |
| 2/26/35 | --- | --- | 1.270 | 1.265 | 1.180 | 1.200 | ---- | --- |
| 3/10/35 | --- | 22° | x | 1.260 | x | 1.180 | ---- | --- |
| 3/25/35 | 21-1/2° | 22° | 1.230 | 1.257 | 1.170 | 1.193 | ---- | --- |
| 4/25/35 | 22° | 22° | 1.218 | 1.240 | 1.157 | 1.179 | 1.056 | 1.055 |
| 6/ 2/35 | 30° | 30° | 1.203 | 1.218 | 1.143 | 1.157 | 1.050 | 1.050 |

x - Up to this point a regular battery hydrometer had been used.

76. To examine the condition of the plates by means of X-rays each group was removed from the container individually, a lower corner of one positive and one negative plate cut off by means of a coping saw and the group immediately returned to the container. These plate sections were then washed in running water for three hours and dried in a vacuum desiccator for 24 hours or more. These sections were then cut into smaller sections and mounted as shown in Plate IB for the X-ray investigation.

77. The plates were measured with a micrometer and studied at the surface, halfway to the center and at the center, the amount of material to be filed away being determined from the original plate thickness in each case and checked with the micrometer while filing.

78. After these studies, all groups were charged and again investigated to check up on the degree of conversion, particle sizes, etc. All examinations were made with copper K alpha radiation at 30 KV, 25 milliamperes, and three hour exposures.

## CONCLUSIONS AND RECOMMENDATIONS

### (a) Facts Established

79. The above work has established the following:

I. Chemistry of Lead and its Compounds with Oxygen.

a. The fundamental X-ray data for the application of X-ray methods to storage cells have been obtained.

b. The basic data on the chemistry of the several lead oxides have been established.

c. Lead Monoxide:

(1) Both modifications of commercial lead monoxide contain sufficient lead carbonate to show the strongest lines of these patterns superimposed on the oxide pattern.

(2) Changes from the one crystal modification to the other cause strain and distortion in the transition stage.

(3) Heating in water causes the orthorhombic form to change to the tetragonal.

(4) Boiling the tetragonal form in water converts it into basic lead carbonate.

d. Minium:

(1) Minium is a definite crystalline compound.

(2) Red lead treated with cold nitric acid produces colloidal lead dioxide.

e. Lead Dioxide:

(1) Lead dioxide from good storage battery plates showed a very distorted crystal structure.

(2) Synthetic lead dioxide did not show this distorted structure.

(3) The large crystalline "lead dioxide" of Simon proved to be $Pb_2O_3$.

f. Lead Sulfate and Basic Sulfates.

(1) Approximately 200 preparations of the basic lead sulfates were made, using several different methods, and their X-ray patterns obtained.

(2) These patterns were found to be composite of three primary patterns.

(3) The three primary patterns are due to three basic sulfates, $4PbO \cdot PbSO_4$, $3PbO \cdot PbSO_4$ and $2PbO \cdot PbSO_4$.

g. Lead Carbonates.

(1) X-ray data for three lead carbonates were obtained.

h. Distortion Studies.

(1) X-ray data showing the distortion effects due to chemical interaction of lead oxides were obtained.

II. Studies of Positive Battery Plates.

80. a. Commercial Batteries.

(1) In old batteries which were "dead" due to the combined effect of working and of standing in charged condition, no evidence of self-discharge was observed in the positive plates.

(2) Particle sizes decrease when passing from the surface to the center of the plate.

(3) In load discharges (as distinguished from self-discharge) the reaction always starts at the surface and progresses inwards.

(4) Charging does not affect the size of any lead dioxide particles which already exist.

(5) In the conversion of the sulfate, smaller lead dioxide particles may be formed.

(6) Lead dioxide starts to grow in grain size with a battery standing idle.

(7) During "self-discharge" the reaction occurs on the inside of the plate.

(8) Distortion of the crystal lattice of lead dioxide was found, especially in the better brands of batteries. This distortion increases towards the center of the plates.

(9) Considerably less time is required to obtain complete conversion in the positive plates than in the negative.

(10) Much more energy is required to completely reverse a plate than electrochemical calculations would indicate.

Lead dioxide is especially slow in changing over to lead.

81. b. Positive Plate Formation Studies:

(1) The "green" plate was composed of lead oxide which exhibited a rather distorted lattice structure.

(2) The height of the electrolyte was very critical. Only a thin film could be permitted over the surface to be studied. More than this would completely absorb the diffracted radiation.

(3) Finely divided lead sulfate was formed as soon as the electrolyte was added to the cell. The growth of this lead sulfate was quite rapid until an optimum size was reached.

(4) Conversion of the lead sulfate into lead peroxide starts at the surface of the grid and progresses radially outward from the grid.

(5) Several weak "fuzzy" extra lines which do not appear in C.P. dioxide patterns are found in these plate formation patterns.

(6) During the conversion not all the planes break over simultaneously since most of the lines representing the longer spacings are more persistent that the others.

(7) The conversion reaction with discharge starts on the surface of the plate and gradually moves inward. Such studies may be of considerable importance in determining the proper plate dimensions for various purposes.

(8) Complete conversion of the lead sulfate into lead peroxide is readily obtained.

III. Studies of Negative Plates

82. a. Commercial Plates

(1) Particle size decreases when passing from the surface to the interior of a plate.

(2) Charging does not affect the size of any lead particles which already exist.

(3) In load discharges the reaction starts at the surface and progresses inwards.

(4) In "self-discharge" the reaction occurs in the interior of the plates.

(5) Lead sulfate from self-discharge is extremely resistant to conversion into lead.

(6) Negative plates required more time for conversion on charge than do positives.

b. Antimony in Negative Plates.

(1) X-ray methods are not well adapted to studying antimony problems.

(2) Optical spectrographic methods are well suited to studying antimony.

(3) In negative plates from batteries, antimony occurs at all depths in the plates.

c. Negative Plate Formation Studies.

(1) The "green" plate was composed almost entirely of the basic sulfate $4PbO \cdot PbSO_4$.

(2) Fine grained lead sulfate formed immediately with the addition of the electrolyte.

(3) Free lead appeared after five hours of formation due to the position of the grid wire with respect to the region studied.

(4) Standing over a period of about four hours produced a considerable amount of lead sulfate on the surface of the lead.

(5) The grain size of the lead sulfate increased rapidly over a period of several days (time forming was in progress).

(6) High electrolyte level cuts out the diffracted radiation or the part of the pattern where the path through the electrolyte is longer, namely at the longer spacings.

(7) Lowering the electrolyte level removed the orientation effects obtained in many of the patterns.

(8) The planes of the lead sulfate crystals do not break down simultaneously since some of the weaker lines in the pattern persist (or perhaps even become stronger) while the strong lines disappear almost entirely in the new pattern. Furthermore, these lines are not found in the new (Pb) pattern.

(9) Grain growth of the lead was very noticeable with cycling (35 cycles).

(10) After thirty-five cycles, the battery was reversed and charged until the formerly negative plate was converted to lead peroxide. After reversal the "close in" spacings were not present. These lines may have been absorbed by the electrolyte, or slow to come in as in all observations previously. The dioxide spacings were otherwise in agreement as regards spacings and intensities. Thereupon the battery was given an intensive charging in the proper direction again, cycled once and an X-ray pattern taken. This pattern showed the coexistence of lead and lead peroxide without the presence of any lead sulfate. The lead during this procedure showed a very decided growth in grain size, although theoretically a decrease was expected as given in a previous Progress Report. Its spacings and intensities were in good agreement with the standard pattern. The dioxide, however, showed an excessive decrease in lattice dimensions, probably due to loss of oxygen from the lattice, as found by LeBlanc and Eberius, without any replacement by other atoms or groups. Decrease in intensities at shorter spacing would suggest excessive distortion or strained conditions in the lattice. Numerous other lines were also present in the pattern which at present have not been identified.

## IV. Studies of Hot-Cold Cycling of Batteries

83. For the sake of completeness and especially for future reference work these results will be given somewhat in detail.

84. A. In charged condition the following results were obtained:

(a) At surface:

No. 1 Positive: Standing had deposited a few large scattered lead sulfate crystals on the surface of the plates. Dioxide crystals showed some grain growth due to standing, but not to charging. Changes in lattice spacings were not observed and foreign lines were entirely absent.

No. 2 Positive: Here, too, a few scattered sulfate crystals had been deposited on the surface; however, less than in No. 1. All this surface was converted by charging. Grain growth, due to standing, was also less. Charging did not alter particle size. Distortion could hardly be recognized and there was no change in lattice dimensions sufficient to be observed. Foreign lines were not present.

No. 1 Negative: A few large scattered sulfate crystals were present. A superimposed pattern which was later identified as $3PbO \cdot PbSO_4$ was obtained before charging. Conversion to lead was complete while the lead had grown to large sized grains (somewhat less than No. 2) while standing. At least it is assumed that the growth was due to standing, or charging conditions. No patterns had been taken from these supposedly new batteries which may have been used slightly previously. Charging had a tendency to smooth out the lines somewhat, perhaps due to the formation of small grained lead upon conversion from the sulfate. Three faint extra lines appeared that could be accounted for by tungsten radiation from the L series.

No. 2 Negative: Pattern before charging contained same superimposed pattern as No. 1 but a little less pronounced. The deposited sulfate crystals were again present. Lead was present in large excess and showed very pronounced grain growth from standing. Charging could hardly account for this growth since it was only the equivalent of one cycle. Charging again smoothed out the lines. The charged pattern showed a considerable amount of lead oxide and again seversl lines due to tungsten radiation.

(b) Halfway to center of plate:

No. 1 Positive: Grain growth of dioxide less than on surface. Sulfate of grainy nature present - about 10 or 15%. No change in lattice spacings. Some evidence of distortion. A new line present before and after charging. (One line, as a rule, is without significance for identification.) Conversion of sulfate to dioxide was complete.

No. 2 Positive: Sulfate present as in No. 1; no lattice changes; grain growth less than on surface; grain size not changed by charging, and distortion effects and new line as in No. 1

No. 1 Negative: Showed lead - lead sulfate ratio of about 50/50 (no reason to be that high) the lead being quite granular and the sulfate of moderate particle size. Sulfate conversion was complete and five rather faint lines are unaccounted for by tungsten radiation.

No. 2 Negative: Grain growth much less than on surface and also less than in No. 1 Contained about 30-40% sulfate of moderate grain size before charging. After charging showed some oxide lines and two lines due to tungsten deposits on the target.

(c) At center of plate:

No. 1 Positive: Distortion effects very pronounced (about 6 or 7 new lines with fuzzy) before and after charging.

A little less sulfate formation than at halfway position. Grain size of sulfate was average. Concerning the dioxide--it is hard to decide on account of the superimposed crystalline sulfate pattern; spacings did not change on charging. One line came out stronger than in standard dioxide pattern (is a combination of dioxide and sulfate).

No. 2 Positive: Distortion effects were very pronounced; twelve new lines definitely crystalline in nature appear after charging of which about six were present before. All new lines found so far seem to belong to the same substance which thus far has not been identified. Somewhat less sulfate than in No. 1. Dioxide grain size unaffected by charging.

No. 1 Negative: Showed nearly same condition as at halfway position; two new lines before and four after charging due to tungsten radiation. A small amount of sulfate remained after charging. The lead showed some large grained structure, very nearly same size as in No. 2.

No. 2 Negative: Sulfate formation less than in No. 1; of average grain size, and conversion complete. The pattern shows a considerable amount of oxide and several lines due to tungsten both before and after charging.

85. B. Results obtained in half-discharged condition:

(a) At surface:

No. 1 Positive: Distortion effects were lacking. New lines were not observed either before or after charging. Plate consisted of about 60% sulfate, quite granular in nature, and was converted completely to dioxide after charging. Dioxide was quite grainy before charging (much less than in charged condition). Charging overshadowed these particles by the formation of an abundance of new small grained material. Changes in lattice spacings were not observed.

No. 2 Positive: Distortion or new lines were not shown. Plate had about same sulfate content as in No. 1 with complete conversion on charging. The dioxide after charging was more grainy than in No. 1. Lattice changes were not observed.

No. 1 Negative: Lead - lead sulfate ratio was approximately 50/50. The lead was very coarse in particle size before charging and possibly even larger after charging. The sulfate was of moderate size - about same as the lead. The pattern showed some oxide and two of the tungsten radiation lines. On charging the sulfate conversion was complete.

No. 2 Negative: Lead - lead sulfate ratio as in No. 1.

Conversion of sulfate complete. Lead of large grain size before charging; sulfate of average. Pattern before charging showed one extra line; after charging it showed a new superimposed pattern in very good agreement with that of fused oxide, which is a mixture of orthorhombic and tetragonal oxides.

The same sample that had been studied after washing was also studied without washing and dipped into collodion instead. This pattern showed a small amount of sulfate but no oxide. One line was stronger than expected. Consequently, oxidation during washing definitely accounts for the oxide formation. On the other hand, if the sulfuric acid is not removed it will react with the finely divided active lead. Washing with alcohol gives somewhat better results.

(b) Halfway to center of plate:

<u>No. 1 Positive:</u> Distortion effects were quite evident and somewhat overshadowed by charging. Several extra lines appeared and lattice changes were not observed. The sulfate was present in about a 50/50 ratio; of moderate grain size and converted over to dioxide completely. The dioxide grain size was smaller than in most of the previous cases.

<u>No. 2 Positive:</u> Distortion and new lines appeared as in No. 1. Sulfate was present to the extent of about 40 or 50% and converted completely on charging with grain size as in No. 1.

<u>No. 1 Negative:</u> Sulfate present in about 50/50 ratio. Particle size much less pronounced than at surface. Charging gave complete conversion. Charged pattern showed some PbO and two lines due to tungsten radiation.

<u>No. 2 Negative:</u> All conditions and behavior very similar to those of No. 1.

(c) At center of plate:

<u>No. 1 Positive:</u> Distortion was quite pronounced; orientation indicated. Sulfate dioxide ratio was about 40/60 before charging. Grain size of sulfate moderate; of dioxide quite small. Five of new lines present in charged state. Conversion of sulfate not quite complete.

<u>No. 2 Positive:</u> Distortion and orientation as in No. 1. Six or seven new lines observed. Dioxide grain size after charging somewhat larger than in No. 1. Sulfate conversion was complete.

<u>No. 1 Negative:</u> Lead - lead sulfate ratio was about 50/50, with particle sizes about the same as at halfway to center. Sulfate conversion complete. Lead grain size rather small

on the average with a few large particles. Four of the lines due to tungsten radiation and some oxide were observed.

No. 2 Negative: Lead - lead sulfate ratio was nearly 60/40. Particle sizes were average, that, however, being large when considered for lead in the interior. Conversion was complete on charging, giving lead grains larger than in No. 1. Considerable amounts of oxide were found while the extra lines due to tungsten were not very pronounced.

86. C. Results obtained in discharged condition:

(a) At surface:

No. 1 Positive: No distortion or new lines were observed. Plates consisted almost entirely of sulfate smaller in grain size than in No. 2. Dioxide after charging showed considerable growth - less, however, than No. 2. Conversion was complete and no change in lattice spacings was observed.

No. 2 Positive: Only a very small amount of dioxide left before charging. The sulfate existed as large particles which gave correspondingly large grained dioxide; larger than No. 1. Distortion, new lines or changes in spacings were not observed.

No. 1 Negative: A small amount of large grained lead was left before charging. The sulfate particle sizes were about average. Complete conversion was not obtained after 162 ampere hours (about 25% sulfate left even if gravity was well up). The lead after charging had approximately the same grain size as the sulfate before charging; hardly any fine grained lead was present at all. After 187 amp. hrs. there was still a small amount of sulfate left (large grains only). The lead still had about the same size as after 162 amp. hrs. and appeared in the ratio as in No. 2 after same charging time. After 235 amp. hrs. a very small amount of sulfate was still found; grain sizes were still excessive and several extra lines corresponding to tungsten radiation were observed.

No. 2 Negative: Only moderately sized sulfate, smaller in particle size than in No. 1, was found before charging. Complete conversion was not fully obtained after 187 amp. hrs. The lead formed had approximately the same grain size as the sulfate (very pronounced). Two of the extra lines due to tungsten radiation were found.

(b) Results halfway to center of plate:

No. 1 Positive: Only a very small amount of dioxide left before charging. The sulfate was reasonably fine in grain size (finer than usual) and conversion was complete. Distortion, new lines or lattice changes were not indicated.

No. 2 Positive: Dioxide - sulfate ratio as in No. 1.

Sulfate considerably larger in grain size than in No. 1. Conversion complete giving grainy dioxide. Distortion was questionable; changes in spacings unobserved and new lines indicated.

No. 1 Negative: Lead still present to the extent of about 10 or 15%. Grain size of sulfate considerably below normal; lead as usual. Incomplete conversion after 162 amp. hrs. (about 10% of the more grainy left). Lead rather coarse grained. Conversion after 187 amp. hrs. still incomplete. Sulfate present in increasing amount from surface on in, which is contrary to results obtained in formation studies. After 235 amp. hrs. a very small amount of sulfate still existed. After charging the lead was mostly very coarse grained. Two of the lines due to tungsten were observed.

No. 2 Negative: Mostly all rather small grained sulfate (as in No. 1). The conversion was quite complete giving rather coarse grained lead. Sulfate particles appeared to be getting smaller with rounded edges. Lead oxide and one faint line due to tungsten were found.

(c) Results at center of plate:

No. 1 Positive: Small amount of dioxide still present. Sulfate relatively fine grained. Some distortion with the appearance of several of new lines was found, one line being quite "fuzzy." No changes in lattice spacings.

No. 2 Positive: Constituents before charging as in No. 1. Sulfate grain size much larger than in No. 1. Distortion somewhat evident; orientation questionable and no change in spacings. Several of the new lines present - one rather "fuzzy."

No. 1 Negative: More lead remained than at midway region; grain size was average. Particle sizes of sulfate somewhat less than expected. Conversion incomplete after 162 amp. hrs.; some large grained sulfate left. Lead was quite granular after charging. After 187 amp. hrs. the lead- lead sulfate ratio was still about 75/25. Only large grained sulfate was found. After 235 amp. hrs. the results were practically identical with the midway region. Now the sulfate existed in decreasing amounts from the surface on in.

No. 2 Negative: Lead more pronounced than at midway region. Sulfate grains rather small (smaller than No. 1). After charging the results were very nearly the same as at midway position except that the extra lines due to tungsten radiation were stronger. The conversion was complete and some oxide observed.

(b) Recommendations

87. It is recommended that the Bureau of Engineering encourage the manufacturers of storage cells to adopt X-ray diffraction methods in their research work as a means of improving the characteristics of Navy storage batteries.

## APPENDIX A

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Table I

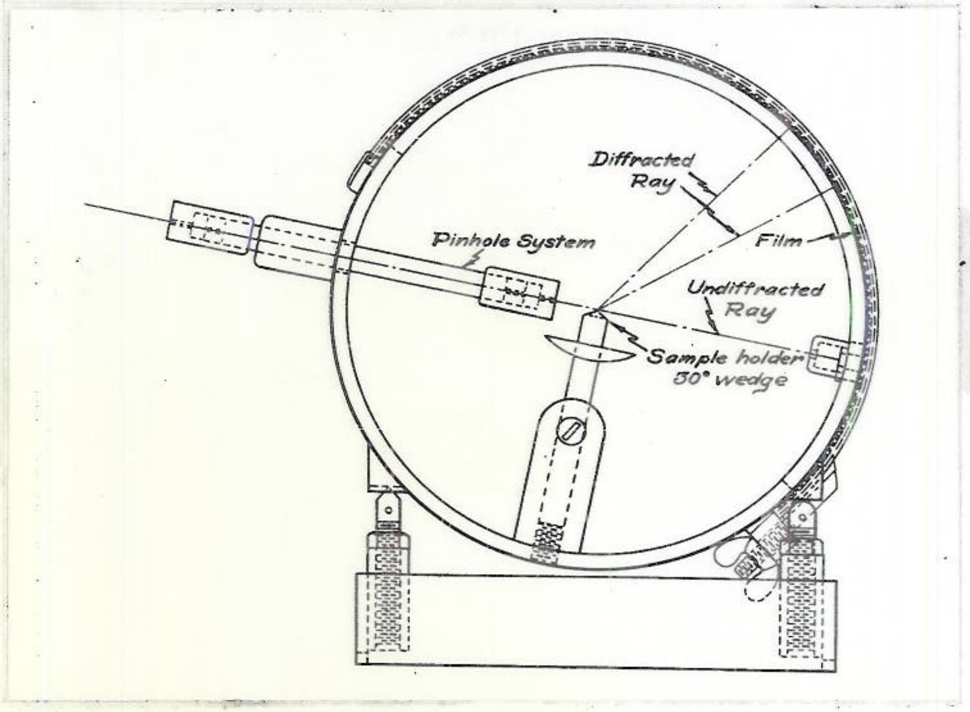
| | | Ratio | | Filtrate | | | | X-ray Results | |
|---|---|---|---|---|---|---|---|---|---|
| Sample | Pattern | $Pb_3O_4$ | $HNO_3$ | Acid or Neutral | Exp. Conditions | Per cent Active $O_2$ | $PbO_x$ | $Pb_3O_4$ | $PbO_2$ |
| 117 | 291 | 1 | 1 | | Room Temp. | 2.41 | $Pb_3O_{4.03}$ or $PbO_{1.343}$ | All | None |
| 118 | 292 | 1 | 1 | | 1 hr. Boil | 2.515 | $Pb_3O_{4.07}$ - $PbO_{1.36}$ | " | " |
| 126 | 300 | 1 | 2 | | Room | 2.99 | $Pb_3O_{4.28}$ - $PbO_{1.427}$ | " | " |
| 127 | 301 | 1 | 2 | | 1 hr. Boil | 3.46 | $Pb_3O_{4.48}$ $PbO_{1.493}$ | Nearly All | Strongest line faintly visible. |
| 128 | 302 | 1 | 3 | | Room | 3.83 | $Pb_3O_{4.63}$ - $PbO_{1.543}$ | Nearly All | Strongest line a little more pronounced. |
| 129 | 303 | 1 | 3 | | 1 hr. Boil | 4.51 | -- | Nearly All | Five of strongest lines coming in. |
| 115 | 289 | 1 | 4 | | Room | | -- | Mixture of both $Pb_3O_4$ in excess and $PbO_2$ lines very fuzzy. | |
| 116 | 290 | 1 | 4 | | 1 hr. Boil | | -- | None | All - good clear cut pattern. |
| 119 | 293 | 1 | 8 | | Room | 5.78 | $PbO_{1.865}$ | " | All - very diffuse pattern - colloidal or distortion? |
| 120 | 294 | 1 | 8 | | 1 hr. Boil | 6.21 | $PbO_{1.929}$ | " | All - good clear cut pattern. |

TABLE II

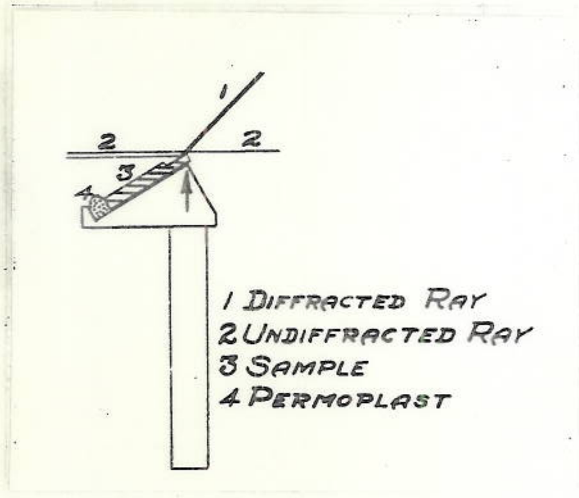
| Pattern | Description | $\%O_2$ | $PbO_x$ |
|---|---|---|---|
| $PbO_2$ | $PbO_2$ from storeroom | 6.13 | x=1.917 |
| | | 6.11 | 1.915 |
| | Different trials with | 6.155 | 1.921 |
| | different strength Kl | 6.16 | 1.921 |
| | solutions | 6.17 | 1.922 |
| $PbO_2$ | $PbO_2$ prepared with $Cl_2$ | 4.87 | 1.729 |
| $Pb_3O_4$ | $PbO_2$ prepared with $H_2O_2$ | 2.17 | 1.31 |
| $Pb_3O_4$ | $Pb_3O_4$ from storeroom | 2.05+ | 1.294 |
| $PbO_2$ | Distorted sample (No. 48) obtained from Dr. Mrgudich | 5.69 | 1.85 |
| $PbO_2$ | Same boiled in $H_2O$ - 1 1/2 hours | 5.69 | 1.85 |
| | Same boiled in $NH_4Ac$ - 1 1/2 hours | 5.96 | |

## TABLE III

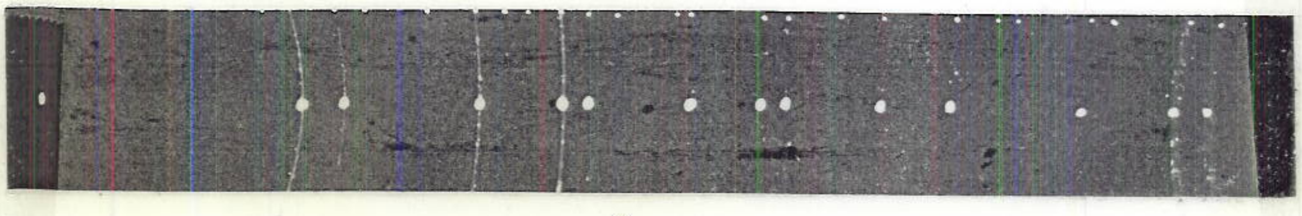
| Mol Ratios | | Order of Effectiveness | |
|---|---|---|---|
| 6 PbO | 1 $Pb(Ac)_2$ | 1 | |
| " | 1/2 $PbCO_3$ | 2 | |
| " | 1 $Pb(NO_3)_2$ | 2 | |
| " | 1 $PbSO_4$ | 3 | |
| " | 1 PbO (ortho) | 4 | |
| " | 1 $BaSO_4$ | 4 | |
| " | 1 $Na_2SO_4$ | 4 | |
| " | 1 $PbF_2$ | New compound and some distortion. | |
| " | 1 $PbCl_2$ | x | PbO was completely destroyed and a new compound formed. |
| | 1/2 $PbCl_2$ | x | |
| " | 1 $PbI_2$ | x | |
| " | 1 $Pb_3O_4$ | Just a mixture. | |
| " | 1 $PbSO_4$ (dry) | Just a mixture. | |


Diffracted Ray
Film
Pinhole System
Undiffracted Ray
Sample holder 30° wedge

a

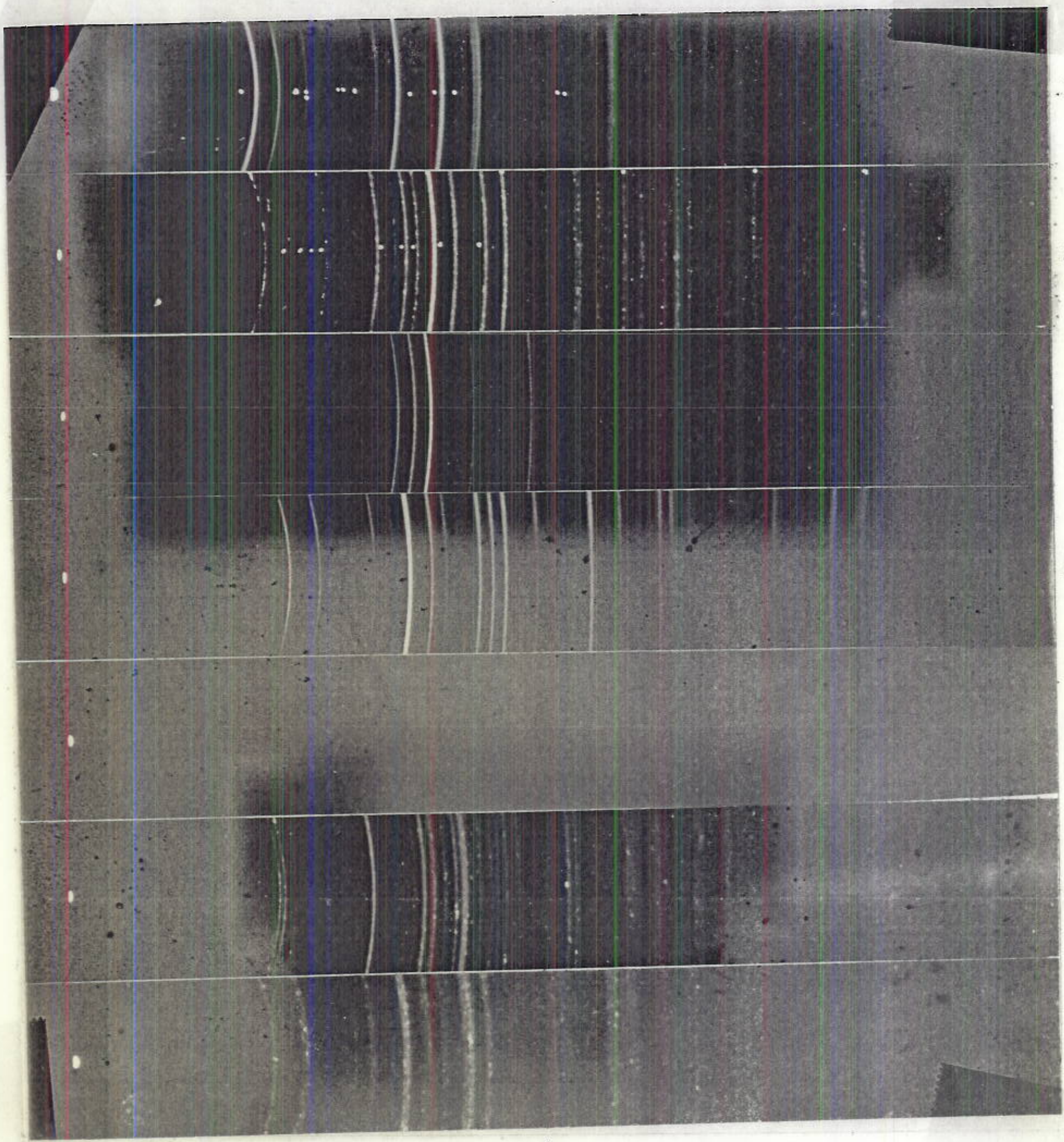

1
2
2
3
4
1 DIFFRACTED RAY
2 UNDIFFRACTED RAY
3 SAMPLE
4 PERMOPLAST

b



c

Plate 1



1-PbO (Tetragonal)

2-PbO (Orthorhombic)

3-$Pb_3O_4$

4-$PbO_2$

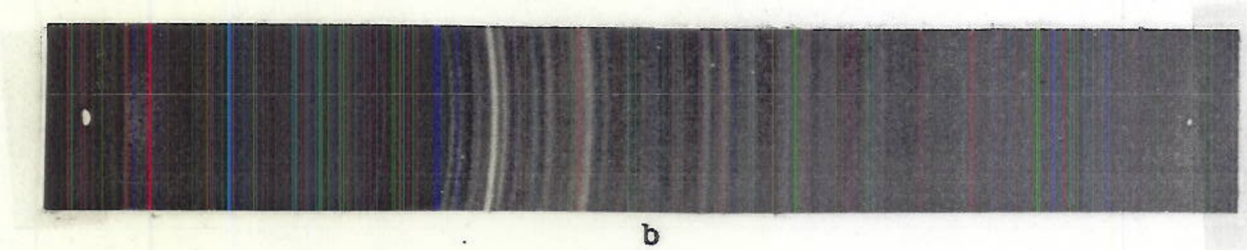
5-$Pb_2O_3$ $3H_2O$

6-$Pb_2O_3$

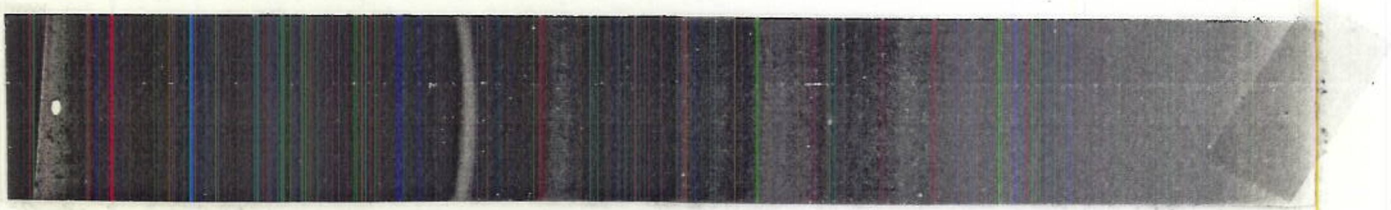
7-$Pb_5O_8$

Plate 2

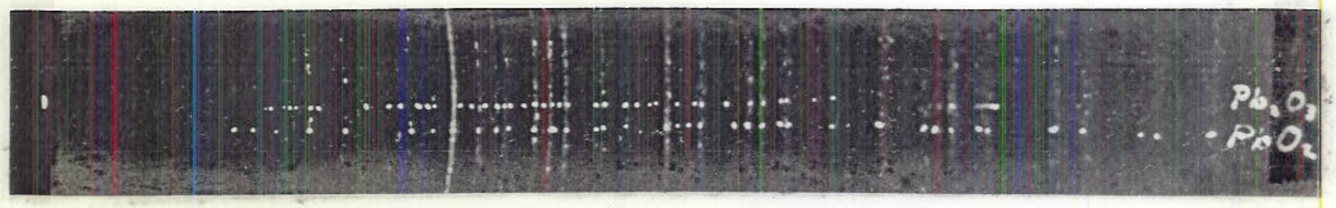
a



b

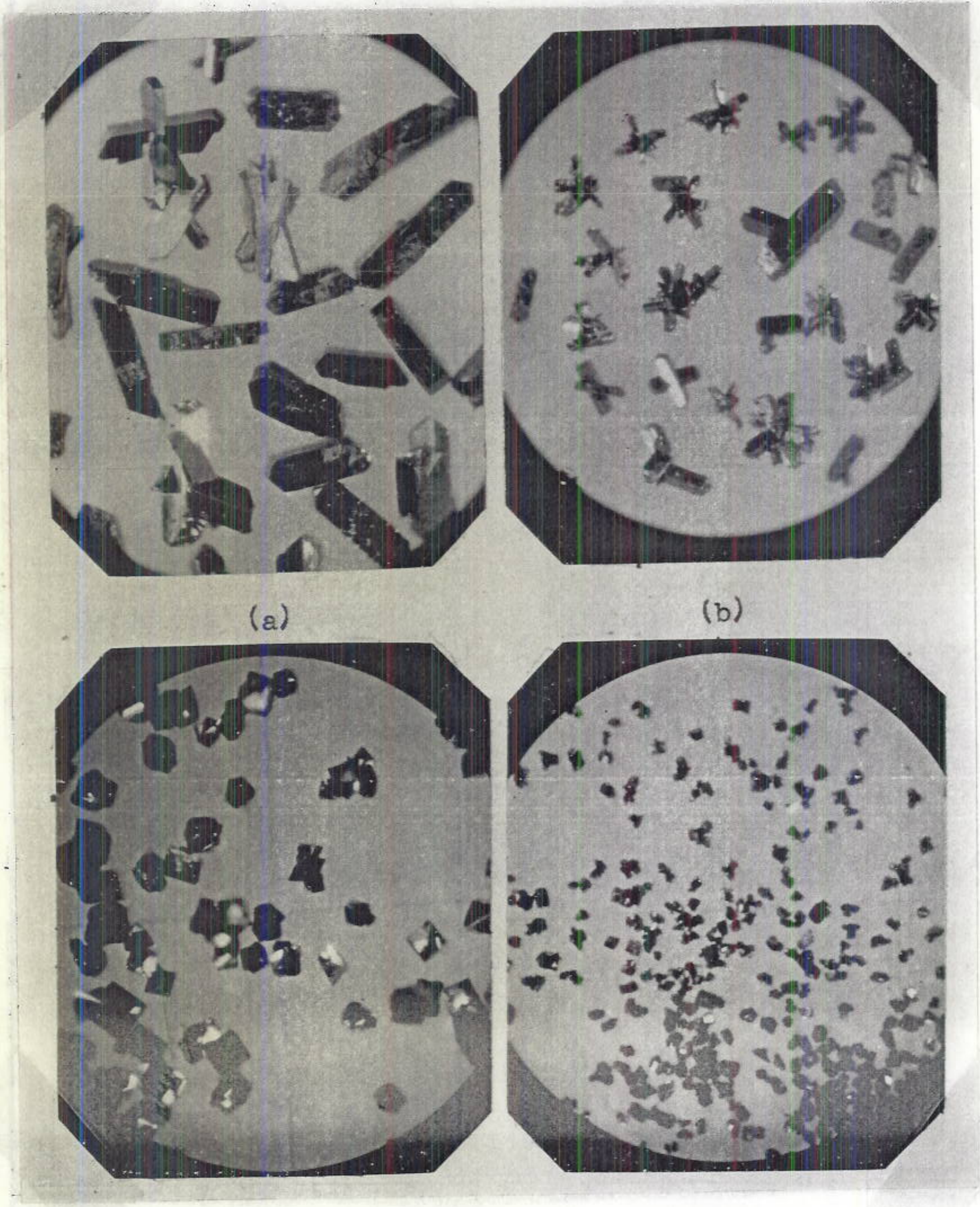


c



d

Plate 3

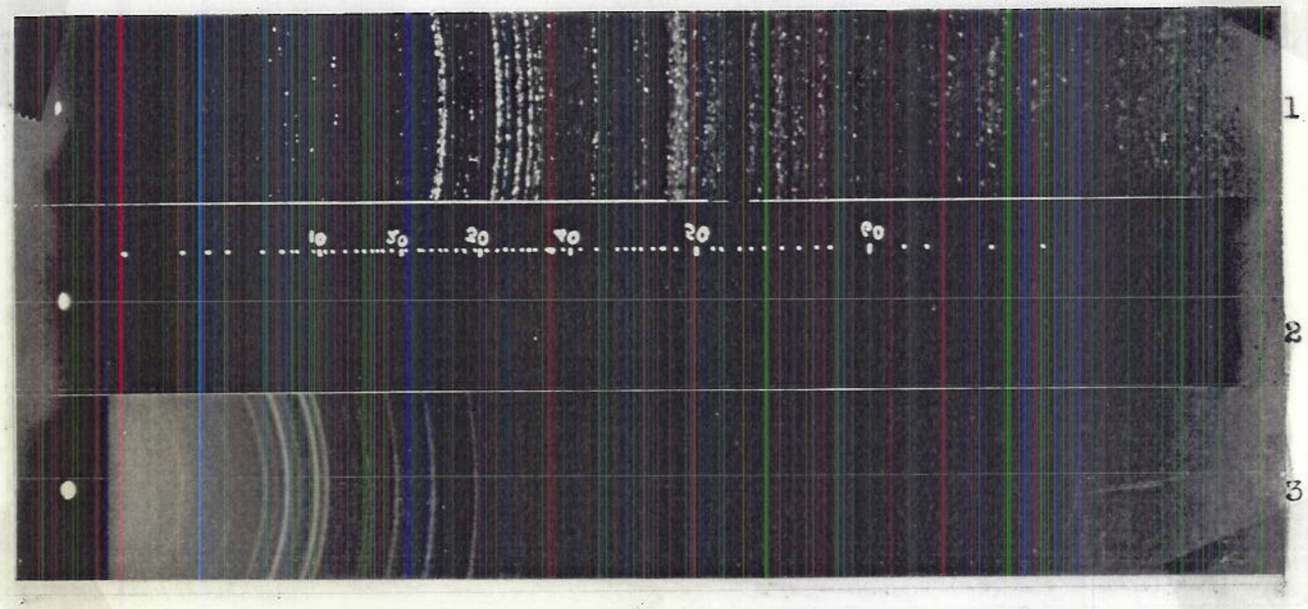


(a) (b)

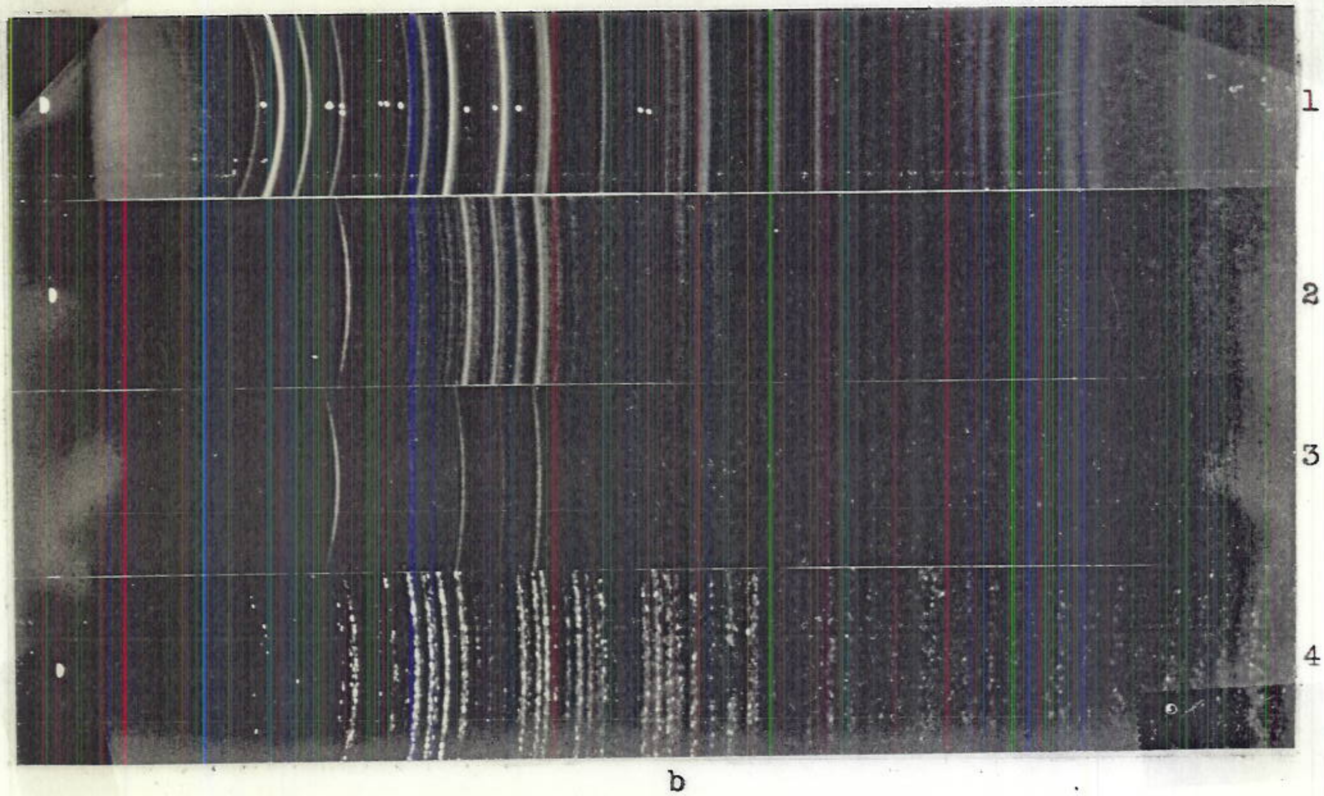
c d

a-$Pb_2O_3$, 10 diameters.
b-$Pb_2O_3$, 9 diameters, crystals from two different preparations.
c-$Pb_5O_8$, 32 diameters.
d-Simon's sample, 32 diameters.

Plate 4



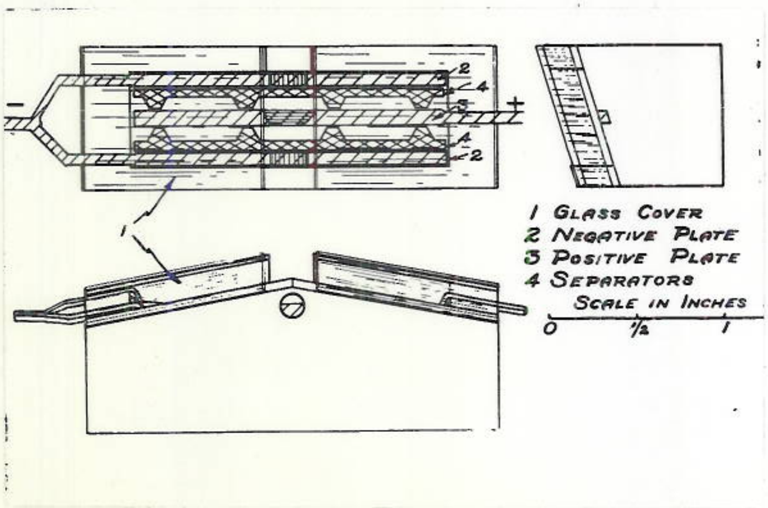
a



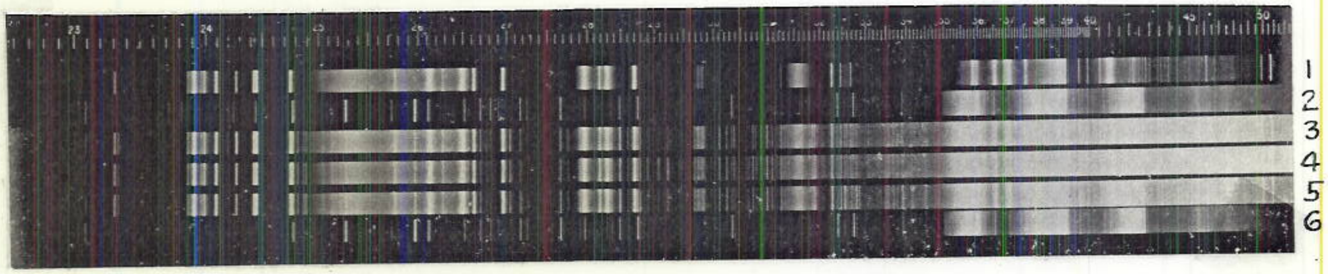
b

1-PbO (tetragonal)
2-Structure I
3-Structure II ($2PbCO_3 \cdot Pb(OH)_2$)
4-Structure III $PbCO_3$

Plate 5



a



b

1-Lead

2-Antimony

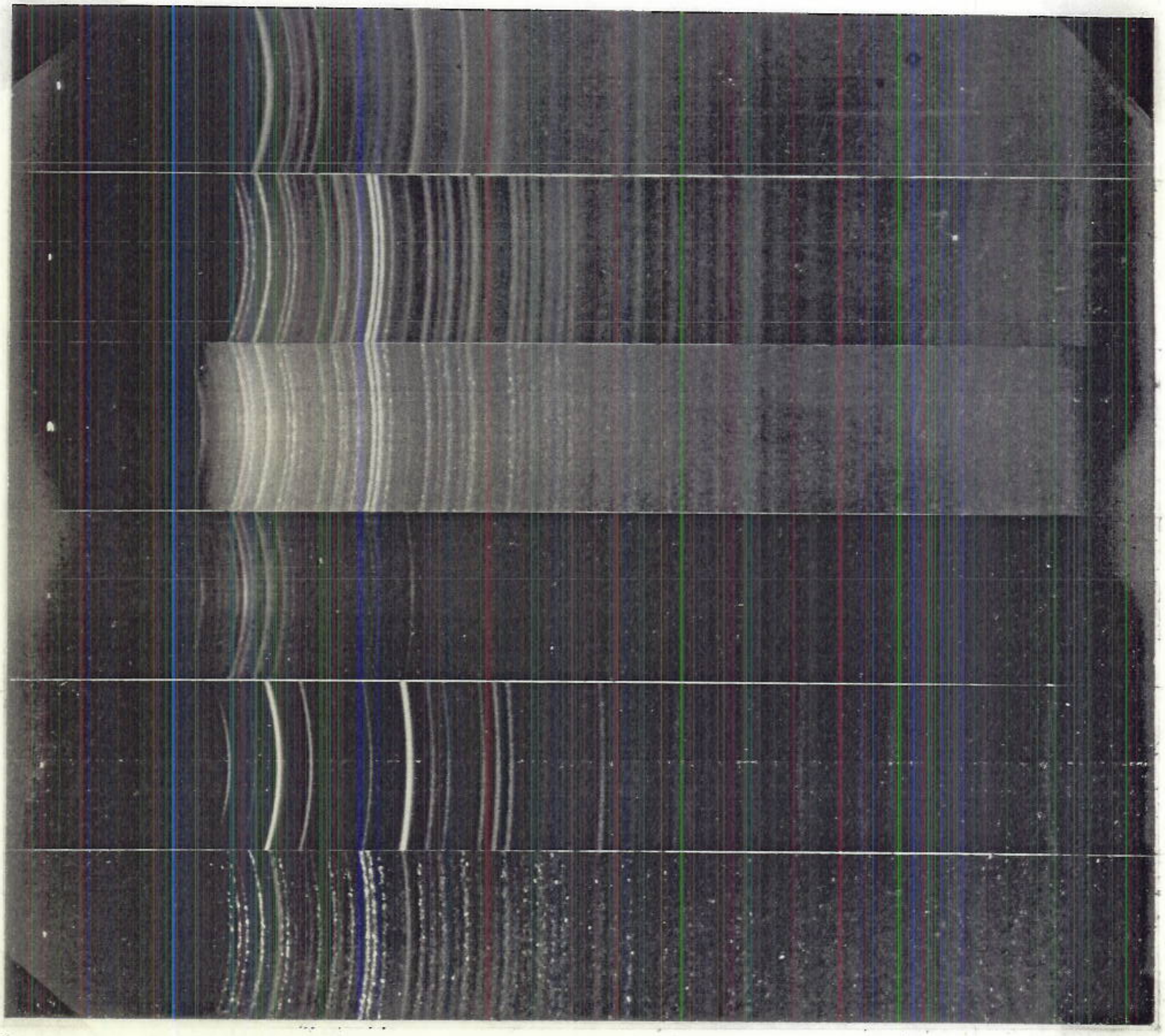
3-Plate:at surface

4-Plate:halfway to center

5-Plate:at center

6-Antimony

Plate 6



1-Green positive plate

2- " " " after $H_2SO_4$ has been added

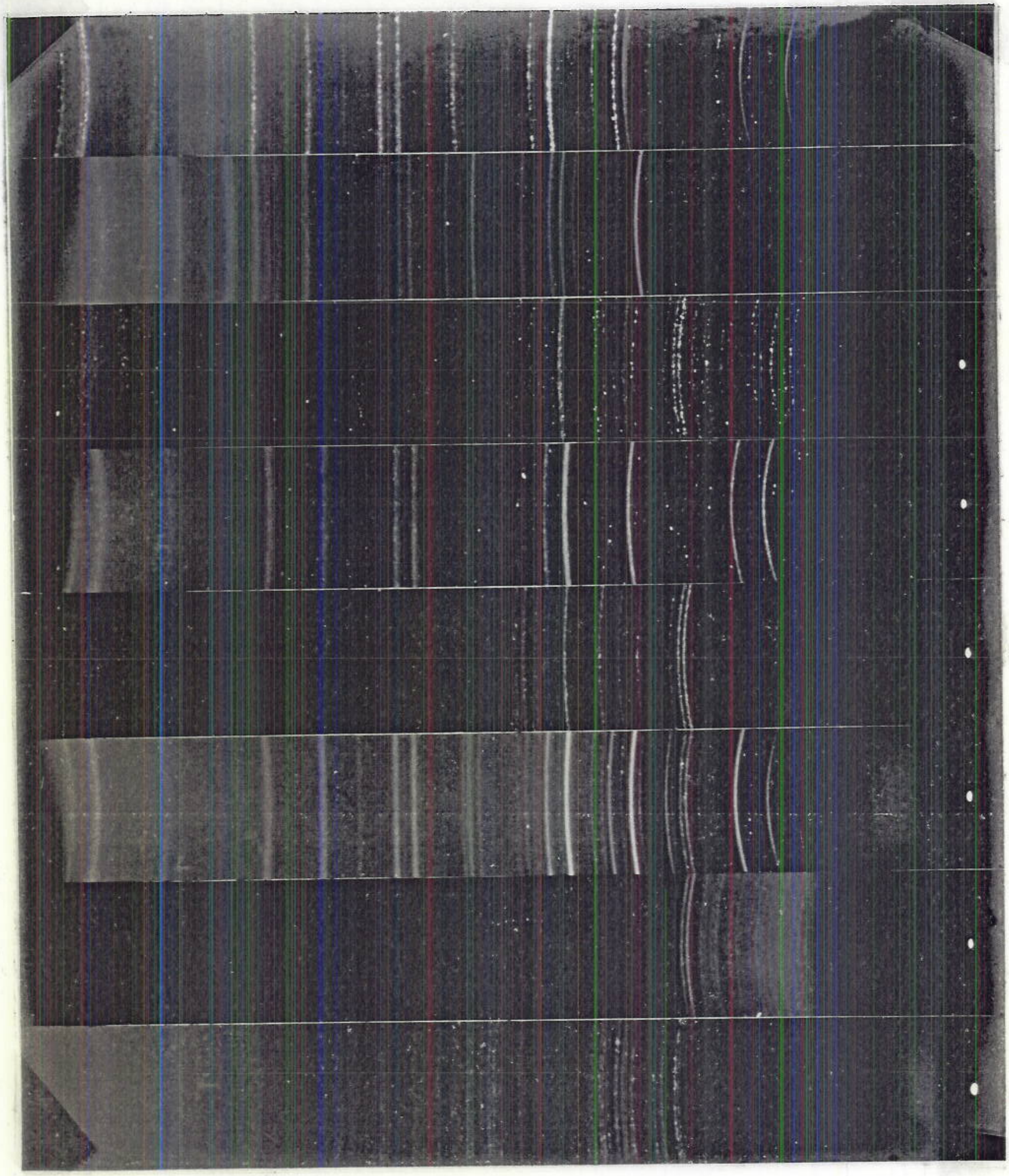
3-Formation time:33 to 37 hours

4- " " :52 to 54 hours

5- " " :66 to 69 hours

6-Condition of plate after discharge

Plate 7



1-Green negative plate
2-Formation time:1 to 5 hrs.
3- " " :31 to 34 hrs.
4-Complete discharge
after 4th. cycle
5-Charged after 34th. cycle
6-Discharged ater 35th. cycle
7-Reversed-now a pos.plate
8-Charged in proper direction
again(as a negative plate)
and cycled once.

Plate 8