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DIAMOND ORDNANCE FUZE LABORATORIES
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THE DETERMINATION OF GASES IN BARIUM CHROMATE
FOR USE IN PYROTECHNIC DELAY AND HEAT MIXTURES

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ABSTRACT

Barium chromate has been found to contribute water vapor and carbon dioxide to gases evolved by the combustion of pyrotechnic delay and heat mixtures in which it is used. A procedure has been developed for accurately measuring the gas-producing tendencies of barium chromate. In this test the barium chromate is heated in a tube furnace and the moisture and carbon dioxide are swept into absorption tubes where they are collected and weighed.

Data are presented to show the effect on the gas-producing tendencies of dried barium chromate samples of the following predrying treatments: exposure to various relative humidities; soaking in distilled water at a pH of 7; and soaking in dilute hydrochloric acid at a pH of 3.

The evaluation of a large number of commercial samples showed that the included moisture content of the dried samples may vary from 0.01% to 0.61% by weight, and the carbon dioxide content may vary from 0.00 to 0.63% by weight.

1. INTRODUCTION

Barium chromate powder is one of the ingredients used in a number of pyrotechnic delay and heat mixtures. The gases evolved during the combustion of these mixtures must be minimized since these gases usually introduce control problems in application of these mixtures in miniaturized ordnance devices.

Gases evolved from burning these powder mixtures containing finely divided metallic fuels, have been analyzed in the mass spectrometer by the Gas Chemistry Section of the National Bureau of Standards, and were found to consist mainly of hydrogen, water vapor, carbon monoxide and carbon dioxide. The hydrogen in these gases originally may have been dissolved in the metallic fuel or it may have been produced by the reaction between the metallic fuel and water vapor. The carbon monoxide may have resulted from a reaction between carbon dioxide and the metallic fuel. The water-gas reaction equilibrium also influences their proportion. The moisture may have been present in any of the constituents, while carbon dioxide can be associated with barium chromate and its impurities depending upon the method used in preparing the barium chromate.

The data reported herein indicate that the contribution of barium chromate to gases evolved by burning these powder mixtures would be expected to be mainly water vapor and carbon dioxide. In order to test this supposition, barium chromate samples were heated in an argon atmosphere and the gases were analyzed in a mass spectrometer by the Gas Chemistry Section of the National Bureau of Standards. The gases evolved by the barium chromate samples were found to be mainly water vapor and carbon dioxide. These gases probably are associated with impurities in the barium chromate or are adsorbed directly on the surface.

It appeared that acceptance tests for barium chromate for use in heat and certain pyrotechnic delay powders should include a measurement of its gas-producing tendencies. Therefore, it was decided to develop a test for measuring the water vapor and carbon dioxide evolved when barium chromate samples are heated to a relatively high temperature. This paper details the development of this test and the effect of the various test parameters.

2. PRELIMINARY TESTS USING OXYGEN GAS

The initial tests were made using oxygen to sweep the gases evolved from the heated barium chromate sample into the absorption tubes. Oxygen was selected because of its ready availability.

2.1 Apparatus

The first combustion train for the determination of moisture and carbon dioxide was assembled as follows. A cylinder of commercial oxygen fitted with a reduction valve was followed by a glass drying tower charged with indicating Drierite. The oxygen sweep rate was measured with a Fisher Flowmeter. A needle valve was placed between the drying tower and the flowmeter to facilitate regulation of the oxygen flow. A Sentry tube furnace was equipped with a sillimanite combustion tube and the combustion tube was closed by a screw-type breech cemented in place with plaster of Paris. The furnace temperature was regulated within $\pm 25^{\circ}\text{F}$. Absorption tubes used were the U type, closed with stopcocks, and the absorbent for the moisture determination was anhydrous magnesium perchlorate. The carbon dioxide absorption tube was charged with Caroxite, an indicating carbon dioxide absorbent, followed by a small charge of anhydrous magnesium perchlorate to guard against loss or gain of moisture. The moisture absorption tube was placed at the exit end of the combustion tube and followed by the carbon dioxide absorption tube. The

complete system was swept with oxygen at varied sweep rates as stated in the procedure. Copper tubing was used to make all connections from the oxygen cylinder into the combustion tube. All other connections were made with pure gum rubber tubing.

2.2 Preparation of Combustion Boats

Combustion boats used to place the sample into the heat zone of the combustion furnace were of glazed porcelain. Before the boats were used for a test they were cleaned in Calgonite solution, distilled-water rinsed and predried at 105°C. The boats were heated in the tube furnace for 15 minutes at the same temperature and sweep rate at which the samples were to be tested. The boat was allowed to cool in air for 3 minutes to prevent breakage due to thermal shock, and then stored in a desiccator until used.

2.3 Combustion System Preparation

It was found necessary to bring the tube furnace to the desired temperature and to sweep the system for at least 20 minutes before test runs. When absorption runs were not being made, it was found advisable to keep the system closed or to have it swept at a moderate rate. This prevented the system from picking up moisture and carbon dioxide from the atmosphere, which would be swept into the absorption tubes during a run, causing an error in the determination.

2.4 Determination of Blank

In order to get an initial weight of the absorption tubes and also to purge the system of any moisture gathered during the shut-down period, the stopcocks of the absorption tubes were opened and the tubes were connected into the system, the moisture tube first, followed by the carbon dioxide tube. The tubes were swept for 20 minutes. They were then disconnected and the stopcocks immediately closed. The absorption tubes were then placed in the balance case to come to equilibrium before being weighed. They were vented, by opening the stopcocks momentarily to equalize the pressure, immediately before being weighed. In weighing, a similar absorption tube was used as a tare. The system was swept with oxygen while the absorption tubes were being weighed. The flow of oxygen was cut to zero with the needle valve and the absorption tubes were again connected in the chain. A predried, cool, empty combustion boat was placed into the heat zone of the combustion tube and the breech closed. The stopcocks on the

absorption tubes and then the needle valve were opened to allow the desired flow of oxygen to sweep the system. The run was made for 20 minutes. The absorption tubes were then disconnected, closed, cooled, vented and weighed as before. The initial weight was subtracted from the weight gain recorded after this blank run. A duplicate blank run was made and the difference in weight gains were averaged to give the blank determination. Blank runs were made with both absorption tubes in the chain and the results of this run was subtracted from all samples run that day. Due to changes in room temperature and humidity these blanks may vary from day to day.

2.5 Determination of Cooling Time of Absorption tubes

Several runs were made to determine the cooling time necessary for the absorption tubes from the time they are removed from the absorption chain to the time they are weighed. This cooling time took place in the balance case. Four runs were made using 5 grams each of barium chromate, and an oxygen sweep time of 20 minutes. After the run was completed, the absorption tubes were removed from the chain and weighed immediately and then at 5-minute intervals up to 15 minutes total cooling time. In two runs there was no weight change between the initial (0) time and the 15-minute cooling time. In two runs there was a weight gain of 0.1 and 0.2 milligram between the initial and 5-minute interval, but none after 5 minutes. From this information it was concluded that 5-minute cooling time between the removal of the tubes from the chain to the weighing of the tubes was sufficient.

2.6 Determination of Collection Time

While making tests with 5-gram samples of barium chromate it was noted that at sweep rates of 100 milliliters per minute and 200 milliliters per minute, moisture from the sample was visible in the entrance arm of the moisture absorption tube 10 and 12 minutes after the start of the run. Because of this condition it was not considered advisable to reduce the collection time of the sample below 15 minutes.

Several runs were made with the absorption tubes in the system for periods of 20, 30 and 40 minutes. No appreciable change was noted when duplicate samples were tested under these conditions. The time of 20 minutes was chosen as the length of the run or collection time, to eliminate the possibility of incomplete absorption of the sample at a shorter time or an unnecessarily long run of 40 minutes.

Later an investigation was made to show that complete absorption definitely took place within the 20-minute period.

2.7 Possible Sources of Moisture in Blanks and Their Elimination

It was found that the moisture blanks appeared to be somewhat higher than desirable and therefore the following modifications were made.

A yellow discoloration was noted on the glass wool plug at the entrance stopcock of the magnesium perchlorate absorption tube after several runs. To prevent this product from being blown over into the absorption tubes a glass wool plug was placed at the tapered exit end of the combustion tube. A fractional combustion unit of the copper oxide type was placed in the system following the tube furnace and preceding the absorption tubes. However, this unit was charged with silver ribbon and operated at a temperature of 707°F (375°C) to react with any chlorine or sulfur compounds swept through the system.

The glass drying tower packed with indicating Drierite was replaced with a brass tower charged with anhydrous magnesium perchlorate. The glass tower was replaced because of sealing difficulties and the danger of breakage due to gas pressure.

The sillimanite combustion tube had been closed by a screw-type breech cemented in place with plaster of Paris. The sillimanite combustion tube was replaced by a Vycor tube which gave longer tube life and was not as easily contaminated with spilled or spattering samples. The Vycor tube was closed at the breech end with a one-hole rubber stopper with a glass tube through the center to admit the gas.

To check the effect of moisture introduced into the system while placing the sample into the furnace, the following tests were made.

The system was swept with oxygen at a rate of 100 milliliters per minute for 40 minutes. The combustion tube was not opened. A run was made for 20 minutes, at the same oxygen flow rate. The weight gain was 0.7 milligram. The combustion tube was opened and the rake, which was used to place and remove boats from the heat zone, was inserted into the heat zone and withdrawn twice. A 20-minute run at the same sweep rate gave a weight gain of 1.4 milligrams. This

operation was repeated making a note of the total time it took to perform the operation. The total time of the operations were 40 and 42 seconds with a weight gain in both instances of 1.4 milligrams. To make conditions extreme during the placing of a sample into the furnace, the operator inhaled and exhaled near the open end of the combustion tube while inserting and withdrawing the rake six times. This operation took a total time of 68 seconds and gave a weight gain in the moisture tube of 1.8 milligrams.

In the conclusion of these tests it was found that with reasonable care in inserting a sample into the heat zone of the combustion tube, using oxygen at a sweep rate of 150 milliliters per minute and a furnace temperature of 1500°F (815°C), inherent moisture in the system should not exceed 1 milligram for a 20-minute run.

3. PRELIMINARY TESTS USING ARGON GAS

Due to the excessively high moisture blanks obtained with oxygen, it was decided to use an inert gas to sweep the system. There was a possibility that the oxygen used to sweep the system was reacting with some of the components of the system to produce moisture. Blank runs were made using argon to sweep the system and 10 blank determinations for moisture gave variations from .2 to .6 milligrams.

3.1 Determination of Complete Absorption at Varied Flow Rates

The purpose of this test was to determine a gas flow that would always be high enough that all the moisture and carbon dioxide would be carried out of the system into the absorption tubes and low enough so that the moisture and carbon dioxide were not carried through the absorption tubes at too fast a rate to be absorbed and thus be swept into the atmosphere.

Before starting this test a run was made to determine the quantity of residual moisture in the system.

With argon sweeping the system at 100 milliliters per minute and operating at a furnace temperature of 1500°F (815°C), two blank runs were made without a boat and without the combustion tube being opened. The absorption tubes were swept for 20 minutes, with weight gains in the moisture tube of 0.3 and 0.2 milligram and weight gains in the carbon dioxide tube of 0.0 and 0.1 milligram.

In order to determine if all the gases were swept out into the absorption tubes at the minimum gas flow of 100 milliliters per minute, 5-gram samples of barium chromate were run in the normal manner with a 20-minute collection time. Before the absorption tubes were removed, the argon flow was shut off. A second set of moisture and carbon dioxide tubes were connected and the argon sweep adjusted to 100 milliliters per minute for another 20 minutes. Eight runs were made and in each case the weight collected in the second tubes was as small as or smaller than the blank, indicating none of the gases evolved by the heated barium chromate were left after the first 20-minute collection period.

The following tests were run in order to determine if the moisture and carbon dioxide evolved from the barium chromate samples were completely absorbed in the absorption tubes, at the maximum flow of 200 milliliters per minute. In this test two sets of moisture absorption tubes were connected in series immediately after the silver furnace, and these were followed by two sets of carbon dioxide absorption tubes in series. Eight runs were made using 5-gram samples of barium chromate and argon flow rate of 200 milliliters per minute. In each case, the weight collected in the second tubes were as small as or smaller than the blank, indicating all of the moisture and carbon dioxide were absorbed completely in the first set of tubes.

The results of these tests indicated that the argon flow could be varied safely between 100 milliliters per minute and 200 milliliters per minute; therefore the argon sweep rate was established at 150 milliliters per minute, midway between the minimum and maximum flows tested. The first six samples reported in Table No. 1 show the results of these tests varying the argon flow rate. The blank runs were made under conditions identical as with those the sample run to compensate for these variations in the flow rate.

3.2 Effect of Combustion Furnace Temperature

The maximum operating temperature of the combustion furnace used for these tests was stated by the manufacturer as being 2000°F (1090°C). As a safety factor, the maximum temperature for the tests was placed at 1800°F (980°C).

As reported in Table No. 1 runs were made at furnace temperature of 1500°F (820°C) and 1800°F (980°C) with very little effect on the moisture and carbon dioxide determinations. The median furnace temperature of 1650°F (900°C) was selected as a standard operating temperature.

3.3 Determination of Collection Time

As discussed in an earlier section of this report the presence of visible moisture condensed in the apparatus upstream of the absorption tubes limited the time of the run to above 15 minutes. Earlier tests also showed that varying the collection time between 20 and 40 minutes had no appreciable effect on the results. However, it was not known if the 20-minute period would be sufficient in all cases. Therefore, tests were run using a temperature of 1500°F (820°C) an argon flow of 150 milliliters per minute and a collection time of 16 minutes. The results of these runs, shown in Table No. 1, indicate that similar results will be obtained for this sample with collection times of 16 and 20 minutes. Therefore, it was believed that a 20-minute collection period should be adopted as standard for all samples.

4. DEVELOPMENT OF SAMPLE PREPARATION

4.1 Effect of Moisture Introduced during Preparation of Samples

Barium chromate often is mixed with other components in a water or a dilute hydrochloric acid slurry whose pH may vary between 7 and 3. After the mixing process is complete the mixtures may be stored under water for indefinite periods and then dried before use. Since the tests outlined in this study were being developed to measure the gas-producing tendencies of barium chromate during its reaction with fuels in the final mixtures, it appeared advisable to determine if the barium chromate samples should be exposed to slurry conditions before analyses were made. Three samples of barium chromate were selected for this study, DOFL Nos. 5, 23, and 30. Since preliminary tests had indicated that preheating barium chromate to relatively high temperatures before use would decrease the gas content, tests were included in which the samples were heated before soaking either in water or dilute hydrochloric acid slurries.

The results of these tests, summarized in Table 2, indicate that barium chromate samples must be dried to constant weight at 105°C before their gas-producing tendencies can be determined; and that the

gas-producing tendencies of a barium chromate sample are not affected by soaking the sample in water or dilute hydrochloric acid with a pH above 3, as long as the sample is dried to constant weight at 105°C before analysis.

4.2 Effect of Humidity

To investigate the effect of atmospheric moisture introduced into the barium chromate during the preparation, manipulation and testing of the sample, constant humidity tests were made. All tests were made with argon sweeping the system at a flow rate of 150 milliliters per minute, combustion furnace temperature of 1650°F (900°C) and a collection time of 20 minutes per run. The sample was dried at 105°C to constant weight and stored in covered weighing bottles over Drierite until used. For a relative humidity of less than 10%, samples were stored in a desiccator over indicating Drierite, at room temperature (24°C). A 60% humidity desiccator was prepared by using a saturated solution of cobaltous chloride (CoCl_2) at a controlled temperature of 35°C. A saturated solution of sodium tartrate ($\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$) stored in a desiccator at room temperature (24°C) was used to produce a 90% humidity.

Blank runs, using empty boats exposed to these humidities were made, to compensate for moisture absorbed in the combustion boats. The sample was weighed and placed in the boat. The boat and sample were exposed to these humidities for time intervals of 22 and 46 hours. Once the boat and sample were placed in the constant-humidity desiccator, the desiccator was not opened until the sample was removed and placed into the combustion furnace for testing. During transfer of the boat and sample from the constant-humidity desiccator into the furnace, they were exposed to the room atmosphere for about 15 seconds. The results of these constant-humidity tests are shown in Table No. 3. All samples for these tests were of barium chromate, DOFL Sample 5.

From these results it was definitely proven that atmospheric moisture did change the moisture content of the barium chromate. In order to ascertain the rapidity with which this change takes place, a 10-gram sample of barium chromate was dried at 105°C for 21 hours. It was covered, removed from the oven and cooled in a desiccator before weighing. The relative humidity of the room at the time of weighing was 23%. The sample was uncovered after the first weighing and left on the balance pan to be weighed at intervals of 10 minutes

for the first 30 minutes and at 30-minute intervals for an additional 90 minutes. The rate of moisture gain as follows,

| <u>Time Interval</u> | <u>Weight Gain during Indicated Period</u> |
|------------------------------|--|
| 10 minutes after initial wt. | 0.0 milligrams |
| Additional 10 minutes | 2.4 milligrams |
| " 10 minutes | 0.7 milligrams |
| " 30 minutes | 0.2 milligrams |
| " 30 minutes | 0.2 milligrams |
| " 30 minutes | 0.0 milligrams |

Because it was quite evident that moisture was being absorbed by the sample during a short exposure time to the room atmosphere, a preliminary sample preparation was established to try to eliminate the error introduced by this absorbed moisture. To determine whether the moisture absorbed through atmospheric exposure could be driven off by heating the sample at 105°C, the following tests were made. A 5-gram sample of barium chromate, DOFL Sample No. 5 was dried at 105°C, to constant weight. After the sample was cooled in a desiccator for 15 minutes and weighed, it was exposed to 90% relative humidity for two hours. The sample was reweighed and showed a weight gain of 1.5 milligrams. It was dried in an oven at 105°C for one hour, cooled in a desiccator for 15 minutes and reweighed. There was a weight loss of 1.9 milligrams. A second sample was tested using the same procedure and it also showed that by heating the sample at 105°C for one hour, the absorbed moisture was driven off.

5. REVISION OF APPARATUS

Thus far in this investigation the absorption tubes used were of the U type with a capacity of 10 milliliters and a charge weight of about 35 grams. These were made for this use on special order because those tubes which were commercially available were so heavy that it was difficult to determine small weight changes due to absorption of either moisture or carbon dioxide. It was suggested that micro absorption tubes be used because they were lighter in weight and readily available commercially. The micro absorption tube also has an advantage over the U type in that it is closed by capillary constrictions which save manipulation of the stopcocks. It was found that the ends of the micro absorption tubes could be left uncovered

during the weighing. It is advisable, however, to close the ends with rubber policemen if the tubes are not in use for a period of several hours to prevent absorption from the atmosphere. When the U-type tubes were replaced by the micro tubes a second chain of micro absorption tubes were introduced into the system as before to check for complete absorption at varied sweep rates. It was found that complete absorption was effected in the first chain of tubes as long as the argon flow was between 100 & 150 milliliters per minute. The results of these tests reported in Table No. 4, indicate that the flow rate when micro tubes are used should be standardized at 125 milliliters per minute.

A Brooks Rotameter Co. Flowmizer replaced the Fisher Flowmeter to give a more accurate measurement of gas flow rate. The Flowmizer had been calibrated at the factory for the flow rate of argon from 0 to 190 milliliters per minute.

6. PRELIMINARY PROCEDURE FOR PREPARING BARIUM CHROMATE SAMPLES

A preliminary procedure for the preparation of barium chromate samples prior to determining moisture and carbon dioxide content was investigated as outlined below.

- a. Sample dried at 105°C to constant weight.
- b. Sample weighed and transferred into combustion boat.
- c. Sample in combustion boat stored in desiccator for twenty four hours.
- d. Dried at 105°C for one hour, cooled in desiccator for one-half hour.
- e. Dried at 105°C for one hour
- f. Test sample in combustion furnace.

Results of tests on these preliminary procedures are shown on Table No. 5. These indicate that the sample should be dried at 105°C for one hour and placed directly into the furnace without cooling.

7. FINAL TEST PROCEDURES

As a result of all the investigations and findings reported above, the following procedures have been established for the determination of moisture and carbon dioxide in barium chromate samples.

7.1 Apparatus

The combustion train used is shown in Figure No. 1. A drying tower charged with anhydrous magnesium perchlorate follows the argon cylinder. A needle valve is placed in the line to facilitate regulation of gas flow. The gas flow is measured with a Brooks Flowmizer. The Sentry tube furnace is equipped with a Vycor combustion tube. The furnace is operated at a temperature of 1650°F (900°C). The furnace temperature is regulated by a variable input controller. The breech end of the combustion tube is closed by a one-hole rubber stopper with a glass tube through the center to admit the argon. To prevent fine particles of the sample from being blown into the system, a glass wool plug is placed at the tapered exit end of the combustion tube.

A fractional combustion unit charged with silver ribbon is placed in the system following the tube furnace, to react with any chlorine and sulfur compounds which might be present. This unit is operated at a temperature of 707°F (375°C.)

Copper tubing is used for all connections from the argon cylinder to entry into the combustion tube. All other connections are made with pure gum rubber tubing. Micro absorption tubes are used, closed by capillary constrictions. The absorbent for the moisture determination is anhydrous magnesium perchlorate, ($Mg(ClO_4)_2$). The carbon dioxide absorption tube is charged with Caroxite, an indicating carbon dioxide absorbent, followed by a small charge of anhydrous magnesium perchlorate.

The complete system is swept with argon at a sweep rate of 125 milliliters per minute.

7.2 Preparation of Combustion Boats

Cores porcelain combustion boats are used to place the sample into the combustion tube. The boats are cleaned in Calgonite solution, distilled-water rinsed and predried at 105°C. If barium chromate from a previous run adheres to the boat, it is removed by cleaning with hydrochloric acid before washing in the Calgonite solution. The boats are heated in the tube furnace for 15 minutes at the same temperature and sweep rate at which the samples are to be run. The boats are cooled in air for three minutes and stored in a desiccator until used.

7.3 Procedure for the Determination of Moisture and Carbon Dioxide in Barium Chromate

7.3.1 Preparation of the Barium Chromate Sample

- a. Dry at 105°C to constant weight.
- b. Weigh a 5-gram sample and transfer into a predried combustion boat.
- c. Dry the sample and the boat at 105°C for one hour.
- d. Transfer directly to combustion furnace and test immediately.

7.3.2 The Determination of Moisture and Carbon Dioxide in the Barium Chromate Sample

- a. Bring the combustion furnace to operating temperature 1650°F (900°C). Sweep system with argon at the desired flow rate (125 milliliters per minute) for 20 minutes.
- b. Connect absorption tubes into the system. The moisture absorption tube is placed first in the chain, followed by the carbon dioxide absorption tube.
- c. Sweep absorption tubes for 20 minutes.
- d. Disconnect the absorption tubes and place them in the balance case to cool for 5 minutes. Weigh to get initial weight.
- e. Repeat step b.
- f. Immediately shut off needle valve.
- g. Place a preheated combustion boat into the heat zone of the combustion furnace and restopper the combustion tube.
- h. Open the needle valve and adjust the sweep rate to 125 milliliters per minute.
- i. Sweep the system for 20 minutes, collecting the blank.
- j. Disconnect the absorption tubes and place them in the balance case to cool for 5 minutes. Weigh. Subtract initial weight (step d) to determine the blank.
- k. Repeat steps b and f.
- l. Place the preheated sample (see sample preparation) into the heat zone of the combustion furnace and restopper the combustion tube.
- m. Repeat steps h, i, and j. Calculate the percentage of moisture and carbon dioxide present.

$$\% = \frac{\text{Wt. Gain}}{\text{Wt. of Sample}} \times 100$$

8. TESTS OF COMMERCIAL SAMPLES

Following the final test procedure 22 samples of barium chromate obtained from various sources were tested. The results of these tests are shown in Table No. 6.

In Table 7, the carbon dioxide contents of these samples determined by the DOFL combustion method are compared with carbon dioxide contents calculated from chemical analysis made by the Chemistry Section of the National Bureau of Standards. A few water analyses also are included in this comparison.

9. CONCLUSION AND RECOMMENDATIONS

A simple and accurate method has been developed for measuring the tendency of barium chromate powder to evolve gas during the combustion of pyrotechnic delay and heat powders in which it is used. The test conditions need not be controlled critically and may be varied over a relatively wide range without affecting the accuracy of the method.

The method of preparing the samples of barium chromate powder for analysis has a marked effect on the analytical results. A standard reproducible procedure for preparing the barium chromate has been developed as a part of the analytical method.

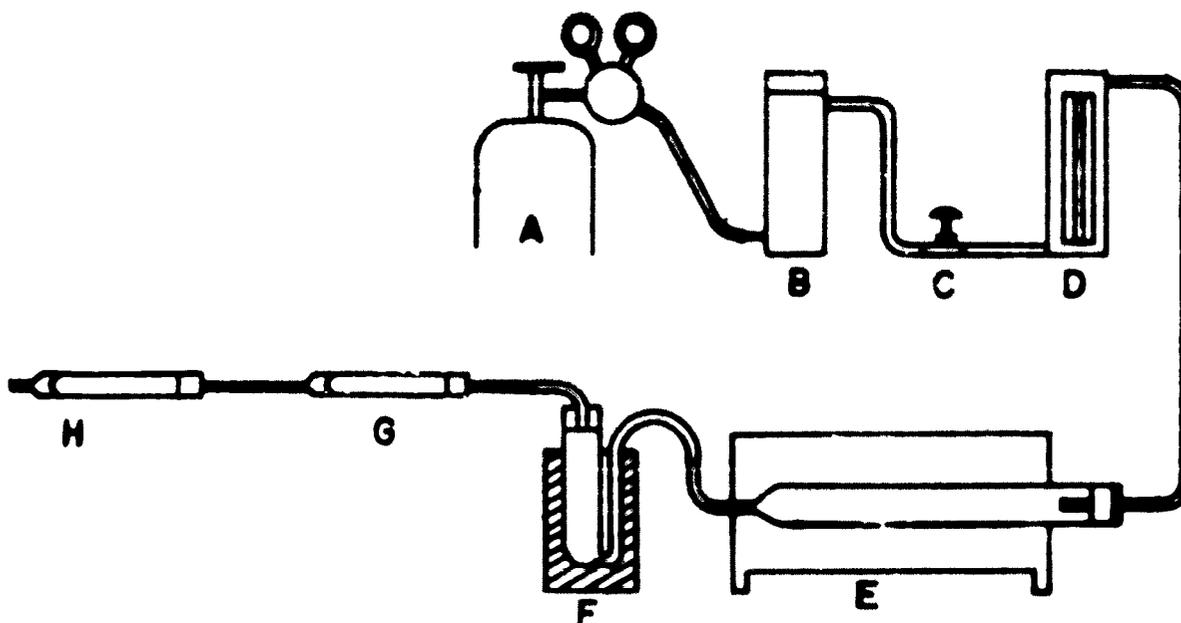
It is recommended that this method be adopted as a part of an acceptance test for barium chromate powder used as an ingredient in delay and heat mixtures.

The moisture content of barium chromate powder is affected by the relative humidity of the atmosphere surrounding it. However, the moisture introduced into barium chromate powders by exposure to high relative humidities, soaking in distilled water, and soaking in dilute hydrochloric acid (pH=3.0) may be removed readily by drying at a temperature of 105°C.

Data presented to show the gas producing tendencies of a number of samples obtained from commercial sources indicate that the moisture content may vary from 0.01% to 0.61% by weight, and the carbon dioxide

content may vary from 0.00 to 0.63% by weight.

It is recommended that the selection of the minimum gas content of barium chromate powders for final specification purposes be deferred until an investigation is made establishing the optimum particle size of barium chromate for certain pyrotechnic delay and heat powders, and its relationship to gas content. However, it is believed that sufficient test data can be readily obtained to permit the establishment of an interim working specification which is urgently needed for particular ordnance applications.



- A. CYLINDER OF ARGON WITH REGULATOR
- B. DRYING TOWER PACKED WITH ANHYDROUS MAGNESIUM PERCHLORATE
- C. NEEDLE VALVE
- D. BROOKS FLOWMIZER
- E. COMBUSTION TUBE IN COMBUSTION FURNACE
- F. FRACTIONAL COMBUSTION UNIT CHARGED WITH SILVER RIBBON
- G. MOISTURE ABSORPTION TUBE CHARGED WITH ANHYDROUS MAGNESIUM PERCHLORATE
- H. CARBON DIOXIDE ABSORPTION TUBE CHARGED WITH CAROXITE FOLLOWED BY ANHYDROUS MAGNESIUM PERCHLORATE

Figure 1. Combustion Apparatus for the determination of Water and Carbon Dioxide in Barium Chromate

Table 1

Effect of Furnace Temperature, Rate of Argon Flow and Length of Run

Barium Chromate, DOFL Sample No. 5,

Sample Preparation - As Received

| $\% \text{H}_2\text{O}$ | $\% \text{CO}_2$ | Furnace Temp. (°F) | Argon Sweep Rate (ml/min) | Length of Run (min) |
|-------------------------|------------------|-----------------------|------------------------------|------------------------|
| .76 | .13 | 1500 | 100 | 20 |
| .77 | .11 | 1500 | 100 | 20 |
| .78 | .12 | 1500 | 150 | 20 |
| .78 | .11 | 1500 | 150 | 20 |
| .76 | .12 | 1500 | 200 | 20 |
| .78 | .12 | 1500 | 200 | 20 |
| .77 | .11 | 1800 | 150 | 20 |
| .78 | .12 | 1800 | 150 | 20 |
| .75 | .11 | 1500 | 150 | 16 |
| .76 | .11 | 1500 | 150 | 16 |
| .77 | .12 | Average | | |

Table 2

METHODS OF SAMPLE PREPARATION

| Sample Preparation | DOFL No. 5 | | DOFL No. 23 | | DOFL No. 30 | |
|---|----------------------|------------------|-------------------|------------------|-------------------|------------------|
| | %H ₂ O | %CO ₂ | %H ₂ O | %CO ₂ | %H ₂ O | %CO ₂ |
| As received | .77 (See Table 1) | .12 | .21 | .02 | .21 | .02 |
| Dried at 105°C for 2 1/2 Hours | .74 | .11 | .19 | .01 | .19 | .01 |
| Dried at 105°C to Constant Weight | .69 | .11 | .20 | .02 | .19 | .01 |
| Wet with Distilled Water, Dried at 105°C for 2 1/2 Hours | .71 | .12 | .19 | .02 | .20 | .01 |
| Wet with Distilled Water, Dried at 105°C for 2 1/2 Hours | .75 | .10 | .19 | .01 | | |
| Wet with Distilled Water, Dried at 105°C to Constant Weight | .76 | .10 | .18 | .01 | | |
| Wet with Distilled Water, Dried at 105°C to Constant Weight | .68 | .12 | .19 | .02 | .18 | .01 |
| Dried at 105°C to Constant Weight | .73 | .11 | .19 | .01 | .19 | .01 |
| Dried at 345°C for 2 Hours | | | .06 | .01 | | |
| Dried at 345°C for 2 Hours, Wet with Distilled Water, Dried at 105°C for 2 1/2 Hours | | | .06 | .00 | | |
| Dried at 345°C for 2 Hours, Wet with Distilled Water, Dried at 105°C for 2 1/2 Hours | | | .08 | .01 | | |
| Dried at 345°C for 2 Hours, Wet with Distilled Water, Dried at 105°C to Constant Weight | | | .11 | .01 | | |
| Dried at 345°C for 2 Hours, Wet with Distilled Water, Dried at 105°C to Constant Weight | | | .10 | .01 | | |
| Dried at 345°C for 2 Hours, Wet with Distilled Water, Dried at 105°C to Constant Weight | | | .10 | .01 | | |
| Dried at 345°C for 2 Hours, Wet with Distilled Water, Dried at 105°C to Constant Weight | | | .06 | .01 | | |
| Dried at 345°C for 2 Hours, Wet with Distilled Water, Dried at 105°C to Constant Weight | | | .07 | .01 | | |
| Dried at 345°C for 2 Hours, Wet with Distilled Water for 2 weeks, Dried at 105°C to Constant Weight | | | .08 | .01 | | |
| Dried at 345°C for 2 Hours, Wet with Distilled Water for 2 weeks, Dried at 105°C to Constant Weight | | | .08 | .01 | | |
| Dried at 650°C for 6 Hours | | | | | .01 | .00 |
| Dried at 650°C for 6 Hours, Wet with Distilled Water, Dried at 105°C to Constant Weight | | | | | .02 | .01 |
| Dried at 650°C for 6 Hours, Wet with Distilled Water, Dried at 105°C to Constant Weight | | | | | .02 | .01 |
| Dried at 650°C for 6 Hours, Wet with Distilled Water, Dried at 105°C to Constant Weight | | | | | .01 | .00 |
| Adjusted to pH 3 with 1% HCl, Dried at 105°C to Constant Weight | .69 | .10 | | | .18 | .01 |
| Adjusted to pH 3 with 1% HCl, Dried at 105°C to Constant Weight | .71 | .11 | | | .18 | .01 |

(All tests were run for 20 minutes at a sweep rate of 150 ml/min argon and a furnace temperature of 1650°F)

Table 3

Constant Humidity Tests

Barium Chromate, DOFL Sample No. 5,

Furnace Temperature - 1650°F (900°C)

Argon Sweep Rate - 150 milliliters per minute

| Humidity | Exposure Time | | | |
|--|-------------------|------------------|-------------------|------------------|
| | 22 Hours | | 46 Hours | |
| | %H ₂ O | %CO ₂ | %H ₂ O | %CO ₂ |
| Less than 10% (Drierite) | .62 | .12 | .62 | .13 |
| | .62 | .12 | .62 | .12 |
| 60% Sat. CoCl ₂ at 35°C | .79 | .11 | .80 | .12 |
| | .80 | .12 | .80 | .11 |
| 90% Sat. Na ₂ C ₄ H ₄ O ₆ · 2H ₂ O | .98 | .13 | 1.00 | .12 |
| | at 24°C 1.00 | .12 | .99 | .12 |

Table 4

Test Results Using Micro Absorption Tubes

Barium Chromate, DOFL Sample No. 5.

Sample Preparation - Dried to Constant Weight at 105°C.

| Argon Sweep Rate (ml/min) | Collection Time (min) | % H ₂ O | % CO ₂ |
|------------------------------|--------------------------|--------------------|-------------------|
| 180-185 | 20 | .69 | .05 |
| | | .70 | .09 |
| | | .65 | .00 |
| 150 | 20 | .70 | .11 |
| | | .73 | .13 |
| 100 | 20 | .70 | .11 |
| | | .69 | .11 |
| 100 | 18 | .72 | .13 |
| | | .73 | .13 |
| | | . | . |
| 125 | 20 | .68 | .12 |
| | | .70 | .13 |

Table No. 5

Preliminary Procedure for the Preparation of Samples

Sample Barium Chromate, DOFL Sample No. 5.

Dry at 105°C to Constant Weight

Weigh 5 gram sample and put in boat

| Store in Desiccator 24 Hours | | Dry at 105°C 1 hour, cool in Desiccator 1/2 hour | | Dry at 105°C 1 hour | |
|---------------------------------|-------------------|--|-------------------|----------------------------|-------------------|
| Test % H ₂ O | % CO ₂ | Test % H ₂ O | % CO ₂ | Test % H ₂ O | % CO ₂ |
| .63 | .12 | .67 | .12 | .60 | .13 |
| .62 | .12 | .67 | .13 | .61 | .13 |

Table No. 6

Combustion Analysis of Barium Chromate Samples

| Sample | % H ₂ O | % CO ₂ |
|-------------|--------------------|-------------------|
| DOFL No. 1 | .51 | .16 |
| | .51 | .17 |
| DOFL No. 2 | .55 | .08 |
| | .53 | .08 |
| DOFL No. 3 | .61 | .04 |
| | .62 | .04 |
| DOFL No. 4 | .59 | .63 |
| | .59 | .62 |
| DOFL No. 5 | .63 | .14 |
| | .62 | .14 |
| DOFL No. 6 | .27 | .15 |
| | .27 | .15 |
| DOFL No. 7 | .32 | .03 |
| | .30 | .02 |
| DOFL No. 8 | .36 | .03 |
| | .36 | .05 |
| | .36 | .05 |
| DOFL No. 9 | .17 | .12 |
| | .15 | .12 |
| DOFL No. 10 | .08 | .01 |
| | .07 | .01 |
| DOFL No. 11 | .11 | .11 |
| | .11 | .13 |
| DOFL No. 12 | .18 | .21 |
| | .17 | .18 |
| DOFL No. 13 | .29 | .17 |
| | .28 | .16 |

| Sample | % H ₂ O | % CO ₂ |
|--------------|--------------------|-------------------|
| DOFL No. 14 | .24 | .01 |
| | .24 | .01 |
| DOFL No. 15 | .42 | .02 |
| | .42 | .01 |
| DOFL No. 16 | .21 | .02 |
| | .19 | .03 |
| DOFL No. 23 | .16 | .01 |
| | .15 | .02 |
| DOFL No. 30 | .17 | .02 |
| | .16 | .01 |
| DOFL No. 97 | .06 | .00 |
| | .06 | .01 |
| DOFL No. 98 | .01 | .00 |
| | .00 | .00 |
| DOFL No. 130 | .09 | .00 |
| | .10 | .00 |
| DOFL No. 131 | .61 | .01 |
| | .59 | .01 |

Table No. 7

Analysis of Barium Chromate Samples

Chemical Analysis by
National Bureau of Standards

Combustion Analysis by
DOFL

| DOFL Sample | % CO ₂ | % Moisture | % CO ₂ | % H ₂ O |
|----------------|-------------------|------------|-------------------|--------------------|
| No. 1 | .04 | | .16 | |
| No. 2 | .05 | | .08 | |
| No. 3 | .05 | | .04 | |
| No. 4 | .58 | | .62 | |
| No. 5 | .03 | | .14 | |
| No. 6 | .10 | | .15 | |
| No. 7 | .09 | .20 | .02 | .31 |
| No. 8 | .00 | | .05 | |
| No. 9 | .02 | .23 | .12 | .16 |
| No. 10 | .01 | .11 | .01 | .07 |
| No. 11 | .17 | | .12 | |
| No. 12 | .29 | | .16 | |
| No. 13 | .01 | | .01 | |
| No. 15 | .02 | | .01 | |
| No. 16 | .02 | | .02 | |

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