DEPARTMENT OF THE INTERIOR

ALBERT B. FALL, Secretary

BUREAU OF MINES

H. FOSTER BAIN, Director

ANALYSIS OF DETONATING AND PRIMING MIXTURES

BY

C. A. TAYLOR and W. H. RINKENBACH

CONTENTS.

4 CONTENTS.

ILLUSTRATIONS.

THE ANALYSIS OF DETONATING AND PRIMING MIXTURES.

By C. A. TAYLOR and W. H. RINKENBACH.

INTRODUCTION.

Many schemes of analysis are published that take up the examination of metals or other substances in a special and comprehensive way and serve as a general basis of procedure to be modified by the analyst to suit his particular need. These basic methods and modifications have been brought to a high state of perfection in various industries, as in the analysis of iron, steel, and coal. Therefore it is comparatively easy for a chemist in one of those industries to find a method that covers his special problem.

In the examination and manufacture of explosives conditions are radically different. New materials and combinations are being tried as explosives, and the variety of both is so great that it is impracticable to give a definite method of analysis applicable to even one class of explosives, such as detonating and priming compositions or dynamites. Consequently, a real need exists for the adaptation of the methods followed in the analysis of stable materials to the sensitive compounds and mixtures used in explosives in order that the analyst will know how to proceed with maximum safety and confidence.

This paper is intended to satisfy part of this need and is a continuation of the publications on explosives analysis from the Pittsburgh laboratory of the Bureau of Mines.[1] The methods given herein are those used in practical work and are not intended to fill the requirements of a research chemist working on a particular compound. However, they do cover the needs of a chemist analyzing explosive compositions and desirous of results that are accurate within the limits of the variation of the mixtures themselves.

The explosives chemical laboratory at Pittsburgh is now preparing a bulletin on explosives, their materials, and analysis.

ACKNOWLEDGMENTS.

---

[1] Snelling, W. O., and Storm, C. G., The analysis of black powder and dynamite, Bull. 51, Bureau of Mines, 1916, 80 pp.; Storm, C. G., The analysis of permissible explosives, Bull. 96, Bureau of Mines, 1916, 88 pp.

GENERAL METHODS.

In analyzing explosives the general practice is to make as many separations as possible by the use of solvents. The subsequent evaporation of the solvent leaves the extracted ingredient chemically unchanged, when it can be weighed and its percentage calculated. The solvent should be driven from explosive compounds by a current of dry air or by spontaneous evaporation at room temperature, precautions being taken to prevent moisture from being deposited on the residue of the explosive by the cooling effect of the evaporating solvent.

The most powerful explosives are comparatively insensitive in solution. Nitroglycerin may be burned in ethereal solution, but this procedure is inadvisable with large quantities, as the ether evaporates very readily.

Adding strong acid or alkali to an explosive is inadvisable unless it is in solution, as the heat evolved in the reactions that sometimes take place may cause the explosion of the entire sample.

All explosives should be kept neutral, as slight acidity causes many compounds to become much more sensitive to shock or heat.

When an unknown explosive compound or mixture is being dried, the temperature should be kept below 75° C., as some substances tend to decompose and become very sensitive at higher temperatures and others are volatile enough to cause considerable loss.

In all analyses there are two steps—the identification of the various ingredients and their separation, or their separation and subsequent identification. The microscope should be used freely in identifying materials and detecting their impurities. With inorganic materials, the usual qualitative tests are used and quantitative separations are then made. The organic compounds, except those in general use which are easily identified through practice, are often difficult to identify. Their physical appearance is carefully noted, the details being studied with the microscope, and their identity is determined by comparison with known materials. If the organic compounds can be separated and purified, they may be easily identified by the system given by Mulliken.[2]

Organic compounds are usually separated from inorganic substances by solvents. When two organic nitro compounds with very similar characteristics are present, such as tetryl and TNT, it may be necessary to take them out in solution together and identify them by color tests. By determining the nitrogen content of the mixture and calculating from the known nitrogen content of the individual substances, it is possible to get results very close to the amounts actually used in manufacture.

---

[2] Mulliken, S. P., A method for the identification of pure organic compounds. New York, 1904, vol. 1, pp. 9–14.

NITROGEN DETERMINATION.

For determining the nitrogen in an organic compound or mixture the Dumas method may be accepted as standard, but must be used with the precautions given in Technical Paper 160.[3]

NITROMETER METHOD.

The du Pont nitrometer [4] is used to determine all organic and inorganic nitrates. It should be remembered that the presence of certain mononitro and dinitro compounds affects the accuracy of this method.

ORNDORFF METHOD.

During the recent war another method was developed by W. R. Orndorff and R. R. Braden, of Cornell University. With proper precautions, this method gives good results. The procedure follows:

Weigh out 0.2 to 0.3 gram of the sample; place it in a 300-c. c. Kjeldahl flask and add 0.1 to 0.2 gram of red phosphorus and 20 c. c. of hydriodic acid (specific gravity, 1.7). When the substance to be analyzed—tetryl, for example—is high in nitrogen, about 1 gram of iodine should be added to the hydriodic acid to insure reduction.

The flask is now heated on a water bath for 1½ hours, and the mixture agitated several times while on the bath. After removal from the bath it is carefully heated over a free flame to gentle boiling, then cooled slightly. Next there are added 1 gram of copper sulphate, 45 grams of potassium sulphate, and 55 c. c. of concentrated sulphuric acid; then the flask and its contents are heated until all the iodine has been driven off. Complete oxidation is indicated if the contents of the flask have a clear greenish-blue color.

The whole is cooled and the ammonia is distilled into a standard N/5 sulphuric acid solution after the acid contents of the flask have been neutralized. When the distillation is complete, the excess of sulphuric acid is titrated with a N/10 sodium hydroxide solution, using methyl red or cochineal as the indicator.

Care should be taken in digesting and distilling the iodine to avoid local overheating. The iodine driven off may be caught and saved by placing a balloon flask over the mouth of the Kjeldahl flask so that it does not touch the neck of the Kjeldahl. If recovery of the iodine is not desired, a current of warm air decreases the time needed for driving it off.

The ammonia is distilled with steam, the sodium hydroxide with which the solution is neutralized and then made alkaline being added

[3] Cope, W. C., and Taylor, G. B., The determination of nitrogen in substances used in explosives: Tech. Paper 160, Bureau of Mines, 1917, pp. 5–10.

[4] Pitman, J. R., Analysis of nitric and mixed acids by Du Pont's modification of the Lunge nitrometer: Jour. Soc. Chem. Ind., vol. 19, 1900, p. 983; Lunge, G., Du Pont's nitrometer: Jour. Soc. Chem. Ind., vol. 20, 1901, pp. 100–102.

cautiously with the steam. Just after the mixture has been made alkaline the ammonia comes over so rapidly that the standard sulphuric acid should be agitated to prevent local saturation and consequent loss of ammonia, or a special tube should be used, as shown in the accompanying sketch (fig. 1). A blank should be run with each set of determinations.
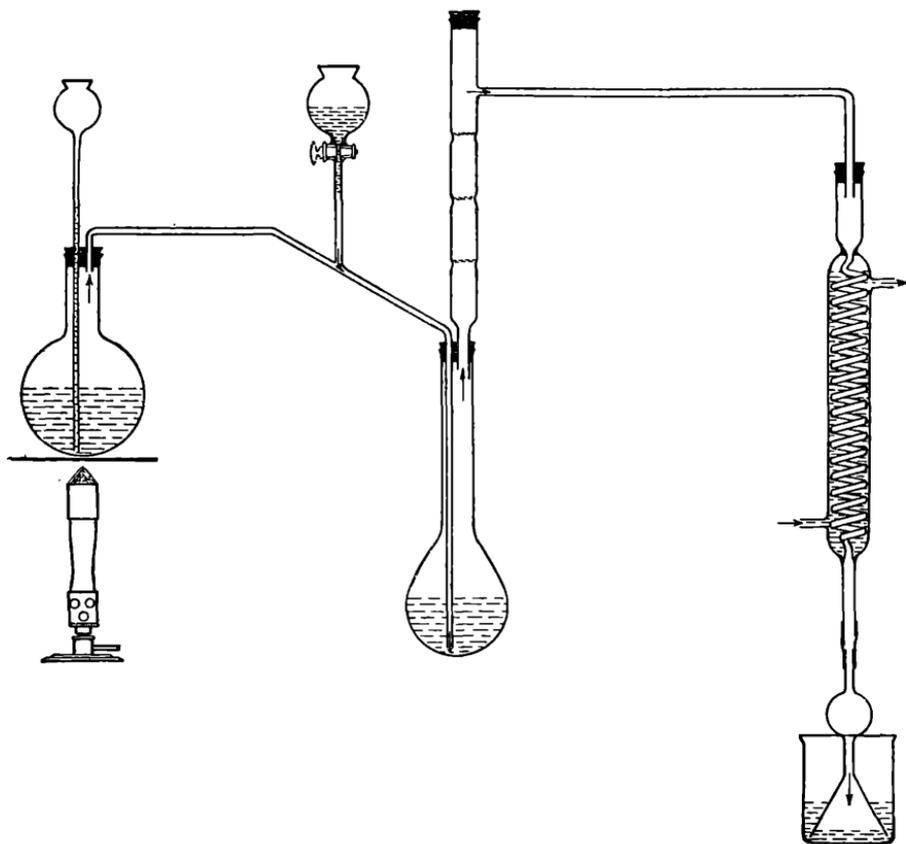
FIGURE 1.—Orndorff nitrogen apparatus.

Occasionally it is necessary to make the ultimate analysis of a compound in order to identify it, but usually such a compound can be identified by appearance, melting point, nitrogen content, crystal form, or other criteria. Two similar organic substances are seldom used together.

The following sources of information have been freely consulted in the writing of this paper: " High Explosives," by E. de W. S. Colver, 1918, New York; " Initialexplosivstoffe " by Richard Escales and A. Stettbacher, Leipzig, 1917; and " Explosives," by Arthur Marshall, London, 1915.

ANALYSIS OF DETONATING COMPOSITIONS.

PHYSICAL TESTS OF INITIATING MATERIALS.

Simple physical methods of testing the efficiency of these initiating materials have been developed. These are:

1. The Trauzl lead-block test.[5]
2. The plate test.[6]
3. The nail test.[7]
4. The sand test.[8]
5. Dupré test.[9]

CHEMICAL ANALYSIS OF INITIATING MATERIALS.

Frequently it is desirable to know the chemical composition of initiating mixtures. The purpose of this paper is to give the analytical procedure to be followed.

Because of the nature of the materials to be handled it is necessary to take special precautions against accidents in the examination of detonators. The following methods and procedure have been used or tested in the explosives chemical laboratory of the United States Bureau of Mines and have proved satisfactory within the limits shown. This paper does not attempt to give exact methods covering all possible materials and mixtures that have been tried at various times, but the general methods and their specific application to some usual and unusual mixtures will suggest other modifications that will be applicable to a new mixture.

MATERIALS OF DETONATING COMPOSITIONS.

The substances and compositions proposed or patented for use as detonating agents include a wide variety of chemical compounds. The lists below are incomplete, but they comprise the most common and many of the more unusual materials found in detonators. Inorganic materials include the following:

LIST OF INORGANIC MATERIALS.

Mercury fulminate ($Hg(ONC)_2$).
Silver fulminate ($Ag(ONC)$).
Lead azide (PbN_6).
Sodium azide (NaN_3).
Mercury azide (HgN_3).

Silver azide (AgN_3).
Silver acetylide (Ag_2C_2).
Nitrogen sulphide (N_4S_4).
Lead thiocyanate ($Pb(SCN)_2$).
Mercury thiocyanate ($Hg(SCN)_2$).

---

[5] Hall, Clarence, and Howell, S. P., Investigations of detonators and electric detonators: Bull. 59, Bureau of Mines, 1913, p. 61.

[6] Ibid., pp. 24–25.

[7] Snelling, W. O., The energy of explosives: Proc. Eng. Soc. Western Pennsylvania, vol. 28, Nov., 1912, p. 673.

[8] Storm, C. G., and Cope, W. C., The sand test for determining the strength of detonators: Tech. Paper 125, Bureau of Mines, 1916, 66 pp.

[9] Dupré, F. H., and Dupré, F. V., 44th Annual Report of His Majesty's Inspectors of Explosives, 1919: London, 1920.

Copper - ammonium   t h i o c y a n a t e ($Cu(NH_3SCN)_2$).

Lead thiosulphate (PbS_2O_3).

Copper - ammonium   t h i o s u l p h a t e ($CuS_2O_3.4NH_3.H_2O$).

Red phosphorus (P).

Sulphur (S).

Aluminum powder (Al).

Manganese dioxide (MnO_2).

Potassium chlorate ($KClO_3$).

Ammonium chlorate (NH_4ClO_3).

Barium chlorate ($Ba(ClO_3)_2$).

Potassium bromate ($KBrO_3$).

Ammonium perchlorate (NH_4ClO_4).

Potassium nitrate (KNO_3).

Ammonium nitrate (NH_4NO_3).

Barium nitrate ($Ba(NO_3)_2$).

Mercury chromate ($HgCrO_4$).

Lead oxide (PbO_2).

Barium oxide (BaO_2).

Barium silicide ($BaSi_2$).

Calcium silicide ($CaSi_2$).

Potassium silicide (K_4Si).

Sodium carbonate (Na_2CO_3).

Potassium bicarbonate ($KHCO_3$).

The organic compounds comprise:

LIST OF ORGANIC MATERIALS.

Trinitrotoluene

Tetranitromethane $C(NO_2)_4$
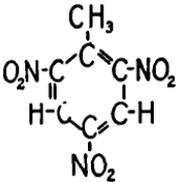
Tetranitraniline
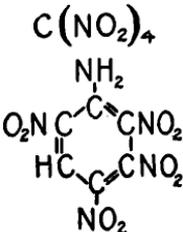
Trinitroxylene

Trinitrophenylmethylnitramine (tetryl)
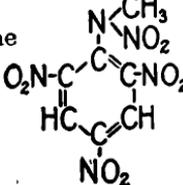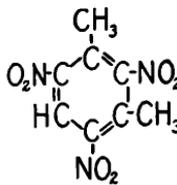
Picric acid

Sugar of milk (lactose) $C_{12}H_{22}O_{11} H_2O$
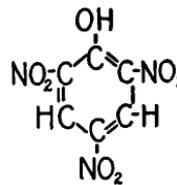
Potassium picrate

Mannitolhexanitrate (nitromannite)

Trinitroresorcin

Hexanitrodiphenyl

LIST OF ORGANIC MATERIALS—continued.

Hexanitrodiphenyloxide
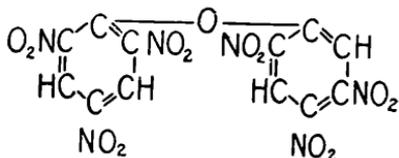
Diphenylamine
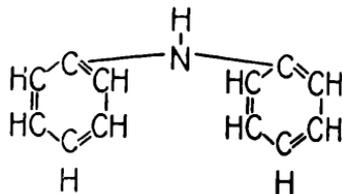
Hexanitrosulphobenzide
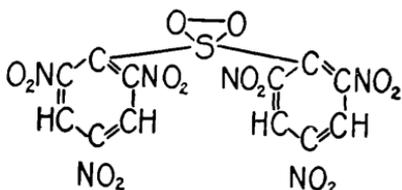
Benzoylperoxide
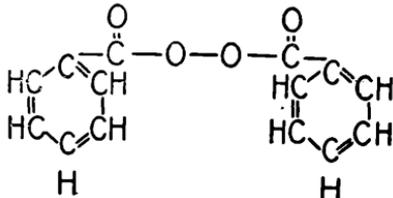
Hexamethylenetriperoxiddiamine
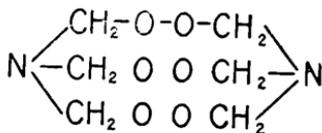
Some of the foregoing materials have been patented, but have never been sold on a commercial scale and probably will not be because of the high cost of production, a tendency to decomposition, or some other unfavorable factor. The methods of analysis given cover all of the initiating detonating compositions in more or less general use and as many of the others as it is possible to include at present.

STRUCTURE OF DETONATORS.

A detonator, often called a blasting cap in commerce and industry, consists of a copper capsule or shell and the inclosed charge. The capsule, closed at one end, is 1 to 2 inches long and has a diameter of approximately three-sixteenths inch. The open end of the cap is made to fit over the end of a safety fuse, on which it is securely crimped. The charge is either entirely compressed or, if loose, is held in place by a reinforcing cap to keep it from falling out on handling and to insure its maximum effect when ignited by the spit from the burning powder core of the fuse.

An electric detonator is of slightly greater diameter than a detonator and has a loose priming charge above the main compressed charge. The two terminals of the electric wires project into the cap through a sulphur plug and are connected by a fine platinum or iron wire termed the " bridge wire." This sulphur plug is pressed into

the copper shell so that the bridge wire is embedded in the priming charge, and it is held in place by a plug of asphalt composition, which also renders the detonator waterproof. Molten sulphur is poured over the asphalt until the cup is entirely filled. The ignition of the charge results from the heating of the bridge wire due to its resistance when an electric current is passed through it. Sketches of the three types of detonators described above are given as figure 2.

METHOD OF REMOVING CHARGES FROM DETONATORS.

To remove the charge from a detonator that has no reinforcing cap it is only necessary to squeeze the sides of the cap gently to loosen the charge, which can then be dumped out. A pair of 6-inch gas pliers may be used; a guard of heavy belting about 8 inches square is kept over the pliers at the rivet. As the cap is squeezed, it should be held at arm length and in such a position that if it should explode the guard will shield the operator. Only gentle pressure should be used and the cap should be deformed as little as possible. After each application of pressure any loosened portion of the charge should be dumped out.

FIGURE 2.—Three types of detonators: 1, detonator of simple type; 2, reinforced detonator; 3, electric detonator. *a,* detonating main charge; *b,* priming charge; *c,* sulphur plug; *d,* asphalt composition; *e,* fused sulphur.

A better method is to roll the detonator carefully between two pieces of smooth hardwood board, dumping out the loosened charge after each rolling.

To remove the charge from a detonator having a reinforcing cap, it is necessary to cut into the open end of the cap with a pair of angle-cutting pliers. The cap is then turned while the pliers hold the piece cut so that a strip of copper in the form of a spiral is torn off. When the reinforcing cap is reached this is loosened and removed, after which charge in the cap is loosened and removed as directed above.

It has been recommended that the following procedure be followed in opening electric detonators: A hole, just large enough to hold the detonator and deep enough so that the top of the charge is just below the surface of the steel, is drilled in a heavy steel block. The cap is then cut off even with the steel surface by a quick blow with a sharp wood chisel. This method is relatively safe so far as danger to the manipulator is concerned, but it is seldom used because frequent explosions will spoil the chisel.

An improvement over this method consists of cutting into the sulphur filling and asphalt, and then peeling the copper down in a
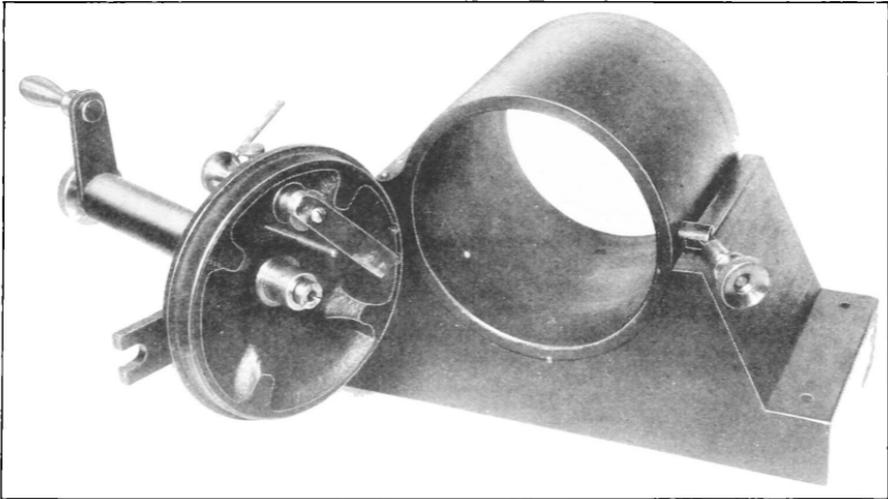
DETONATOR HOLDER.

spiral until the plugs are loosened enough to be withdrawn easily. During this process the detonator should be held in the hand or in a pair of gas pliers. Extreme care should be taken not to cut into the portion of the shell containing the charge.

The explosives chemical laboratory, with the assistance of the instrument makers of the bureau, has built an apparatus for holding the detonator and cutting through the cap at any desired point by a sharp knife or rotating disk. The mechanism is so arranged that should a charge explode the operator would be fully protected. As yet, however, no explosions have occurred when this apparatus has been used. Plate I is a photograph of the detonator holder.

As soon as the detonator is opened, the loose priming charge is emptied out, weighed, and analyzed separately. The main charge is loosened by squeezing or rolling and removed as described above.

SAMPLING.

Usually the charge from each detonator is analyzed separately. When the charge consists of a priming and a main charge, or a "booster" and a main charge, care is taken to remove, weigh, and analyze each part separately.

As the condition of a single detonator affects the whole blast, information is usually sought in the analysis as to the variations in a lot of detonators rather than the average composition of a lot. However, when the average composition is sought, it is best to open several detonators and to mix the similar parts, thus making a blend or composite of corresponding parts of the charge. The analysis is then run in duplicate or triplicate. The weight of each portion of each charge is recorded in order that an average may be taken.

In one series, the weight of the charge in the different grades of detonators using the fulminate and chlorate mixture ran as follows, when taken from the detonators:

Weight of charge in detonator.

No.	Weight of charge, grams.	No.	Weight of charge, grams.
1	0.30	5	0.75
2	.40	6	1.00
3	.52	7	1.50
4	.65	8	2.00

When a loose wad of nitrocellulose is used as a priming charge in an electric detonator, this wad averages from 0.02 to 0.025 gram in weight, irrespective of the size of the detonator. When a loose fulminate or fulminate-chlorate mixture is used for the priming charge, its average weight is usually a trifle over 0.3 gram. These quantities suffice to cover the bridge wire and insure ignition.

Typical analyses of detonating compositions containing the more usual ingredients used commercially are given on the following pages.

DETERMINING MOISTURE IN DETONATING MIXTURES.

Moisture is seldom determined in detonating mixtures, for the latter are usually dry and must remain so if the proper results are to be obtained. The moisture content is usually but a few hundredths of 1 per cent.

If for any reason it is advisable that moisture be determined, the procedure is as follows: The contents of one or two detonators are spread out on a tared 3-inch watch glass and weighed, then kept for three days in a sulphuric acid desiccator which holds a small beaker containing mercury. The beaker of mercury is placed in the desiccator in order that a constant mercury-vapor pressure may be maintained, as if this is not done any metallic mercury contained in fulminate is apt to volatilize, causing the figure for moisture to be entirely too high. At the end of three days the watch glass and sample are again weighed and the loss is taken as moisture.

METHODS OF ANALYZING DETONATING MIXTURES.

SIMPLE ANALYSIS OF A DETONATING MIXTURE CONTAINING FULMINATE AND CHLORATE.

Fulminate may be tested for qualitatively [10] by bringing the substance to be tested into contact with a solution made up of 20 to 25 parts of a 5 per cent solution of potassium bromate and 4 to 5 parts of concentrated hydrochloric acid. The development of blue color indicates the presence of a fulminate.

The following method is used when it is desired to get a fairly accurate idea of the fulminate and potassium-chlorate contents of a simple detonating mixture of these two compounds without taking into consideration any impurities they may contain.

A sample of approximately 1 gram is weighed out, transferred to a small beaker, and digested in the cold with distilled water. It is then caught on a dried and weighed filter or in a Gooch or alundum crucible and given several washes with distilled water, the filtrate and the washes being retained. For a 1-gram sample it is not necessary to use more than 100 c. c. of water for all purposes.

The residue of mercury fulminate left on the filter or crucible is dried for three hours at 50° C., care being taken not to exceed this temperature. After cooling, the residue is weighed, and the increase is taken as mercury fulminate.

As some of the mercury fulminate is present in the filtrate, it is necessary to determine the amount. Half or all of the filtrate-wash

---

[10] Langhans, A., Reaktion des Knallquecksilbers mit Halogenaten und Hypohalogenaten : Jour. prakt. Chem., Bd. 98, 1918, pp. 255–314.

solution is taken, rendered strongly ammoniacal, and the mercury in it precipitated as with hydrogen sulphide, continuing the passing through of the hydrogen sulphide until the cold solution is saturated with the gas. The mixture is then brought just to the boiling point, allowed to cool to air temperature, and caught on a filter or Gooch crucible previously dried at 110° C. The precipitate is washed several times with distilled water containing a small amount of ammonium sulphide, dried at 110° C., and weighed. The weight of the precipitate is multiplied by the factor 1.22327, which gives the corresponding weight of mercury fulminate. This calculated weight should be added to that found previously and the whole calculated to a percentage basis.

A check on the foregoing is obtained by determining the chlorate content in half the filtrate-wash solution.[11] This is done by adding 5 c. c. of a 30 or 40 per cent solution of formaldehyde, a measured 50 c. c. of N/10 silver nitrate. and a few drops of nitric acid to the solution contained in a flask or beaker. The mixture is heated for half an hour on the steam bath with occasional shaking. Silver chloride is precipitated according to the reaction:

$$KClO_3 + 3 \ HCHO + AgNO_3 = 3 \ HCOOH + AgCl + KNO_3$$
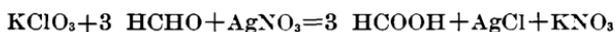
The amount of chlorate reduced may be determined either by filtering off, washing, drying, and weighing the precipitated silver chloride or by titrating the excess silver nitrate with N/10 NH$_4$CNS, according to Volhard, using a ferric alum indicator. The presence of the excess of formaldehyde has no effect on the titration of the excess silver nitrate.

The weight of silver nitrate reduced is calculated to potassium chlorate (1 c. c. of N/10 AgNO$_3$=.012256 gram KClO$_3$), and this is calculated to a percentage basis on the whole sample.

A simple detonator composition often contains a small amount of a binding material. If both fulminate and chlorate are determined directly, the difference between 100 per cent and their sum will give a fairly accurate idea of the amount of binder present.

In European detonators ammonium chlorate is sometimes mixed with the potassium chlorate. If ammonia is found qualitatively, it is determined quantitatively by distilling a water extract of the detonator charge with sodium hydroxide in the usual way, catching the distilled ammonia in standardized sulphuric acid and titrating the excess sulphuric with standardized sodium hydroxide, using a cochineal indicator.

---

[11] Storm, C. G., The analysis of permissible explosives : Bull. 96, Bureau of Mines, 1916, pp. 63–64.

ANALYSIS OF A MIXTURE OF FULMINATE AND CHLORATE FOR FREE MERCURY.

Mercury fulminate frequently contains free mercury to a greater or less degree, and occasionally it is desirable to determine how much is present in a fulminate-chlorate detonating mixture that is under investigation.

For a simple fulminate-chlorate mixture this is done as follows: A sample of from 1 to 5 grams of the detonating mixture is weighed out, transferred to a previously dried and weighed filter or crucible, and washed with distilled water to remove the chlorate. It is then washed with more than enough concentrated ammonia to dissolve all the fulminate present, then washed with dilute ammonia and distilled water.

The residue should consist of metallic mercury and any binding material and phlegmatizer present. If inspection shows metallic mercury alone, this is directly determined by drying the filter or crucible and its contents in a sulphuric acid desiccator containing a small beaker half full of mercury, and weighing. If matter other than metallic mercury is found in the residue, the mercury is dissolved on the filter or crucible with dilute nitric acid (20 per cent). The filtrate and water-washes therefrom are combined and the mercury determined by precipitation in ammoniacal solution with hydrogen sulphide, filtering, washing, drying at 110° C., and weighing. The weight of mercuric sulphide multiplied by 0.862165 gives the corresponding weight of metallic mercury, which is calculated to per cent of the sample taken.

The above method for a simple mixture can be extended to more complex mixtures if desired.

A solution of sodium thiosulphate may be used instead of ammonia to dissolve the mercury fulminate, and the volumetric method devised according to a process first used by Brownsdon, and based by him on the fact that sodium hydroxide is produced in the reaction, may be employed here.

DETAILED ANALYSIS OF A DETONATING COMPOSITION CONTAINING FULMINATE AND CHLORATE.

Occasionally it may be desirable to make a thorough analysis of a fulminate-chlorate detonating composition in order to get all available data. Such analyses are rarely made, and definite and exact knowledge of the nature and origin of all the impurities which may be present, particularly after some decomposition has occurred, is lacking.

IMPURITIES.

The fulminate may contain the impurities mentioned below:

1. *Metallic mercury.* Although all of the mercury may be dissolved in the nitric acid when the reaction incident to the mixing of the alcohol and nitric acid-nitrate solution has proceeded for some time, some metallic mercury may be thrown out and contaminate the finished product.

2. *Oxalic acid.* The presence of oxalic acid is due to oxidation of the alcohol in the manufacturing process and to incomplete subsequent purification.

3. *Free nitric acid.* The presence of free nitric acid in commercial fulminate is due to incomplete washing of the crude product during manufacture.

4. *Chlorine and hydrochloric acid.* Gray fulminate is frequently purified (in reality bleached) with hydrochloric acid, which usually results in not all of this acid being removed.

5. *Mercurous chloride.* The presence of mercurous chloride is also due to the use of hydrochloric acid for bleaching gray fulminate.

6. *Copper chloride.* Gray fulminate is sometimes bleached with cuprous chloride, which explains the presence of the latter.

7. *Basic mercuric salts.* Practically nothing is known as to the causes or nature of basic mercuric salts.

The chlorate may contain the following impurities:

1. *Chloride.* The presence of chloride is due to the method of manufacture and to incomplete purification of the crude product.

2. *Potassium bromate.* All potassium chloride from the Stassfurt deposits contains bromide, which is converted into bromate when the chloride is converted to chlorate by electrolytic methods.

METHODS OF ANALYSIS.

1. *Metallic mercury.* A sample of the detonator charge weighing between 1 and 5 grams is transferred to a dried and weighed filter or crucible where it is washed with water, and then with concentrated ammonia. The filter or crucible is then dried in a calcium-chloride desiccator containing a little mercury in a beaker and weighed, the weight being taken as metallic mercury; if inspection shows the presence of other insoluble matter, the mercury without drying, is dissolved on the filter with dilute nitric acid, and then precipitated from ammoniacal solution with hydrogen sulphide.

2. *Oxalic acid.* The ammoniacal solution that results from combining the filtrate and the washes in the foregoing process is treated with a dilute solution of c. p. calcium chloride, a little ammonium nitrate solution being added first. The mixture is allowed to stand for 12

hours after it is brought to boiling. The calcium oxalate precipitated is then filtered off and can be determined either by weighing as such or by titration in a 5 per cent sulphuric acid solution at 85 to 95° C. with approximately $N/20$ potassium permanganate solution.

3. *Nitric acid.* A preliminary qualitative test of the detonator charge may be made with blue litmus paper, which will not be turned red by thoroughly washed fulminate, or the diphenylamine test may be used. For quantitative work, the total acidity of the sample is determined by agitating the sample (preferably about 5 grams in weight) with 100 c. c. of water and titrating with $N/10$ sodium hydroxide, using phenolphthalein as indicator. The result is calculated to per cent of nitric acid. From this figure are to be subtracted any values found for oxalic and hydrochloric acids.

4. *Chlorides and hydrochloric acid.* A sample of the detonator charge weighing between 5 and 10 grams, if possible, is leached with distilled water. The filtrate and several washes are combined and the chloride and hydrochloric acid present determined either by precipitation of silver chloride with subsequent drying and weighing, or by titration with a $N/10$ silver nitrate solution. The result should be calculated to either chloride or hydrochloric acid as indicated by other impurity determinations.

5. *Mercurous chloride.* The presence of mercurous chloride is determined by washing a sample of the charge thoroughly with cold concentrated hydrochloric acid[12] and testing the residue with ammonia. For a quantitative determination, a 5-gram sample of the charge is washed on a previously dried and weighed crucible with concentrated hydrochloric acid. Mercurous chloride and metallic mercury are left behind. If examination has shown nothing else in the residue, the crucible can be dried in a sulphuric acid desiccator containing a beaker of mercury and weighed. Subtraction of the weight of metallic mercury previously found will give the weight of mercurous chloride. If, however, other substances are in the residue, the chloride and metallic mercury are dissolved out in aqua regia, the residue washed several times with water, and the total mercury in the filtrate and washings determined by precipitation with hydrogen sulphide. The weight of mercuric sulphide equivalent to the weight of metallic mercury is calculated and subtracted from that found. The remaining mercuric sulphide is calculated to mercurous chloride.

6. *Copper.* Copper found as an impurity in fulminate may be present as fulminate or chloride. The manner of combination is not definitely known, but the metal is assumed to be present as cuprous chloride. It should be determined in a solution containing all of the fulminate, as follows: Precipitate the mercury and copper from

---

[12] Escales, Richard, and Stettbacher, A., Initialexplosivstoffe: Leipzig, 1917, p. 142.

an ammoniacal solution with hydrogen sulphide and wash with very dilute ammonium sulphide; then wash with warm dilute nitric acid which dissolves any copper sulphide present. The filtrate is tested for copper with ammonia (blue coloration) and any copper found present is reprecipitated from ammoniacal solution with hydrogen sulphide. This is washed on the filter with very dilute ammonium sulphide, dried at 100° C. and weighed as CuS, or ignited to CuO and weighed as such. It is then calculated to cuprous chloride.

$$CuS \times 1.03544 = CuCl.$$
$$CuO \times 1.24456 = CuCl.$$
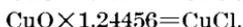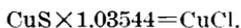
7. *Potassium bromate.*[13] A 2-gram sample is dissolved in 100 c. c. of water and any undissolved fulminate filtered off and washed. Five c. c. of a 10 per cent solution of potassium iodide and an equal quantity of normal hydrochloric acid are added to the combined filtrate and washes. Not more than a trace of blue color should appear within 10 minutes. A blank test is made, using 100 c. c. of water for comparison. The method is made quantitative by the titration of the liberated iodine with $N/10$ $Na_2S_2O_3$ after the treated solution has stood in the dark for one hour.

ANALYSIS OF A DETONATING MIXTURE CONTAINING FULMINATE, CHLORATE, AND TETRYL.

Among the newer types of detonators are those containing a chlorate-fulminate mixture over a compressed charge of tetryl (trinitrophenylmethylnitramine).

The charges are ordinarily so placed that they can be separated mechanically. Under these circumstances the fulminate-chlorate mixture is analyzed as directed before, the purity of the tetryl being established by a determination of its melting point, which should be between 127.5° and 129° C., but never below 127.5° C. Determination of acidity may also be desirable, and is done by boiling a 10-gram sample with 50 c. c. of distilled water, filtering, washing with distilled water, and titrating the filtrate and washes with $N/10$ sodium hydroxide, using several drops of phenolphthalein as an indicator. Acid-free tetryl has an acid reaction and is slightly soluble in water, so 0.2 c. c. of $N/10$ sodium hydroxide must be allowed for this. The result is calculated to per cent of sulphuric acid. The nitrogen content, which is 24.4 per cent for pure tetryl, may also be determined and the purity calculated from this.

Sometimes an accurate and complete separation of the two charges is impossible. In that event the combined charges of two or three detonators are weighed out and transferred to a filter or crucible

---

[13] Zeitschrift für das gesamte Schiess-und Sprengstoffwesen : Jahrg. 8, 1913, p. 102.

previously dried at 100° C. and weighed. The chlorate and some of the fulminate are extracted with distilled water, the filtrate being saved. In this solution chlorate and fulminate are determined as directed before (see p. 14).

If a determination of free mercury is not required the crucible and its contents are dried for five hours at 70° C., cooled, and weighed. The fulminate is then dissolved out on the filter with approximately 30 per cent warm hydrochloric acid, followed by about five washings with distilled water. Then the crucible and its contents are dried for three hours at 110° C., cooled, and weighed. The loss in weight represents fulminate and should be added to the fulminate found in the water extract. The residue in the filter or crucible may be regarded as tetryl and calculated to the percentage basis as such, but if information is desired regarding any additional insoluble impurities that may be present, the residue may be dissolved out with acetone, benzene, or orthonitrotoluene, and the crucible again dried and weighed to determine the loss in weight, which is regarded as tetryl.

ANALYSIS OF A ·DETONATING COMPOSITION CONTAINING FULMINATE, CHLORATE, AND TNT.

Fulminate-chlorate-TNT detonating compositions are analyzed in exactly the same way as fulminate-chlorate-tetryl compositions. The melting point of TNT is 80.6° C., but its "setting point" is usually determined instead, 79.6° C. being regarded as the minimum for satisfactory TNT. In determining acidity, it is not necessary to subtract from the sodium hydroxide reading to compensate for the acidity of the substance, as is necessary with tetryl. Pure TNT contains 18.5 per cent nitrogen, therefore a determination of the nitrogen content will serve as a criterion of the purity of the sample under inspection. The TNT in solution in acetone or benzene may be recovered, identified, and tested to determine its melting point and nitrogen content.

If it is desired to determine the amount of free mercury present, the drying and weighing after the water extraction are followed by the extraction of (1) the TNT and (2) the fulminate in turn with (1) acetone, benzol, or orthonitrotoluene and (2) concentrated ammonia. The filter or crucible is dried and weighed after each extraction, the loss in weight being taken as TNT and fulminate respectively. After the ammonia extraction the drying should be done in a desiccator containing calcium chloride and a little metallic mercury. The metallic mercury remaining is then determined either by direct weighing or by solution in dilute nitric acid and precipitation in ammonical solution with hydrogen sulphide, as directed before.

ANALYSIS OF DETONATING COMPOSITIONS CONTAINING FULMINATE, CHLORATE, NITROMANNITE, AND NITROCELLULOSE.

Fulminate-chlorate-nitromannite-nitrocellulose detonating compositions are analyzed in four stages as follows:

1. The chlorate and some of the fulminate are extracted with water in the usual way, the chlorate and mercury in the solution being determined by reduction with formaldehyde and precipitation with hydrogen sulphide. The crucible or filter containing the residue is dried for five hours at 50° C.

2. The remaining fulminate is extracted with concentrated ammonia, then washed with dilute ammonia and distilled water. If preferred, hydrochloric acid (1:3) may be used. The crucible and its contents are again dried at 50° C. for five hours. The loss in weight is taken as fulminate, but this can be checked by aliquoting the solution and precipitating the mercury with hydrogen sulphide in the usual way.

3. The nitromannite (hexanitromannitol) is removed by extraction with alcohol, benzene, or absolute ether. After drying for five hours at 70° C., the loss in weight is taken as nitromannite. The result can be checked by throwing the nitromannite out of the alcoholic solution with water, filtering, drying at 50° C., and weighing.

4. The residue may be regarded as nitrocellulose, but if the result is to be checked and the presence of other substances investigated, the residue may be extracted with acetone and the crucible dried and weighed. The loss is nitrocellulose.

ANALYSIS OF PRIMING CHARGES IN DETONATORS.

An initial priming charge is placed in some detonators to set off the actual detonating charge. This priming charge is always taken out of the detonator separately, weighed, and given a separate analysis. If it consists solely of nitrocellulose it need only be weighed and identified. The course of analysis of several typical priming charges is given below:

ANALYSIS OF AN INITIATOR CONTAINING FULMINATE AND NITROCELLULOSE.

Samples taken from one or more detonators are weighed and transferred to a filter or crucible that has been previously dried at 100° C., cooled, and weighed. The fulminate is thoroughly extracted with 30 per cent hydrochloric acid, the residue of nitrocellulose is washed several times with distilled water, and the crucible and contents are dried for five hours at 70° C., cooled, and weighed. The loss in weight is taken as fulminate and the weight of the residue is regarded as nitrocellulose, both weights being calculated to a percentage basis.

The analysis of an initiator containing loose fulminate and chlorate is carried out in the same manner as that described for a fulminate-chlorate detonating composition.

ANALYSIS OF AN INITIATOR CONTAINING CHLORATE AND PICRIC ACID.

A weighed sample is transferred to a dried, tared filter or crucible. The picric acid is extracted with ether or benzene. The filter and residue of potassium chlorate are dried at 100° C. for five hours, cooled, and weighed. The loss in weight represents picric acid; the residue represents chlorate. This latter may be checked by dissolving with water, reducing with formaldehyde in the presence of nitric acid and an excess of silver nitrate, and back-titrating with N/10 ammonium thiocyanate.

An alternative method is to extract the chlorate and some of the picric acid with distilled water and to determine the chlorate in the solution by reduction with formaldehyde as directed above.

ANALYSIS OF A PRIMING COMPOSITION FOR DETONATORS, CONTAINING LEAD NITRATE AND TETRYL OR LEAD NITRIDE AND TNT.

The lead nitride is used as a priming charge over the organic nitro compounds, and with sufficient care these can be separated as the charge is removed, then weighed and identified.

If it is impossible to keep the nitride and the nitro compound separated, they are thoroughly mixed and an analysis of the mixture is made as follows:

Weigh a sample of from 1 to 5 grams and transfer it to a filter or alundum crucible that has been previously dried at 100° C. and weighed. The tetryl or the TNT as the case may be, is extracted with absolute ether, orthonitrotoluene, or some other solvent. The crucible with its content of residual lead nitride is carefully dried at 50° C., cooled, and weighed.

ANALYSIS OF PERCUSSION PRIMING COMPOSITIONS.

DIFFERENTIATION BETWEEN PRIMERS AND DETONATORS.

When a detonator is used, it is desired that the detonation wave shall cause a detonation in the main blasting charge; any flame which may be produced is of secondary consideration. Primers, on the other hand, are used to supply a flame at a definite time and place for the purpose of ignition only; detonation is not desired.

NATURE OF PRIMING COMPOSITIONS.

Two classes of primers are in use:

(1) Those containing mercury fulminate, and (2) those which do not, such as the sulphocyanate mixtures.

Antimony sulphide or ground glass is used in practically all primers to increase the sensitivity to friction. They all contain an oxidizing and a reducing agent, one or both of which might be classed as sensitizing materials. By themselves they may be very stable and insensitive, but in the proper mixtures they tend to form gaseous products very easily.

Sulphur is one of the most common substances of this type. Alone it is very insensitive and burns slowly in the air, but when mixed intimately with a strong oxidizing agent, such as potassium nitrate or potassium chlorate, the reaction between them becomes very rapid when once started. A black powder mixture of sulphur, charcoal, and nitrate is very effective as a second-order explosive. It is too insensitive to act as a satisfactory priming mixture, but if potassium chlorate is substituted for potassium nitrate and the charcoal is eliminated the basis of a primer is obtained. Usually, however, more active reducing agents than sulphur are used.

Potassium chlorate is the best-known oxidizing agent for primers. Its only disadvantage is that in combustion potassium chloride is formed, tending to cause after-corrosion in the barrels if used in guns; hence, if so used, proper precautions should be taken to prevent this corrosion.[14]

PRIMER COMPOSITION MATERIALS.

INORGANIC.

Mercury fulminate ($Hg(ONC)_2$).
Lead azide (PbN_6).
Sodium azide (NaN_3).
Potassium nitrate (KNO_3).
Barium nitrate ($Ba(NO_3)_2$).
Lead nitrate ($Pb(NO_3)_2$).
Antimony sulphide (Sb_2S_3).
Phosphorus sulphide (P_4S_3).
Nitrogen sulphide (N_4S_4).
Red phosphorus (P).
Sulphur (S).
Carbon (C).
Powdered glass.
Potassium carbonate (K_2CO_3).
Sodium carbonate (Na_2CO_3).
Barium carbonate ($BaCO_3$).
Lead ammonium thiosulphate ($PbS_2O_3.2(NH_4)_2S_2O_3$).

Potassium chlorate ($KClO_3$).
Calcium chlorate ($Ca(ClO_3)_2$).
Potassium perchlorate ($KClO_4$).
Mercury chromate ($HgCrO_4$).
Lead chromate ($PbCrO_4$).
Lead oxide (PbO_2).
Barium oxide (BaO_2).
Antimony oxide (Sb_2O_3).
Potassium permanganate ($KMnO_4$).
Silver permanganate ($AgMnO_4$).
Silver acetylide (Ag_2C_2).
Potassium silicide (K_4Si).
Barium silicide ($BaSi_2$).
Calcium silicide ($CaSi_2$).
Lead thiocyanate ($Pb(SCN)_2$).
Copper thiocyanates.
Copper ammonium thiosulphate $CuS_2O_3.2(NH_4)_2S_2O_3$.

[14] Huff, Wilbert T., The cause and prevention of after-corrosion in the bores of fire-arms: Jour. Ind. Eng. Chem., vol. 39, 1920, p. 862.

ORGANIC.

Trinitrotoluene
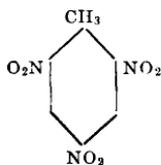
Hexanitrosulphobenzide
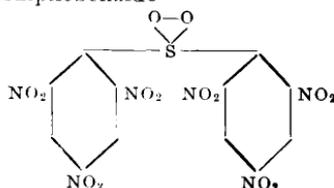
Picric acid
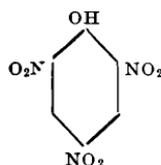
Hexanitrodiphenyl
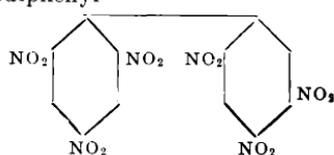
Potassium picrate
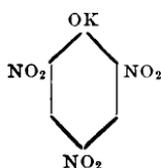
Lead trinitroresorcinate
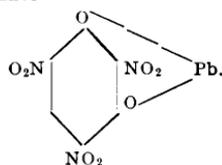
Benzoyl peroxide
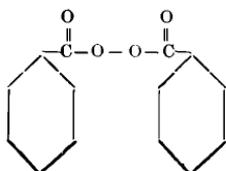
Diazoaminobenzene
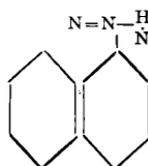
Diphenylamine
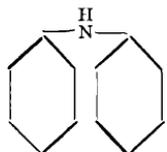
Trinitronitranilide
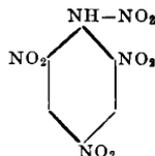
Hexamethylenetriperoxiddiamine
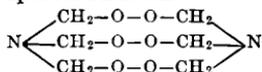
Nitropentaerythritol
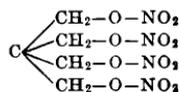
Primers are much more sensitive than detonators, for they are made to ignite by percussion. Accordingly, when primer caps are being opened, it is necessary to handle them more carefully than detonators, but as the charge is very much smaller, there is but little danger of severe injury.

The individual charge is so small that it is only with the more simple mixtures that it is possible to make an analysis on a single charge with any accuracy. Accordingly, the charges are withdrawn from as many caps as is convenient and the weight of each is recorded

so as to ascertain the average charge weight as well as the variation in charges. A composite sample of all opened is made, therefore the result reported is the average of a number.

SAMPLING.

When taking out the charge from the primer, the anvil is first removed and the cap tapped to loosen and jar out the charge. When this work is being done it is well to wear heavy gloves to prevent injury to the hands. The following procedure is recommended as being the safest.

The ordinary pliers used for holding primers are modified so that the opening on one side of the jaws is covered. The primer is held with the anvil toward the open side and about flush with the side of the jaws; then, while the cap is held with the pliers in such a way that it can be seen only in a mirror set at an angle of about 45 degrees on the desk, the anvil is pried or pulled out by a sharp hook. After the anvil has been removed the charge is usually jarred out, but if the charge resists this method, it may be loosened by a maple or orangewood stick with a sharp point. If the charge does ignite during any part of the foregoing, the only damage is the loss of the charge, as the gloves will protect the hands.

IDENTIFICATION OF PRIMER MATERIALS.

Probably the most difficult part of the analysis of primer charges is the identification of the compounds used. The sample is usually so small that not many tests can be made upon it. One of the first steps taken, and often the only one necessary to give a fair idea of the substance used, is the making of a careful examination of the sample under the microscope. For this work a binocular microscope is best, but the usual type with a comparatively low magnification is also very satisfactory. Occasionally it is necessary to pick out a few crystals of some compound on which to make special qualitative tests, and to crystallize out small quantities on a slide in order to note crystal form and growth. Some of the compounds may be identified by the ordinary qualitative tests for bases, acids, and other compounds or elements. A thorough qualitative examination is always worth while, however, and is often essential before it is possible to obtain accurate quantitative results.

Primers are so varied in composition that it is impossible to work out a general scheme of analysis which may be followed. Identifications may, however, follow a partial quantitative separation. In the following pages several methods that are adapted to different mixtures will be outlined. They do not cover all the possible combinations, nor all the substances that may be combined in primers, but do cover most of the materials in common use.

DETERMINATION OF MOISTURE.

Moisture is not usually determined. In order that the composition may be effective it must be kept dry, and it is therefore usually protected by a coating of shellac or collodion. The charge is so small, and so much time is required to remove it, that a moisture determination could not be accurate. When the analysis is for the purpose of determining the cause of misfires the condition of the charge should be carefully noted under a microscope before the charge is removed. If it seems that the moisture content may be high the moisture may be determined by weighing several primers on a watch glass and exposing them for three days in a sulphuric acid desiccator. As a check, in order to be sure that the loss was not surface moisture, the same number of empty caps should be weighed at the same time and the moisture figure corrected accordingly.

ANALYSIS OF SINGLE PRIMERS.

If single primers contain a mercury fulminate, antimony sulphide, and potassium chlorate mixture only, the charge of about 0.02 gram is too small to give good results with the average quantitative methods.

Brownsdon [15] developed a volumetric method for determining mercury fulminate, based on the fact that sodium thiosulphate reacts with mercury fulminate to form free sodium hydroxide, which may then be titrated with standard acid which is suitable for use here.

In order to standardize the solutions the fulminate is weighed into a porcelain dish and about 1 gram of sodium thiosulphate in solution is added. A drop of phenolphthalein indicator is added and the solution is titrated to slight acidity with N/50 sulphuric acid, after which back-titration is effected with N/50 sodium hydroxide.

The procedure in the actual analysis is identical. After the titration is completed, the supernatant liquor is decanted through a small filter and the antimony sulphide is washed five times with hot water, the wash water being decanted through the filter each time. The filter is then dried at 105° C., then the sulphide is dissolved off with hot concentrated hydrochloric acid. The filtrate is caught in the porcelain dish containing the bulk of the sulphide residue, and the dish heated on the water-bath until all of the H_2S is driven off. The solution should not be evaporated to less than 3 c. c. The solution is transferred to a 100-c. c. Erlenmeyer flask and about 1 gram of tartaric acid added. At this point there should be about 25 c. c. of solution. A drop of phenolphthalein is now added and the mixture is brought near the neutral point with ammonium hy-

droxide.   Great care should be taken not to add an excess of ammonia or the basic chloride will precipitate out and will not go back into solution if the mixture is again made acid.   The solution is now made neutral by the addition of small amounts of solid sodium bicarbonate.   An excess of 0.5 gram of sodium bicarbonate and 2 c. c. of clear starch solution are then added and titration with N/100 iodine solution is carried out.

The iodine may be standardized against arsenious oxide.   This is done by weighing arsenious oxide into a porcelain dish, adding 10 c. c. of N/10 sodium hydroxide and a drop of phenolphthalein, and acidifying with concentrated hydrochloric acid.   An excess of sodium bicarbonate is now added, followed by the starch solution. The mixture is then titrated with N/100 iodine solution.

The potassium chlorate is figured by difference.   If ground glass is also present, it may be determined by washing, drying, and weighing the insoluble residue.

By using stronger solutions this procedure may be applied to the analysis of a composite of charges from several primers.

ANALYSES OF TYPICAL PRIMING MIXTURES.

ANALYSIS OF A PRIMING COMPOSITION CONTAINING FULMINATE, ANTIMONY SULPHIDE, CHLORATE, AND GLASS.

The usual type of priming composition contains only four ingredients—mercuric fulminate, antimony sulphide, potassium chlorate, and glass—hence its analysis is not difficult and is carried out in the following manner:

A weighed sample is placed in a beaker and treated with 100 c. c. of water; 5 c. c. of 1:5 sulphuric acid is added, and the solution is brought to a boil.   Hydrogen sulphide is passed through the solution for about 30 minutes in order to precipitate the antimony and mercury.

The beaker and its contents are allowed to cool and the mixture of sulphides is filtered off.   Hydrogen sulphide water is used to wash the precipitate.   The filtrate and wash waters are caught in a porcelain or silica evaporating dish and evaporated.   There should be present sufficient sulphuric acid to decompose all the chlorate present.   When all the chlorine has been driven off—that is, toward the end of the evaporation, when the yellowish green color in the liquid has disappeared—the liquid is transferred to a weighed platinum dish.   The evaporation of the solution is finished in this dish. After the residue has been brought to dryness, excess acid is driven off by stronger heating, and finally the dish and its contents are strongly ignited with the blast.   The factor for the conversion of potassium sulphate to potassium chlorate is 0.70327.

The filter containing the powdered glass and the mixture of sulphides is placed in a beaker and mixed with 5 c. c. of concentrated hydrochloric acid (1.19) and 2 c. c. of a 50 per cent solution of tartaric acid. The mixture is warmed on the water-bath with frequent stirring until the solids have been thoroughly disintegrated. The beaker is then covered with a watch-glass and 1 c. c. of concentrated nitric acid is added from a pipette. Warming with stirring is continued for a short time. The solution is then diluted with a little water and filtered on an ashless filter. The powdered glass is washed with hot water, and the filter with its contents is dried, placed in a weighed porcelain crucible, ignited over a Bunsen burner, cooled, and weighed.

The filtrate from the powdered glass is heated to boiling and the mercury and antimony precipitated out with a stream of hydrogen sulphide for 30 minutes. The beaker and its contents cooled to air temperature and the sulphides are filtered off on a weighed filter, the washing being done with hydrogen sulphide water. Either a porcelain crucible or a silica dish of a capacity of 80 to 100 c. c., previously ignited and weighed, is now placed under the funnel. The antimony sulphide is dissolved out on the filter with ammonium sulphide and washed down with hot water. If this is done carefully, the crucible or dish will be only two-thirds full. The mercury sulphide remaining on the filter is washed with hot water, alcohol, ether, and carbon bisulphide, dried at $110°$ C., and weighed. The factor for conversion to fulminate is 1.22327. The antimony solution is evaporated on the water-bath, the residue is oxidized with concentrated nitric acid (1.42) and taken down two or three times with fuming nitric acid, and finally ignited carefully over a blast. The factor for the conversion of antimony oxide to antimony sulphide is 1.16716.

ANALYSIS OF A PRIMING COMPOSITION CONTAINING CHLORATE, ANTIMONY SULPHIDE, LEAD SULPHOCYANIDE, AND TNT.

This composition is chiefly notable for the reason that it contains no fulminate. It has been successfully used in military practice. The method of analysis is as follows:

The TNT is first extracted from a weighed sample with ether. The sample is dried and reweighed and the loss in weight is taken as TNT.

The residue is now washed with a water solution of potassium nitrate, thus dissolving the potassium chlorate and the lead sulphocyanide. The loss in weight after drying is recorded. The residue consists of antimony sulphide and is weighed as such.

The solution containing potassium chlorate and lead thiocyanate is treated with an excess of N/10 silver nitrate solution, with sub-

sequent heating to the boiling point. After it has stood over night in a dark place, the silver thiocyanide is filtered on a dried and tared Gooch filter, dried at 100° C., and weighed. The factor for conversion to lead thiocyanate is 1.03635.

The filtrate and wash waters are combined and 5 c. c. of 40 per cent formaldehyde and several of nitric acid are added. The chlorate is then reduced to chloride by boiling. The chloride formed is determined by weighing the precipitated silver chloride.

ANALYSIS OF A PRIMING COMPOSITION CONTAINING RED PHOSPHORUS, LEAD PICRATE, AND BARIUM NITRATE.

A weighed sample of the primer is transferred to a beaker and treated with distilled water, which dissolves the barium nitrate and some of the lead picrate. A large excess of hydrochloric acid is now added, completing the solution of the lead picrate.

The mixture is filtered on a dried and tared filter, and the residue of red phosphorus washed with water. The filter is then dried at 70° C. and weighed, the weight of the residue being taken as red phosphorus.

The lead is precipitated from the acid filtrate and wash waters with a stream of hydrogen sulphide. The use of paper pulp is advised, as this assists coagulation of the lead sulphide. After the mixture has been brought to the boiling point, it is cooled, then filtered, and the lead sulphide washed with hydrogen-sulphide water.

Barium is precipitated from the filtrate and wash water with sulphuric acid. The factor for the conversion of barium sulphate to barium nitrate is 1.1197.

If it is desired to check the lead, the lead sulphide is dissolved in nitric acid and precipitated as sulphate.

ANALYSIS OF A PRIMING COMPOSITION CONTAINING POTASSIUM CHLORATE, ANTIMONY SULPHIDE, LEAD NITRATE, AND TNT.

A weighed sample of the primer is first extracted with ether, which removes the TNT. The loss in weight is taken as representing this constituent.

The residue is then extracted with water, which dissolves out the chlorate and the lead nitrate. After it has been dried the residue is weighed and regarded as antimony sulphide. If desired, this may be checked by dissolving the residue in hydrochloric and tartaric acids, precipitating the sulphide, igniting to oxide, and weighing as such.

On account of the fact that only a very small sample is usually available, but one determination can be made on the chlorate-lead nitrate solution, the other compound being found by difference. Lead may be precipitated as sulphate, chlorate determined as chlo-

ride after reduction by formaldehyde, or potassium determined by one of several methods. This choice rests with the individual analyst, but probably the simplest method is to determine chlorate by titration as chloride as previously directed in this paper (see p. 18). After calculation to chlorate, the lead nitrate is found by difference.

ANALYSIS OF A PRIMING COMPOSITION CONTAINING POTASSIUM CHLORATE, ANTIMONY SULPHIDE, LEAD NITRATE, TNT, AND GLASS.

The analysis of this composition is carried out in exactly the same manner as that outlined for the composition containing all these ingredients except powdered glass, with the following exception:

After the priming composition is washed with potassium nitrate solution, the insoluble residue will consist of glass and antimony sulphide instead of the sulphide alone. This is dried and weighed. The sulphide is then dissolved out with hydrochloric and tartaric acids and the glass residue washed with hot water, ignited, and weighed. The loss in weight may be taken as antimony sulphide, but if it is desired to check this the antimony may be precipitated from the filtrate and determined as already described.

ANALYSIS OF A PRIMING COMPOSITION CONTAINING FULMINATE, LEAD PICRATE, ANTIMONY SULPHIDE, BARIUM NITRATE, AND BARIUM CHLORATE.

A weighed sample of the priming composition is given a wash with water to dissolve out the barium nitrate, the solution being decanted into a filter. The residue is next given several washes with dilute hydrochloric acid (30 per cent), these also being decanted into the filter. Everything but the antimony sulphide should now be completely in solution. This latter is put into solution with hydrochloric and tartaric acids and added to the combined filtrates previously obtained.

The lead, mercury, and antimony are now precipitated from a slightly acid solution with hydrogen sulphide. The sulphides are filtered off and washed on the filter with water containing hydrogen sulphide.

The barium in the filtrate is determined by precipitation with sulphuric acid, the resultant barium sulphate being weighed up. $BaSO_4 \times 1.1197 = Ba(NO_3)_2$.

The mixture of sulphides is removed to a beaker and treated with nitric acid of specific gravity 1.2. The whole is warmed and the antimony and lead sulphides are dissolved. The mercury sulphide remaining is filtered off on a tared Gooch filter and washed with water, alcohol, ether, and carbon bisulphide; dried at 110° C.; and weighed. The factor for conversion to mercury fulminate is 1.22327.

The filtrate containing the antimony and lead is treated with a little sulphuric acid and evaporated until dense fumes of sulphur trioxide are given off. It is allowed to cool, then diluted with several times its volume of water. The lead sulphate settles out on standing, and is filtered off, dried, and weighed. $PbSO_4 \times 2.2469 = [C_6H_2(NO_2)_3O]_2Pb.H_2O$.

The antimony in the filtrate is thereupon precipitated with hydrogen sulphide, filtered, washed, ignited to oxide, cooled, and weighed. The factor for conversion of the oxide to sulphide is 1.16716.

Barium carbonate is used in this mixture in a small amount and merely as an antacid, hence it is not necessary to make a quantitative determination of this ingredient.

ANALYSIS OF A PRIMING COMPOSITION CONTAINING SILVER PERMANGANATE, ANTIMONY, SULPHIDE, TNT, AND RED PHOSPHORUS.

A weighed sample of the priming composition is extracted with ether, the loss in weight being taken as TNT. The dried and weighed residue is treated with water, which dissolves out the silver permanganate. About 100 c. c. of water, which will dissolve about a gram of the salt at room temperature, should be used. The loss in weight may be checked by precipitation of the silver as chloride or by titration in hot solution of the permanganate radical with standardized oxalic acid in the presence of sulphuric acid.

The weighed residue is now treated with hydrochloric acid and a 50 per cent solution of tartaric acid, which dissolve out the antimony sulphide. The residue is dried and weighed, its weight being taken as red phosphorus. The loss in weight is taken as antimony sulphide, but this may be checked by precipitation with hydrogen sulphide and ignition to oxide if desired.

ANALYSIS OF A COMPLEX NONCORROSIVE PRIMING COMPOSITION.

A number of noncorrosive priming compositions have been evolved. Between them they contain the following ingredients:

Mercury fulminate ($Hg(ONC)_2$).
Barium carbonate ($Ba(NO_3)_2$).
Barium carbonate ($BaCO_3$).
Antimony sulphide (Sb_2S_3).
Lead peroxide (PbO_2).

Lead chromate ($PbCrO_4$).
Powdered glass.
Picric acid ($C_6H_2(NO_2)_3OH$).
Potassium silicate ($KSiO_3$).

No one primer contains all of these substances. What is present is first determined qualitatively. Outlines for the analysis of a typical composition follows:

ANALYSIS OF A PRIMING COMPOSITION CONTAINING FULMINATE, ANTIMONY SULPHATE, BARIUM NITRATE, PICRIC ACID, AND GLASS.

A weighed sample is transferred to a weighed filter or crucible and extracted with absolute ether, which removes the picric acid. The

residue is dried at 50° C., cooled, and weighed. The loss in weight is taken as picric acid. The ether-picric acid solution may be evaporated to dryness with desiccated air and identification tests, such as determination of the melting point and the nitrogen content, made on the solid picric acid.

The dried residue is now washed with water, thereby dissolving the barium nitrate and some of the fulminate. The filtrate and wash waters are made up to volume and aliquoted. Barium is determined on one portion by precipitation as sulphate, which is calculated back to the nitrate. The factor for this conversion is 1.1197. Fulminate dissolved is determined upon another portion by precipitation from ammoniacal solution with hydrogen sulphide.

The residue after the water extract is transferred to a beaker and treated with 100 c. c. of water and 5 c. c. of 1:5 sulphuric acid. The mercury and antimony are then thrown out as sulphides with hydrogen sulphide. These are redissolved by the addition of 5 c. c. of hydrochloric acid and 2 c. c. of a 50 per cent solution of tartaric acid. The mixture is warmed on the water bath with frequent stirring until the solids have been disintegrated. The beaker is then covered with a watch glass and 1 c. c. of concentrated nitric acid is added from a pipette. Warming with stirring is continued ·for a short time. The solution is then diluted with a little water and filtered with an ashless filter. The powdered glass is washed with hot water and ignited in a weighed porcelain crucible.

The filtrate from the powdered glass is heated to boiling and the mercury and antimony precipitated out with a stream of hydrogen sulphide for 30 minutes. The beaker and its contents are allowed to cool to air temperature and the sulphides are filtered off on a weighed filter, the washing being done with hydrogen sulphide water. An 80 to 100 c. c. porcelain crucible or a silica dish of the same capacity, previously ignited and weighed, is now placed under the funnel. The antimony sulphide is dissolved out on the filter with ammonium sulphide and washed down with hot water. If this is done carefully, the crucible or dish will be only two-thirds full. The mercury sulphide remaining on the filter is washed with hot water, alcohol, ether, and carbon bisulphide, dried at 110° C., and weighed. The factor for conversion to fulminate is 1.22327. The antimony solution is evaporated on the water bath; the residue is oxidized with concentrated nitric acid (1.42), taken down two or three times with fuming nitric acid, and, in conclusion, carefully ignited over a blast lamp. The factor for the conversion of antimony trioxide to antimony sulphide is 1.16716.

PUBLICATIONS ON INVESTIGATIONS OF EXPLOSIVES.

A limited supply of the following publications of the Bureau of Mines has been printed and is available for free distribution until the edition is exhausted. Requests for all publications can not be granted, and to insure equitable distribution applicants are requested to limit their selection to publications that may be of especial interest to them. Requests for publications should be addressed to the Director, Bureau of Mines.

The Bureau of Mines issues a list showing all its publications available for free distribution as well as those obtainable only from the Superintendent of Documents, Government Printing Office, on payment of price of printing. Interested persons should apply to the Director, Bureau of Mines, for a copy of the latest list.

PUBLICATIONS AVAILABLE FOR FREE DISTRIBUTION.

BULLETIN 48. The selection of explosives used in engineering and mining operations, by Clarence Hall and S. P. Howell. 1914. 50 pp., 3 pls., 7 figs.

BULLETIN 59. Investigations of detonators and electric detonators, by Clarence Hall and S. P. Howell. 1913. 73 pp., 7 pls., 6 figs.

BULLETIN 96. The analysis of permissible explosives, by C. G. Storm. 1916. 88 p., 3 pls., 7 figs.

TECHNICAL PAPER 7. Investigations of fuse and miners' squibs, by Clarence Hall and S. P. Howell. 1912. 19 pp.

TECHNICAL PAPER 17. The effect of stemming on the efficiency of explosives, by W. O. Snelling and Clarence Hall. 1912. 20 pp., 11 figs.

TECHNICAL PAPER 78. Specific-gravity separation applied to the analysis of mining explosives, by C. G. Storm and A. L. Hyde. 1914. 14 pp.

TECHNICAL PAPER 125. The sand test for determining the strength of detonators, by C. G. Storm and W. C. Cope. 1916. 68 pp., 2 pls., 5 figs.

TECHNICAL PAPER 145. Sensitiveness to detonation of trinitrotoluene and tetranitromethylaniline, by G. B. Taylor and W. C. Cope. 1916. 11 pp., 1 pl.

TECHNICAL PAPER 160. The determination of nitrogen in substances used in explosives, by W. C. Cope and G. B. Taylor. 1917. 46 pp., 4 figs.

TECHNICAL PAPER 162. Initial priming substances for high explosives, by G. B. Taylor and W. C. Cope. 1917. 32 pp.

TECHNICAL PAPER 234. Sensitiveness of explosives to frictional impact, by S. P. Howell. 1919. 17 pp., 2 pls., 1 fig.

TECHNICAL PAPER 243. Development of liquid-oxygen explosives during the war, by G. S. Rice. 1920. 46 pp., 2 pls., 6 figs.

PUBLICATIONS THAT MAY BE OBTAINED ONLY THROUGH THE SUPERINTENDENT OF DOCUMENTS.

BULLETIN 51. The analyses of black powder and dynamite, by W. O. Snelling and C. G. Storm. 1913. 80 pp., 5 pls., 5 figs. 10 cents.

BULLETIN 66. Tests of permissible explosives, by Clarence Hall and S. P. Howell. 1913. 313 pp., 1 pl., 6 figs. 25 cents.

TECHNICAL PAPER 12. The behavior of nitroglycerin when heated, by W. O. Snelling and C. G. Storm. 1912. 14 pp., 1 pl., 2 figs. 5 cents.

TECHNICAL PAPER 146. The nitration of toluene, by E. J. Hoffman. 1916. 32 pp. 5 cents.

○