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PROGRESS REPORT ON DETERMINATION OF CHEMICAL COMPOSITION

OF SLOW EXPLOSIVES

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ABSTRACT

An outline of the work which has been done to date on the determination of the chemical composition of bonded slow explosives is presented. The explosives considered are a mixture of ammonium picrate-barium nitrate-plastic, a mixture of T.N.T.-barium nitrate-plastic, and various metal picrates (in an unbonded condition). Preliminary data are presented which indicate that the quantitative determination of these individual components, and water, by the methods developed, is possible.

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Introduction

On the basis of preliminary experimental work (6) it was felt that a bonded explosive mixture consisting of $Ba(NO_3)_2$, a suitable explosive (either ammonium picrate or T.N.T.), and a thermosetting plastic of the phenol-formaldehyde, resorcinol, or melamine type would most likely be used. In addition, it was thought advisable to prepare and test various of the metal picrates. Inasmuch as the reproducibility of the explosive properties of these materials depends upon their chemical composition, the necessity for the development of rapid, accurate methods for determining the chemical composition became apparent. This report deals with the development of these methods.

General Method of Attack

A. Mixed Explosives

Before any quantitative determination of the relative amounts of the individual components of the two "mixed" explosives (T.N.T.-$Ba(NO_3)_2$-plastic and ammonium picrate-$Ba(NO_3)_2$-plastic) could be made, it was first necessary to find a means of separation of these components. The method which at once suggested itself was that of selective solubility. Accordingly, the individual components (before bonding) were subjected to the action of various solvents and reagents.

The following table summarizes the results obtained in the case of those solvents which are of greatest interest:

TABLE I

Effect of Solvents on Pure Components

Solvent

Pure Component	NH$_4$OH(con)	Acetone	H$_2$O	(C$_2$H$_5$)$_2$O	CH$_3$OH	CHCl$_3$	C$_6$H$_6$
Ba(NO$_3$)$_2$	Sol.	Insol.	Sol.	Insol.	Insol.	Partly Sol.	Partly Sol.
T.N.T.	Partly Sol. Pink Sol'n.	Sol. Pink Sol'n.	Insol.	Sol.	Insol.	Sol.	Sol.
NH$_4$ Picrate	Sol. Red Sol'n.	Insol.	Sol. (hot)	Insol.	Sol.	Insol.	Insol.
Uncured Resorcinol Plastic	Sol. Red Sol'n.	Sol. Red Sol'n.	Insol.	Insol.	Sol. (slow) Red Sol'n.	Partly Sol.	Partly Sol.
Partly Cured* Resorcinol Plastic	Sol. Dark Sol'n.	Partly Sol.	Insol.	Insol.	Partly Sol.	----	----

*Heated in oven at about 105°C for 36 hours. It was later found that this temperature was too low for curing.

The above descriptions as to whether a component is soluble or insoluble in a given solvent are strictly qualitative, no attempt having been made to determine quantitatively the degree of solubility. The appearance of a pink, red, or dark color is indicative of decomposition.

From Table I several different methods of separation are at once evident. However, certain of these methods which involve dissolving of the plastic had to be abandoned when it was shown that in order to obtain the required mechanical

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strength, the plastic must be completely cured. This complete

curing renders the plastic inert. Thus for the case of the

cured T.N.T. mixtures the following procedure should be the

most satisfactory:

1. Dissolve $Ba(NO_3)_2$ in H_2O.

2. Dissolve T.N.T. in $(C_2H_5)_2O$, $CHCl_3$, or C_6H_6.

3. Leaves plastic.

For the ammonium picrate mixtures:

1. Dissolve $Ba(NO_3)_2$ and ammonium picrate in hot H_2O.

2. Determine barium chemically.

3. Leaves plastic.

A number of rough determinations on the mixed explosives

were run in order to determine the applicability of the above

methods. Although some difficulty was experienced in dissolving

the ammonium picrate mixture (this was accomplished by the use

of boiling and stirring), these methods were found to be suitable

for the separation of the individual components. These preliminary

runs, in which the percentage of the individual components was

determined by weight difference only, brought out the need for

the development of suitable chemical means for the quantitative

determination of these components in order to achieve a satis-

factory degree of accuracy.

This problem was simplified at this point in that it was

decided to discontinue development work on the T.N.T. mixture

due to its inherent disadvantages; the low melting point of

T.N.T. makes proper curing of the plastic impossible. Thus

it was necessary to develop methods for use with the ammonium picrate mixtures only. Analysis of the problem indicated that direct determination of barium and nitrogen should be sufficient.

B. Metal Picrates

The work on the metal picrates was undertaken at a somewhat later date than that on the mixed explosives. In this connection it was realized that water would have a profound effect upon the explosive characteristics of the picrates. Therefore, in addition to finding a satisfactory method for the determination of the picrate present, a great deal of effort was expended in finding a suitable method for the determination of small amounts of water.

Determination of Barium

For the direct determination of barium in the ammonium picrate mixture, the volumetric chromate method was used. This method consists in precipitating barium chromate in a neutral solution (found to be preferable) or a solution buffered with a mixture of acetic acid and sodium acetate (21). This precipitate is then washed with water, dissolved in dilute hydrochloric acid, treated with potassium iodide, and titrated against standard thiosulfate to an iodine end-point. Other investigators (4, 18, 25) have shown, as have these experiments, that the following precautions are helpful:

> 1. To prevent oxidation of the iodide by air, and at the same time to allow the reaction to proceed, the concentration of the acid must be maintained around 0.2 N. Thus it is recommended that the precipitate be dissolved in as dilute acid as possible, the potassium iodide then be added, and the final concentration of the acid then be adjusted.

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2. Allow sufficient time for the reaction to proceed.

3. Add sufficient potassium iodide.

A fairly large number of barium determinations were made using both the ammonium picrate mixture and barium picrate. Table II lists the results which were obtained.

TABLE II

Determination of Barium

Run #	Substance	% Barium
1	75% $Ba(NO_3)_2$ - 25% NH_4 Pic. - Resin	37.15, 35.21
2	Ba Picrate	22.59, 22.21
3	Ba Picrate	23.20, 23.26, 22.86 (maximum possible for pure Ba Picrate = 23.15%)
4	Ba Picrate	22.23, 22.09
5	Ba Picrate	22.22, 22.21
6	$Ba(NO_3)_2$ Resin	48.20, 48.27
7	$Ba(NO_3)_2$ - NH_4 Pic. - Resin	9 (approx.)

A check sample was run with a known amount of dried reagent grade $Ba(NO_3)_2$. The error was found to be 0.85%.

Considering the results of Table II, Run #1 was a sample of 75-25 $Ba(NO_3)_2$ - ammonium picrate-resin explosive. On a barium nitrate basis, these results are 75.16% and 71.24%. The error is due to mechanical loss brought about by using too large samples, thus necessitating excess washing.

Runs 2-5 were made on samples of barium picrate prepared by Julius Feit. All samples were supposed to be the same, the only apparent difference being due to the varying lengths of time during which the samples remained in the dessicator. Runs 2-4 were determined by the usual chromate method; run 5 is the result of a sulfate precipitation as run by the analytical chemical group under Mr. Potratz. Since these results vary a great deal with respect to the water present (from .05 to 1.47 moles of water per mole of barium picrate), and since the detonation velocity depends upon the amount of water, a direct method for the determination of water was felt to be advisable.

The sample for run 6, consisting of $Ba(NO_3)_2$ and resin, was supplied by Hugh Bryce. This sample was prepared in a manner different from the ordinary and had a very high compressive strength. The results are excellent, having an average deviation from the mean of less than 1 part per 1000.

The sample for run 7, supplied by Lester Guttman, exhibited anamolous phenomena regarding its explosive properties. The reason for this behavior was readily apparent when it was found that although the lens was supposed to contain 50% $Ba(NO_3)_2$, it actually contained only about 18% $Ba(NO_3)_2$.

Determination of Water

For the determination of water in either the metal picrates or the ammonium picrate mixtures, a large number of methods were investigated. Among the methods considered were the use of acetyl chloride and pyridine for titrimetric determination (23),

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conductrometric titrations using acetic anhydride in glacial
acetic acid (8), thermal decomposition measuring the evolution
of hydrogen from the reaction of sodium metal on sulfuric acid
(16), thermal decomposition absorbing the carbon and hydrogen
combustion products, the use of the Grignard reagent (2, 12,
13, 14), the Karl Fischer method using sulfur dioxide and iodine
dissolved in pyridine (1, 5, 10, 11, 15, 24, 28), the use of the
reaction between calcium hydride and water (20), the use of sodium
triphenyl methyl dissolved in ethyl ether (22), the use of
napthoxydichlorophosphine (3), a manometric procedure using
lithium chloride monohydrate (7), and the distillation method
of Rodman (19).

After consideration of all these methods from the standpoints
of difficulty to be encountered with hydrates and impurities,
speed of operation, simplicity of apparatus, and accuracy to be
obtained, the Karl Fischer method was decided upon as being the
most suitable.* This method was felt to be inherently inaccurate
due to the presence of an unknown amount of plastic in the case of
the metal picrates. These considerations were paramount in deciding
upon a direct method for water.

The method for the direct determination of water, developed
by Karl Fischer (10), depends upon the action of I_2, SO_2 and
pyridine upon water. The Fischer reaction, as amended by Smith,
Bryant, and Mitchell (24), is as follows:

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*However, a sample of barium picrate was given to the analytical
chemistry group under Mr. Potratz for determination by combustion
and direct measurement of the gases involved. The results obtained
were very poor.

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$$I_2 + SO_2 + CH_3OH + 3 \; \bigcirc\!\!\!N + H_2O \longrightarrow$$

$$3 \; \bigcirc\!\!\!\overset{+}{N}\!\!H + 2I^- + CH_3SO_4^-$$
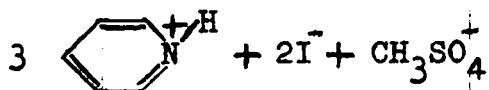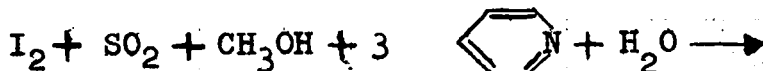
Side reactions also occur. The end-point for this reaction has been determined colorimetrically or potentiometrically. This method has met with success in quite a large number of varying applications.

The main parts of the apparatus were supplied by Group CM-15, who had attempted to use this method for the determination of water in uranyl sulfate. It is similar to that described by Almy, Griffin, and Wilcox (1) with certain modifications such as the use of similar electrodes, capillary burette tips, double drierite tubes, etc. Figure 1 shows the set-up. The apparatus shown in Figure 1 was assembled with the thought uppermost in mind of excluding atmospheric moisture from the reactants. Accordingly, all inlet and outlet points are protected by drierite-filled tubes. Also, the bakelite stopper was ground to fit tightly into the titrating flask, and the holes drilled through it to allow entrance of the burette tips, platinum electrode, and stirrer are as small as possible. The bakelite stopper and ground glass joints were used (rather than rubber connections or rubber or neoprene stoppers) due to the deleterious effects of the Karl Fischer reagent upon these substances. The Karl Fischer reagent storage bottle is protected from light by a covering of dark paper. In order to use, the reagent or methanol solution is merely pumped up into the burette, and then by changing the position of the 3-way stopcock, the appropriate amount of solution is drained into the titrating

flask. After use, the screw clamps are tightened in order to further protect the solutions from atmospheric moisture. The entire apparatus is mounted on a strong frame.

Inasmuch as the colorimetric end-point (from orange to yellow) was found to be unsatisfactory, a potentiometric "titrimeter," based upon the "dead-stop end-point" method of Foulk and Bowden (9) and developed further by other investigators (17, 26, 27) was supplied by the electronics department for this installation.

At the present time little data are available concerning the practicability of this method for determining the moisture present in the samples under consideration. However, by using the method of procedure outlined below, the moles of water per mol of standard $BaCl_2 \cdot 2H_2O$ was determined as 1.99. In general, this procedure follows closely that given by Almy, Griffin, and Wilcox (1) and repeated in the Eimer and Amend pamphlet (28) with which they accompany the made-up Karl Fischer reagent which they supply. It is felt advisable, however, to present this procedure here so that it will be readily available for other project investigators.

A. Procedure for Determination of Water by Karl Fischer Method

    1. Preparation of Reagent

        It was found that a good quality reagent could be prepared by mixing:

        169 gm I_2 (resublimed) - from K-Stock
        511 ml methanol - synthetic as obtained directly
             from the barrel and
        425 ml pyridine - Eastman Kodak as supplied
             by K-Stock

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These materials were mixed in an Erlenmeyer flask which was then placed in an ice-bath in a hood. To this solution were then added

128 gm SO$_2$

Although heat was liberated, the amount was not excessive. Therefore, it was possible to add the SO$_2$ in 35-40 minutes. (this figure is a great deal less than that reported by Johnson (10).), with only small SO$_2$ loss. The amount of SO$_2$ added was determined by weighing the flask before and after the SO$_2$ addition in order to allow for any losses. Since this reagent changes strength very rapidly when first made up and then more slowly, it is advisable not to attempt any standardization for approximately 24 hours after making a fresh batch, and then daily standardization is necessary. The possibility of predicting the strength at any given time by means of an extrapolated graph has been suggested.

It is also possible to purchase the previously prepared Karl Fischer reagent from Eimer and Amend (#2028). This is supplied in the form of two solutions, which are not mixed until ready for use in order to avoid deterioration.

2. Standardization of Reagent

After preparation of the reagent, it is next necessary to standardize it. This is done by comparing its strength to that of the methanol-water mixture against which it is to be titrated. (The strength of the methanol-water mixture may be known or unknown at this point.) Therefore, approximately 20 ml. of the reagent are placed in the titrating

flask, the stirrer is started, and the methanol-water mixture is added until the end-point is reached. It is recommended that the strength of the methanol-water mixture be adjusted so that 1½ to 2½ times as much methanol is required as reagent (30 to 50 ml. methanol). It was found necessary to dilute the methanol as obtained from K Stock with water in order to give the correct ratio. This ratio, called R for purposes of calculation, which is the ml. of reagent divided by the ml. of methanol-water, must be determined daily. It was found this value could be determined within 1 part per 1000 on separate samples.

3. Determination of End-Point

In order to accurately determine the end-point, the operating and calibrating instructions accompanying the titrimeter are closely followed. The polarizing current is kept at zero, and the scale factor at 50 until the electrodes are in contact with the reagent. When this occurs, the polarizing current and the scale factor are set at their proper values to give the most satisfactory reading of the end-point. Experimentally, these values have been determined at 10 and 1 respectively.

With the reagent only in the titrating flask, and the titrimeter adjusted as above, no current will be flowing through the solution due to polarization, and the indicator will register zero. With the addition of the methanol-water solution, the dark brown iodine color of the reagent

will gradually become a light orange. At approximately
the end-point this light orange will turn a light yellow.
Slightly before the end-point is reached, the titrimeter
indicator needle will begin to waver, until at the final
drop (which may not appear to coincide exactly with the
color change) it will begin a slow steady rise which will
not stop until the indicator needle goes off scale at the
upper end beyond 10. The amount of methanol-water mixture
required to accomplish this is taken as the end-point.

4. Standardization of Methanol-Water Mixture

The methanol-water mixture may be standardized by
weighing about 0.15 gm. of water from a Lunge weighing bottle
into the titrating flask, adding excess Karl Fischer reagent,
and titrating to the end-point with the methanol-water
mixture. From the information thus obtained the factor
F_{I_2}, the grams of water per ml. of reagent and F_{alc}, the
grams of water per ml. of methanol may be calculated as
follows:

$$F_{I_2} = \frac{gm.\ water}{ml.\ of\ I_2\ reagent - (ml.\ of\ alcohol\ x\ R)}$$

and $F_{alc} = F_{I_2}\ x\ R$

Some difficulty was at first experienced in preventing
evaporation of the water during weighing. However, with
the arrival of the Lunge weighing bottle and by allowing
it, when full, to reach equilibrium with the air before
weighing, no further difficulty was encountered.

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It is also possible to buy standard methanol (1 ml. -
1 mg. H_2O) from Eimer and Amend (#2027).

5. Determination of Water in an Unknown Sample

A known amount of the sample to be tested (enough to
contain approximately 0.15 gm. water) is weighed into the
titrating flask. Since the primary purpose is to deter-
mine the water of hydration, rather than surface moisture,
the samples are kept in a dessicating flask before weighing
and run as soon as possible after weighing. A measured
amount of methanol-water mixture is then added, and the
mixture is stirred for a sufficient time to see if all
the solid will go into solution. Regardless of whether
or not this occurs, a measured excess of I_2 reagent is then
added. If the material has not yet gone into solution,
stirring is continued. If solution is now obtained, the
results may be considered satisfactory, and the sample is
then back-titrated with the methanol-water mixture. If
solution has not been obtained, alternate methods such as
the use of ethylene glycol, severe shaking (5), and heat
have been suggested.

In the case of the picrates, a pyridine-picrate addition
compound is formed upon the addition of the Karl Fischer
reagent to the picrate-methanol solution. However, it is
thought that the tendency for the water to be used up in
the Karl Fischer reaction is greater than the tendency
for the water to be trapped as a hydrate in this compound.

Thus no error should be introduced due to the formation of this compound. As yet, insufficient data are available to support this stand.

Using the information obtained by the method outlined above, the per cent of water present in a sample may be calculated as follows:

$$\% \text{ of } H_2O =$$

$$\frac{(\text{ml. of } I_2 \text{ Reagent} - \text{ml. of methanol} \times R) \times F_{I_2} \times 100}{\text{grams of sample}}$$

6. Results Obtained

The results obtained by the use of the Karl Fischer method are incomplete at the present time. Other than the check sample of $BaCl_2 \cdot 2H_2O$ which has already been mentioned, and the establishment of this method on a firm working basis, few unknowns have been run. Preliminary indications are that a precision of around 0.2% (at least for those samples which are soluble) is readily obtainable. The accuracy is probably on the order of 0.5%.

Determination of Picrate

Some thought has been given the matter of the determination of the amount of picrate present. It was decided this could best be done by determining the nitrogen. Comparison of the various methods available for the determination of nitrogen resulted in the selection of the Kjeldahl method as being most satisfactory for the present problem, involving ammonium picrate. No experimental work has yet been done.

Recommendations

At the present time, the mixtures under consideration are two in number. The components of these mixtures may be listed as follows:

Mixture 1	Mixture 2
$Ba(NO_3)_2$	Metal Picrate
NH_4 Pic.	H_2O
Plastic	

On the basis of the work which has been completed, it is recommended that the following procedures be carried out:

Mixture 1

1. Dissolve all but the plastic in hot water. An estimate of the plastic may be made at this time by weight difference.

2. The barium may be determined by chromate precipitation and subsequent titration with thiosulfate. Although good results have been obtained by this method, it is quite slow, involving thorough washing of both the sample when it is being dissolved and of the chromate precipitate. The first washing will, of course, always be necessary. A method may be found whereby the second can be eliminated.

3. It should then be possible to determine the nitrogen in the ammonium picrate by the Kjeldahl method. Complete development of this method must be done.

4. A check on the plastic may now be made by difference. If small amounts of surface moisture or impurities are

present, they will be included as plastic.

Mixture 2

1. It should be possible to determine the amount of picrate present by a Kjeldahl determination of nitrogen as in mixture 1 above. Experimental work will indicate whether this method is applicable for all picrates or ammonium picrate only.

2. Present indications are that the Karl Fischer method for the determination of water will prove satisfactory. Insoluble picrates will give trouble, but methods have been suggested to overcome this. This phase of the work is actively being carried forward at the present time.

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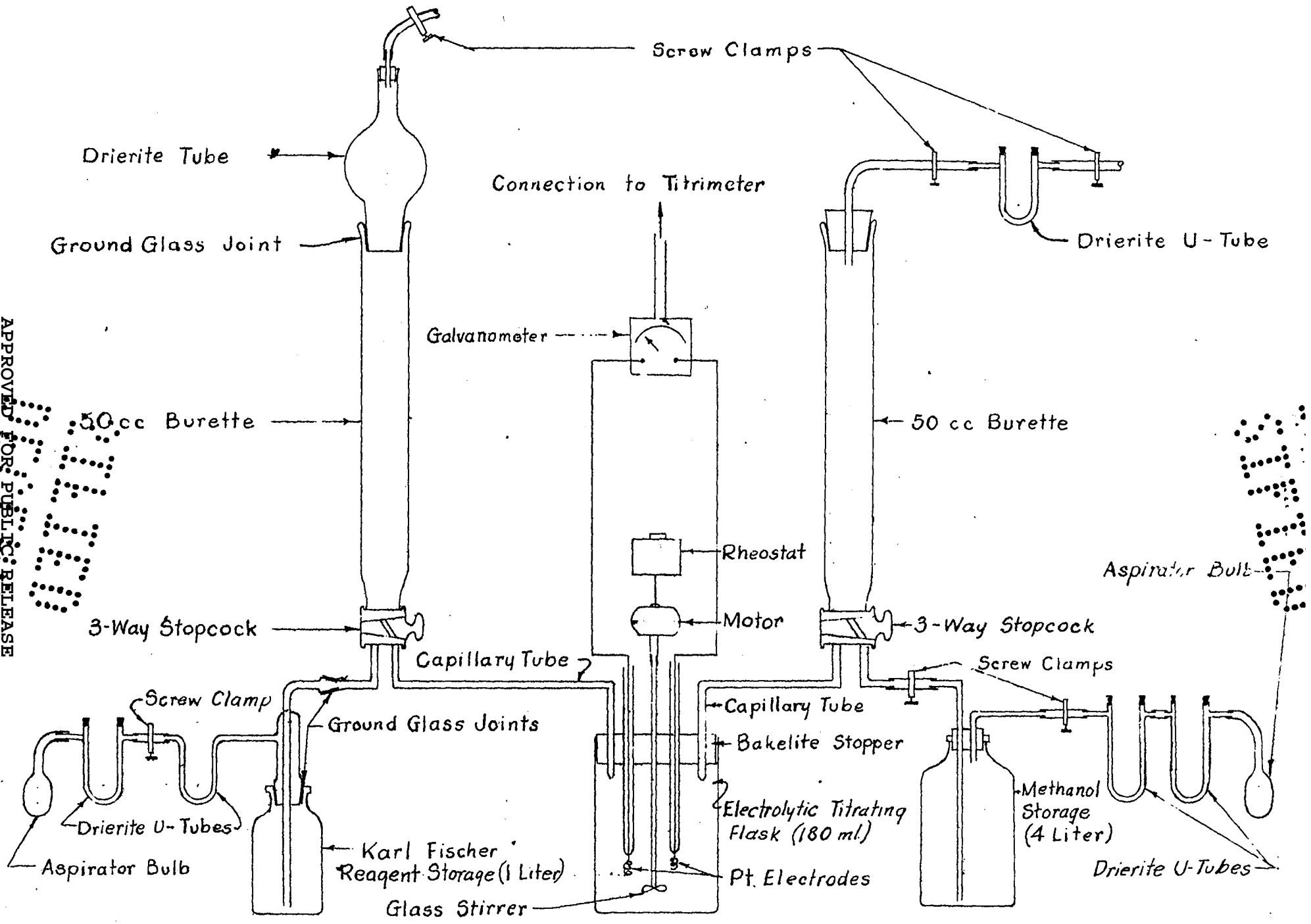
FIG. 1
DIAGRAM OF WATER-DETERMINATION ASSEMBLY