

# Apparatus for the Determination of Minor Components of a Gas Mixture

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The apparatus is primarily for the determination of the components occurring in low partial pressures in a gas mixture, and which ordinarily cannot be determined with satisfactory accuracy because of the significant sorption and desorption of major components in the reagents intended for the removal of the minor ones. Small amounts of solid and liquid reagents are used in the apparatus, and combustions, as well as absorptions, can be performed. The apparatus can be made a separate unit or part of a standard apparatus for volumetric chemical gas analysis.

## 1. Introduction

There comes a time in the life of every exasperated gas analyst when he tires of cleaning liquid reagents from parts of the apparatus not intended to contain them, and the tendency of solutions to wander out of bounds prompts the desire to substitute less nomadic solid reagents. And there are times when the analyst is discouraged by conventional analyses that have indicated minor constituents that did not exist in the samples analyzed, or lost small but significant portions of major constituents. Errors caused by the solubility of components in a reagent not intended for their removal have long been a problem in gas analysis. During 1938 the apparatus described here was designed to eliminate such errors of solubility, at least within the significance of the better volumetric systems. Prior to this, the idea had been used in determining carbon dioxide in air captured in the stratosphere [1],<sup>1</sup> and for the determination of ethylene oxide in carbon dioxide [2]. Part of this apparatus was illustrated and briefly mentioned in a paper [3] describing modifications of what was then our volumetric gas analysis apparatus.

The determination of constituents of small partial pressures has been successfully done by Bone and Wheeler, whose apparatus seems to be one of the standard types used in England [4]. This apparatus requires the addition of a small amount of fresh reagent for each absorption conducted, and while this minimizes the errors of solubility associated with the ordinary volumetric apparatus (usually referred to as an Orsat), this gain in accuracy is obtained by a considerable inconvenience in operation. Analysts in general have shown too great an impatience ever to accept the Bone and Wheeler procedure. So they have put up with errors of solubility.

Errors caused by solubility have long been recognized and even talked about, but it took a demonstration like the cooperative analysis of a sample of natural gas by 30 laboratories working with Subcommittee D-3-VII (Analysis of Gaseous Fuels) of the American Society for Testing Materials to bring a full realization of the magnitude of these errors [5].

The determination of oxygen was particularly interesting because there was no significant amount of oxygen in the sample. One- or two-tenths of a percent of oxygen is usually reported in the analysis of a natural gas, and the extent to which oxygen really does occur has long been a question. Of 294 analyses reported, 124 (only 42 percent) correctly indicated no oxygen; 58 (about 20 percent) indicated 0.1 percent of oxygen, which may be considered the average error of solubility that experience has shown may be expected; and 69 (about 23 percent) indicated 0.2 percent of oxygen, which should have been the maximum error caused by solubility alone. However, 24 and 19 analyses indicated 0.3 and 0.4 percent, respectively, and these values round off a probability curve.

Errors of solubility can be minimized by using small amounts of solid reagents and liquid reagents in reaction tubes designed to confine them. The reaction tubes can be connected to the distributor of the gas analysis apparatus in such a way that the manipulations involved are more easily performed than in the case with the ordinary volumetric apparatus employing liquids in pipet. Actually, the reaction tubes form an integral part of the distributor, and a reaction is conducted by simply passing gas from the buret through the tube and into a reservoir over mercury, just as though the gas were being passed through the distributor itself.

The apparatus can be made a separate unit or a part of the conventional gas analysis apparatus.

## 2. The Separate Unit

The separate unit is independent of the regular one ordinarily used for volumetric analysis. It is possible to do a complete absorption-combustion analysis with this unit, even with gases of average composition, but it is primarily intended for the determination of components of a mixture that occur in small amounts. If the type of analysis performed requires the determination of components present in both large and small amounts, the apparatus described in section 3 is the one to use.

The various reaction tubes of this unit are permanently sealed to the distributor, which may be made in 1, 2, or 3 sections, as desired. A natural

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<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

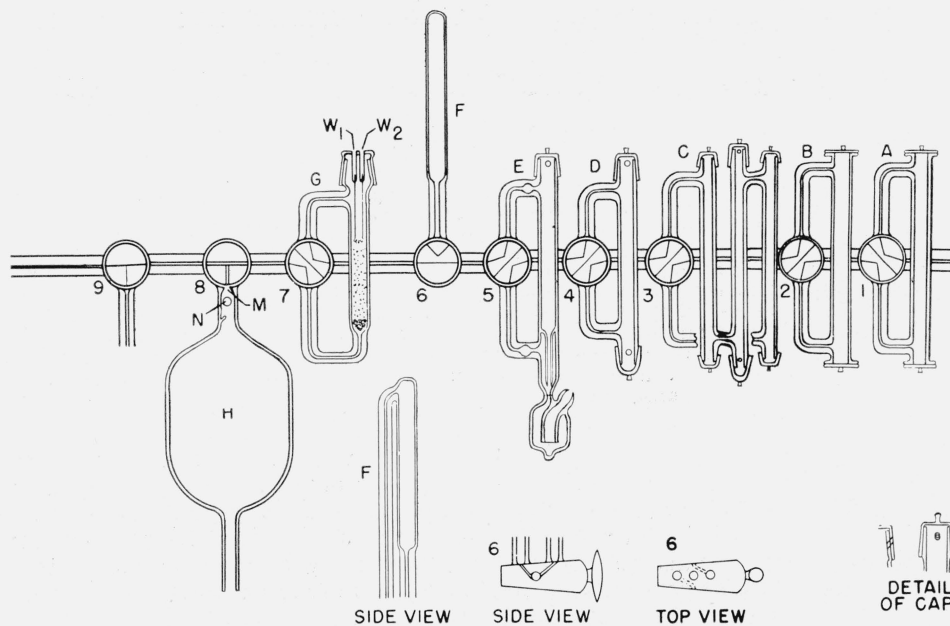


FIGURE 1. *Separate unit.*

division would be to include absorption tubes in one section (see fig. 1, stopcocks 1 to 5, inclusive), combustion tubes in a second (cocks 6 and 7), and the reservoir and connection for the pipet containing alkaline pyrogallol solution in the third (cocks 8 and 9). In arranging the section for absorptions, the particular needs of the work to be done will often indicate a simplification of the apparatus shown.

If the distributor is made in a single section, the total length (60 cm) makes it advisable to use 10-mm outside diameter capillary tubing for the horizontal member, and the vertical members are 8-mm outside diameter, and all bores are 2 mm. When the distributor is divided, the sections are connected with 12/2 interchangeable spherical joints, such as terminate the distributor at both ends.

The buret used with this unit is not shown, but is just like the one previously described [6], complete with the special compensator-manometer, except that the top 45 ml of the buret itself is a pear-shaped bulb. The stem of the buret is graduated in the standard manner [6], but as the over-all length is the same and the volume only half that of the regular buret, the stem may be marked in intervals of 0.1 ml rather than 0.2 ml, which is advantageous for analysis of this kind, and the standard water jacket and frame may be used.

As previously noted, the reaction tubes are integral parts of the distributor and are designed to use small amounts of either solid or liquid reagents. They are connected by stopcocks with keys bored so that in one position the reaction tube is bypassed, and in another position gas from the buret enters the bottom of the reaction tube and leaves the top traveling left into the distributor on its way to the mercury-filled reservoir. The various tubes will be briefly described.

Reaction tubes A and B (fig. 1) are alike, and are for solid reagents. The ends of these tubes are closed with flat caps ground to fit the ground flat flanges at the top and bottom of the tubes. These joints may be sealed with a low-melting thermoplastic cement or with a heavy lubricant. The caps have glass spurs to hold retaining springs or rubber bands in place. These tubes are ordinarily used with a desiccant, such as phosphorous pentoxide on glass wool or calcium sulfate, in the event a dry analysis is done; or with Ascarite for the removal of carbon dioxide and other acid gases.

Reaction tube C may be used with solid reagents, or the central tube may be used with a liquid reagent on glass wool while the outer tubes contain solid reagents. For example, a few drops of fuming sulfuric acid in the middle tube, and a packing of glass wool and Ascarite in the outer tubes, may be used to determine small amounts of unsaturated hydrocarbons in fuel gases; or calcium sulfate in the outer tubes and Hopcalite in the middle tube will serve to remove small amounts of carbon monoxide from the gas sample. When a liquid reagent is used in the central tube it is introduced through holes in the top cap and top male grinding of the tube, which may be made to coincide by rotating the cap. For convenience in filling, the open position is at the front of the tube, and the holes are drilled at a downward angle (fig. 1) to permit insertion of the nozzle of a medicine dropper, from which the reagent is transferred. The excess and spent reagents are removed through a similar arrangement at the bottom of the tube, again using the medicine dropper. Dropping bottles may be used for the convenient storage of reagents.

Tube D is for liquid reagents, and is like the middle tube of C except for internal diameter. Glass wool

or glass tape is ordinarily used as a packing to hold solutions. The diameter of this tube will permit another packing—a central glass rod wound with a helix of glass wicking, which snugly fills the annular space, thus providing a relatively long path for the gas to travel.

Tube E is designed to permit coating the packing with fresh reagent several times during an absorption. One charge of reagent may also last for quite a few analyses. The solution is placed in the lower reservoir and forced up over the packing by compressing a rubber bulb attached to the top outlet of this reservoir. The in-seal tube just above the reservoir allows the solution to ascend the reaction tube without entering the left-hand capillary to stopcock 5 (which is closed during this procedure). The solution is brought to an etched mark on the neck just above the reservoir (before each gas volume is measured) by a screw clamp on the rubber bulb attached at the top of the reservoir.

Tube F is for combustion with a catalyst heated by an outer tube furnace. Copper oxide is ordinarily used.

Tube G is a combustion tube containing a platinum helix fastened to two platinum leads of much larger diameter than the helix. Contact to power leads is made through two mercury-filled wells ( $W_1$ ,  $W_2$ ) in the top cap. This cap is fastened to the combustion tube with a high-melting thermoplastic cement, and is cooled with strong air jets during a combustion. A packing of fine quartz sand acts as a safe flashback trap. The combustible gases are premixed with oxygen before burning.

Tube H is a mercury-filled reservoir, which confines the gases passed through the reaction tubes, and delivers them back to the buret. For convenience in displacing gas from the reservoir, a ground spherical ball N fits against ground 45-degree seat M. The seat is ground snugly into the bottom lead of the T-cock 8, presenting essentially no dead space. The ball cuts off the flow of mercury as the gas is delivered from the reservoir with a volumetric reproducibility better than could be obtained by adjustment to an etched mark, and with far greater ease.

A pipet of the distributor-tip type [7] is connected to stopcock 9. This furnishes the nitrogen necessary as a flushing, or sweeping, gas used to transfer the sample as required throughout the apparatus.

### 3. Procedure for an Analysis With the Separate Unit

#### 3.1. Preparation of Transfer Gas

The sweeping or transfer gas that may be needed is prepared by absorbing oxygen from air, and storing over the alkaline pyrogallol solution in the pipet connected to stopcock 9. The recently developed pyro solution should be used [8]. The distributor, all reaction tubes, and the arm of the manometer connected to the distributor are adjusted to the reference compensator pressure.

#### 3.2. Procedure for an Absorption With Solid Reagents

The gas sample is measured and then transferred at the approximate rate of 100 ml/min through the first reaction tube (with all other tubes bypassed) to the reservoir H. The gas contained in the arm of the manometer connected to the distributor is displaced into the buret, and then transferred through the reaction tube. If it is important to keep the reagent at the exit of the reaction tube fresh, the residual gas is returned from the reservoir to the buret with the reaction tube bypassed, but if the condition of the reagent at the exit of the reaction is not important, the residual gas is returned through the tube. The cycle is repeated until all significant reaction has occurred as shown by no further contraction. The pressure in the buret, distributor, and reaction tube are adjusted to the reference pressure, and the volume of the residual gas is measured.

#### 3.3. Procedure for Absorption With Liquid Reagents

When the nitrogen is prepared at the beginning of the analysis, and all reaction tubes are filled with it, the liquid reagents to be used are introduced at the top of each of the reaction tubes designed to contain them. A very slow flow of nitrogen from the buret will prevent air from entering the reaction tube during introduction of the solution, but if there is any reason to suspect air contamination, a few final passages into the pyrogallol may be made. The final nitrogen balance is made after the introduction of the liquid reagents. The actual procedure for absorptions is the same as that outlined for absorptions with solid reagents.

#### 3.4. Procedure for Combustion

The procedure for combustion with copper oxide does not differ from the routine ordinarily described. Inasmuch as carbon dioxide, which may be produced, is strongly absorbed on a cooling catalyst, it is best to start and stop with the catalyst hot. The initial nitrogen balance should be made with this in mind.

The combustion over the hot platinum helix is apt to be more complete than the conventional slow combustion. The residual sample from the absorption analysis is stored in the reservoir while the oxygen (or air) for the combustion is measured. These two gases are mixed by passing back and forth between reservoir and buret, and then the mixture is passed over the glowing platinum helix and thence through the flashback trap to the reservoir at the approximate rate of 20 ml/min. The gas in the arm of the manometer connected to the distributor is displaced and passed through the combustion tube. After this, the residual mixture in the reservoir may be below the explosive limit, and this gas may be passed back over the platinum to the buret. However, the safety of this procedure should be established by experience. The cycle is continued until no further significant reaction occurs. Carbon diox-

ide in the products of combustion is absorbed in Ascarite contained in one of the reaction tubes. In some analyses it is advantageous to absorb the carbon dioxide during the combustion procedures. For example, methane and ethane (and other hydrocarbons) calculated from contraction and carbon dioxide produced are seriously in error, whereas calculation from contraction, carbon dioxide produced, and oxygen consumed, will give more accurate results [9]. In such cases, the removal of carbon dioxide during the course of the combustion will result in a more rapid and possibly more complete combustion.

### 3.5. General Procedure

When the gas sample, or a part of it, has entered a reaction tube, some of the residue remaining in the tube is reactive with respect to the rest of the analysis. It is obvious that with each successive reaction the gas in formerly used tubes must enter the tube used for each new reaction. Bringing all the gas into the reactive zone is quite easily done with this apparatus. In the more conventional volumetric apparatus, passing the gas into a succession of absorption pipets or correcting for reactive residues by the calibrated distributor procedure [6] is considerably more trouble.

The apparatus must be operated in an area of reasonably constant temperature. One single reaction tube when filled with reagent contains about 3.5 ml of gas, so that an error of about 0.01 ml/deg C change in temperature could be made in comparing volumes before and after an absorption. The error with a double or triple reaction tube would be almost proportionately greater. The accumulative error for a complete analysis, using every reaction pipet shown, would be about 0.2 ml/deg C. This is too great, and temperature corrections should be applied if the laboratory is not suitably conditioned. The volumes of the various reaction tubes are easily determined by evacuation and subsequent filling from the buret. For more accurate work involving very small changes in volume, reaction tubes of smaller volume than those shown should be used. As this apparatus is likely to be put to special uses, it should be tailored to fit.

## 4. Reaction Tubes Adapted to Standard Volumetric Apparatus

The average analytical demand may not require a complete separate unit of the kind just described. Instead, the standard volumetric apparatus will usually be employed for the analysis of most gas mixtures, but as most mixtures are apt to contain one or more components in small percentages, the reaction tubes might well be employed for part of the analysis. Fortunately, they are neatly adaptable to the standard apparatus. This may be done with a set of special connectors and interchangeable spherical ground-glass joints. The reaction tubes may be connected across 2 T-cocks of a distributor, or better yet, to one cock of the type designed to pass

gas into and out of a closed tube, or bypass the tube. Such units are commercially available. These reaction tubes, their connectors, and the distributor section designed for them are shown in figures 2, 3, and 4. The connectors and the basic reaction tube for solids or liquids upon glass wool or tape are shown in figure 2. The tube itself is shown at A. With connector D it forms a single reaction tube that fits the outlets of the special distributor stopcock shown at G, figure 4. With connector C, two of A make a double reaction tube, and with connector B and another of A added to the double tube, a triple reaction tube is assembled. The special tube for absorptions requiring several applications of fresh reagent is shown at F, figure 3; its connector is F of figure 2. The slow-combustion tube is shown at G, figure 3; its connector is G of figure 2. The copper-oxide tube is shown at H, figure 3; it needs no connector unless keyed into two T-cocks of a standard distributor, in which case two of connector H (fig. 2) will serve to bring it to the proper upward position. The mercury-filled reservoir, K of figure 3 may be connected to a T-cock of the standard distributor if space permits, but the combustion pipet of the standard apparatus will serve for this reservoir, albeit not so neatly. Figure 4 shows a five-cock standard distributor with a two-cock section for reaction tubes. The special section is placed next to the buret (which is to the right but not shown). This arrangement serves for many types of analysis involving absorption and combustion. The five T-cocks will accommodate the slow combustion pipet and the two pairs of absorption pipets prescribed in the American Society for Testing Materials standard method for the analysis of natural gases and other fuel gases of similar type [10]. A copper-oxide tube may be connected at stopcock H. Stopcock G will accommodate any of the reaction tubes, including the triple reaction tube mentioned in the above ASTM standard for the determination of the small amounts of unsaturated hydrocarbons that may be in some natural gases or similar fuels.

It is apparent that this type of apparatus can conveniently meet the needs of both special and regular problems, and perhaps occasionally stimulate the imagination of the more enthusiastic analysts. For example, the possibility of conducting an entire analysis with dry gases has been mentioned. If this is done, it will probably be best to dry the sample en route to the buret, although water vapor in the sample may be determined volumetrically if the walls of the buret are carefully equilibrated with respect to the sample before the initial measurement of the sample. Working without water has distinct advantages. The buret remains clean, and the position of the mercury meniscus is determined with less eye strain and perhaps greater precision than is the case when films or droplets of water are on the buret walls. There is no error caused by a change in the amount of water above the mercury in the buret or by solution of any gas in the water here or in the combustion pipet. (Water formed in the combustion pipet evaporates into the dried gas passed back into

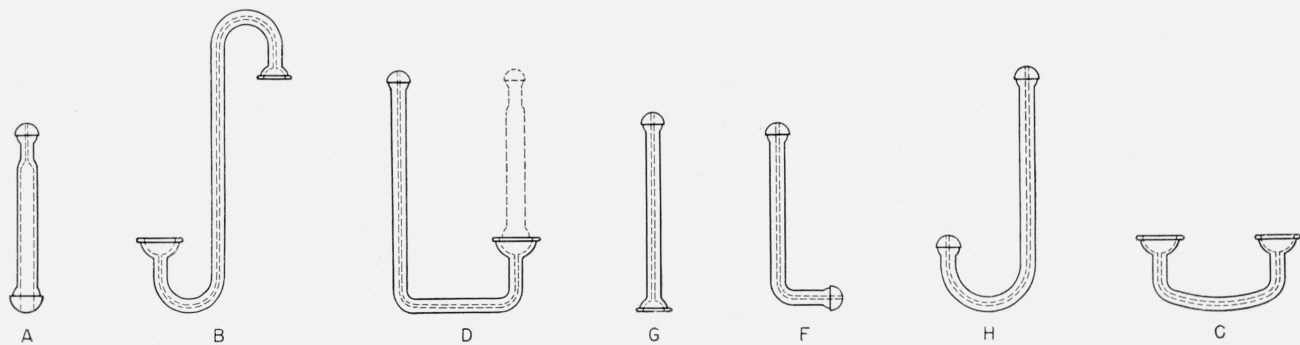


FIGURE 2. Connectors for reaction tubes.

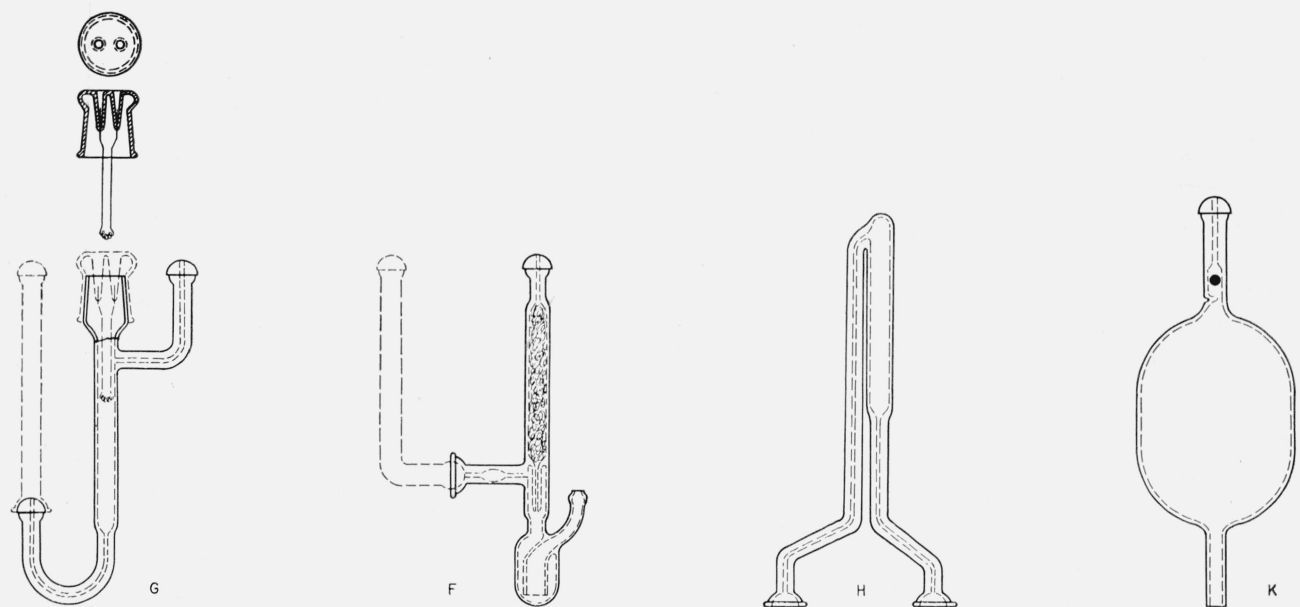


FIGURE 3. Special reaction tubes and reservoir.

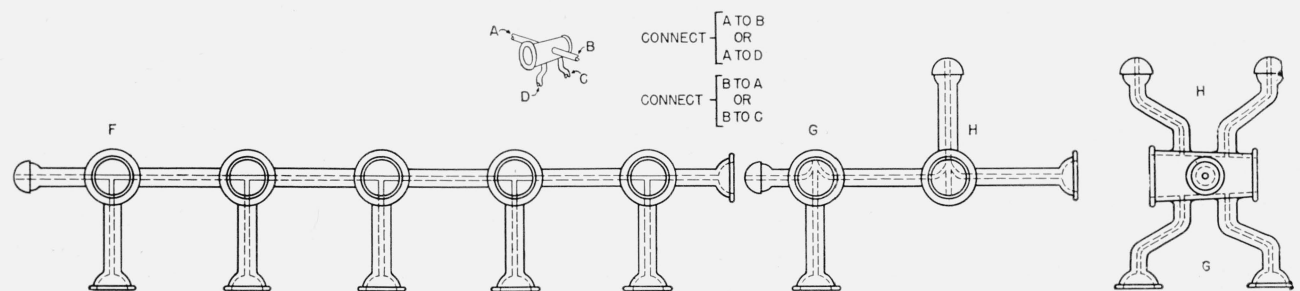


FIGURE 4. Distributor sections.



it during the combustion and is removed by the desiccant.) It should be noted that prolonged use of Ascarite during dry analyses may remove so much water from it that the rate of absorption of carbon dioxide on this reagent is considerably reduced. Although the likelihood of a general conversion to dry analyses is not great, every analyst should have the satisfying experience of performing a few. On the other hand, a wet analysis can be made much more dependably by interposing a saturator in the reaction tube nearest the buret, rather than the desiccant proposed for a dry analysis. One of the greatest and most frequently occurring errors in volumetric analysis is caused by failure to saturate properly each measured gas with water vapor. Samples of compressed gases, and residues returned from desiccating reagents, are often not completely saturated. The time required for saturation may be very long if water vapor must be supplied from liquid in the lower parts of the buret because the vapor travels slowly by diffusion and convection in tubes of this size.

## 5. References

- [1] Martin Shepherd, National Geographic Society, U. S. Army Air Corps stratosphere flight of 1935 in the balloon Explorer II, Stratosphere Series No. **2**, 117 (1936).
- [2] Joseph R. Branham and Martin Shepherd, J. Research NBS **22**, 171 (1939) RP1175.
- [3] Martin Shepherd, J. Research NBS **26**, 351 (1941) RP1382.
- [4] George Lunge and H. R. Ambler, Technical gas analysis (D. Van Nostrand Co., Inc., New York, N. Y., 1934).
- [5] Martin Shepherd, J. Research NBS **38**, 19 (1947) RP1759.
- [6] Martin Shepherd, BS J. Research **6**, 121 (1931) RP266.
- [7] Martin Shepherd, BS J. Research **4**, 747 (1930) RP177; Joseph R. Branham and Edward C. Sperling, J. Research NBS **22**, 701 (1939) RP1214; Martin Shepherd, J. Research NBS **26**, 351 (1941) RP1382.
- [8] Marthada V. Kilday, J. Research NBS **45**, 43 (1950) RP2112.
- [9] Martin Shepherd, Anal. Chem. **22**, 881 (1950).
- [10] Am. Soc. Testing Materials, Philadelphia, ASTM designation: D 1136-50T (1950).

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