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MODIFICATIONS OF APPARATUS FOR VOLUMETRIC GAS ANALYSIS

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ABSTRACT

This paper describes modifications of the volumetric gas analysis apparatus originally described in this journal, volume 6, page 121 (1931), Research Paper 266. These modifications include new pipettes, particularly a new type designed for use with small amounts of solid or liquid reagents. The new equipment is not intended to replace, but rather to supplement the apparatus previously reported.

CONTENTS

During the course of experimental studies in gas analysis, the apparatus, which was first described in this journal in 1931, has been modified in some respects. These modifications are described herein. They may be regarded as optional and are not offered as required changes of the original apparatus, unless otherwise noted. They seem of sufficient interest to report at this time, especially in view of the fact that it is unlikely that a general revision of the design of the original volumetric unit will be described for some time.

It will be convenient, in the interest of economy of space, to refer to the previous description of the apparatus. This will be done by citing the number of the paper, RP266. For the further convenience of those who are familiar with this publication, the various modifications will be discussed in the same order as that in which the parts were described in the original paper.

I. THE BURETTE

Most of the users of this apparatus, including men in our own laboratory, have found it convenient to supply the nitrogen used as a diluent during analysis by treating air with the pyrogallol solution. This automatically eliminates the necessity for the atmospheric bore of the stopcock affixed to the top of the burette (RP266, p. 123, fig. 1, stopcock 2). This bore had better be omitted unless the user particularly desires it.

Analysts have long wished for a burette to which no correction need be applied, and some time ago the advent of the KPG precision-bore tubing, made by Schott u. Genossen, offered the possibility of fulfilling this wish. It should be possible to construct such a burette at no great additional cost, since the actual *units* employed in its calibration do not matter, so long as they compare strictly one with another. In addition, the use of diluent nitrogen eliminates the necessity for measuring volumes smaller than approximately 5 ml, so that the destruction of the uniform bore at the very top of the burette where the cock must be sealed on is a matter of no concern. With these two facts in mind, the calibration should offer very attractive possibilities to the manufacturer. Instead of locating at least 5 and preferably 10 points along the tube by repeated weighings of mercury, and *then* setting up the dividing machine with the proper ratios for each of these measured intervals, the machine could merely be set to rule equal intervals of, say, 1.5 mm each along the length of a precision-bore tube. The only point which would have to be located would be one near the top of the tube, so that the first line engraved would leave above it a whole number of whatever the unit happened to be. If the same size precision bore were always used, as it should be, the location of this one point could be easily accomplished by means of an auxiliary volumetric apparatus already designed. This would so greatly reduce the cost of calibration and engraving that the additional cost of the precision-bore tube would be nearly canceled. The analyst when relieved of the irksome obligation of applying corrections would, without doubt, be glad to pay the slight premium that might be necessary to obtain this advantage.

We had one such burette constructed from tubing of foreign manufacture. The bore was so uniform that any 10-ml interval throughout its length equalled any other 10-ml interval within ± 0.01 ml. This tubing is not generally available, and a source of tubing of sufficiently uniform bore has not been located in this country. As worldly matters are disposed at present, we hope that an ambitious American manufacturer will undertake the production of this item.

II. BURETTE ILLUMINATOR

The reflecting mirror type of illuminator shown in RP266, page 124, figure 3, has been discarded, because of complaints that it provided insufficient illumination at the lower portion of the burette. The feature of the reading shield (fig. 2 of the same reference) has been retained. In one instance this shield has been mounted as was the illuminator of figure 3, but a 3-volt lamp with a ground-glass diffusing screen was placed back of it. In another instance the apparatus was placed within 4 feet of a white wall, and strong light reflected from this was sufficient when the reading shield was used. The new fluorescent daylight lamps of the 30-watt length give good illumination for the necessary observations. Equipped with a strip of black curtain traveling as a belt over pulleys at top and bottom of the lamp, and with a suitable slit in the curtain, which is adjusted to the position of the mercury meniscus, an excellent illuminator can be made at modest cost.

III. MANOMETER-COMPENSATOR

The manometer-compensator has been simplified so that it can be made entirely by the glassblower. Instead of terminating the two electric leads from the manometer with binding posts, fastened in place by cement, these leads, one from the cap and one from the dome of the compensator (see RP266, p. 125, fig. 4), end in small glass cups into which a drop of mercury is put. The wires from the current source are then dipped into this mercury to provide the connection. For some work, the compensator has been modified by projecting the lower tube slightly into the top bulbed portion by means of a ring seal. This construction affords a small ring into which water is put. This serves to supply water from both the top and bottom regions of the compensator tube and so insures proper saturation.[1] The modified manometer-compensator is shown in figure 1.

A miniature neon lamp on a 110-volt circuit may be used to replace the 3-volt miniature lamp across the manometer contact. This will eliminate a battery and condenser.

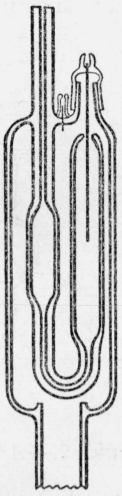

FIGURE 1.—*Modified manometer-compensator (top section only).*

IV. DISTRIBUTOR AND ABSORPTION PIPETTES

In general, no permanent change has been made in the distributor other than the addition of tee cocks to accommodate additional pipettes in experimental models. Experimental study, however, has clearly indicated the desirability of duplicate pipettes for potassium hydroxide and pyrogallate solutions in the case of fuel-gas analysis—one pair for the absorption analysis preceding the combustion, the other for the absorption of carbon dioxide and excess oxygen after the combustion. This arrangement largely avoids significant errors arising from the physical solution of various components in these solutions, and is desirable for exact work, but it increases the number of tee cocks of the distributor from four to six. The 120° cock (RP266, p. 131, fig. 5, cock 9) can be omitted. If a fractional combustion tube is desired, it can be included by adding a single cock of the type illustrated in figure 2.

Further experimental work with solid reagents and small amounts of liquid reagents has disclosed some interesting possibilities, and eventually apparatus to accommodate such reagents will be more fully described. The apparatus so far used is sketched in part in figure 2. Since the small tubes used to hold the reagents act virtually as parts of the distributor, they can properly be discussed at this time. At the beginning of the analysis, the tubes (as well as the distributor) are filled with nitrogen, at the pressure of the compensator. The gas is passed through the tubes by using the combustion pipette as one reservoir and the burette as the other. The stopcocks are bored so that gas may be bypassed, or made to loop the loop, through an absorbing tube. The handle of the cock indicates the bypassed

[1] J. R. Branham, *Saturation by water in gas analysis compensators*, J. Research NBS **18**, 59 (1937) RP962.

position; the position of connection to the tubes is indicated by lines on the key and barrel of the cock. Tubes 1 and 2 are designed for use with small amounts of liquid reagents. These reagents are injected and removed by means of medicine droppers whose nozzles are inserted through the atmospheric bores in the ground caps at top and bottom. The caps are bored diagonally downward to facilitate this operation. The reagent is supported on glass wool, or various forms of glass wicking and cloth, which may be wound upon glass rods to present a long helical path for the gas. Tubes 3 and 4 are designed for solid reagents, and are capped with flat ground plates at bottom and top. These plates may be lubricated and held in place by springs, or cemented in place with a suitable thermoplastic. Tube 4 has been used with a desiccant in performing analyses during which all the gases were

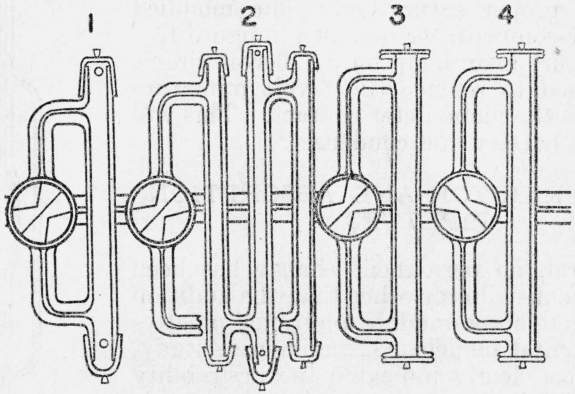

FIGURE 2.—*Apparatus for solid reagents and small amounts of liquid reagents.*

measured dry instead of saturated with water vapor.[2] The same arrangement has been used with a gasometric method for the determination of ethylene oxide in carbon dioxide.[3]

Two new absorption pipettes of the bubbling type have been developed since the description of the one with a perforated platinum plate at the exit (RP266, p. 133, fig. 9). One designed by J. R. Branham and E. O. Sperling, which employs a Pyrex slotted disk, has already been described.[4] The other has been available for some time through the Fish-Schurman Corporation of New York, N. Y., and will probably be obtainable shortly in Pyrex glass. In this model, the gas stream is divided by means of a light-walled sintered glass thimble sealed to the exit (fig. 3). The thimble has been made in two porosities, *G2* and *G3* (see the Fish-Schurman catalog). The thimble of finer porosity was slightly more efficient than the platinum-tipped pipette; that of coarser porosity was slightly less efficient, but proved to be the better choice because it decreases the back pressure. From the practical viewpoint, all three of these distributor pipettes are equally efficient, and all are about equal in cost. The Branham-Sperling type with slotted Pyrex disk is not yet available commercially. From a view-

[2] J. R. Branham, Martin Shepherd, and Shuford Schuhmann, *Critical study of the determination of carbon monoxide by combustion over platinum in the presence of excess oxygen.* (Publication pending.)

[3] J. R. Branham and Martin Shepherd, *Gasometric method and apparatus for the analysis of mixtures of ethylene oxide and carbon dioxide*, J. Research NBS, 22 171 (1939) RP1175.

[4] J. R. Branham and E. O. Sperling, *Bubbler tip of Pyrex glass for difficult absorptions*, J. Research NBS 22, 701 (1939) RP1214.

point of general performance, there is little choice. The slotted-disk type is the most rugged of the three; the sintered-thimble type shows the least tendency to clog with repeated absorptions of nearly pure oxygen; and the platinum-tipped type exhibits the least tendency to form slugs of reagent in the inlet tube.

In addition to the above, the pipette shown in figure 4 was designed for use with small samples of gas, say 10 ml, such as are employed in the ordinary Haldane type of analysis. This pipette has a perforated platinum plate 10 mm in diameter.

V. COMBUSTION PIPETTE

The Weaver-Ledig combustion pipette (RP266, p. 136, fig. 10) has been slightly modified. The stopcock at the top (cock 11 of the above-

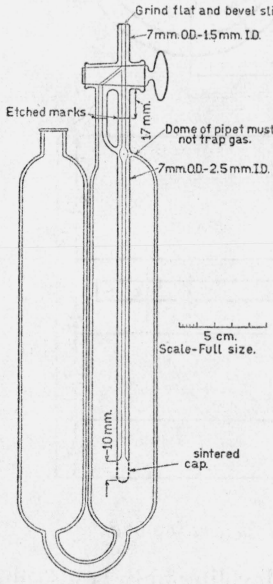

FIGURE 3.—*Absorption pipette with distributor tip of sintered glass.*

FIGURE 4.—*Absorption pipette for small volumes of gas.*

A, Perforated platinum plate.

mentioned figure) has been eliminated, because of the tendency for lubricant from this source to work down into the pipette. The two "stainless" steel caps (2–2 of the same figure) have been provided with 1-mm rods of platinum threaded into the bottom of the cap and extending inside the tapered sleeve of the cap along the longitudinal axis. These rods insure good electric contact if the "stainless" steel becomes corroded. (Products of corrosion can, of course, be removed from inside the original type of cap.)

VI. APPARATUS SUPPORT

Two modifications of the original support (RP266, p. 140) have been made. The first is necessary, the second entirely optional.

The rheostat has been covered so that mercury accidentally spilled will not collect upon wires which are sometimes warm. This is desir-

able in the interest of health, since the danger of too much mercury vapor in air is now well known. An autotransformer can be used instead of the ordinary rheostat.

If it is desired, a sliding support can be substituted for the fixed rings used to support the leveling bulb connected to the burette. A clever arrangement was called to our attention by N. R. White, of this Bureau, and improved by H. W. Bailey, of the Bureau's instrument

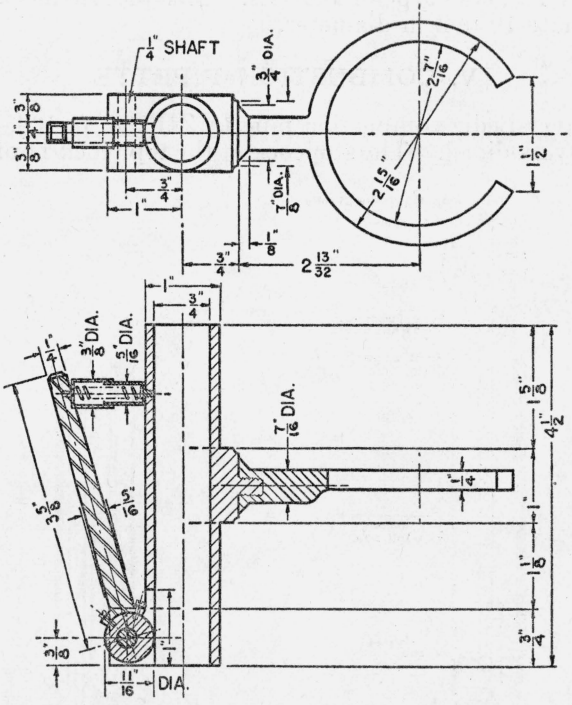

FIGURE 5.—*Sliding support for leveling bulb.*

shop. The sliding ring supporting the leveling bulb is attached to an eccentric cam which bears upon the guide rod and so locks the ring securely in place. The cam is released by pressing a hand lever. The position of the cam is adjustable. The arrangement is shown in figure 5.

These modifications account for new features developed and tried since the first description of our volumetric gas analysis apparatus. They are of sufficient value to pass along to the present or prospective users of this apparatus, but do not constitute any formal change in the original model, other than noted as necessary in the foregoing text. Before announcing definite alterations, further experimental work will be necessary. In general, however, a six-pipette model has proved to be more useful than the four-pipette model, since it permits more accurate work in combustion and additional outlets for special problems.

WASHINGTON, November 14, 1940.

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