Under the conditions of the distillation no separation of the bromine isotopes is to be feared, as the constancy in composition of the fractionated material also indicates.

The analyses of titanium tetrachloride and titanium tetrabromide thus agree in yielding the value 47.90 for the atomic weight of titanium.

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NOTES

Alkali Earth Metals in Saccharate Solutions and their Use in Alkalimetry.—Theoretically it would be most desirable to find some substance the equivalent weight of which could be directly weighed out, put into solution and diluted to a given volume to yield a standard of predetermined normality that would not require standardization or adjustment. The writer has been carrying on some work in an attempt to realize, partially at least, this ideal.

To this end different materials that would yield calcium oxide have been converted to that substance or to calcium hydroxide and have been dissolved to form a standard solution in a 30% cane sugar. These attempts were successful in so far as the attainment of the final results were concerned, but so much time was consumed that the method was not considered practical. In the course of further investigations, it was found that samples of metallic calcium in the form of 0.05 inch wire and about 96% pure went into solution at the rate of 1 g. in about eight minutes, on the average. In the ten cases tried a solution of predetermined normality was obtained, employing, of course, a correction factor to allow for the impurities. The calcium was obtained from the General Electric Company and, though impure, was so uniform that samples from different parts of the lots were found to yield identical solutions. The chief impurity is metallic magnesium which, together with its oxide, is almost insoluble in 30% sucrose, a fact that might be employed in separating small amounts of magnesium from large percentages of calcium especially in the analysis of metallic calcium. It would seem easy to eliminate this impurity by employing pure calcium chloride as an electrolyte instead of that obtained as a by-product from magnesian bitterns.

Another source of impurity is the rapid tarnishing of clean surfaces of metallic calcium when exposed to moist air, as reported in the literature. The film so formed is slow to appear in ordinary air and since it is very thin and consists of a high calcium compound, the error from this source seems negligible; however, it can easily be sandpapered off from the warm metal much as rust is removed from standard iron wire. The warm calcium which does not tarnish readily can then be enclosed in a suitable weighing bottle, cooled and weighed. The metal used in the above experiments was weighed in the open air with excellent results.

Some doubts seem to exist as to whether it would be feasible to produce c. p. metallic calcium. The very recent notable success of Syracuse University in producing 99.9+% metallic barium, a more reactive metal than calcium, should satisfactorily answer this question. In addition, The American Magnesium Corporation in a letter to the writer stated that that company has produced metallic calcium analyzing 99.98% metal. Moreover, it is common knowledge that very pure metallic sodium, still more reactive than the alkali-earth metals, has been produced commercially for years in enormous quantities at a reasonable price.

The size of wire is an important factor in the production of metal suitable for analytical work. Half-inch sticks are too large, as solubility is too slow; 0.05 inch wire is rather small, as the length of a tenth-equivalent is too great for convenience. One-eighth inch sticks would probably be most suitable so that the length of a tenth-equivalent weight would be convenient.

To ascertain whether or not the solution of calcium saccharate so prepared was suitable for general analytical work, titrations of carbonic acid, acid potassium phthalate and succinic acid were carried out with satisfactory results, employing the common indicators. To further test out the solution in actual practice, samples were distributed to members of the chemical faculty for general use. These reported that the solutions were as satisfactory as the bases commonly employed.

The purpose of these notes is to interest, if possible, some producer of metallic calcium to furnish this element in sufficient purity to satisfy the requirements as outlined and at a non-prohibitive price. The successful accomplishment of this object seems attainable by attention to the exclusion of magnesium from the electrolyte employed in the method now used. The financial rewards of such a course seem to be assured because it would enable the chemist to prepare, with a single weighing, a standard alkali of predetermined normality, carbonate free and ready for use without previous standardization by an auxiliary substance.

Contribution from the
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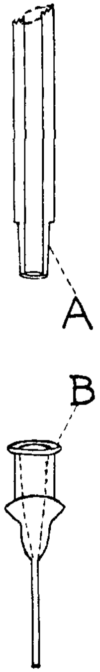
A Pipet for Micro-Analyses.—The accurate delivery of small amounts of fluid is essential for micro-analyses. Folin[1] has stated that the Ostwald pipet is accurate to the order of 0.1%. Van Slyke and Neill[2] have improved this. They calibrate between marks and place a stopcock under the bottom mark. Their pipet is excellent for introducing fluids into the Van Slyke gas apparatus but is not equally practicable for other uses. Unless the end is washed a variable and unknown amount of fluid clings to the tip.

The pipet which we use is a modification of Van Slyke's, with a glass Luer adapter sealed to the bottom end. This ground end fits snugly into a hypodermic needle B of small gage, 18–23, which is cut off horizontally and ground on a stone. Trevan and Bainbridge[3] have shown that drops of the order of 0.00015 cc. can be removed from such a needle tip. For corrosive liquids a platinum needle may be used.

A test of the amount delivered indicated a surprising degree of accuracy. One worker obtained for a given pipet the following weights of water: 0.9982, 0.9981 and 0.9980 g. A second investigator weighed the water delivered from the same pipet as 0.9982 and 0.9983 g.



A, ground glass Luer adapter which fits into B; B, a hypodermic needle. Drawing is actual size.

Fig. 1.

Contribution from the
Laboratory of
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Apparatus for Micro-Filtration.—The centrifuge tube technique for the separation and washing of precipitates has been very useful for micro-analyses. In the course of development of a method for potassium, however, a small amount of material was lost when the supernatant fluid was poured off. To overcome this difficulty the following form of apparatus was devised (Fig. 1).

The principle is that of a Caldwell crucible. The filter is made by mounting a one inch funnel in a Witt filtering apparatus (this is essentially a suction flask with a ground glass removable top so that the filtrate may be recovered in a small inner container. If the precipitate only is to be saved, an ordinary suction flask is satisfactory). Into the

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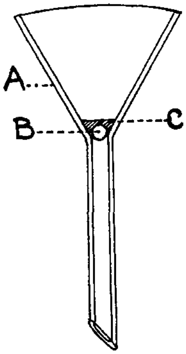
[1] Folin, *J. Biol. Chem.*, **21**, 198 (1915).

[2] Van Slyke and Neill, *ibid.*, **61**, 532 (1924).

[3] Trevan and Bainbridge, *Biochem. J.*, **20**, 423 (1926).

funnel, A, a glass pearl, B, is dropped and over the bead is poured a suspension of finely shredded asbestos, C, to form a layer about $^1/_{32}$ of an inch thick. The mat is allowed to drain and suction is applied (see Fig. 1).



A—one inch glass funnel; B—small glass pearl or bead; C—mat of fine grained asbestos. Drawing is $^3/_4$ actual size.

Fig. 1.

The precipitate and mother liquor are transferred to the micro-filter and the filtrate is removed by gentle suction. One drop of fluid is sufficient to wash the precipitate on the mat. With intermittent suction a precipitate can easily be washed five to ten times with one cc. of solution.

To remove the precipitate the funnel is inverted and a glass rod is inserted into the stem. Precipitates such as calcium, sodium, potassium, phosphorus, etc., that are to be dissolved before determination may be dissolved either on the mat, or in a separate container after removal together with the mat. In the latter case, a second filtration through the same apparatus gives a solution free of asbestos.

The materials for this micro-filter are at hand in every laboratory. They are inexpensive. During a year of use not a single determination has been lost.

Contribution from the Laboratory
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CORRECTION

Through the work of Paul S. Roller[1] it has come to my attention that the signs of two terms in Equation 10 of my paper on titration[2] are incorrectly recorded. The term $3K_WK_A{}^{-2}$ in the coefficient of $(H^+)^3$ should be negative, as should also the last term of the equation. I wish also to confirm the result obtained by Roller by an independent method concerning the limiting strength of acid necessary for appearance of an inflection in titration with a strong base, the values of the ionization constants given in my paper for this case being too large, due to a numerical error, by one power of ten.

E. D. Eastman

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[1] Roller, This Journal, **50**, 1 (1928).

[2] Eastman, *ibid.*, **47**, 332 (1925).