SEMIMICRO QUANTITATIVE ORGANIC ANALYSIS

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PREFACE

This book is the outcome of a number of years' experience in dealing with the analytical phase of research upon the chemistry of natural products. The materials dealt with were available in moderate quantities but not in amounts that would permit the use of the standard macromethods. The microsystem of Pregl suggested itself as a means of meeting the situation, but after some experimenting, it was abandoned. This step was taken with reluctance because Pregl's system is a powerful tool which for many types of work and circumstances is indispensable. Nevertheless the limitations imposed by it were in conflict with the conditions under which the work had to be done. Without presenting details concerning these factors, the essential circumstances were that all the activities pertaining to the main work program, such as the preparation of raw materials, their purification, the preparation of derivatives, various syntheses, and the analysis of these products, had to be done in a none too spacious laboratory which fundamentally was ill suited for Pregl's analytical technique.

It was obvious, therefore, that under the conditions enumerated a system of analysis in which a middle course, or the so-called semimicro method, would have to be employed. At the time this problem presented itself such an idea was well established and reference to it was frequently made both orally and in the literature, but no attempt had been made to gather together into a practical system such work as had been done. With the wealth of fundamental information available as a result of the researches of Pregl and his students, it was not difficult to develop smoothly working methods of the type desired and there soon emerged a successful plan in which analytical samples ranging from 10 to 25 mg. were employed.

It was found that operations upon quantities of this magnitude compared favorably in economy of time, space, and reagents with the Pregl system, and in addition they could be conducted with much less detail where laboratory conditions were not extremely exacting. It was thus possible to conduct these analytical operations, along with other work, in a very satisfactory manner. As the various procedures required were evolved and successfully used over a period of time, it was suggested that some of them be published in the Journal of the Official Association of Agricultural Chemists. This was for the purpose of having them on record should the Association wish to consider them for official or tentative methods. During the course of several years the procedures most frequently used were thus published and because of their generally favorable reception it appeared that a compilation of all of them in one place, together with certain other useful material, would be desirable. The present book is the outcome, but it should be noted that in many cases experience and new developments have dictated changes tending toward simplicity, economy, or both. Thus, for example, the treatment of carbon and hydrogen, and to a lesser extent the Dumas nitrogen method, is quite different from the procedures published in the Journal of the Association of Official Agricultural Chemists several years ago. Thus the material presented is largely the author's treatment of the analytical procedures for the determination of the more common elements and groups encountered in his work. While it is not all-inclusive, it is hoped that it will be helpful, or at least suggestive, to other workers.

It may, however, appear that this outline as well as the absence of a discussion of, or a bibliography of the entire field, gives the work too restrictive a character. This is believed to be more apparent than real. In the first place, if one eliminates special procedures for individual substances in which the average analyst has little interest, there is not an extensive literature upon semimicro analytical methods for organic compounds. Second, the methods included are all well tested and satisfactory and embrace the greater part of the field required in an average organic laboratory. There are, to be sure, references that might be quoted but have not been included for lack of confirmatory work. Certain others, unfortunately, make claims that cannot be verified. The reason is probably due to inadequate details, or presentation, or both, but the inclusion of such material is deemed of little value and would serve only to enlarge the book. The basic purpose which consistently has been attempted throughout is not to compile a reference book but rather to present in as brief a manner as possible simple working, well tested methods, which can be followed to a successful conclusion.

The term semimicro analysis is now a popular expression in American chemical literature. In quantitative analysis it usually includes methods in which samples of the order of 10 to 50 mg. are used. However, in view of the definition of microanalysis* adopted by the editorial board of the Industrial and Engineering Chemistry and accepted by many workers, the term should be discontinued. According to the definition, microanalysis is a determinative chemical procedure in which the quantities dealt with are not more than one-tenth as large as used in customary laboratory practice. Work with samples of 10 to 25 mg. thus falls within this range and should be designated accordingly. Nevertheless, a poll taken recently at a meeting of the Microchemical Society of New York indicated that the term quantitative micro organic analysis would be interpreted as meaning a system in which samples of less than 10 mg. were employed. This, in spite of the

* *Ind. Eng. Chem., Anal. Ed.* **11**, 111 (1939).

acceptance of the above definition, seems to be generally prevalent and consequently the more popular term, semimicro analysis, is retained. Whether or not this course is correct, its retention does have the advantage of keeping the system herein outlined from confusion with the one associated with Pregl and his school.

Finally, it is desired to thank the Editors of the Journal of the Association of Official Agricultural Chemists and of the Industrial and Engineering Chemistry for permission to reproduce certain material published by the author in these Journals. Thanks are also extended to Mr. Fred Acree, Jr., for valuable suggestions concerning the Dumas nitrogen determination. The author is especially grateful to his wife who typed the entire manuscript, assisted in proofreading, and helped in many ways which made the preparation of the book possible.

Chevy Chase, Md. E. P. CLARK

Chapter I

Introduction

Under this heading several topics will be discussed which are pertinent to the general subject of quantitative semimicro organic analysis. Some of them could be treated equally as well under specific determinations, but it is thought that if this were done the digressions might confuse in the actual working procedures.

It is not intended to dwell upon subjects adequately treated in other texts, but rather to call attention to certain information not as generally utilized as it should be. In attempting this it is admittedly difficult to decide what should or should not be included, but the criterion adopted is to consider matters which, from experience in teaching and in aiding others, have been most often helpful. Among these the analytical balance will receive first attention.

THE ANALYTICAL BALANCE

A balance suitable for semimicro analytical work should operate easily and with reasonable rapidity and be capable of reproducing weighings to 0.02 mg. Several such instruments are now available, but among them one known as the Seko semimicro balance (Plate 1) has two outstanding features that are especially desirable. First, it is a magnetically damped aperiodic instrument. The reason for preferring this to a free oscillating type balance is that with the former the zero point is found without counting swings or estimating their amplitude. Wear on the bearings is greatly reduced and fatigue from eye strain is diminished. The second feature to which reference is made is a clever mechanical amplifying device for reading the scale divisions. It employs a graduated disk geared to an auxiliary pointer extending through the base of the balance case. This operates in such a manner that when the balance comes to rest the auxiliary pointer can be brought directly in line with the regular pointer and, under these conditions, the scale readings at the zero or load rest point are indicated on the disk. Because of the gear ratio used these divisions can be estimated easily to .02 of a unit.

Without entering into a discussion of the mechanical details of these devices which are available in the advertising literature of the manufacturers, it is believed that they constitute the most important advances in balance construction that have occurred in a long time.

The foregoing does not imply that a special balance must of necessity be available for semimicro analytical work. Any good instrument will do provided it is sufficiently sensitive. The accuracy of .02 mg. is suggested in order to cover the demands for the entire analytical system to be presented. However, many of the determinations may well be carried out with a balance of inferior sensitivity. Frequently so-called ordinary analytical balances have sufficient sensitivity, or may be made to have by various adjustments or alterations, as, for example, converting them to aperiodic

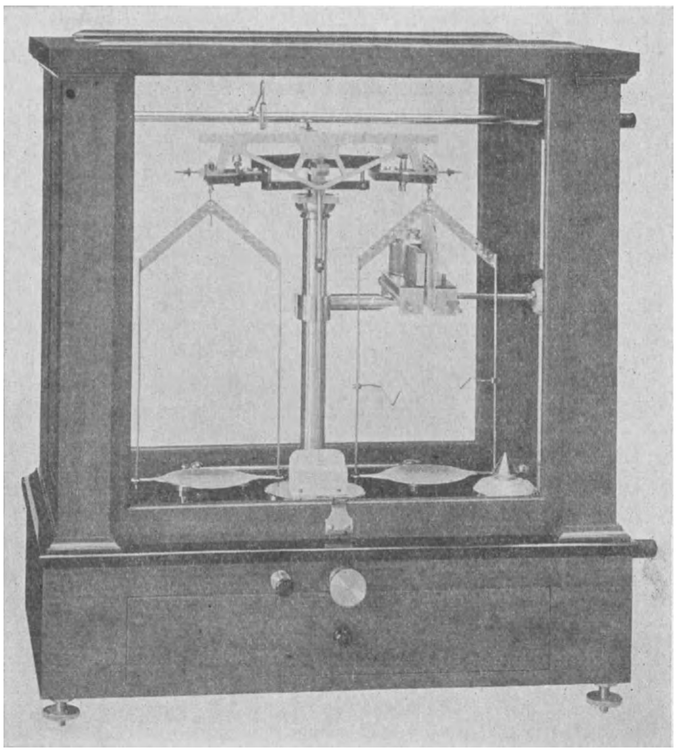


Plate 1
Seko Aperiodic Semimicro Balance
(Courtesy Seederer-Kohlbush Co.)

type instruments, to meet the requirements for all semimicro analytical work. The criterion of workability in all such cases is that the sensitivity of the instrument must be commensurate with the size of the sample to be used. This idea has been amply verified by Niederl, Niederl, Nagel, and Benedetti-Pichler[1] in which very good results were obtained by using microanalytical procedure and an ordinary analytical balance sensitive to

[1] J. B. Niederl, V. Niederl, R. H. Nagel, and A. A. Benedetti-Pichler, *Ind. Eng. Chem., Anal. Ed.* **11**, 412 (1939).

.022 mg. In the same article a table showing the relationship which must exist between the sensitivity of a balance and the practical size of the sample to be taken was presented. Because of its importance this table is reproduced herewith.

Analytical balances are among our most sensitive instruments. Most of them are very good but there is still room for improvement. At this point it is desired to suggest a combination of features which, if incorporated into a single balance, would undoubtedly produce an instrument of superior performance. First, it should be aperiodic and equipped with the amplifying scale reading device as mentioned before. Second, it should have a keyboard rider mechanism as developed by the Ainsworth Company of Denver, Colorado; and finally, the balance case should be constructed of $\frac{3}{16}''$ sheet copper for the purpose of maintaining an isothermal condition within.* There would of necessity be certain small glass windows to admit light to

TABLE I

Relationship Between the Precision of a Balance and the Practical Size of a Sample to be Weighed

Precision of Balance	Practial Size of Sample
mg.	*mg.*
.001	3–5
.002	4–6
.005	5–8
.010	6–10
.020	8–12

the beam, index plate, and graduated disk, with possibly certain simple optical arrangements for the proper direction of light upon these. The construction of such a balance would require research and cooperation between the two firms whose patents are involved, but there is little doubt that the results would produce a considerable advance in analytical procedure.

Temperature Effects Upon the Balance. As implied in the foregoing, temperature changes within the balance during the operation are important. They are, in fact, the cause of most errors in weighing which in turn give rise to errors in critical analytical procedures. A metal case, as suggested, would automatically maintain an isothermal condition within the balance, even in a general working room (see molecular weight determination,

* As far as is known, Professor A. H. Corwin of Johns Hopkins University was the first to use a metal case to maintain an isothermal condition within a balance. Several years ago he showed the author a reconstructed balance having among other excellent innovations this type of case. It is hoped Professor Corwin will publish his experiences in this field to arouse interest in the subject.

Chapter XI). However, with the equipment at present available certain precautions must be observed to reduce temperature errors to a minimum. The most effective way this may be done is to place the balance in a small insulated room or closet in which a constant temperature at least two degrees above that outside is maintained. Electrical heating with the necessary temperature control devices is best for the purpose.

Another way by which temperature effects may be greatly minimized is to use long forceps for handling weights, tares, and apparatus within the balance. Such instruments can be made by soldering weight forceps to the tips of crucible tongs and then cutting off the connecting end. Also specially shaped tips for various purposes may be made of sheet steel, monel metal, or nickel, covering their critical parts with cork or chamois, and then soldering these pieces to crucible tongs. The author uses three such instruments in his work. One is for handling fractional weights and other small objects, another is used for brass weights and bulky pieces, and a third is designed especially to handle the absorption tubes in the carbon and hydrogen determination. With such instruments, manipulations within the balance may be made with the hand at least four inches from the case.

Lighting Arrangements. Frequently lighting arrangements are sources of trouble, but the recently introduced fluorescent balance lamps largely eliminate them. Experiments to ascertain the best location for such a lamp have shown that practically no disturbance is caused when it is placed at the top of the balance case, either directly in front of the sash or on top of the case as near the sash as possible. A satisfactory spot light to illuminate the pointer and scale is also required. It can be made by cutting the reflector end from a flash light, connecting it to a small transformer of the door bell type, and directing the resulting narrow beam of light from some distance upon the scale. This device is an essential expedient, not only for the purpose of giving good illumination, but also to prevent the pointer from appearing coincident with its shadow.

Cleaning Agate Bearings. Aside from the foregoing suggestions, it is presumed that those interested in the branch of analytical chemistry under treatment are familiar with the general principles concerned with the use and operation of a balance. However, there are several important points to be discussed which text-books and classroom instruction usually omit. The first pertains to cleaning the knife edges and bearings of a balance either in the assembling of a new instrument or in the care of one which has been in operation for some time. A very effective method used by some balance makers is to wipe agate parts with a thin wedge of soft wood until, with the aid of a strong magnifier, they all seem to be free from dust and lint. A match shaved to the shape of a thin wedge makes an ideal appliance for the purpose.

Notches, Riders, and Weights. All micro, semimicro and certain other types of balances have notched beams for riders. In some cases, as with the Seko balance to which reference has been made, two sets of notches are employed. One is for 1 mg. increments and the other is for 10 mg. increments. One mg. riders function satisfactorily for micro or semimicro work, but heavier ones do not; hence their use is discouraged. Apparently the reason for this is that the riders do not repeatedly seat themselves in an identical manner and so large riders give erratic readings. While the differences observed with riders for 10 mg. increments are small, their magnitudes are such that they can not be ignored in semimicro work.

Another factor to be taken into consideration is the assigned values of the notches. The notches are cut with dividing engines which assures fairly equal distribution, but other factors entering into the manufacture of a balance beam usually result in assigned values less accurate than the corresponding weights of a good set. It follows, therefore, that the relationships between the notches, rider, and weights of a set must be determined if accurate analytical work is to be realized. There is no difficulty in doing this but it frequently happens that the arithmetical treatment of the data involved is confusing. An example of a calibration procedure is therefore given.

Calibration of Notches and Weights. The first operation is to determine the value of the notches in terms of a standard. A satisfactory way of doing this is the following: Place a 1 mg. weight upon the left-hand pan of the balance and the rider on the 0 notch. Observe the zero point, then move the rider to the 1 mg. notch and determine the number of scale divisions the pointer moves. This gives the scale divisions for the 1 mg. notch. The rider is then returned to the 0 notch, the rest point is determined, and finally the rider is again placed in the 1 mg. notch and the first value redetermined. This gives three values, the average of which is taken as final. This is shown schematically as follows:

	Wt. on L.-H. Pan 1 mg. Rider 0	Wt. on L.-H. Pan 1 mg. Rider 1 mg.	Difference = Scale Divisions per mg.	
Scale Divisions	4.52	.51	1	4.01
	4.50	.50	2	3.99
			3	4.00
Average				4.00

(The value is that assigned to the first notch in Table II.)

The process is then continued with each notch, *i.e.*, the next step is to place a 2 mg. weight on the left-hand pan, the rider is placed on first, the

1 mg., then the 2 mg., and finally back to the 1 mg. notch and the average deflections in scale divisions are determined in each position. The average gives the value for the 2 mg. notch, and so on. Finally the 9 mg. or 10 mg. notch, whichever the case may be, is checked against a 10 mg. weight of the set to be used. Since the deviations of the mg. notches from the assigned values are usually very small, the average of all values of scale divisions per mg. may be taken as the true one. The results obtained from an actual calibration are presented in Table II.

An inspection of this table reveals that the rider is slightly heavy as compared with the 10 mg. weight from the set and that the assigned values of the notches deviate but slightly from the average.

TABLE II

Comparison of 1 mg. Notches in Terms of Scale Divisions and mg.

I Notches	II Scale Divisions per mg.	III Deviation from Average S.D.	IV Correction	V Value of Notches
			mg.	*mg.*
1	4.00	+.002	+.0050	1.0050
2	4.00	+.002	+.0050	2.0100
3	3.97	−.001	−.0025	3.0075
4	4.00	+.002	+.0050	4.0125
5	3.95	−.003	−.0075	5.0050
6	3.99	+.001	+.0025	6.0075
7	3.97	−.001	−.0025	7.0050
8	3.97	−.001	−.0025	8.0025
9	3.97	−.001	−.0025	9.0000
Average..	3.98	10 mg. weight = 9 mg. rider + 3.88 Scale Divisions		

Next, the weights to be used are compared among themselves and the results calculated to notch values. These data are then assembled in some such form as given in Table III.

When this has been done the values of the notches and weights are brought together as in Table IV.

At this stage it is desirable to employ redistributed values to eliminate excessive corrections. By inspection, or a little experimenting, it will be seen that if the 100 mg. weight is chosen as a standard of assigned value the corrections will be more uniform. With a really good set of weights and a rider to match such redistributed values may be relatively small and many actually eliminated.

In the operation the 100 mg. weight becomes 99.652 mg., the actual comparative value, and the other weights and notches would be in direct pro-

TABLE III

Comparison of Weights

Comparison	Value of Weights in Terms of Notches
	mg.
10 mg. = 9 mg. + 3.88 S.D. (.975 mg.)	9.975
10 mg. = 10′ mg.	9.975
20 mg. = 10 mg. + 10′ mg.	19.950
50 mg. = Σ 49 mg. + 3.71 S.D. (.932 mg.)	49.832
100 mg. = Σ 99 mg. + 3.66 S.D. (.920 mg.)	99.652
100 mg. = 100′ mg.	99.652
200 mg. = 100 mg. + 100′ mg. − .25 S.D.	199.241
500 mg. = Σ 499 mg. + 3.75 S.D. (.942 mg.)	498.219
1 g. = Σ 999 mg. + 3.62 S.D. (.910 mg.)	996.406
2 g. = Σ 1,999 mg. + 4.12 S.D. (1.035 mg.)	1992.937
2 g. = 2′ g.	1992.937

TABLE IV

Assembled Values of Notches and Weights from Tables II and III, their Redistributed Values and Practical Corrections

I Assigned Values	II Comparative Values	III Redistributed Values	IV Correction	V Practical Corrections
	mg.		*mg.*	*mg.*
1 mg.	1.0050	.9965	+.0085	+.01
2 "	2.0100	1.9930	+.0170	+.02
3 "	3.0075	2.9895	+.0180	+.02
4 "	4.0125	3.9861	+.0264	+.02
5 "	5.0050	4.9826	+.0224	+.02
6 "	6.0075	5.9791	+.0284	+.03
7 "	7.0050	6.9756	+.0294	+.03
8 "	8.0025	7.9722	+.0303	+.03
9 "	9.0000	8.9687	+.0313	+.03
10 "	9.975	9.9652	+.010	+.01
10′ "	9.975	9.9652	+.010	+.01
20 "	19.950	19.9304	+.020	+.02
50 "	49.832	49.826	+.006	+.01
100 "	99.652	99.652	0	0
100′ "	99.652	99.652	0	0
200 "	199.241	199.304	−.063	−.06
500 "	498.219	498.260	−.041	−.04
1 g.	996.406	996.520	−.114	−.11
2 "	1992.937	1993.04	−.633	−.63
2′ "	1992.937	1993.04	−.633	−.63

portion. Instead of solving the laborious equations involved in these calculations, the same results may be obtained by a simple procedure suggested by Richards.[2] It is based upon the properties of small numbers in the presence of large ones and is carried out as follows: From Table IV the 100 mg. weight has the value 99.652 mg. with respect to all the other weights and notches. If this value is placed in Column III and then aliquots of it are taken for all the other values (for example, 10 mg. will be represented by 0.1 of 99.652 or 9.9652, etc.), the redistributed values of Column III will be obtained. The difference between the values of Column III and Column II gives the corrections to be applied to each weight and notch. Column IV gives these values rounded off to the second decimal place, or the practical corrections to be applied to each assigned value. When these corrections are obtained it is well to place them on a card attached to the balance so that they may be readily seen and mentally added to the readings made on the balance.

One more consideration is essential, namely, the preparation of a table showing the scale divisions corresponding to fractions of a mg. Such a card,

TABLE V

Scale Divisions Corresponding to Fractions of 1 mg.

	0	1	2	3	4	5	6	7	8	9
0		02	05	08	10	13	15	18	20	23
1	25	28	30	33	35	38	40	43	45	48
2	50	53	55	58	60	63	65	68	70	73
3	75	78	80	83	85	88	90	93	95	98

shown in Table V, should be placed beside the one showing weight corrections. To give an example of its use, it may be seen at once that if the pointer comes to rest, say at 2.7 scale divisions, it corresponds to .68 mg.

Weighing. In connection with the process of weighing it is good practice, whenever possible, to use tares for all types of apparatus. Their use saves time, necessitates less manipulation within the balance and, where they are of the same size and material as that weighed, they compensate for buoyancy of air and adsorption of moisture. All these and other factors, in the aggregate, tend toward accuracy.

Small tares may be made of wire, sheet brass, or lead and are usually lighter than the object to be weighed. For heavier objects small flasks of 1 to 5 ml. capacity may be filled with small lead shot. However, in all cases where possible, such as filter and absorption tubes, small flasks, etc., it is always best to use an object of the same size and shape as that to be weighed.

[2] T. W. Richards, *J. Am. Chem. Soc.* **22,** 144 (1900).
See also F. C. Eaton, *ibid.* **54,** 3261 (1932).

The use of cigarette papers, or fractions thereof, is especially useful for weighing solids for analysis. When a number of pieces are cut from a book at the same time they usually balance each other within a few tenths of a mg. In some determinations the sample and paper upon which it is weighed may be introduced into the reaction flask together without causing error. In the case of the Kjeldahl nitrogen determination the paper actually aids the combustion. In fact, some types of nitro compounds, *i.e.*, those not highly nitrated, may be reduced and kjeldahlized by this procedure.[3]

VOLUMETRIC PROCEDURES

Standard Acid. Decinormal hydrochloric acid and .05 *N* iodine solutions are two primary volumetric standards required in the work under consideration.

A standard decinormal hydrochloric acid solution is most easily and accurately prepared by diluting a weighed quantity of a constant boiling acid to

TABLE VI

Composition of Constant Boiling Hydrochloric Acid Solution

Barometric Pressure	Per Cent HCl. Vacuum Wt. Basis	Grams of Distillate Containing 1 mol. of HCl. Air Weight Basis
770	20.197	180.407
760	20.221	180.193
750	20.245	179.979
740	20.269	179.766
730	20.293	179.555

a definite volume.[4] Constant boiling hydrochloric acid is stable and when sealed in glass may be preserved indefinitely. It is prepared by distilling a solution of equal volumes of concentrated hydrochloric acid and water from a glass stoppered Claisen flask, discarding the first three-quarters of the distillate, and collecting as much of the last quarter as is desired. A platinum star or crimped sheet of the metal should be placed in the flask to prevent bumping. The barometric pressure at the time of distillation must be known; then by the use of Table VI[5] the quantity of the reagent required for any volume of a standard solution may be ascertained.

Since the relationship between the values in the first and last columns are for practical purposes linear, the quantity of boiling acid containing one mol of the hydrochloric acid at any pressure, within the range given, may be calculated readily. For example, the 10 mm. change in pressure between

[3] A. Elek and H. Sabotka, *J. Am. Chem. Soc.* **48**, 501 (1926).

[4] G. A. Hulett and W. D. Bonner, *J. Am. Chem. Soc.* **31**, 390 (1909).

[5] C. W. Foulk and M. Hollingsworth, *J. Am. Chem. Soc.* **45**, 1220 (1923).

760 and 750 mm. makes a change of .214 g. of distillate containing 1 mol of acid. Therefore at 755 mm. the change would be one-half of .214 g., or .107 g., which, added to 179.979 or subtracted from 180.193, gives 180.086 g. of distillate required for 1 mol of acid at the 755 mm. pressure.*

The following suggestion for accurately weighing the reagent may be helpful. An Erlenmeyer flask of appropriate size is accurately tared upon the analytical balance. The reagent is then weighed in it as accurately as possible with a rough balance, after which the flask and its contents are returned to the analytical balance and the final weighing is made by adding or subtracting small quantities of acid with a bent capillary pipette. The latter is a thin walled tube, such as that used in making melting point tubes, bent 90° about one and a half inches from its end. With it acid can be picked up by capillary action or discharged by touching the side of the flask. A solution prepared as outlined is usually accurate to about one part in 5,000.

Standard Iodine Solution. Twentieth normal iodine solution is used primarily to standardize thiosulfate solution. For this purpose a potassium iodate or potassium hydrogen iodate solution is made so that when used with an excess of potassium iodide and acid it yields a definite quantity of iodine according to the equation

$$KIO_3 + 5KI + 3H_2SO_4 \rightarrow 3K_2SO_4 + 3I_2 + 3H_2O.$$

Therefore, a solution which will be .05 N with respect to iodine will contain $(\frac{1}{6})$ $(\frac{1}{20})$ (214.02) or 1.7835 g. of potassium iodate per liter. A corresponding solution of acid potassium salt will contain $(\frac{1}{12})$ $(\frac{1}{20})$ (389.95) or 1.6248 g. per liter. These iodates are readily prepared in a high state of purity[6] and have a large molecular weight. They are stable in the air and their solutions keep indefinitely, all of which make them ideal standards.

Standard Alkali Solutions. Barium hydroxide is the preferable base from which to make standard alkali solutions. The base is a strong one, it is sufficiently soluble for all practical purposes and, most important of all, its solutions automatically keep themselves free from carbonate. Storage and handling of standard alkali solutions deserve more consideration than they usually receive. They cannot be stored in glass and the usual expedient of keeping them in paraffin lined bottles is not recommended for the reason that traces of grease from the lining soon cause a burette to drain poorly. The best containers are silver or silver lined flasks. Copper also makes a good second choice. In either case these can be made by silver-smiths at reasonable cost so there is really little excuse for not using them. In all cases, however, it is not expedient to trust the titer of any alkaline solution very

* For an extension of the table to lower pressures see *J. Am. Chem. Soc.* **52,** 1747 (1930).

[6] P. A. Shaffer and A. F. Hartmann, *J. Biol. Chem.* **45,** 376 (1920).

long. The quantity to be used for a short time should be standardized before it is used. In routine analysis, or when an alkali is used frequently, an ensemble as shown schematically in Fig. 1 is convenient and gives the best possible protection to a solution. The 500 ml. flask and the 4 mm. delivery tube from the flask to the burette are made of pure silver. The burette is

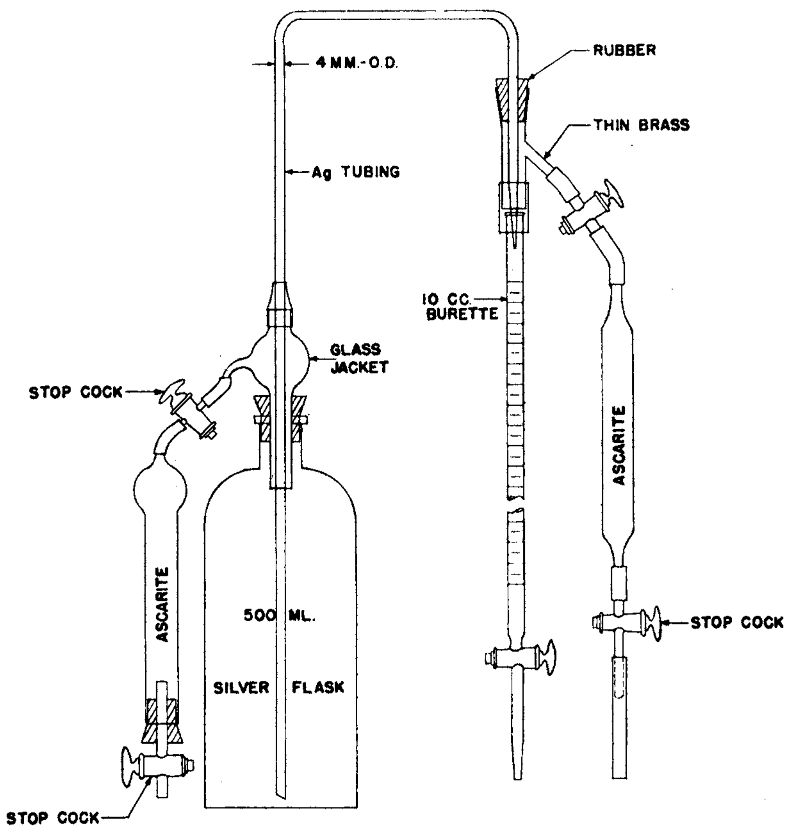


Fig. 1
Alkali Titration Apparatus

filled by drawing the solution from the flask to the burette by gentle suction from the mouth.

Should occasions arise in which barium hydroxide cannot be used, standard, carbonate-free sodium hydroxide may be prepared by the excellent method of Kolthoff.[7] In this procedure, the carbonate is removed with calcium hydroxide. The operation is simple and convenient, and a high grade product is obtained.

[7] J. M. Kolthoff, *Z. anal. Chem.* **61**, 48 (1922).

One liter of approximately normal solution of sodium hydroxide is treated with a suspension of calcium hydroxide made by slaking 5 g. of good grade calcium oxide in some of the sodium hydroxide solution. The mixture is vigorously shaken occasionally for at least an hour, then allowed to settle. As much as is required of the clear solution is drawn off and diluted to 0.1 normal with carbon dioxide-free water. Such a 0.1 normal solution will contain only from 1 to 2 mg. of calcium per liter, which for all practical purposes is insignificant.

Standard Thiosulfate Solution. Many directions are available for preparing standard sodium thiosulfate solution, but the critical analysis of the subject made by Mayr and Kirschbaum[8] has shown that the best procedure is as follows: Four and one-half liters of distilled water is boiled until it has a volume of four liters. Upon cooling it to about 50° the thiosulfate and 40 ml. of sugar fermentation amyl alcohol, *i.e.*, 1 per cent, are added and dissolved. Upon cooling to room temperature it is ready for standardization and use. Five hundredths normal is the strength usually employed in the methods to be described, but should dilutions be necessary, a stock solution of 1 per cent amyl alcohol prepared as above should be available as a diluent.

A starch solution used as an iodine indicator in all reactions where an excess of iodine is present may be rendered permanent by saturating it with mercuric iodide.

Diluting Standard Solutions. Standard solutions used in semimicro analysis are, for the most part, of the order of .01 to .02 normal. It is not good practice to keep such solutions very long, but rather to make dilutions from stronger ones as the need arises. This can be done quickly and accurately by pipetting the necessary quantity of strong solution and diluting it to the required volume. For small volumes the Oswald-Folin pipettes of 1 to 10 ml. capacity are recommended. They have remarkably accurate delivery for in actual calibrations replications of delivery have always been better than 1 part in 10,000. This does not mean, however, that the assigned value of delivery from the mark is always correct. Standard pipettes are recommended for larger volumes but care should be exercised in choosing those with well ground tips. In all cases pipettes and burettes used for critical determinations should be calibrated.

Cleaning Volumetric Glassware. Volumetric accuracy of high order can be attained only when drainage of the apparatus is perfect. This in turn demands scrupulous cleanliness which can best be attained by treating the glassware with a hot solution of chromic acid in concentrated sulfuric acid. An excellent cleaning mixture is prepared by adding 1,500 ml. of concentrated sulfuric acid to a hot solution of 200 g. of crystalline sodium dichro-

[8] C. Mayr and E. Kirschbaum, *Z. anal. Chem.* **73,** 321 (1928).

mate in 100 ml. of water. For best results the liquid should be heated to about 100°, but no hotter.

MISCELLANEOUS EQUIPMENT

Sand Bath. An electrically heated sand bath has a wide range of utility in analytical work and, for some purposes, such as evaporating or boiling solutions, it is superior to other methods of heating.

Specifications for a useful form of such an apparatus are given in Fig. 2[9] and it is shown in operation in Plate 2, p. 14. It consists of a transite box

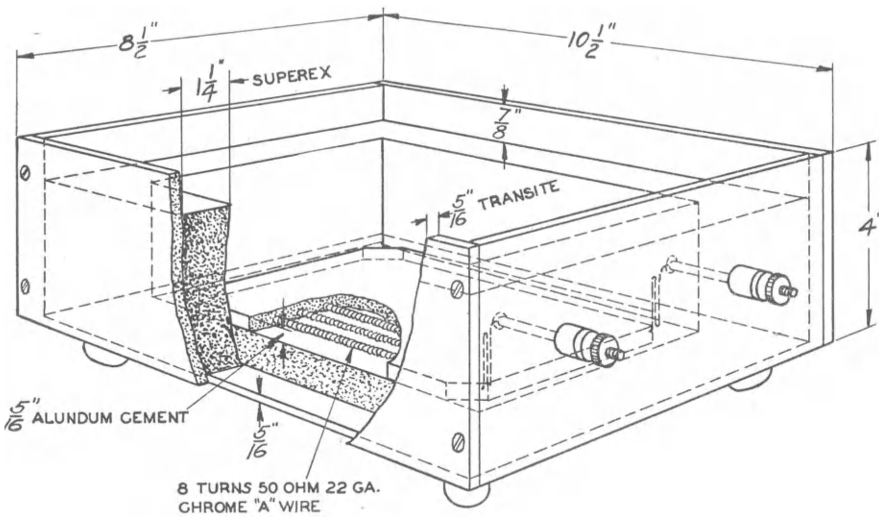


FIG. 2
An Electrically Heated Sand Bath
(Courtesy Journal Association of Official Agricultural Chemists)

assembled with machine screws and supported near its four bottom corners by 3″ metal studs. It is lined as shown with $1\frac{1}{4}$ inch superex insulation (a Johns-Manville product) equipped with a heating element placed in the bottom of the box, and filled to within a half inch of the top with clean silica sand.

During operation the temperature of the surface sand increases from the sides to the center of the box and the temperature within the sand increases with its depth. With these characteristics any rate of heating is possible.

Tablet Machine. Samples in tablet form are frequently required and are made by compressing the material in a mold. Several commercial machines for making approximately 5 mg. tablets are available, but they are of little use in the present work. Larger ones are necessary and must be made.

[9] E. P. Clark, *J. Assoc. Official Agr. Chem.* **16,** 418 (1933).

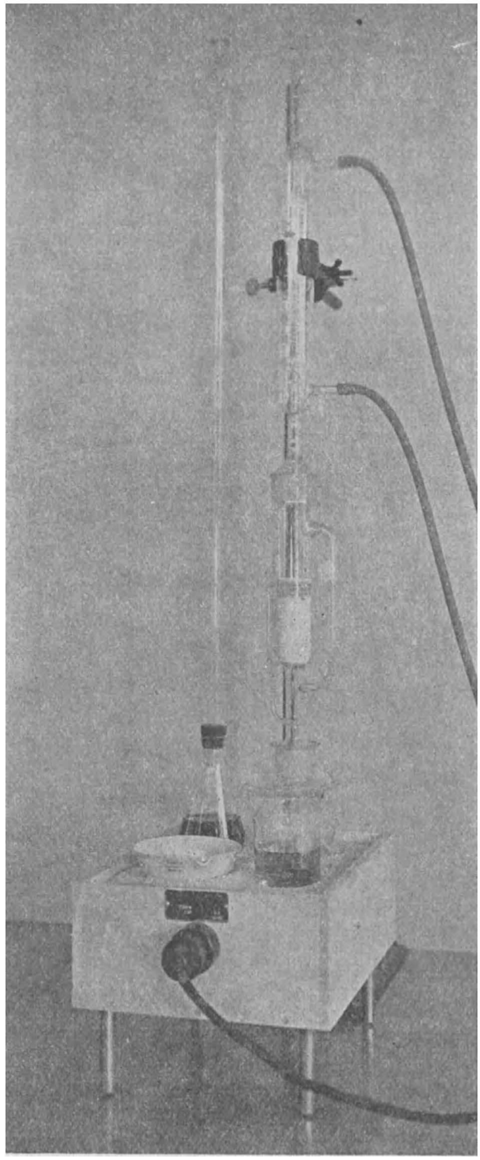


Plate 2
An Electrically Heated Sand Bath in Operation

Specifications for a machine of very simple construction is suggested in Fig. 3.

The truncated cone C fits snugly in the recess of the section of the steel bar A. The top and bottom surfaces of C are flush with the terminus of the hole B and the bottom of A respectively. The apparatus thus assembled is placed upon a heavy metal plate, the sample is introduced into B, the plunger D is inserted and pressed firmly against the sample with a punch machine or its equivalent. D is then removed, C falls out upon lifting A, and the auxiliary plunger E is used to force the tablet from the mold. The plunger D should be hardened so that it will not bend under pressure. A sodium press or an ordinary vise is a good substitute in lieu of a punch machine. It is advisable to have two such machines, one to make tablets approximately $\frac{1}{8}''$ in diameter and the other for larger ones about $\frac{3}{16}''$ in diameter.

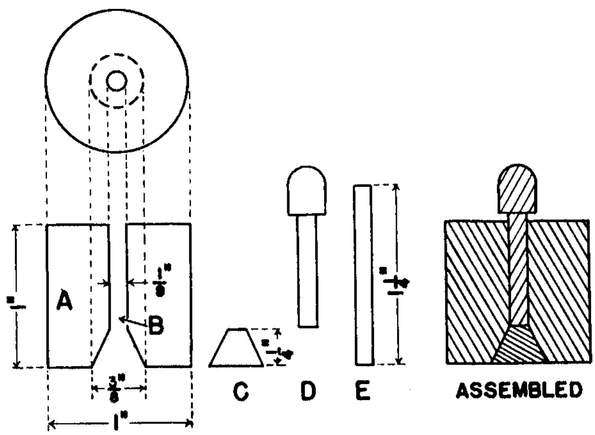


FIG. 3
A Simple Convenient Tablet Machine

The formation of tablets by compression usually leaves them so highly charged that they adhere to the punch. However, the static may be quickly dissipated by placing the tablet upon a metal plate grounded to a water or gas line and ionizing the air about it with a brush discharge from a vacuum leak tester.

Filtering Apparatus. Filtering liquids to collect precipitates, such as silver halides, the yellow phosphomolybdate precipitate, and the like, is best accomplished with the syphon filtering apparatus suggested by Pregl.[10]

[10] F. Pregl, Quantitative Organic Microanalysis, page 97. Translated from the Fourth German Edition by E. Beryl Daw, P. Blakiston's Sons & Co., Philadelphia (1937). Future references to Pregl will be indicated by his name and page number only with this edition understood.

It is shown schematically in Fig. 4 and is self-explanatory. To filter a liquid, the sintered glass filter tube C with the syphon D is placed in the adaptor B attached to the 250 ml. suction flask A, the liquid to be filtered is brought in position as shown at E and the precipitate and mother liquors are sucked into the filtering tube. Several small quantities of wash liquid are used to rinse the container, the syphon is removed and the wall of the filter is

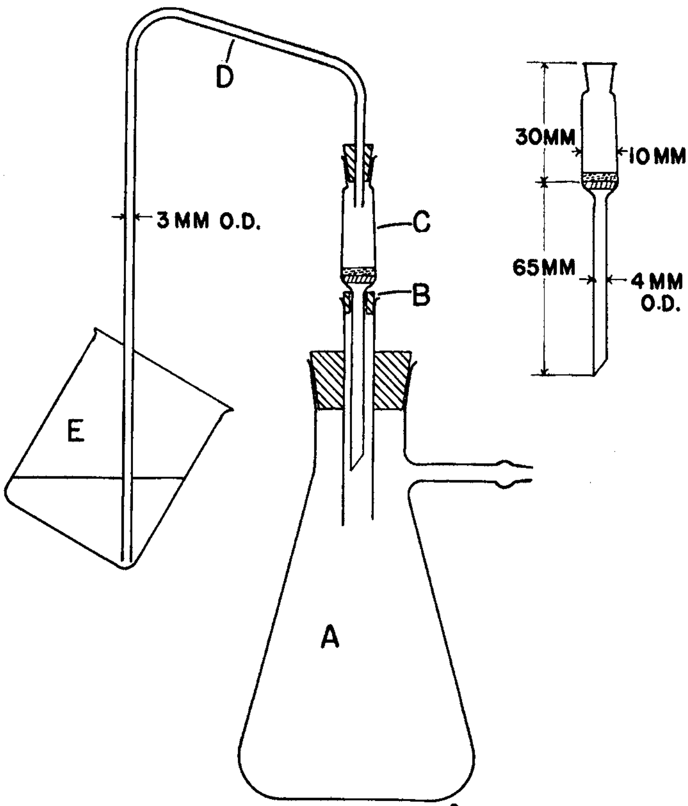


Fig. 4
Pregl's Syphon Filtering Apparatus

washed with a small stream of liquid from a wash bottle. The tube is then ready to dry as conditions demand.

Because sintered glass filter tubes are easily and quickly made, even by amateur glass blowers, specifications for a more desirable size than the standard commercial article are given. These tubes when made of thin walled glass and rather coarse sintered plates, to be covered with a mat of fine asbestos, are light in weight, are not larger than necessary, and they filter rapidly and retain all precipitates for which they are used.

The sintered glass plates are made as follows: Four circular recesses of proper dimensions bored close together in a small thin piece of graphite plate are filled level full with ground pyrex glass which passes through a 40 but is retained by a 50 mesh screen. The mold is then placed in a small closed electric heater, such as a macrokjeldahl digester or a Cenco hot cone heater, which has previously been brought to its maximum temperature. Two to three minutes is usually sufficient to sinter the glass for proper porosity and strength, but this must be determined by experiment. As soon as the first lot is finished the mold may be refilled and the process repeated. The finished plates are placed in position in the tube shell and sealed quickly with a fine hot oxygen flame from a jeweler's hand torch.

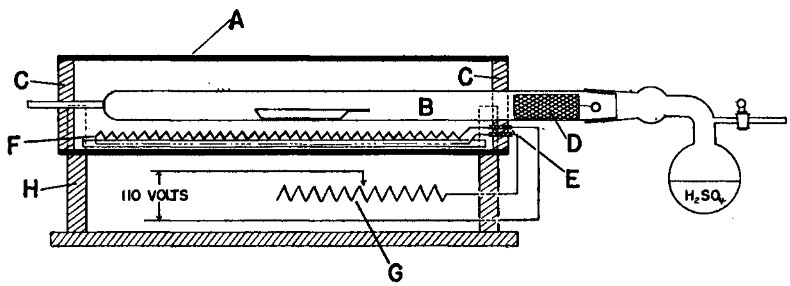


FIG. 5
An Electrically Heated Vacuum Drier

A, A standard 4″ × 20″ section of heavy duty pyrex tubing.
B, 1¾″ × 22″ pyrex tube.
C, C, Cork discs.
D, Copper screen basket containing pellet form KOH.
E, Glass capillary tubing insulator.
F, 100 ohm #30 chromel-C wire stretched upon asbestos board painted with sodium silicate.
G, 45 ohm variable resistance or variable voltage regulator.
H, Wooden cradle.

Drying Apparatus. The usual apparatus for drying analytical samples is the Abderhalden Dryer. This is a jacketed tube holding various dehydrating or absorbing agents, capable of being evacuated, and is heated by the vapors of various boiling liquids. There are many designs of the instrument but an electrically heated one has advantages over any of the vapor heated types in that any desired temperature may be approximately obtained by adjusting a rheostat; fire hazards are eliminated, condensing water is unnecessary and the apparatus occupies a minimum amount of space. These reasons are, therefore, sufficient for its recommendation.

Fig. 5 shows a drier of fairly large size which is used not only for treating analytical samples, but for preparative ones as well.[11] It is, of course, possible to change the dimensions to give an apparatus of any desired size.

[11] E. P. Clark, *Ind. Eng. Chem.* **19**, 306 (1928).

Determination of Moisture. In certain not infrequent cases, substances take up moisture from the air so rapidly that it is impossible to weigh them in the usual manner. Some materials, as for example, dry proteins and even some crystalline substances, adsorb moisture so quickly that they will take up as much as 10 to 15 per cent of moisture within a few seconds. These difficulties are negotiated by weighing the analytical sample in an air dried condition and making a simultaneous moisture determination in order that the results of the main analysis may be calculated to an anhydrous basis.

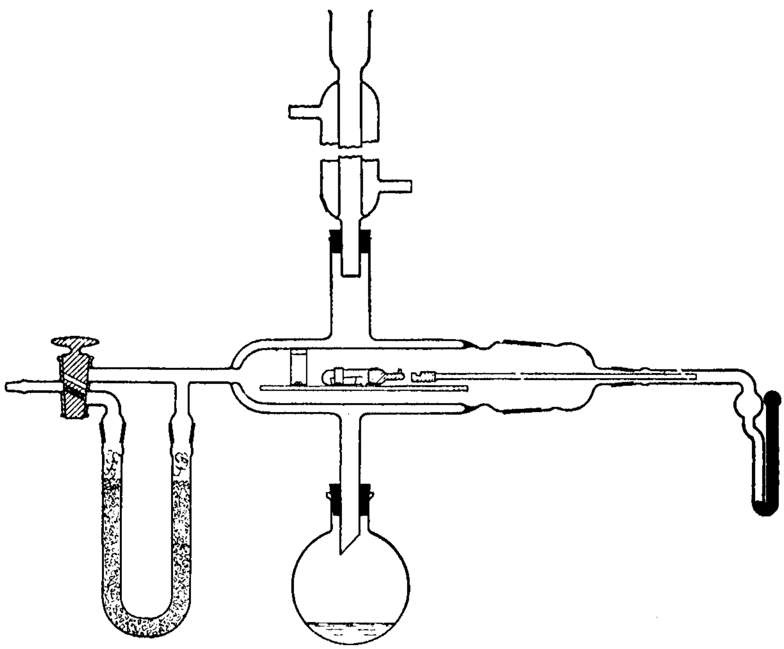


FIG. 6
Drier With Pig and Boat in Place

Moisture determinations thus involved are made by placing a definite quantity of air dried material in a special weighing tube called a "pig" and drying it in a vacuum drier. Perfectly dry air is then admitted to the apparatus, and the tube is tightly closed. Then the dryer is opened, and the still closed tube is again weighed. The moisture content of the sample is represented by the loss of weight incurred. In order that the pig may be closed or opened within the drier, the latter must be modified for the purpose. Milner and Sherman[12] have described such an apparatus which ope-

[12] R. T. Milner and M. S. Sherman, *Ind. Eng. Chem., Anal. Ed.* **8**, 427 (1936).

rates very satisfactorily. It is shown in Figs. 6 and 7 and their description of it is as follows:

"A vapor bath maintains a constant temperature as in the ordinary Abderhalden. The two-way stopcock can be turned to permit evacuation or the drying of incoming air, the latter entering through a very fine capillary cemented in the plug of the cock and then through the U-tube containing the desiccant. Colored anhydrite (anhydrous calcium sulfate) has proved very satisfactory as a drying agent. The other end of the tube carries two ground joints, a large one for introducing the plate holding the pig and a small one to hold the brass rod used to open and close the pig while the sample is in the drier. A closed-end mercury manometer is used to seal the small ground joint and to indicate leaks if present when the apparatus is evacuated over night."

When only a single analysis is required, both the moisture and other determination may be made on the same sample. The procedure to follow is

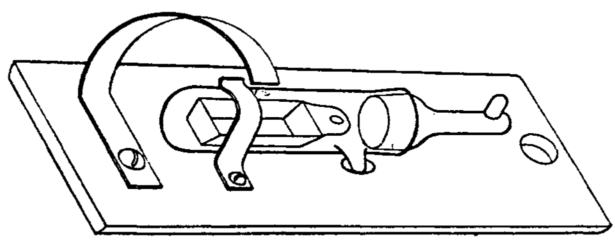


FIG. 7
Detail of Pig Held in Place

that given by Milner and Sherman (l.c.). Before the sample is weighed the pig and empty boat are dried and capped in the apparatus. The sample is then weighed and dried and the result recorded. The pig is opened and the sample allowed to come to equilibrium with the moisture of the air during 30 to 60 minutes. The pig is reweighed. The gain in weight upon exposure to the air is the quantity of moisture in the analyzed sample which must be considered in calculating the results to a dry basis.

Melting Point Apparatus. The determination of melting points is probably the first actual microdetermination ever made. It is a very important operation and is without doubt the most frequent one made in the organic chemical laboratory. A simple but efficient apparatus for the purpose is suggested. It operates smoothly without attention and removes much tedium from the Rast molecular weight determination to be discussed later.

In principle it is a modified Thiele apparatus with mechanical circulation of the heating medium. It is shown schematically in Fig. 8 and is self-explanatory. A few remarks, however, may be helpful. The shaft holding

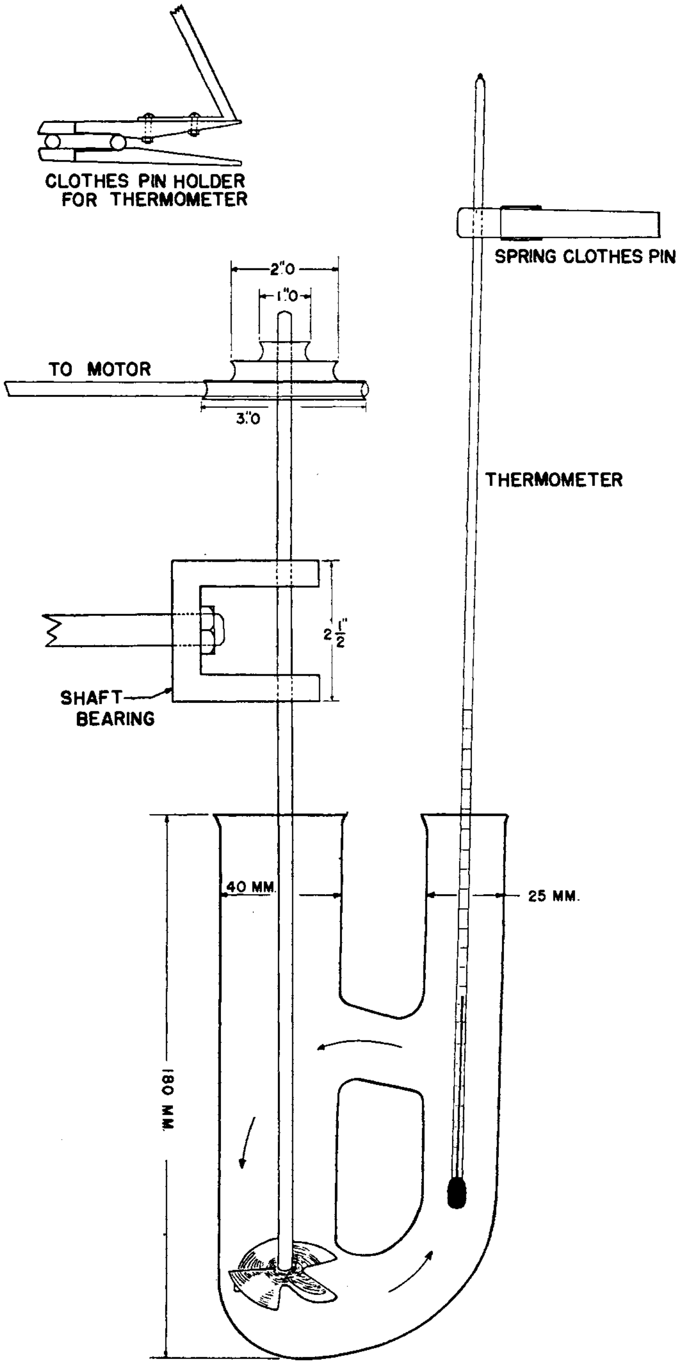


FIG. 8
Melting Point Apparatus

the turbin should be made of $\frac{1}{4}''$ brass stock and the vanes of the turbin are best constructed of sheet nickel or monel metal. They may be either silver soldered or attached to the drive shaft with a machine screw. The shaft bearing and in fact all metal parts should be carefully machined so as to give a well balanced assembly. The motor used to drive the shaft should be fairly large (of the order of $\frac{1}{20}$ H.P.) so that when its speed is reduced appreciably it still will have power enough to maintain a constant speed.

The best bath liquid for all around use is Monsanto's Aroclor 1248. Melting points up to 360°C. may be made with this liquid.

Another important accessory is an optical system capable of magnifying 6 or 8 diameters attached to a stand with three dimensional movement. The most desirable instrument is a dissecting binocular microscope. This is

TABLE VII

List of Chemicals and their Melting Points for Checking Melting Point Thermometers

	°C.
Benzoic Anhydride	39.
Thymol	49.4
Naphthalene	80.8
Acetanilide	114.2
Benzoic Acid	122.5
Salicylic Acid	159.8
Ammonium Nitrate	169.6
Anisic Acid	184.2
Silver Nitrate	212.
Carbazole	246.
Oxanilide	252.
Anthraquinone	285.
Isonicotinic Acid	317.

expensive and may be prohibitive in many instances, but some sort of magnification is imperative.

Calibration of the Melting Point Thermometer. A thermometer for the melting point apparatus should be carefully selected and calibrated under the conditions it is to be used. The calibration is made by checking the thermometer readings against the fusion values of a series of pure compounds whose melting points are sharp and accurately known. Such a list is given in Table VII.

The Determination of Melting Points. The melting point of a substance is determined by observing the temperature at which the material changes from the solid to the liquid phase. The observation is made in a long thin walled tube 1.5 × 100 mm. sealed at one end. The material is tamped in the bottom of the tube by dropping it several times through a 2 foot section of 6 mm. I. D. glass tubing held on a metal plate. The tube is then placed on the thermometer and held securely with a snugly fitting loop of copper bronze spring the coils of which are approximately 1.5 mm. in diameter. Heat is applied to the apparatus, the stirring mechanism is started, and the substance is observed until it melts. The thermometer is then read, which gives the information sought.

The Determination of Boiling Points. Boiling points of liquids may be made with the same apparatus and with much of the same technique as is used for melting point determinations. A piece of melting point tubing 1 to 1.5 mm. in diameter is heated and quickly drawn so as to form a cone about 2 cm. long and no thicker than a coarse hair at the tip where it is broken off. The tip is placed in the liquid under examination and the cone is allowed to fill 5 to 8 mm. by capillary action. The tip is instantly sealed in a hot flame so that a minute air bubble is trapped between the liquid and the seal. The filled tube thus obtained is placed upon the thermometer of the melting point apparatus, heat is applied to the circulating liquid, and stirring is commenced. As the temperature rises the bubble becomes larger and larger, forcing the liquid in the tube higher and higher. Just before the boiling point is reached the liquid begins to quiver and then it rises very rapidly. When the top of the expanded bubble reaches the surface of the heating liquid the temperature is read from the thermometer and this is the boiling point of the liquid under examination.

THE CALCULATION OF EMPIRICAL FORMULAS FROM ANALYTICAL DATA

The last subject to be discussed in the present chapter is that of calculating empirical formulas from analytical data. It may appear to some that the subject is irrelevant and unnecessary, but experience has convinced the author that it is not. Two of several reasons for this is that instances of impossible formulas are recorded in the literature and similar errors have been encountered in reviewing papers submitted to various journals for publication.

The subject is treated in most text-books but only in a superficial way. Simple examples are explored sufficiently far to truthfully say that "it can be seen by inspection" that the formula is so and so. Many such examples do exist, but the majority are not so simple and hence a need exists for a general procedure.

The analytical methods to be discussed in succeeding chapters give the percentage composition of the elements and groups of a compound, but for practical purposes these must be expressed in terms of chemical formulas. Let us take an example of a compound of carbon, hydrogen, and oxygen which upon analysis gave the following results:

C, 58.72%; H, 5.92%; O, 35.36%.

These figures imply that in 100 g. of the substance there are 58.72 g. of carbon, 5.92 g. of hydrogen, and 35.36 g. of oxygen. In other words, the unit expressed is grams of each element per 100 g. of material. In a chemical formula, however, units are different for each element. Thus, when carbon is considered, the unit is expressed by C which represents an atomic weight of the element. Now, as 100 g. of the compound under discussion contains 58.72 g. of carbon and each unit of carbon is 12 g., there are 58.72 divided by 12, or 4.9 units of carbon present. In like manner there are 5.92 units of hydrogen and 2.2 units of oxygen in the compound. The substance therefore contains carbon, hydrogen, and oxygen in the proportion of 4.9 to 5.92 to 2.2 units respectively. When these numbers are each divided by 2.2, the smallest of the series, another set of values is obtained in which the same ratios are maintained. The values are 2.23, 2.68, and 1. This is where the usual discussion of the subject stops, but it is not always possible, as in the present case, to see what factor it is necessary to use in order to have all values whole numbers—the condition demanded by the definition. It may be easily found, however, if the results thus far obtained are tabulated and the operations continued in the manner to be indicated.

	C	H	O
(1)	58.72	5.92	35.6
(2)	4.9	5.92	2.2
(3)	2.23	2.68	1
(4)	4.46	5.36	2
(5)	6.8	8.05	3
(6)	8.92	11.7	4
(7)	11.5	13.4	5
(8)	13.4	16.1	6
(9)	15.6	18.7	7
(10)	17.8	21.4	8
(11)	20.05	24.1	9
(12)	22.3	26.8	10
(13)	24.6	29.5	11
(14)	27.8	32.2	12
(15)	29	34.9	13

Series (1) represents the elementary composition as found by analysis. Series (2) represents the relative number of atoms of each element in the compound as found by dividing the percentage composition by the atomic weights of the elements. Series (3) is a new set of values having the same ratios as in (2) found by dividing each value by 2.2, the smallest number of the series. The succeeding series are obtained by multiplying each element in (3) by 2, 3, 4, etc.

From inspection of the table and without further information, Series (11) would be the proper choice to make, since for all practical purposes the numbers are integers. This would mean that the substance would have the formula $C_{20}H_{24}O_9$ which according to theory contains 58.80 per cent carbon, and 5.92 per cent hydrogen. It may be argued, however, that several other sets of values, *i.e.*, Series (6), (8), (10), (12), (14) and (15) would answer probably as well. In making a choice between the formulas which could be derived from the table, the following rule concerning the composition of molecules with elements having odd valences will be useful. The rule states that *the number of elements in a molecule having odd valences must be equal to an even number*. This rule is a direct corollary of the theory of the tetravalency of carbon. It at once eliminates Series (10), (12), and (15) so there then remain only four formulas from which to choose, namely, those derived from Series (6), (8), (11), and (14). Of these, Series (6) and (8) diverge too far from whole numbers to be considered. Series (14) may possibly do. According to theory this C_{27} compound demands 59.11 per cent carbon and 5.88 per cent hydrogen. The theoretical hydrogen is too close to that found experimentally to be of differential significance, but the theoretical carbon is too far removed from that actually found to be due to experimental error. The only choice, therefore, is the $C_{20}H_{24}O_9$ formula previously chosen. This then is the empirical formula of the compound.

In most actual cases, as with the one under discussion, other analytical data, such as results from molecular weight, alkoxyl, or carboxyl determinations are also available. Such supplementary information not only indicates the proper formula to choose, but also establishes the molecular formula of the compound.

CHAPTER II

THE DETERMINATION OF CARBON AND HYDROGEN

In principle the determination of carbon and hydrogen is one of the simplest of analytical operations; but in practice it requires skill and manipulative ability. The reaction involved is simply burning a substance in oxygen and collecting and weighing the carbon dioxide and water formed.

This determination was the first one investigated by the author in developing a semimicro system of analysis.[1] The work was very encouraging for from it there emerged a satisfactory procedure that was used extensively for a number of years. However, as experience was gained and mechanical and chemical developments pertaining to the field appeared, it became obvious that the procedure, and especially the equipment, could be simplified. During this period also microchemical apparatus became available on the American market. All this led to the adoption of some changes, particularly those concerned with the use of standard glass equipment. The revised procedure has proved itself equally as good as the former and will therefore be presented.

Apparatus. The equipment essential to the determination is a furnace, a combustion tube with its filling in which the sample is burned, absorption tubes for collecting and weighing the carbon dioxide and water, a device for purifying oxygen, and several other auxiliary items to be described later. All the glass items are standard micro combustion apparatus obtainable from supply houses. A schematic drawing of the ensemble is shown in Fig. 9. In order that the reader may become familiar with the purpose of these items as they are described, a skeleton outline of the procedure is presented.

The sample to be burned is placed in a platinum boat in the combustion tube between A and B. Tank oxygen is passed through the pressure regulator D and dried in E. It then passes through the purifier C, thence to the bubble counter F, the ascarite and anhydrous magnesium perchlorate tube G, and finally into the combustion tube. The units A and B are maintained at about 550°, and heat is slowly applied to the sample by advancing A in its direction. H is a device for removing nitrogen oxides if present, and the two tubes I and J collect the water and carbon dioxide respectively. The function of the Mariotte bottle K is to measure the volume and pressure of the gases passing through the system. With this general outline specific considerations may be undertaken.

The Furnace. Several types of micro combustion furnaces are available

[1] E. P. Clark, *J. Assoc. Official Agr. Chem.* **16**, 413 (1933).

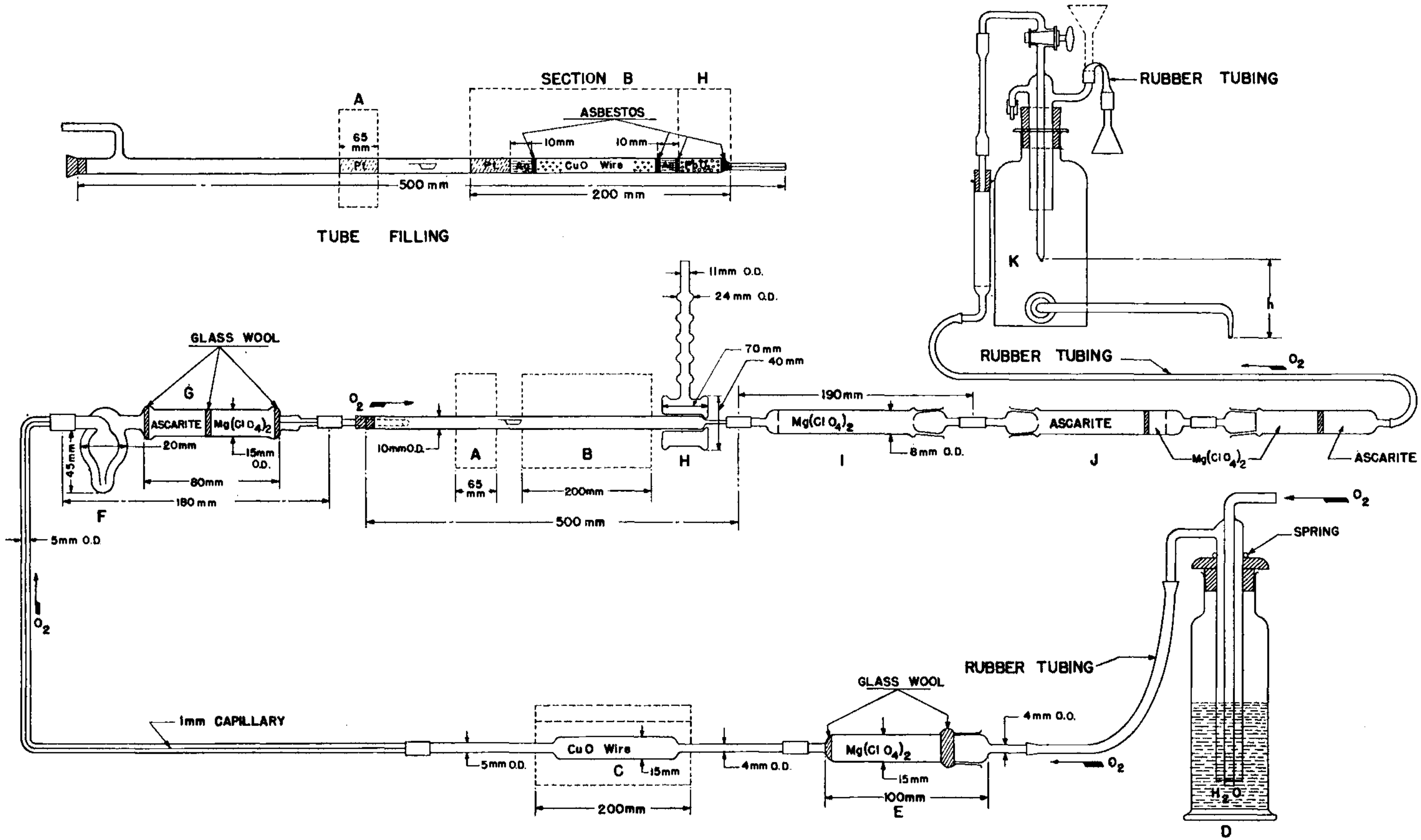


FIG. 9
Combustion Train for the Semimicro Determination of Carbon and Hydrogen

from supply houses. They are all good, and adequate descriptions of them may be found in catalogues of principal dealers. Most of them are electrically heated and are of the split core design; that is, they are built in two sections and are assembled with hinges so that they may be opened and removed from the tube while still in operation. This design, Fig. 10, was evolved primarily because of its desirability in the Dumas nitrogen determination, but is really of no advantage in the carbon and hydrogen determination. Such furnaces are somewhat expensive and it may happen that an analyst will prefer to build one himself, not only to reduce cost,

Fig. 10
A Split Core Type of Combustion Furnace
(Courtesy Fisher Scientific Co.)

but to incorporate features that he particularly likes. As a helpful suggestion, specifications for one which functions perfectly, is inexpensive, and easy to construct is shown in Fig. 11. It is susceptible to minor changes if desired, but its main recommendation is its low heat radiation factor.

Construction of the Furnace. Fig. 11 is for the most part self-explanatory. The furnace B is simply an open transite box lined with superex insulation,* with a loose cover of the same material. A nickel or monel metal tube is used to support and equalize the temperature of the combustion tube, and heat is supplied by a chromel resistance placed underneath the tube. The

* A Johns Manville high temperature insulator marketed in blocks of various sizes.

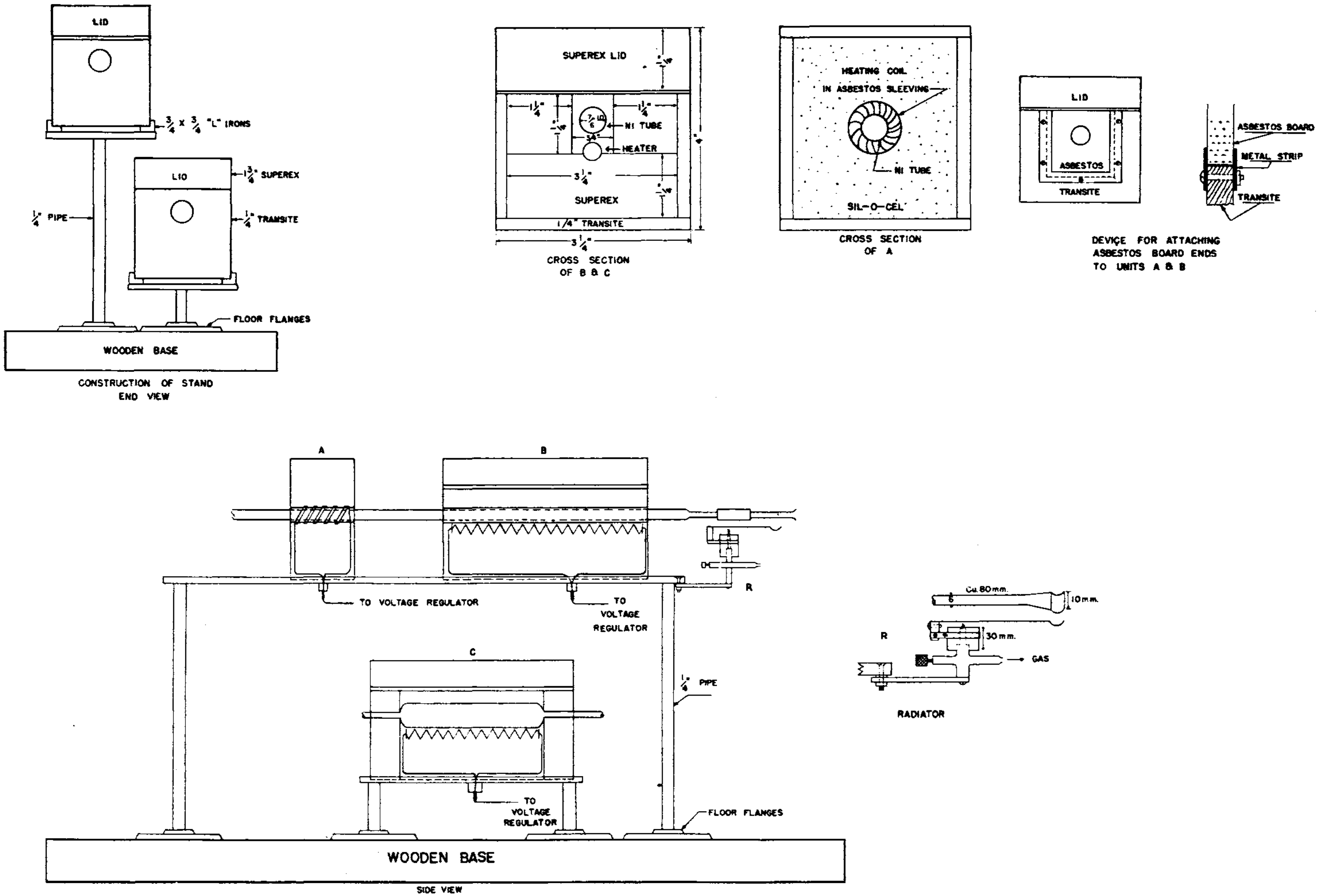


FIG. 11
Outline of the Construction of the Box Type Combustion Furnace

following details are pertinent to the construction. The exposed superex within the box and the entire lid are painted with a thin aqueous paste of Rutland furnace cement to give a clean hard surface. The heating coil is made of chromel A wire in the following manner: A length of 24 gauge wire of 32 ohms resistance is closely wound and secured upon a $\frac{3}{8}''$ section of light metal tubing. It is then heated to redness and plunged into water, a treatment that removes all resilience from chromel wire. The coil is removed from the form by twisting it somewhat in the opposite direction from which it was wound and the individual turns of the coil are separated by pulling them apart. However, to compensate for end heat losses, they are more closely spaced at the ends than in the central part of the unit. Because of its shortness the burner unit A is best built as a closed unit and insulated with Cil-o-sel. In this case the nickel core through which the combustion tube passes is insulated with mica sheets split to such thickness that they can be wrapped around the tube without breaking. The mica is tied in place with thin cotton thread. The resistance wire (35 ohms of 25 gauge chromel C), made as directed above on a $\frac{1}{4}''$ form, is inserted in a tube of braided asbestos sleeving and then wrapped as closely as possible around the mica covered nickel core, and the ends are secured to the lead wires. The end pieces of both A and B are made of asbestos board instead of transite to reduce heat conduction. Means of regulating the temperatures of the three heating units A, B, and C must be provided. This may be done by the use of adequate rheostats or by variable voltage regulators. The latter are the more expensive of the two but they are much more desirable and are well worth the added expense. Should it be found necessary to use rheostats, one of 25 ohm resistance is suitable for section A, while 11 ohm instruments are satisfactory for both sections B and C.

The Tube Filling. The combustion tube, used either in the above or a commercial furnace, is of standard microdimensions. It contains various reagents, some of which act as combustion catalysts and others to eliminate interfering elements which may be present in the sample. The nature and relative positions of these substances are shown in Fig. 9. A roll of platinum foil or screen is employed as a catalyst to assist combustion. Silver gauze removes halogens and sulfur and lead peroxide removes any nitrogen oxides that may be formed by the combustion of nitrogenous materials. A roll of platinum gauze at A is a baffle to prevent vapors of partially burned substance from diffusing counter to the direction of the oxygen stream.

The lead peroxide reagent is the only one necessary to prepare. It is made in the following manner which is according to the latest directions of Pregl.[2] A quantity of lead peroxide is heated and occasionally stirred for two hours on the steam bath with concentrated nitric acid. After allowing the mixture

[2] Pregl, page 35.

to stand for one to two hours, it is washed by decantation with distilled water until free from nitric acid. The mud is then spread upon a plate, almost dried, and cut into 2 mm. cubes with a knife or spatula. The pieces are rolled in a wide-mouthed bottle until they are largely rounded. Then they are screened to remove the fine particles. When the small grains thus prepared are placed in the combustion tube they require about 6 hours' heating before they are ready for use.

The Pressure Regulator and Gas Purifier. The pressure regulator D is a simple bell gas-holder which delivers gas regularly at a definite water head. It consists of a wide-mouthed bottle about 240 mm. high and 60 mm. wide. It is half filled with water and its mouth is closed with a wooden cap. The bell is a glass tube 20 mm. in diameter and 200 mm. long, having a small tube sealed through the center of the closed end and reaching to its lower open end. The upper end of the sealed-in tube is attached to the oxygen supply. The bell is held in position and may be adjusted by coiled springs. The outlet of the bell conducts the gas to the anhydrous magnesium perchlorate drying tube E, and thence to the purifier C. The latter is a tube containing broken pieces of about 20 gauge copper oxide wire and is heated in a furnace. As indicated in Fig. 11, the furnace is the same as B except that the ends are insulated with superex to reduce end radiation as much as possible. When operating it is maintained at a temperature of about 550°. If the oxygen supply is pure this is not necessary, but it has been the experience of the writer that all tank oxygen has some impurities, or if not, a small but appreciable quantity of such material finds its way into the gas from the rubber connections. After leaving the preheater or purifier, the gas passes through the units F and G. F is a bubble counter containing concentrated sulfuric acid. G is an ascarite and magnesium perchlorate tube to remove carbon dioxide and water which may have been formed. From here the gas enters the combustion tube and is utilized in burning the sample and sweeping out the products of combustion.

The Lead Peroxide Heater. Lead peroxide, used to react with nitrogen dioxide, should this be formed in the combustion of the sample, is a critical material in that it will take up or lose moisture over a wide range of fairly high temperatures. Therefore, in order that it may be used successfully, it must be maintained at a definite temperature. This is done by placing the portion of the combustion tube containing it in the device H. It is an all glass vapor jacketed heater in which a small quantity of paracymene or purified decalin (decahydro naphthalene) is boiled with a microburner. The vapors surrounding the lead peroxide thus maintain the reagent at the necessary constant temperature.

The Absorption Tubes. The absorption tubes I and J collect the water and carbon dioxide respectively. I contains anhydrous magnesium perchlorate, and J contains ascarite except for a 2 cm. zone of perchlorate at its terminal end. The reagents are held in place by small plugs of glass wool at the ends of the tubes. To prevent blocking of the ascarite tube, to assure its use for eight or ten combustions, two sections of 1 mm. melting point tubing are inserted in the fore end of the absorbent. One tube, ca. 13 mm. long, is placed in the reagent to the depth of 10 mm.; the other tube, ca. 23 mm. long, is embedded in the reagent to a depth of 20 mm. These tubes are readily dropped in place as the absorption tube is filled. The ground stoppers are sealed with Krönig's glass cement (1 part white wax and 4 parts rosin). It should be connected to the combustion tube through the end opposite the ground-in stopper. This is to prevent the cement from becoming warm with consequent danger of loosening.

A third tube attached to J, one-half of which contains ascarite and the other half anhydrous magnesium perchlorate, is used only as a guard tube and is never weighed. The two reagents are separated by a thin zone of glass wool. This also applies wherever the two reagents are in the same tube, *i.e.*, the ascarite tube and in G. The rubber connections for the absorption train are sections of a good grade antimony combustion tubing and are lubricated by forcing a swab slightly moistened with glycerine through them. An extremely thin film of glycerine thus applied to the bore of the connections assures ease of assembling and dismantling the train and is practically essential.

The Mariotte Bottle. The final piece of apparatus in the assembly is the Mariotte bottle K, which serves to measure the volume of gas passing through the apparatus and also to maintain a sufficiently reduced pressure to partly overcome the internal friction of the system. By the combined use of it and the regulator D, the pressure within the system at the junction of the absorption train and combustion tube should be essentially that of the atmosphere. Usually the positive pressure in the regulator about neutralizes the negative pressure in the Mariotte bottle. Its operation is readily seen from the diagram. The water head h is a measure of the vacuum produced. In order to assure easy movement of the delivery tube, the stopper through which it is attached must be cork. The device through which the gas enters the bottle is chosen so that the water delivered may be easily returned to the bottle after the combustion.

When the entire equipment, with the exception of the absorption train, is assembled, the units A, B, and C are heated to ca. 550°C. (a dull red heat), and oxygen is passed through the system for 2 hours. Sufficient heat is also applied to the paracymene bath to keep the vapors of the hydrocarbon constantly refluxing from the lower bulb of the condenser. Attention is directed to the mistake so frequently made of heating the combustion tube to excessively high temperatures. A bright red heat is not only unnecessary but undesirable as the glass may soften, become distorted or even fuse to the reagents, which will cause the tube to crack.

The Combustion. Having previously adjusted the water head in the pressure regulator and the Mariotte bottle to deliver about 5 ml. per minute under the conditions previously stated, the entire assembly is connected and heat is applied to purifier C, Section B, and the paracymene heater H. Oxygen is passed through the system and when B and C are approximately 550°C. (a dull red heat) and the paracymene is refluxing, the platinum baffle in Section A is removed and about 10 mg. of a pure compound, such as sugar, contained in a standard microcombustion boat is placed between sections A and B. The platinum baffle is replaced,* the tube is closed with a rubber stopper, and heat is applied to the burning unit A. In case the split core type combustion furnace is used, a collar of heavy copper tubing placed over the combustion tube outside the furnace takes the place of the burning unit A. The copper collar is heated with a gas burner and functions in every way as does the closed unit A. As the temperature rises, the burn-

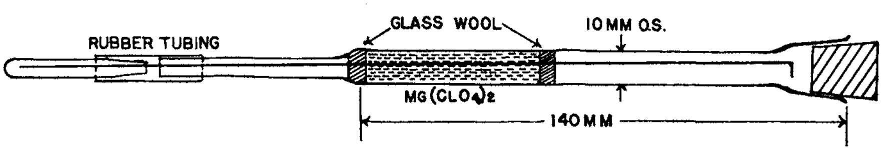


Fig. 12
Desiccator for Handling Platinum Baffle

ing starts and is controlled by the rate at which the burner approaches the sample. It must be such that a slow, steady combustion will occur so as to require approximately 20 minutes for the actual operation. When finished the burner will completely cover the boat.

After this operation is completed the heat in Section A is turned off and the combustion tube is swept out by continuing the flow of oxygen for approximately 25 minutes. During the combustion and sweeping of the tube a gentle flame is occasionally applied to the end of the combustion tube near the connection of the absorption train. This occasional heating prevents moisture from condensing in the cooler part of the combustion tube and, in like manner, the radiator arm r, held against the capillary of the water tube, automatically keeps moisture from condensing there. This

* The baffle coil may be removed or introduced into the combustion tube without contamination of moisture by the use of a desiccator type of device shown in Fig. 12. After the baffle is moved toward the end of the combustion tube, it is caught by the hook, drawn into the desiccator and the latter closed. The reverse process is, of course, used to introduce it into the combustion tube following the boat.

device is a strip of sheet copper, heated with a minute flame from a micro-burner attached to the furnace support by a movable arm. The end of the radiator is bent in the form of a half cylinder to snugly fit the under half of the absorption tube capillary. It is adjusted with enough tension to be held in place. When it is removed, it is pressed down and swung out of place. Only sufficient heat is applied to the radiator to keep moisture from condensing in the tube capillary while oxygen is flowing.

As the flow of oxygen through the system continues the absorption train is disconnected from the combustion tube and the Mariotte bottle. The guard tube on the absorption train is left open but the water tube is closed with a rubber nipple, and the train is allowed to adjust itself for ten minutes to the temperature of the balance room. The tubes are then disconnected and the capillary ends stoppered with nipples until just before they are placed on the balance for weighing. In this as well as other operations with the tubes, it is good practice to hold them by the capillary ends during all necessary manipulations. An expedient found serviceable in this connection, especially during warm, humid weather, is to rinse the hands with a little alcohol and dry them with a towel. They will then remain dry for quite some time.

The carbon dioxide tube is weighed first. The rubber nipples are removed and the capillary ends and any part of the tube touched by the hands are carefully wiped with a small piece of chamois. The openings of the ends are also wiped with a small cotton covered applicator. The tube is then taken by the special tongs mentioned in Chap. I and placed on the left-hand pan of the balance. Another tube of the same size, but slightly lighter than the one weighed, is used as a tare on the right pan of the balance. Any difference of atmospheric changes, buoyancy of the air, or other factors which may occur between weighing is eliminated in this way.

After being weighed the tubes are again assembled and connected to the combustion tube. Approximately 10 mg. of the material to be analyzed, which has previously been weighed in a platinum boat to 0.01 mg., is placed in the tube and burned as directed for the sugar sample. The time required for its combustion is usually 20 minutes, but this varies somewhat depending upon the nature of the substance. After the system has been swept out and the tubes allowed to cool the latter are weighed in the same order as before. The increase in weight of the magnesium perchlorate and ascarite tubes is, of course, due to the water and carbon dioxide formed during the combustion. From these values the percentage of carbon in the compound is found as follows:

$$\frac{(\text{wt. of } CO_2 \text{ found})(0.2727)(100)}{\text{wt. of sample}} = \%\ \text{carbon}$$

Likewise hydrogen is found as follows:

$$\frac{(\text{wt. of } H_2O \text{ found})(0.1119)(100)}{\text{wt. of sample}} = \% \text{ hydrogen present}$$

The above directions are for solids and high boiling liquids which usually include the majority of the materials to be analyzed. If, however, the substance is a volatile liquid, or even a solid with very high vapor pressure, modifications must be introduced. When the substance is a volatile liquid, it is weighed in a small section of melting point tubing with a capillary end. The tube is weighed and the liquid is introduced by warming the bulb to expand the air and then inverting the open neck under the liquid. The bulb with the liquid is sealed and weighed again. Before introducing the material into the combustion tube the capillary is scratched with a glass knife and broken. The two parts are then placed in the boat and quickly introduced into the combustion tube. Substances which are moderately volatile are vaporized by the heat from the platinum baffle some distance away so that heat immediately about the boat is unnecessary until at the close of the combustion. Other substances still more volatile may require some cooling to prevent too rapid vaporization. Directing a fine blast of air upon the combustion tube directly over the substance is usually sufficient. In burning highly volatile substances, the boat with the substance is placed in the combustion tube some distance from the furnace. As a rule in such instances, some form of cooling is also necessary.

Notes. The preliminary burning of a small sample of sugar or other material is to establish an equilibrium in the entire system comparable to that which exists during an actual determination. This is especially important when the lead peroxide unit is employed, because this reagent is particularly sensitive to environmental changes. It is only done, however, at the beginning of a day's series of analyses.

When the work warrants, it is strongly suggested that two combustion tubes be available, one having lead peroxide for use in burning nitrogenous compounds, and another without the lead peroxide for use in burning nitrogen-free compounds. When the latter is used the paracymene unit is removed. These tubes may be readily interchanged, and when a considerable number of nitrogen-free compounds are to be analyzed, time is saved in sweeping out the apparatus and the elimination of a critical reagent is accomplished.

According to Friedrich,[3] the most effective way to use lead peroxide is to spread thinly 0.2 to 0.3 g. of dry reagent in a boat and place it in the paracymene section of the combustion tube. This quantity is claimed to be good for only about 12 mg. of picric acid, or its equivalent of nitro groups, or

[3] A. Friedrich, *Mikrochemie* **23**, 129 (1937).

25 mg. of other substances. The statement is contrary to the directions of most workers and does not conform to the prevalent use of lead peroxide. The use of the reagent in this manner would also require a rubber stopper rather than the capillary end of the combustion tube. The writer has not as yet investigated this point, and consequently no comment can be made. However, it is an important consideration which should be carefully substantiated. Lead peroxide is not an ideal reagent for the purpose for which it is used. This statement is obvious from the numerous attempts made to find a better one. Several have been suggested[4,5,6] but their desirability has not been substantiated. Consequently, until this is done the best choice is still lead peroxide.

Burning the substance in oxygen followed by sweeping the system with air has long since been discontinued. When the absorption tubes are handled as directed there appears to be no displacement of oxygen by air during the weighing operation. The small capillary ends of the tubes and the fact that they are always in a horizontal position when open, contributes largely to this. In any event, careful checking has shown no differences in either way. Consequently, oxygen is used exclusively and thus the operation and equipment are simplified.

A simple stand to hold the absorption train when attached to the combustion tube may be made by suspending chromel wire rings from hooks in a small wooden bar attached to a ring stand upon which the tube may rest. This arrangement assures flexibility and freedom from accident.

The rubber connections are always kept in the microdesiccator with the platinum boats when not in use. It prevents the rubber from absorbing moisture and other gases.

The determination of carbon and hydrogen is perhaps the most critical determination in all organic analysis, and the literature upon the subject is very extensive. To review it adequately would undoubtedly require as much space as this entire book. The greater part of it, however, deals with mechanical devices and procedures to attain greater precision. Many of these, when critically analyzed, are found ineffectual, for the innovations introduced frequently nullify other safety arrangements. After all, the simpler the procedure and equipment, the better the method. It is, of course, true that individual compounds behave characteristically and modifications must be introduced for each. On the whole, a simple procedure, such as the one presented in the foregoing, will adequately take care of a great proportion of encountered research compounds.

[4] A. H. Corwin, Paper presented at Rochester meeting, Am. Chem. Soc., Sept. 9, 1939.

[5] A. Dombrowski, *Mikrochemie* **28**, 136 (1940).

[6] P. J. Elving and W. R. McElroy, *Ind. Eng. Chem., Anal. Ed.* **13**, 660 (1941).

There are, however, certain procedures for specific classes of compounds or types of problems that are invaluable. One of these is the wet combustion method for carbon alone. Van Slyke and Folch[7] have developed an excellent manometric method for this work that is very precise and is applicable to very small samples. The method may frequently be used to determine trace metals by forming organic derivatives, purifying them without actually isolating them and finally, determining the carbon in the compound and thereby arriving at the quantity of metal under investigation. The procedure is more often required in biochemical research, hence the reader is referred to the original literature.

[7] D. D. Van Slyke and J. Folch, *J. Biol. Chem.* **136,** 509 (1940).

CHAPTER III

THE DETERMINATION OF NITROGEN BY THE KJELDAHL METHOD

The Kjeldahl method for determining nitrogen is one of the most accurate and easily performed procedures in organic analysis. The operations consist of burning the substance in sulfuric acid containing certain other reagents that assist the combustion both by raising the boiling point of the acid and by acting as catalysts. When the substance is completely burned its nitrogen remains in the acid mixture as ammonium acid sulfate. This salt is then decomposed with alkali and the liberated ammonia is distilled into a receiver and titrated with standard acid. The method has quite general applicability, and the equipment necessary is simple and inexpensive. It has many modifications as a result of its development and perfection but it can be stated with confidence, based upon thousands of determinations, that the Gunning-Arnold-Dyer Modification of combustion with the boric acid method of titrating the ammonia is the most desirable procedure.

This system is applicable to practically all classes of animal and vegetable materials, pyridine and quinoline derivatives, purines, pyrimidines, amines, amides, oximes, and such substances as carbazole, hydrazobenzene, and indigotin. By modifying the method according to Friedrich, *et al.*,[1] the nitrogen in hydrazines, osazones, and nitro, nitroso, azo, and even certain diazo compounds may be determined with a high degree of precision.

Apparatus. The apparatus recommended for semimicro or even micro quantities consists of two parts, the digester (Fig. 13) and the Parnas-Wagner Kjeldahl distilling apparatus (Fig. 14).[2] The distilling ensemble is as simple and easily operated as is consistent with accuracy. A gas heated digester may replace the electrically heated one if desired.

The operation of the distillation apparatus is as follows: Steam generated in 1 by a resistance coil immersed in distilled water passes through the trap 2. The quantity of steam delivered is controlled by, preferably, a variable voltage regulator or a rheostat. When 3 and 4 are closed (4 is closed by removing the funnel from a wire hook and allowing it to hang by the rubber connection, thus crimping the tubing), steam passes through the distilling flask 5, thence through the condenser 7,.to the collection flask 6. To empty the distilling flask 5, the heating current is broken. Immediately the liquid in 5 is emptied into 2. The current is again made; 3 is opened, allowing the liquid in 2 to pass to the waste, and wash water is admitted

[1] A. Friedrich, E. Kühaas, and R. Schnürch, *Z. physiol. Chem.* **216,** 68 (1933).
[2] T. K. Parnas and R. Wagner, *Biochem. Z.* **125,** 253 (1921).

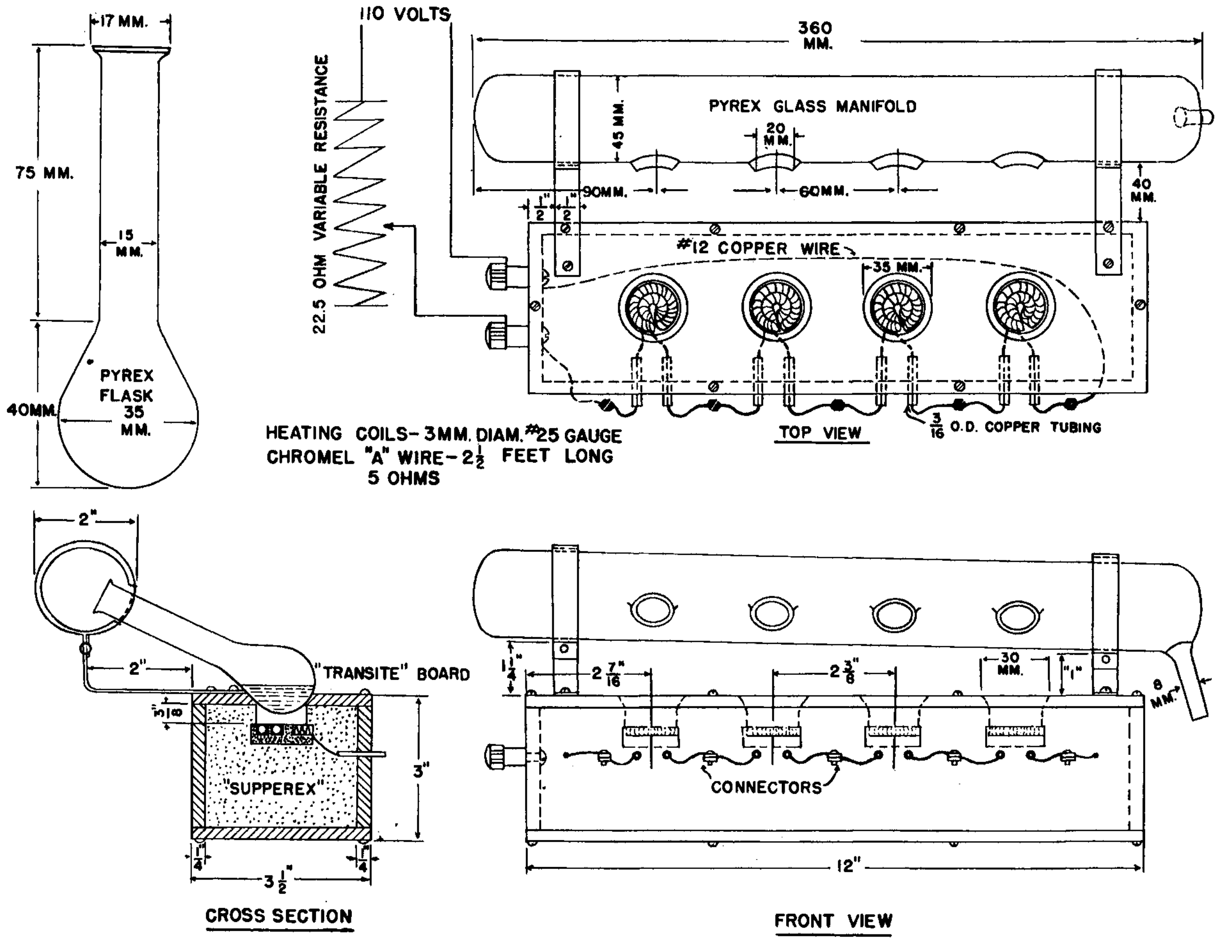


Fig. 13
Electrically Heated Micro or Semimicro Kjeldahl Digester

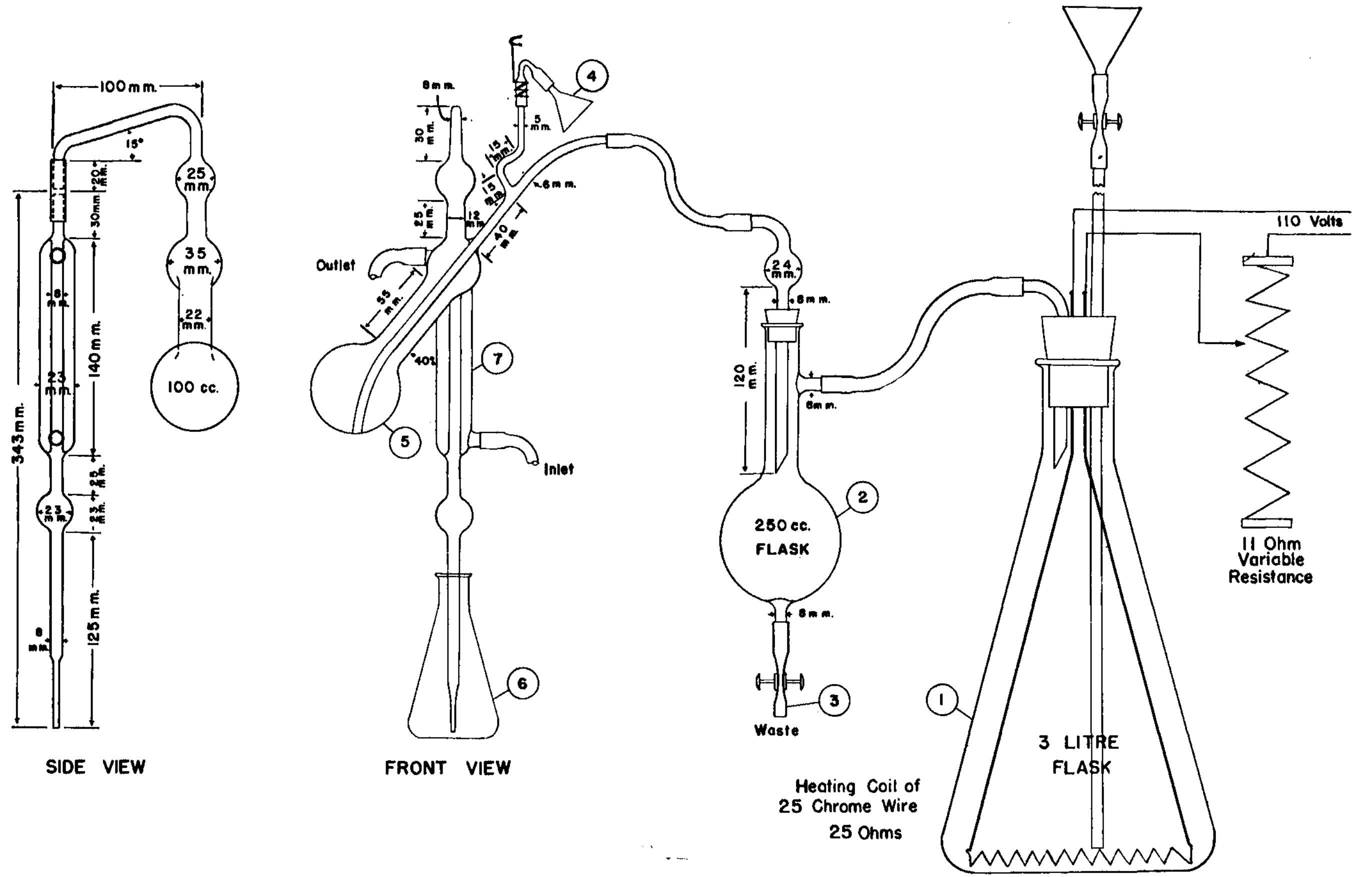


Fig. 14
Parnass-Wagner Electrically Operated Micro or Semimicro Kjeldahl Distilling Apparatus

to 5 through 4; 3 and 4 are then closed, and the operation is repeated, which rinses 5, thus conditioning the apparatus for the next distillation.

Procedure. Approximately 10 mg. of substance weighed upon a 15 × 25 mm. piece of cigarette paper, 40 mg. of mercuric oxide, 0.5 g. of potassium sulfate, and 1.5 ml. of sulfuric acid are placed in a Kjeldahl flask, the dimensions of which are shown in Fig. 1. The flask with its contents is gently heated on the digester until frothing ceases, when the temperature is increased until the mixture vigorously boils and the vapors of the acid rise to within 5 cm. of the mouth of the flask. The total time of digestion should be an hour, and the mixture should be colorless during the latter half of this period. A longer combustion period, for any reason, does no harm. The digest is then cooled, a drop of alcohol is added, and the mixture is again heated until it becomes colorless. When the acid mixture has cooled it is ready for distillation.

With the distillation apparatus in working order and steam having been passed through it for some time, 3 and 4 are opened (the funnel 4 is placed upon the wire support in an upright position), the rubber connection between 2 and 5 is closed with haemostatic forceps, and the acid mixture in the digestion flask, diluted with about 8 ml. of water, is transferred through the funnel 4 to 5. The transfer is made quantitatively by rinsing the flask with four 3 ml. portions of water. Before the transfer is made it is expedient to cover the lip of the digestion flask with a thin film of vaseline to prevent the liquid from running down the outside. Sufficient sodium hydroxide is added through 4 to neutralize the acid and render the final liquid strongly alkaline. A 40 per cent solution of sodium hydroxide containing 5 per cent of crystalline sodium thiosulfate is used for this purpose. It is washed into the distilling flask 5 with 2–3 ml. of water, and the system is closed at this point; 3 is then closed, the connection between 2 and 5 is opened, and a small flame is applied to 5. Almost immediately distillation begins. The condensate containing the ammonia is collected in flask 6, containing 2 ml. of 4 per cent boric acid solution and 1 drop of a 0.1 per cent ethanolic solution of methyl red. The distillation is continued with the adapter under the acid solution until 8 ml. of distillate has been collected. The flask is then lowered until the adapter is above the contents of the flask, and the distillation is continued until approximately 1 ml. more of distillate is collected. During this time the outside of the delivery tube is washed with a little water in a fine stream from a wash bottle. The rate of distillation should be so adjusted that the boiling in 5 will not be so violent as to carry over any of its contents mechanically. The condensing water in 7 should also be adjusted so that the temperature of the condensate will not be above 40°C. at the end of the distillation.

The ammonia received in the boric acid solution is titrated with 0.02 *N* HCl, a burette graduated to 0.05 ml. being used.

A blank due to reagents should be determined and subtracted from the burette reading. The percentage of nitrogen in the sample is then calculated as follows:

$$\frac{(\text{ml. of } 0.02\, N \text{ HCl used})(0.28)(100)}{\text{weight of sample}} = \% \text{ of nitrogen},$$

where 0.28 is the number of mg. of nitrogen equivalent to 1 ml. of 0.02 *N* acid.

The Friedrich Method for N–N, NO, and NO_2 Linkages. Substances containing N–N, NO, and NO_2 linkages must be pretreated before Kjeldahlization. In the case of nitro and nitroso groups there are several ways to bring about the necessary reduction, but since the Friedrich method is the only one of general applicability capable of handling all three functional groups, it is presented.

Approximately 10 mg. of substance weighed upon a cigarette paper as previously indicated, is placed in a digestion flask; 1 ml. of constant-boiling hydriodic acid is added, and the mixture is gently refluxed for 45 minutes. More heat is then applied until approximately 0.7 ml. of the hydriodic acid has been slowly distilled from the flask; 0.5 g. of potassium sulfate, 1 ml. of water, and 1.5 ml. of sulfuric acid are added to the concentrate; and the mixture is heated on the digester until most of the water has been removed. After the digest has been cooled, 1 ml. of water is again added and the distillation is repeated. (The purpose of this operation is to remove with steam the liberated iodine, and if this is not accomplished with 2 ml. of water another ml. may be added and the process repeated.) The digest is then cooled and 40 mg. of mercuric oxide is added, after which the kjeldahlization and distillation are completed in the usual way.

Discussion of the Method. Cups with appropriate handles may be made to advantageously dispense the mercuric oxide and the potassium sulfate.

Samples of solid materials, permanent in the air, are most easily weighed upon a tared piece of cigarette paper. This paper, with the sample, is then slipped into the digestion flask with the other reagents and the combustion is started at once. The paper not only does no harm but actually aids in the digestion process as a fairly efficient reducing agent. Elek and Sabotka,[3] using sugar as a carbohydrate reducing agent, have proposed a very satisfactory method for the Kjeldahl determination of nitrogen in certain types of nitro compounds, *i.e.*, those not highly nitrated. In this procedure the semimicro charge used for the digestion is 10 mg. of substance, 40 mg. of mercuric

[3] A. Elek and H. Sabotka, *J. Am. Chem. Soc.* **48**, 501 (1926).

oxide, 0.5 g. of potassium sulfate, 100 mg. of sugar, and 3 ml. of sulfuric acid. Heat must be applied cautiously until the initial foaming subsides, after which the digestion is conducted as usual. The quantity of alkali required to render the digest alkaline, and a new blank on the reagents must be determined.

As stated above, the method is satisfactory for the type of compounds here suggested but contrary to the claims of its authors, results on highly nitrated products are always low.

Much misunderstanding exists as to the time necessary to remove the ammonia quantitatively from the digest after it has been rendered alkaline. Experiments conducted to clarify this point have shown that under the conditions of the determination the quantity of distillate recommended to be collected is ample. For example, digests containing 5 mg. of ammonia were distilled at different rates. In all cases the first 4 ml. contained most of the ammonia, the fifth ml. gave a good test (Nessler's reagent), the sixth gave only a faint test, and the seventh was negative.

The object of adding sodium thiosulfate with the alkali is to convert the mercury used as a catalyst to mercuric sulfide. The complex substances formed by mercuric sulfate and ammonia are not readily decomposed by alkali; therefore, if the mercury is not removed, low values are likely to result. Sodium thiosulfate is efficient for this purpose and is convenient when used in the manner indicated. Neuberg[4] gives the following equation for the reaction:

$$\mathrm{Hg}\begin{array}{c}\mathrm{NH_3}\\ \diagup \qquad \diagdown\\ \diagdown \qquad \diagup\\ \mathrm{NH_3}\end{array}\mathrm{SO_4} + \mathrm{Na_2S_2O_3} + \mathrm{H_2O} \rightarrow \mathrm{HgS} + \mathrm{Na_2SO_4} + \mathrm{(NH_4)_2SO_4}.$$

He suggests that the thiosulfate may be used in the solid form in the proportion of 2 parts of crystalline salt to 1 part of mercuric oxide. However, the method indicated is preferable. In neutralizing the digest mixture it is necessary to have an excess of alkali present, but not enough to decompose the mercuric sulfide. When this happens the mixture usually turns yellow and metallic mercury distills into the receiver. During distillation the contents of the distilling flask should always be black from the mercuric sulfide.

The recommended boric acid procedure has been exhaustively tested and has been found to be entirely satisfactory, as many published reports have indicated. Its accuracy is as high as the classical method, and its advantages are that measurement of an excess of standard acid is not necessary, no

[4] C. Neuberg, *Beitr. Chem. Physiol. Path.* **2**, 214 (1902).

standard alkali is required, and faint or uncertain end points due to the effect of carbon dioxide are not encountered. In most cases where results have been unsatisfactory they appear to have been due to excessive quantities of boric acid and indicator and attempts to reach a so-called neutral end point. In titrations of this type the end point should be the change in color from the indefinite intermediate neutral range to a distinct pure color formed by an excess acid. Under the conditions of the above procedure 0.01 ml. of 0.01 N acid brings this about.

The concept that the Kjeldahl method is inapplicable to many compounds is generally prevalent. At times this appears in the literature as a direct statement but most frequently it is implied where the nitrogen in many simple compounds is determined by the less convenient Dumas method. The Kjeldahl procedure undoubtedly has its limitations, but only the cases of certain semicarbazones have come to the author's attention. Some of the alkaloids and related compounds require longer digestion than is specified in the above procedure, but they do yield their nitrogen to the Kjeldahl method. For example, it has been found that the atropine and quinine types of alkaloids require 2 hours' digestion for complete kjeldahlization and a quantitative yield of nitrogen. In general, however, the Kjeldahl method as here modified has a wider range of usefulness than any other procedure.

The use of samples of the order of 5–10 mg. assumes that they are weighed upon a balance accurate to 0.02 mg. If such an instrument is not available, the usual analytical balance may be used with equal success provided samples of about 20 mg. are taken. The procedure and quantity of reagents are the same as directed for 10 mg. samples except that it is expedient to use 0.04 N acid for titration.

The Kjeldahl method is especially well adapted to the determination of nitrogen in solutions, extracts, or biological fluids. An accurate procedure has been published[5] for the determination of urea in Folin-Wu blood filtrates in which the apparatus here described was used. In connection with the development and use of this method there emerged a more convenient indirect way of obtaining the same results. From a clinical standpoint the findings are very precise.

The number of mg. of non-protein nitrogen in 100 ml. of blood is determined by the Kjeldahl procedure upon 5 ml. of the Folin-Wu filtrate. Fifteen mg. subtracted from this value gives the number of mg. of urea nitrogen per 100 ml. of blood.

[5] Clark and Collip, *J. Biol. Chem.* **67**, 621 (1926).

CHAPTER IV

THE DUMAS METHOD FOR THE DETERMINATION OF NITROGEN

The principle involved in the determination of nitrogen by the Dumas method is that of burning a substance with the aid of cupric oxide in an atmosphere of pure carbon dioxide and collecting and measuring, over strong potassium hydroxide solution, the nitrogen thus formed. The procedure is frequently spoken of as an absolute method, but it is no more so, in so far as it is universal, than is the Kjeldahl method. It has advantages as well as disadvantages. Two of the former that might be mentioned are first, it is indispensable for the analysis of a certain limited number of compounds. A case in point is that in which Pregl[1] states that the diazoketones, $R \cdot CO \cdot CHN_2$, cannot be analyzed by any other known procedure; and second, it is desirable as a means of checking the Kjeldahl method in doubtful cases. Some of the obvious disadvantages are that the method is not rapid when only an occasional determination is required; some substances have a tendency to form non-combustible nitrogenous charcoals which cause low values; and certain compounds cannot be analyzed by the method at all. Some of these circumstances leave no choice as to the procedure to be used, but with the great majority of substances encountered, it will be determined largely by the analyst's preference. Whichever he may decide upon, the fact remains that the Dumas method is an integral part of a system of organic analysis.

Apparatus. The apparatus required for the determination consists of a combustion furnace, a properly filled combustion tube in which the sample is burned, an azotometer to collect and measure the nitrogen, and a carbon dioxide generator. The assembly of these items is shown in Fig. 15.

The Combustion Furnace. This determination, as well as that of carbon and hydrogen, is arranged to utilize commercial apparatus as far as possible. The split core type combustion furnace mentioned in the carbon and hydrogen determination is very desirable, but the box-type furnace, also described, will do equally as well. The only disadvantage it has is that a little more time is required to cool the apparatus between repeated determinations.

As mentioned in the carbon and hydrogen determination, the split core type furnace requires a collar of heavy copper tubing placed over the combustion tube outside the furnace and forward of the sample. It is used as a burning unit and is heated with a gas burner. It, or the box burner unit, is synonymous with the burner in either type furnace.

[1] Pregl, page 87.

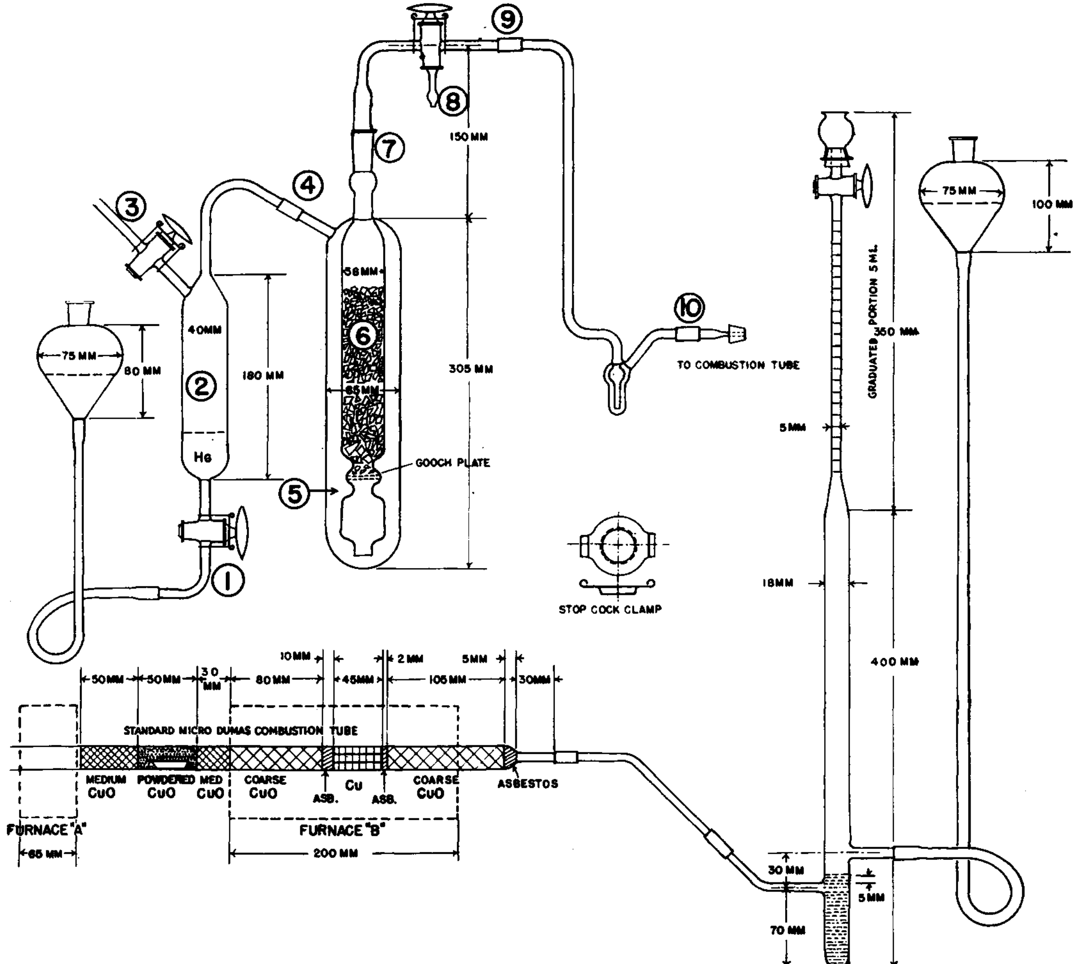


FIG. 15
Apparatus for the Determination of Nitrogen by the Dumas Method

The Tube Filling. Commercial micro pyrex Dumas nitrogen combustion tubes are available from most supply houses. They are the best to use since they are standardized as to size and shape and are made of special glass to withstand the conditions to which they must be subjected. The filling of the tube consists of two reagents, copper oxide and granular copper. Copper oxide is recommended in three grades. The first, or coarse grade, is 28 gauge copper oxide wire broken into 2 to 5 mm. lengths. The medium grade is copper oxide wire broken sufficiently to pass a 40 mesh sieve, and the third is a powder which will pass a 60 mesh sieve. Before using these preparations they should be strongly ignited in oxygen for at least two hours. The oxygen is then replaced with carbon dioxide, and after a time the reagents are permitted to cool in the continued stream of carbon dioxide. The preparations should be placed in small containers and stored in a tight fruit jar, or other such device, filled with carbon dioxide.

Granular copper is prepared from the medium sized oxide by reduction with hydrogen. A quantity of the oxide, placed in a tube through which hydrogen passes, is moderately heated in a combustion furnace. Under these conditions the oxide is readily and completely reduced.

The drawing in Fig. 15 indicates the relative positions of the various reagents when filled, ready for the combustion. Starting from the end of the tube to be attached to the azotometer, coarse copper oxide and the granular copper are held in position by plugs of asbestos. It is referred to as the permanent filling since it is not changed during many determinations. The remainder is changed for each determination and hence is designated as the temporary filling.

The Azotometer. This part of the apparatus is patterned after the standard microazotometer, but is larger. The narrow graduated section has a capacity of 5 ml. and can be readily read to 0.01 ml. Further specifications can be ascertained from the drawing. Unfortunately, no semimicro azotometer has yet been placed on the market and must be built. It is not difficult to do, however, as it may be made from an accurate 10 ml. burette, the stopcock of which is removed and sealed to the top end of the instrument. The blank space between the graduations and the cock should be roughly 0.5 ml. The burette tip is removed and the graduated portion is sealed at the 5 ml. mark to the large section of the apparatus. The graduated portion and the blank space between the cock and the zero mark are then accurately calibrated. Mercury is placed in the lower part of the instrument so that its level is 5 mm. above the gas inlet side tube and the rest of the azotometer is filled through the leveling bulb with Pregl's so-called 50 per cent potassium hydroxide solution.[2]

[2] Pregl, page 76.

This reagent is prepared by dissolving 200 g. of potassium hydroxide in 200 ml. of water. Five grams of finely powdered barium hydroxide are then added and the mixture is shaken occasionally for several hours. After the insoluble material has settled, the clear supernatant liquid is decanted and is ready for use in the azotometer.

The Carbon Dioxide Generator. The only necessary qualification of a carbon dioxide generator of whatever design is that it yield a pure product. Such carbon dioxide, when passed at the usual speed into the column of strong alkali in the azotometer, quite suddenly disappears except for so-called micro bubbles. These are of only pin point dimensions when they reach the top of the apparatus and yield no measurable quantity of residual gas during two to three hours' run.

Several good generators have been described[3] and others, equally as effective, have been seen. The one shown in the figure and to be described is preferred simply because it is easy to make and is readily portable.[4]

The carbon dioxide is formed by the action of dilute hydrochloric acid upon prepared marble. Clean, dense marble, broken into pieces that will pass through the ground joint (7), is immersed in water in a beaker covered with a watch-glass, and alternately boiled and cooled for several days. It is then placed in (6), the ground joint (7) is sealed with glyptol resin[5] (8) is closed and (5) is three-fourths filled with approximately 20 per cent hydrochloric acid. A few small pieces of marble are dropped through (4) to permit the evolved carbon dioxide to help sweep the acid free of air. The mercury reservoir (2) is connected with (5) through (4) by means of prepared rubber tubing. Short sections of good grade antimony (red) rubber tubing are immersed in molten paraffin contained in a round-bottomed flask heated on a steam bath. The system is evacuated with an oil pump until gas ceases to be evolved, after which the vacuum is removed. The flask is then left on the steam bath for another half hour, when the tubing is removed and thoroughly wiped inside and out. Rubber tubing thus treated and used for connections will not cause contamination of pure carbon dioxide. The ends of the glass tubing at this connection, as well as at (9) and (10), should be flush with each other and covered with cellogrease (or a similar stopcock lubricant). The cocks (1), (3), and (8) should be equipped with stopcock clamps as shown.[6]

When the apparatus is assembled (1) and (8) are closed, and an oil vacuum pump is connected to (3) and (8), (closed). At first the evacuation

[3] E. J. Poth, *Ind. Eng. Chem., Anal. Ed.* **3,** 202 (1931); O. R. Trautz and J. B. Niederl, *ibid.* **3,** 151 (1931), and E. W. Lowe and W. S. Guthmann, *ibid.* **4,** 440 (1932).

[4] E. P. Clark, *J. Assoc. Official Agr. Chem.* **16,** 575 (1933).

[5] T. P. Sager and R. G. Kennedy, Jr., *Physics* **1,** 352 (1931).

[6] See A. F. Roe, *Science* **77,** 566 (1933).

through (3) must be carefully controlled with a screw pinch clamp, but after a good vacuum is attained the clamp is removed. After the system has been pumped for 10 minutes (3) is closed and (8) is opened, which causes the acid to rise in (6) to the marble. The vacuum connection to (8) is closed for a short time by pinching the rubber connection to the pump and then suddenly releasing it and closing it in such a way that the acid surges onto the marble and generates sufficient carbon dioxide to cause some of it to pass out of (6) through (5) and into (2). At first, however, care must be taken that the reaction is not too violent. Several repetitions of this process will cause sufficient carbon dioxide to accumulate in (2) to produce a pressure equal to or slightly higher than that of the atmosphere. In filling (2) with carbon dioxide, (1) is cracked from time to time to determine by means of the flow of the mercury the pressure in B. When atmospheric pressure is attained, (1) is opened and the pressure in (2) is adjusted to approximately 10 cm. of mercury by means of the leveling bulb. The bubble counter and connection (10) leading to the combustion tube is then attached and the apparatus is ready for use.

Charging the Tube. To charge the tube for a combustion it is taken from the furnace and all but the temporary filling is removed. A section of about 70 mm., immediately before the asbestos plug holding the granulated copper, is filled with coarse copper oxide. This is followed with a 20 mm. section of medium oxide and 10 mm. of the powdered oxide. The boat containing 15 to 25 mg. of substance, depending upon its nitrogen content, is then filled with copper oxide powder and introduced into the tube next to the filling already introduced. More of the oxide powder is added and the tube is rotated so as to intimately mix the sample and the powder. More powdered oxide is added to well cover the boat and is finally followed by a 30–50 mm. section of medium oxide. This completes the charge, and the tube is replaced in the furnace. The azotometer and the carbon dioxide generator are connected and the combustion is started.

The Combustion. The burner is placed some distance forward of the boat, and heat is applied to both the burner and the combustion furnace. The potassium hydroxide is removed from the azotometer by lowering the leveling bulb and opening the stopcock. A fairly rapid stream of carbon dioxide is then passed through the system to completely flush out the air. As soon as a dull red heat is attained in both heating sections, the potassium hydroxide solution is returned to the azotometer and it is observed to see whether the residual bubbles from the absorption of the carbon dioxide are pin-point size. If not, the system requires further sweeping out, but if they are, the azotometer is completely filled with the potassium hydroxide solution, including some in the reservoir above the stopcock. The rate of flow of carbon dioxide is reduced to approximately 1.5 ml. per minute and the burner is moved toward the sample. As the latter becomes sufficiently hot, combustion of the substance begins, as is indicated by a more rapid flow of carbon dioxide into the azotometer. The burning, controlled by the rate at which the burner is caused to approach the sample, must be such that a slow even stream of gas is evolved. Approximately twice as many bubbles as come from the generator is a desirable speed, and at such a rate approximately 20 minutes is required for the actual combustion.

When the burning is completed, the rate of flow of the bubbles passing into the azotometer reassumes that set by the generator. The heating in both units is then discontinued,* and a fairly rapid stream of carbon dioxide is passed through the tube in order to sweep all the nitrogen into the azotometer. When the residual bubbles become pin-point in size, as in the beginning of the operation, the procedure is completed. The azotometer is disconnected, and after a few minutes the volume of gas is read.

In calculating the percentage of nitrogen in the sample the following formula is used:

$$\text{Wt. of nitrogen in mg.} = \frac{1.2507\,(V)\,(P - P')\,(273)}{(760)\,(273 + t)},$$

$$= \frac{(0.4493)\,(V)\,(P - P')}{(273 + t)},$$

where V = the corrected azotometer reading; P = the barometric pressure; P′ = the aqueous tension of the potassium hydroxide solution used; and t the temperature of the gas.

The values for P′ for the potassium hydroxide solution prepared as directed are approximately those shown in Table VIII.†

In the usual micro Dumas method several corrections are applied to the nitrogen volume as read. As indicated by Trautz[7] these are: (1) the occluded air in the temporary filling, (2) the wall error of the azotometer, (3) the contamination of the carbon dioxide, and (4) the vapor pressure of the potassium hydroxide solution. In the procedure outlined only the first of these is significant. The copper oxide used as the temporary filling, when prepared and stored as recommended, contains only a very small quantity of occluded gas not absorbed by the potassium hydroxide solution. This value, however, should be determined for each lot of reagent, and also on the same lot after an appreciable interval of time. This is done by burning a

* If the split core type furnace is used, it is opened and removed from the tube.

† The solution upon which these values were obtained was made from a good C. P. grade of potassium hydroxide containing 16.5 per cent moisture. 100 ml. of the solution contained 61.5 g. of potassium hydroxide.

[7] O. Trautz, *Mikrochemie* **9**, 300 (1931).

sample of nitrogen-free substance under the conditions governing a regular combustion. Concerning the other three factors enumerated it has been found that an azotometer of the size described has, after 15 minutes, no measurable wall error; the carbon dioxide from the generator, assembled as outlined, or any other equally as good, is of such purity that no measurable residual gas is formed during a combustion; and finally, the formula suggested for calculating the nitrogen formed involves the correction for the vapor pressure of the potassium hydroxide solution.

Notes. Previous to the popularity of the Kjeldahl method for the determination of nitrogen in research compounds, the Dumas method was used almost exclusively. For this reason it is undoubtedly true that many more substances have been analyzed by the latter than by the former method.

TABLE VIII

The Vapor Pressure of Pregl's so-called 50 Per Cent Potassium Hydroxide Solution at Temperatures from 15° to 35°C.

t	P′ in mm.	t	P′ in mm.
15	5.5	26	9.3
16	5.7	27	9.8
17	6.0	28	10.4
18	6.4	29	10.9
19	6.7	30	11.4
20	7.0	31	12.0
21	7.3	32	12.6
22	7.6	33	13.1
23	8.0	34	13.6
24	8.4	35	14.0
25	8.9		

However, little real improvement was made in the method until Pregl began to apply it to micro quantities. The many inherent errors of the macro method then became significant and efforts were undertaken to correct them. This resulted in what is now a very efficient procedure. The main improvements are good sources of carbon dioxide, a modified filling containing metallic copper, alkali which does not foam, and the use of more copper oxide mixed with the sample to assure complete combustion.

There are various procedures and modified techniques but they all recognize the above factors and are largely a question of the analyst's preference. Some time ago the writer[4] described an outline in which the operation was similar to the carbon and hydrogen determination in that the sample was placed in a loaded copper cartridge which was introduced into the combustion tube. This enabled repeated determinations to proceed without cooling the main furnace or removing the tube. This method gave results which were entirely satisfactory. The present outline is essentially that of the older one and has deviated from it only in so far as is necessary to employ standard micro equipment.

Some chemists prefer to use ground joints on each end of the combustion tube and to evacuate the charged tube with a high vacuum oil pump. Several such evacuations, followed by filling with pure carbon dioxide, remove all residual air from the temporary filling and do not require the introduction of a reagent blank.

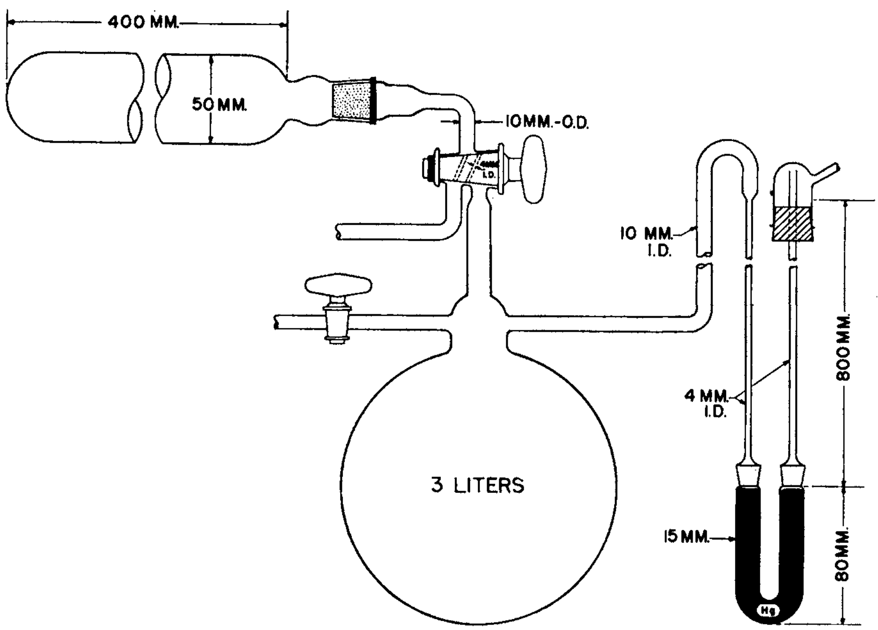


FIG. 16
Carbon Dioxide Generator in which the Gas is Evolved by Heating Sodium Bicarbonate

The problem of the preparation of pure carbon dioxide has been solved in several ways. Besides the action of acid upon marble, or upon potassium bicarbonate solution, other methods have been used and are recommended. One such[8] employs solid carbon dioxide with adequate safety devices. Several generators have been seen in operation in which carbon dioxide is obtained by heating sodium bicarbonate. These set-ups appeared somewhat awkward but they gave a very high grade gas.

A suggestion for a generator of this type is submitted in Fig. 16. It is

[8] E. B. Hershberg and G. W. Wellwood, *Ind. Eng. Chem., Anal. Ed.* **9**, 303 (1937).

simple to build and is fairly compact. A high vacuum oil pump evacuates the system, the cock is then closed and gentle heat is applied back and forth to all the bicarbonate until the apparatus is filled with carbon dioxide. It is again evacuated and the process repeated. Two or three such operations give a gas of the high grade required. A pressure of approximately 25 cm. of mercury is a satisfactory head for operation.

It should be borne in mind, however, that there is little difference in the choice of generators provided they give a high grade gas. Exceptions may occur where one form may be more easily assembled than another, but otherwise it is largely a question of an analyst's personal choice.

Very satisfactory combustion boats for the determination are made by bending copper foil to the usual shape. The dimensions suggested are 45 × 5 × 5 mm. They may be cleaned after each determination by reduction with hot methanol. A boat is heated to redness and quickly dropped into a small test tube containing a drop of methanol. The alcohol immediately ignites, and is almost completely consumed. As soon as the flame recedes within the tube, the latter is connected to a vacuum line and the whole system is allowed to cool and dry under reduced pressure.

CHAPTER V

THE DETERMINATION OF HALOGENS

There are undoubtedly more methods for the determination of halogens in organic compounds than for any other element. As a rule, such circumstances result from attempting to improve inadequate procedures, but in the present case this is not so. The reason is found entirely in the fact that the halogens readily lend themselves to quantitative reactions. The various procedures are quite diversified in principle and also in applicability, but, in all cases, the operation consists of destroying the organic compound and converting the halogen into ionic form in which state it is estimated. Some of the methods are of a general character, while others are for specific purposes. One or the other may have certain operative advantages, but they seldom differ greatly in accuracy. Examples of both types will be detailed, and the choice is then left to the analyst to decide which best answers his particular needs. The first procedure to be discussed is the Rauscher ethanolamine method which undoubtedly ranks as first in importance.

THE ETHANOLAMINE-SODIUM METHOD

This method, published by Rauscher,[1] has been shown by him to have general application, and his results have been quite thoroughly tested. By this procedure all three halogens in either aliphatic or aromatic combination are readily converted to ionic halogens which are then determined gravimetrically. The method is not only reasonably rapid, but requires very simple apparatus and technique, all of which commends it as one of the best available procedures.

Outline of Method. Approximately 25 mg. of substance contained in a 25 ml. 14/20 ground joint, round-bottomed flask is dissolved in 1 ml. of dioxane and 2 ml. of ethanolamine. A 150 mm. Liebig condenser is attached, 0.25 g. of sodium is added, and the mixture is refluxed 0.5 hour, or until the sodium is dissolved. Upon cooling, 10 ml. of water and 4 ml. of concentrated nitric acid are added through the condenser. If appreciable solid material from the reaction separates, the liquid is filtered. If not, or only a turbidity is formed, the liquid is transferred to a small beaker and the flask is thoroughly washed with water. The total volume of the final liquid should be about 30 ml. It is then treated with an excess of 0.1 *N* silver nitrate solution, gently heated on the steam or sand bath to coagulate the silver halide, and set aside in the dark to settle and clear.

In the meantime sintered glass filter tubes are prepared for collecting the

[1] W. H. Rauscher, *Ind. Eng. Chem., Anal. Ed.* **9**, 296 (1937).

precipitate. Mats of asbestos, about 1 mm. thick, made from an aqueous suspension of long, soft asbestos fibers, are laid uniformly upon the sintered plates of the filter tubes. These are tamped in place with a glass rod, washed further with water, then with alcohol, and finally dried at 125°. When removed from the oven they are cooled in the open and weighed. In the latter operation one of the prepared tubes is used as a tare.

When these are prepared and the reaction mixture is ready to filter, the precipitates are transferred to the filter tube by Pregl's syphon filtering apparatus, page 15. The precipitate is washed first with water, then with acetone, and finally with alcohol. Acetone is specifically used in this operation to remove any organic material resulting from the dehalogenation process. The tare should be treated exactly as the tube or tubes containing silver halide. All tubes are then dried, cooled, and weighed as before. The silver halide found gives the information necessary for calculating the percentage of halogen in the sample.

Notes. Commercially available dioxane contains appreciable quantities of halogen and must be purified before use.

Three hundred ml. of dioxane, 15 ml. of ethanolamine, and 5 g. of sodium are refluxed for three hours. The condenser is then changed for distillation and the bulk of the dioxane is distilled. The product contains some ethanolamine, but for the purpose for which it is used it is unimportant. Ethanolamine, even after redistillation, also appears to contain traces of halogen. Two ml. of the amine usually gives a blank of 0.24 mg. of silver halide. Blanks should, therefore, be run on new lots of reagents.

At times more dioxane than specified is required to dissolve the sample. This does no harm even to the extent of two to three extra ml. of solvent.

Non-volatile liquids may be weighed in small glass boats; more volatile ones may be weighed in sealed ampules and crushed under the reagent before adding the sodium. Danger from loss of such samples may be avoided by delaying the boiling and allowing a longer reaction time.

Rauscher[2] also reported a modification of his method which permits the determination of aliphatic and aromatic halogens in the presence of each other. It is undoubtedly a useful procedure for certain problems. The method, however, is really one for determining active and inactive halogens.

THE CARIUS METHOD

The Carius method for the determination of halogens is an old and reliable one. In its macro form it has been more widely used in the past than any other. It is easily performed, the reactions are straightforward, and the results are accurate. However, it is not entirely general in its applicability for the literature records compounds that cannot be analyzed by it. There

[2] W. H. Rauscher, *Ind. Eng. Chem., Anal. Ed.* **9**, 503 (1937).

are also other compounds whose analysis involves so much difficulty that other methods are preferable. Such substances, fortunately, are relatively few, so that in general the method is an excellent one to employ.

The reactions involved in the determination consist of burning the substance in a sealed tube with fuming nitric acid in the presence of silver nitrate. These conditions cause the organic halogen to be converted to silver halide. This, when collected and weighed, gives the information necessary for the calculation of the percentage of halogen in the sample.

The semimicro method is essentially the same as that used in the macro system except that approximately 20 to 25 mg. samples are employed. It entails only a corresponding refinement in weighing the sample and the resulting silver halide and the use of apparatus of appropriate size.

Apparatus. Specifications for the equipment required are presented in Fig. 17. The bomb furnace consists of a cylindrical section of aluminum or other metal (A) provided with wells to contain the bomb tubes and thermometer. It is surrounded with a heating coil and insulator and is provided with a heavy, loose-fitting, cast iron protective cap (B). Heat is applied from a 110-volt power line and is regulated by a 45-ohm sliding resistance.*

Bomb tubes of either pyrex or soft glass of the size indicated have never failed at 300°C. The design of the sample tube (c) with the small rod attached is chosen to prevent silver halides from adhering to the bomb tube. This difficulty frequently occurs when an ordinary sample tube rests on the bottom of small-bore Carius tubes.

Procedure. The bomb tube is charged with approximately 60 mg. of silver nitrate crystals and 0.3 ml. of fuming nitric acid. The sample tube, containing approximately 25 mg. of substance in the form of a tablet, is inserted in the bomb tube, which is then sealed and placed in the furnace. The length of the tube should be such that about 1 cm. of the sealed capillary end extends into the recess of the loose cap (B). The temperature of the furnace is gradually raised to 300°C. at which point it is kept for several hours. The usual procedure is to charge the furnace in the morning; bring it to the required temperature, which is maintained during the remainder of the working day; then allow it to cool during the night. The next morning the tube is opened,† and the silver halide is washed into a small beaker and

* This apparatus is now available from the American Instrument Co., Silver Spring, Md.

† The same precautions should be observed in opening the tubes as are used in the macromethod. The cap B is carefully removed, and, with a hand torch, a small hot flame is applied to the sealed tip of the capillary. When the glass softens it is blown out as the internal pressure is released. The tube is then removed, scratched with a glass knife about two inches from the bottom and broken in the usual way with a hot tip of a glass rod.

transferred by the syphon filtering apparatus to a filter tube. The procedure to be followed is the same as indicated in the Rauscher method. The silver

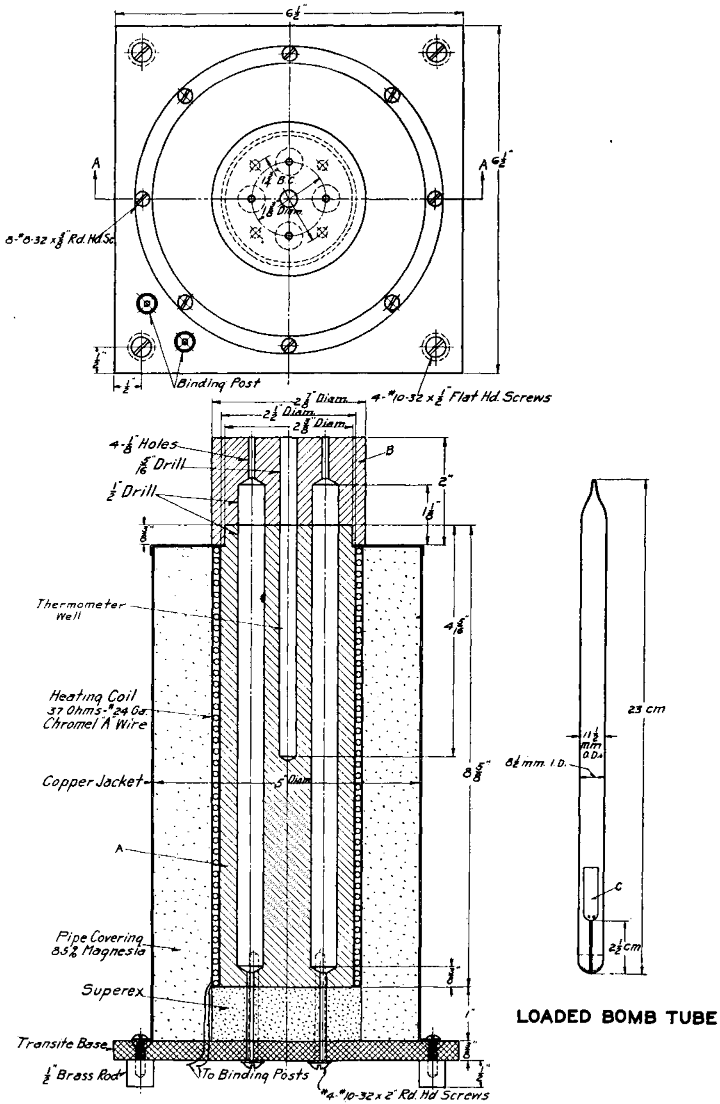


FIG. 17
Semimicro Carius Furnace

halide is well washed, first with water then with alcohol, and dried at 125°C. The tube is removed from the oven, cooled to room temperature in the open, and weighed. In this operation another tube, prepared and treated exactly the same as the one containing the silver halide, is used as a tare. This point is again emphasized here as the operation compensates for moisture adsorbed by the asbestos pad and frequently eliminates an otherwise appreciable error.

Note. In lieu of a Carius furnace as described, a simple substitute made of two concentric pieces of gas pipe is satisfactory. The temperature of the device can be easily controlled with a small gas flame and is rapidly heated and cooled. As a safety precaution, when in use, it should be shielded and placed in a hood or in some out-of-the-way place. Fig. 18 shows its construction.

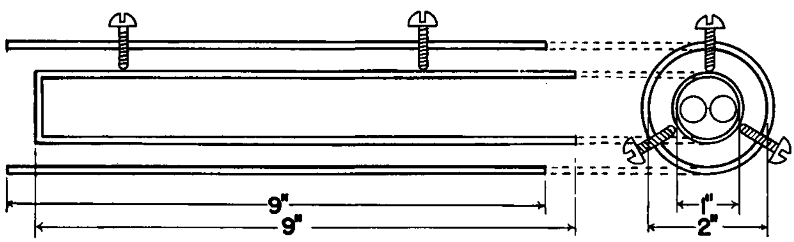


FIG. 18
Inexpensive Substitute for Carius Furnace

THE SODIUM PEROXIDE FUSION METHOD

The two foregoing procedures are the most important ones, but others of more restricted applicability are equally as useful.

Perhaps the most popular of these is the sodium peroxide fusion method devised by Pringsheim[3] and later refined by American chemists. This method, adapted to semimicro quantities, is satisfactory for chlorine and iodine, but in the writer's hands it fails for bromine. The reason for this has not been ascertained, although much time has been devoted to it. The problem appears to be paradoxical since the macromethod gives entirely satisfactory results. Chlorine may be determined quickly and accurately either gravimetrically or volumetrically, but iodine is best determined volumetrically.

Principle of the Method. The reaction involved in the fusion is the destruction of the organic material with sodium peroxide which converts any chlorine to sodium chloride and iodine to sodium iodate. These ionic halogens are then treated in different ways, depending upon circumstances. The solution of the fused mass from chloro compounds is boiled, acidified, filtered, precipitated with an excess of silver nitrate, and the resulting silver

[3] H. Pringsheim, *Ber. chem. Ges.* **36**, 4244 (1903).

chloride is collected and weighed. If the method is to be volumetric, the boiled, acidified solution is precipitated with an excess of standard silver nitrate solution, the silver chloride is removed by filtration, and the excess silver is titrated with standard potassium iodide, using starch and iodine as an indicator. When iodine is concerned, the solution of the fusion mixture is boiled and treated with sodium bisulfite to quantitatively remove traces of hydrogen peroxide. The liquid is then acidified and the iodine reoxidized to iodate and titrated.

Method. The reaction is carried out in a Parr micro peroxide fusion bomb. This is essentially a special alloy 14 $\times$ 30 mm. cup and lid which can be securely sealed.

Twenty to twenty-five mg. of material is placed in the bottom of the Parr bomb and is covered with a 1 g. measure of the sodium peroxide fusion mixture.* The bomb is quickly sealed and, while held with a pair of crucible tongs, a fine hot flame from a jeweler's oxygen torch is applied to a single point near the top of the fusion mixture. In a moment the mixture ignites. This can always be recognized by a characteristic sensation through the tongs. Immediately the bomb is cooled in a little water in a crystallizing dish, after which it is opened and placed in a 100 ml. tall form beaker. Just enough water is added to cover the bomb, a watch glass is placed over the beaker and the liquid is gently heated until a fairly rapid reaction occurs. When the fused mass is dissolved the cup is removed and washed and the solution is boiled for a few minutes to decompose the hydrogen peroxide formed. Subsequent operations depend upon the halogen under investigation and the method by which it is to be determined.

Chlorine. *A. Gravimetric:* The solution is boiled until effervescence ceases. It is then acidified with nitric acid (approximately 2.5 ml.) and filtered. An excess of silver nitrate is added and the mixture is heated in the usual way to coagulate the silver chloride. The latter is then collected on a filter tube and washed with water and alcohol. It is dried and weighed as previously directed for silver halide and the results calculated to the percentage of chlorine in the sample.

* This reagent is an intimate mixture of 10 g. of sodium peroxide, 1.2 g. of powdered potassium nitrate and 0.45 g. of granulated sugar. [See J. F. Lemp and H. J. Boderson, *J. Am. Chem. Soc.* **39**, 2069 (1917).] It may be prepared by shaking the ingredients in a glass stoppered bottle amply wrapped with a towel. A safer way is to mix the materials in a macro Parr bomb if one is available. While the preparation is an explosive mixture, no case is known where it has spontaneously ignited if kept dry. Nevertheless, extreme caution should be exercised in handling it. It should be kept dry. It should not be weighed, but dispensed with a measure since it is very hygroscopic and no more should be prepared at a time than is to be immediately used. A safety glass shield should be interposed between the operator and the stock fusion mixture during handling and dispensing.

B. Volumetric: The volumetric procedure is the same as above to the point where nitric acid is added. From here on, an excess of standard silver nitrate solution (1 ml. equivalent to 1 mg. of chlorine) is added and boiled to coagulate the silver chloride. The clear solution is filtered through a sintered glass filter and collected in a 125 ml. Erlenmeyer flask. About 2 ml. of starch indicator and a fresh saturated aqueous solution of iodine,* in the proportion of one volume of the reagent to five of the filtrate, is added. The liquid is titrated with a standard potassium iodide solution to the appearance of a blue color. From the relationships between the quantity of standard silver nitrate and potassium iodide used, and the actual titer of the silver nitrate, as well as the volume ratio between both standards, the quantity of chlorine is readily calculated.

Iodine. The volumetric iodine determination is conducted in the same way as directed for chlorine to the point where the solution of the fusion mass is boiled until effervescence ceases. From here on the procedure is as follows: Two ml. of a 10 per cent sodium sulfite solution is added and the liquid is gently boiled for 10 minutes, then cooled. Three ml. of acetic acid and 15 drops of bromine are added and the liquid is thoroughly stirred until all sulfite is oxidized and it has a deep reddish brown color due to bromine. After 5 minutes, the excess of bromine is reduced with about 8 drops of concentrated formic acid, and any bromine vapor is removed from the flask with a current of air. Finally 0.5 g. of potassium iodide, and 10 ml. of 10 *N* sulfuric acid is added and the liberated iodine is titrated with .05 *N* thiosulfate solution. One-sixth of the iodine represents the quantity present in the sample.

Notes. The silver nitrate-potassium iodide titration is very sensitive and has a wide range of usefulness. It may be employed in any determination in which it is possible for an element or group to be converted to an equivalent quantity of ionic silver.

Silver nitrate and potassium iodide are permanent in dry air and can thus be weighed as dry salt. However, it may be preferable to determine the silver content of the standard solution gravimetrically and check the potassium

* This reagent is prepared by shaking pure powdered iodine with several 200 ml. portions of water acidulated with sulfuric acid. A saturated distilled water solution of the washed iodine is then made by vigorously shaking the two components together. If the iodine is very pure the resulting reagent will give no blue color with starch; but if a color does develop, dilute silver nitrate solution is added portionwise until the point is just reached at which no color is produced. The principle involved in the use of this indicator is that *pure iodine does not give a blue color with starch*, but the minutest trace of an iodide reacts with iodine to form KI_3, which is responsible for the well known blue starch and iodine color reaction. The removal of iodides by washing the powdered iodine with water is at times successful, but with some specimens this can be accomplished only by adding sufficient silver ions.

iodide against it. Silver nitrate solution will keep indefinitely if properly protected, and the potassium iodide standard keeps very well also. The iodide solution should have the same molal concentration as the silver nitrate.

In titrating silver against an iodide the end point is reached when all silver ions are removed. When this occurs further iodide immediately reacts with free iodine of the indicator to form KI_3 which in turn produces a blue color with starch. The iodine indicator solution is not stable, especially in light, and therefore should not be used for more than a few hours. As its preparation requires only a few minutes, no inconvenience is caused by its frequent renewal.

The reactions involved in the volumetric iodine determination are those outlined by Vieböck and Breckner[4] which Vieböck and Schwappach[4] employed so effectively in their volumetric alkoxyl determinations. They are explained in Chapter VIII.

THE LIEPERT VOLUMETRIC METHOD FOR IODINE

The Liepert volumetric iodine method as given by Friedrich[5] is an accurate, refined procedure and is frequently preferred to all others. The method consists in burning the sample with oxygen in a platinum-filled combustion tube and collecting the liberated iodine in 5 per cent sodium hydroxide solution. The iodine is oxidized to iodate, which is reacted with an excess of acid and potassium iodide, and the liberated iodine is determined with thiosulfate.

Specifications for the apparatus adapted to semimicro conditions are presented in Fig. 19. The combustion tubing is the same as that recommended for the determination of carbon and hydrogen and the fillings conform to the dimensions of the combustion furnace previously described.

Procedure. Approximately 10 to 25 mg. of material in a platinum boat is placed in the combustion tube and burned as described in the carbon and hydrogen determination except that the Mariotte bottle is not used. The end of the combustion tube has a long bent tip which dips into 5 ml. of 5 per cent sodium hydroxide solution contained in a test tube. At frequent intervals a small flame is applied to the iodine, which collects in the cool portion of the constricted end of the combustion tube and is driven past the right-angled bend. When the combustion is completed and the tube (except the portion which dips into the alkali) is swept free of iodine, the connection to the oxygen supply is replaced by a small rubber tube; with slight suction from the mouth applied to the tube, the alkali is drawn repeatedly over the

[4] F. Vieböck, and Associates, *Ber. chem. Ges.* **63**, 2818, 3207 (1930).

[5] A. Friedrich, Die Praxis der quantitativen organischen Mikroanalyse, p. 102 (1933).

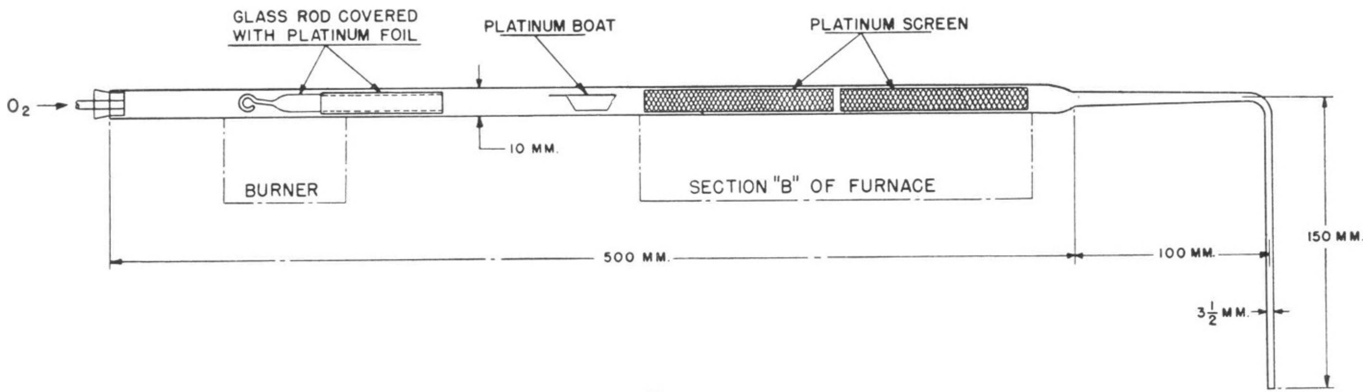


FIG. 19
Tube Filling for the Determination of Iodine by the Liepert Method

iodine until it is dissolved. By the same procedure the tube is then washed several times with a few ml. of water. To the combined alkaline liquid and washings is added 5 ml. of a 10 per cent solution of potassium acetate in glacial acetic acid and followed by 0.1 ml. of bromine (10 drops of bromine from a medicine dropper with a tip 2 mm. outside diameter and a 1 mm. bore). The liquids are thoroughly mixed and diluted to approximately 100 ml., after which the remaining bromine is reduced with a few drops in excess of 90 per cent formic acid. One-half gram of potassium iodide is then dissolved in the liquid, about 5 ml. of 10 per cent sulfuric acid is added, and the liberated iodine is titrated with 0.05 *N* thiosulfate. One-sixth of the iodine liberated represents the iodine in the original sample.

ALIPHATIC IODINE

Aliphatic iodine may be determined more rapidly and conveniently by utilizing the reactions involved in the alkoxyl determination than in any other way. The reactions are

$$\text{(A)} \qquad RI + Br_2 \rightarrow RBr + IBr$$

$$\text{(B)} \qquad IBr + 2Br_2 + 3H_2O \rightarrow HIO_3 + 5HBr$$

After the process is completed the iodine is determined in the same manner as outlined in the Liepert method. The semimicro procedure follows:

Approximately 20 mg. of substance is weighed upon a tared piece of cigarrette paper 12 × 25 mm. The paper and its contents are placed in a 25 × 140 mm. test tube, and 10 ml. of a 10 per cent solution of potassium acetate in glacial acetic acid containing 0.1 ml. of bromine is added. If the sample dissolves immediately it is allowed to stand for 5 minutes after which the liquid is heated to boiling and permitted to cool for 15 minutes. If the sample does not dissolve readily, it is heated at once and allowed to stand for 15 minutes. Liquids are conveniently weighed in sealed, small bore, melting-point tubes, which are then crushed in the bromine reagent. From this point the procedure is the same as that for solids. After the indicated time, 150 ml. of water is used to wash the reaction mixture into a flask containing 5 ml. of a 25 per cent aqueous sodium acetate solution. Sufficient 90 per cent formic acid is then added to reduce the excess bromine, after which 1 gram of potassium iodide and 5 ml. of 10 per cent sulfuric acid are added. The liberated iodine is titrated with 0.05 *N* thiosulfate, one-sixth of which represents the quantity of iodine in the sample.

CHAPTER VI

THE DETERMINATION OF SULFUR

All methods for the analysis of organic sulfur involve the complete oxidation of the substance and the determination of the resulting sulfuric acid. The usual procedure for estimating the acid is to convert it to barium sulfate and weigh it as such. There are several ways of doing this but the most popular appears to be the Carius method in which the oxidation and formation of barium sulfate is accomplished in one operation. This is brought about by heating the substance in a sealed tube with fuming nitric acid and barium chloride. The resulting barium sulfate is removed from the bomb and after certain purifications it is weighed.

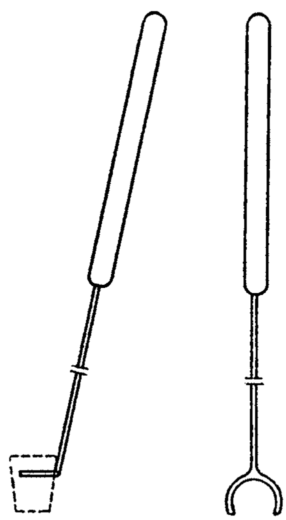


FIG. 20
Hooks for Handling Micro Platinum Crucibles

Both micro and macro methods involving this outline are largely used and, in studying possibilities for a semimicro procedure, it appeared to be the best all-around choice. Such a procedure has been developed[1] and has been used sufficiently to conclude that for general purposes it is entirely satisfactory.

Apparatus. The apparatus required for the method is the same as that described in connection with the determination of halogens by the Carius method except that standard micro platinum Gooch crucibles with asbestos pads are used in place of the sintered glass filtering tubes.

Procedure. A sample of the material, made into a pellet of approximately 25 mg., is placed in the sample tube, which is introduced into the glass bomb containing approximately 100 mg. of barium chloride and 0.3 ml. of fuming nitric acid. The bomb tube is sealed, heated to 300°C. for 6 hours or more, cooled, and opened, and the barium sulfate is transferred to a 30 ml. beaker in the manner described in the directions for halogens. The contents of the beaker are evaporated to dryness, on a sand bath, and the residue is treated with 10 ml. of 5 per cent hydrochloric acid. The liquid is again evaporated to dryness, after which the residue is digested with hot water, and the barium sulfate is transferred to a weighed

[1] E. P. Clark, *J. Assoc. Official Agr. Chem.* **18**, 476 (1935).

platinum Gooch crucible with the aid of a small stirring rod, a fine stream of water from a wash bottle, and a little alcohol.

The crucible is prepared by placing in it a mat of asbestos, washing it with water and alcohol, heating to redness for 5 minutes, cooling upon a brass block, and weighing it in the same manner as directed for glass filter tubes in the preceding chapter. Another crucible prepared and treated like the one in which the barium sulfate is collected must be used as a tare. The heating is done most conveniently in a porcelain crucible placed in an electric heater, such as a Cenco hot-cone heater. The introduction and removal of the crucible are best done with a small hook, as shown in A, Fig. 20, made of No. 15 B & S gauge wire. A similar straight hook, shown in B, is convenient for placing crucibles on the balance and removing them.

After the barium sulfate has been transferred, the crucible is heated to redness, cooled, and washed with 5 per cent hydrochloric acid. The crucible is again heated to redness, allowed to cool, and weighed. The percentage of sulfur in the sample is calculated from the quantity of barium sulfate found.

Note. A micro method employing a sodium peroxide fusion for converting sulfur to sulfate has been described by Elek and Hill.[2] According to these authors, this procedure gives satisfactory results and should therefore be readily adapted to semimicro quantities. The author has had no experience with the method, but as soon as opportunity permits, it is his intention to investigate it.

[2] A. Elek and D. W. Hill. *J. Am. Chem. Soc.* **55**, 3479 (1933).

Chapter VII

The Determination of Phosphorus

The determination of organic phosphorus is analogous to that of sulfur in that the organic material must be destroyed and the phosphorus oxidized to a state (orthophosphate) that can be estimated. Some of the methods available for the oxidation are Kjeldahlization with sulfuric acid and hydrogen peroxide or nitric acid, or both; fusion with nitrate and potassium hydroxide; and sodium peroxide fusion.[1] Of these the Kjeldahl procedure requires less attention and offers advantages. The alkali-nitrate fusion is rapid, but frequently causes spattering, while the sodium peroxide fusion method is rapid and straightforward. However, certain experiences with the Kjeldahl and sodium peroxide methods have led the writer to question these, especially the Kjeldahl procedure.

The latter is an old and often used method but is subject to the criticism that phosphoric acid may be lost by volatilization in the digestion process. Furthermore, the conditions to which the digest is subjected may form meta or pyrophosphates. The sodium peroxide fusion method gives complete combustion without question, but it probably also yields meta or pyrophosphates which, after acidification, require considerable boiling to convert them to orthophosphates. Whatever may be the true circumstances, the writer's limited experience with organic phosphorus has been of such a nature that these controversial subjects have been neglected and the alkali-nitrate fusion method, which has always given accurate results, has been adopted.

THE ALKALI-NITRATE FUSION METHOD FOR CONVERTING ORGANIC PHOSPHORUS TO ORTHOPHOSPHATE

For semimicro quantities the alkali-nitrate fusion method is conducted as follows: Twenty to fifty mg. of material, depending upon the phosphorus content, is placed in a silver crucible and intimately mixed with about 0.7 g. of a powdered 4–1 mixture of potassium hydroxide and potassium nitrate. A small silver rod, flattened at one end, is used for mixing the components and is left in the crucible. The mixture is then covered with 0.5 g. more of the alkali-nitrate reagent and the fusion is begun. Heat from a small burner is gently applied to the top of the crucible in such a way that the reaction is slowly but steadily controlled until foaming largely ceases. More heat is then applied until the mass becomes completely oxidized as shown by its white appearance. Upon cooling it is dissolved from the crucible, transferred to a

[1] A. Elek and D. W. Hill, *J. Am. Chem. Soc.* **55,** 3479 (1933).

125 ml. Erlenmeyer flask, with 75 ml. of water, acidified to congo red with nitric acid, and slowly simmered until its volume is 50 ml. These operations convert the phosphorus to orthophosphates in which condition it may be estimated.

WOY'S PROCEDURE FOR WEIGHING THE PHOSPHORUS AS PHOSPHOMOLYBDIC ANHYDRIDE

It is preferred to determine the phosphorus, converted to inorganic form, by the method of Woy.[2] This is done by precipitating the phosphate as ammonium phosphomolybdate and, after purification, it is converted to and weighed as phosphomolybdic anhydride. The reason for choosing this method is that the operation is simple, the product has a definite composition, $P_2O_5 \cdot 24MoO_3$, and above all, it eliminates the ritual and the arbitrary factors involved in the micro methods of Lieb and others.[3] It is of interest that Woy accurately determined quantities of phosphorus well within the range of present day micro methods.

Several reagents to be immediately described are required for the procedure.

Reagents Required for Woy's Method

1. Aqueous ammonium molybdate solution, 30 g. of salt in 1 liter.
2. Aqueous ammonium nitrate solution, 340 g. of salt in 1 liter of solution.
3. Twenty-five per cent of nitric acid.
4. Wash liquid. An aqueous solution containing 50 g. ammonium nitrate and 40 ml. nitric acid in water to make 1 liter.
5. Aqueous 8 per cent ammonia solution.

Formation of the Yellow Precipitate. The neutralized digest from the fusion, having been concentrated to 50 ml., is treated with the required quantities of 25 per cent nitric acid and ammonium nitrate reagent, approximately ascertained from Table IX.

The solution is heated just short of boiling and the required quantity of ammonium molybdate solution, heated to boiling, is added. This is done by whirling the phosphate solution and adding the molybdate reagent to the center of the rotating liquid. The whirling is continued for one minute, then it is set aside to cool. The yellow precipitate forms at once and the separation is quantitative. After the liquid is cooled, the precipitate is separated from its mother liquor by decantation through a small filter and washing the flask and precipitate upon the filter with several portions, in all about 30 ml., of wash liquid. It is then dissolved from the filter with 10 ml. of 8 per cent ammonia and the solution is collected in the flask containing the bulk of the

[2] R. Woy, *Chem. Ztg.* **21**, 441 (1897).

[3] Pregl, page 126.

yellow precipitate. The filter is washed first with 30 ml. of water followed with 20 ml. of ammonium nitrate solution. One ml. of ammonium molybdate solution is added to the filtrate, the liquid is heated just short of boiling, and is reprecipitated as outlined above by adding 20 ml. of hot 25 per cent nitric acid.

After the mixture cools, the precipitate is transferred with the syphon filtering apparatus to a previously heated (525°C.) and weighed filter tube with an asbestos mat. The precipitate and the flask are washed with the special wash liquid and finally with alcohol. The filter tube is heated to approximately 525°C. in a muffle, or other convenient apparatus, until the yellow precipitate changes to a steel blue color. This indicates that the reaction is complete. The tube is then removed from the furnace, cooled in

TABLE IX

Quantities of Reagents Required to Precipitate P_2O_5 as the Yellow Precipitate

mg. P_2O_5 Present	ml. of NH_4NO_3 Sol.	ml. of 25 per cent HNO_3	ml. of Ammonium Molybdate Sol.
10	20	10	15
5	20	10	15
2	15	5	10
1	15	5	10

the open, and weighed. Another tube, treated exactly as that with the sample, is used as a tare.

The product is phosphomolybdic anhydride whose composition is $P_2O_5 \cdot 24MoO_3$. The factor for its phosphorus content is 0.01724 (log. 23654), therefore the percentage of phosphorus in the sample is given by the expression

$$\frac{(\text{Wt. of } P_2O_5 \cdot 24MoO_3)\ (.01724)\ (100)}{\text{Wt. of sample taken}} = \%\ \text{P}.$$

Note. The reprecipitation of the yellow precipitate is essential for two reasons: First, it accomplishes a purification; and second, it renders the precipitate filterable by the syphon arrangement. The phosphomolybdate when first precipitated adheres tenaciously to the flask and cannot be removed by the syphon method. However, when it is washed, dissolved, and again reprecipitated, no trouble is encountered.

CHAPTER VIII

THE DETERMINATION OF METHOXYL AND ETHOXYL GROUPS

The most satisfactory method for the determination of alkoxyl groups is the slightly modified volumetric procedure of Vieböck and Schwappach.[1,2]

The operations consist of the hydrolysis of the ether linkage with hydriodic acid and phenol according to the equation

$$\acute{R}OR + HI \rightarrow \acute{R}OH + RI$$

The alkyl iodide thus formed is swept through the apparatus with carbon dioxide and collected in an acetic acid solution of potassium acetate containing bromine. Under these conditions the following transformations occur in which the iodine is oxidized to iodate.

$$\text{(a)} \qquad RI + Br_2 \rightarrow RBr + IBr.$$

$$\text{(b)} \qquad IBr + 2Br_2 + 3H_2O \rightarrow HIO_3 + 5HBr.$$

The latter is determined in the following way: The reaction mixture is diluted with water, a sodium acetate buffer is added, and the excess bromine is destroyed with formic acid. When this is done the liquid is acidified with sulfuric acid, potassium iodide is added, and the liberated iodine is titrated with thiosulfate. Thus one alkoxyl group is equivalent to six atoms of iodine.

Apparatus and Reagents. The apparatus recommended for performing this determination on a semimicro scale is shown in Fig. 21. Also the following special reagents are required:

1. A glacial acetic acid solution of potassium acetate in which 10 g. of the salt is dissolved in sufficient glacial acetic acid to make 100 ml.
2. An aqueous sodium acetate solution in which 25 g. of the salt is dissolved in sufficient water to make 100 ml.
3. Ninety per cent formic acid.
4. Bromine free from iodine.
5. Constant boiling hydriodic acid.
6. Phenol.

Procedure. Approximately 10 mg. of substance is weighed upon a tared piece of cigarette paper 12 × 25 mm. The paper and its contents are placed in the bottom of the boiling flask, A, together with a boiling rod.* Two ml.

[1] Vieböck and Schwappach, *Ber. Chem. Ges.* **63**, 2818 (1930).

[2] E. P. Clark, *J. Assoc. Official Agr. Chem.* **15**, 136 (1932); **22**, 622 (1939).

* The boiling rod used here is a glass tube approximately 60 mm. long, 3.5 mm. outside diameter, with a 1 mm. bore. It is sealed at one end and also closed about 10 mm.

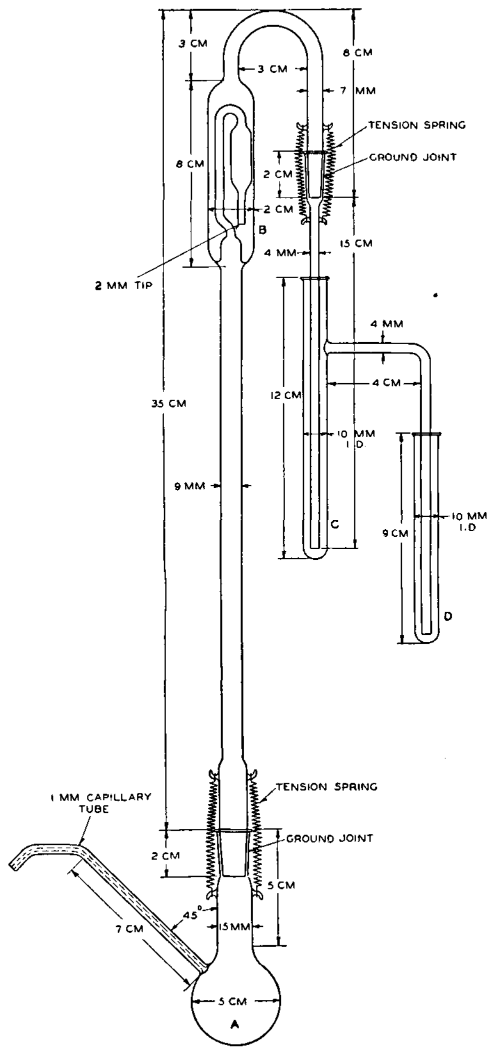


FIG. 21
Semimicro Alkoxyl Apparatus
(Courtesy Journal Association of Official Agricultural Chemists)

of constant boiling hydriodic acid and one ml. of melted phenol are added. The flask is connected by tension springs to the remainder of the apparatus which consists of the trap, B, containing a little water, and the receivers C

from the other. The open end is fire polished. When this is placed in the flask with the open end down, it will cause uniform boiling indefinitely so long as sufficient heat is constantly applied to the liquid.

and D. The receivers contain 5 ml. of the acetic acid solution of potassium acetate to which has been added 10 drops of bromine (about 0.1 ml.). Approximately two-thirds of the bromine reagent is placed in C and the remainder in D. Carbon dioxide is passed through the apparatus from the capillary side arm of the boiling flask at a uniform rate of about 25 bubbles a minute and the liquid is gently boiled by means of a mantled micro burner that will cause the vapors of the boiling liquid to rise about half way up the air condenser. Usually 45 minutes is sufficient for quantitative hydrolysis and is the time generally allowed unless indications point to an unusual circumstance.

The apparatus is then disconnected and the contents of the receivers are carefully washed into a 250 ml. Erlenmeyer flask containing 5 ml. of the 25 per cent aqueous sodium acetate solution. The excess bromine is reduced with 8 to 10 drops of 90 per cent formic acid. Any bromine vapor in the flask is removed by drawing air over the liquid from a vacuum line or by blowing air over the solution. The contents of the flask are then diluted with water to approximately 100 ml. Five-tenths of a gram of potassium iodide and 5 ml. of 10 per cent sulfuric acid are added and the liberated iodine is titrated with 0.05 N thiosulfate solution. From the equations given before, 1 ml. of 0.05 N thiosulfate is equivalent to 0.2586 mg. of methoxyl (OCH_3) or 0.3754 mg. of ethoxyl (OC_2H_5).

Notes. Tank carbon dioxide is the most convenient source of this gas if it is used in connection with a pressure regulator of the type employed in the carbon and hydrogen determination. The pressure should be equivalent to a 25 cm. column of water. The gas outlet from the regulator should have the following accessories in the order given; a glass stop-cock, a bubble counter, and a rubber connection in which is inserted a section of #16 gauge wire. Fine adjustment is obtained by a screw clamp on the section of the tubing containing the wire.

Hydriodic acid, as ordinarily prepared, readily decomposes and as a consequence it frequently contains appreciable quantities of free iodine. For the purpose at hand such a reagent is undesirable, first, because of the danger of some iodine passing through the apparatus and reacting with the bromine reagent; and second, because any liberated iodine causes the hydriodic acid to be proportionately diluted.

Another consideration concerning the hydriodic acid is that all samples, which have been tested, give an appreciable blank when used for alkoxyl determinations.

By treating commercially available hydriodic acid according to the outline which follows, a colorless acid solution, largely if not entirely free from alkoxyl blank, can be obtained.

One pound of constant boiling hydriodic acid solution, contained in a liter flask with a ground-in air condenser, is heated to 100° and treated with 5 ml. of 50 per cent hypophosphorous acid in excess of that necessary to reduce any free iodine if present. The solution is heated to boiling and a stream of carbon dioxide is passed through the liquid while it refluxes three hours. The condenser is next changed so that the liquid distills and the first 20 ml. of distillate are discarded. The acid which remains in the flask is that which is used in the alkoxyl determination. Although the acid thus prepared

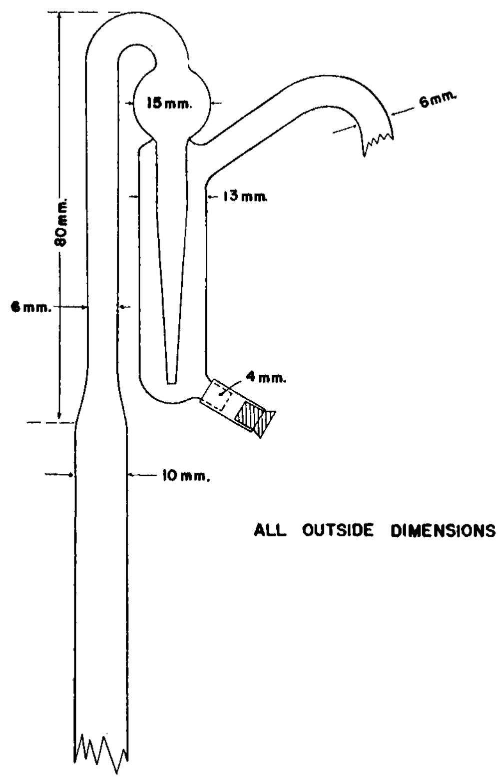


Fig. 22
Alternative Scrubber for Alkoxyl Apparatus

meets the necessary requirements, blanks on all the reagents used in the procedure should be determined.

A convenient method for preparing hydriodic acid[3] for this, as well as for the Friedrich-Kjeldahl procedure, has been published by the writer. Its preparation is little more troublesome than the foregoing purification process but, if good grade reagents are used, it is superior to commercial

[3] E. P. Clark, *Ind. Eng. Chem., Anal. Ed.* **10**, 677 (1938).

products. The preparation of the acid involves the well known reduction of iodine with hypophosphorous acid and the scrubbing of the resulting constant-boiling liquid with carbon dioxide.

For the purpose 254 g. of iodine and 185 g. of water are heated to about 50°C. in a 500 ml. flask with a ground-joint condenser, and 66 g. of 50 per cent hypophosphorous acid are added portionwise at such a rate that the mixture boils continuously until the iodine is reduced. Heat is applied to the flask and the boiling is continued for 3 hours, during which time a stream of carbon dioxide is passed through the solution. The position of the reflux condenser is then changed to allow distillation and the constant-boiling hydriodic acid is collected. The yield is 447 g. The preparation is stored in dark bottles and preserved by the addition of 1 ml. of 50 per cent hypophosphorous acid.

There are many designs of apparatus for alkoxyl determinations, but the one given is very simply fabricated and it can readily be adapted to the determination of higher alkoxyls by slipping a water jacket over the air condenser and scrubber and heating the entire apparatus to the necessary temperature. An alternative design of the scrubber part is shown in Fig. 22. It is more compact but is not suited for the estimation of higher alkoxyls.

As pointed out in the Kjeldahl method for nitrogen, it is assumed that samples of the order of 10 mg. are weighed upon a balance accurate to 0.02 mg. In special fields of work, methoxyl determinations are frequently required in routine processes, and a balance of the type indicated is not available. Where this is so, a regular analytical balance may be used equally as well if 20 mg. samples are analyzed. The procedure and quantities of reagents are the same throughout as given for the smaller samples.

A useful application of the alkoxyl method is that of indirectly determining hydroxyl groups in certain circumstances.

The number of hydroxyl groups in alcoholic or phenolic substances is most frequently ascertained by replacing the hydroxyl hydrogen with acetyl groups and determining the latter. Methods for these analytical procedures are presented in Chapter IX, but they sometimes fail and indirect approaches to the problem must be used. The outline of Hill[4] is often successful. Instead of using acetic anhydride as the acylating reagent, methoxy- or ethoxyacetic anhydride is employed, thus giving alkoxylated derivatives. These, when analyzed for alkoxyl groups, give an accurate and trustworthy answer to the number of acyl groups present.

Ethoxyacetic anhydride is available on the American market. Methoxyacetic anhydride may be readily prepared by the Williamson synthesis, provided a good fractionation column is available for purifying the intermediate methoxyacetyl chloride and also the final anhydride.

[4] D. W. Hill, *J. Am. Chem. Soc.* **56**, 993 (1934).

CHAPTER IX

THE DETERMINATION OF ACETYL GROUPS

Conditions frequently arise that require acetyl (CH_3CO-) determinations. Various natural products are esters of acetic acid, but the substances most frequently encountered are acetyl derivatives of hydroxylated compounds prepared for the purpose of finding the number of hydroxyl hydrogens substituted by acyl. An acetyl determination on such materials, together with other information, is usually sufficient to show the number of hydroxyl groups present in the mother substance.

Most of the available acetyl methods are grouped in two classes. The principle involved in the first consists of aqueous acid hydrolysis followed by the distillation and estimation of the acetic acid formed; in the second class alcoholic acid hydrolysis is followed by the distillation of the resulting ethyl acetate along with the excess of alcohol, and finally the estimation of the acetyl in the ethyl acetate by hydrolysis with an excess of standard alkali. This is frequently spoken of as the transesterification procedure.

The first type is inapplicable to many classes of compounds, because aqueous acids will not affect hydrolysis. The second type of procedure is, in general, more reliable and simple when applied to macro samples, but for small quantities it fails because the ethyl acetate cannot be completely hydrolyzed without employing a standard alkali solution too strong to yield accurate results. Both procedures also suffer from the fact that they are too time-consuming, or the apparatus or manipulative details required are too complicated.

The semimicro procedure to be presented[1] is based upon a different principle and is largely free from the disadvantages enumerated. With few exceptions it has given uniformly good results with all compounds upon which it has been tried, and its accuracy is also well within the range for which it is intended. The method involves (1) the hydrolysis of the acetyl compound with *N* ethanolic potassium hydroxide; (2) the dilution of the reaction mixture to a definite volume with strong magnesium sulfate solution acidified with sulfuric acid; and (3) the distillation and titration of the liberated acetic acid. The first operation must be done differently, depending upon whether the substance under investigation is an O- or an N-acetyl compound. Otherwise the procedure is the same for all acetates.

Apparatus. The apparatus required for the determination is shown in Fig. 23 and is self-explanatory. It will be recognized that the steam generator is the same as used in the Kjeldahl nitrogen determination.

[1] E. P. Clark, *Ind. Eng. Chem., Anal. Ed.* **8,** 487 (1936); **9,** 539 (1937).

Method. *O-Acetyl Compounds.* A 10 to 20 mg. sample of the material to be analyzed is weighed upon a 12 × 24 mm. piece of cigarette paper and placed, with the paper, in the distilling flask, B. Two ml. of *N* ethanolic potassium hydroxide are then added, and the liquid is heated to boiling or until the sample is dissolved. After 4 minutes 18 ml. of magnesium sulfate-sulfuric acid solution, made by dissolving 100 g. of crystalline salt and 1.5 g. of concentrated sulfuric acid in sufficient water to make 180 ml., are added. Steam, generated in flask A, is then passed through the apparatus, and flask B is heated with a small flame in such a manner that the liquid in

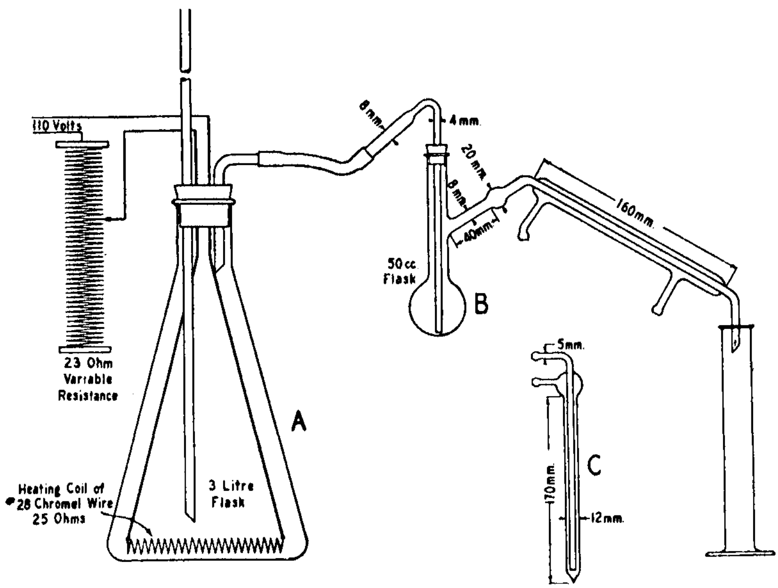


FIG. 23
Apparatus for the Semimicro Determination of Acetyl
(Courtesy Journal Industrial Engineering Chemistry)

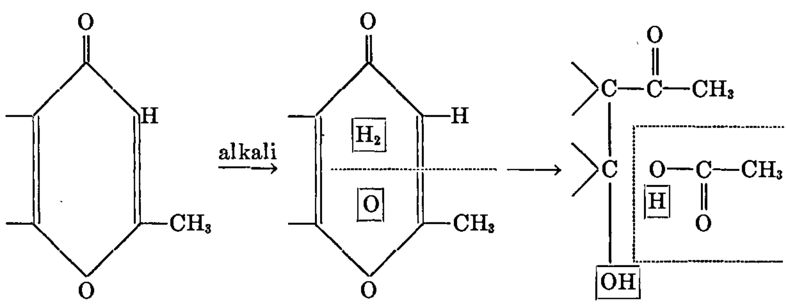
the flask distills at a fairly rapid rate and is concentrated to 15 ml. during the collection of 50 ml. of distillate. The latter is titrated with 0.02 *N* barium hydroxide with phenol red as an indicator. A blank must be run on the reagents and the resulting correction applied to the titration.

N-Acetyl Compounds. By modifying the above procedure it may be applied to many N-acetyl compounds. The sample, placed in the distilling flask, is dissolved in 2 ml. of *N* *n*-butanolic potassium hydroxide solution. The condenser, C, is placed in the flask, and the mixture is refluxed for 1 hour. The procedure is then the same as for O-acetyl compounds.

Notes. As previously indicated, the method, with few exceptions, has given uniformly good results with all compounds upon which it has been tried. These exceptions, however, indicate its limitations, for unsatisfactory results are obtained with substances that react with alkali to give products, which upon acidification, are volatile with steam and will affect the titration. Acetyl salicylic acid may be cited as an example. Free salicylic acid is somewhat volatile with steam, under the conditions of the experiment, and that which passes over is titrated with the acetic acid. The results are well over six per cent of theory. However, this may be overcome by running a blank on an equivalent quantity of the unacetylated acid, and deducting the results from the value obtained upon the acetyl compound. This procedure in general may be utilized with good results.

It is also possible that O-acetyl compounds may be encountered which react slowly because of their insolubility, but which would react upon longer boiling. In such cases correct results should be obtained by running a blank upon the reagents under the conditions of the experiment.

There are still other types of materials which, while not acetyl compounds, give acetic acid upon treatment with alkali. As an example the action of alkali upon certain 1,4 pyrones may be cited.[2]



Here the alkali breaks the pyrone ring to give a mol of acetic acid.

Notwithstanding the fact that the acetyl determination is not as satisfactory nor as precise as could be desired, it is an important analytical tool. The method here presented is more generally applicable and simpler to perform than others and is thus believed to be a real contribution to the subject.

[2] E. Späth and W. Gruber, *Ber. chem. Ges.* **71**, 106 (1938).

CHAPTER X

THE DETERMINATION OF THE NEUTRALIZATION EQUIVALENT

The neutralization equivalent is defined as the number of grams of substance required to neutralize one liter of normal alkali. In micro or semimicro procedures the practical unit is the milligram equivalent, or .001 of the above. The term, therefore, may be called the milligram neutralization equivalent and its definition stated as the number of milligrams of substance required to neutralize 1 ml. of normal alkali.

The determination of the constant is simply the alkalimetric titration of an acid substance or, in other words, the estimation of hydrogen capable of ionization. It is usually considered, and generally is, a determination of carboxyl groups, but this does not always follow, for many non-carboxylated compounds may produce ionic hydrogen even to a greater extent than some true acids and consequently may be titrated. Such values are usually as important as those from acids.

Procedure. Samples of the order of 15 to 30 mg. are weighed upon a small piece of cigarette paper and placed in a 50 ml. Erlenmeyer flask. Ten ml. of water and a drop of phenolphthalein indicator are added and the liquid is titrated to a definite pink with .02 N barium hydroxide solution. If the substance is soluble and the material is a fairly strong true acid, the end point is sharp and is reached at once; if it is insoluble, the liquid is heated and the alkali is added portionwise. In many instances, especially if the acid is a weak one, it is preferable to add an excess of alkali, dissolve, neutralize the acid, and back titrate with acid. This procedure, in general, is the safest and when used cresol red is a better indicator than phenolphthalein. The end point is chosen as the color change from the indefinite intermediate neutral range to a distinct pure yellow formed by an excess of acid. Usually 0.01 ml. of 0.02 normal acid brings this about. Whichever way it is done, the value of the constant is found from the quantity of alkali consumed. An example is presented as a model from which to calculate the results.

23.73 mg. of material required 4.15 ml. of .919 $\times$ .02 normal barium hydroxide solution.

This 4.15 ml. of standard base equals 3.815 ml. of .02 normal, or 7.63 ml. of .01 normal alkali. Therefore if 23.73 mg. of substance requires 7.63 ml. of 0.01 N alkali, 3.11 mg. of substance requires 1 ml. of .01 normal alkali. This follows from the proportion

$$\frac{23.73}{7.63} = \frac{X}{1}; \qquad X = 3.11$$

Since the alkali is 0.01 normal, the neutralization equivalent will be 100 times 3.11 or 311.

If the acid is monobasic the value corresponds to its molecular weight. If, however, it is polybasic the molecular weight will be a submultiple of it.

Notes. As previously indicated, some phenols behave as fairly strong organic acids. When this is true they will frequently titrate to a sharp end point. With others, however, they are too weakly acid to give a definite end point. If both phenolic and carboxyl groups are present, the latter usually titrates rapidly to neutralization, but the end point is not sharp because the phenolic hydroxyl continues slowly to use more alkali. Fairly good estimates of the carboxyl end point may be had but the values are not at all precise.

Lactones are neutralized only slowly, hence with this class of compounds better results are always obtained by using an excess of alkali, heating the solution and then back titrating with acid.

In some instances, the extreme insolubility of a substance makes it expedient to use some alcohol as a solvent. The alcohol should be perfectly neutral, and the volume ratio between the alkali and a standard acid under the exact conditions of the experiment should be ascertained to determine any effect of the alcohol.

CHAPTER XI

THE DETERMINATION OF MOLECULAR WEIGHTS

Two methods for the determination of molecular weights are especially adaptable to a semimicro system of analysis. The most important of these is the Signer method[1] employing the principle of isothermal distillation, while the other is the Rast method[2] based upon the classical freezing point depression law of Raoult.

Of the two, the Signer method as recently improved by the writer[3] is far more reliable and accurate. In fact, the results which can be obtained by the judicious use of the procedure are such that many questions heretofore unanswerable can now be solved with ease.

The Rast method is simple, fairly rapid, and gives good results with certain compounds, but with others it fails. The difficulty is that, except with acids which cannot be determined, there is no way of telling when it is to be relied upon. Nevertheless, valuable data have been obtained with it and the method doubtless will continue to be of importance.

THE SIGNER METHOD

Outline and Apparatus. The experiment consists in permitting two solutions, one a standard and the other the unknown, in an evacuated system, with solvent vapors in contact, to arrive at vapor-pressure equilibrium by isothermal distillation. Arrangements must be available for determining the volumes of each solution. The apparatus used to realize this is shown in Fig. 24. Its dimensions are such as to make possible accurate measurements of 1.5 to 1.7 ml. of liquid. The solutions usually employed are approximately 0.1 molar, from which it follows that the usual quantity of substance necessary for a determination varies from 20 to 50 mg.

Method. The samples of standard and unknown material, in the form of pellets, are weighed and dropped through the open side arms of the apparatus, so that one bulb receives the standard and the other the unknown.

The filling tubes are then constricted near their bases to facilitate subsequent sealing. As soon as the glass cools, 2 ml. of solvent are added to each bulb, after which one tube is sealed at its constriction. As the seal is made, a very gentle stream of dry air should be blown through the tube to prevent vapors of the solvent from coming in contact with the hot glass. The system is then evacuated from a line in which is interposed 1 meter of 1 mm. capil-

[1] R. Signer, *Ann. Chem.* **478**, 246 (1930).
[2] K. Rast, *Ber. Chem. Ges.* **55**, 1051, 3727 (1922).
[3] E. P. Clark, *Ind. Eng. Chem., Anal. Ed.* **13**, 820 (1941).

lary tubing, and in this manner approximately 0.3 ml. of solvent is distilled from each bulb. While distillation continues, the constricted part of the connecting tube is sealed with a soft gas-oxygen flame. The closed evacuated system then contains two solutions containing definite quantities of standard and unknown material arranged as outlined above. Therefore, if the entire apparatus is isothermally insulated, solvent will distill from the solution of greater vapor pressure to the one of less, until equilibrium is established. When this occurs the volumes of the two solutions will be constant and equimolar. These volumes may then be read by tilting the apparatus and draining the solutions into the graduated side arms. Five minutes are arbitrarily taken for this purpose.

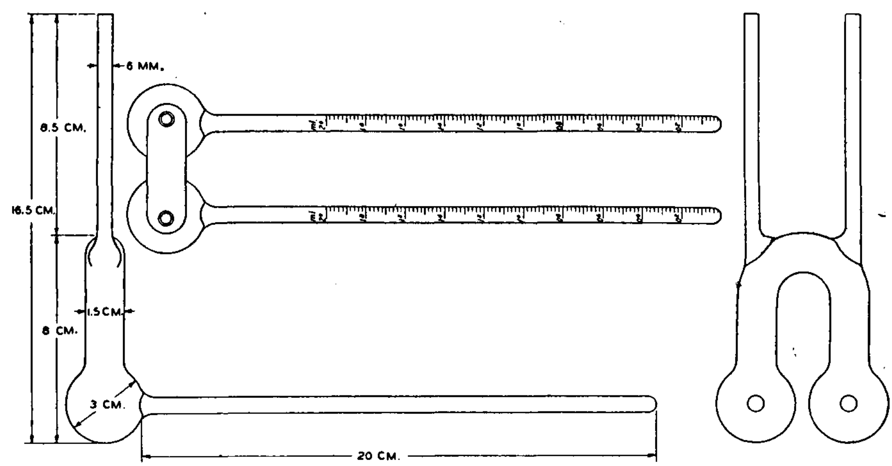


FIG. 24
Signer Semimicro Molecular Weight Apparatus
(Courtesy Journal Industrial Engineering Chemistry)

With the data thus available, it follows from Raoult's law that

$$M_1 = \frac{G_1 M V}{G V_1}$$

where M, V, and G are, respectively, the molecular weight, volume of solution, and weight of the standard, and M_1, V_1, and G_1 are the corresponding values of the unknown. In practice, the volumes are read every 1 to 3 days, depending upon the solvent used, until they become constant. The results thus obtained may be plotted (volume against time) and, if the experiment is progressing normally, smooth typical curves are obtained as presented in Figs. 25, 26, and 27.

The essential experimental factor in this determination is the maintenance of the apparatus in an isothermal condition. A very simple way to do this is to conduct the experiment at room temperature in a heavy metal container, such as an aluminum pressure cooker, which has a high thermal

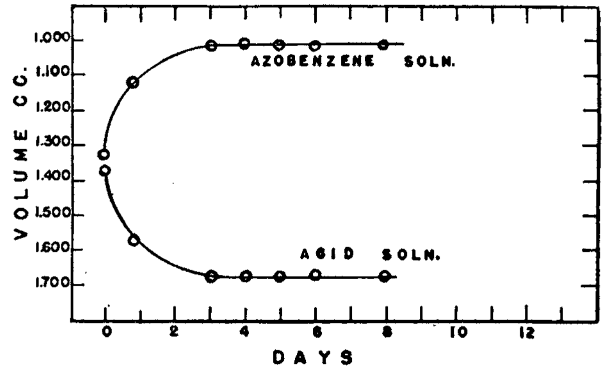


FIG. 25
Azobenzene—*o*-Chlorobenzoic Acid
Solvent, ether; solutions, 0.1416 molar at equilibrium. Molecular weight of *o*-chlorobenzoic acid 156.5; found 158

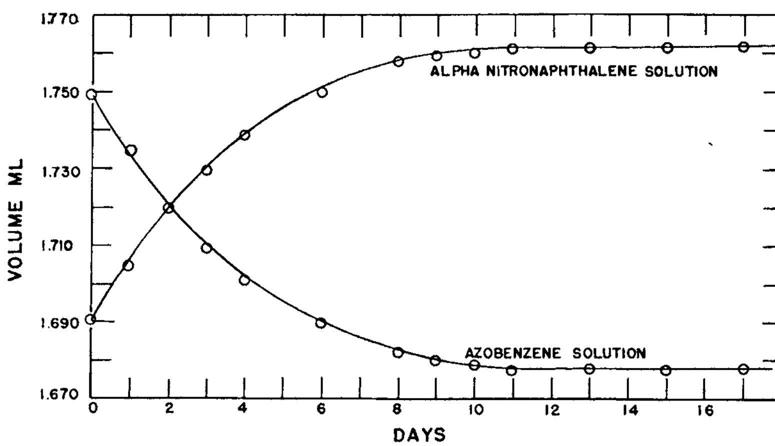


FIG. 26
Azobenzene—α-Nitronaphthalene
Solvent, acetone; solutions, 0.0932 molar at equilibrium. Molecular weight of α-nitronaphthalene 173.1; found 173.7

conductivity. Under these conditions the time necessary for a pair of solutions to reach equilibrium is greater than at elevated temperatures, but the simplicity of the procedure and the accuracy of the results warrant its use. The duration of the experiment is also dependent upon the concentration of the solutions, their relative molarity when prepared, and the solvent used. The best solvents are those with high vapor pressures. Table X gives a list of suggested solvents with their boiling points at standard conditions.

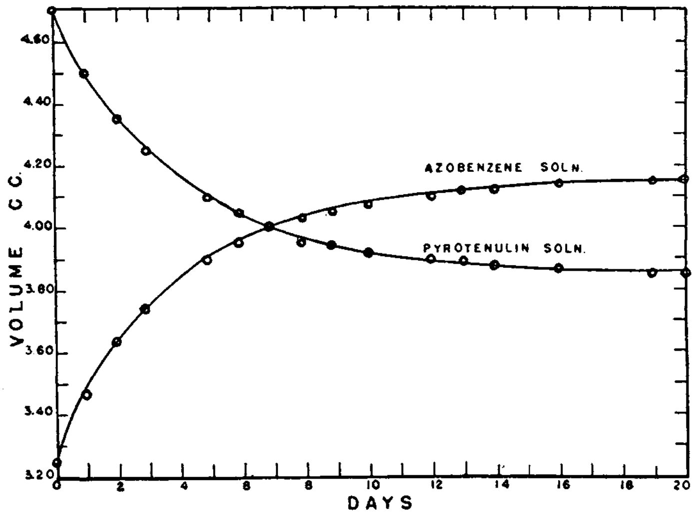


FIG. 27
Azobenzene-Pyrotenulin
Solvent, chloroform; solutions, 0.1367 molar at equilibrium. Molecular weight of pyrotenulin 288.3; found 288.4

TABLE X

Suggested Solvents for Signer Molecular Weight Determination and their Boiling Points at Standard Conditions

Substance	B. P.
	°C.
Ethyl ether	34.5
Ethyl bromide	38.
Methylene chloride	40.1
Ethyl formate	54.3
Acetone	56.5
Methyl acetate	57.1
Chloroform	61.3

Azobenzene is an excellent standard where organic solvents are used. It is easily purified, is permanent in the air, and is readily soluble in most solvents, and the color of its solution distinguishes it from the unknown.

Notes. An examination of Figs. 25, 26, and 27 gives a fair approximation of the rate of distillation of several solvents at a temperature of 25 to 27°C.

They adequately show the relationship between the rate of distillation and the vapor pressure of the solvents used. The temperature effect upon distillation may, in a rough way, be had by comparing the time necessary for a pair of acetone solutions of approximately the same molarity to come to equilibrium at 30° and 40°C. In the first case seven days were required, while at 40° equilibrium was established in only three days.

Work is in progress attempting to devise a means of working at higher temperatures so that other solvents, as benzene, dioxane, and pyridine may be used. The approach that is being followed is to allow the tubes to come to equilibrium in a sealed heavy copper container immersed in a relatively hot constant temperature water bath. Results so far obtained indicate that the method will be successful, but several mechanical difficulties will have to be overcome before a final statement can be made.

THE RAST METHOD

The Rast method for the determination of molecular weights is based upon the well known principle of the depression of the freezing point of a

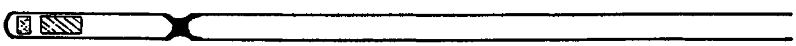


FIG. 28
A Sealed Rast Semimicro Molecular Weight Tube
(natural size)

solution. It is unique, however, in that camphor is used as a solvent. This compound, because of its large freezing point depression constant, permits the determination to be performed with an ordinary thermometer and melting point apparatus.

Method. In the semimicro system of analysis a solution whose composition is of the order of 5 mg. of material dissolved in 50 mg. of camphor is used for a determination. The difference between the melting point of this and the pure solvent gives the value Δ in the classical molecular weight formula. These values are determined by the outline that follows:

The sample and camphor as a tablet and cylinder respectively, made with the $\frac{1}{8}$ inch tablet machine, page 13, are sealed in the bottom of a thin-walled, soft glass tube, 4 mm. inside diameter, Fig. 28. A satisfactory way by which this may be done is to wrap the tube for a distance of 15 mm. from its closed end with several layers of filter paper, dip it in water for cooling purposes, and seal the tube 10 mm. above the wet paper with a fine oxygen flame. The next operation is to melt the camphor and obtain a homogeneous solution of the two components. The camphor may be melted by placing the tube in a glycerine bath at 180° and solution of the sample is best accomplished by withdrawing and vigorously shaking the mixture. Since the melt quickly solidifies, the process must be repeated several times until complete solution is obtained. Preliminary to the melting point determination, the burner for the melting point apparatus is adjusted to raise the temperature of the circulating bath 1°C. per minute within a range of 5°C. near the fusion point of the solution. It is also necessary to adjust a light source behind the bath to give a bright, diffused beam through the melt. The tube containing the solution is then attached to a long-stemmed thermometer, graduated from 140 to 230°C. in 0.2°C. divisions (a commercially available size) and placed in the melting point apparatus. The bath is quickly heated with an auxiliary burner to approximately the fusion point of the solution. The adjusted burner is then substituted for the auxiliary one and the heating continued. As the temperature rises (1°C. per minute), the appearance of the solution undergoes a series of characteristic changes until finally individual crystals separate, slowly settle to the bottom of the tube, and melt. For the purpose at hand, the melting point of the solution is defined as the temperature at which the last crystal finally disappears.

Several replications of the value thus obtained are necessary. The melt is sufficiently cooled (usually 1 to 2°) to cause the formation of crystals. Heat is again applied and the melting operation is repeated. The average of all the values obtained is taken as the melting point of the solution.

The entire operation is repeated with the camphor used as the solvent. The difference between the two averaged values is the depression Δ in the molecular weight formula

$$M = \frac{KS}{S'\Delta}$$

where S is the weight in milligrams of the solute; S′ is the weight in milligrams of the solvent, and K, 40,000, is the freezing point depression constant for camphor.

Notes. The constant for camphor is usually given as 40,000, as indicated above. This value, however, appears to vary with the source of the camphor. Some specimens have been known to be as low as 37,000. It is therefore expedient to determine the constant of the camphor used with several pure compounds known to give reliable results. Some common materials satisfactory for the purpose are acetanilide, chloranthraquinone, sulfonal, azobenzene, and naphthalene.

It may usually be assumed that the method is trustworthy if the repeated melting points obtained are consistent. If, on the other hand, each replication gives a value lower than the preceding one, it indicates decomposition and the values are meaningless.

Melted camphor is an unusually good solvent for most organic substances. Because of this, the Rast method has given valuable information on compounds practically insoluble in usual molecular weight solvents. Occasions arise, however, when concentrations less than 10 per cent must be used. This will lessen the accuracy of the result; but even with 5 per cent solutions the values are quite reliable.

Solvents other than camphor, with similar characteristics, have been used for molecular weight determinations and, according to published statements, they have given satisfactory results. Some of these follow:

Pirsch[4] has reported the use of several satisfactory substances among which are camphene, bornylamine, and camphoquinone.

Camphene, M. P. 49°C.; K = 31,000.

It is stated to have good solvent qualities.

Bornylamine, M. P. 164°C.; K = 40,600.

Because of its basic properties it is especially useful for alkaloids and other basic substances.

Camphoquinone, M. P. 190°C.; K = 45,700.

It is said to be useful for substances of high melting points.

Giral[5] recommends exaltone (cyclopentadecanone) for sterols, carotenoids, azo dyes, and many quinones.

Exaltone, M. P. 65.6°; K = 21,300.

Wilson and Heron[6] have recently recommended:

Cyclohexanol, M. P. 24.6°–24.8°C.; K = 37,700.

It is a fairly general solvent, but is unsuited for heavily halogenated compounds.

[4] J. Pirsch, *Ber. Chem. Ges.* **65**, 862, 1227 (1932); **66**, 349 (1933).
[5] F. Giral, *Chemical Abstracts* **29**, 6489 (1935).
[6] H. N. Wilson and H. E. Heron, *J. Soc. Chem. Ind.* **60**, 168 (1941).

CHAPTER XII

THE DETERMINATION OF VOLATILE FATTY ACIDS

The determination of volatile fatty acids is a powerful tool in many fields of chemical and biological work. It may be used in the identification and estimation of volatile acids formed under conditions of food spoilage, in fermentation reactions, and purely organic transformations.

When only one acid is involved the method gives a positive identification and an accurate estimation of it. With a mixture of two acids the same is usually true, but if the determination is not so precise, it is frequently the most accurate one available. When more than two acids are together, some or all of them may be identified and some may be determined. The method has been successfully employed in all types of problems to which reference has been made and is used extensively as a referee method for the evaluation of spoilage in canned fish.[1]

Principle of the Method. The method which was proposed by Dyer[2] is based on the principle that when a dilute solution of a volatile fatty acid is steam distilled at constant volume, there is, at any given stage, a definite and characteristic relationship between the quantity of acid in the flask and that in the distillate. Dyer used a 500 ml. distilling flask and maintained the volume of the liquid distilled at 150 ml. Under these conditions the *distillation constant of an acid* is defined as the percentage of the original acid in the flask that is found in the first 100 ml. of distillate. This may be restated thus: If t = the total acid in the flask; t_1 = the acid in the first 100 ml. of distillate; then the distillation constant

$$C = \frac{100\, t_1}{t}.$$

When, under these conditions, a dilute solution of a pure acid, such as acetic or butyric, is distilled and the percentages of the original acid in given volumes of distillate are plotted against these volumes on semilogarithmic coordinates as indicated in Fig. 29, a straight line is obtained. The slopes of all the lines so obtained for the various acids are different and characteristic. For a mixture of acids a curved line is obtained, and the nature of its slope is, to some extent, indicative of the acids present. These properties are utilized for the identification and determination of the various acids of the group.

[1] F. Hillig and E. P. Clark, *J. Assoc. Official Agr. Chem.* **21**, 688 (1938).
[2] D. C. Dyer, *J. Biol. Chem.* **28**, 445 (1917).

A critical study of the method[3] has revealed that the distillation constants of the various acids depend largely upon the size and design of the apparatus, and to some extent upon the rate of distillation. The values recorded by Dyer are obtained, therefore, only under the exact conditions used by him, and since the instructions given in his paper are inadequate, his results are not reproducible. This is not important, however, for new values may be determined readily with a new ensemble and set of conditions. In fact, it is best for an analyst in this field to use his own assembly and determine the constants of the acids in which he is interested. This

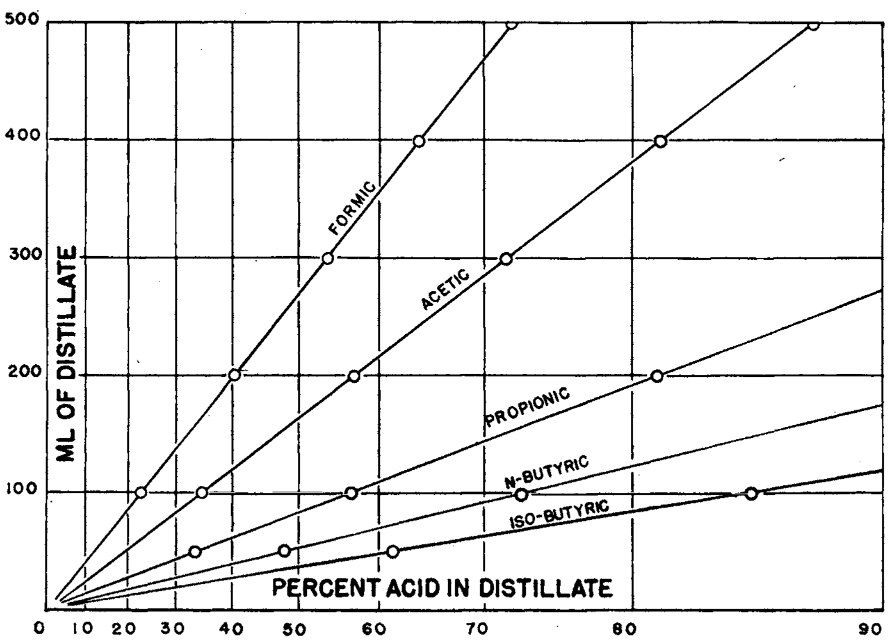


Fig. 29
Rates of Distillation of Several Volatile Fatty Acids, as Determined by the Modified Dyer Method

does not affect the general principle of the method and gives more accurate results.

Apparatus and Method. An apparatus, easily assembled, and well suited for the determination is shown in Fig. 30. Steam is generated by the electrically operated boiler and accurately and smoothly controlled by a rheostat or variable voltage regulator. The liquid in the distilling flask, containing from 10 to 100 mg. of free acid, is maintained at 150 ml. (marked on the flask), while the rate of distillation is so regulated by the flow of

[3] E. P. Clark and F. Hillig, *J. Assoc. Official Agr. Chem.* **21,** 684 (1938).

steam and a small flame under the flask that 100 ml. of distillate is collected in 30 minutes. A paper mantle, with cellophane windows surrounding the entire flask is very helpful in maintaining constant conditions.

The distilled acid is titrated with barium hydroxide solution with phenolphthalein as an indicator. The strength of standard alkali should range from 0.02 to 0.1 normal, depending upon the quantity of acid dealt with. The titrations are carried to a definite end point by comparison with the color of an equal volume of standard (pH 8.6) buffered solution and indi-

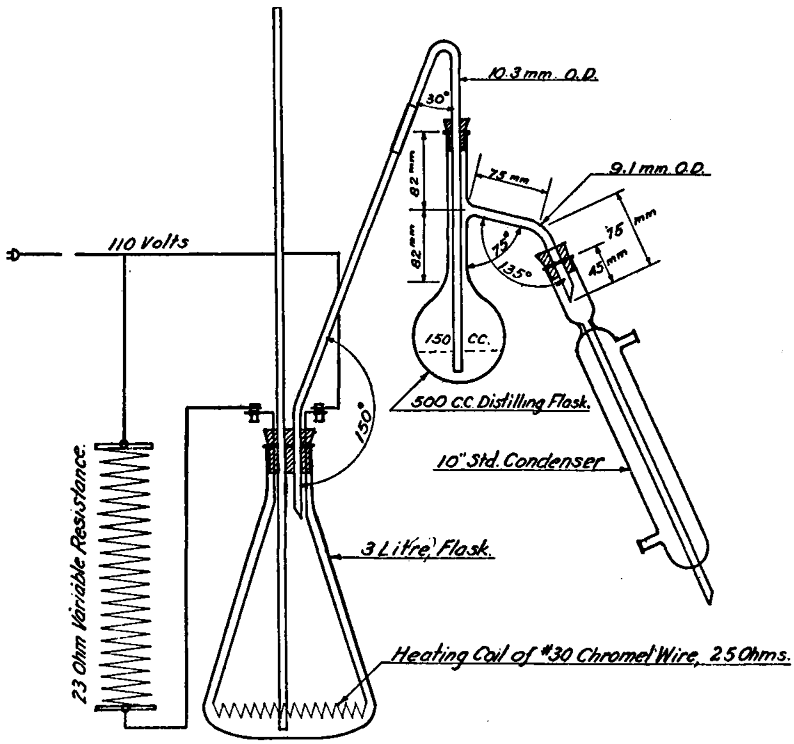


Fig. 30
Distillation Assembly for Determining Volatile Fatty Acids

cator contained in a stoppered flask the same size as that used in the titration. Titration blanks are determined with the same volume of water freshly distilled from the apparatus. When these precautions are taken, the results are remarkably accurate.

In Table XI are given the distillation constants (the value for the first 100 ml.) and rates of distillation of a few of the more common volatile acids as determined by the above procedure.

Figure 29 is a graphical representation of some of these data.

Interpretation of Results. For purposes of clarity in showing the manner in which the method may be utilized, two practical problems will be explained. The first is a simple case involving only one acid.[4]

Gossypol, when treated with 50 per cent potassium hydroxide, yielded apogossypol and a volatile acid. The acid was recovered from the reaction mixture, neutralized with alkali and concentrated. The resulting liquid was placed in the distilling flask, acidified to congo red with sulfuric acid, diluted to a volume of 150 ml. and distilled as outlined. The results when plotted gave a straight line whose slope was that of formic acid. These facts showed that only formic acid was under consideration.

TABLE XI

Distillation Constants and Rate of Distillation of Several Common Volatile Fatty Acids

(The figures under each acid represent the percentage of the acid in the flask at the beginning of the distillation that comes over in the indicated volume of distillate. The first 100 cc. fraction is the distillation constant.)

Distillate	Formic	Acetic	Propionic	n-Butyric	Iso-butyric
cc.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
25	6.0	10.4	19.0	28.1	38.7
50	12.0	19.3	34.0	48.1	62.2
75	17.4	27.5	47.0	62.5	76.6
100	*23.0*	*34.7*	*56.8*	*72.8*	*85.6*
200	40.5	57.2	81.3	92.45	97.82
300	54.0	71.7	92.0	97.90	99.67
400	64.1	81.1	96.45	99.42	
500	72.1	87.5	98.45	99.84	
600	78.4	91.80	99.34		
700	83.3	94.55	99.72		
800	87.0	96.42	99.87		
900	90.0	97.65			
1000	92.2	98.43			

The isolation of the acid from the reaction mixture had to be done in such a manner that the quantity of acid obtained was known only approximately. An accurate value was therefore calculated from the results used to obtain the distillation curve. The procedure employed is a useful one and illustrates the versatility of the method.

Let t = the total titration, i.e., all the acid in the distillation flask (unknown)

t_1 = the titration of the first 100 ml. fraction (known)

t_2 = the titration of the second 100 ml. fraction (known)

C = the distillation constant (known)

[4] E. P. Clark, *J. Biol. Chem.* **78**, 159 (1928).

By definition it follows that

$$C = \frac{100\, t_1}{t} = \frac{100\, t_2}{t - t_1} \cdots .$$

Therefore by algebraic transformations

$$t = \frac{t_1^2}{t_1 - t_2}$$

Substituting the values for t_1 and t_2 in this formula, the quantity of acid recovered from the reaction was calculated. The use of the method, therefore, showed the nature and quantity of the acid formed in the reaction.

The second more complicated example from the same series of studies[5] is presented to illustrate further applications of the procedure.

Gossypol when oxidized in a limited way with alkaline permanganate gave, among other things, a mixture of volatile acids. These were collected, neutralized, and distilled as outlined in the foregoing experiment. From an examination of the distillation curve obtained (Fig. 31) it was possible to make certain deductions concerning the nature of the acid distillate. First, as the curve was not a straight line, more than one acid was present. Second, in the beginning the curve passed between the distillation curves of *n*-butyric and isobutyric acids which thus indicated the presence in the mixture of the latter. Third, as the curve crossed the distillation curve of acetic acid, the presence of formic acid was shown, and finally, the slope of the curve strongly indicated the presence of acetic acid. These conclusions were verified by applying specific confirmatory tests and by preparing certain characteristic derivatives of the respective acids.

A quantitative determination of the individual acids was then undertaken. First a definite quantity of the mixed acids was refluxed with an excess of mercuric oxide to destroy the formic acid. The resulting mixture was then cooled and transferred to a distilling flask. Sufficient sulfuric acid was added to dissolve all the unchanged mercuric oxide and to render the solution strongly acid. The acetic and isobutyric acids remaining in the mixture were then completely recovered by steam distillation, and titrated. Eighty-five and six-tenths ml. of 0.1 normal alkali was required. The difference between the original mixed acids taken and the recovered acetic and isobutyric acids gave the quantity of formic acid in the mixture.

The neutralized distillate containing the acetic and isobutyric acids was evaporated, acidified, and distilled in order to obtain the distillation constant of the mixture. It was then possible to calculate the quantities of acetic and isobutyric acid present. The distillation constant found was 56.3. This and the distillation constants for both acetic and isobutryric

[5] E. P. Clark, *J. Biol. Chem.* **77**, 81 (1928).

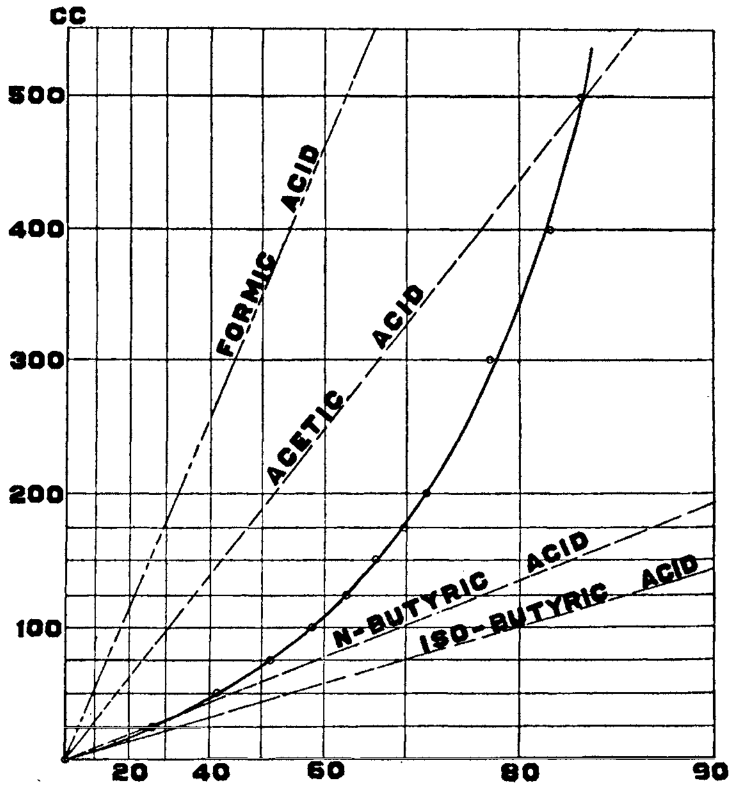


FIG. 31
Distillation Curve of the Volatile Fatty Acids Obtained by Alkaline Permanganate Oxidation of Gossypol
The distillation curves of formic, acetic, *n*-butyric, and isobutyric acids are given for comparison. The abscissas represent the percentages of the total acids distilled (107 ml. of 0.1 N acid) which were found in definite fractions of the distillate, while the volumes in ml. of these fractions are represented by the ordinates

acids were set up and solved according to the method of alligation.[6] The following form and solution resulted.

	56.3
85.6	34.7
21.6	29.3

The numbers 34.7, 56.3, and 85.6 are the distillation constants respectively of acetic acid, the mixture of acids and isobutyric acid. The values 21.6 and 29.3 are obtained by subtracting 34.7 from 56.3, and placing the result

[6] Remington's Practice of Pharmacy, 8th Ed., E. F. Cook and C. H. La Wall, J. B. Lippincott Co., Philadelphia, 1936, page 86.

under 85.6; and that obtained by subtracting 56.3 from 85.6 is placed under 34.7. The rule to follow is to link a quantity which is less with one which is greater.

The interpretation of these results is that of 50.9 parts (the sum of 21.6 and 29.3), corresponding to 85.6 ml. of 0.1 *N* alkali necessary to neutralize the mixed acid; 29.3 parts represent the acetic acid present, and 21.6 parts represent the isobutyric acid. Thus, since 85.6 ml. of 0.1 normal alkali equals 50.9 parts, one part equals 85.6 divided by 50.9, or 1.681 ml. of 0.1 *N* alkali for each part. Therefore

$1.681 \times 29.3 = 49.24$ ml. of 0.1 *N* alkali is the equivalent of acetic acid, and $1.681 \times 21.6 = 36.31$ ml. of 0.1 *N* alkali is the equivalent of isobutyric acid.

Thus, in this problem involving a mixture of three acids, the method was used successfully to identify the acids and *determine* the quantity of each present.

The two examples presented indicate the most frequent uses of the method, but other applications are possible as well. The procedure is not restricted to the volatile fatty acids alone, but may be applied to any acid appreciably volatile with steam. The technique may also be applied to very small quantities of acids as indicated by the following experiment.

Five ml. of 0.02 *N* acetic acid was distilled in the usual way and the distillate titrated with 0.02 *N* barium hydroxide solution. The values obtained were $t_1 = 1.54$ ml.; $t_2 = 1.07$ ml.; $t_3 = .72$ ml.; $C = 30.8$ (the apparatus was different in several respects from the one recommended). The t_1, t_2, and t_3 values gave a perfectly straight line, and the calculated value for t using the formula

$$t = \frac{t_1^2}{t_1 - t_2}$$

was 5.04 ml. of .02 *N* alkali.

CHAPTER XIII

SOME USEFUL TABLES

TABLE XII

Gravimetric Factors

Given	Sought	Factor	Log
CO_2	C, 12.01	.2727	43559
H_2O	H, 1.008	.1119	04884
AgCl	Cl, 35.46	.24738	39337
AgBr	Br, 79.92	.42556	62896
AgI	I, 126.92	.5405	73283
$P_2O_5 \cdot 24MoO_3$	P, 30.98	.01724	23654
$BaSO_4$	S, 32.06	.1374	13782

TABLE XIII

Barometer Corrections

For Temperature

Glass Scale (Bunsen) mm. to be deducted						Brass Scale (Delcros) mm. to be deducted					
t°C.	Reading					t°C.	Reading				
	700	720	740	760	780		700	720	740	760	780
1	0.120	0.123	0.127	0.130	0.133	1	0.113	0.116	0.119	0.123	0.126
2	0.2	0.2	0.3	0.3	0.3	2	0.2	0.2	0.2	0.3	0.3
3	0.4	0.4	0.4	0.4	0.4	3	0.3	0.4	0.4	0.4	0.4
4	0.5	0.5	0.5	0.5	0.5	4	0.5	0.5	0.5	0.5	0.5
5	0.6	0.6	0.6	0.7	0.7	5	0.6	0.6	0.6	0.6	0.6
6	0.7	0.7	0.8	0.8	0.8	6	0.7	0.7	0.7	0.7	0.8
7	0.8	0.9	0.9	0.9	0.9	7	0.8	0.8	0.8	0.9	0.9
8	1.0	1.0	1.0	1.0	1.1	8	0.9	0.9	1.0	1.0	1.0
9	1.1	1.1	1.1	1.2	1.2	9	1.0	1.0	1.1	1.1	1.1
10	1.2	1.2	1.3	1.3	1.3	10	1.1	1.2	1.2	1.2	1.3
11	1.3	1.4	1.4	1.4	1.5	11	1.2	1.3	1.3	1.4	1.4
12	1.4	1.5	1.5	1.6	1.6	12	1.4	1.4	1.4	1.5	1.5
13	1.6	1.6	1.7	1.7	1.7	13	1.5	1.5	1.6	1.6	1.6
14	1.7	1.7	1.8	1.8	1.9	14	1.6	1.7	1.7	1.7	1.8
15	1.8	1.8	1.9	2.0	2.0	15	1.7	1.8	1.8	1.8	1.9
16	1.9	2.0	2.0	2.1	2.1	16	1.8	1.9	1.9	2.0	2.0
17	2.0	2.1	2.2	2.2	2.3	17	1.9	2.0	2.0	2.1	2.1
18	2.2	2.2	2.3	2.3	2.4	18	2.0	2.1	2.2	2.2	2.3
19	2.3	2.3	2.4	2.5	2.5	19	2.1	2.2	2.3	2.3	2.4
20	2.4	2.5	2.5	2.6	2.7	20	2.3	2.3	2.4	2.5	2.5
21	2.5	2.6	2.7	2.7	2.8	21	2.4	2.5	2.5	2.6	2.7
22	2.6	2.7	2.8	2.9	2.9	22	2.5	2.6	2.6	2.7	2.8
23	2.8	2.8	2.9	3.0	3.1	23	2.6	2.7	2.8	2.8	2.9
24	2.9	3.0	3.0	3.1	3.2	24	2.7	2.8	2.9	2.9	3.0
25	3.0	3.1	3.2	3.3	3.3	25	2.8	3.0	3.1	3.0	3.2
26	3.1	3.2	3.3	3.4	3.5	26	2.9	3.1	3.1	3.2	3.3
27	3.2	3.3	3.4	3.5	3.6	27	3.1	3.2	3.2	3.3	3.4
28	3.4	3.4	3.5	3.6	3.7	28	3.2	3.3	3.3	3.4	3.5
29	3.5	3.6	3.7	3.8	3.9	29	3.3	3.4	3.5	3.6	3.7
30	3.6	3.7	3.8	3.9	4.0	30	3.4	3.5	3.6	3.7	3.8

TABLE XIV

Atomic and Molecular Formulas and Some of Their Multiples

Hydrogen

		log
H	1.008	00346
2	2.016	30449
3	3.024	48058
4	4.032	60552
5	5.040	70243
6	6.048	78161
7	7.056	84856
8	8.064	90655
9	9.072	95770
10	10.08	00346
11	11.09	04493
12	12.10	08279
13	13.10	11727
14	14.11	14953
15	15.12	17955
16	16.13	20763
17	17.14	23401
18	18.14	25864
19	19.15	28217
20	20.16	30449
21	21.17	32572
22	22.18	34596
23	23.18	36511
24	24.19	38364
25	25.20	40140
26	26.21	41847
27	27.22	43489
28	28.22	45056
29	29.23	46583
30	30.24	48058
31	31.25	49485
32	32.26	50866
33	33.26	52192
34	34.27	53491
35	35.28	54753
36	36.29	55979
37	37.30	57171
38	38.30	58320
39	39.31	59450
40	40.32	60552
41	41.33	61627
42	42.34	62675
43	43.34	63689
44	44.35	64689
45	45.36	65667
46	46.37	66624
47	47.38	67560

Carbon

		log
C	12.01	07954
2	24.02	38057
3	36.03	55666
4	48.04	68160
5	60.05	77851
6	72.06	85769
7	84.07	92464
8	96.08	98263
9	108.09	03378
10	120.10	07954
11	132.11	12093
12	144.12	15872
13	156.13	19348
14	168.14	22567
15	180.15	25563
16	192.16	28366
17	204.17	30999
18	216.18	33481
19	228.19	35829
20	240.20	38057
21	252.21	40176
22	264.22	42196
23	276.23	44127
24	288.24	45975
25	300.25	47748
26	312.26	49451
27	324.27	51090
28	336.28	52670
29	348.29	54194
30	360.30	55666
31	372.31	57090
32	384.32	58469

Oxygen

		log
O	16.00	20412
2	32.00	50515
3	48.00	68124
4	64.00	80618
5	80.00	90309
6	96.00	98227
7	112.00	04922
8	128.00	10721
9	144.00	15836
10	160.00	20412
11	176.00	24551
12	192.00	28330

Nitrogen

		log
N	14.008	14638
2	28.016	44741
3	42.024	62350
4	56.032	74844
5	70.040	84535
6	84.048	92453

Chlorine

		log
Cl	35.46	54974
2	70.92	85077
3	106.38	02686
4	141.84	15180
5	177.30	24871
6	212.76	32789

Bromine

		log
Br	79.92	90266
2	159.84	20369
3	239.76	37978
4	319.68	50472
5	399.60	60163
6	479.52	68081

Iodine

		log
I	126.92	10353
2	253.84	40456
3	380.76	58065
4	507.68	70559
5	634.60	80250
6	761.52	88168

OCH_3

		log
1	31.03	49178
2	62.06	79281
3	93.09	96890
4	124.12	09384
5	155.15	19075
6	186.18	26993

OC_2H_5

		log
1	45.06	65379
2	90.12	95482
3	135.18	13091

$COCH_3$

		log
1	43.04	63387
2	86.08	93490
3	129.12	11099
4	172.16	23593
5	215.20	33284
6	258.24	41202

TABLE XV

The Carbon and Hydrogen Percentage and Molecular Weights of a Series of CHO Compounds from C_{15} to C_{32} Frequently Encountered Among Natural Products and Their Derivatives

The Molecular Weights are in Italicized Type

C_{15}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	210.26	*226.26*	*242.26*	*258.26*	*274.26*	*290.26*	*306.26*	*322.26*	*338.26*
H_{14}	85.68	79.62	74.36	69.76	65.69	62.06	58.82	55.90	53.26
	6.71	6.24	5.82	5.46	5.14	4.86	4.61	4.38	4.17
	212.28	*228.28*	*244.28*	*260.28*	*276.28*	*292.28*	*308.28*	*324.28*	*340.28*
H_{16}	84.86	78.92	73.75	69.21	65.21	61.64	58.44	55.55	52.94
	7.60	7.07	6.60	6.20	5.84	5.52	5.23	4.97	4.74
	214.29	*230.29*	*246.29*	*262.29*	*278.29*	*294.29*	*310.29*	*326.29*	*342.29*
H_{18}	84.07	78.23	73.15	68.68	64.73	61.22	58.06	55.21	52.63
	8.47	7.88	7.37	6.92	6.52	6.16	5.85	5.56	5.30
	216.31	*232.31*	*248.31*	*264.31*	*280.31*	*296.31*	*312.31*	*328.31*	*344.31*
H_{20}	83.28	77.55	72.55	68.16	64.27	60.80	57.68	54.87	52.32
	9.32	8.68	8.12	7.63	7.19	6.80	6.46	6.14	5.86
	218.33	*234.33*	*250.33*	*266.33*	*282.33*	*298.33*	*314.33*	*330.33*	*346.33*
H_{22}	82.51	76.88	71.97	67.64	63.81	60.39	57.31	54.54	52.02
	10.16	9.47	8.86	8.33	7.86	7.43	7.06	6.71	6.40
	220.34	*236.34*	*252.34*	*268.34*	*284.34*	*300.34*	*316.34*	*332.34*	*348.34*
H_{24}	81.76	76.22	71.39	67.13	63.36	59.98	56.95	54.21	51.72
	10.98	10.24	9.59	9.01	8.51	8.05	7.65	7.28	6.94
	222.36	*238.36*	*254.36*	*270.36*	*286.36*	*302.36*	*318.36*	*334.36*	*350.36*
H_{26}	81.02	75.58	70.82	66.63	62.91	59.58	56.59	53.88	51.42
	11.79	11.00	10.30	9.69	9.15	8.67	8.23	7.84	7.48
	224.37	*240.37*	*256.37*	*272.37*	*288.37*	*304.37*	*320.37*	*336.37*	*352.37*
H_{28}	80.29	74.95	70.27	66.14	62.47	59.19	56.23	53.56	51.13
	12.58	11.74	11.01	10.36	9.79	9.27	8.81	8.39	8.01
	226.39	*242.39*	*258.39*	*274.39*	*290.39*	*306.39*	*322.39*	*338.39*	*354.39*
H_{30}	79.58	74.32	69.72	65.65	62.04	58.80	55.88	53.24	50.83
	13.36	12.48	11.70	11.02	10.41	9.87	9.38	8.94	8.53
	228.41	*244.41*	*260.41*	*276.41*	*292.41*	*308.41*	*324.41*	*340.41*	*356.41*
H_{32}	78.87	73.71	69.18	65.17	61.61	58.41	55.53	52.92	50.55
	14.12	13.20	12.39	11.67	11.03	10.46	9.94	9.48	9.05

TABLE XV—*Continued*

C_{16}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
H_{14}	*222.27* 86.45 6.35	*238.27* 80.65 5.92	*254.27* 75.57 5.55	*270.27* 71.10 5.22	*286.27* 67.13 4.93	*302.27* 63.57 4.67	*318.27* 60.38 4.43	*334.27* 57.49 4.22	*350.27* 54.86 4.03
H_{16}	*224.29* 85.67 7.19	*240.29* 79.97 6.71	*256.29* 74.98 6.29	*272.29* 70.57 5.92	*288.29* 66.66 5.60	*304.29* 63.15 5.30	*320.29* 60.00 5.04	*336.29* 57.14 4.80	*352.29* 54.55 4.58
H_{18}	*226.30* 84.91 8.02	*242.30* 79.31 7.49	*258.30* 74.39 7.02	*274.30* 70.01 6.61	*290.30* 66.19 6.25	*306.30* 62.74 5.92	*322.30* 59.62 5.63	*338.30* 56.80 5.36	*354.30* 54.24 5.12
H_{20}	*228.32* 84.16 8.83	*244.32* 78.65 8.25	*260.32* 73.82 7.74	*276.32* 69.54 7.30	*292.32* 65.74 6.90	*308.32* 62.32 6.54	*324.32* 59.25 6.22	*340.32* 56.46 5.92	*356.32* 53.93 5.66
H_{22}	*230.34* 83.42 9.63	*246.34* 78.01 9.00	*262.34* 73.25 8.45	*278.34* 69.04 7.97	*294.34* 65.29 7.54	*310.34* 61.92 7.15	*326.34* 58.88 6.80	*342.34* 56.13 6.48	*358.34* 53.63 6.19
H_{24}	*232.35* 82.70 10.41	*248.35* 77.37 9.74	*264.35* 72.69 9.15	*280.35* 68.54 8.63	*296.35* 64.84 8.16	*312.35* 61.52 7.74	*328.35* 58.52 7.37	*344.35* 55.80 7.02	*360.35* 53.33 6.71
H_{26}	*234.37* 81.99 11.18	*250.37* 76.75 10.47	*266.37* 72.14 9.84	*282.37* 68.05 9.28	*298.37* 64.40 8.78	*314.37* 61.13 8.34	*330.37* 58.17 7.93	*346.37* 55.48 7.57	*362.37* 53.03 7.23
H_{28}	*236.38* 81.29 11.94	*252.38* 76.14 11.18	*268.38* 71.60 10.51	*284.38* 67.57 9.92	*300.38* 63.97 9.39	*316.38* 60.74 8.92	*332.38* 57.81 8.49	*348.38* 55.16 8.10	*364.38* 52.74 7.74
H_{30}	*238.40* 80.60 12.68	*254.40* 75.53 11.89	*270.40* 71.07 11.18	*286.40* 67.09 10.56	*302.40* 63.54 10.00	*318.40* 60.35 9.50	*334.40* 57.46 9.04	*350.40* 54.84 8.63	*366.40* 52.45 8.25
H_{32}	*240.42* 79.93 13.42	*256.42* 74.94 12.58	*272.42* 70.54 11.84	*288.42* 66.63 11.19	*304.42* 63.12 10.60	*320.42* 59.97 10.07	*336.42* 57.12 9.59	*352.42* 54.53 9.15	*368.42* 52.16 8.76

TABLE XV—*Continued*

C_{17}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	234.28	*250.28*	*266.28*	*282.28*	*298.28*	*314.28*	*330.28*	*346.28*	*362.28*
H_{14}	87.15	81.58	76.67	72.33	68.45	64.96	61.82	58.96	56.36
	6.02	5.64	5.30	5.00	4.73	4.49	4.27	4.07	3.89
	236.30	*252.30*	*268.30*	*284.30*	*300.30*	*316.30*	*332.30*	*348.30*	*364.30*
H_{16}	86.40	80.92	76.10	71.81	67.99	64.55	61.44	58.62	56.04
	6.83	6.39	6.01	5.67	5.37	5.10	4.85	4.63	4.43
	238.31	*254.31*	*270.31*	*286.31*	*302.31*	*318.31*	*334.31*	*350.31*	*366.31*
H_{18}	85.67	80.28	75.53	71.31	67.54	64.14	61.07	58.28	55.74
	7.61	7.13	6.71	6.34	6.00	5.70	5.43	5.18	4.95
	240.33	*256.33*	*272.33*	*288.33*	*304.33*	*320.33*	*336.33*	*352.33*	*368.33*
H_{20}	84.95	79.65	74.97	70.81	67.09	63.74	60.71	57.95	55.43
	8.39	7.86	7.40	6.99	6.62	6.29	5.99	5.72	5.47
	242.35	*258.35*	*274.35*	*290.35*	*306.35*	*322.35*	*338.35*	*354.35*	*370.35*
H_{22}	84.25	79.03	74.42	70.32	66.65	63.34	60.34	57.62	55.13
	9.15	8.59	8.08	7.64	7.24	6.88	6.56	6.26	5.99
	244.36	*260.36*	*276.36*	*292.36*	*308.36*	*324.36*	*340.36*	*356.36*	*372.36*
H_{24}	83.55	78.42	73.88	69.84	66.21	62.95	59.99	57.29	54.83
	9.90	9.29	8.75	8.27	7.84	7.46	7.11	6.79	6.50
	246.38	*262.38*	*278.38*	*294.38*	*310.38*	*326.38*	*342.38*	*358.38*	*374.38*
H_{26}	82.86	77.81	73.34	69.36	65.78	62.56	59.63	56.97	54.54
	10.64	9.99	9.42	8.90	8.44	8.03	7.66	7.31	7.00
	248.39	*264.39*	*280.39*	*296.39*	*312.39*	*328.39*	*344.39*	*360.39*	*376.39*
H_{28}	82.20	77.22	72.82	68.89	65.36	62.17	59.28	56.65	54.24
	11.36	10.67	10.06	9.52	9.03	8.59	8.19	7.83	7.50
	250.41	*266.41*	*282.41*	*298.41*	*314.41*	*330.41*	*346.41*	*362.41*	*378.41*
H_{30}	81.53	76.64	72.30	68.42	64.94	61.79	58.94	56.34	53.95
	12.08	11.35	10.71	10.13	9.62	9.15	8.73	8.34	7.99
	252.43	*268.43*	*284.43*	*300.43*	*316.43*	*332.43*	*348.43*	*364.43*	*380.43*
H_{32}	80.88	76.06	71.78	67.96	64.52	61.42	58.60	56.02	53.67
	12.78	12.02	11.34	10.74	10.19	9.70	9.26	8.85	8.48

TABLE XV—*Continued*

C_{18}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	250.32	*266.32*	*282.32*	*298.32*	*314.32*	*330.32*	*346.32*	*362.32*	*378.32*
H_{18}	86.36	81.17	76.57	72.47	68.78	65.45	62.42	59.67	57.14
	7.25	6.81	6.43	6.08	5.77	5.49	5.24	5.01	4.79
	252.34	*268.34*	*284.34*	*300.34*	*316.34*	*332.34*	*348.34*	*364.34*	*380.34*
H_{20}	85.67	80.56	76.03	71.98	68.34	65.05	62.06	59.33	56.84
	7.99	7.51	7.09	6.71	6.37	6.07	5.79	5.53	5.30
	254.36	*270.36*	*286.36*	*302.36*	*318.36*	*334.36*	*350.36*	*366.36*	*382.36*
H_{22}	84.99	79.96	75.49	71.50	67.90	64.65	61.70	59.01	56.54
	8.72	8.20	7.75	7.34	6.97	6.63	6.33	6.05	5.80
	256.37	*272.37*	*288.37*	*304.37*	*320.37*	*336.37*	*352.37*	*368.37*	*384.37*
H_{24}	84.32	79.37	74.97	71.03	67.48	64.27	61.35	58.69	56.24
	9.44	8.88	8.39	7.95	7.55	7.19	6.86	6.57	6.29
	258.39	*274.39*	*290.39*	*306.39*	*322.39*	*338.39*	*354.39*	*370.39*	*386.39*
H_{26}	83.66	78.79	74.44	70.56	67.06	63.88	61.00	58.37	55.95
	10.14	9.55	9.03	8.55	8.13	7.75	7.40	7.08	6.78
	260.40	*276.40*	*292.40*	*308.40*	*324.40*	*340.40*	*356.40*	*372.40*	*388.40*
H_{28}	83.02	78.21	73.93	70.10	66.64	63.51	60.66	58.05	55.66
	10.84	10.21	9.65	9.15	8.70	8.29	7.92	7.58	7.27
	262.42	*278.42*	*294.42*	*310.42*	*326.42*	*342.42*	*358.42*	*374.42*	*390.42*
H_{30}	82.38	77.65	73.43	69.64	66.23	63.13	60.31	57.74	55.37
	11.52	10.86	10.27	9.74	9.26	8.83	8.44	8.08	7.75
	264.44	*280.44*	*296.44*	*312.44*	*328.44*	*344.44*	*360.44*	*376.44*	*392.44*
H_{32}	81.75	77.09	72.93	69.19	65.82	62.76	59.98	57.43	55.09
	12.20	11.50	10.88	10.33	9.82	9.37	8.95	8.57	8.22
	266.45	*282.45*	*298.45*	*314.45*	*330.45*	*346.45*	*362.45*	*378.45*	*394.45*
H_{34}	81.13	76.54	72.40	68.75	65.42	62.40	59.64	57.12	54.81
	12.86	12.13	11.48	10.90	10.37	9.89	9.46	9.06	8.69
	268.47	*284.47*	*300.47*	*316.47*	*332.47*	*348.47*	*364.47*	*380.47*	*396.47*
H_{36}	80.52	75.99	71.95	68.31	65.02	62.04	59.31	56.82	54.53
	13.52	12.76	12.08	11.47	10.92	10.41	9.96	9.54	9.15

TABLE XV—*Continued*

C_{19}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	262.33	*278.33*	*294.33*	*310.33*	*326.33*	*342.33*	*358.33*	*374.33*	*390.33*
H_{18}	86.99	81.99	77.53	73.53	69.93	66.66	63.68	60.96	58.46
	6.91	6.52	6.16	5.85	5.56	5.30	5.06	4.85	4.65
	264.35	*280.35*	*296.35*	*312.35*	*328.35*	*344.35*	*360.35*	*376.35*	*392.35*
H_{20}	86.32	81.39	77.00	73.06	69.50	66.27	63.32	60.63	58.16
	7.63	7.19	6.80	6.45	6.14	5.85	5.59	5.36	5.14
	266.37	*282.37*	*298.37*	*314.37*	*330.37*	*346.37*	*362.37*	*378.37*	*394.37*
H_{22}	85.67	80.81	76.48	72.57	69.07	65.88	62.97	60.31	57.86
	8.33	7.85	7.43	7.06	6.71	6.40	6.12	5.86	5.62
	268.38	*284.38*	*300.38*	*316.38*	*332.38*	*348.38*	*364.38*	*380.38*	*396.38*
H_{24}	85.02	80.24	75.97	72.13	68.65	65.50	62.62	59.99	57.57
	9.01	8.51	8.05	7.65	7.28	6.94	6.64	6.36	6.10
	270.40	*286.40*	*302.40*	*318.40*	*334.40*	*350.40*	*366.40*	*382.40*	*398.40*
H_{26}	84.39	79.68	75.46	71.67	68.24	65.12	62.28	59.67	57.28
	9.69	9.15	8.67	8.23	7.84	7.48	7.15	6.85	6.58
	272.41	*288.41*	*304.41*	*320.41*	*336.41*	*352.41*	*368.41*	*384.41*	*400.41*
H_{28}	83.77	79.12	74.96	71.22	67.83	64.75	61.94	59.36	56.99
	10.36	9.78	9.27	8.81	8.39	8.01	7.66	7.34	7.05
	274.43	*290.43*	*306.43*	*322.43*	*338.43*	*354.43*	*370.43*	*386.43*	*402.43*
H_{30}	83.15	78.57	74.47	70.77	67.43	64.38	61.60	59.05	56.70
	11.02	10.41	9.87	9.38	8.94	8.53	8.16	7.83	7.51
	276.45	*292.45*	*308.45*	*324.45*	*340.45*	*356.45*	*372.45*	*388.45*	*404.45*
H_{32}	82.54	78.03	73.98	70.33	67.03	64.02	61.27	58.74	56.42
	11.67	11.03	10.46	9.94	9.48	9.05	8.66	8.30	7.98
	278.46	*294.46*	*310.46*	*326.46*	*342.46*	*358.46*	*374.46*	*390.46*	*406.46*
H_{34}	81.95	77.49	73.50	69.90	66.63	63.66	60.94	58.44	56.14
	12.31	11.64	11.04	10.50	10.01	9.56	9.15	8.78	8.43
	280.48	*296.48*	*312.48*	*328.48*	*344.48*	*360.48*	*376.48*	*392.48*	*408.48*
H_{36}	81.36	76.97	73.03	69.47	66.24	63.30	60.61	58.14	55.86
	12.94	12.24	11.61	11.05	10.53	10.07	9.64	9.25	8.88

TABLE XV—*Continued*

C_{20}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	274.34	*290.34*	*306.34*	*322.34*	*338.34*	*354.34*	*370.34*	*386.34*	*402.34*
H_{18}	87.56	82.73	78.41	74.52	70.99	67.79	64.86	62.17	59.70
	6.61	6.18	5.92	5.63	5.36	5.12	4.90	4.70	4.51
	276.36	*292.36*	*308.36*	*324.36*	*340.36*	*356.36*	*372.36*	*388.36*	*404.36*
H_{20}	86.92	82.16	77.90	74.05	70.57	67.40	64.51	61.85	59.40
	7.30	6.90	6.54	6.22	5.92	5.66	5.41	5.19	4.99
	278.38	*294.38*	*310.38*	*326.38*	*342.38*	*358.38*	*374.38*	*390.38*	*406.38*
H_{22}	86.28	81.60	77.39	73.60	70.16	67.02	64.16	61.53	59.11
	7.97	7.53	7.15	6.80	6.48	6.19	5.92	5.68	5.46
	280.39	*296.39*	*312.39*	*328.39*	*344.39*	*360.39*	*376.39*	*392.39*	*408.39*
H_{24}	85.67	81.04	76.89	73.14	69.75	66.65	63.82	61.21	58.82
	8.63	8.16	7.74	7.37	7.02	6.71	6.43	6.16	5.92
	282.41	*298.41*	*314.41*	*330.41*	*346.41*	*362.41*	*378.41*	*394.41*	*410.41*
H_{26}	85.05	80.49	76.40	72.70	69.34	66.28	63.48	60.90	58.53
	9.28	8.78	8.34	7.93	7.57	7.23	6.93	6.65	6.39
	284.42	*300.42*	*316.42*	*332.42*	*348.42*	*364.42*	*380.42*	*396.42*	*412.42*
H_{28}	84.45	79.95	75.91	72.26	68.94	65.91	63.14	60.59	58.24
	9.92	9.39	8.92	8.49	8.10	7.74	7.42	7.12	6.84
	286.44	*302.44*	*318.44*	*334.44*	*350.44*	*366.44*	*382.44*	*398.44*	*414.44*
H_{30}	83.86	79.42	75.43	71.82	68.54	65.55	62.81	60.29	57.96
	10.56	10.00	9.50	9.04	8.63	8.25	7.91	7.59	7.30
	288.46	*304.46*	*320.46*	*336.46*	*352.46*	*368.46*	*384.46*	*400.46*	*416.46*
H_{32}	83.27	78.89	74.95	71.39	68.15	65.19	62.48	59.98	57.68
	11.18	10.60	10.07	9.59	9.15	8.76	8.39	8.06	7.75
	290.47	*306.47*	*322.47*	*338.47*	*354.47*	*370.47*	*386.47*	*402.47*	*418.47*
H_{34}	82.69	78.38	74.49	70.97	67.76	64.84	62.15	59.68	57.40
	11.80	11.18	10.63	10.12	9.67	9.25	8.87	8.51	8.19
	292.49	*308.49*	*324.49*	*340.49*	*356.49*	*372.49*	*388.49*	*404.49*	*420.49*
H_{36}	82.12	77.86	74.02	70.55	67.38	64.48	61.83	59.38	57.12
	12.41	11.76	11.19	10.66	10.18	9.74	9.34	8.97	8.63

TABLE XV—*Continued*

C_{21}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	288.37	*304.37*	*320.37*	*336.37*	*352.37*	*368.37*	*384.37*	*400.37*	*416.37*
H_{20}	87.46	82.86	78.72	74.98	71.58	68.47	65.62	62.99	60.57
	6.99	6.62	6.29	5.99	5.72	5.47	5.24	5.04	4.84
	290.39	*306.39*	*322.39*	*338.39*	*354.39*	*370.39*	*386.39*	*402.39*	*418.39*
H_{22}	86.85	82.32	78.23	74.53	71.17	68.09	65.27	62.68	60.28
	7.64	7.24	6.88	6.55	6.26	5.99	5.74	5.51	5.30
	292.40	*308.40*	*324.40*	*340.40*	*356.40*	*372.40*	*388.40*	*404.40*	*420.40*
H_{24}	86.26	81.78	77.75	74.09	70.77	67.73	64.94	62.37	59.99
	8.27	7.84	7.46	7.11	6.79	6.50	6.23	5.98	5.75
	294.42	*310.42*	*326.42*	*342.42*	*358.42*	*374.42*	*390.42*	*406.42*	*422.42*
H_{26}	85.66	81.25	77.27	73.66	70.37	67.36	64.60	62.06	59.71
	8.90	11.84	8.03	7.65	7.31	7.00	6.71	6.45	6.20
	296.43	*312.43*	*328.43*	*344.43*	*360.43*	*376.43*	*392.43*	*408.43*	*424.43*
H_{28}	85.08	80.73	76.79	73.23	69.97	67.00	64.27	61.75	59.42
	9.52	9.03	8.59	8.19	7.83	7.50	7.19	6.91	6.65
	298.45	*314.45*	*330.45*	*346.45*	*362.45*	*378.45*	*394.45*	*410.45*	*426.45*
H_{30}	84.51	80.21	76.32	72.80	69.58	66.64	63.94	61.45	59.14
	10.13	9.62	9.15	8.73	8.34	7.99	7.67	7.37	7.09
	300.47	*316.47*	*332.47*	*348.47*	*364.47*	*380.47*	*396.47*	*412.47*	*428.47*
H_{32}	83.94	79.69	75.86	72.38	69.20	66.24	63.61	61.15	58.86
	10.74	10.19	9.70	9.26	8.85	8.48	8.14	7.82	7.53
	302.48	*318.48*	*334.48*	*350.48*	*366.48*	*382.48*	*398.48*	*414.48*	*430.48*
H_{34}	83.38	79.19	75.40	71.96	68.82	65.94	63.29	60.85	58.59
	11.33	10.76	10.25	9.78	9.35	8.96	8.60	8.27	7.96
	304.50	*320.50*	*336.50*	*352.50*	*368.50*	*384.50*	*400.50*	*416.50*	*432.50*
H_{36}	82.83	78.69	74.95	71.55	68.44	65.59	62.97	60.55	58.31
	11.92	11.32	10.78	10.30	9.85	9.44	9.06	8.71	8.39
	306.51	*322.51*	*338.51*	*354.51*	*370.51*	*386.51*	*402.51*	*418.51*	*434.51*
H_{38}	82.28	78.20	74.51	71.14	68.07	65.25	62.66	60.26	58.04
	12.50	11.88	11.31	10.80	10.34	9.91	9.52	9.15	8.81

TABLE XV—*Continued*

C_{22}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	302.40	*318.40*	*334.40*	*350.40*	*366.40*	*382.40*	*398.40*	*414.40*	*430.40*
H_{22}	87.37	82.98	79.01	75.41	72.11	69.10	66.32	63.76	61.39
	7.33	6.97	6.63	6.33	6.05	5.80	5.57	5.35	5.15
	304.41	*320.41*	*336.41*	*352.41*	*368.41*	*384.41*	*400.41*	*416.41*	*432.41*
H_{24}	86.80	82.46	78.54	74.98	71.72	68.73	65.99	63.45	61.10
	7.95	7.55	7.19	6.86	6.57	6.29	6.04	5.81	5.59
	306.43	*322.43*	*338.43*	*354.43*	*370.43*	*386.43*	*402.43*	*418.43*	*434.43*
H_{26}	86.23	81.95	78.07	74.55	71.33	68.37	65.66	63.15	60.82
	8.55	8.13	7.74	7.39	7.08	6.78	6.51	6.26	6.03
	308.44	*324.44*	*340.44*	*356.44*	*372.44*	*388.44*	*404.44*	*420.44*	*436.44*
H_{28}	85.66	81.44	77.61	74.13	70.94	68.02	65.33	62.84	60.54
	9.15	8.70	8.29	7.92	7.58	7.26	6.98	6.71	6.47
	310.46	*326.46*	*342.46*	*358.46*	*374.46*	*390.46*	*406.46*	*422.46*	*438.46*
H_{30}	85.11	80.93	77.15	73.71	70.56	67.67	65.01	62.54	60.26
	9.74	9.26	8.83	8.44	8.08	7.74	7.44	7.16	6.90
	312.48	*328.48*	*344.48*	*360.48*	*376.48*	*392.48*	*408.48*	*424.48*	*440.48*
H_{32}	84.56	80.44	76.70	73.30	70.18	67.32	64.68	62.25	59.98
	10.32	9.82	9.36	8.95	8.57	8.22	7.90	7.60	7.32
	314.49	*330.49*	*346.49*	*362.49*	*378.49*	*394.49*	*410.49*	*426.49*	*442.49*
H_{34}	84.02	79.95	76.26	72.89	69.81	66.98	64.37	61.95	59.71
	10.90	10.37	9.89	9.45	9.05	8.69	8.35	8.04	7.74
	316.51	*332.51*	*348.51*	*364.51*	*380.51*	*396.51*	*412.51*	*428.51*	*444.51*
H_{36}	83.48	79.46	75.81	72.49	69.44	66.64	64.05	61.66	59.44
	11.47	10.91	10.41	9.96	9.54	9.15	8.80	8.47	8.16
	318.52	*334.52*	*350.52*	*366.52*	*382.52*	*398.52*	*414.52*	*430.52*	*446.52*
H_{38}	82.95	78.98	75.38	72.09	69.07	66.30	63.74	61.37	59.17
	12.02	11.45	10.93	10.45	10.01	9.61	9.24	8.90	8.58
	320.54	*336.54*	*352.54*	*368.54*	*384.54*	*400.54*	*416.54*	*432.54*	*448.54*
H_{40}	82.43	78.51	74.95	71.69	68.71	65.97	63.43	61.09	58.91
	12.58	11.98	11.44	10.94	10.49	10.07	9.68	9.32	8.99

TABLE XV—*Continued*

C_{23}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	316.42	*332.42*	*348.42*	*364.42*	*380.42*	*396.42*	*412.42*	*428.42*	*444.42*
H_{24}	87.30	83.10	79.28	75.80	72.61	69.68	66.98	64.48	62.16
	7.64	7.28	6.94	6.64	6.36	6.10	5.87	5.65	5.44
	318.44	*334.44*	*350.44*	*366.44*	*382.44*	*398.44*	*414.44*	*430.44*	*446.44*
H_{26}	86.74	82.59	78.82	75.38	72.23	69.33	66.65	64.17	61.87
	8.23	7.84	7.48	7.15	6.85	6.58	6.32	6.09	5.87
	320.45	*336.45*	*352.45*	*368.45*	*384.45*	*400.45*	*416.45*	*432.45*	*448.45*
H_{28}	86.20	82.10	78.37	74.97	71.85	68.98	66.33	63.88	61.60
	8.81	8.39	8.01	7.66	7.34	7.05	6.78	6.53	6.29
	322.47	*338.47*	*354.47*	*370.47*	*386.47*	*402.47*	*418.47*	*434.47*	*450.47*
H_{30}	85.66	81.61	77.93	74.56	71.48	68.63	66.01	63.58	61.32
	9.38	8.93	8.53	8.16	7.82	7.51	7.23	6.96	6.71
	324.49	*340.49*	*356.49*	*372.49*	*388.49*	*404.49*	*420.49*	*436.49*	*452.49*
H_{32}	85.13	81.13	77.49	74.16	71.10	68.29	65.69	63.28	61.05
	9.94	9.47	9.05	8.66	8.30	7.98	7.67	7.39	7.13
	326.50	*342.50*	*358.50*	*374.50*	*390.50*	*406.50*	*422.50*	*438.50*	*454.50*
H_{34}	84.60	80.65	77.05	73.76	70.74	67.95	65.38	62.99	60.78
	10.50	10.01	9.56	9.15	8.78	8.43	8.11	7.82	7.54
	328.52	*344.52*	*360.52*	*376.52*	*392.52*	*408.52*	*424.52*	*440.52*	*456.52*
H_{36}	84.08	80.18	76.62	73.36	70.37	67.62	65.07	62.71	60.51
	11.05	10.53	10.07	9.64	9.25	8.88	8.55	8.24	7.95
	330.53	*346.53*	*362.53*	*378.53*	*394.53*	*410.53*	*426.53*	*442.53*	*458.53*
H_{38}	83.57	79.71	76.20	72.97	70.01	67.29	64.76	62.42	60.24
	11.59	11.05	10.56	10.12	9.71	9.33	8.98	8.65	8.35
	332.55	*348.55*	*364.55*	*380.55*	*396.55*	*412.55*	*428.55*	*444.55*	*460.55*
H_{40}	83.06	79.25	75.77	72.59	69.66	66.96	64.46	62.14	59.98
	12.12	11.57	11.06	10.60	10.17	9.77	9.41	9.07	8.75
	334.57	*350.57*	*366.57*	*382.57*	*398.57*	*414.57*	*430.57*	*446.57*	*462.57*
H_{42}	82.56	78.79	75.36	72.20	69.31	66.63	64.15	61.86	59.72
	12.65	12.08	11.55	11.07	10.62	10.21	9.83	9.48	9.15

TABLE XV—*Continued*

C_{24}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	330.45	*346.45*	*362.45*	*378.45*	*394.45*	*410.45*	*426.45*	*442.45*	*458.45*
H_{26}	87.23	83.20	79.53	76.16	73.07	70.23	67.59	65.15	62.87
	7.93	7.57	7.23	6.93	6.64	6.39	6.15	5.92	5.72
	332.46	*348.46*	*364.46*	*380.46*	*396.46*	*412.46*	*428.46*	*444.46*	*460.46*
H_{28}	86.70	82.72	79.09	75.05	72.70	69.88	67.27	64.85	62.60
	8.49	8.10	7.74	7.42	7.12	6.84	6.59	6.35	6.13
	334.48	*350.48*	*366.48*	*382.48*	*398.48*	*414.48*	*430.48*	*446.48*	*462.48*
H_{30}	86.18	82.24	78.65	75.36	72.33	69.54	66.96	64.56	62.32
	9.04	8.63	8.25	7.91	7.59	7.30	7.02	6.77	6.54
	336.50	*352.50*	*368.50*	*384.50*	*400.50*	*416.50*	*432.50*	*448.50*	*464.50*
H_{32}	85.66	81.77	78.22	74.96	71.97	69.21	66.65	64.27	62.05
	9.59	9.15	8.75	8.39	8.05	7.75	7.46	7.19	6.95
	338.51	*354.51*	*370.51*	*386.51*	*402.51*	*418.51*	*434.51*	*450.51*	*466.51*
H_{34}	85.15	81.31	77.80	74.58	71.61	68.87	66.34	63.98	61.79
	10.12	9.67	9.25	8.87	8.51	8.19	7.89	7.61	7.35
	340.53	*356.53*	*372.53*	*388.53*	*404.53*	*420.53*	*436.53*	*452.53*	*468.53*
H_{36}	84.64	80.85	77.37	74.19	71.25	68.54	66.03	63.70	61.52
	10.66	10.18	9.74	9.34	8.97	8.63	8.31	8.02	7.75
	342.54	*358.54*	*374.54*	*390.54*	*406.54*	*422.54*	*438.54*	*454.54*	*470.54*
H_{38}	84.15	80.39	76.96	73.81	70.90	68.22	65.73	63.41	61.26
	11.18	10.68	10.23	9.81	9.42	9.06	8.73	8.43	8.14
	344.56	*360.56*	*376.56*	*392.56*	*408.56*	*424.56*	*440.56*	*456.56*	*472.56*
H_{40}	83.65	79.94	76.55	73.43	70.55	67.89	65.43	63.13	61.00
	11.70	11.18	10.71	10.27	9.87	9.50	9.15	8.83	8.53
	346.58	*362.58*	*378.58*	*394.58*	*410.58*	*426.58*	*442.58*	*458.58*	*474.58*
H_{42}	83.17	79.50	76.14	73.05	70.20	67.57	65.13	62.85	60.74
	12.22	11.68	11.18	10.73	10.31	9.93	9.57	9.23	8.92
	348.59	*364.59*	*380.59*	*396.59*	*412.59*	*428.59*	*444.59*	*460.59*	*476.59*
H_{44}	82.69	79.06	75.74	72.68	69.86	67.25	64.83	62.58	60.48
	12.72	12.16	11.65	11.18	10.75	10.35	9.98	9.63	9.31

TABLE XV—*Continued*

C_{25}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	344.47	*360.47*	*376.47*	*392.47*	*408.47*	*424.47*	*440.47*	*456.47*	*472.47*
H_{28}	87.16	83.29	79.75	76.50	73.51	70.74	68.17	65.78	63.55
	8.19	7.83	7.50	7.19	6.91	6.65	6.41	6.18	5.97
	346.49	*362.49*	*378.49*	*394.49*	*410.49*	*426.49*	*442.49*	*458.49*	*474.49*
H_{30}	86.65	82.83	79.33	76.11	73.14	70.40	67.85	65.49	63.28
	8.73	8.34	7.99	7.67	7.37	7.09	6.83	6.60	6.37
	348.51	*364.51*	*380.51*	*396.51*	*412.51*	*428.51*	*444.51*	*460.51*	*476.51*
H_{32}	86.15	82.37	78.91	75.72	72.79	70.07	67.55	65.20	63.01
	9.37	8.95	8.48	8.14	7.82	7.53	7.26	7.01	6.77
	350.52	*366.52*	*382.52*	*398.52*	*414.52*	*430.52*	*446.52*	*462.52*	*478.52*
H_{34}	85.66	81.92	78.49	75.34	72.43	69.74	67.24	64.92	62.75
	9.78	9.35	8.96	8.60	8.27	7.96	7.67	7.41	7.16
	352.54	*368.54*	*384.54*	*400.54*	*416.54*	*432.54*	*448.54*	*464.54*	*480.54*
H_{36}	85.17	81.47	78.08	74.96	72.08	69.42	66.94	64.63	62.48
	10.29	9.85	9.44	9.06	8.71	8.39	8.09	7.81	7.55
	354.55	*370.55*	*386.55*	*402.55*	*418.55*	*434.55*	*450.55*	*466.55*	*482.55*
H_{38}	84.68	81.03	77.67	74.59	71.74	69.09	66.64	64.36	62.22
	10.80	10.33	9.91	9.51	9.15	8.81	8.50	8.21	7.94
	356.57	*372.57*	*388.57*	*404.57*	*420.57*	*436.57*	*452.57*	*468.57*	*484.57*
H_{40}	84.21	80.59	77.27	74.21	71.39	68.77	66.34	64.08	61.96
	11.31	10.82	10.38	9.97	9.59	9.24	8.91	8.60	8.32
	358.59	*374.59*	*390.59*	*406.59*	*422.59*	*438.59*	*454.59*	*470.59*	*486.59*
H_{42}	83.73	80.15	76.87	73.85	71.05	68.46	66.05	63.80	61.70
	11.86	11.36	10.89	10.46	10.07	9.70	9.36	9.04	8.74
	360.60	*376.60*	*392.60*	*408.60*	*424.60*	*440.60*	*456.60*	*472.60*	*488.60*
H_{44}	83.03	79.73	76.48	73.48	70.71	68.15	65.76	63.53	61.45
	12.30	11.78	11.30	10.85	10.44	10.06	9.71	9.38	9.08
	362.62	*378.62*	*394.62*	*410.62*	*426.62*	*442.62*	*458.62*	*474.62*	*490.62*
H_{46}	82.80	79.30	76.09	73.12	70.38	67.83	65.47	63.26	61.19
	12.79	12.25	11.75	11.29	10.87	10.48	10.11	9.77	9.45

TABLE XV—*Continued*

C_{26}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	360.52	*376.52*	*392.52*	*408.52*	*424.52*	*440.52*	*456.52*	*472.52*	*488.52*
H_{32}	86.61	82.93	79.55	76.44	73.56	70.88	68.40	66.08	63.92
	8.95	8.57	8.22	7.90	7.60	7.32	7.07	6.83	6.60
	362.53	*378.53*	*394.53*	*410.53*	*426.53*	*442.53*	*458.53*	*474.53*	*490.53*
H_{34}	86.13	82.49	79.15	76.06	73.21	70.56	68.10	65.80	63.66
	9.45	9.05	8.69	8.35	8.03	7.74	7.47	7.22	6.99
	364.55	*380.55*	*396.55*	*412.55*	*428.55*	*444.55*	*460.55*	*476.55*	*492.55*
H_{36}	85.66	82.05	78.74	75.69	72.86	70.24	67.80	65.53	63.40
	9.95	9.54	9.15	8.80	8.47	8.16	7.88	7.62	7.37
	366.56	*382.56*	*398.56*	*414.56*	*430.56*	*446.56*	*462.56*	*478.56*	*494.56*
H_{38}	85.19	81.62	78.35	75.32	72.52	69.93	67.51	65.25	63.14
	10.45	10.01	9.61	9.24	8.90	8.58	8.28	8.00	7.74
	368.58	*384.58*	*400.58*	*416.58*	*432.58*	*448.58*	*464.58*	*480.58*	*496.58*
H_{40}	84.72	81.20	77.95	74.96	72.19	69.61	67.21	64.98	62.88
	10.94	10.48	10.07	9.68	9.32	8.99	8.68	8.95	8.12
	370.60	*386.60*	*402.60*	*418.60*	*434.60*	*450.60*	*466.60*	*482.60*	*498.60*
H_{42}	84.26	80.77	77.56	74.60	71.85	69.30	66.92	64.70	62.63
	11.42	10.95	10.52	10.11	9.74	9.40	9.07	8.77	8.49
	372.61	*388.61*	*404.61*	*420.61*	*436.61*	*452.61*	*468.61*	*484.61*	*500.61*
H_{44}	83.80	80.35	77.18	74.24	71.52	68.99	66.64	64.44	62.38
	11.90	11.41	10.96	10.54	10.16	9.80	9.46	9.15	8.86
	374.63	*390.63*	*406.63*	*422.63*	*438.63*	*454.63*	*470.63*	*486.63*	*502.63*
H_{46}	83.35	79.94	76.79	73.88	71.19	68.68	66.35	64.18	62.13
	12.38	11.87	11.40	10.98	10.58	10.20	9.85	9.53	9.23
	376.64	*392.64*	*408.64*	*424.64*	*440.64*	*456.64*	*472.64*	*488.64*	*504.64*
H_{48}	82.91	79.53	76.41	73.54	70.87	68.38	66.07	63.90	61.88
	12.85	12.32	11.84	11.39	10.98	10.59	10.24	9.90	9.59
	378.66	*394.66*	*410.66*	*426.66*	*442.66*	*458.66*	*474.66*	*490.66*	*506.66*
H_{50}	82.46	79.12	76.04	73.19	70.54	68.08	65.79	63.64	61.63
	13.31	12.77	12.27	11.81	11.39	10.99	10.62	10.27	9.95

TABLE XV—*Continued*

C_{27}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	372.53	*388.53*	*404.53*	*420.53*	*436.53*	*452.53*	*468.53*	*484.53*	*500.53*
H_{32}	87.05	83.46	80.16	77.11	74.28	71.66	69.21	66.92	64.79
	8.66	8.30	7.97	7.67	7.39	7.13	6.89	6.66	6.45
	374.54	*390.54*	*406.54*	*422.54*	*438.54*	*454.54*	*470.54*	*486.54*	*502.54*
H_{34}	86.58	83.46	79.76	76.74	73.94	71.34	68.91	66.65	64.53
	9.15	8.78	8.43	8.11	7.81	7.54	7.28	7.04	6.82
	376.56	*392.56*	*408.56*	*424.56*	*440.56*	*456.56*	*472.56*	*488.56*	*504.56*
H_{36}	86.11	82.60	79.37	76.38	73.60	71.02	68.62	66.37	64.27
	9.64	9.24	8.88	8.55	8.24	7.95	7.68	7.43	7.19
	378.57	*394.57*	*410.57*	*426.57*	*442.57*	*458.57*	*474.57*	*490.57*	*506.57*
H_{38}	85.66	82.18	78.98	76.02	73.27	70.71	68.33	66.10	64.01
	10.12	9.71	9.33	8.98	8.65	8.35	8.07	7.81	7.56
	380.59	*396.59*	*412.59*	*428.59*	*444.59*	*460.59*	*476.59*	*492.59*	*508.59*
H_{40}	85.20	81.76	78.59	75.66	72.94	70.40	68.04	65.83	63.80
	10.59	10.17	9.77	9.41	9.07	8.75	8.46	8.19	7.93
	382.61	*398.61*	*414.61*	*430.61*	*446.61*	*462.61*	*478.61*	*494.61*	*510.61*
H_{42}	84.75	81.35	78.21	75.30	72.61	70.10	67.75	65.56	63.51
	11.07	10.62	10.21	9.83	9.48	9.15	8.85	8.56	8.29
	384.62	*400.62*	*416.62*	*432.62*	*448.62*	*464.62*	*480.62*	*496.62*	*512.62*
H_{44}	84.31	80.94	77.83	74.95	72.28	69.79	67.47	65.30	63.26
	11.53	11.07	10.65	10.25	9.89	9.55	9.23	8.93	8.65
	386.64	*402.64*	*418.64*	*434.64*	*450.64*	*466.64*	*482.64*	*498.64*	*514.64*
H_{46}	83.87	80.54	77.46	74.61	71.96	69.49	67.19	65.03	63.01
	11.99	11.52	11.08	10.67	10.29	9.94	9.61	9.30	9.01
	388.65	*404.65*	*420.65*	*436.65*	*452.65*	*468.65*	*484.65*	*500.65*	*516.65*
H_{48}	83.43	80.14	77.09	74.26	71.64	69.19	66.91	64.77	62.76
	12.45	11.96	11.50	11.08	10.69	10.32	9.98	9.66	9.36
	390.67	*406.67*	*422.67*	*438.67*	*454.67*	*470.67*	*486.67*	*502.67*	*518.67*
H_{50}	83.00	79.74	76.72	73.92	71.32	68.90	66.63	64.51	62.52
	12.90	12.39	11.92	11.49	11.08	10.71	10.36	10.03	9.72

TABLE XV—*Continued*

C_{28}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	386.55	*402.55*	*418.55*	*434.55*	*450.55*	*466.55*	*482.55*	*498.55*	*514.55*
H_{34}	87.00	83.54	80.34	77.39	74.64	72.08	69.69	67.45	65.35
	8.87	8.51	8.19	7.89	7.61	7.35	7.10	6.87	6.66
	388.57	*404.57*	*420.57*	*436.57*	*452.57*	*468.57*	*484.57*	*500.57*	*516.57*
H_{36}	86.54	83.12	79.96	77.03	74.30	71.77	69.40	67.18	65.10
	9.34	8.97	8.63	8.31	8.02	7.74	7.49	7.25	7.03
	390.58	*406.58*	*422.58*	*438.58*	*454.58*	*470.58*	*486.58*	*502.58*	*518.58*
H_{38}	86.10	82.71	79.58	76.67	73.98	71.46	69.11	66.91	64.85
	9.81	9.42	9.06	8.73	8.43	8.14	7.87	7.62	7.39
	392.60	*408.60*	*424.60*	*440.60*	*456.60*	*472.60*	*488.60*	*504.60*	*520.60*
H_{40}	85.65	82.30	79.20	76.32	73.65	71.16	68.83	66.64	64.59
	10.27	9.87	9.50	9.15	8.83	8.53	8.25	7.99	7.74
	394.62	*410.62*	*426.62*	*442.62*	*458.62*	*474.62*	*490.62*	*506.62*	*522.62*
H_{42}	85.22	81.90	78.82	75.97	73.32	70.85	68.54	66.38	64.35
	10.73	10.31	9.92	9.57	9.23	8.92	8.63	8.36	8.10
	396.63	*412.63*	*428.63*	*444.63*	*460.63*	*476.63*	*492.63*	*508.63*	*524.63*
H_{44}	84.78	81.50	78.45	75.63	73.00	70.55	68.26	66.11	64.10
	11.18	10.75	10.35	9.97	9.63	9.30	9.00	8.72	8.45
	398.65	*414.65*	*430.65*	*446.65*	*462.65*	*478.65*	*494.65*	*510.65*	*526.65*
H_{46}	84.35	81.10	78.09	75.29	72.69	70.26	67.98	65.85	63.85
	11.63	11.18	10.77	10.38	10.02	9.69	9.37	9.08	8.80
	400.66	*416.66*	*432.66*	*448.66*	*464.66*	*480.66*	*496.66*	*512.66*	*528.66*
H_{48}	83.93	80.71	77.72	74.95	72.37	69.96	67.71	65.60	63.61
	12.08	11.61	11.18	10.78	10.41	10.07	9.74	9.44	9.15
	402.68	*418.68*	*434.68*	*450.68*	*466.68*	*482.68*	*498.68*	*514.68*	*530.68*
H_{50}	83.51	80.32	77.36	74.62	72.06	69.67	67.43	65.34	63.37
	12.52	12.04	11.59	11.18	10.80	10.44	10.11	9.79	9.50
	404.70	*420.70*	*436.70*	*452.70*	*468.70*	*484.70*	*500.70*	*516.70*	*532.70*
H_{52}	83.09	79.93	77.00	74.28	71.75	69.38	67.16	65.08	63.13
	12.95	12.46	12.00	11.58	11.18	10.81	10.47	10.15	9.84

TABLE XV—*Continued*

C_{29}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	400.58	*416.58*	*432.58*	*448.58*	*464.58*	*480.58*	*496.58*	*512.58*	*528.58*
H_{36}	86.95	83.61	80.51	77.64	74.97	72.47	70.14	67.95	65.89
	9.06	8.71	8.39	8.09	7.81	7.55	7.31	7.08	6.87
	402.59	*418.59*	*434.59*	*450.59*	*466.59*	*482.59*	*498.59*	*514.59*	*530.59*
H_{38}	86.51	83.21	80.14	77.30	74.65	72.17	69.85	67.68	65.64
	9.51	9.15	8.81	8.50	8.21	7.94	7.68	7.44	7.22
	404.61	*420.61*	*436.61*	*452.61*	*468.61*	*484.61*	*500.61*	*516.61*	*532.61*
H_{40}	86.08	82.81	79.77	76.95	74.32	71.87	69.57	67.42	65.39
	9.97	9.59	9.23	8.91	8.60	8.32	8.05	7.80	7.57
	406.63	*422.63*	*438.63*	*454.63*	*470.63*	*486.63*	*502.63*	*518.63*	*534.63*
H_{42}	85.65	82.41	79.40	76.61	74.01	71.57	69.29	67.16	65.15
	10.41	10.02	9.65	9.31	9.00	8.70	8.42	8.16	7.92
	408.64	*424.64*	*440.64*	*456.64*	*472.64*	*488.64*	*504.64*	*520.64*	*536.64*
H_{44}	85.23	82.02	79.04	76.27	73.69	71.28	69.02	66.90	64.90
	10.85	10.44	10.06	9.71	9.38	9.08	8.79	8.52	8.26
	410.66	*426.66*	*442.66*	*458.66*	*474.66*	*490.66*	*506.66*	*522.66*	*538.66*
H_{46}	84.81	81.63	78.68	75.94	73.38	70.98	68.74	66.64	64.66
	11.29	10.87	10.48	10.11	9.77	9.45	9.15	8.87	8.61
	412.67	*428.67*	*444.67*	*460.67*	*476.67*	*492.67*	*508.67*	*524.67*	*540.67*
H_{48}	84.40	81.25	78.33	75.61	73.07	70.69	68.47	66.38	64.42
	11.72	11.29	10.88	10.50	10.15	9.82	9.51	9.22	8.95
	414.69	*430.69*	*446.69*	*462.69*	*478.69*	*494.69*	*510.69*	*526.69*	*542.69*
H_{50}	83.99	80.87	77.97	75.28	72.76	70.41	68.20	66.13	64.18
	12.15	11.70	11.28	10.89	10.53	10.19	9.87	9.57	9.29
	416.71	*432.71*	*448.71*	*464.71*	*480.71*	*496.71*	*512.71*	*528.71*	*544.71*
H_{52}	83.58	80.49	77.62	74.95	72.45	70.12	67.93	65.88	63.94
	12.58	12.11	11.68	11.28	10.90	10.55	10.22	9.91	9.62
	418.72	*434.72*	*450.72*	*466.72*	*482.72*	*498.72*	*514.72*	*530.72*	*546.72*
H_{54}	83.18	80.12	77.27	74.63	72.15	69.84	67.67	65.63	63.71
	13.00	12.52	12.08	11.66	11.28	10.91	10.57	10.26	9.96

TABLE XV—*Continued*

C_{30}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	414.60	*430.60*	*446.60*	*462.60*	*478.60*	*494.60*	*510.60*	*526.60*	*542.60*
H_{38}	86.90	83.67	80.68	77.89	75.28	72.85	70.56	68.42	66.40
	9.24	8.89	8.58	8.28	8.00	7.74	7.50	7.27	7.06
	416.62	*432.62*	*448.62*	*464.62*	*480.62*	*496.62*	*512.62*	*528.62*	*544.62*
H_{40}	86.48	83.28	80.31	77.55	74.97	72.55	70.29	68.16	66.16
	9.68	9.32	8.99	8.68	8.39	8.12	7.87	7.63	7.40
	418.64	*434.64*	*450.64*	*466.64*	*482.64*	*498.64*	*514.64*	*530.64*	*546.64*
H_{42}	86.06	82.90	79.95	77.21	74.65	72.26	70.01	67.90	65.91
	10.11	9.74	9.40	9.07	8.77	8.49	8.23	7.98	7.75
	420.65	*436.65*	*452.65*	*468.65*	*484.65*	*500.65*	*516.65*	*532.65*	*548.65*
H_{44}	85.65	82.51	79.60	76.88	74.34	71.97	69.74	67.64	65.67
	10.54	10.16	9.80	9.46	9.15	8.86	8.58	8.33	8.08
	422.67	*438.67*	*454.67*	*470.67*	*486.67*	*502.67*	*518.67*	*534.67*	*550.67*
H_{46}	85.24	82.13	79.24	76.55	74.03	71.68	69.47	67.39	65.43
	10.97	10.57	10.20	9.85	9.53	9.22	8.94	8.67	8.42
	424.68	*440.68*	*456.68*	*472.68*	*488.68*	*504.68*	*520.68*	*536.68*	*552.68*
H_{48}	84.84	81.76	78.90	76.22	73.73	71.39	69.20	67.13	65.19
	11.39	10.98	10.59	10.24	9.90	9.59	9.29	9.01	8.75
	426.70	*442.70*	*458.70*	*474.70*	*490.70*	*506.70*	*522.70*	*538.70*	*554.70*
H_{50}	84.44	81.39	78.55	75.90	73.43	71.11	68.93	66.88	64.95
	11.81	11.38	10.99	10.62	10.27	9.95	9.64	9.36	9.09
	428.72	*444.72*	*460.72*	*476.72*	*492.72*	*508.72*	*524.72*	*540.72*	*556.72*
H_{52}	84.04	81.02	78.20	75.58	73.12	70.82	68.67	66.63	64.72
	12.23	11.79	11.38	11.00	10.64	10.30	9.99	9.69	9.42
	430.73	*446.73*	*462.73*	*478.73*	*494.73*	*510.73*	*526.73*	*542.73*	*558.73*
H_{54}	83.65	80.65	77.86	75.26	72.83	70.55	68.40	66.39	64.49
	12.64	12.18	11.76	11.37	11.00	10.66	10.33	10.03	9.74
	432.75	*448.75*	*464.75*	*480.75*	*496.75*	*512.75*	*528.75*	*544.75*	*560.75*
H_{56}	83.26	80.29	77.53	74.95	72.53	70.27	68.14	66.14	64.25
	13.04	12.58	12.15	11.74	11.36	11.01	10.68	10.36	10.07

TABLE XV—*Continued*

C_{31}	O	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9
	428.63	*444.63*	*460.63*	*476.63*	*492.63*	*508.63*	*524.63*	*540.63*	*556.63*
H_{40}	86.86	83.73	80.83	78.11	75.58	73.20	70.97	68.87	66.89
	9.41	9.07	8.75	8.46	8.18	7.93	7.69	7.46	7.24
	430.65	*446.65*	*462.65*	*478.65*	*494.65*	*510.65*	*526.65*	*542.65*	*558.65*
H_{42}	86.45	83.36	80.47	77.78	75.27	72.91	70.69	68.61	66.64
	9.83	9.48	9.15	8.85	8.56	8.29	8.04	7.80	7.58
	432.66	*448.66*	*464.66*	*480.66*	*496.66*	*512.66*	*528.66*	*544.66*	*560.66*
H_{44}	86.05	82.98	80.13	77.46	74.96	72.62	70.43	68.36	66.41
	10.25	9.88	9.54	9.23	8.93	8.65	8.39	8.14	7.91
	434.68	*450.68*	*466.68*	*482.68*	*498.68*	*514.68*	*530.68*	*546.68*	*562.68*
H_{46}	85.65	82.61	79.78	77.13	74.66	72.34	70.16	68.10	66.17
	10.67	10.29	9.94	9.61	9.30	9.01	8.74	8.48	8.24
	436.69	*452.69*	*468.69*	*484.69*	*500.69*	*516.69*	*532.69*	*548.69*	*564.69*
H_{48}	85.26	82.24	79.44	76.81	74.36	72.06	69.89	67.85	65.93
	11.08	10.69	10.32	9.98	9.66	9.36	9.08	8.82	8.57
	438.71	*454.71*	*470.71*	*486.71*	*502.71*	*518.71*	*534.71*	*550.71*	*566.71*
H_{50}	84.86	81.88	79.10	76.50	74.06	71.78	69.63	67.61	65.70
	11.49	11.08	10.71	10.36	10.03	9.72	9.43	9.15	8.89
	440.73	*456.73*	*472.73*	*488.73*	*504.73*	*520.73*	*536.73*	*552.73*	*568.73*
H_{52}	84.48	81.52	78.76	76.18	73.76	71.50	69.37	67.36	65.46
	11.89	11.48	11.09	10.73	10.39	10.07	9.77	9.48	9.22
	442.74	*458.74*	*474.74*	*490.74*	*506.74*	*522.74*	*538.74*	*554.74*	*570.74*
H_{54}	84.09	81.16	78.42	75.87	73.47	71.22	69.11	67.11	65.23
	12.29	11.86	11.47	11.09	10.74	10.41	10.10	9.81	9.54
	444.76	*460.76*	*476.76*	*492.76*	*508.76*	*524.76*	*540.76*	*556.76*	*572.76*
H_{56}	83.71	80.80	78.09	75.56	73.18	70.95	68.85	66.87	65.00
	12.69	12.25	11.84	11.46	11.10	10.76	10.44	10.14	9.86
	446.77	*462.77*	*478.77*	*494.77*	*510.77*	*526.77*	*542.77*	*558.77*	*574.77*
H_{58}	83.33	80.45	77.76	75.25	72.89	70.68	68.59	66.63	64.78
	13.08	12.63	12.21	11.82	11.45	11.10	10.77	10.46	10.17

TABLE XV—*Continued*

C_{32}	O	O_2	O_3	O_4	O_5	O_6	O_7		O_9
	442.66	*458.66*	*474.66*	*490.66*	*506.66*	*522.66*	*538.66*	*554.66*	*570.66*
H_{42}	86.82	83.79	80.97	78.33	75.85	73.53	71.35	69.29	67.35
	9.56	9.23	8.92	8.63	8.36	8.10	7.86	7.63	7.42
	444.67	*460.67*	*476.67*	*492.67*	*508.67*	*524.67*	*540.67*	*556.67*	*572.67*
H_{44}	86.43	83.43	80.63	78.01	75.55	73.25	71.08	69.04	67.11
	9.97	9.63	9.32	9.00	8.72	8.45	8.20	7.97	7.74
	446.69	*462.69*	*478.69*	*494.69*	*510.69*	*526.69*	*542.69*	*558.69*	*574.69*
H_{46}	86.04	83.06	80.29	77.69	75.26	72.97	70.82	68.79	66.87
	10.38	10.02	9.69	9.37	9.08	8.80	8.54	8.28	8.07
	448.70	*464.70*	*480.70*	*496.70*	*512.70*	*528.70*	*544.70*	*560.70*	*576.70*
H_{48}	85.65	82.70	79.95	77.37	74.96	72.69	70.56	68.54	66.64
	10.78	10.41	10.06	9.74	9.44	9.15	8.88	8.63	8.39
	450.72	*466.72*	*482.72*	*498.72*	*514.72*	*530.72*	*546.72*	*562.72*	*578.72*
H_{50}	85.27	82.34	79.62	77.06	74.67	72.41	70.30	68.30	66.41
	11.18	10.80	10.44	10.11	9.79	9.50	9.22	8.96	8.71
	452.74	*468.74*	*484.74*	*500.74*	*516.74*	*532.74*	*548.74*	*564.74*	*580.74*
H_{52}	84.89	81.99	79.28	76.75	74.37	72.14	70.04	68.05	66.18
	11.58	11.18	10.81	10.47	10.14	9.84	9.55	9.28	9.03
	454.75	*470.75*	*486.75*	*502.75*	*518.75*	*534.75*	*550.75*	*566.75*	*582.75*
H_{54}	84.51	81.64	78.96	76.44	74.09	71.87	69.78	67.81	65.95
	11.97	11.56	11.18	10.83	10.49	10.18	9.88	9.60	9.34
	456.77	*472.77*	*488.77*	*504.77*	*520.77*	*536.77*	*552.77*	*568.77*	*584.77*
H_{56}	84.14	81.29	78.63	76.14	73.80	71.60	69.53	67.57	65.72
	12.36	11.94	11.55	11.18	10.84	10.52	10.21	9.92	9.65
	458.78	*474.78*	*490.78*	*506.78*	*522.78*	*538.78*	*554.78*	*570.78*	*586.78*
H_{58}	83.77	80.95	78.31	75.84	73.51	71.33	69.27	67.33	65.50
	12.74	12.31	11.91	11.54	11.18	10.85	10.54	10.24	9.96
	460.80	*476.80*	*492.80*	*508.80*	*524.80*	*540.80*	*556.80*	*572.80*	*588.80*
H_{60}	83.40	80.60	77.99	75.53	73.23	71.07	69.02	67.09	65.27
	13.12	12.68	12.27	11.89	11.52	11.18	10.86	10.56	10.27

Table XVI

A FIVE PLACE TABLE

of

LOGARITHMS OF NUMBERS

from

1 to 10,000

N.	L. 0	1	2	3	4	5	6	7	8	9
100	00 000	043	087	130	173	217	260	303	346	389
101	432	475	518	561	604	647	689	732	775	817
102	860	903	945	988	*030	*072	*115	*157	*199	*242
103	01 284	326	368	410	452	494	536	578	620	662
104	703	745	787	828	870	912	953	995	*036	*078
105	02 119	160	202	243	284	325	366	407	449	490
106	531	572	612	653	694	735	776	816	857	898
107	938	979	*019	*060	*100	*141	*181	*222	*262	*302
108	03 342	383	423	463	503	543	583	623	663	703
109	743	782	822	862	902	941	981	*021	*060	*100
110	04 139	179	218	258	297	336	376	415	454	493
111	532	571	610	650	689	727	766	805	844	883
112	922	961	999	*038	*077	*115	*154	*192	*231	*269
113	05 308	346	385	423	461	500	538	576	614	652
114	690	729	767	805	843	881	918	956	994	*032
115	06 070	108	145	183	221	258	296	333	371	408
116	446	483	521	558	595	633	670	707	744	781
117	819	856	893	930	967	*004	*041	*078	*115	*151
118	07 188	225	262	298	335	372	408	445	482	518
119	555	591	628	664	700	737	773	809	846	882
120	918	954	990	*027	*063	*099	*135	*171	*207	*243
121	08 279	314	350	386	422	458	493	529	565	600
122	636	672	707	743	778	814	849	884	920	955
123	991	*026	*061	*096	*132	*167	*202	*237	*272	*307
124	09 342	377	412	447	482	517	552	587	621	656
125	691	726	760	795	830	864	899	934	968	*003
126	10 037	072	106	140	175	209	243	278	312	346
127	380	415	449	483	517	551	585	619	653	687
128	721	755	789	823	857	890	924	958	992	*025
129	11 059	093	126	160	193	227	261	294	327	361
130	394	428	461	494	528	561	594	628	661	694
131	727	760	793	826	860	893	926	959	992	*024
132	12 057	090	123	156	189	222	254	287	320	352
133	385	418	450	483	516	548	581	613	646	678
134	710	743	775	808	840	872	905	937	969	*001
135	13 033	066	098	130	162	194	226	258	290	322
136	354	386	418	450	481	513	545	577	609	640
137	672	704	735	767	799	830	862	893	925	956
138	988	*019	*051	*082	*114	*145	*176	*208	*239	*270
139	14 301	333	364	395	426	457	489	520	551	582
140	613	644	675	706	737	768	799	829	860	891
141	922	953	983	*014	*045	*076	*106	*137	*168	*198
142	15 229	259	290	320	351	381	412	442	473	503
143	534	564	594	625	655	685	715	746	776	806
144	836	866	897	927	957	987	*017	*047	*077	*107
145	16 137	167	197	227	256	286	316	346	376	406
146	435	465	495	524	554	584	613	643	673	702
147	732	761	791	820	850	879	909	938	967	997
148	17 026	056	085	114	143	173	202	231	260	289
149	319	348	377	406	435	464	493	522	551	580
150	609	638	667	696	725	754	782	811	840	869
N.	**L. 0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

P. P.

	44	**43**	**42**
1	4,4	4,3	4,2
2	8,8	8,6	8,4
3	13,2	12,9	12,6
4	17,6	17,2	16,8
5	22,0	21,5	21,0
6	26,4	25,8	25,2
7	30,8	30,1	29,4
8	35,2	34,4	33,6
9	39,6	38,7	37,8

	41	**40**	**39**
1	4,1	4,0	3,9
2	8,2	8,0	7,8
3	12,3	12,0	11,7
4	16,4	16,0	15,6
5	20,5	20,0	19,5
6	24,6	24,0	23,4
7	28,7	28,0	27,3
8	32,8	32,0	31,2
9	36,9	36,0	35,1

	38	**37**	**36**
1	3,8	3,7	3,6
2	7,6	7,4	7,2
3	11,4	11,1	10,8
4	15,2	14,8	14,4
5	19,0	18,5	18,0
6	22,8	22,2	21,6
7	26,6	25,9	25,2
8	30,4	29,6	28,8
9	34,2	33,3	32,4

	35	**34**	**33**
1	3,5	3,4	3,3
2	7,0	6,8	6,6
3	10,5	10,2	9,9
4	14,0	13,6	13,2
5	17,5	17,0	16,5
6	21,0	20,4	19,8
7	24,5	23,8	23,1
8	28,0	27,2	26,4
9	31,5	30,6	29,7

	32	**31**	**30**
1	3,2	3,1	3,0
2	6,4	6,2	6,0
3	9,6	9,3	9,0
4	12,8	12,4	12,0
5	16,0	15,5	15,0
6	19,2	18,6	18,0
7	22,4	21,7	21,0
8	25,6	24,8	24,0
9	28,8	27,9	27,0

P. P.

N.	L. 0	1	2	3	4	5	6	7	8	9
150	17 609	638	667	696	725̄	754	782	811	840	869
151	898	926	955	984	*013	*041	*070	*099	*127	*156
152	18 184	213	241	270	298	327	355	384	412	441
153	469	498	526	554	583	611	639	667	696	724
154	752	780	808	837	865̄	893	921	949	977	*005
155	19 033	061	089	117	145	173	201	229	257	285̄
156	312	340	368	396	424	451	479	507	535̄	562
157	590	618	645	673	700	728	756	783	811	838
158	866	893	921	948	976	*003	*030	*058	*085	*112
159	20 140	167	194	222	249	276	303	330	358	385̄
160	412	439	466	493	520	548	575̄	602	629	656
161	683	710	737	763	790	817	844	871	898	925̄
162	952	978	*005	*032	*059	*085	*112	*139	*165	*192
163	21 219	245	272	299	325	352	378	405̄	431	458
164	484	511	537	564	590	617	643	669	696	722
165	748	775̄	801	827	854	880	906	932	958	985̄
166	22 011	037	063	089	115	141	167	194	220	246
167	272	298	324	350	376	401	427	453	479	505
168	531	557	583	608	634	660	686	712	737	763
169	789	814	840	866	891	917	943	968	994	*019
170	23 045̄	070	096	121	147	172	198	223	249	274
171	300	325	350	376	401	426	452	477	502	528
172	553	578	603	629	654	679	704	729	754	779
173	805̄	830	855̄	880	905̄	930	955̄	980	*005̄	*030
174	24 055̄	080	105̄	130	155̄	180	204	229	254	279
175	304	329	353	378	403	428	452	477	502	527
176	551	576	601	625	650	674	699	724	748	773
177	797	822	846	871	895	920	944	969	993	*018
178	25 042	066	091	115	139	164	188	212	237	261
179	285	310	334	358	382	406	431	455̄	479	503
180	527	551	575	600	624	648	672	696	720	744
181	768	792	816	840	864	888	912	935	959	983
182	26 007	031	055̄	079	102	126	150	174	198	221
183	245	269	293	316	340	364	387	411	435̄	458
184	482	505	529	553	576	600	623	647	670	694
185	717	741	764	788	811	834	858	881	905̄	928
186	951	975̄	998	*021	*045̄	*068	*091	*114	*138	*161
187	27 184	207	231	254	277	300	323	346	370	393
188	416	439	462	485	508	531	554	577	600	623
189	646	669	692	715	738	761	784	807	830	852
190	875	898	921	944	967	989	*012	*035	*058	*081
191	28 103	126	149	171	194	217	240	262	285̄	307
192	330	353	375	398	421	443	466	488	511	533
193	556	578	601	623	646	668	691	713	735	758
194	780	803	825̄	847	870	892	914	937	959	981
195	29 003	026	048	070	092	115̄	137	159	181	203
196	226	248	270	292	314	336	358	380	403	425̄
197	447	469	491	513	535̄	557	579	601	623	645̄
198	667	688	710	732	754	776	798	820	842	863
199	885	907	929	951	973	994	*016	*038	*060	*081
200	30 103	125̄	146	168	190	211	233	255̄	276	298

N. L. 0 1 2 3 4 5 6 7 8 9

P. P.

	29	**28**
1	2,9	2,8
2	5,8	5,6
3	8,7	8,4
4	11,6	11,2
5	14,5	14,0
6	17,4	16,8
7	20,3	19,6
8	23,2	22,4
9	26,1	25,2

	27	**26**
1	2,7	2,6
2	5,4	5,2
3	8,1	7,8
4	10,8	10,4
5	13,5	13,0
6	16,2	15,6
7	18,9	18,2
8	21,6	20,8
9	24,3	23,4

	25
1	2,5
2	5,0
3	7,5
4	10,0
5	12,5
6	15,0
7	17,5
8	20,0
9	22,5

	24	**23**
1	2,4	2,3
2	4,8	4,6
3	7,2	6,9
4	9,6	9,2
5	12,0	11,5
6	14,4	13,8
7	16,8	16,1
8	19,2	18,4
9	21,6	20,7

	22	**21**
1	2,2	2,1
2	4,4	4,2
3	6,6	6,3
4	8,8	8,4
5	11,0	10,5
6	13,2	12,6
7	15,4	14,7
8	17,6	16,8
9	19,8	18,9

N.	L. 0	1	2	3	4	5	6	7	8	9
200	30 103	125̄	146	168	190	211	233	255̄	276	298
201	320	341	363	384	406	428	449	471	492	514
202	535	557	578	600	621	643	664	685	707	728
203	75̄0	771	792	814	835	856	878	899	920	942
204	963	984	*006	*027	*048	*069	*091	*112	*133	*154
205	31 175	197	218	239	260	281	302	323	345̄	366
206	387	408	429	45̄0	471	492	513	534	555	576
207	597	618	639	660	681	702	723	744	765̄	785
208	806	827	848	869	890	911	931	952	973	994
209	32 015̄	035	056	077	098	118	139	160	181	201
210	222	243	263	284	305̄	325	346	366	387	408
211	428	449	469	490	510	531	552	572	593	613
212	634	654	675̄	695̄	715	736	756	777	797	818
213	838	858	879	899	919	940	960	980	*001	*021
214	33 041	062	082	102	122	143	163	183	203	224
215	244	264	284	304	325̄	345̄	365̄	385	405	425
216	445	465	486	506	526	546	566	586	606	626
217	646	666	686	706	726	746	766	786	806	826
218	846	866	885	905	925	945	965	985̄	*005̄	*025̄
219	34 044	064	084	104	124	143	163	183	203	223
220	242	262	282	301	321	341	361	380	400	420
221	439	459	479	498	518	537	557	577	596	616
222	635	655̄	674	694	713	733	753	772	792	811
223	830	85̄0	869	889	908	928	947	967	986	*005
224	35 025̄	044	064	083	102	122	141	160	180	199
225	218	238	257	276	295	315̄	334	353	372	392
226	411	430	449	468	488	507	526	545	564	583
227	603	622	641	660	679	698	717	736	755	774
228	793	813	832	851	870	889	908	927	946	965̄
229	984	*003	*021	*040	*059	*078	*097	*116	*135	*154
230	36 173	192	211	229	248	267	286	305̄	324	342
231	361	380	399	418	436	455	474	493	511	530
232	549	568	586	605̄	624	642	661	680	698	717
233	736	754	773	791	810	829	847	866	884	903
234	922	940	959	977	996	*014	*033	*051	*070	*088
235	37 107	125	144	162	181	199	218	236	254	273
236	291	310	328	346	365̄	383	401	420	438	457
237	475̄	493	511	530	548	566	585̄	603	621	639
238	658	676	694	712	731	749	767	785	803	822
239	840	858	876	894	912	931	949	967	985̄	*003
240	38 021	039	057	075	093	112	130	148	166	184
241	202	220	238	256	274	292	310	328	346	364
242	382	399	417	435	453	471	489	507	525̄	543
243	561	578	596	614	632	65̄0	668	686	703	721
244	739	757	775̄	792	810	828	846	863	881	899
245	917	934	952	970	987	*005	*023	*041	*058	*076
246	39 094	111	129	146	164	182	199	217	235̄	252
247	270	287	305̄	322	340	358	375	393	410	428
248	445	463	480	498	515	533	550	568	585	602
249	620	637	655̄	672	690	707	724	742	759	777
250	794	811	829	846	863	881	898	915	933	950
N.	L. 0	1	2	3	4	5	6	7	8	9

P. P.

	22	21
1	2,2	2,1
2	4,4	4,2
3	6,6	6,3
4	8,8	8,4
5	11,0	10,5
6	13,2	12,6
7	15,4	14,7
8	17,6	16,8
9	19,8	18,9

	20
1	2,0
2	4,0
3	6,0
4	8,0
5	10,0
6	12,0
7	14,0
8	16,0
9	18,0

	19
1	1,9
2	3,8
3	5,7
4	7,6
5	9,5
6	11,4
7	13,3
8	15,2
9	17,1

	18
1	1,8
2	3,6
3	5,4
4	7,2
5	9,0
6	10,8
7	12,6
8	14,4
9	16,2

	17
1	1,7
2	3,4
3	5,1
4	6,8
5	8,5
6	10,2
7	11,9
8	13,6
9	15,3

P. P.

N.	L. 0	1	2	3	4	5	6	7	8	9
250	39 794	811	829	846	863	881	898	915	933	950
251	967	985̄	*002	*019	*037	*054	*071	*088	*106	*123
252	40 140	157	175̄	192	209	226	243	261	278	295̄
253	312	329	346	364	381	398	415̄	432	449	466
254	483	500	518	535̄	552	569	586	603	620	637
255	654	671	688	705	722	739	756	773	790	807
256	824	841	858	875̄	892	909	926	943	960	976
257	993	*010	*027	*044	*061	*078	*095̄	*111	*128	*145
258	41 162	179	196	212	229	246	263	280	296	313
259	330	347	363	380	397	414	430	447	464	481
260	497	514	531	547	564	581	597	614	631	647
261	664	681	697	714	731	747	764	780	797	814
262	830	847	863	880	896	913	929	946	963	979
263	996	*012	*029	*045	*062	*078	*095̄	*111	*127	*144
264	42 160	177	193	210	226	243	259	275	292	308
265	325̄	341	357	374	390	406	423	439	455	472
266	488	504	521	537	553	570	586	602	619	635̄
267	651	667	684	700	716	732	749	765̄	781	797
268	813	830	846	862	878	894	911	927	943	959
269	975	991	*008	*024	*040	*056	*072	*088	*104	*120
270	43 136	152	169	185̄	201	217	233	249	265̄	281
271	297	313	329	345̄	361	377	393	409	425̄	441
272	457	473	489	505̄	521	537	553	569	584	600
273	616	632	648	664	680	696	712	727	743	759
274	775	791	807	823	838	854	870	886	902	917
275	933	949	965̄	981	996	*012	*028	*044	*059	*075
276	44 091	107	122	138	154	170	185	201	217	232
277	248	264	279	295̄	311	326	342	358	373	389
278	404	420	436	451	467	483	498	514	529	545̄
279	560	576	592	607	623	638	654	669	685̄	700
280	716	731	747	762	778	793	809	824	840	855
281	871	886	902	917	932	948	963	979	994	*010
282	45 025̄	040	056	071	086	102	117	133	148	163
283	179	194	209	225̄	240	255	271	286	301	317
284	332	347	362	378	393	408	423	439	454	469
285	484	5̄00	515̄	530	545	561	576	591	606	621
286	637	652	667	682	697	712	728	743	758	773
287	788	803	818	834	849	864	879	894	909	924
288	939	954	969	984	*000	*015̄	*030	*045̄	*060	*075̄
289	46 090	105̄	120	135̄	15̄0	165̄	180	195̄	210	225̄
290	240	255̄	270	285̄	300	315̄	330	345̄	359	374
291	389	404	419	434	449	464	479	494	509	523
292	538	553	568	583	598	613	627	642	657	672
293	687	702	716	731	746	761	776	790	805	820
294	835̄	85̄0	864	879	894	909	923	938	953	967
295	982	997	*012	*026	*041	*056	*070	*085	*100	*114
296	47 129	144	159	173	188	202	217	232	246	261
297	276	290	305̄	319	334	349	363	378	392	407
298	422	436	451	465	480	494	509	524	538	553
299	567	582	596	611	625	640	654	669	683	698
300	712	727	741	756	770	784	799	813	828	842
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P. P.

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6	10,8	10,2	9,6	9,0	8,4
7	12,6	11,9	11,2	10,5	9,8
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9	16,2	15,3	14,4	13,5	12,6

P. P.

N.	L. 0	1	2	3	4	5	6	7	8	9
300	47 712	727	741	756	770	784	799	813	828	842
301	857	871	885	900	914	929	943	958	972	986
302	48 001	015	029	044	058	073	087	101	116	130
303	144	159	173	187	202	216	230	244	259	273
304	287	302	316	330	344	359	373	387	401	416
305	430	444	458	473	487	501	515	530	544	558
306	572	586	601	615̄	629	643	657	671	686	700
307	714	728	742	756	770	785̄	799	813	827	841
308	855	869	883	897	911	926	940	954	968	982
309	996	*010	*024	*038	*052	*066	*080	*094	*108	*122
310	49 136	150	164	178	192	206	220	234	248	262
311	276	290	304	318	332	346	360	374	388	402
312	415	429	443	457	471	485	499	513	527	541
313	554	568	582	596	610	624	638	651	665	679
314	693	707	721	734	748	762	776	790	803	817
315	831	845̄	859	872	886	900	914	927	941	955̄
316	969	982	996	*010	*024	*037	*051	*065̄	*079	*092
317	50 106	120	133	147	161	174	188	202	215	229
318	243	256	270	284	297	311	325̄	338	352	365
319	379	393	406	420	433	447	461	474	488	501
320	515̄	529	542	556	569	583	596	610	623	637
321	651	664	678	691	705̄	718	732	745	759	772
322	786	799	813	826	840	853	866	880	893	907
323	920	934	947	961	974	987	*001	*014	*028	*041
324	51 055̄	068	081	095̄	108	121	135̄	148	162	175̄
325	188	202	215	228	242	255	268	282	295	308
326	322	335	348	362	375	388	402	415̄	428	441
327	455̄	468	481	495̄	508	521	534	548	561	574
328	587	601	614	627	640	654	667	680	693	706
329	720	733	746	759	772	786	799	812	825	838
330	851	865̄	878	891	904	917	930	943	957	970
331	983	996	*009	*022	*035	*048	*061	*075̄	*088	*101
332	52 114	127	140	153	166	179	192	205	218	231
333	244	257	270	284	297	310	323	336	349	362
334	375̄	388	401	414	427	440	453	466	479	492
335	504	517	530	543	556	569	582	595	608	621
336	634	647	660	673	686	699	711	724	737	750
337	763	776	789	802	815̄	827	840	853	866	879
338	892	905̄	917	930	943	956	969	982	994	*007
339	53 020	033	046	058	071	084	097	110	122	135
340	148	161	173	186	199	212	224	237	25̄0	263
341	275	288	301	314	326	339	352	364	377	390
342	403	415	428	441	453	466	479	491	504	517
343	529	542	555̄	567	580	593	605	618	631	643
344	656	668	681	694	706	719	732	744	757	769
345	782	794	807	820	832	845̄	857	870	882	895
346	908	920	933	945	958	970	983	995	*008	*020
347	54 033	045	058	070	083	095	108	120	133	145
348	158	170	183	195	208	220	233	245	258	270
349	283	295̄	307	320	332	345̄	357	370	382	394
350	407	419	432	444	456	469	481	494	506	518
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P. P.

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P. P.

N.	L. 0	1	2	3	4	5	6	7	8	9
350	54 407	419	432	444	456	469	481	494	506	518
351	531	543	555	568	580	593	605	617	630	642
352	654	667	679	691	704	716	728	741	753	765
353	777	790	802	814	827	839	851	864	876	888
354	900	913	925	937	949	962	974	986	998	*011
355	55 023	035	047	060	072	084	096	108	121	133
356	145	157	169	182	194	206	218	230	242	255
357	267	279	291	303	315	328	340	352	364	376
358	388	400	413	425	437	449	461	473	485	497
359	509	522	534	546	558	570	582	594	606	618
360	630	642	654	666	678	691	703	715	727	739
361	751	763	775	787	799	811	823	835	847	859
362	871	883	895	907	919	931	943	955	967	979
363	991	*003	*015	*027	*038	*050	*062	*074	*086	*098
364	56 110	122	134	146	158	170	182	194	205	217
365	229	241	253	265	277	289	301	312	324	336
366	348	360	372	384	396	407	419	431	443	455
367	467	478	490	502	514	526	538	549	561	573
368	585	597	608	620	632	644	656	667	679	691
369	703	714	726	738	750	761	773	785	797	808
370	820	832	844	855	867	879	891	902	914	926
371	937	949	961	972	984	996	*008	*019	*031	*043
372	57 054	066	078	089	101	113	124	136	148	159
373	171	183	194	206	217	229	241	252	264	276
374	287	299	310	322	334	345	357	368	380	392
375	403	415	426	438	449	461	473	484	496	507
376	519	530	542	553	565	576	588	600	611	623
377	634	646	657	669	680	692	703	715	726	738
378	749	761	772	784	795	807	818	830	841	852
379	864	875	887	898	910	921	933	944	955	967
380	978	990	*001	*013	*024	*035	*047	*058	*070	*081
381	58 092	104	115	127	138	149	161	172	184	195
382	206	218	229	240	252	263	274	286	297	309
383	320	331	343	354	365	377	388	399	410	422
384	433	444	456	467	478	490	501	512	524	535
385	546	557	569	580	591	602	614	625	636	647
386	659	670	681	692	704	715	726	737	749	760
387	771	782	794	805	816	827	838	850	861	872
388	883	894	906	917	928	939	950	961	973	984
389	995	*006	*017	*028	*040	*051	*062	*073	*084	*095
390	59 106	118	129	140	151	162	173	184	195	207
391	218	229	240	251	262	273	284	295	306	318
392	329	340	351	362	373	384	395	406	417	428
393	439	450	461	472	483	494	506	517	528	539
394	550	561	572	583	594	605	616	627	638	649
395	660	671	682	693	704	715	726	737	748	759
396	770	780	791	802	813	824	835	846	857	868
397	879	890	901	912	923	934	945	956	966	977
398	988	999	*010	*021	*032	*043	*054	*065	*076	*086
399	60 097	108	119	130	141	152	163	173	184	195
400	206	217	228	239	249	260	271	282	293	304
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P. P.

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P. P.

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400	60 206	217	228	239	249	260	271	282	293	304
401	314	325	336	347	358	369	379	390	401	412
402	423	433	444	455	466	477	487	498	509	520
403	531	541	552	563	574	584	595	606	617	627
404	638	649	660	670	681	692	703	713	724	735
405	746	756	767	778	788	799	810	821	831	842
406	853	863	874	885	895	906	917	927	938	949
407	959	970	981	991	*002	*013	*023	*034	*045	*055
408	61 066	077	087	098	109	119	130	140	151	162
409	172	183	194	204	215	225	236	247	257	268
410	278	289	300	310	321	331	342	352	363	374
411	384	395	405	416	426	437	448	458	469	479
412	490	500	511	521	532	542	553	563	574	584
413	595	606	616	627	637	648	658	669	679	690
414	700	711	721	731	742	752	763	773	784	794
415	805	815	826	836	847	857	868	878	888	899
416	909	920	930	941	951	962	972	982	993	*003
417	62 014	024	034	045	055	066	076	086	097	107
418	118	128	138	149	159	170	180	190	201	211
419	221	232	242	252	263	273	284	294	304	315
420	325	335	346	356	366	377	387	397	408	418
421	428	439	449	459	469	480	490	500	511	521
422	531	542	552	562	572	583	593	603	613	624
423	634	644	655	665	675	685	696	706	716	726
424	737	747	757	767	778	788	798	808	818	829
425	839	849	859	870	880	890	900	910	921	931
426	941	951	961	972	982	992	*002	*012	*022	*033
427	63 043	053	063	073	083	094	104	114	124	134
428	144	155	165	175	185	195	205	215	225	236
429	246	256	266	276	286	296	306	317	327	337
430	347	357	367	377	387	397	407	417	428	438
431	448	458	468	478	488	498	508	518	528	538
432	548	558	568	579	589	599	609	619	629	639
433	649	659	669	679	689	699	709	719	729	739
434	749	759	769	779	789	799	809	819	829	839
435	849	859	869	879	889	899	909	919	929	939
436	949	959	969	979	988	998	*008	*018	*028	*038
437	64 048	058	068	078	088	098	108	118	128	137
438	147	157	167	177	187	197	207	217	227	237
439	246	256	266	276	286	296	306	316	326	335
440	345	355	365	375	385	395	404	414	424	434
441	444	454	464	473	483	493	503	513	523	532
442	542	552	562	572	582	591	601	611	621	631
443	640	650	660	670	680	689	699	709	719	729
444	738	748	758	768	777	787	797	807	816	826
445	836	846	856	865	875	885	895	904	914	924
446	933	943	953	963	972	982	992	*002	*011	*021
447	65 031	040	050	060	070	079	089	099	108	118
448	128	137	147	157	167	176	186	196	205	215
449	225	234	244	254	263	273	283	292	302	312
450	321	331	341	350	360	369	379	389	398	408
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P. P.

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450	65 321	331	341	350	360	369	379	389	398	408
451	418	427	437	447	456	466	475	485	495	504
452	514	523	533	543	552	562	571	581	591	600
453	610	619	629	639	648	658	667	677	686	696
454	706	715	725	734	744	753	763	772	782	792
455	801	811	820	830	839	849	858	868	877	887
456	896	906	916	925	935	944	954	963	973	982
457	992	*001	*011	*020	*030	*039	*049	*058	*068	*077
458	66 087	096	106	115	124	134	143	153	162	172
459	181	191	200	210	219	229	238	247	257	266
460	276	285	295	304	314	323	332	342	351	361
461	370	380	389	398	408	417	427	436	445	455
462	464	474	483	492	502	511	521	530	539	549
463	558	567	577	586	596	605	614	624	633	642
464	652	661	671	680	689	699	708	717	727	736
465	745	755	764	773	783	792	801	811	820	829
466	839	848	857	867	876	885	894	904	913	922
467	932	941	950	960	969	978	987	997	*006	*015
468	67 025	034	043	052	062	071	080	089	099	108
469	117	127	136	145	154	164	173	182	191	201
470	210	219	228	237	247	256	265	274	284	293
471	302	311	321	330	339	348	357	367	376	385
472	394	403	413	422	431	440	449	459	468	477
473	486	495	504	514	523	532	541	550	560	569
474	578	587	596	605	614	624	633	642	651	660
475	669	679	688	697	706	715	724	733	742	752
476	761	770	779	788	797	806	815	825	834	843
477	852	861	870	879	888	897	906	916	925	934
478	943	952	961	970	979	988	997	*006	*015	*024
479	68 034	043	052	061	070	079	088	097	106	115
480	124	133	142	151	160	169	178	187	196	205
481	215	224	233	242	251	260	269	278	287	296
482	305	314	323	332	341	350	359	368	377	386
483	395	404	413	422	431	440	449	458	467	476
484	485	494	502	511	520	529	538	547	556	565
485	574	583	592	601	610	619	628	637	646	655
486	664	673	681	690	699	708	717	726	735	744
487	753	762	771	780	789	797	806	815	824	833
488	842	851	860	869	878	886	895	904	913	922
489	931	940	949	958	966	975	984	993	*002	*011
490	69 020	028	037	046	055	064	073	082	090	099
491	108	117	126	135	144	152	161	170	179	188
492	197	205	214	223	232	241	249	258	267	276
493	285	294	302	311	320	329	338	346	355	364
494	373	381	390	399	408	417	425	434	443	452
495	461	469	478	487	496	504	513	522	531	539
496	548	557	566	574	583	592	601	609	618	627
497	636	644	653	662	671	679	688	697	705	714
498	723	732	740	749	758	767	775	784	793	801
499	810	819	827	836	845	854	862	871	880	888
500	897	906	914	923	932	940	949	958	966	975
N.	L. 0	1	2	3	4	5	6	7	8	9

P. P.

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P. P.

N.	L. 0	1	2	3	4	5	6	7	8	9	P. P.
500	69 897	906	914	923	932	940	949	958	966	975	
501	984	992	*001	*010	*018	*027	*036	*044	*053	*062	
502	70 070	079	088	096	105	114	122	131	140	148	
503	157	165	174	183	191	200	209	217	226	234	
504	243	252	260	269	278	286	295	303	312	321	
505	329	338	346	355	364	372	381	389	398	406	
506	415	424	432	441	449	458	467	475	484	492	
507	501	509	518	526	535	544	552	561	569	578	9
508	586	595	603	612	621	629	638	646	655	663	1 | 0,9
509	672	680	689	697	706	714	723	731	740	749	2 | 1,8
510	757	766	774	783	791	800	808	817	825	834	3 | 2,7
511	842	851	859	868	876	885	893	902	910	919	4 | 3,6
512	927	935	944	952	961	969	978	986	995	*003	5 | 4,5
513	71 012	020	029	037	046	054	063	071	079	088	6 | 5,4
514	096	105	113	122	130	139	147	155	164	172	7 | 6,3
515	181	189	198	206	214	223	231	240	248	257	8 | 7,2
516	265	273	282	290	299	307	315	324	332	341	9 | 8,1
517	349	357	366	374	383	391	399	408	416	425	
518	433	441	450	458	466	475	483	492	500	508	
519	517	525	533	542	550	559	567	575	584	592	
520	600	609	617	625	634	642	650	659	667	675	
521	684	692	700	709	717	725	734	742	750	759	8
522	767	775	784	792	800	809	817	825	834	842	1 | 0,8
523	850	858	867	875	883	892	900	908	917	925	2 | 1,6
524	933	941	950	958	966	975	983	991	999	*008	3 | 2,4
525	72 016	024	032	041	049	057	066	074	082	090	4 | 3,2
526	099	107	115	123	132	140	148	156	165	173	5 | 4,0
527	181	189	198	206	214	222	230	239	247	255	6 | 4,8
528	263	272	280	288	296	304	313	321	329	337	7 | 5,6
529	346	354	362	370	378	387	395	403	411	419	8 | 6,4
530	428	436	444	452	460	469	477	485	493	501	9 | 7,2
531	509	518	526	534	542	550	558	567	575	583	
532	591	599	607	616	624	632	640	648	656	665	
533	673	681	689	697	705	713	722	730	738	746	
534	754	762	770	779	787	795	803	811	819	827	
535	835	843	852	860	868	876	884	892	900	908	7
536	916	925	933	941	949	957	965	973	981	989	1 | 0,7
537	997	*006	*014	*022	*030	*038	*046	*054	*062	*070	2 | 1,4
538	73 078	086	094	102	111	119	127	135	143	151	3 | 2,1
539	159	167	175	183	191	199	207	215	223	231	4 | 2,8
540	239	247	255	263	272	280	288	296	304	312	5 | 3,5
541	320	328	336	344	352	360	368	376	384	392	6 | 4,2
542	400	408	416	424	432	440	448	456	464	472	7 | 4,9
543	480	488	496	504	512	520	528	536	544	552	8 | 5,6
544	560	568	576	584	592	600	608	616	624	632	9 | 6,3
545	640	648	656	664	672	679	687	695	703	711	
546	719	727	735	743	751	759	767	775	783	791	
547	799	807	815	823	830	838	846	854	862	870	
548	878	886	894	902	910	918	926	933	941	949	
549	957	965	973	981	989	997	*005	*013	*020	*028	
550	74 036	044	052	060	068	076	084	092	099	107	
N.	L. 0	1	2	3	4	5	6	7	8	9	P. P.

N.	L. 0	1	2	3	4	5	6	7	8	9	P. P.
550	74 036	044	052	060	068	076	084	092	099	107	
551	115	123	131	139	147	155	162	170	178	186	
552	194	202	210	218	225	233	241	249	257	265	
553	273	280	288	296	304	312	320	327	335	343	
554	351	359	367	374	382	390	398	406	414	421	
555	429	437	445	453	461	468	476	484	492	500	
556	507	515	523	531	539	547	554	562	570	578	
557	586	593	601	609	617	624	632	640	648	656	
558	663	671	679	687	695	702	710	718	726	733	
559	741	749	757	764	772	780	788	796	803	811	
560	819	827	834	842	850	858	865	873	881	889	
561	896	904	912	920	927	935	943	950	958	966	**8**
562	974	981	989	997	*005	*012	*020	*028	*035	*043	1 | 0,8
563	75 051	059	066	074	082	089	097	105	113	120	2 | 1,6
564	128	136	143	151	159	166	174	182	189	197	3 | 2,4
565	205	213	220	228	236	243	251	259	266	274	4 | 3,2
566	282	289	297	305	312	320	328	335	343	351	5 | 4,0
567	358	366	374	381	389	397	404	412	420	427	6 | 4,8
568	435	442	450	458	465	473	481	488	496	504	7 | 5,6
569	511	519	526	534	542	549	557	565	572	580	8 | 6,4
570	587	595	603	610	618	626	633	641	648	656	9 | 7,2
571	664	671	679	686	694	702	709	717	724	732	
572	740	747	755	762	770	778	785	793	800	808	
573	815	823	831	838	846	853	861	868	876	884	
574	891	899	906	914	921	929	937	944	952	959	
575	967	974	982	989	997	*005	*012	*020	*027	*035	
576	76 042	050	057	065	072	080	087	095	103	110	
577	118	125	133	140	148	155	163	170	178	185	
578	193	200	208	215	223	230	238	245	253	260	
579	268	275	283	290	298	305	313	320	328	335	
580	343	350	358	365	373	380	388	395	403	410	**7**
581	418	425	433	440	448	455	462	470	477	485	1 | 0,7
582	492	500	507	515	522	530	537	545	552	559	2 | 1,4
583	567	574	582	589	597	604	612	619	626	634	3 | 2,1
584	641	649	656	664	671	678	686	693	701	708	4 | 2,8
585	716	723	730	738	745	753	760	768	775	782	5 | 3,5
586	790	797	805	812	819	827	834	842	849	856	6 | 4,2
587	864	871	879	886	893	901	908	916	923	930	7 | 4,9
588	938	945	953	960	967	975	982	989	997	*004	8 | 5,6
589	77 012	019	026	034	041	048	056	063	070	078	9 | 6,3
590	085	093	100	107	115	122	129	137	144	151	
591	159	166	173	181	188	195	203	210	217	225	
592	232	240	247	254	262	269	276	283	291	298	
593	305	313	320	327	335	342	349	357	364	371	
594	379	386	393	401	408	415	422	430	437	444	
595	452	459	466	474	481	488	495	503	510	517	
596	525	532	539	546	554	561	568	576	583	590	
597	597	605	612	619	627	634	641	648	656	663	
598	670	677	685	692	699	706	714	721	728	735	
599	743	750	757	764	772	779	786	793	801	808	
600	815	822	830	837	844	851	859	866	873	880	
N.	L. 0	1	2	3	4	5	6	7	8	9	P. P.

N.	L. 0	1	2	3	4	5	6	7	8	9
600	77 815	822	830	837	844	851	859	866	873	880
601	887	895	902	909	916	924	931	938	945	952
602	960	967	974	981	988	996	*003	*010	*017	*025
603	78 032	039	046	053	061	068	075	082	089	097
604	104	111	118	125	132	140	147	154	161	168
605	176	183	190	197	204	211	219	226	233	240
606	247	254	262	269	276	283	290	297	305	312
607	319	326	333	340	347	355	362	369	376	383
608	390	398	405	412	419	426	433	440	447	455
609	462	469	476	483	490	497	504	512	519	526
610	533	540	547	554	561	569	576	583	590	597
611	604	611	618	625	633	640	647	654	661	668
612	675	682	689	696	704	711	718	725	732	739
613	746	753	760	767	774	781	789	796	803	810
614	817	824	831	838	845	852	859	866	873	880
615	888	895	902	909	916	923	930	937	944	951
616	958	965	972	979	986	993	*000	*007	*014	*021
617	79 029	036	043	050	057	064	071	078	085	092
618	099	106	113	120	127	134	141	148	155	162
619	169	176	183	190	197	204	211	218	225	232
620	239	246	253	260	267	274	281	288	295	302
621	309	316	323	330	337	344	351	358	365	372
622	379	386	393	400	407	414	421	428	435	442
623	449	456	463	470	477	484	491	498	505	511
624	518	525	532	539	546	553	560	567	574	581
625	588	595	602	609	616	623	630	637	644	650
626	657	664	671	678	685	692	699	706	713	720
627	727	734	741	748	754	761	768	775	782	789
628	796	803	810	817	824	831	837	844	851	858
629	865	872	879	886	893	900	906	913	920	927
630	934	941	948	955	962	969	975	982	989	996
631	80 003	010	017	024	030	037	044	051	058	065
632	072	079	085	092	099	106	113	120	127	134
633	140	147	154	161	168	175	182	188	195	202
634	209	216	223	229	236	243	250	257	264	271
635	277	284	291	298	305	312	318	325	332	339
636	346	353	359	366	373	380	387	393	400	407
637	414	421	428	434	441	448	455	462	468	475
638	482	489	496	502	509	516	523	530	536	543
639	550	557	564	570	577	584	591	598	604	611
640	618	625	632	638	645	652	659	665	672	679
641	686	693	699	706	713	720	726	733	740	747
642	754	760	767	774	781	787	794	801	808	814
643	821	828	835	841	848	855	862	868	875	882
644	889	895	902	909	916	922	929	936	943	949
645	956	963	969	976	983	990	996	*003	*010	*017
646	81 023	030	037	043	050	057	064	070	077	084
647	090	097	104	111	117	124	131	137	144	151
648	158	164	171	178	184	191	198	204	211	218
649	224	231	238	245	251	258	265	271	278	285
650	291	298	305	311	318	325	331	338	345	351
N.	L. 0	1	2	3	4	5	6	7	8	9

P. P.

	8		7		6
1	0,8	1	0,7	1	0,6
2	1,6	2	1,4	2	1,2
3	2,4	3	2,1	3	1,8
4	3,2	4	2,8	4	2,4
5	4,0	5	3,5	5	3,0
6	4,8	6	4,2	6	3,6
7	5,6	7	4,9	7	4,2
8	6,4	8	5,6	8	4,8
9	7,2	9	6,3	9	5,4

P. P.

N.	L. 0	1	2	3	4	5	6	7	8	9	P. P.
650	81 291	298	305	311	318	325	331	338	345	351	
651	358	365	371	378	385	391	398	405	411	418	
652	425	431	438	445	451	458	465	471	478	485	
653	491	498	505	511	518	525	531	538	544	551	
654	558	564	571	578	584	591	598	604	611	617	
655	624	631	637	644	651	657	664	671	677	684	
656	690	697	704	710	717	723	730	737	743	750	
657	757	763	770	776	783	790	796	803	809	816	
658	823	829	836	842	849	856	862	869	875	882	
659	889	895	902	908	915	921	928	935	941	948	
660	954	961	968	974	981	987	994	*000	*007	*014	
661	82 020	027	033	040	046	053	060	066	073	079	7
662	086	092	099	105	112	119	125	132	138	145	1 | 0,7
663	151	158	164	171	178	184	191	197	204	210	2 | 1,4
664	217	223	230	236	243	249	256	263	269	276	3 | 2,1
665	282	289	295	302	308	315	321	328	334	341	4 | 2,8
666	347	354	360	367	373	380	387	393	400	406	5 | 3,5
667	413	419	426	432	439	445	452	458	465	471	6 | 4,2
668	478	484	491	497	504	510	517	523	530	536	7 | 4,9
669	543	549	556	562	569	575	582	588	595	601	8 | 5,6
670	607	614	620	627	633	640	646	653	659	666	9 | 6,3
671	672	679	685	692	698	705	711	718	724	730	
672	737	743	750	756	763	769	776	782	789	795	
673	802	808	814	821	827	834	840	847	853	860	
674	866	872	879	885	892	898	905	911	918	924	
675	930	937	943	950	956	963	969	975	982	988	
676	995	*001	*008	*014	*020	*027	*033	*040	*046	*052	
677	83 059	065	072	078	085	091	097	104	110	117	
678	123	129	136	142	149	155	161	168	174	181	
679	187	193	200	206	213	219	225	232	238	245	
680	251	257	264	270	276	283	289	296	302	308	
681	315	321	327	334	340	347	353	359	366	372	6
682	378	385	391	398	404	410	417	423	429	436	1 | 0,6
683	442	448	455	461	467	474	480	487	493	499	2 | 1,2
684	506	512	518	525	531	537	544	550	556	563	3 | 1,8
685	569	575	582	588	594	601	607	613	620	626	4 | 2,4
686	632	639	645	651	658	664	670	677	683	689	5 | 3,0
687	696	702	708	715	721	727	734	740	746	753	6 | 3,6
688	759	765	771	778	784	790	797	803	809	816	7 | 4,2
689	822	828	835	841	847	853	860	866	872	879	8 | 4,8
690	885	891	897	904	910	916	923	929	935	942	9 | 5,4
691	948	954	960	967	973	979	985	992	998	*004	
692	84 011	017	023	029	036	042	048	055	061	067	
693	073	080	086	092	098	105	111	117	123	130	
694	136	142	148	155	161	167	173	180	186	192	
695	198	205	211	217	223	230	236	242	248	255	
696	261	267	273	280	286	292	298	305	311	317	
697	323	330	336	342	348	354	361	367	373	379	
698	386	392	398	404	410	417	423	429	435	442	
699	448	454	460	466	473	479	485	491	497	504	
700	510	516	522	528	535	541	547	553	559	566	
N.	L. 0	1	2	3	4	5	6	7	8	9	P. P.

N.	L. 0	1	2	3	4	5	6	7	8	9	P. P.
700	84 510	516	522	528	535	541	547	553	559	566	
701	572	578	584	590	597	603	609	615	621	628	
702	634	640	646	652	658	665	671	677	683	689	
703	696	702	708	714	720	726	733	739	745	751	
704	757	763	770	776	782	788	794	800	807	813	
705	819	825	831	837	844	850	856	862	868	874	
706	880	887	893	899	905	911	917	924	930	936	
707	942	948	954	960	967	973	979	985	991	997	7
708	85 003	009	016	022	028	034	040	046	052	058	1 | 0,7
709	065	071	077	083	089	095	101	107	114	120	2 | 1,4
710	126	132	138	144	150	156	163	169	175	181	3 | 2,1
711	187	193	199	205	211	217	224	230	236	242	4 | 2,8
712	248	254	260	266	272	278	285	291	297	303	5 | 3,5
713	309	315	321	327	333	339	345	352	358	364	6 | 4,2
714	370	376	382	388	394	400	406	412	418	425	7 | 4,9
715	431	437	443	449	455	461	467	473	479	485	8 | 5,6
716	491	497	503	509	516	522	528	534	540	546	9 | 6,3
717	552	558	564	570	576	582	588	594	600	606	
718	612	618	625	631	637	643	649	655	661	667	
719	673	679	685	691	697	703	709	715	721	727	
720	733	739	745	751	757	763	769	775	781	788	
721	794	800	806	812	818	824	830	836	842	848	6
722	854	860	866	872	878	884	890	896	902	908	1 | 0,6
723	914	920	926	932	938	944	950	956	962	968	2 | 1,2
724	974	980	986	992	998	*004	*010	*016	*022	*028	3 | 1,8
725	86 034	040	046	052	058	064	070	076	082	088	4 | 2,4
726	094	100	106	112	118	124	130	136	141	147	5 | 3,0
727	153	159	165	171	177	183	189	195	201	207	6 | 3,6
728	213	219	225	231	237	243	249	255	261	267	7 | 4,2
729	273	279	285	291	297	303	308	314	320	326	8 | 4,8
730	332	338	344	350	356	362	368	374	380	386	9 | 5,4
731	392	398	404	410	415	421	427	433	439	445	
732	451	457	463	469	475	481	487	493	499	504	
733	510	516	522	528	534	540	546	552	558	564	
734	570	576	581	587	593	599	605	611	617	623	
735	629	635	641	646	652	658	664	670	676	682	
736	688	694	700	705	711	717	723	729	735	741	5
737	747	753	759	764	770	776	782	788	794	800	1 | 0,5
738	806	812	817	823	829	835	841	847	853	859	2 | 1,0
739	864	870	876	882	888	894	900	906	911	917	3 | 1,5
740	923	929	935	941	947	953	958	964	970	976	4 | 2,0
741	982	988	994	999	*005	*011	*017	*023	*029	*035	5 | 2,5
742	87 040	046	052	058	064	070	075	081	087	093	6 | 3,0
743	099	105	111	116	122	128	134	140	146	151	7 | 3,5
744	157	163	169	175	181	186	192	198	204	210	8 | 4,0
745	216	221	227	233	239	245	251	256	262	268	9 | 4,5
746	274	280	286	291	297	303	309	315	320	326	
747	332	338	344	349	355	361	367	373	379	384	
748	390	396	402	408	413	419	425	431	437	442	
749	448	454	460	466	471	477	483	489	495	500	
750	506	512	518	523	529	535	541	547	552	558	
N.	L. 0	1	2	3	4	5	6	7	8	9	P. P.

N.	L. 0	1	2	3	4	5	6	7	8	9	P. P.
750	87 506	512	518	523	529	535	541	547	552	558	
751	564	570	576	581	587	593	599	604	610	616	
752	622	628	633	639	645	651	656	662	668	674	
753	679	685	691	697	703	708	714	720	726	731	
754	737	743	749	754	760	766	772	777	783	789	
755	795	800	806	812	818	823	829	835	841	846	
756	852	858	864	869	875	881	887	892	898	904	
757	910	915	921	927	933	938	944	950	955	961	
758	967	973	978	984	990	996	*001	*007	*013	*018	
759	88 024	030	036	041	047	053	058	064	070	076	
760	081	087	093	098	104	110	116	121	127	133	
761	138	144	150	156	161	167	173	178	184	190	**6**
762	195	201	207	213	218	224	230	235	241	247	1 | 0,6
763	252	258	264	270	275	281	287	292	298	304	2 | 1,2
764	309	315	321	326	332	338	343	349	355	360	3 | 1,8
765	366	372	377	383	389	395	400	406	412	417	4 | 2,4
766	423	429	434	440	446	451	457	463	468	474	5 | 3,0
767	480	485	491	497	502	508	513	519	525	530	6 | 3,6
768	536	542	547	553	559	564	570	576	581	587	7 | 4,2
769	593	598	604	610	615	621	627	632	638	643	8 | 4,8
770	649	655	660	666	672	677	683	689	694	700	9 | 5,4
771	705	711	717	722	728	734	739	745	750	756	
772	762	767	773	779	784	790	795	801	807	812	
773	818	824	829	835	840	846	852	857	863	868	
774	874	880	885	891	897	902	908	913	919	925	
775	930	936	941	947	953	958	964	969	975	981	
776	986	992	997	*003	*009	*014	*020	*025	*031	*037	
777	89 042	048	053	059	064	070	076	081	087	092	
778	098	104	109	115	120	126	131	137	143	148	
779	154	159	165	170	176	182	187	193	198	204	
780	209	215	221	226	232	237	243	248	254	260	
781	265	271	276	282	287	293	298	304	310	315	**5**
782	321	326	332	337	343	348	354	360	365	371	1 | 0,5
783	376	382	387	393	398	404	409	415	421	426	2 | 1,0
784	432	437	443	448	454	459	465	470	476	481	3 | 1,5
785	487	492	498	504	509	515	520	526	531	537	4 | 2,0
786	542	548	553	559	564	570	575	581	586	592	5 | 2,5
787	597	603	609	614	620	625	631	636	642	647	6 | 3,0
788	653	658	664	669	675	680	686	691	697	702	7 | 3,5
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791	818	823	829	834	840	845	851	856	862	867	
792	873	878	883	889	894	900	905	911	916	922	
793	927	933	938	944	949	955	960	966	971	977	
794	982	988	993	998	*004	*009	*015	*020	*026	*031	
795	90 037	042	048	053	059	064	069	075	080	086	
796	091	097	102	108	113	119	124	129	135	140	
797	146	151	157	162	168	173	179	184	189	195	
798	200	206	211	217	222	227	233	238	244	249	
799	255	260	266	271	276	282	287	293	298	304	
800	309	314	320	325	331	336	342	347	352	358	
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802	417	423	428	434	439	445	450	455	461	466	
803	472	477	482	488	493	499	504	509	515	520	
804	526	531	536	542	547	553	558	563	569	574	
805	580	585	590	596	601	607	612	617	623	628	
806	634	639	644	650	655	660	666	671	677	682	
807	687	693	698	703	709	714	720	725	730	736	
808	741	747	752	757	763	768	773	779	784	789	
809	795	800	806	811	816	822	827	832	838	843	
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816	169	174	180	185	190	196	201	206	212	217	5 | 3,0
817	222	228	233	238	243	249	254	259	265	270	6 | 3,6
818	275	281	286	291	297	302	307	312	318	323	7 | 4,2
819	328	334	339	344	350	355	360	365	371	376	8 | 4,8
820	381	387	392	397	403	408	413	418	424	429	9 | 5,4
821	434	440	445	450	455	461	466	471	477	482	
822	487	492	498	503	508	514	519	524	529	535	
823	540	545	551	556	561	566	572	577	582	587	
824	593	598	603	609	614	619	624	630	635	640	
825	645	651	656	661	666	672	677	682	687	693	
826	698	703	709	714	719	724	730	735	740	745	
827	751	756	761	766	772	777	782	787	793	798	
828	803	808	814	819	824	829	834	840	845	850	
829	855	861	866	871	876	882	887	892	897	903	
830	908	913	918	924	929	934	939	944	950	955	**5**
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841	480	485	490	495	500	505	511	516	521	526	
842	531	536	542	547	552	557	562	567	572	578	
843	583	588	593	598	603	609	614	619	624	629	
844	634	639	645	650	655	660	665	670	675	681	
845	686	691	696	701	706	711	716	722	727	732	
846	737	742	747	752	758	763	768	773	778	783	
847	788	793	799	804	809	814	819	824	829	834	
848	840	845	850	855	860	865	870	875	881	886	
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856	247	252	258	263	268	273	278	283	288	293
857	298	303	308	313	318	323	328	334	339	344
858	349	354	359	364	369	374	379	384	389	394
859	399	404	409	414	420	425	430	435	440	445
860	450	455	460	465	470	475	480	485	490	495
861	500	505	510	515	520	526	531	536	541	546
862	551	556	561	566	571	576	581	586	591	596
863	601	606	611	616	621	626	631	636	641	646
864	651	656	661	666	671	676	682	687	692	697
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866	752	757	762	767	772	777	782	787	792	797
867	802	807	812	817	822	827	832	837	842	847
868	852	857	862	867	872	877	882	887	892	897
869	902	907	912	917	922	927	932	937	942	947
870	952	957	962	967	972	977	982	987	992	997
871	94 002	007	012	017	022	027	032	037	042	047
872	052	057	062	067	072	077	082	086	091	096
873	101	106	111	116	121	126	131	136	141	146
874	151	156	161	166	171	176	181	186	191	196
875	201	206	211	216	221	226	231	236	240	245
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881	498	503	507	512	517	522	527	532	537	542
882	547	552	557	562	567	571	576	581	586	591
883	596	601	606	611	616	621	626	630	635	640
884	645	650	655	660	665	670	675	680	685	689
885	694	699	704	709	714	719	724	729	734	738
886	743	748	753	758	763	768	773	778	783	787
887	792	797	802	807	812	817	822	827	832	836
888	841	846	851	856	861	866	871	876	880	885
889	890	895	900	905	910	915	919	924	929	934
890	939	944	949	954	959	963	968	973	978	983
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892	95 036	041	046	051	056	061	066	071	075	080
893	085	090	095	100	105	109	114	119	124	129
894	134	139	143	148	153	158	163	168	173	177
895	182	187	192	197	202	207	211	216	221	226
896	231	236	240	245	250	255	260	265	270	274
897	279	284	289	294	299	303	308	313	318	323
898	328	332	337	342	347	352	357	361	366	371
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9	3,6

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903	569	574	578	583	588	593	598	602	607	612	
904	617	622	626	631	636	641	646	650	655	660	
905	665	670	674	679	684	689	694	698	703	708	
906	713	718	722	727	732	737	742	746	751	756	
907	761	766	770	775	780	785	789	794	799	804	
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909	856	861	866	871	875	880	885	890	895	899	
910	904	909	914	918	923	928	933	938	942	947	
911	952	957	961	966	971	976	980	985	990	995	**5**
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919	332	336	341	346	350	355	360	365	369	374	8 | 4,0
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921	426	431	435	440	445	450	454	459	464	468	
922	473	478	483	487	492	497	501	506	511	515	
923	520	525	530	534	539	544	548	553	558	562	
924	567	572	577	581	586	591	595	600	605	609	
925	614	619	624	628	633	638	642	647	652	656	
926	661	666	670	675	680	685	689	694	699	703	
927	708	713	717	722	727	731	736	741	745	750	
928	755	759	764	769	774	778	783	788	792	797	
929	802	806	811	816	820	825	830	834	839	844	
930	848	853	858	862	867	872	876	881	886	890	
931	895	900	904	909	914	918	923	928	932	937	**4**
932	942	946	951	956	960	965	970	974	979	984	1 | 0,4
933	988	993	997	*002	*007	*011	*016	*021	*025	*030	2 | 0,8
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942	405	410	414	419	424	428	433	437	442	447	
943	451	456	460	465	470	474	479	483	488	493	
944	497	502	506	511	516	520	525	529	534	539	
945	543	548	552	557	562	566	571	575	580	585	
946	589	594	598	603	607	612	617	621	626	630	
947	635	640	644	649	653	658	663	667	672	676	
948	681	685	690	695	699	704	708	713	717	722	
949	727	731	736	740	745	749	754	759	763	768	
950	772	777	782	786	791	795	800	804	809	813	
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951	818	823	827	832	836	841	845	850	855	859	
952	864	868	873	877	882	886	891	896	900	905	
953	909	914	918	923	928	932	937	941	946	950	
954	955	959	964	968	973	978	982	987	991	996	
955	98 000	005	009	014	019	023	028	032	037	041	
956	046	050	055	059	064	068	073	078	082	087	
957	091	096	100	105	109	114	118	123	127	132	
958	137	141	146	150	155	159	164	168	173	177	
959	182	186	191	195	200	204	209	214	218	223	
960	227	232	236	241	245	250	254	259	263	268	
961	272	277	281	286	290	295	299	304	308	313	**5**
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963	363	367	372	376	381	385	390	394	399	403	2 | 1,0
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965	453	457	462	466	471	475	480	484	489	493	4 | 2,0
966	498	502	507	511	516	520	525	529	534	538	5 | 2,5
967	543	547	552	556	561	565	570	574	579	583	6 | 3,0
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969	632	637	641	646	650	655	659	664	668	673	8 | 4,0
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971	722	726	731	735	740	744	749	753	758	762	
972	767	771	776	780	784	789	793	798	802	807	
973	811	816	820	825	829	834	838	843	847	851	
974	856	860	865	869	874	878	883	887	892	896	
975	900	905	909	914	918	923	927	932	936	941	
976	945	949	954	958	963	967	972	976	981	985	
977	989	994	998	*003	*007	*012	*016	*021	*025	*029	
978	99 034	038	043	047	052	056	061	065	069	074	
979	078	083	087	092	096	100	105	109	114	118	
980	123	127	131	136	140	145	149	154	158	162	**4**
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984	300	304	308	313	317	322	326	330	335	339	4 | 1,6
985	344	348	352	357	361	366	370	374	379	383	5 | 2,0
986	388	392	396	401	405	410	414	419	423	427	6 | 2,4
987	432	436	441	445	449	454	458	463	467	471	7 | 2,8
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989	520	524	528	533	537	542	546	550	555	559	9 | 3,6
990	564	568	572	577	581	585	590	594	599	603	
991	607	612	616	621	625	629	634	638	642	647	
992	651	656	660	664	669	673	677	682	686	691	
993	695	699	704	708	712	717	721	726	730	734	
994	739	743	747	752	756	760	765	769	774	778	
995	782	787	791	795	800	804	808	813	817	822	
996	826	830	835	839	843	848	852	856	861	865	
997	870	874	878	883	887	891	896	900	904	909	
998	913	917	922	926	930	935	939	944	948	952	
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