INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION

21,800 Copies of This Issue Printed

Vol. 31, Consecutive No. 3

January 15, 1939

Harrison E. Howe, Editor

Vol. 11, No. 1

Publication Office: Easton, Pa.

Editorial Office: Room 706, Mills Building, Washington, D. C.
Telephone: National 0848. Cable: Jiechem (Washington)

Advertising Department: 332 West 42nd Street, New York, N. Y.
Telephone: Bryant 9-4430

Published by the American Chemical Society, Publication Office, 20th & Northampton Sts., Easton, Pa. Entered as second-class matter at the Post Office at Easton, Pa., under the Act of March 3, 1879, as 48 times a year. Industrial Edition monthly on the 1st; Analytical Edition monthly on the 15th; News Edition on the 10th and 20th. Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918.

Annual subscription rates: INDUSTRIAL AND ENGINEERING CHEMISTRY complete $6.00; (a) INDUSTRIAL EDITION $3.00; (b) ANALYTICAL EDITION $2.50; (c) NEWS EDITION $1.50; (a) and (b) together, $5.00. Foreign postage to countries not in the Pan American Union, $2.40, (a) $1.20; (b) $0.60; (c) $0.60. Canadian postage one-third these rates. Single copies: (a) $0.75; (b) $0.50; (c) $0.10. Special rates to members.

No claims can be allowed for copies of journals lost in the mails unless such claims are received within sixty days of the date of issue, and no claims will be allowed for issues lost as a result of insufficient notice of change of address. (Ten days' advance notice required.) "Missing from files" cannot be accepted as the reason for honoring a claim. Charles L. Parsons, Business Manager, Mills Building, Washington, D. C., U. S. A.

INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION ◆ Harrison E. Howe, Editor

Photoelectric Methods in Analytical Chemistry

RALPH H. MÜLLER

New York University, Washington Square College, New York, N. Y.

PHOTOELECTRIC photometry has been an established branch of applied physics for half a century. The comparatively recent application of these methods to chemical problems has been very useful to the analyst, the physical chemist, and the biochemist. The best resources of optics and electronics are required in this field and abundant literature is widely scattered in numerous journals and monographs. In this review the writer has attempted to epitomize the more important facts and methods which are essential in chemical applications. Particular stress is placed upon the number of excellent monographs in the fields of optics and electronics. (These are collected ahead of the rest of the bibliography and referred to by letters in the body of the paper. Specific references in a monograph contain the page number; thus, *N*, p. 245, refers to page 245 of the monograph by Henny.) They afford instrumental and theoretical approaches which are largely untouched.

Photometry and Colorimetry

The terms "colorimetry," "the colorimeter," and "colorimetric analysis" all suggest to the chemist definite concepts as familiar as the balance or other tools of the analytical laboratory. The physicist reserves these terms for those means of specifying color or for the measurement of color stimuli (*L*, *M*, *71*). His terminology is undoubtedly correct and although a conservative estimate would indicate the present use of about 25,000 "colorimeters" in this country alone, the chemist will probably have to define his concepts more clearly.

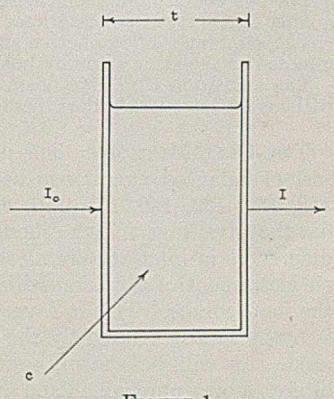


FIGURE 1
$\log_{10} I_0/I = kct = E$

To state the problem more definitely, it may be resolved into two categories:

1. The measurements are to describe the color of a system in unambiguous, reproducible terms. The problem might be to define the color of a dyed fabric, an oil sample, an impure organic compound, or a natural product. This is a true colorimetric problem in the sense of the physicist's definition. Its solution demands a complete spectrophotometric analysis, or abridged methods in terms of trichromatic coefficients either of which may be reduced to the standard I. C. I. observer. The necessary data may be obtained either visually or photoelectrically. The complete treatment of this question is beyond the scope of this review; the best statement and approach to date are given by Gibson (*71*).

2. The measurements are to furnish information on the concentration of a colored substance, or the color produced by that substance when appropriate reagents are added. If there is a definite functional relationship between the intensity or "depth" of this color and the concentration, we shall be able to use such measurements for analytical purposes. In addition, such measurements may be used to study anomalies in the system itself, the existence of equilibria, or incompleteness of reaction and other physico-chemical aspects. If the system is measured with sensibly monochromatic light (filters) the process is then one of photometry.

Our main interest in this discussion will be the elaboration of problems encountered in the second category.

DEFINITIONS. In terms of Figure 1, let monochromatic light of intensity I_0 strike the solution of thickness, t, the concentration of colored substance in this solution being c. The emergent intensity is I. According to Lambert-Beer's law [usually referred to in this form, although Lambert's work was anticipated by Bouguer in 1729 (see *M*, p. 24)] we have

$$I = I_0\, 10^{-kct}$$

If c is expressed in moles per liter and t in centimeters, k is the molecular extinction coefficient, I/I_0 is the transmission, T, and $\log_{10} I_0/I = E$ (the extinction). It follows that $E = kct$ and $-\log T = E$.

Corrections for reflection at the surface of the liquid or the container are neglected, as most instruments contain comparison cells with pure solvent or standard solution. In the Duboscq colorimeter the depths of two solutions are varied until a match is obtained, under which condition

$$E_1 = E_2$$

or

$$kc_1l_1 = kc_2l_2$$

from which

$$\frac{c_1}{c_2} = \frac{l_2}{l_1}$$

If monochromatic light is used, the above procedure is a truly photometric matching and will be rigorous to the extent that Beer's law is obeyed by the system. Usually, how-

ever, white light is employed and the conditions are not as rigorously defined as implied by the above equations. Nevertheless, over a limited concentration range, the thickness and respective concentrations are inversely related.

Photoelectric Methods

The substitution of photocells for the eye has been accomplished in a number of ways. It is advisable to classify them and discuss each in turn.

In general it may be said that the adaptation of photocells to existing visual instruments is poor practice and wholly inadvisable. The uninitiated are inclined to place a photocell at the ocular of a microscope, spectrometer, refractometer, or "colorimeter" and then expect extraordinary results. The optics of these instruments are designed to accommodate the optical properties of the human eye and the available light is by no means most efficiently utilized by a photocell put in place of the eye (*M*, p. 422).

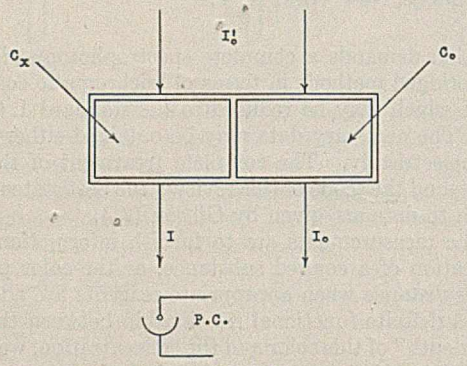


FIGURE 2. PHOTOMETRIC COMPARISON WITH PURE SOLVENT

Photoelectric methods are so attractive, and have offered so much promise of high precision and relief from fatiguing effort, that they have often been seized upon and utilized with little regard for sound principle. Little ordered progress can result from the use of instruments that require empirical calibration for each substance that is to be determined and over the entire concentration range. We expect our balances, refractometers, polarimeters, and potentiometers to yield direct measurements in terms of grams, refractive index, rotation in degrees, and potential differences in volts directly, with no particular reference to any substance. We insist upon a definite functional relationship (preferably direct) between the instrumental indication and the property in question. This is not too much to expect of a photoelectric photometer.

The ideal instrument would respond to any region of the visible spectrum with equal precision, indicating transmission or the extinction. The source would be monochromatic, so that the extinction would be a linear function of the concentration for any system which obeys Beer's law. No commercial instrument fulfilling these requirements has been offered. It is true that Hardy's photoelectric spectrophotometer does satisfy these requirements, but this instrument was designed for the vastly more complex problem of color analysis (true colorimetry) and its cost is naturally greater than the simplicity of our problem warrants. Many systems, including commercially available instruments, have been suggested which approach the specification. Others have been recommended in which the sole criterion of success is the author's ability to analyze a given substance under rigorously standardized conditions.

In general, it is preferable to effect a photometric match or balance and use the photocell merely to indicate this state. On the other hand, it may be desirable to use the photocurrent as a measure of the unbalance, in which case it is necessary to have constant assurance that the photocell responds linearly with the light intensity.

SINGLE-CELL METHODS. *A.* If we illuminate a rectangular cell, containing in one compartment pure solvent, $c = 0$, and in the other compartment a solution of concentration C_x, with a parallel beam of monochromatic light, the light which strikes the photocell may be called I_0 when $c = 0$ is in the path. Upon substitution of the solution the beam will be reduced to intensity I. If the photocell response is linear, the respective photocurrents will measure I/I_0 which is the transmission, or $\log I_0/I$ gives the extinction, E (Figure 2).

This principle requires (1) constancy of the light source during the interval required to interchange the absorption cells, (2) linear response of the photocell, and (3) stability of the circuit used to measure the photoelectric current. An alternative procedure, which eliminates requirement 2, is to decrease I_0 by introducing a compensating wedge, variable aperture, or polarizing equipment, until the response is identical for the two absorption cells.

The method has often been criticized by proponents of double photocell circuits, but very precise results have been obtained which show unquestionable reliability (*85*, *142*, *144*, *175*).

B. Flicker Methods. A single photocell is used and a homogeneous beam is directed alternately through the solution and solvent by a rotating or vibrating shutter, (*B; I*, p. 200; *184*), total reflecting prism (*K*, *2*), or a mirror or rotating Rochon prism. The transition from one medium to the other must be smooth with no intervening dark period. Compensation is effected in the reference system until the emergent beams striking the photocell are of equal intensity. Any unbalance will give rise to a pulsating photocurrent. With or without amplification this pulsating current can be detected by short-period electrometers or galvanometers (*D*, p. 169), or the latter may be fed with the photocurrent after it has passed through a commutator which is driven synchronously with the scanning device (*X*, p. 228; *184*). A tuned amplifier with telephone, or bridge-balance indicator may be used.

It is difficult to set any upper limit for the precision of this method. It is undoubtedly set by the optical refinements of the instrument. In any projected design it is wise to keep in mind the recommendations of Hardy (*M*, p. 294).

The two beams under comparison must have the same spectral quality and state of polarization.

The same area of the active surface of the cell must be illuminated at the same angle by both beams in rapid succession.

The transition from one beam to the other must take place without an intervening dark period.

TWO-CELL METHODS. The use of two photocells in some sort of balanced circuit has been used extensively (*48*, *78*, *118*, *132*, *137*, *140*, *173*, *180*, *226*, *229*, *236*). The method has the advantage of high differential sensitivity, in that only differences in intensity are measured. If properly designed, an instrument of this kind will compensate for variations in the light source. This is a very useful characteristic but it is by no means assured by the mere fact that two cells are used. As will be shown, some twin-cell circuits are definitely more unreliable and unstable than substitution methods employing a single cell.

This principle may be utilized in several ways:

1. The two photocells are illuminated from a common source, preferably monochromatic, and solution and solvent are placed in the respective beams. Assuming that the cells were initially adjusted for equal response, the net response will now be a measure of the absorption due to the solution (*78*, *118*, *137*, *140*). Successful operation requires (*a*) linear response of both photo-

cells; (*b*) identical color sensitivity for the two cells, if white light is used. This is not important if monochromatic light is used, provided condition (*a*) is satisfied.

2. The above arrangement is used, but optical compensation is effected in the beam passing through the solvent. When the net response of the photocells is reduced to zero, the amount of light absorption is obtained in terms of the compensating device.

Linearity of response of both cells is still required unless compensation is effected in the absorbing branch (intensity increased to the same extent that the solution decreases it). Requirement (*b*) in the preceding method holds equally in this case.

3. The optical arrangement is similar to that of a Duboscq colorimeter, and the principle, that concentration and solution depth are inversely related, is employed (*11*, *77*). Two photocells intercept the respective beams (preferably monochromatic) and the depth of one solution is varied until standard and unknown transmit equally, as indicated by a net photocurrent of zero. There are many commendable features in this method. For a limited concentration range, the demands upon strict monochromaticity of the source are less than in other methods. However, the optical design of the instrument presents great difficulties. The beams passing through the long variable layers must be strictly parallel and adequate stops must be provided to eliminate stray or reflected light. For this reason, existing visual instruments of this type cannot be converted to the photoelectric equivalent with any degree of success. The best criterion of successful design is the ability to secure reproducible settings which are independent of the total cup depth.

In all balanced arrangements, "reasonably" monochromatic light must be used if any simple physical interpretation of the results is desired. Similarly, when compensation is effected in the comparison beam, the functional relationship between the compensator and the quantity which is being measured should be known. For example, a nonselective wedge, if carefully made, will change the light intensity logarithmically with linear displacement, and under this condition its displacement will be a linear function of the concentration of any colored substance that obeys Beer's law. One instrument which used a white light source and an arbitrary slit mechanism for compensation actually reached the commercial production stage. It was beautifully made by a well-known company. The instrumental indications bore no recognizable relationship to the concentration; indeed, they were even irregular but withal highly reproducible. The enormous burden of point-by-point calibration rendered it valueless for general utility.

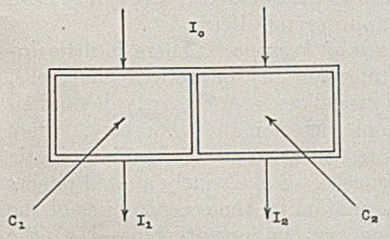


FIGURE 3. PHOTOMETRIC COMPARISON WITH STANDARD SOLUTION
$C_1/C_2 = \log I_1/\log I_2$

Where precise results in absolute terms are desired the compensation method is preferable. Under these conditions fluctuations of the light source are of little consequence. Since all photoelectric methods possess the inherent possibility of continuous indication and eventually automatic registration or control, it is of interest to see to what extent direct measurement of the photocurrent will be reliable.

Some generalization of this procedure may be of interest. For work of the highest precision it is advantageous to compare an unknown solution with one of identical nature but of a known concentration, preferably of the order of magnitude of the unknown. The results may be expected to be somewhat more accurate than a comparison with pure solvent, because the extinction coefficient can be independent of the concentration only if the light is strictly monochromatic. In general, if the main spectral line is accompanied by n other lines, for each of which the solution exhibits a characteristic extinction coefficient, then the total extinction will be given by (*85*, *107*):

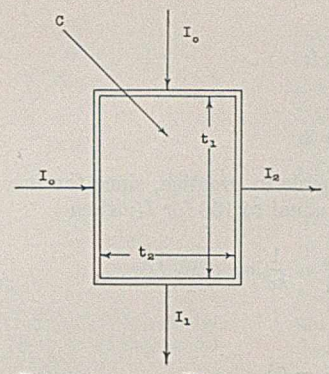


FIGURE 4. PHOTOMETRIC COMPARISON AT TWO THICKNESSES
Without reference solution
$C = 1/(t_1 - t_2) \times \log I_2/I_1$

$$E = \log \frac{I_0}{I} = \log \frac{\sum_0^n I_n}{\sum_0^n I_n 10^{-\epsilon_n cd}} = \bar{\epsilon} cd$$

where $\bar{\epsilon}$ represents the average extinction coefficient for the heterogeneous light. Of course, the magnitude of this error also depends upon the nature of the solution. For a gray (neutral) colored solution the error would be zero (ϵ = constant, independent of λ); for one with a sharp absorption band it might be very considerable, especially if one worked along the steep sides of the band.

This all implies that relative measurements of concentration can be made more precisely than an absolute measurement of the extinction coefficient. Table I, taken from Kortüm's paper (*107*), illustrates a case in which the extinction coefficient for a given system could be determined to no better than ±0.5 per cent, whereas the concentration of a single solution compared with a known solution of the same order of magnitude could be determined to within ±0.02 per cent.

TABLE I. CONCENTRATION MEASUREMENTS

(C_s = 8.892 × 10^{-5} mole per liter; d_s = 1.0917 cm.; d_x = 1.9944 cm.)

C_x Mole/liter
4.982 × 10^{-5}
4.980
4.979
4.979
4.980
4.978
Av. 4.980 × 10^{-5} ± 0.001

This advantage may be realized in practice for any of the methods discussed above by substituting a standard solution for the solvent. Under these conditions the respective intensities emerging from unknown solution and standard solution (Figure 3) will be given by

$$\frac{C_x}{C_s} = \frac{\log I_x}{\log I_s}$$

An alternative scheme, which the writer has not seen described, would seem to offer some advantages. The unknown solution is contained in a rectangular absorption cell, and is viewed alternately through one side (Figure 4) (thickness of layer = t_1) and then through the other side (thickness of layer = t_2) either by rotating the cell through exactly 90° or by a suitable arrangement of prisms in the optical train. For the two positions we get:

$$\log I_0 = kCt_1 + \log I_1$$
$$\log I_0 = kCt_2 + \log I_2$$

or

$$kCt_1 + \log I_1 = kCt_2 + \log I_2$$

and

$$C = \frac{1}{k(t_1 - t_2)} \log \frac{I_2}{I_1}$$

Now let

$$t_1 > t_2$$

then

$$I_2 \geq I_1$$

Further simplification is possible in practice, since the instrumental reading may be set equal to 100 for I_1; then

$$c = \frac{1}{k(t_1 - t_2)} \log \frac{I_2}{I_1} = \frac{1}{kd} \log (0.01\ I_2)$$

where

$$d = (t_1 - t_2)$$

Photoelectric Cells

In modern instruments practically only two types of photocells are employed: the high-vacuum cell and the barrier-layer type. Special forms for particular problems will be mentioned later.

VACUUM PHOTOCELL. A highly evacuated cell with a composite cesium cathode may be taken as typical of this class. For a central anode cell we may discuss the characteristics in terms of Figure 5.

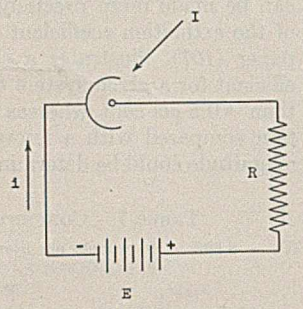


FIGURE 5. VACUUM PHOTOCELL

The cell is illuminated with light of intensity I, and under the influence of the applied potential, E, an electron current, i, flows through the load, R. Here R may represent an appropriate galvanometer or the input resistor of an amplifier. For constant illumination current i will increase with applied potential E as shown in Figure 6, indicating the saturation characteristic above a certain potential. For successively higher intensities similar curves are obtained (I_2, I_3, I_4, etc.). At very high intensities true saturation is not attained and this is commonly observed with central anode cells. Most commercial cells are of this type. Their total output is greater than cells of the central cathode type which give saturation currents with nearly zero applied potential (*O*, p. 422; *91*). It follows that for precise photometry some minimum potential, E_m, must be applied across the cell in order that saturation currents may be obtained for all intensities that are likely to be encountered. If we now plot the corresponding saturation currents against the corresponding light intensities a straight line should result (Figure 7). Returning to Figure 5 we note that the potential across the cell is always less than E, by an amount equal to the voltage drop across R. In other words

$$E_c = E - Ri \qquad (1)$$

This is especially important where amplification is used, for in this case the coupling resistor is usually chosen as high as possible ($R < 50$ megohms). Care must be exercised that the resulting Ri drop is not too large, thus bringing the potential

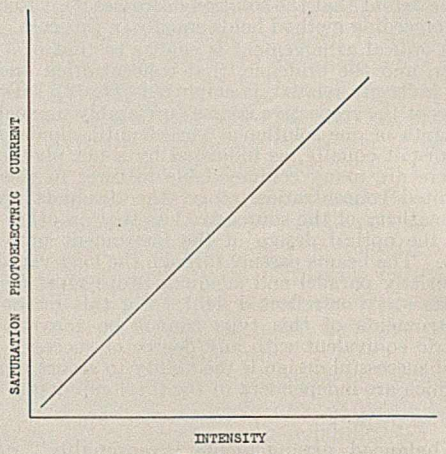


FIGURE 7

across the cell to a value below the minimal E_m. A conservative choice in E will be 10 per cent in excess of E_m after the above correction has been calculated. An excessively high potential is undesirable because there can be no gain in response but only increasing contribution to leakage currents.

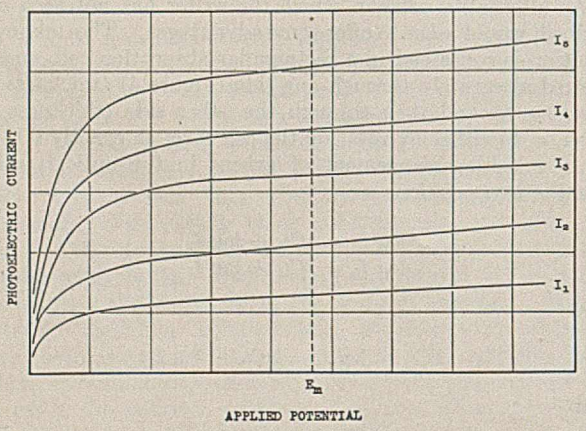


FIGURE 6. SATURATION CHARACTERISTICS OF A CENTRAL-ANODE VACUUM PHOTOCELL

Color Sensitivity. The response of a vacuum photocell to different regions of the spectrum depends upon the nature of the cathode surface and its treatment during manufacture (*F*, p. 161). Since most cells which are manufactured are used in sound-picture installations or for industrial control work, and are illuminated by incandescent lamp sources, they are purposely treated to accentuate the response to long wave lengths in order to utilize most efficiently the radiation from such sources. This is a decided disadvantage for colorimetric work; indeed, most of the infrared from such sources must be screened off by appropriate filters.

Fatigue and Nonlinearity of Response. There is little information available on the reliability of modern photocells. We have inherited many prejudices from the early days when cells were individually constructed in the laboratory. They undoubtedly bear little resemblance to the semiautomatic production of present-day cells. Some widely quoted papers (*B*, *92*) give detailed information on the eccentricities of the photocell but neglect one very important point—i. e., the characteristics of the light source which is used in such tests.

In general it is advisable to use null or rapid substitution methods of photometry in which the cell is merely used as an indicator of photometric balance. Nevertheless it would be interesting to know just how reliable a good cell can be. It turns out that a photocell might better be used to study the constancy of a light source than for the converse test of cell stability or linearity. Simple considerations show why this is so. Let us imagine a vacuum cell to be illuminated with the unfiltered radiation from a 6-volt automobile lamp. Let V designate the lamp voltage and I the resultant photocurrent. Over a very wide range the empirical relationship (Equation 2) holds (*144*).

$$I = kV^n \qquad (2)$$

The constant, n, has a value between 3 and 4. In other words, if we expect to reproduce the photocurrent, I, to within ± 0.1 per cent, the lamp voltage must not vary by more

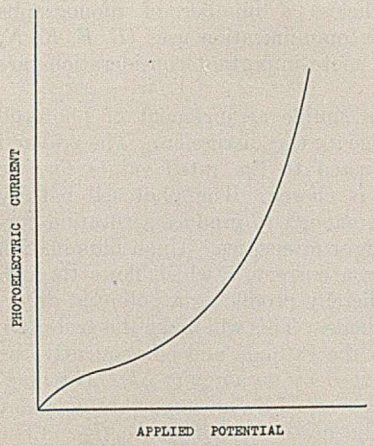


FIGURE 8. CHARACTERISTIC OF GAS-FILLED PHOTOCELL

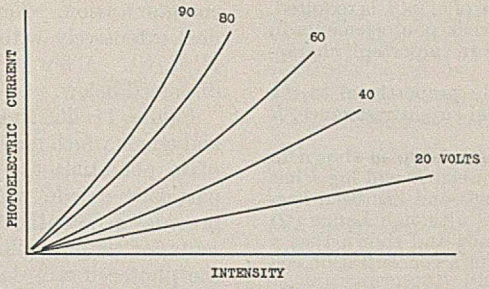


FIGURE 9. INTENSITY-CURRENT CURVES FOR GAS-FILLED PHOTOCELL AS A FUNCTION OF APPLIED POTENTIAL

than a few millivolts. Even if such a lamp is operated from storage batteries on the optimum portion of their discharge curve, this constancy will not be obtainable for more than a few seconds at a time. Any statements made without an exact statement of the condition of the source are therefore pointless. Some significant and interesting life tests on vacuum cells have been reported (*I*, p. 36). The response of several cells was automatically recorded for a period of 12,000 hours, under sensibly constant illumination. Whatever variations in photocurrent did arise, were common to all the cells and undoubtedly arose from temporary fluctuations in the common source.

It is generally agreed that the strict proportionality between photocurrent and light intensity is a fundamental law of photoelectricity, but its realization in practice demands a carefully designed and constructed cell (*O*, p. 32).

Gas-Filled Cells. The sensitivity of the cell described above may be increased greatly by admitting a small amount of rare gas. Argon at about 0.2-mm. pressure is usually used. Ionization currents are superimposed on the primary photoelectric current and the response may be increased tenfold. Figure 8 shows typical characteristics of a gas-filled cell. Very few modern schemes of photometry utilize the gas-filled cell for the following reasons:

Linearity of response is approached as the potential applied to the cell is reduced, and is attained near the ionization potential of the gas. Under these conditions the cell is really behaving like a vacuum cell and all the advantages of amplification by ionization have disappeared (Figure 9).

If modulated light is used, gas cells show a definite lag in response.

High-gain amplifiers with adequate stability are available which entirely offset the slight gain obtained by the use of gas-filled cells.

Special Cells. The high-vacuum cell is available in many sizes and shapes, with a choice of cathode and envelope material (*F*, p. 161). Cells sensitive to the ultraviolet are commercially available. Some of the products of television research will undoubtedly be available in the future; the multiplier tubes of Zworykin (*239*) and Farnsworth (*F*, p. 214) are notable examples. In these tubes the primary photoelectrons are made to collide with a sensitive surface from which secondary electrons are emitted. This process may be repeated many times with a gain of 4 to 8 at each stage. A single multiplier phototube thus yields an output comparable with a cell–multistage amplifier combination with the added advantage that the ratio of signal to noise is increased approximately one thousand fold. Cells with split cathodes and multiple cathodes have been designed for special problems (R. C. A. 920). The iconoscope, a mosaic consisting of myriads of photoelements electronically scanned, is an integral part of one important method of television.

BARRIER-LAYER CELLS. The most recent addition to the family of light-sensitive devices is the barrier-layer cell, variously termed the dry-disk, blocking layer, photovoltaic, or Sperrschicht cell, or by trade names such as Photronic (Weston) or Photox (Westinghouse). The apparent, but deceptive, simplicity of these cells undoubtedly accounts for the recent interest which has arisen in many fields in the application of photoelectric methods. The recent monograph by Lange (*Q*) gives an excellent account of the discovery, development, and properties of these cells. The second volume deals with applications and instruments.

Properties and Characteristics. These cells consist essentially of a plate of copper or iron upon which a semiconducting layer of cuprous oxide or selenium is grown. The semiconductor is covered by a light-transmitting layer of metal—gold, platinum, copper, or lead—which serves as a collector electrode. Upon illumination through the transparent electrode an electron cur-

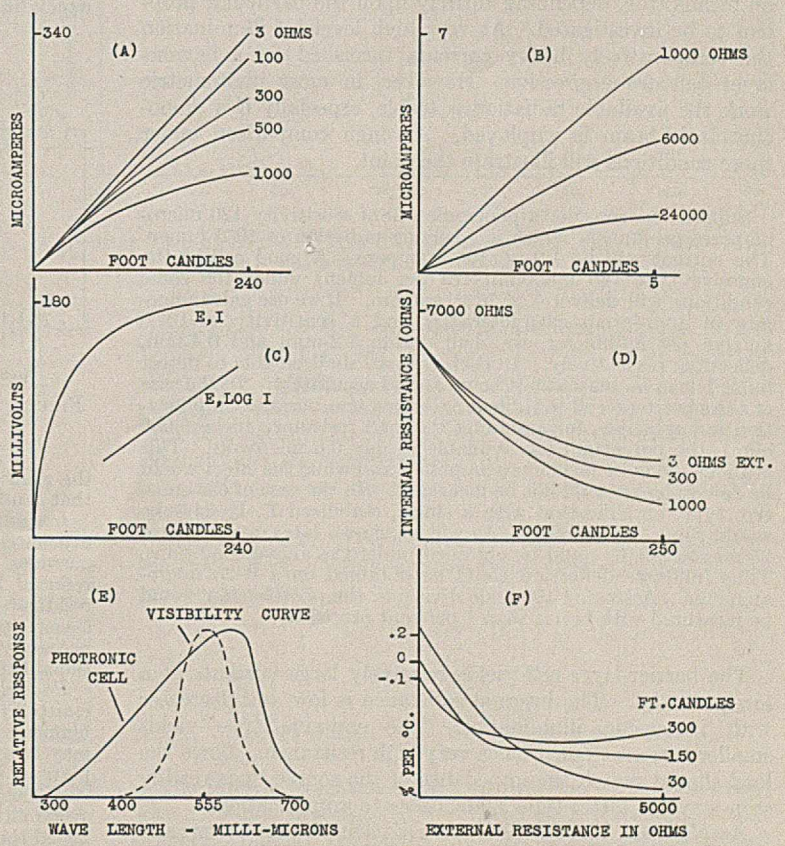


FIGURE 10. PHOTRONIC CELL CHARACTERISTICS

rent flows. In this type no auxiliary source of e. m. f. is required. For this reason Lange has termed these cells photoelements in analogy with galvanic elements. The more important characteristics are represented in Figure 10.

The photocurrent is very nearly directly proportional to the light intensity for low values of the external circuit resistance, R (Figure 10, A and B).

The open circuit e. m. f.–intensity relationship is shown in Figure 10, C. The linear relationship between E and log I has interesting possibilities for colorimetry (*146*) and has been neglected or overlooked in American practice, although Lange (*Q*) has accounted for it on theoretical grounds and shown that a formal analogy with the Nernst equation for a concentration cell predicts the observed phenomenon.

The "internal resistance" of the cell decreases with increasing illumination (Figure 10, D).

The temperature coefficient is complex and is a function of the external circuit resistance (Figure 10, F).

The spectral response extends from the x-ray region to about 1 to 1.2 M in the infrared. The ordinary cell with a glass window exhibits a response curve as shown in Figure 10, E. Filters have been designed to adjust this response to approximate that of the average human eye (*54*, *55*, *65*, *153*).

The average cell has an output of about 120 microamperes per lumen. The best high-vacuum cell of the photoemissive type yields 40 to 60 microamperes per lumen. For high levels of illumination robust instruments such as micro- or milliammeters may be used with barrier-layer cells. In direct sunlight 10 milliamperes have been obtained.

Special Types. For special applications, cells with a differential connection have been designed; a split cell for comparing two adjacent illuminated fields is available, as well as ocular eyepiece types which fit a microscope draw tube. Giant cells, consisting of a number of elements connected in parallel, are available (*Q*).

Comparison of Emissive and Barrier-Layer Types. It is important to keep in mind the relative advantages and limitations of each type of cell. There has been a tendency in some circles to regard the barrier-layer cell as vastly superior and simpler than the photoemissive type. This is by no means true, depending entirely upon the particular problem to be investigated. At very high levels of illumination the comparatively heavy currents furnished by a barrier-layer cell are impressive. However, in most photometric work the available radiation is feeble, especially if a monochromatic beam is employed. A rough comparison under these conditions will illustrate the point.

Suppose we consider a photronic cell of sensitivity 120 microamperes per lumen, which is receiving radiation of 10^{-6} lumen. The current will be 1.2×10^{-10} ampere. A good cell of the emissive type (40 microamperes per lumen) under the same conditions will deliver 4×10^{-11} ampere. If we use galvanometers of appropriate characteristics and a sensitivity of 10^{-10} ampere per millimeter, we shall obtain 1.2-mm. and 0.4-mm. deflection, respectively. In each case we shall be able to detect light, but in no sense can it be measured accurately. In the case of the photronic cell the dilemma is genuine because amplification is impossible, for assuming the load resistance to be 5,000 ohms, the potential drop available is only 0.6 microvolt. This is about the noise level of an amplifier, and while the effect would be detectable it could not be measured. In the case of the emissive type, amplification with a single, stabilized F. P. 54 tube would solve the problem. As will be shown later, a current of 25 microamperes could be obtained under the above conditions. Thus full-scale deflection could be obtained on a 0–25 microammeter. Assuming 100 scale divisions, the photocurrent could be measured with better than 1 per cent precision.

The barrier-layer cell yields relatively large currents at a low potential. The internal resistance is low and decreases with increasing illumination. The emissive type yields smaller currents, but it has a very high resistance. Since the load should match the impedance of the source, it is readily seen why the latter type is amenable to amplification.

Amplifiers. The vast literature of vacuum-tube theory and application is directed largely to its most important field, communication. Nevertheless a number of monographs deal extensively with noncommunication uses (*E*, *F*, *K*, *N*, *P*, *R*, *S*). A few of the more important considerations are discussed below.

Figure 11 illustrates a simple arrangement of photocell and triode which may serve for this discussion. The grid and plate potentials are adjusted to the rated values for the particular triode which is chosen. The photocell battery provides a potential high enough to produce saturation currents for the prevailing light intensities. Upon illumination the photocell will deliver a current, i, which flows through the high resistance, R, thereby producing a potential difference, Eg', across its terminals. This will make the grid more negative with respect to the cathode and consequently the plate current will be reduced by an amount ΔI. The magnitude of this change is governed by an important constant of the triode known as the mutual conductance, G_M. (The advent of multigrid tubes has necessitated a more specific designation, *Sp*, termed the grid-plate transconductance.) Its value is given by:

$$G_M = \left(\frac{\partial I_p}{\partial E_g}\right) E_p \qquad (3)$$

It is expressed in units of reciprocal ohms $\times 10^{-6}$ and designated micromhos. For a given tube the value depends upon the plate and grid potentials. An average value suitable for the circuit of Figure 11 is 1,000 micromhos. This means that a change in Eg' of 1 volt will produce a change in plate current of $\Delta I_p = 1$ milliampere.

Let us suppose that the triode has this value for G_M. If R is equal to 10 megohms, then a photocurrent of 10^{-7} will produce a change of plate current of 1 milliampere. The gain is therefore $10^{-3}/10^{-7} = 10^4$ or ten thousand fold. This is a very conservative case and by no means approaches the limit to which this process can be extended. The factors which limit indefinite gain are as follows:

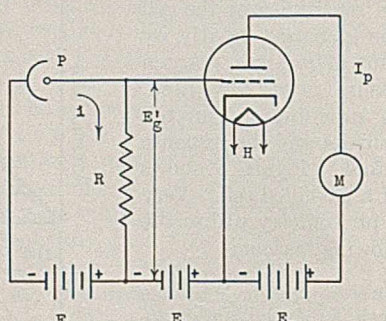


Figure 11. Triode-Photocell Circuit

Grid Currents. While the grid exerts its control primarily electrostatically, yet in high-gain tubes with large values of G_M, the grid does collect some electrons and a finite current flows in the grid circuit. It is obvious that the magnitude of this grid current limits the small currents which can be measured in the input circuit.

Insulation. Leakage currents between tube elements, over the glass envelope and at socket terminals, set limits to the gain that can be realized in practice.

Ionization Currents. Although modern tubes are very highly evacuated, there is sufficient gas present to furnish positive ion currents. If the potentials applied to the tube elements are reduced to low values (below the ionization potentials of the residual gases) this disturbance can be eliminated. This entails a very considerable reduction in gain but it can be overcome, if necessary, by succeeding stages of amplification of the conventional type.

Photoelectrons and Soft X-Rays. Photoelectrons may be emitted from the metal tube elements because of light from the filament or indirectly heated cathode, and similar disturbances may arise from the soft x-rays emitted by bombardment of the plate by electrons.

Special electrometer tubes have been developed in which systematic studies of the above-mentioned difficulties have established the correct design. The General Electric FP. 54 tube was the first of this class (*131*). In appropriate circuits, currents as

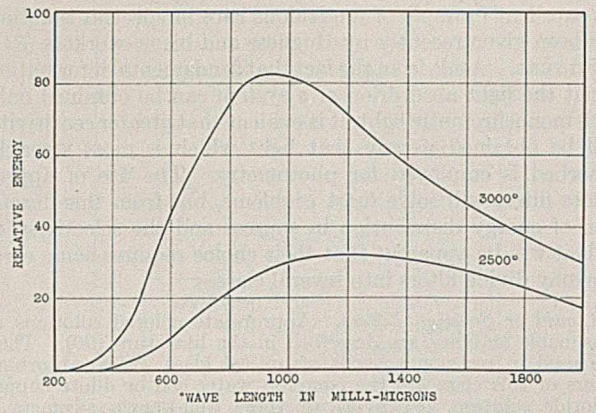


FIGURE 12. ENERGY DISTRIBUTION OF INCANDESCENT SOURCE

low as 30 electrons per second have been measured (*41*) with this tube. Other electrometer tubes are the Western Electric Company's D-96475 and the R. C. A. A-154. Westinghouse manufactures semielectrometer tubes of the inverted triode type, the DRH-506 and DRH-507. A further compromise between commercial and electrometer tubes is afforded by their RJ-550 and RJ-553.

In general, it should be emphasized that many commercial triodes if operated at subnormal voltages will approach electrometer tube performance. The low gain may be made up by subsequent stages of amplification in the conventional manner.

Light Sources

TUNGSTEN LAMPS. The tungsten incandescent lamp is one of the most convenient and widely used sources for photoelectric measurements. The energy distribution throughout the spectrum is not ideal for the purpose, as may be seen from Figure 12, particularly if it is used with a red-sensitive cesium cell. The effect of this energy distribution is best illustrated by noting the effective response of a cesium (blue response) cell when used with this type of illuminant (Figure 13). The importance of these simple considerations cannot be overemphasized. If we keep in mind that most of the energy is in the infrared and very little at the shorter wave lengths it will be seen that all sensitivity curves and effective filter transmission curves may be displaced considerably when they are used with an incandescent source.

TABLE II. VALUES OF n

Characteristic	Value of n W, vacuum	W, gas-filled
Lumens, volts	3.5	3.6
Watts, volts	1.6	1.5
Lumens per watt, volts	1.9	2.1
Lamp life, lumens per watt	−7.0	−6.8

A general expression similar to Equation 2 may be used to define the characteristics of tungsten lamps (*61*). Thus

$$\frac{X_1}{X_2} = \left(\frac{V_1}{V_2}\right)^n$$

The best-known values for exponent n for some properties as a function of lamp voltage, V, are given in Table II.

Lamp-life ratings would seem to be primarily of economic interest, but actually it is advantageous to choose a light source somewhat larger than required and operate it at slightly subnormal voltage. Replacement and possibly necessary recalibration are therefore less frequent. Industrial experience has indicated that this practice applies to electronic equipment in general, and satisfactory performance after 20,000 hours' use has been reported. On the other hand, moderate overloading enhances the brilliance and occasions a favorable shift of energy distribution. This is exemplified by the photoflood lamps used in photography. It is obvious that several factors will govern the choice of operating conditions.

Low-voltage lamps may be operated from storage batteries or transformers. For the former, a well-charged battery should be used and only over the optimum portion of the discharge curve. The use of a voltmeter across the lamp terminals is pointless except as a rough indication of the operating voltage. Unless a suppressed zero instrument is available it can be seen from Equation 2 that the photocurrent is a much more sensitive indicator of lamp conditions than a voltmeter. If it is necessary to know the lamp voltage, a volt box in combination with a simple potentiometer reading to ±0.1 millivolt will suffice.

Operation from a step-down transformer is very convenient and fairly constant illumination can be obtained by special

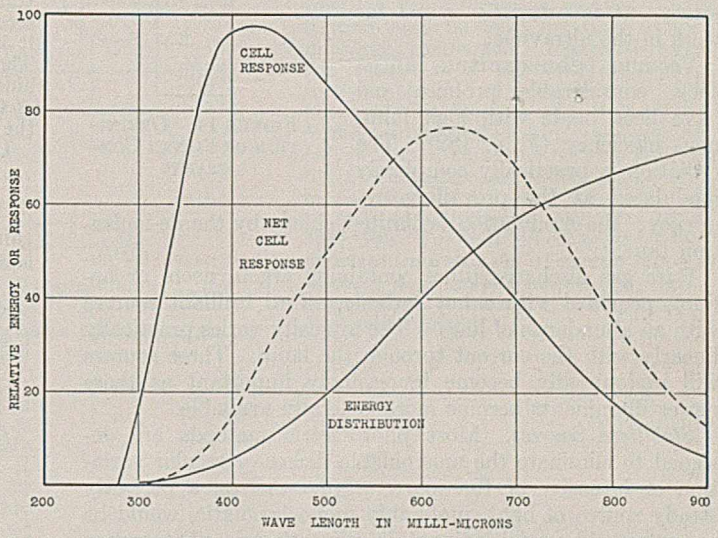


FIGURE 13. EFFECT OF ENERGY DISTRIBUTION OF THE SOURCE UPON PHOTOCELL RESPONSE

transformers of the three-legged saturation type (Ward Leonard Mfg. Co., Mt. Vernon, N. Y.). In all cases of alternating current operation an appreciable modulation of the light occurs, owing to slight cooling of the filament on each half cycle. The photocurrent will be partially modulated at twice the line frequency (usually 120 cycles). This is important in some cases, especially where amplification is employed.

MERCURY ARC. The modern mercury arc is a most convenient source, yielding several strong groups of lines in the visible spectrum.

	Å.
Yellow	5791; 5770
Green	5461
Blue	4358; 4348, 4339
Violet	4079; 4047
Near ultraviolet	3663.3; 3662.8; 3655; 3650

The intensity of these lines as a function of lamp wattage was carefully investigated by Küch and Retschinsky and others (*58, 59, 60, 112, 166*). The absolute intensities as well as the relative values depend upon many factors such as lamp

dimensions, current, voltage, ambient temperature, etc. Individual lines can be isolated with reasonable purity by filter combinations. The ordinary mercury pool–cathode type is subject to considerable flicker even in a well-ballasted circuit. If a high-voltage storage battery is available, the lamp may be operated steadily enough to permit measurements by the substitution method. In photometric methods of the balanced or null type, the flicker is of no consequence, provided that there is no asymmetric displacement of the source.

The rare gas–mercury vapor discharge tubes are very stable, owing to the absence of liquid mercury. The intensity varies almost directly with the current through the lamp. Owing to the rare gas excitation, the mercury resonance lines are favored and the visible lines are relatively weak. As exemplified by the Hanovia S2537 lamp, about 40 per cent of the radiant energy is emitted by the first resonance line—2537 Å.—the tube is feebly luminous and not uncomfortably warm. It is primarily suited for work in the ultraviolet.

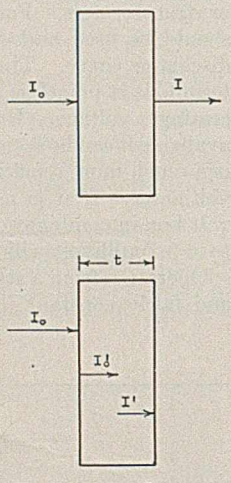


FIGURE 14. DEFINITION OF FILTER CONSTANTS

Vacuum tube–excited lamps show considerable promise and have been made with high luminous efficiency (*F*, p. 182). The radiation is practically completely modulated at the prevailing frequency; the modulation is limited chiefly by the de-ionization time.

Rare gas discharge tubes containing argon, neon, or helium, provided with a hot cathode, afford brilliant sources with an abundance of lines. The intensity varies practically linearly with the current through the lamp. These sources will undoubtedly become increasingly important as these newer illuminants become more generally available.

Stabilized Sources. Most photometric methods are designed to eliminate the unavoidable flicker or secular variation of intensity of the source. Nevertheless, a perfectly steady source of light, preferably monochromatic, would be an extremely useful adjunct in photoelectric photometry. Some successful attempts in this direction include: lamp excited by a generator driven by a synchronous motor; lamp excited by a generator with vacuum-tube field control (*F*, *K*, *N*, *R*); lamp current controlled by a saturable reactor (thyratron control, *F*, *K*, *N*, *R*); and current stabilized by a power tube shunt (*87*).

These methods are characterized by an attempt to furnish a very constant source of current. It is likely that photoelectric control of the source itself is more promising, inasmuch as the light intensity usually varies exponentially with the current or voltage.

Monochromators and Filters

All but the crudest photoelectric measurements demand some approximation to monochromaticity of the light source. For the highest precision and work requiring information of a fundamental nature, spectral isolation, preferably with a double monochromator, is necessary. Naturally, considerable reduction in intensity accompanies this process. Stray or scattered radiation is an important factor; this can be avoided by supplementing the monochromator with filters or by using a second monochromator. It is beyond the scope of this review to discuss this subject in detail; it is dealt with in numerous papers and manufacturers' bulletins (*H*, *M*). An excellent example of meticulous care in spectral isolation has been given recently by Hogness and his co-workers (*84*).

FILTERS. Aside from the fact that fundamental information about the light absorption of a system can be obtained only with monochromatic light, it is evident that greater sensitivity will be obtained if only that light which is most strongly absorbed is employed for photometry. The use of appropriate filters will solve most problems, but from this discussion of energy distribution in sources and the selectivity of cells it will be apparent that their choice requires some care. We may divide filters into several classes.

Liquid or Solution Filters. Appropriate colored solutions of reasonable stability are described in the literature (*90*). They are used in rectangular cells of optical glass. Heat-absorbing filters of this class are the common water cell or dilute copper chloride solution. (The use of these well-known adjuncts is burdened with the appearance of bubbles and for this reason heat-absorbing glass filters are gradually replacing them.) In general, this class of filter is used only when no glass filter of the desired transmission is obtainable.

Glass Filters. These are available in great variety, the Corning and Jena filters being the best known. Typical transmission values are available in bulletins of the Corning Glass Co., Schott, Jena, and also in handbooks (*82*, *89*). The transmission, *T*, for a given wave length refers to the ratio of light intensity leaving the second surface to that incident upon the first surface. The transmittance, C_t, is the ratio of intensity incident upon the second surface to that leaving the first surface: In other words, it is the transmission corrected for surface losses (Figure 14). These are due primarily to nonselective reflection and usually amount to 4 per cent at each surface. Following the notation of Gage (*65*) we may relate these quantities to the thickness of the filter.

Let

T = transmission of the piece of glass
C = transmittance per mm. of glass
C_t = transmittance for t mm. of glass
t = thickness
β = $\log_{10}$ transmittance for 1-mm. thickness.

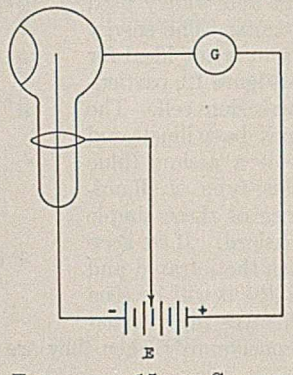


FIGURE 15. SIMPLE PHOTOMETER WITH VACUUM PHOTOCELL

Then from the above

$$T = 0.92\ C_t$$

(due to 8 per cent loss by reflection) or

$$C_t = T/0.92$$

Since $C_t = C^t$, $\log_{10}$ transmittance $= \log_{10} C_t = t$, which may be written

$$\beta t = \log_{10}(T/0.92) = \log_{10} T - 0.0362$$

Gage (*65*) has given a typical example of how the thickness of two pieces of glass of known spectral transmission may be computed in order to reduce the response curve of a photronic

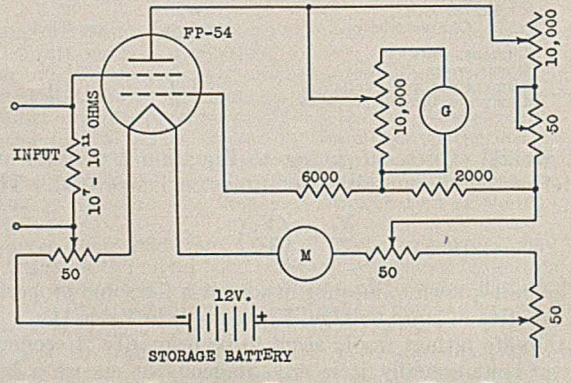


FIGURE 16. STABILIZED ELECTROMETER TUBE CIRCUIT
Suitable for photoelectric measurements

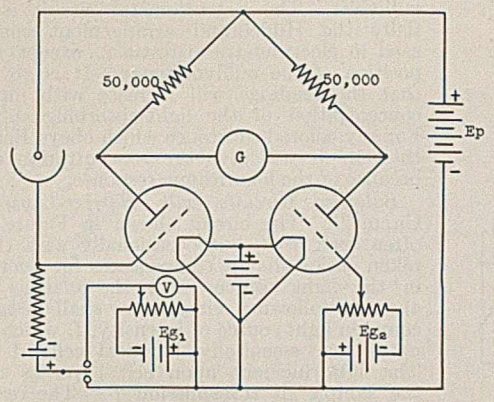


FIGURE 17. VACUUM-TUBE BRIDGE CIRCUIT FOR PHOTOELECTRIC PHOTOMETRY

cell to that of the average eye. For the more exacting problem of computing filters for use with a photocell such that the trichromatic coefficients may be obtained in terms directly reducible to the standard I. C. I. observer, Gibson (*71*) has prepared an excellent summary.

Gelatin Filters. Thin films of gelatin in which dyes have been incorporated provide very useful filters, usually mounted between plates of clear optical glass. The Wratten (*43*) filters are typical of this class and are widely used, especially in photography. They are usually more selective than glass filters but they must be handled with great care, especially with respect to overheating. Some of them lack permanence because of thermal and photochemical changes, although these limitations are clearly indicated by the manufacturers. In cases where their use is preferred, it is advisable to introduce the filter in a position most remote from the light source in order to minimize thermal effects. It must not be inferred that gelatin filters stand alone in their susceptibility to heat. Selenium glass filters and probably others are perceptibly affected by increase in temperature and this must be kept in mind at all times.

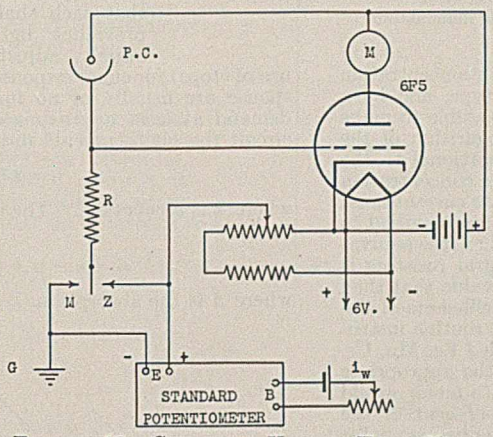


FIGURE 18. SENSITIVE VACUUM-TUBE VOLTMETER
With precise input compensation for photoelectric photometry

CIRCUITS. Some circuits are obviously straightforward and understandable; others have been recommended by chemists because they solved the problem in hand. Wherever possible, the writer has attempted to analyze and interpret them physically in order to evaluate their general utility.

Photoemissive Type, A, (for single-cell methods with vacuum photo cells). 1. For moderately high intensities the simple arrangement of Figure 15 is satisfactory. A guard ring is attached to the photocell as shown in order to minimize leakage. A galvanometer of sensitivity 10^{-10} ampere per mm. is satisfactory. For some work an Ayrton shunt in the galvanometer circuit is very convenient. Its value should leave the galvanometer slightly underdamped. Another great convenience is to supplement the usual scale with a logarithmic scale (*85*). This simplifies the computation of extinction values.

2. The general aspects of amplification have been discussed. Figure 16 shows a typical stabilized circuit using an electrometer tube and a sensitive galvanometer (*N*, p. 91). The theory and design of stabilized circuits are discussed in several papers (*42, 192, 214, 219*).

3. The use of vacuum tubes in bridge circuits is exemplified by several examples. In Figure 17 two tubes form adjacent arms of a Wheatstone bridge. When the photocell is dark, the grid bias on the right-hand tube is adjusted until the bridge is balanced. Upon illumination of the photocell, the plate resistance of the left-hand tube decreases and the bridge becomes unbalanced. Balance is then restored by changing the grid bias of this tube. The voltmeter, *V*, indicates a potential which is equal to the *iR* drop in the grid resistor. This, of course, is directly proportional to the photocurrent. In modern practice a twin triode would be used because the common heater and related factors would enhance the stability. Bridge circuits of this sort are less sensitive than the equivalent single-tube circuit, but they are more stable.

4. The 6F5 circuit shown in Figure 18 has been used extensively in the writer's laboratory (*68*). It is simply a vacuum-tube voltmeter with a convenient direct-reading bias adjustment. When the photocell is darkened, the zero bias is adjusted to give a standard plate current reading. When the cell is illuminated with light coming through the solvent, I_0, the dials of the potentiometer box are set at unity (1.0000) and the working current is adjusted until the standard plate current is again obtained. Now when the solution is interposed (intensity = I) the potentiometer dial and slide wire are adjusted until the standard plate current is again obtained. The potentiometer now indicates the transmission directly. Since $-\log T = kc$ these transmission values enable one to calculate the concentration. In addition, the working current may be measured very simply and can be admitted to the potentiometer in calculated amount for each type of determination (specific values of the extinction coefficient, k).

5. For those methods in which two beams strike a single cell alternately (method *B*) alternating current amplification may be used for the pulsating unbalance-component. Figure 19 shows the connection of photocell cathode directly to the grid of the first tube. Low potentials are used on this tube in conformity with electrometer tube practice (*M*, p. 294). This tube may be followed by a multistage amplifier, terminating in the voltage coil of a wattmeter (*N*, p. 425) or a thyratron controller (*N*, p. 426; *80*). For null indication the bridge balance indicator of Garman is well suited. It achieves a sensitivity of a few microvolts, by means of a single multielectrode tube (*66*).

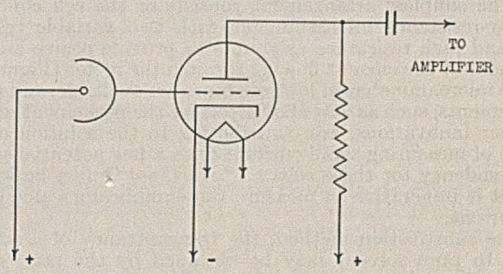


FIGURE 19. PHOTOCELL PREAMPLIFIER CONNECTION
With differential sensitivity independent of illumination level

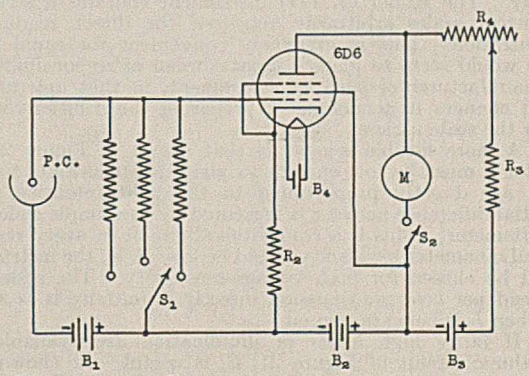


FIGURE 20. PHOTOMETER WITH LOGARITHMIC RESPONSE
Linear in concentration units

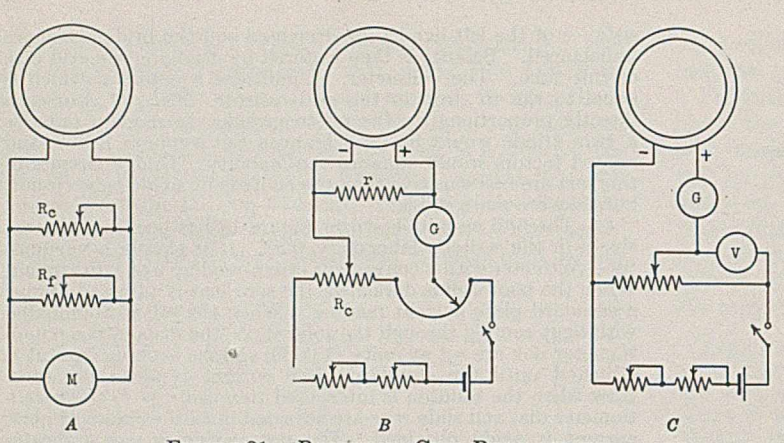


FIGURE 21. PHOTRONIC CELL PHOTOMETERS

A. Measurement of short-circuit current
B. Potentiometric measurement of current
C. Measurement of open-circuit e. m. f.

Logarithmic response at high levels of illumination

6. Figure 20 is a direct-reading arrangement (concentration units). The 6D6 tube is of the remote cutoff type, and by a suitable choice of the cathode resistor, R_2, it is possible to make the plate current directly proportional to the logarithm of the input voltage (*147*). Since this voltage is proportional to the light intensity, the plate meter can be calibrated in concentration units directly. The normal component of the plate current must be balanced out, since the logarithmic relation cannot extend to zero plate current. This is an advantage, however; it is equivalent to a suppressed zero meter. A choice of grid resistors is available; indeed, these can be selected of such value that they stand in the ratio of the respective extinction coefficients of the various substances which are to be analyzed. A routine instrument would therefore bear a selector switch labeled Fe, Mn, Cr, Cu, etc., each representing an input resistor of the appropriate value to suit the extinction coefficient. The plate meter would bear a linear scale reading in micrograms or per cent of the desired constituent. A calibrated shunt would be necessary for the plate meter.

Barrier-Layer Type, B. 1. We have seen that the short-circuit current in this type is very nearly directly proportional to the light intensity, provided the external circuit resistance is low. The simplest arrangement consists of the cell connected to a low-resistance microammeter with two variable resistors of low and high resistance as shunts to provide coarse and fine adjustment of the current flowing through the meter (Figure 21). Suitable microammeters of low resistance are available, and recent improvements, such as new alloy steels for the permanent magnet and other innovations, are contributing to the solution of this problem of measuring small currents from a low potential source.

The tendency for these cells to "overshoot" must be kept in mind; it is imperative to measure the equilibrium value of the photocurrent.

By the substitution method, the transmittancy of a solution relative to pure solvent may be obtained by the ratio of the corresponding photocurrents. In instruments embodying this principle the meter is usually calibrated in 100 divisions, so that the transmission may be read directly. Logarithmic scales have been provided enabling one to read extinction values directly. The Kuder (*5, 111*) instrument contains a series of translucent scales arbitrarily engraved for direct reading of concentration. This is extremely convenient for rapid work but it would seem to place a great burden of responsibility on the manufacturer of such an instrument, in that any unwarranted changes in technique of preparing the solutions would render the scale useless.

2. A more flexible scheme is that shown in Figure 21, *B*. Resistor r must be low enough to allow photocurrents to flow which are directly proportional to the light intensity. The potential difference across r is measured by the simple slide-wire potentiometer. This is a conventional circuit in every respect. The galvanometer resistance should be low—i. e., the instrument should be chosen for high voltage-sensitivity. The slide wire will read per cent transmission directly if initially it is set at 100 when I_0 is being measured.

3. If fairly high levels of illumination are available the logarithmic circuit of Figure 21, *C*, is useful. As shown previously, the open circuit e. m. f. of a barrier-layer cell is directly proportional to the logarithm of the light intensity. For the average cell this relationship prevails for potentials above 60 millivolts. The potentiometer circuit is essentially the Hildebrand arrangement commonly used in electrometric titrations, except for the position of the millivoltmeter. It is so chosen that the readings will increase with increasing concentration of the light-absorbing substance. For any colored substance which obeys Beer's law this circuit will give the concentration directly because of the logarithmic response.

Balanced Circuits with Barrier-Layer Cells. Circuit 1. The circuit shown in Figure 22 has often been used, but occasionally with the mistaken notion that it compensates for fluctuations in the light source. For the analysis of this and the following circuits we shall designate a common light source of intensity, I, which illuminates two essentially identical cells, 1 and 2. The light incident upon cell 1 passes through the sample of transmission T. The respective photocurrents, i_1 and i_2, flow through the galvanometer in opposite directions. In this and the remaining cases, absolutely identical photocells are not necessary. It is merely assumed that each shall exhibit linear response over the prevailing light intensities and that they are initially adjusted (by virtue of position or the use of stops) for equal response. Slight differences in spectral response are usually of no importance, since most applications demand at least approximately monochromatic light. In this circuit the photocurrents in the two branches are

$$i_1 = kTI \text{ and } i_2 = kI$$

where k is a constant. The net current through the galvanometer is

$$i_g = i_2 - i_1 = kI(1 - T) = kIA \qquad (3)$$

where A is the absorption.

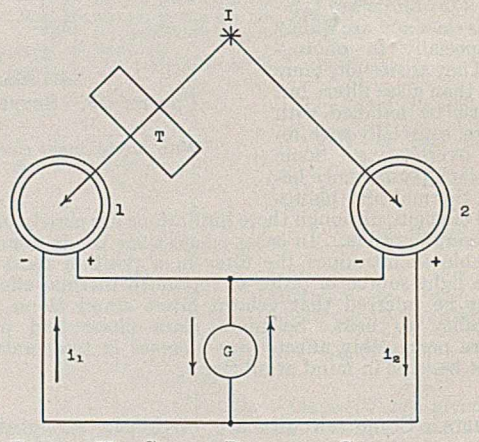


FIGURE 22. SIMPLE BALANCED CIRCUIT FOR BARRIER-LAYER CELLS

With a constant source the galvanometer will indicate the absorption directly. If the galvanometer sensitivity is adjusted by means of appropriate shunts it may be set to read full scale (100 divisions) when $T = 0$—i. e., when no light strikes cell 1. Under these conditions the scale will indicate per cent absorption.

We may seek the condition for compensation for source fluctuations by differentiating Equation 3

$$di_g = kdI - kTdI$$

Setting

$$\frac{di_g}{dI} = 0$$

we find that $kTI = kI$ or $T = 1$.

In other words, fluctuations in response will be a minimum when the transmission of the sample is unity and the circuit has the doubtful distinction of perfect compensation when it is not in use. However, if optical compensation is used the compensating feature can be retained.

Circuit 2 (Figure 23). In this arrangement the two photocurrents, i_1 and i_2, flow through variable resistors R_1 and R_2.

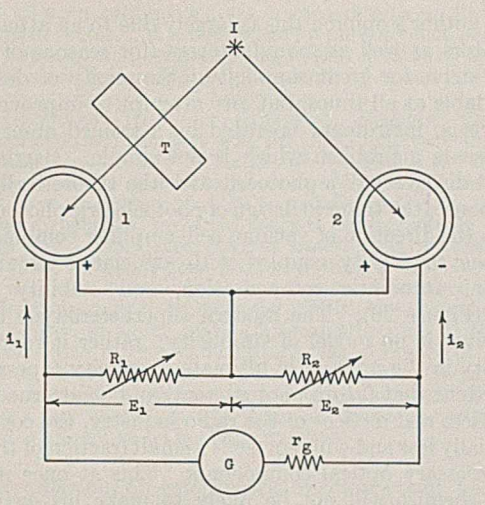


FIGURE 23. BALANCED CIRCUIT POSSESSING COMPENSATION FOR SOURCE FLUCTUATIONS

Values for the latter may be found such that the potential drops, E_1 and E_2, are equal, under which circumstances the galvanometer will show zero deflection. The circuit was suggested by Wilcox (*227*). No circuit analysis was given and the following treatment which has been confirmed by experiment may be of interest.

As before

$$i_1 = kTI \quad \text{and } E_1 = kTIR_1$$
$$i_2 = kI \quad \text{and } E_2 = kIR_2$$

at balance $E_1 = E_2$ and therefore $kTIR_1 = kIR_2$ or

$$T = \frac{R_2}{R_1}$$

The transmission of the sample is given by the ratio of the resistor settings necessary to establish balance. Various convenient arrangements are possible—for example, R_2 may be a Kohlrausch slide wire and R_1 an ordinary resistor of the radio "potentiometer" type. The slide wire is set at 100 with the sample removed and balance is established with R_1. The sample is then introduced and balance is re-established with the slide wire. The per cent transmission is indicated directly on the slide wire. Both resistors should have very low values for the reasons before-mentioned.

Compensation for source variations is inherent in this circuit. The current through the galvanometer is

$$i_g = \frac{E_2 - E_1}{r_g} = \frac{kIR_2 - kTIR_1}{r_g} \qquad (4)$$

Differentiating

$$\frac{di_g}{dI} = \frac{kR_2}{r_g} - \frac{kTR_1}{r_g}$$

For

$$\frac{di_g}{dI} = 0$$

we get

$$T = \frac{R_2}{R_1}$$

From this result we see that the fluctuations due to source variations will be at a minimum when the resistors are set in the ratio of the transmission, which is precisely what is done in the process of balancing the circuit. This may be confirmed experimentally in simple fashion. Writing Equation 4 in increment form,

$$\Delta i_g = \frac{k\Delta I}{r_g}(R_2 - TR_1) = \frac{k\Delta IR_1}{r_g} \times \left(\frac{R_2}{R_1} - T\right)$$

Since R_2/R_1 is the transmission, any value of R_2/R_1 may be designated as a virtual transmission, T'. The last equation becomes:

$$\frac{\Delta i_g}{\Delta I} = \frac{kR_1}{r_g}(T' - T) = a\Delta T$$

where

$$a = \frac{kR_1}{r_g}$$

Figure 24 shows values obtained and plotted according to the above equation. In this test R_1 was held constant and the intensity of the common source was changed by known amounts, ΔI. The corresponding galvanometer deflections, Δi_g, were noted. Several values of $\Delta i_g/\Delta I$ were measured for different settings of R_2. In each case ΔT could be computed from the value of $R_2/R_1 - T$. These are the abscissas of Figure 24, which shows that the fluctuations approach zero as the difference between R_2/R_1 and T (the true transmission) approaches zero. The limiting case is most simply shown by setting R_2/R_1 equal to the true transmission. The light source may now be dimmed almost to extinction without causing any perceptible galvanometer deflection.

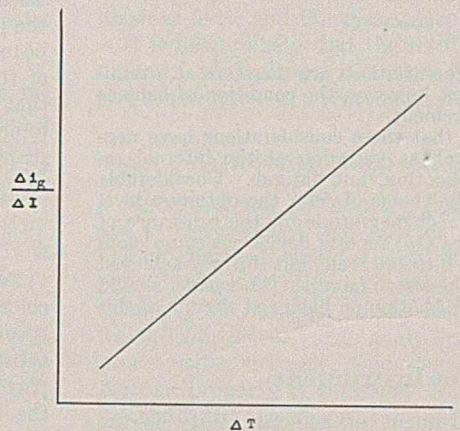


FIGURE 24

Circuit 3 (Figure 25). This arrangement with various modifications has been widely employed. Brice (*19*) has given an analysis of this and related circuits. Neglecting secondary factors, this method may be used to obtain transmission values with good compensation for source variations. Figure 25 shows that the galvanometer may be considered as fed by two cells through universal shunts. In the right-hand branch, R may take the form of a low-resistance Kohlrausch slide wire.

The opposing currents through the galvanometer may be written

$$i_{g_1} = kTI\frac{a}{R + r_g}$$
$$i_{g_2} = kI\frac{x}{R + r_g}$$

At balance these currents are equal; hence

$$x = Ta$$

In other words, x, the slide-wire setting, is directly proportional to the transmittancy; indeed, if the initial adjustment is so arranged that when $T = 1.00$, x is set at its maximum value,

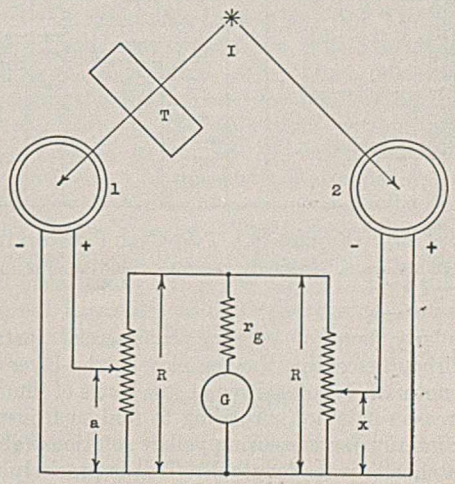


FIGURE 25. BALANCED CIRCUIT
Direct reading, with compensation for source fluctuations

R (100 or 1,000 scale divisions), and a is varied until balance is established, then all successive values of T will be given by x directly. Whenever electrical balance is established, the arrangement should be independent of source fluctuation, as may be seen by differentiating the expression for the net current through the galvanometer.

$$i_{g_n} = \frac{kIx}{R + rg} - \frac{kTIa}{R + rg} = cIx - cTIa$$

where

$$c = \frac{k}{R + rg}$$

$$\frac{di_{g_n}}{dI} = cx - cTa$$

for

$$\frac{di_g}{dI} = 0, \; x = Ta$$

Fluctuations due to source variations are therefore at a minimum when $x = Ta$, which is, however, the condition of balance as obtained during a measurement.

It should be emphasized that these considerations have neglected secondary factors such as variation of the internal resistance of the cells, overshooting, and fatigue. Considerable care must be exercised in the choice of cells, the optimum level of illumination, and the correct magnitude for the resistance of the measuring circuit. Brice (*19*) reports deviations of no more than 0.1 to 0.2 division on a 0 to 100 scale, but this was achieved by a very careful study of the above factors. This paper should be consulted for detailed information on balanced circuits of this type.

Choice of Instrument

The most reliable instrument of general utility is the spectrophotometer. All colorimetric problems can be referred to the complete information which a photometric curve affords. Compromise instruments like the gradation photometer are less costly and enable one to obtain an abridged spectrophotometric analysis. For colorimetric chemical analysis the visual Duboscq colorimeter is still the most versatile and useful instrument. Despite the fact that most of the photoelectric instruments discussed above may be as sensitive or more sensitive than the best visual instrument, their use is at present restricted to specific applications. This

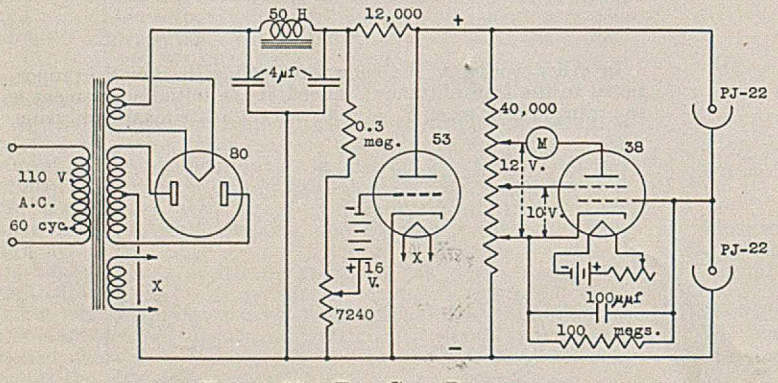


FIGURE 26. TWO-CELL PHOTOMETER

With high differential sensitivity and tube stabilization of the high-voltage source

is particularly true of existing commercial instruments. Almost without exception they employ barrier-layer cells and these are notoriously insensitive at low levels of illumination. For this reason it is not surprising to find such instruments decidedly inferior for measuring yellow solutions (absorption of light at shorter wave lengths). This is precisely the difficulty which the user of a visual colorimeter wishes to avoid; he usually abhors the task of matching yellow solutions.

In the author's opinion this is largely due to an attempt of investigators as well as manufacturers (for reasons of economy) to strive for great simplicity. Simplicity of design is commendable at all times, but any attempt to improve upon a good visual instrument operated by a trained observer at once presents a problem which is not simple. Barring the imminent discovery of a photocell with the theoretically possible response, the trend in design of photoelectric photometers will be in the direction of vacuum cell–amplifier combinations of extreme sensitivity coupled with associated circuits for regulation, automatic compensation, and stability maintenance (Figure 26). The modern superheterodyne broadcast receiver is no model of simplicity; rather it represents complexity in the interest of ultimate simplicity (operation). To the extent that future photometers can be patterned after the practices and devices of the radio industry, the costs will be materially less and will represent a small fraction of the cost of the necessary optical components. This at once implies that the chemist will not be likely to make his own photometer; there are probably few who would attempt to construct an analytical balance, though essentially it is a much simpler instrument.

Colorimetric Analysis

To illustrate a typical case we shall assume that a suitable color reaction has been selected; further, that it shall be specific for the substance in question or that all interfering substances have been separated or transformed into complexes, etc., which prevent such interference. In most of the careful work reported in the literature, these chemical aspects are adequately treated. The optical problem now reduces to the following steps:

1. The region of maximum light absorption must be determined. This is best done with a spectrophotometer or gradation photometer. For the better-known substances, absorption spectra may be found in the literature. If these instruments are not available a hand spectroscope will afford a rough estimate of the region of maximum absorption. Even a rough guess (complementary color) is no bar to successful selection of the appropriate region, but the chance of selecting the most suitable region is roughly in proportion to the elegance of the measurement.

2. The light source is now provided with means for selecting this region of the spectrum. The most elegant procedure is to use a monochromator. Next in order of choice is a discontinuous source with suitable filters or a continuous source with composite filters. In every case the energy distribution of the source must be combined with the filter characteristic, as explained in Figure 13. In any case some sort of filter must be used. Results obtained with "white" light not only show poor differential sensitivity but the interpretation of the results will be difficult.

3. Rate of reaction studies, however simple, must now be made, in order to be sure that the maximum light absorption is being measured. A simple plot of transmission against time after mixing will show how much time must elapse before measurements are made. This is best done at several concentrations, especially since higher order kinetics may be involved. The same procedure will detect and evaluate the rate of bleaching or fading if it occurs in this system. At this point the analyst should not be surprised if he encounters a system in which the rate of color formation is almost equaled by the rate of fading. The literature of colorimetric analysis is replete with examples, and some are the basis of lengthy polemics.

4. It is now assumed that we shall employ a photometer which is direct-reading in transmission or extinction values or that the functional relationship between light intensity and instrumental indication is known. A series of solutions of known concentration is measured and the extinction coefficient is then calculated. It will be evident that this constant is really an "effective extinction coefficient," especially if filters have been used to render the light approximately monochromatic. To this

extent all such calibrations are burdened with an instrumental constant or factor. It is only when all photoelectric photometers employ strictly monochromatic light that a table of appropriate extinction coefficients will be of general value and will eliminate the necessity of individual calibration.

5. Interpretation of Results. Reliable photometric measurements of this sort will provide immediate information concerning the validity of Beer's law. Despite the many contradictions in the literature, very careful and precise measurements have indicated that it is usually applicable, including colloidal dispersions, provided there is no appreciable change in particle size. There are obvious cases, such as concentrated cupric salts, in which very profound changes in color are associated with dilution and in such instances pronounced deviations from Beer's law are to be expected. With the exception of such obvious cases, in which many physical properties of the system would lead one to expect deviations, the existence of a definite extinction coefficient at a given wave length is to be regarded as a fundamental physical property of the system. The failure of Beer's law should not be claimed unless the experimental method is known to be beyond reproach.

This criterion of colorimetric reactions will become increasingly important as photometric practice becomes more precise and reliable. At the present time our fund of color reactions is very large, although, unfortunately, very few have been investigated rigorously enough to satisfy the above criteria. Indeed it may be said that we have far too many methods; that few will survive critical examination. It is not the object of this review to discuss these reactions in detail nor even to question the expediency of certain proposed tests, but rather to emphasize the need for rigorous optical and physico-chemical examination of each reaction. As a rule the purely analytical aspects such as selectivity, interference, etc., have been adequately investigated.

Photometric Titrations

The type of measurement just discussed places a heavy burden of responsibility upon a single photometric measurement. Ordinary volumetric analysis permits high precision because a relatively large volume of reagent can be measured to within one drop. The actual color change at the end point is rarely estimated (in the optical sense) to better than 5 or 10 per cent, yet this change is sufficiently abrupt to afford sufficient precision. Photoelectric methods have been used to detect such changes (*16*, *76*, *96*, *140*, *142*, *173*, *193*, *194*); indeed, titrations can be performed automatically (*149*) when a large number of routine analyses warrant the necessary elaboration in equipment. In a larger sense, however, photometric titrations may supplement or replace the ordinary photometric procedure. The well-known "duplication method" of colorimetry involves the treatment of the unknown with a large excess of reagent. In a comparison vessel filled with excess reagent, a standard solution of the substance is added in amount sufficient to match the color of the unknown sample. The conditions necessary for the success of this method are completely discussed in standard texts and will not be repeated here (*105*).

For those systems in which it is applicable, the photoelectric method may be used in a number of ways—for example, a sensitive twin-cell photometer may be used to indicate the point at which the two solutions have identical transmissions. A more laborious but very precise procedure involves a measurement of the transmission at uniform intervals during the titration. If Beer's law is obeyed, a plot of $-\log T$ (extinction) will be a linear function of the amount of reagent. Moreover, if the color reaction follows a definite stoichiometric law a sharp inflection may be expected in the extinction lines when reagent and substance react in equivalent amount. The technique is reminiscent of conductance titrations; indeed, the average straight lines may be considerably more reliable than the individual points. The latter method is useful in clearing up certain points of theoretical interest. By this method it has been shown (*148*) that the gold method for estimating bromides really involves the $AuBr_4^-$ ion as the light-absorbing species, not a wholly unexpected result, but more convincing than indirect reasoning or supposition. Similarly, certain peculiarities of the starch-iodine system have been studied in this manner (*147*).

It is likely that studies of this sort would be profitable in the case of most colored substances in solution. In too many cases the composition of the colored substance has been inferred from the nature of the solid phase which can be obtained from the solution, or as one often suspects, from the ease with which an equation may be balanced in an elementary textbook. A classic example is the familiar reaction between ferric and thiocyanate ions (*190*, p. 284).

It is not unlikely that the results obtainable by the technique of photoelectric titrations would warrant the design and construction of a recording photometer.

Automatic Inspection and Control

Modern trends in industry show increasing use of automatic measurement and control. Many operations are in reality chemical analyses, but the operator has been dispensed with and self-regulated, self-calibrated instruments take over the burden. Of the various properties of a system which lend themselves to analytical purposes, one may mention density, viscosity, conductance, dielectric constant, etc. No one property is superior; there is hardly ever a "best method," but the choice of the determining property and the means of measuring it are governed by the circumstances. The cases which will be mentioned are those which solved the problem satisfactorily even though alternative schemes might have been used. Photoelectric methods have been used for the obvious chore of counting objects, classifying, and grading according to size, color, or temperature (incandescence) (*F*, *I*, *K*, *N*, *Q*, *R*, *U*). Distinctly optical criteria of a system naturally lend themselves to photoelectric methods—for example, turbidity, color, gloss, refractive index, optical activity, and opacity (smoke).

The conventional methods of colorimetric analysis have been reduced to automatic practice, usually by the expedient of by-passing (bleeding) a portion of the system, sampling, then injecting an appropriate reagent, after which the mixture is photometered. The measurement in this case may be in absolute terms or relative to an arbitrary standard. Usually a conventional electrical recorder (recording potentiometer or Wheatstone bridge) provides a permanent record. For control it is fitted with limit relays which initiate appropriate corrective measures (addition of acid or alkali, change of temperature or pressure, etc.). Such installations are further complicated by the need for auxiliary equipment, as, for example, periodic self-calibration, antihunting mechanisms, or circuits to prevent overcompensation. Unless elaborate precautions of this sort are provided by intelligent engineering design, the instrument or controller is likely to act like an unruly monster. The fundamental idea behind most photoelectric controls is relatively simple, but reference to typical installations (*K*, p 230; *2*, *53*) shows the expenditure of great ingenuity and care in the realization of the scheme from an engineering point of view.

Applications

While it is obvious that any suitable colorimetric reaction may be treated by appropriate photoelectric means, it may be helpful to record some instances of actual problems which have been solved by the use of photoelectric cells. Further

possibilities are to be gleaned from standard treatises on colorimetry (*190*, *233*). Photoelectric instruments have been used in the analysis or measurement of water (*3*, *17*, *113*, *172*, *187*, *218*, *221*), gas (*21*, *22*, *74*, *120*, *191*), foods (*151*, *230*), steel (*9*, *194*), textiles (*4*, *20*, *179*, *185*, *189*), leather (*12*), titrations (*16*, *76*, *96*, *140*, *173*, *193*, *194*), combustion (*170*), colloids (*181*), serum (*155*), oils (*13*, *123*, *127*, *178*, *202*, *203*), beer (*35*, *110*, *199*), fertilizers (*135*), sugar (*83*, *177*, *196*), chlorophyll (*73*, *188*), pH (*122*, *124*, *125*, *143*, *150*), reaction kinetics (*18*, *79*, *98*, *138*, *176*), dust (*100*), indicators (*125*, *182*), dyes (*94*, *157*), clinical (*25*, *37*, *38*, *45*, *46*, *101*, *103*, *121*, *168*, *175*), sedimentation (*136*), turbidity (*26*, *64*, *76*, *95*, *97*, *99*, *102*, *126*, *150*, *198*), carbon dioxide (*22*), hydrogen sulfide (*21*), alkalies (*93*), alkaline earths (*93*), and bacteria (*7*).

Conclusions

The current literature indicates a widespread and increasing interest in photoelectric methods. Measurements have been reported which exceed in precision and reliability the values which can be obtained with the very best visual instruments (*85*, *107*, *125*, *128*, *129*, *130*, *133*, *158*, *159*, *238*). These results are invariably obtained with instruments which embody sound optical theory and practice and the best resources of electrical measurements. They are usually photoelectric spectrophotometers, and are necessarily elaborate and expensive. Simple compromise instruments have been described in great number and are justified by reasons of expediency, elimination of fatigue, or greater speed of operation. They rarely justify exaggerated claims of superiority over existing visual instruments.

Photoelectric cells are available in great variety and at low cost. Circuit adjuncts such as improved meters, vacuum tubes, thyratrons, and indicator tubes are increasingly available and in many cases have been designed specifically for use with photocells. Countless circuit possibilities have been published in various papers and monographs, but a very small fraction of these have been applied to chemical problems.

Applications have been directed for the most part to analysis, and therefore have served as an improved adjunct to the highly developed field of colorimetric analysis. In addition they have served a useful purpose in pH measurements, kinetics, and the study of the composition of colored solutes.

The increasing number of problems and the complexity and diversity of modern devices seem to imply that future research will require greater cooperation between the chemist and the radio engineer or that each shall become more fully acquainted with the problems and resources of the other field. Specifically, the engineer is unaware of the nature and needs of the chemist's problems. Similarly, the chemist is, in most cases, unfamiliar with the possibilities of electronic circuits and how they may be modified to suit his purpose. One is constantly surprised by the spirit of "rediscovery" which seems to pervade the chemical literature dealing with photoelectric photometry. For this reason, the writer has listed in the bibliography a separate group of monographs. Repeated reference is made in the body of this paper to these sources; indeed, the review can be considered as little more than a summary of the advice and good counsel which is to be found in these sources.

Acknowledgment

The author is greatly indebted to his colleagues, R. L. Garman and M. E. Droz; the latter for material aid in preparing the manuscript, and both for helpful discussion and criticism.

Literature Cited

Monographs

(A) Allen, H. S., "Photoelectricity," 2nd ed., New York, Longmans, Green & Co., 1925.
(B) Anderson, J. S., "Photoelectric Cells and Their Applications," Physical and Optical Society of London, 1930.
(C) Becker, A., "Lichtelektrische Wirkung. Handbuch der Experimentalphysik," Vol. XXIII, Leipzig, Akademische Verlagsgesellschaft, 1938.
(D) Campbell, N. R., and Ritchie, Dorothy, "Photoelectric Cells," London, Sir Isaac Pitman and Sons, 1929.
(E) Chaffee, E. L., "Theory of Thermionic Vacuum Tubes," New York, McGraw-Hill Book Co., 1933.
(F) Fink, D. G., "Engineering Electronics," New York, McGraw-Hill Book Co., 1938.
(G) Fleischer, R., and Teichmann, H., "Die lichtelektrische Zelle und ihre Herstellung," Dresden, Th. Steinkopff, 1932.
(H) Forsythe, W. E., "Measurement of Radiant Energy," New York, McGraw-Hill Book Co., 1937.
(I) Geffken, H., Richter, H., and Winckelmann, J., "Die lichtempfindliche Zelle als technisches Steuerorgan," Berlin, J. Schneider, 1933.
(J) Gudden, B., "Lichtelektrische Erscheinungen," Berlin, Julius Springer, 1928.
(K) Gulliksen, F., and Vedder, E., "Industrial Electronics," New York, John Wiley & Sons, 1935.
(L) Hardy, A. C., "Handbook of Colorimetry," Cambridge, Mass., Technology Press, 1936.
(M) Hardy, A. C., and Perrin, F. H., "Principles of Optics," New York, McGraw-Hill Book Co., 1932.
(N) Henny, Keith, "Electron Tubes in Industry," 2nd ed., New York, McGraw-Hill Book Co., 1937.
(O) Hughes, A. L., and DuBridge, L. A., "Photoelectric Phenomena," New York, McGraw-Hill Book Co., 1932.
(P) Koller, L., "Physics of Electron Tubes," New York, McGraw-Hill Book Co., 1934.
(Q) Lange, G., "Die Photoelemente und ihre Anwendung," 2 vols., Leipzig, J. A. Barth, 1936.
(R) McArthur, E. D., "Electronics and Electron Tubes," New York, John Wiley & Sons, 1936.
(S) Morecraft, J., "Electron Tubes," New York, John Wiley & Sons, 1933.
(T) Sewig, R., "Objektive Photometrie," Berlin, Julius Springer, 1935.
(U) Simon, H., and Suhrmann, R., "Lichtelektrische Zellen und ihre Anwendung," Berlin, Julius Springer, 1932.
(V) Walker, R. C., and Lance, F. M., "Photoelectric Cell Applications," London, Sir Isaac Pitman and Sons, 1933.
(W) Weigert, F., "Optische Methoden der Chemie," Leipzig, Akademische Verlagsgesellschaft, 1927.
(X) Zworykin, V., and Wilson, E., "Photocells and Their Applications," 2nd ed., New York, John Wiley & Sons, 1932.

Bibliography

(1) Aimot, Georges, German patent 602,294 (September 4, 1934); French patent 747,092. Photoelectric apparatus for determining permeability of paper, fabric, etc., to liquids.
(2) Alfriend, J. V., Jr., *Elec. Eng.*, 52, 601–4 (1933). Light-sensitive process control.
(3) Andrew, N. N., and Andrieva, E. V., *J. Gen. Chem.* (U. S. S. R.), 4, 594–7 (1934). Photoelectric cell in analysis of natural waters.
(4) Angel and Co., H. Reeve, *Silk J.*, 6, 43–4 (1930). Photoelectric colorimeter.
(5) Armstrong, E. L., and Kuder, M. L., *J. Lab. Clin. Med.*, 21, 181–7 (1935). Limitations of colorimetric analysis.
(6) Aten, A. H. W., Galema, N., and Goethals, C. A., *Chem. Weekblad*, 31, 258–64 (1934). Objective colorimeter.
(7) Avtonomova, E. S., and Stossel, F. A., *Biochem. Z.*, 274, 220–30 (1934). Nephelometric method for determination of number of microbes in bacterial suspensions with aid of photoelectric cell.
(8) Baden, M. W., U. S. patent 1,938,004 (1934). Photoelectric colorimeter.
(9) Bendig, M., and Hirschmüller, H., *Z. anal. Chem.*, 92, 1–7 (1933). Determination of manganese, iron, and titanium with photoelectric colorimeter of B. Lange.
(10) Berg, Wilhelm, German patent 296,050 (1911). Photoelectric colorimeter.
(11) Bernheim, G., and Revillon, G., *Ann. fals.*, 29, 5–10 (1936). Application of photoelectric measurements to Duboscq colorimeter.
(12) Boldracco, G., *Boll. ufficiale staz. sper. ind. pelli mat. concianti*, 13, 104–10 (1935). Measuring decolorization of sole leather.

(13) Bolton, E. R., and Williams, K. A., *Analyst*, 60, 447–54 (1935). Color measurements of oils and other liquids.
(14) Boutry, G. A., *Compt. rend.*, 202, 1580–2 (1936). Talbot's law in photoelectric photometry.
(15) Boutry, G. A., "Les phénomènes photoélectriques et leurs applications"; T. IV, "Différences de potentiel photoélectrique"; T. V. "Photométrie photoélectrique (mesure des courants)"; T. VI, "Photométrie photoélectrique (mesure des flux)," Paris, Hermann & Cie., *C. A.*, 30, 3726 (1936).
(16) Boyer, W. J., IND. ENG. CHEM., Anal. Ed., 10, 175 (1938).
(17) Brambel, C. E., and Cowles, R. P., *Science*, 85, 340–2 (1937). Determination of phosphorus in estuarine waters.
(18) Brauer, Gerhard, *Z. physik. Chem.*, B26, 71–80 (1934). Photoelectric photometer for measurements of reaction kinetics.
(19) Brice, B. A., *Rev. Sci. Instruments*, 8, 279 (1937).
(20) Buehring, F., *Melliand Textilber.*, 13, 137–8, 210–12, 264–5 (1932). Measurements of white shades.
(21) Burton, M. F., *Gas*, 12, No. 5, 41, 60, 62 (1936). Photocolorimeter for determination of hydrogen sulfide in natural gas.
(22) Bycichin and Laska, *Chem. Listy*, 30, 149–50 (1936). Photoelectric colorimeter for determining carbon dioxide in air.
(23) Campo, A. del, Burriel, F., and García Escolar, L., *Anales soc. espaň. fis. quím.*, 34, 829–34 (1936). New methods of photoelectric determination.
(24) Campo, A. del, Burriel, F., and García Escolar, L., *Bol. acad. cienc.* (Madrid), 2, No. 7, 10–13 (1936). Method of photoelectric analysis.
(25) Canals, E., and Hortala, A., *Bull. soc. chim. biol.*, 14, 1273–8 (1932). Photoelectric colorimeter.
(26) *Ibid.*, 15, 1535–51 (1933). Photoelectric cell in nephelometry.
(27) Carranza, Fortunato, *Bol. soc. quím. Peru*, 1, No. 5, 7–27 (1935). Colorimetric chemical analysis.
(28) Colla, Silvia, *Boll. soc. ital. biol. sper.*, 8, 315–17 (1933). Use of photoelectric cell with selective light as assay method.
(29) Constable, F. H., and Radiovisor Parent, Ltd., British patent 369,261 (Nov. 15, 1930). Photometric apparatus.
(30) Corin, C., and Degard, Charles, *Ind. chim. belg.*, [2] 5, 481–90 (1934). Photoelectric cells in analytical chemistry.
(31) Cuboni, E., *Bull. inst. sieroterap. milanese*, No. 6 (1927). Photoelectric colorimeter.
(32) Davuidov, A. L., and Avrunina, A. M., *Zavodskaya Lab.*, 5, 927–31 (1936). Selenium photocolorimeter and its use in chemical analysis.
(33) Davuidov, A. L., and Stefanovski, V. F., *Ibid.*, 3, 640–5 (1934). Photoelements in colorimetry.
(34) Desbleck, L. B., *Electrician*, 99, 8 (1927).
(35) Deux, Yves, *Petit J. brasseur*, 43, 1002–4 (1935); *Chem. Zentr.*, 1936, I, 2460. Photoelectric cells in brewery operation.
(36) Digand, C., *Ann. chim. anal. chim. appl.*, 13, 1–5, 33–54, 65–72 (1931).
(37) Diller, I. M., *J. Biol. Chem.*, 115, 315–22 (1936). Photoelectric colorimeter.
(38) *Ibid.*, 118, 161–2 (1937). Turbidity in uric acid determinations with special reference to photoelectric colorimeter.
(39) Dolinek, A., *Listy Cukrovar.*, 49, 203–5 (1930); *Z. Zuckerind. Czechoslovak. Rep.*, 55, 376–8 (1931).
(40) Donovan, D. K., *Paper Ind.*, 18, 663–4 (1936). Reducing color to black and white.
(41) DuBridge, L. A., *Phys. Rev.*, 37, 392 (1931).
(42) DuBridge, L. A., and Brown, H., *Rev. Sci. Instruments*, 4, 532 (1933).
(43) Eastman Kodak Co., Bulletin on Wratten Filters, 14th ed., Rochester, N. Y., 1936.
(44) Eddy, C. W., and DeEds, Floyd, IND. ENG. CHEM., Anal. Ed., 9, 12–14 (1937). Determination of phosphorus.
(45) Evelyn, K. A., *J. Biol. Chem.*, 115, 63–75 (1936). Stabilized photoelectric colorimeter with light filters.
(46) Evelyn, K. A., and Cipriani, A. J., *Ibid.*, 117, 365–9 (1937). Photoelectric microcolorimeter.
(47) Exton, W. G., U. S. patent 1,954,925 (April 17, 1934). Photoelectric apparatus for measuring turbidities, colors, etc.
(48) Exton, W. G., U. S. patent 1,971,443 (Aug. 28, 1934). Electrooptical system for measuring concentrations, color, or turbidity of fluids.
(49) Fairbrother, Fred, and Tuck, J. L., *Trans. Faraday Soc.*, 32, 624–33 (1936). Photoelectric measurement of absorption of sodium resonance radiation.
(50) Felix, K. S., Helmrich, and Wanderscheck, H., *Wochschr. Brau.*, 45, 312–16 (1928).
(51) Felix, K. S., and Wanderscheck, H., German patent 529,309 (1927).
(52) Fink, D. G., *Electronics*, 7, 181 (June, 1934).
(53) Fogle, M. E., *Trans. Electrochem. Soc.*, 69, (preprint, 1936). Application of photronic photocell to chemical processes.
(54) *Ibid.*, 69, 443, 1936.
(55) Fogle, M. E., *Trans. Illum. Eng. Soc.*, 31, 773 (1936).
(56) Fonteyne, R., *Natuurw. Tijdschr.*, 17, 10–25 (1935). New photoelectric spectrophotometer. Systematic errors of photoelectric spectrophotometer.
(57) Fonteyne, R., and Smet, P. de, *Mikrochemie*, 13, 289–304 (1933) (in French). Microdetermination of ethyl alcohol and glycerol with aid of colorimetry and photoelectric cell containing selenium.
(58) Forbes, G. S., and Harrison, G., *J. Am. Chem. Soc.*, 47, 2449 (1925).
(59) Forbes, G. S., and Harrison, G., *J. Optical Soc. Am.*, 11, 99 (1925).
(60) *Ibid.*, 12, 55 (1926).
(61) Fowle, F. F., "Standard Handbook for Electrical Engineers," p. 1652, New York, McGraw-Hill Book Co., 1933.
(62) Fritz, R., *Chimie & Industrie*, 33, 541–5 (1935). Photoelectric cell in paint and varnish industry.
(63) Fugita, Akiji, and Sakamoto, Toshimasa, *J. Biochem.* (Japan), 25, 193–205 (1937). Photoelectric determination of extinction coefficients of solutions.
(64) Furman, N. H., and Low, G. W., Jr., *J. Am. Chem. Soc.*, 57, 1588 (1935).
(65) Gage, H. P., *J. Optical Soc. Am.*, 27, 159 (1937).
(66) Garman, R. L., IND. ENG. CHEM., Anal. Ed., 7, 319 (1935). Electronic bridge balance indicator for conductance measurements.
(67) Garman, R. L., and Droz, M. E., *Ibid.*, 7, 341 (1935). Line-operated vacuum tube voltmeter.
(68) Garman, R. L., and Müller, R. H., manuscript in preparation.
(69) Geffcken, H. H., and Richter, H. R., (to Radio Patents Corp.), U. S. patent 1,985,085 (Dec. 18, 1934). Photoelectric comparison system for determining the intensity of light rays.
(70) Gheorghin, T. D., *Ann. Physik*, 20, 133–242 (1933). Gas photoelectric cells in photometric measurements.
(71) Gibson, K. S., *B. Standards Letter Circ.* LC. 473 (July 9, 1936).
(72) Gibson, K. S., *J. Research Natl. Bur. Standards*, 14, 545–52 (1935) (Research paper 785). Filter for obtaining light at wave length 560 mμ.
(73) Godnev, T. N., and Kalischewitz, S. W., *Planta*, 25, 194–6 (1936); *Compt. rend. acad. sci. U. R. S. S.*, N.S., 2, No. 2, 77–9 (1936) (in English). Determination of chlorophyll by Lange's colorimeter.
(74) Gollnow, G., *Gas- u. Wasserfach*, 75, 848–9 (1932).
(75) Gonzalez, Felix, *IX Congr. intern. quím. pura aplicada* (*Madrid*), 6, 70–6 (1934, pub. 1936). Photoelectric cell in analytical chemistry.
(76) Goodhue, L. D., IND. ENG. CHEM., Anal. Ed., 10, 52 (1938). Turbidimetric titration of small amounts of nicotine.
(77) Goudsmit, A., Jr., and Summerson, W. H., *J. Biol. Chem.*, 111, 421–33 (1935). New type of photoelectric colorimeter.
(78) Halban, H. von, and Eisner, H., *Helv. Chim. Acta*, 18, 724 (1935).
(79) Hamai, Senzo, *Bull. Chem. Soc. Japan*, 10, 43–50 (1935). Studying substitution and decomposition reactions by photoelectric cell. Absorption of light of wave lengths 3650 and 4360 A. by vapors of halogen derivatives of ethane.
(80) Hardy, A. C., and Cunningham, F. W., U. S. patents 1,806,197, 1,806,198, 1,806,199 (1931).
(81) Hatch, R. S., and Hanff, H. A., *Paper Trade J.*, 97, No. 26, 34–6 (1933). Razek-Mulder color analyzer and its use for measurement of pulp and paper color.
(82) Hodgman, C. D., and Lange, N. A., "Handbook of Chemistry and Physics," Cleveland, Ohio, Chemical Rubber Publishing Co.
(83) Höppner, K., *Deut. Zuckerind.*, 61, 789–91 (1936). Photoelectric cells in sugar industry.
(84) Hoffmann, E., *Kolloid Z.*, 79, 154–5 (1937). Dispersoid analysis with photo (voltaic) cell.
(85) Hogness, T. R., Zscheile, F. P., Jr., and Sidwell, A. E., Jr., *J. Phys. Chem.*, 41, 379–415 (1937). Spectrophotometry apparatus for ultraviolet and visible spectral regions, construction, calibration, and application to chemical problems.
(86) Howlett, L. E., *Can. J. Research*, 14A, 38–42 (1936). Photoelectric photometer.
(87) Hughes, H. K., and Hurka, R. J., *Rev. Sci. Instruments*, 6, 289 (1935).
(88) Hummel, F. C., and Willard, H. H., IND. ENG. CHEM., Anal. Ed., 10, 13 (1938).
(89) International Critical Tables, Vol. 5, p. 271, New York, McGraw-Hill Book Co., 1929.
(90) *Ibid.*, Vol. 7, p. 160.
(91) Ives, H. E., *Bell. System Tech. J.*, 5, 320 (1926). Photoelectric cells, central cathode type.
(92) Ives, H. E., and Kingsbury, E. F., *J. Optical Soc. Am.*, 21, 541 (1931). Photoelectric cells in colorimetry.
(93) Jansen, W. H., Heyes, J., and Richter, C. *Z. physik. Chem.*, A174, 291–300 (1935). Spectral analysis for determination

of alkalies and alkaline earths. Direct photoelectrometric estimation of alkalies.
(94) Jongbloed, J., *Nederland. Tijdschr. Geneeskunde*, 81, 943–4 (1937). Objective determination of reduction of methylene blue.
(95) Jonnard, R., and Stutinski, F., *Compt. rend. soc. biol.*, 112, 1023–6 (1933). Nephelometric determinations with cuprous oxide cell.
(96) Kasai, Yenya, and Takii, Shigeyoshi, *Repts. Imp. Ind. Research Inst. Osaka, Japan*, 16, No. 3, 1–12 (1935). Photoelectric titrations with selenium cells.
(97) Kidde, Walter, and Co., Inc., British patent 369,514 (August 25, 1931). Apparatus for detecting presence of suspended matter in fluids.
(98) King, C. V., and Jacobs, M. B., *J. Am. Chem. Soc.*, 53, 1704 (1931). Oxidation of iodide ion by S_2O_8. Kinetics of reaction in highly dilute silver solution.
(99) Klages, B., and Klumb, H., *Physik. Z.*, 37, 724–6 (1936). Application of tubular scattered-light cells to measurement of light-scattering in disperse systems.
(100) Knodel, Adolf (to Farbenind, I. G.), German patent 642,167 (Feb. 24, 1937). Recording dust content of gases.
(101) Kofman, T., *Bull. soc. chim. biol.*, 15, 623–36 (1933). Biological applications of photoelectric cells of semiconducting type.
(102) Kofman, T., *Compt. rend. soc. biol.*, 112, 478–80 (1933). Nephelometry by means of cuprous oxide photoelectric cell.
(103) *Ibid.*, 112, 481–2 (1933). Application of cuprous oxide photoelectric cell to colorimetric examination of blood.
(104) Kohn, H., *Neues Jahrb. Mineral., Geol., Beilage Bd.*, A72, 156–97 (1936). Applicability of photoelectric cells to photometric measurements on crystals.
(105) Kolthoff, I. M., and Sandell, E. B., "Textbook of Quantitative Inorganic Analysis," New York, Macmillan Co., 1936.
(106) Kondo, Kinsuke, and Murayama, Masashi, *J. Chem. Soc. Japan*, 57, 772–93 (1936). Colorimetric determination by application of photoelectric cell.
(107) Kortüm, G., *Angew. Chem.*, 50, 193–204 (1937). Physical methods in the chemical laboratory. Photoelectric spectrophotometry.
(108) Kroll, W., *Metall u. Erz*, 31, 105–7 (1934). Application of barrier-film photocells in spectrography.
(109) Krumholz, P., *Mikrochemie*, 20, 227–35 (1936). Objective microphotometry.
(110) Krumholz, P., Pickholz, S., and Hamburg, H., *Brau- u. Malzind.*, 36, 75–7, 86–91 (1936). Objective determination of color in worts and beers.
(111) Kuder, M. L., U. S. patent 2,048,554 (July 21, 1936). Colorimeter apparatus (with photoelectric cell) suitable for clinical laboratories.
(112) Küch, R., and Retschinsky, T., *Ann. Physik*, 20, 563 (1906).
(113) Kuznetsov, N., and Moiseev, A., *Zavodskaya Lab.*, 5, 1325–8 (1936).
(114) Lange, B., *Chem. Fabrik*, 5, 457–9 (1932).
(115) *Ibid.*, 1934, 45–7. New photoelectric colorimeter.
(116) Lange, B., German patent 546,676 (1930).
(117) Lange, B., *Naturwiss.*, 19, 103–7, 128–32 (1931).
(118) Lange, B., *Physik. Z.*, 31, 964–9 (1930).
(119) Lange, B., *Sprechsaal*, 65, 255–6, 275–7, 293–5 (1932).
(120) Leau, E. G., French patent 792,561 (Jan. 6, 1936). Photoelectric gas detector.
(121) Lesure, A., Thomas, A., and Levagne, J., *J. pharm. chim.*, 17, 5–21, 49–61 (1933). Photoelectric cell applications in biological chemistry.
(122) Lothian, G. F., *Trans. Faraday Soc.*, 33, 1239–43 (1937). Photoelectric method of measuring pH values with indicator solutions.
(123) McDill, R. D., U. S. patent 2,082,252 (June 1, 1937). Apparatus for inspecting or photoelectric testing materials such as engine oils by transmitted light.
(124) Martin, H. S., and Janney, T. A., U. S. patent 1,943,684 (Jan. 16, 1934). Controlling hydrogen-ion concentration of flowing solutions.
(125) Mason, R. B., and Kilpatrick, Martin, *J. Am. Chem. Soc.*, 59, 572–8 (1937). Relative acid strengths in normal butyl alcohol.
(126) Matsui, M., Noda, F., and Iwai, S., *J. Soc. Chem. Ind. Japan*, 36, suppl. bind., 691–2 (1933). Measurement of concentration and dispersity of suspensions by photoelectric cell.
(127) Maw, F. J., U. S. patent 2,015,949 (Oct. 1, 1935). Slide for use with lubricating oils or other liquids to be examined with light-sensitive apparatus.
(128) Mehlig, J. P., Ind. Eng. Chem., Anal. Ed., 10, 136 (1938).
(129) Mellon, M. G., *Ibid.*, 9, 51 (1937).
(130) Mellon, M. G., and Kasline, C. T., *Ibid.*, 7, 187 (1935).
(131) Metcalf, G. F., and Thompson, B. J., *Phys. Rev.*, 36, 1849 (1930).
(132) Meunier, Paul, *Bull. soc. chim. biol.*, 19, 113–18 (1937). Electrophotometer of opposed selenium cell type for colorimetric and opacimetric work.
(133) Michaelson and Liebhavsky, *Gen. Elec. Rev.*, 39, 445 (1936).
(134) Mikhal'chuk, B., *Novosti Tekhniki*, Nos. 40–41, 43 (1936). Photoelectric method for determination of phosphoric and silicic acids.
(135) Mikhal'chuk, B. V., and Brutskus, E. G., *Zavodskaya Lab.*, 6, 161–71 (1937). Photoelectric colorimeter and application to analysis of fertilizer.
(136) Milbauer, Jar., *Sbornik Masarykovy Akad. Práce* 9, No. 7, 1 (1935); *Chem. Obzor*, 11, abstract sect., 65 (1935). Sedimentometer.
(137) Millikan, G. A., *J. Physiol.*, 79, 152–7 (1933). Simple photoelectric colorimeter.
(138) Millikan, G. A., *Proc. Roy. Soc.* (London), A155, 277–92 (1936). Velocity of rapid reactions. Portable microapparatus applicable to extended range of reactions.
(139) Mohler, H., and Benz, H., *Mitt. Lebensm. Hyg.*, 25, 161–5 (1934). Photoelectric estimation of furfurol and methanol.
(140) Müller, Friedrich, *Z. Elektrochem.*, 40, 46–51 (1934).
(141) Müller, Friedrich, and Dürichen, Walter, *Chem. Fabrik*, 1935, 267–9. Photoelectric analysis with changing light.
(142) Müller, R. H., Ind. Eng. Chem., Anal. Ed., 7, 223–6 (1935). Photoelectric methods in macro- and microanalysis.
(143) Müller, R. H., *Mikrochemie*, 10, 285–96 (1931).
(144) *Ibid.*, 11, 353–68 (1932).
(145) Müller, R. H., U. S. patent 2,043,589 (June 9, 1936). Photoelectric colorimeter.
(146) Müller, R. H., and Kinney, G. F., *J. Optical Soc. Am.*, 25, 342–6 (1935). Photoelectric colorimeter with logarithmic response.
(147) Müller, R. H., and McKenna, M. H., *J. Am. Chem. Soc.*, 58, 1017–20 (1936). Starch-iodine system.
(148) Müller, R. H., and McKenna, M. H., unpublished results.
(149) Müller, R. H., and Partridge, H. M., Ind. Eng. Chem., Anal. Ed., 3, 167–71 (1931).
(150) Mueller, W. S., *Food Research*, 2, 51–4 (1937). Photoelectric Tyndallmeter.
(151) Napoli, Iginio, *Ann. chim. applicata*, 27, 258–62 (1937). Colorimetric determination of P_2O_5 in foods.
(152) Nutting, R. D., *Textile Research*, 5, 391–400 (1935). Interpretation of data obtained with spectrophotometers of polarizing type.
(153) O'Brien, B., *J. Optical Soc. Am.*, 22, 427 (1932).
(154) Osborn, R. A., *J. Assoc. Official Agr. Chem.*, 17, 135–41 (1934). Photoelectric cell arrangement for measuring small quantities of certain impurities in reagent chemicals.
(155) Ostroumova, E. E., and Goldenberg, V. A., *J. Physiol.* (U. S. S. R.), 21, 263–9 (1936). Kinetics of serum colloid by electrolytes at various ages.
(156) Partridge, H. M., Ind. Eng. Chem., Anal. Ed., 4, 315 (1932).
(157) Pineo, O. W., *Am. Dyestuff Reptr.*, 22, 470–4 (1933). Application of spectrophotometric color analysis to dyeing.
(158) Preston, J. S., and Cuckow, F. W., *Proc. Phys. Soc.* (London), 48, 869–80 (1936). Photoelectric spectrophotometer of high accuracy.
(159) *Ibid.*, 49, 189 (1937). Photoelectric spectrophotometer of high accuracy.
(160) Prinsen, F. B. A., French patent 762,015 (Apr. 3, 1934). Photometer functioning by means of photoelectric cell.
(161) Race, C. N., U. S. patent 1,739,373 (1929).
(162) Rappaport, Friedrich, Austrian patent 144,341 (Jan. 10, 1936). Photoelectric apparatus for colorimetric analysis.
(163) Razek, Joseph, *Paper Ind.*, 16, 171–3 (1934). Color analysis and specification.
(164) *Ibid.*, 16, 407–9 (1934). Color analysis and specification.
(165) Razek, Joseph, and Mulder, P. J., British patent 349,565 (1929).
(166) Reeve, L., *J. Phys. Chem.*, 29, 39, 713 (1925); 30, 1427 (1926).
(167) Reimann, S. P., *Proc. Soc. Exptl. Biol. Med.*, 23, 520–3 (1926).
(168) Renaudin, J., *Bull. soc. chim. biol.*, 18, 301–4 (1936). Opacimetric determinations in biology by means of photoelectric cell.
(169) Reynolds, W. E., and Hext, A. R., U. S. patent 1,961,913 (June 5, 1934). Colorimeter with photoelectric cell.
(170) Rose, R. A., Wilson, G. C., and Benedict, R. R., *S. A. E. Journal*, 39, 459–68T (1936). Photoelectric (engine) combustion analysis.
(171) Ruby, W. R., *Iowa State College J. Sci.*, 11, 100–2 (1936). Quantitative chemical analysis using photon counter.
(172) Rumpf, P., *Bull. soc. chim.*, 53, 84–95 (1933).
(173) Russell, W. W., and Latham, D. S., Ind. Eng. Chem., Anal. Ed., 6, 463–4 (1934).
(174) Sandera, K., *Commun. New Intern. Assoc. Testing Materials* (Zurich), Group D, 225–7 (1930).

(175) Sanford, A. H., Sheard, Charles, and Osterberg, A. E., *Am. J. Clin. Path.*, 3, 405–20 (1933). Photelometer in clinical laboratory.
(176) Sborgi, Umberto, *Atti congr. nazl. chim. pura applicata, 5th Congr., Rome*, 1935, Pt. I, 531–43 (1936). Investigations in chemical kinetics by means of photoelectric colorimeter.
(177) Schewe, Heinrich, and Blomberg, Gustav (to Siemans-Schuckert Werke), German patent 643,303 (Apr. 5, 1937). Photoelectric regulating device for sugar evaporators.
(178) Schoenberg, V. A., British patent 419,339 (Nov. 9, 1934); see U. S. patent 1,940,373. Method and photometric apparatus for testing liquids, such as oil, for contamination.
(179) Scott, W. M., *Textile World*, 79, 886–9 (1931).
(180) Seifert, Rudolf, *Süddeut. Apoth.-Ztg.*, 73, 597–8 (1933). Colorimetry with photoelectric cells.
(181) Selwyn, E. W. H., *J. Sci. Instruments*, 10, 116–18 (1933). Photoelectric instrument for comparing strengths of colored solutions.
(182) Sewig, Rudolf, *Naturwissenschaften*, 25, 321–4 (1937). Development of photoelectric cells.
(183) Sewig, Rudolf, and Müller, Friedrich, *Chem. Fabrik*, 1934, 25–7. Photoelectric measurement of adsorption and color change (of indicators).
(184) Sharp, C. H., and Kinsley, C., *Elec. World*, 87, 823 (1926).
(185) Sheldon, H. H. (to Sheldon Electric Corp.), U. S. patent 2,022,-327 (Nov. 26, 1936). Apparatus (with photoelectric cell) for comparison of colors such as those of textile materials.
(186) Sheldon, H. H., and Lorenz, C. F. (to Sheldon Electric Corp.), U. S. patent 1,971,317 (Aug. 21, 1934). Color comparison system (with light-sensitive cells).
(187) Shvedov, V. P., *J. Applied Chem.* (U. S. S. R.), 10, 940–5 (in German 945, 1937). Photocell for colorimetric determination of fluorides in drinking water.
(188) Singh, B. N., and Anantha, N. K., *Current Sci.*, 5, 416–18 (1937). New method and apparatus for quantitative determination of chlorophyll.
(189) Smith, R. B. (to Weston Electrical Instrument Corp.), U. S. patent 1,974,880 (Sept. 25, 1934). Apparatus (with light-sensitive cells) for comparing shades of cloth.
(190) Snell, F. D., and Snell, C. T., "Colorimetric Methods of Analysis," 2 vols., New York, D. Van Nostrand Co., 1936–38.
(191) Société française des regulateurs universels Arca, French patent 811,031 (Apr. 5, 1937). Photoelectric apparatus for testing gases.
(192) Soller, W., *Rev. Sci. Instruments*, 3, 416 (1932).
(193) Somiya, Takayuki, *IX Congr. intern. quím. pura aplicada* (Madrid), 6, 63–9 (1934, pub. 1936). Application of neon lamp and cuprous oxide photoelectric cell to volumetric analysis.
(194) Somiya, Takayuki, and Nakamura, Yoshio. *J. Soc. Chem. Ind. Japan*, 38, suppl. binding, 262–6 (1935). Application of copper–cuprous oxide cell and determination of vanadium in special high-speed steel.
(195) Sommer, H., and Jacoby, F. C., *Milliand Textilber.*, 13, 204–5 (1932). Measurement of quantities of light in examination of fastness to light.
(196) Spengler, O., and Landt, E., *Z. Ver. deut. Zuckerind.*, 81, 13–24 (1931).
(197) States, M. N., *Oil & Soap*, 12, No. 1, 2–4 (1935). Photelometer and color measurements.
(198) Stier, T. J. B., Arnold, W., and Stannard, J. N., *J. Gen. Physiol.*, 17, 383–92 (1934). Photoelectric densitometer for use with suspensions.
(199) Stockhausen, F., and Windisch, F., *Wochschr. Brau.*, 45, 231 (1928).
(200) Stone, Charles W. (to British Thompson-Houston Co., Ltd.), British patent 404,065 (Jan. 11, 1934). Color analyzer, employing photoelectric device.
(201) Stone, Clarence G., and Edelman, Abraham, U. S. patent 2,020,492 (Nov. 5, 1935). Photoelectric color comparator.
(202) Story, B. W. (to Socony-Vacuum Oil Co.), U. S. patent 2,043,-816 (June 9, 1936). Colorimeter (with photoelectric cell) for testing oils.
(203) Story, B. W., and Kalichevsky, V. A., IND. ENG. CHEM., Anal. Ed., 5, 214–17 (1933).
(204) Strafford, Norman, *Analyst*, 61, 170–7 (1936). Colorimetric analysis by photoelectric cell.
(205) Strelkow, S. A., *Sotsialist. Rekonstruktsiya i Nauka*, No. 4, 80–98 (1935). Photoelectric cells in chemical control and analysis.
(206) Styer, C. A. (to Westinghouse Elec. & Mfg. Co.), U. S. patent 1,977,359 (Oct. 16, 1934). Chemical analysis system employing photosensitive devices.
(207) Suhrmann, R., *Chem. Ztg.*, 61, 245–7 (1937). Photoelectric cells and their application in chemical industry.
(208) Suklin, V. A., and Petin, N. N., *Zavodskaya Lab.*, 5, 763–5 (1936). Photometric examination with photocell.
(209) Thiel, A., *Ber.*, 68B, 1015–23 (1935). New colorimetric methods and related measurements.
(210) Tönnies, H. F., U. S. patent 2,067,843 (Jan. 12, 1937). Photoelectric photometer.
(211) Toussaint, Rene, *Recherches inventions*, 16, 251–4 (1935). Matching colors and measuring fastness.
(212) Traver, A. E. (to Socony-Vacuum Corp.), U. S. patent 2,042,-281 (May 26, 1936). Comparative colorimeter.
(213) Troland, L. F., U. S. patent 1,971,737 (1934).
(214) Turner, L. A., and Siegelin, C. O., *Rev. Sci. Instruments*, 4, 429 (1933).
(215) Turrell, F. M., and Waldbauer, Louis, *Proc. Iowa Acad. Sci.*, 42, 63–6 (1935). Photoelectric colorimeter in measurement of concentration of colored substances in solution.
(216) *Ibid.*, 42, 67–70 (1935). Bibliography on photoelectric cells in plant investigations.
(217) Twyman, F., and Perry, J., U. S. patent 1,775,148 (1930).
(218) Vainshtein, G. M., *Zavodskaya Lab.*, 6, 206–9 (1937). Determination of transparency and turbidity of tap and industrial water at a distance with aid of copper oxide photoelectric cell.
(219) Van Voorhis, S. N., and Harnwell, G. P., *Rev. Sci. Instruments*, 5, 244 (1934).
(220) Waibel, Ferdinand, *Wiss. Veröffentl. Siemens-Werken*, 14, No. 2, 32–40 (1935). Quantitative flame spectral analysis.
(221) Watson, W., and Wier, E. McG., *Surveyor*, 92, 43–4 (1937). Relationship between turbidity measurement and B. O. D. and suspended solids determination.
(222) Weil, Arthur, *Science*, 79, 593 (1934). Photoelectric colorimeter.
(223) Wein, S., U. S. patent 1,779,574 (1931).
(224) Werkenthin, M., *Gaz. Cukrownicza*, 75, 235–45 (1934). Subjective colorimetry and photoelectric colorimeter of Lange.
(225) Whalen, F. C., and Radiovisor Parent, Ltd., British patent 350,703 (1930).
(226) Wilcox, L. V., IND. ENG. CHEM., Anal. Ed., 6, 167–9 (1934). Photronic colorimeter and application to determination of fluoride.
(227) Wildermuth, F., *Arch. ges. Physiol.*, 183, 91–108 (1920).
(228) Wilson, E. D., *Trans. Electrochem. Soc.*, 69, (preprint, 1936). Comparison of photoemissive and photovoltaic devices in measuring radiant energy.
(229) Withrow, R. B., Shrewsbury, C. L., and Kraybill, H. R., IND. ENG. CHEM., Anal. Ed., 8, 214–19 (1936). Precision photoelectric colorimeter.
(230) Woidich, Karl, *Oesterr. Chem.-Ztg.*, 39, No. 11, 88–9 (1936). Photoelectric colorimeter in food research.
(231) Yamamoto, Kenichi, and Abe, Mochiyuki, *Bull. Waseda Applied Chem. Soc.*, 21, 1–16 (1933). Studies in colorimetry with photoelectric tube.
(232) *Ibid.*, 25, 1–10 (1935). Studies in colorimetry with the photoelectric tube (abstracts in English).
(233) Yoe, J. H., "Photometric Chemical Analysis," Vol. I, "Colorimetry," 1928, Vol. II, "Nephelometry," 1929, New York, John Wiley & Sons.
(234) Yoe, J. H., and Crumpler, T. B., IND. ENG. CHEM., Anal. Ed., 7, 281–4 (1935). Photoelectric colorimeter.
(235) Zelazny, A., *Gaz. Cukrownicza*, 76, 337–42 (1935). Objective photoelectric colorimeter in factory laboratory.
(236) Zinzadze, Ch., IND. ENG. CHEM., Anal. Ed., 7, 280–1 (1935). Photoelectric photometers for use in colorimetry.
(237) Zscheile, F. P., Jr., *Cold Spring Harbor Symposia Quant. Biol.*, 3, 108–15 (1935). Quantitative photochemical study of plant cell's photosynthetic system.
(238) Zscheile, F. P., Jr., Hogness, F. R., and Young, T. F., *J. Phys. Chem.*, 38, 1–11 (1934). Precision and accuracy of photoelectric method for comparison of low light intensities involved in measurement of absorption and fluorescence spectra.
(239) Zworykin, V., *Electronics*, 7, 242 (1934); 8, 10 (1935).

RECEIVED September 2, 1938.

The Action of Ethanolamine on Woody Tissue

L. E. WISE, F. C. PETERSON, AND W. M. HARLOW
New York State College of Forestry, Syracuse, N. Y.

IN 1937 Van Beckum and Ritter (*8*) published a revised technique for the determination of holocellulose, which represents very nearly the total carbohydrate fraction of the cell wall, as well as part of the methoxyl and the larger share of the acetyl groups present in the original wood. In their modification, these investigators used alternate treatments with chlorine and 95 per cent ethyl alcohol containing 3 per cent of monoethanolamine. In August, 1935, the first experiments with pure anhydrous ethanolamine and dry wood were carried out at Syracuse.

In the authors' first experiments oven-dried wood samples [large-tooth aspen (nomenclature of species according to *7*), which had been subjected to complete analysis by Richard D. Freeman] were extracted with monoethanolamine, just below the boiling point of the solvent (about 168° C.) for 5.25 hours. One hundred cubic centimeters of the base were used for about 3 grams of wood. At the end of the extraction the material was filtered by suction and washed with water until the filtrates were colorless. The brown residue was dried to constant weight. A lignin determination (made by the cold sulfuric acid method of the U. S. Forest Products Laboratory, *6*) showed that 2.62 per cent of lignin remained in the pulp. Based on the original dry wood, this corresponded to 1.73 per cent of lignin.

A summative analysis thus showed the following:

Total loss of wood on extraction with ethanolamine	33.80
Residual lignin	1.73
Cross and Bevan cellulose (determined by R. D. Freeman)	64.42
Total	99.95

A very similar result was obtained by the ethanolamine extraction of spruce wood.

In another experiment (with a view towards complete delignification) 1 gram of oven-dried beech heartwood sawdust was extracted for 5 hours with 50 cc. of ethanolamine in an oil bath kept at approximately 170° C., so that the solvent in contact with the wood was just below the boiling point. Heating could be carried out satisfactorily in an Erlenmeyer flask, fitted with a funnel, covered with a watch glass. Cork or rubber stoppers were avoided.

The mixture was diluted with 50 cc. of water and the residue collected on a fritted-glass crucible, washed with water, and then bleached for 20 minutes with water saturated with chlorine, in a covered beaker but without removing the cellulose residue from the crucible at any time. The contents of the crucible were sucked dry, and the crucible was then filled with a solution of sulfurous acid. After standing 3 minutes this was removed by suction, and the residue washed with water. Crucible and residue were then placed in hot aqueous 3 per cent sodium sulfite solution for 0.5 hour, during which time a faint pink color developed. Although the residue after washing was white, chlorine water, water, sulfurous acid solution, and water successively were again passed through the crucible to assure a final bleach. The residue was thoroughly washed with water containing a trace of ammonia, and the crucible and residue were dried to constant weight.

The following results were obtained:

Ethanolamine cellulose	60.4, 60.5
Cross and Bevan cellulose on the same sample, determined by R. D. Freeman (av. of 3 determinations)	60.7

Although the analytical procedure by the ethanolamine method given for beechwood should be checked with a large number of woods, it seems probable that it will yield a residue comparable to Cross and Bevan cellulose. If so, it has much to recommend it over the procedure for isolating the latter. No preliminary extractions are required, and the manipulations are much simpler.

More recently Harlow and Wise (*2*), determining cellulose in the woody portions of rhizomes of brake fern, obtained 29.4 per cent of cellulose (by the Cross and Bevan method), and 30.0 per cent of cellulose (by extraction with pure ethanolamine, followed by mild successive treatments with hydrochloric acid, chlorine water, water, sulfurous acid, and water).

Evidently this anhydrous ethanolamine delignification gives a residue corresponding very closely to Cross and Bevan cellulose, and removes from the wood not only most of the lignin, but also a large amount of the "cellulosan" fraction and extraneous materials.

In 1925 Ritter (*5*) chlorinated thin sections of wood and observed the treated sections with a microscope. Delignification resulted in a separation of the cells, presumably by the dissolution of the middle lamella. Similar experiments were subsequently made by one of the authors (*1*) and it was further noted that the lignin in the secondary walls could be removed by mild chlorination before appreciably attacking that in the middle lamella, as shown by the effect of 72 per cent sulfuric acid on such treated material. The substance (presumably a precursor of coniferyl aldehyde, *3*) responsible for the phloroglucinol color test for "lignin" was also removed upon mild chlorination of thin wood sections.

Visual Effect of Monoethanolamine

To determine the visual effect, shown by the microscope, of monoethanolamine on thin (10μ) transverse sections of woody tissue (cut from blocks of dry sapwood, previously aspirated under cold water, and stored in 15 per cent ethyl alcohol), sections of red pine, sitka spruce, red alder, and catalpa were allowed to stand in the cold reagent (15° C.) for a number of weeks and examined periodically for possible evidences of delignification.

After 3 days portions of the sections were removed, washed in water, and treated with phloroglucinol reagent and 72 per cent sulfuric acid, respectively. In the first instance the typical scarlet color obtained on untreated material was not seen but rather an orange-red appeared. Treatment with the acid did not produce any visible disintegration of walls resistant in untreated sections.

After 2 weeks in cold ethanolamine the characteristic red color with phloroglucinol failed to develop, and all sections were yellowish. At this point the secondary walls of the two conifers, and the vessel walls in red alder, showed signs of partial disintegration when immersed in acid. At the end of 3.5 months' treatment with ethanolamine, the secondary walls disintegrated almost completely when subjected to 72 per cent sulfuric acid. In all cases a middle lamella network (Kerr and Bailey's "compound middle lamella," *4*) remained, indicating that the cold reagent, although able to remove the secondary cell-wall lignin, did not appreciably attack that of the central layers. Wood sections of cottonwood, white fir, tupelo, chestnut, red spruce, eastern red cedar, and lodgepole pine were treated for 10 days at 28° C. and results similar to those noted above (at 15° C.) were obtained.

Experiments with boiling ethanolamine on sections of red pine, sitka and red spruces, southern white cedar, Deodar cedar (*Cedrus deodar*), bigtree, eastern white pine, western hemlock, and Douglas fir, gave results comparable to those at lower temperatures, except that delignification was accomplished in a fraction of the time necessary in the cold, and further, the true middle lamella or intercellular substance was attacked and almost, if not entirely, removed. Usually

from 2 to 6 hours were necessary to delignify sections to the point where the cells barely adhered to each other, and were completely soluble in 72 per cent sulfuric acid.

In all cases the visual effect of boiling monoethanolamine on wood sections seemed the same as that obtained by subjecting them to chlorination, or bromination followed by hot dilute sodium sulfite, or 10 per cent ammonium hydroxide. These results appear to reinforce the analytical data which indicate that the amounts of "ethanolamine cellulose" and Cross and Bevan cellulose isolated from a given sample are approximately the same.

Literature Cited

(1) Harlow, W. M., N. Y. State Coll. Forestry, *Tech. Pub.* 24 (1933).
(2) Harlow, W. M., and Wise, L. E., *Am. J. Botany*, 25, 217–19 (1938).
(3) Hoffmeister, C., *Ber.*, 60, 2062 (1927).
(4) Kerr, T., and Bailey, I. W., *J. Arnold Arboretum*, 15, 327–49 (1934).
(5) Ritter, G. J., IND. ENG. CHEM., 17, 1194 (1925).
(6) Sherrard, E. C., and Harris, E. E., *Ibid.*, 24, 103 (1932).
(7) Sudworth, G. B., U. S. Dept. Agr., *Misc. Circ.* 92 (1927).
(8) Van Beckum, W. G., and Ritter, G. J., *Paper Trade J.*, 104, No. 19, 49 (1937).

RECEIVED September 10, 1938.

Determining Organic Carbon in Soils

A Modification of the Chromic Acid Reduction Method

E. R. PURVIS AND GEO. E. HIGSON, JR.
Virginia Truck Experiment Station, Norfolk, Va.

THE current popularity of rapid chemical tests as a means for estimating the crop-producing power of a soil makes desirable a rapid method for determining the organic carbon content of the soil. The chromic acid reduction method as proposed by Schollenberger (*3*, *4*), with its various modifications, is being widely used for this purpose. Constant and reproducible results may be obtained with this method, as has been shown by Degtjareff (*2*) and by Allison (*1*). Although Allison found that the method recovered but 86.9 per cent of the carbon present when compared to the standard furnace combustion method, this percentage recovery was so near constant for the sixty-six soils studied that by use of a factor (carbon found by chromic acid reduction multiplied by 1.15) he obtained almost identical results with the two methods.

Although considerably faster than furnace combustion, the Schollenberger method still consumes considerable time when a number of determinations are made. A modification which would eliminate the necessity of heating each determination separately, without impairing accuracy, would greatly reduce the time factor and would prove of considerable value in those laboratories where a large number of determinations of soil organic matter are made in routine analysis. Various modifications have been suggested, but in these changes the accuracy of the method is usually sacrificed. This paper presents data obtained in an attempt to overcome this difficulty, and describes a procedure that has given results in close agreement with those obtained by the original Schollenberger method.

Briefly stated, the chromic acid reduction method consists of oxidizing the organic carbon in a small sample of soil (0.2 to 0.5 gram) with a measured quantity of standardized chromic acid in sulfuric acid, and determining the extent of reduction of the chromic acid by titration with 0.2 *N* ferrous ammonium sulfate, using diphenylamine as the indicator.

Walkley and Black (*5*) proposed that the oxidation of the organic matter be induced by the heat of reaction between sulfuric acid and water, but claimed a recovery of only 60 to 86 per cent of the carbon present. Allison (*1*) found the maximum temperature obtained in this reaction to approximate 124° C. and stated that this is insufficient to recover a definite fraction of the organic carbon present in different soils.

Degtjareff (*2*) proposed two modifications. In one he brought about the oxidation of the organic carbon by the addition of a mixture of chromic acid and hydrogen peroxide to the soil sample. Walkley and Black (*5*) showed that this method gives entirely fictitious results, since the hydrogen peroxide reacts differently with chromic acid in the presence of soil than in the corresponding blank. Degtjareff's other proposal consisted in oxidizing the organic matter by heating the acid-soil mixture for 10 minutes at 165° C. in a sulfuric acid bath. He stated that the chromic acid oxidizing solution, prepared by heating for one-half hour at 165° C., shows no change in titer when run according to the above procedure. This would seem to conflict with Schollenberger's inference of the importance of temperature-time relationship upon the stability of the chromic acid oxidizing solution. Schollenberger specified that the acid-soil mixture be heated to 175° C. in approximately 90 seconds over an open flame. Tests show that even this brief heating reduces the titer of the 10-ml. aliquot of a 0.408 *N* chromic acid solution to 0.396 *N*, the loss being due to evaporation and reduction of the chromic acid in direct contact with the glass container which may reach a temperature of 800° C. when heated by an open flame.

To test Degtjareff's proposal, 10-ml. portions of chromic acid solution were placed in 25 by 150 mm. test tubes and heated for 10 minutes in a sulfuric acid bath at various temperatures. The results obtained are presented in Table I.

TABLE I. TEST OF DEGTJAREFF'S METHOD

Temperature of H_2SO_4 Bath	Normality of Chromic Acid	Loss in Normality
° *C.*		
100	0.408	0.000
120	0.408	0.000
140	0.400	0.008
160	0.382	0.026
180	0.336	0.072

Although a number of samples could be oxidized at once by this method, the accuracy of the procedure is greatly impaired. The partially reduced chromic acid solution in the tube containing soil would naturally lose less in titer than would the stronger solution in the blank determination. In a determination where the normality of the blank chromic acid solution was reduced 0.026, a soil was found to contain 2.10 per cent of organic carbon. The same soil showed only 1.74 per cent of organic carbon when higher heating reduced the normality of the blank by 0.072.

It would seem that the accuracy of the method depends upon bringing about a rapid oxidation of the organic matter by heating to a temperature sufficiently high to ensure complete oxidation in as short a time as possible in order to prevent loss of titer in the 10-ml. aliquot of the chromic acid solution due to evaporation and reduction. As an electric oven seemed to offer a means of accomplishing this purpose, the oven shown in Figures 1 and 2 was constructed.

A metal trough, 12.5 × 11.25 × 30 cm. (5 × 4.5 × 12 inches), was made of Cop-r-loy. The ends, sides, and bottom of this trough were lined with two thicknesses of 0.8-cm. (0.3-inch) asbestos board which was held in place by refractory cement. Next 16 meters (52 feet) of No. 24 Chromel C wire were coiled and fastened to one side of a false bottom of asbestos board cut to fit snugly in the bottom of the box. The wire was then tapped as shown in Figure 2, the completed heating unit drawing approximately 1,440 watts when operated on a 120-volt current.

For the top of the oven, two pieces of asbestos board were cemented together, and ten 2.66-cm. (1.06-inch) holes were drilled through the top in two tiers, providing a close fit for test tubes 25 mm. in diameter. To prevent the test tubes from resting directly on the heating unit, a strip of 0.6-cm. (0.25-inch) mesh screen wire was placed approximately 3.75 cm. (1.5 inches) above the heating unit in the oven. This permitted only 3.1 cm. (1.25 inches) of the test tube to be exposed to the direct heat of the oven, thereby reducing the heated surface of the glass and the loss by evaporation.

TABLE II. TEST OF OVEN HEATING

Soil Type	Organic Carbon: Heated to 175° C. in open flame in 90 seconds	Organic Carbon: Heated to 175° C. in oven in 3 minutes
	%	%
Sassafras sandy loam	0.65	0.64
Norfolk fine sandy loam	0.80	0.80
Elkton sandy loam	2.33	2.36
Keyport sandy loam	2.58	2.61
Dismal swamp peat	5.22	5.28

The completed oven is capable of an operating temperature of approximately 400° C., and this temperature is sufficient to raise that of 10 ml. of chromic acid solution inserted in a 25 by 150 mm. test tube to 175° C. in approximately 3 minutes. Furthermore, the normality of the chromic acid solution is reduced by only 0.008, just two-thirds the reduction brought about by heating to 175° C. in 90 seconds over an open flame. This lower loss in titer is explained by the lower maximum heat of the oven (400° C.) when compared to that of an open flame (approximately 800° C.), and by the fact that only the lower third of the test tube is heated, the balance of the tube acting as a condenser.

To test oven heating with open-flame heating, five soils varying in organic matter content were chosen. The results, presented in Table II, show that oven heating is quite as satisfactory as heating over an open flame. Ten samples may be oxidized in 3 minutes, the tubes removed from the oven, placed in cold water to be titrated later, and ten fresh tubes inserted in the oven. One hundred samples may be oxidized within an hour with a greater uniformity of heating than is possible where an open flame is used.

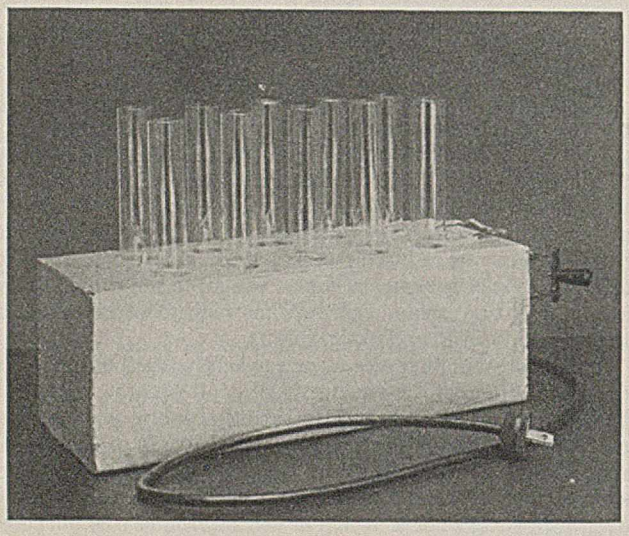


FIGURE 1. OVEN

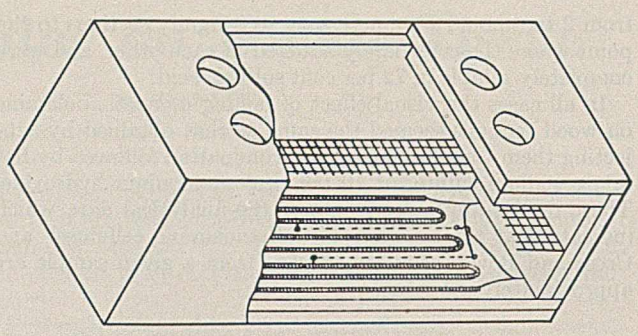


FIGURE 2. DIAGRAM OF OVEN

In the course of the foregoing investigation another minor modification, dealing with the preparation of the chromic acid oxidizing solution, was made in Schollenberger's procedure. It is recommended that this solution be prepared as follows:

Place 10 grams of powdered potassium dichromate, previously oven-dried at 100° C. for one hour, and 500 ml. of a 1 to 1 mixture of phosphoric and sulfuric acids in a 1-liter flask. Then heat the flask in a boiling water bath for 1 hour, occasionally stirring the mixture. Solution of the salt will be complete and the titer of the solution will remain constant, closely approximating 0.4 *N* in oxidizing power. The advantage of this modification is twofold. It eliminates the necessity of later adding phosphoric acid to activate the diphenylamine indicator during the titration with ferrous ammonium sulfate, and by changing the ratio of phosphoric to sulfuric acid from 1 to 2, to 1 to 1, a much sharper end point for the titration is obtained. The substitution of the phosphoric acid for half the sulfuric acid in the oxidizing solution in no way affects the strength of this solution.

Summary

An investigation of the temperature-time relationship in the determination of the organic carbon of the soil by the chromic acid reduction method is reported. A laboratory-constructed electric oven which provides a uniform method of oxidizing ten samples in 3 minutes is described, along with a modification in the preparation of the chromic acid solution which saves time and increases the sharpness of the end point during the titration with ferrous ammonium sulfate.

Literature Cited

(1) Allison, L. E., *Soil Sci.*, 40, 311–20 (1935).
(2) Degtjareff, W. Th., *Ibid.*, 29, 239–45 (1930).
(3) Schollenberger, C. J., *Ibid.*, 24, 65–8 (1927).
(4) *Ibid.*, 31, 483–6 (1931).
(5) Walkley, A., and Black, I. A., *Ibid.*, 37, 29–38 (1934).

RECEIVED September 19, 1938.

Prevention of Sticking of Buret Stopcocks

EDWIN E. MACZKOWSKE
National Bureau of Standards, Washington, D. C.

AFTER considerable trouble with burets used for sodium hydroxide solution, sodium thiosulfate solution, and other reagents, it was found that the sticking of buret stopcocks, when not in use, may be prevented by simply keeping the lower part of the buret containing the stopcock immersed in a beaker of distilled water.

RECEIVED December 2, 1938.

Determination of Fluorine

With Special Reference to Analysis of Natural Phosphates and Phosphatic Fertilizers

D. S. REYNOLDS AND W. L. HILL
Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

THE determination of fluorine in most materials requires its separation from other constituents of the sample. For this separation volatilization (or distillation) methods, being relatively rapid, have been favored whenever the fluorine-bearing constituents were readily soluble in acid, whereas fusion with alkali compounds with subsequent separation of the fluorine by rather cumbersome precipitation methods has been the rule with acid-insoluble materials. The chief carrier of fluorine in natural phosphates is apatite (*12*), and calcium fluoride has been identified in a few instances as a constituent of phosphate rock. Fortunately, both compounds can be treated successfully by distillation methods. On the other hand, fusion with alkali fluxes is not very effective in decomposing apatite (*22*).

The volatilization method (*25, 27*) used prior to about 5 years ago was not entirely satisfactory. One of the principal difficulties arose from the interfering effect of gelatinous silica, which renders the method inapplicable to materials that contain acid-decomposable silicates (*23*). Furthermore, the method of Reynolds and Jacob (*22*), involving fusion and acid extraction of the sample with subsequent precipitation of the fluorine as lead chlorofluoride, was very tedious and gave low results on some types of phosphate rock, such as Tennessee blue rock and Florida waste-pond phosphates.

The publication of a volumetric method by Willard and Winter (*28*) in 1933 marks a great forward step in the analysis of fluorine-containing materials. In simplicity of requisite apparatus, ease of manipulation, speed, and quality of results, this is far superior to any other known method for the analysis of a wide variety of materials.

In the original procedure fluorine is (1) separated from the sample (fused with alkali carbonate if the fluorine compounds are not decomposed by acid) by distillation with sulfuric acid or perchloric acid and (2) determined in the neutralized distillate, after the addition of an equal volume of ethyl alcohol, by titration with standard thorium nitrate with the use of zirconium-alizarin indicator. Armstrong (*2*) omitted the zirconium salt from the indicator used for titrating very small amounts of fluorine. Because of the greater sensitivity of the simplified indicator to changes in the pH of the solution during titration, it was not satisfactory for the titration of several milligrams of fluorine in a slightly buffered solution (*20*), such as was used at that time. Later, the advent of the use of a buffer solution (*16*) to control the pH during titration made the addition of a zirconium salt to the indicator unnecessary for the titration of the larger quantities of fluorine. The almost constant attention required to maintain the temperature of distillation within the permissible range by the frequent additions of small quantities of water to the distilling flask was overcome by means of a form of steam distillation (*24*).

With the foregoing improvements the Willard and Winter method has been used in this laboratory on a wide variety of natural phosphates and phosphatic products. A number of observed interfering factors have been investigated from time to time—for example, the effect of neutral salts on the titration, and the uncertainty of the results obtained on pyritiferous samples. The results of these studies are presented in this paper.

Several factors that cause interference in the determination of fluorine were studied by distilling the sample with perchloric, phosphoric, or sulfuric acid and titrating the distilled fluorine with thorium solution.

The titration is markedly affected by orthophosphate, sulfate, and hypochlorite ions and to a much less extent by alkali, borate, and sulfide ions. In the concentration range studied arsenite, chlorate, and silicate ions have no observable effect. Interference is greatly reduced and a sharper end point is obtained when the titration medium is an aqueous instead of an alcoholic solution.

Difficulties arise from substances, such as (1) aluminum compounds and gelatinous silica, that retard the distillation of fluorine, and (2) the distilling acid, phosphate, pyritic sulfur, organic materials, and halogens other than fluorine, that are incompletely separated from the fluorine and cause trouble in the subsequent titration. When perchloric acid is used as the distilling acid, the distillates of most types of phosphate rocks studied carry negligible quantities of perchlorate and phosphate. The separation of fluorine from pyritic sulfur and organic matter is improved by distilling the sample in the presence of an excess of permanganate.

Preparation of Pure Sodium Fluoride

Hoffman and Lundell (*14*) prepared a sodium fluoride of high purity from sodium bicarbonate and redistilled hydrofluoric acid by a modification of the method used by McAdam and Smith (*19*) in their atomic weight work. The authors prepared a very good grade of sodium fluoride from reagents meeting A. C. S. specifications as follows:

Evaporate 100 grams of 48 per cent hydrofluoric acid in a platinum dish to about two-thirds of its volume. Heat 20 grams of sodium bicarbonate and 75 ml. of distilled water in a platinum dish until the salt dissolves. Filter with the aid of a hard-rubber funnel, and to the clear solution add slowly with constant stirring (platinum rod) the entire amount of prepared acid. Heat the acid solution carefully until the carbon dioxide is expelled and the solution becomes clear, then evaporate it to dryness, and gradually increase the temperature to 350° to 400° C. If a

flame is used, provision should be made to protect the salt from contact with combustion gases. Continue the gentle ignition under the hood until the escape of hydrofluoric acid ceases, and finally ignite the product to constant weight in a muffle furnace at 650° C. Theoretical yield, 10 grams.

As shown volumetrically by comparing its thorium nitrate titer with that of a sodium fluoride of known purity (prepared and carefully analyzed several years ago by C. M. Smith of the Division of Insecticide Investigations, Bureau of Entomology and Plant Quarantine), and also gravimetrically by conversion to sodium sulfate, the product prepared by the authors by the foregoing procedure was 99.7 per cent sodium fluoride.

Titration of Alkali Fluoride with Thorium Nitrate Solution

Besides the titration medium and the presence of interfering substances, the factors that affect the titration of alkali fluoride with thorium nitrate include pH of the solution, concentration of the indicator, fluoride concentration, and temperature. In the work reported here, the pH of the solution was controlled with the aid of a buffer solution (prepared by neutralizing to phenolphthalein 200 ml. of 1 *M* monochloroacetic acid with alkali hydroxide, adding to the neutralized solution 200 ml. of the 1 *M* chloroacetic acid, and diluting to 1 liter), which with a few indicated exceptions was used at the rate of 0.5 ml. per 10 ml. of initial volume (V_i) of the solution for titration. One drop of indicator solution (0.1 per cent solution of sodium alizarin sulfonate) was used for each 10 ml. of initial aqueous solution. With the amounts of fluorine involved in this work the observed effect of indicator concentration is about the same as that noted by Dahle *et al.* (*5*) in the titration of smaller quantities of fluorine. For example, in the titration of 3.8 mg. of fluorine in 50 ml. of aqueous solution the authors found that a 50 per cent decrease or increase in indicator concentration changed the titer +0.04 or −0.04 ml., respectively, of 0.04 *N* thorium nitrate. All titrations were made at room temperature (20° to 30° C.). An increase in temperature results in slightly lower titers.

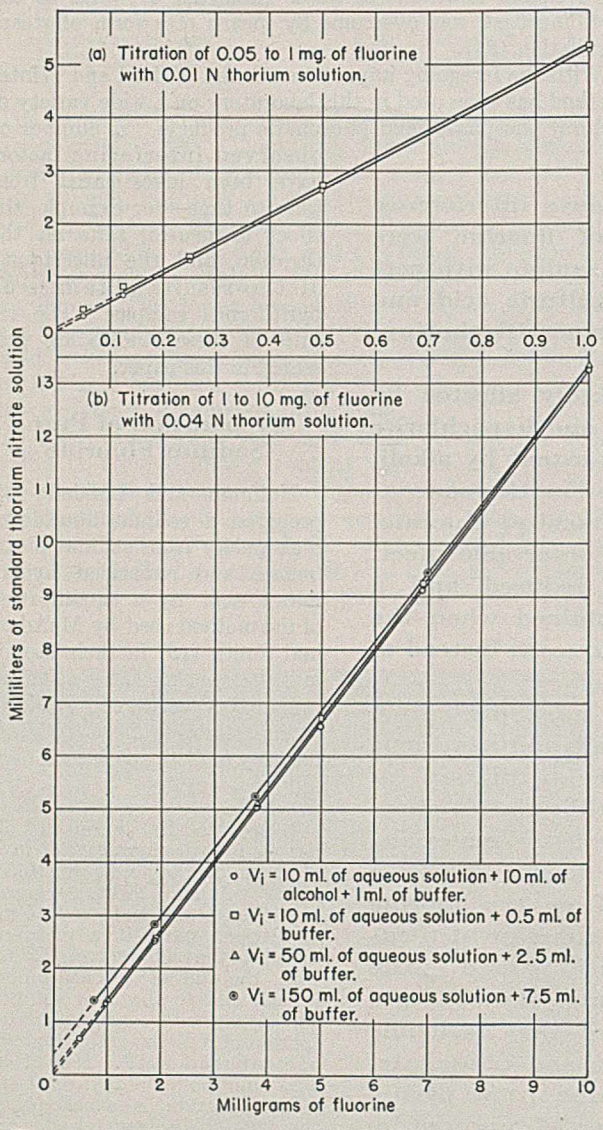


FIGURE 1. STANDARDIZATION OF THORIUM NITRATE SOLUTION AGAINST SODIUM FLUORIDE

By titration of 0.05 to 10 mg. of fluorine in aqueous and alcoholic solutions

THE TITRATION MEDIUM. Willard and Winter titrated in 50 per cent alcohol. Although Armstrong (*1*) showed that the alcohol can be omitted in the titration of up to 0.01 mg. of fluorine in buffered solution, only recently Rowley and Churchill (*26*) have proposed that the titration of larger quantities be conducted in aqueous solution. The omission of alcohol would be a desirable simplification.

In Figure 1 are shown several curves plotted from results obtained by titrating different quantities of sodium fluoride with thorium nitrate solution with and without the use of alcohol. In each case the curves are sensibly straight lines over the useful part of the range. Furthermore, the linear relationship holds for quantities of fluorine up to 50 mg. at least (results not shown). The blank titration is somewhat larger in aqueous than in alcoholic solutions, and for a given normality of thorium nitrate it increases with V_i (Figure 1, *b*). With moderately small quantities of fluorine the results for aqueous solutions depart from a straight line in the vicinity of 0.1 mg. of fluorine, whereas the results for alcoholic solutions do not (Figure 1, *a*). Aside from this behavior, which occurs near the lower limit of the range for 0.01 *N* thorium nitrate, aqueous solution is just as satisfactory as an alcoholic medium for the titration of pure solutions of sodium fluoride. The authors' experience, in general, confirms the observation of Rowley and Churchill (*26*) that a more distinct end point is obtained in aqueous solution; however, the sharpness of the end point is affected considerably by the initial volume, even though the concentration of the indicator be kept constant.

The observation of Lockwood (*18*) that a sharper end point is obtained in glycerol-water solution than in ethanol-water solution could not be confirmed by the authors.

INTERFERING IONS. Willard and Winter (*28*) state that "Any ion that forms a precipitate or a nondissociated salt with fluorine or thorium interferes with the titration—e. g., Ca^{++}, Ba^{++}, Fe^{+++}, Al^{+++}, PO_4^{---}, etc." Hoskins and Ferris (*16*) give quantitative data on the permissible concentrations of a number of ions likely to be met in the distillates of natural materials. Their experiments, which were confined to negative ions (halogen, NO_3^-, ClO_4^-, SO_3^{--}, AsO_3^{---}, SO_4^{--}, AsO_4^{---}, and PO_4^{---}) in alcoholic solution, show that an appreciable effect appears when the halogen, nitrate, or perchlorate concentration reaches about 0.1 *M*, whereas the permissible concentration of the other ions is of the order of 10^{-3} *M*, or less. Quantitative data on the effect of barium chloride and carbon dioxide have appeared recently (*10*). As far as the authors are aware no one has published data on the effect of alkali ions, or the interference of ions, with the exception of Cl^- and ClO_4^- (*1*, *9*), when the titration is made in aqueous solution.

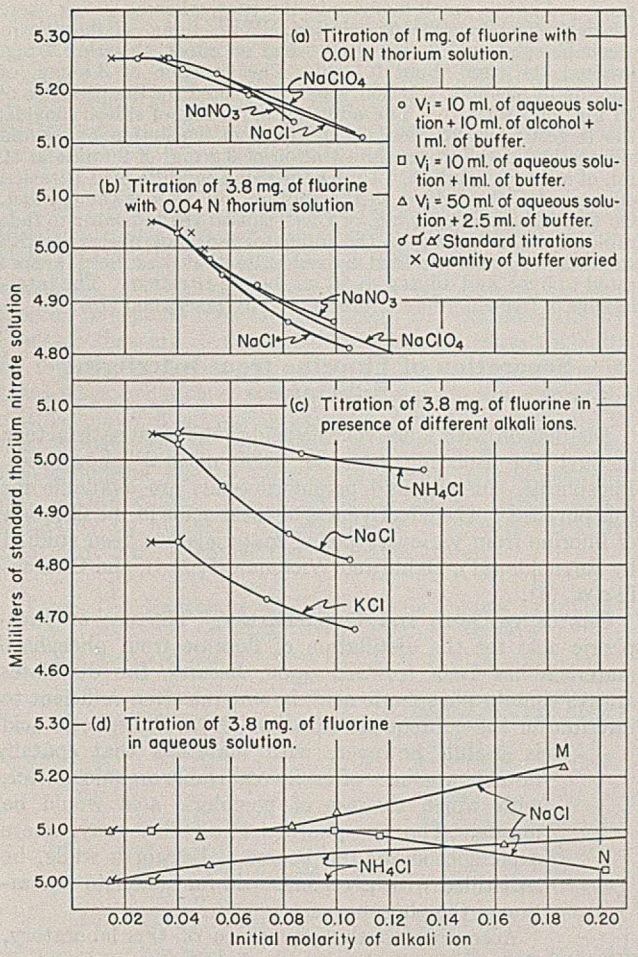


FIGURE 2. EFFECT OF ALKALI CHLORIDES, NITRATE, AND PERCHLORATE ON THE TITRATION OF ALKALI FLUORIDE WITH THORIUM NITRATE

Certain ions, such as chloride, nitrate, and perchlorate, cause low results in alcoholic solution, whereas others, such as sulfate and orthophosphate, give rise to high results. Furthermore, the effects of chloride, nitrate, and perchlorate are quantitatively very much the same, which suggests the possibility of the accompanying alkali ion being the principal source of the interference. If this be true, account must be taken of the alkali ion introduced in the fluorine salt and in the buffer. Accordingly, the effects of the ions are shown graphically (Figure 2) by plotting the titers against the molarity of the alkali ion at the beginning of the titration. For titrations in alcoholic solution the concentration is reckoned on the basis of the aqueous solution before the addition of alcohol.

With 1 mg. of fluorine in alcoholic solution (Figure 2, *a*) the salt effect becomes noticeable at about 0.03 *M*, or less than one-third of the concentration reported (*16*) to be permissible in the titration of approximately 0.05 mg. of fluorine in 50 ml. of alcoholic solution, and with 3.8 mg. of fluorine about the same threshold concentration is indicated (Figure 2, *b*). Accordingly, the concentrations of sodium ion in which sodium fluoride is usually titrated (standard titrations, Figure 2) are below (Figure 2, *a*) or above (Figure 2, *b*) the threshold of interference in alcoholic solution, depending upon the quantity of fluorine that is involved. Moreover, alteration of the sodium concentration by varying the volume of buffer also gave results (Figure 2, *b*) that follow the course of the curves for the other salts. These variations in the amount of buffer had only a slight effect on the pH of the titrated solution (Table I). The observation that the addition of these salts to the solution towards the end of the titration produces little or no effect on the titer indicates that the interference arises from reactions that occur during the initial stages of the titration when the fluoride concentration is greatest.

As a probable explanation of the effect of sodium ion the formation of insoluble compounds, such as Na_2ThF_6 (*13*, p. 606), suggests itself; thus the possibility of potassium or ammonium salts causing less interference than sodium salts becomes apparent. To investigate this point a dilute solution of hydrofluoric acid was prepared and adjusted to a suitable concentration by titration with thorium solution in the customary manner, and standard solutions of potassium fluoride and ammonium fluoride were prepared by neutralizing aliquots of this solution. Aliquots (3.8 mg. of fluorine) of these standard fluoride solutions, with and without the addition of alkali chloride, were titrated with thorium nitrate, using a buffer prepared from the respective alkali hydroxide. The results are plotted in Figure 2, *c*, and for comparison the sodium chloride curve (Figure 2, *b*) is reproduced. The ammonium ion interferes to a much less extent than the sodium ion. In the potassium system the standard titration is considerably lower than the corresponding titer in the sodium system; furthermore, the effect of added alkali chloride is also somewhat less.

TABLE I. EFFECT OF BUFFER CONCENTRATION, ALKALI-ION CONCENTRATION AND NATURE OF ALKALI ION ON pH OF TITRATED SOLUTION

Fluorine Present	Alkali System[a]	Alkali Chloride Added	Volume of Buffer Solution	Titer in Terms of 0.04 *N* Thorium Solution	pH of Titrated Solution[b]
Mg.		*Mg.*	*Ml.*	*Ml.*	
		Titration in Alcoholic Solution[c]			
3.8	Sodium	None	0.5	5.05	3.29
3.8	Sodium	None	1.0	5.03	3.30
3.8	Sodium	None	2.0	5.02	3.24
3.8	Sodium	50	1.0	4.81	3.28
3.8	Potassium	None	1.0	4.85	3.40
3.8	Ammonium	None	1.0	5.05	3.50
3.8	Ammonium	50	1.0	4.98	3.40
		Titration in Aqueous Solution[d]			
1.0	Sodium	None	2.5	1.40	2.86
3.8	Sodium	None	1.25	5.02	2.92
3.8	Sodium	None	2.5	5.09	2.82
3.8	Sodium	None	5.0	5.10	2.78
10.0	Sodium	None	2.5	13.35	2.87
3.8	Sodium	1,000	2.5	5.21	2.80
3.8	Potassium	None	2.5	4.97	2.90
3.8	Ammonium	None	2.5	5.00	3.00
3.8	Ammonium	1,000	2.5	5.14	2.90

[a] Sodium (or potassium or ammonium) ion was the only alkali ion present in the solution.
[b] Determined with the glass electrode by L. M. White of this bureau.
[c] Initial volume was 10 ml. of aqueous solution, 10 ml. of alcohol, and the indicated volume of buffer.
[d] Initial volume was 50 ml. of aqueous solution and the indicated volume of buffer.

In aqueous solution the interference effects of alkali chlorides, nitrates, and perchlorates become noticeable (Figure 2, *d*) when the total initial sodium concentration is 0.08 to 0.1 *M*, depending upon the initial volume of the titrated solution, or about three times the threshold concentration in alcoholic solution. In the larger volume the titer in both the sodium and the ammonium systems was increased by relatively large quantities of alkali chloride (Figure 2, *d*), whereas low titers were observed in the other cases (Figure 2). In contrast to the type of salt interference that gives rise to low results, this effect, observed to be more general in the system of ammonium salts, is not lessened when the addition of alkali chloride is withheld until the titration is nearly completed. Moreover, it does not appear to be attributable to pH effects—for example, after titration

both solutions M and N (Figure 2, *d*) had a pH value of 2.90 (glass electrode).

Of the negative ions that cause high results the orthophosphate and sulfate ions were investigated (Figure 3). Orthophosphate ion apparently titrates quantitatively, an observation also noted by Hoskins and Ferris (*16*), and must be excluded when titrating in alcoholic solution (Figure 3, *a*). With aqueous solutions the situation is improved a little, in which case the presence of the equivalent of 0.1 mg. of PO_4^{---} would be expected to cause less than 1 per cent error for amounts of fluorine in excess of 1 mg. when the initial volume is 50 ml.

The interference of sulfate in alcoholic solution depends upon the amount of fluorine present (Figure 3, *b*), as is also indicated by recent data of others (*10*). Sulfate interference has been attributed (*16*) on the basis of conductivity data to the slight dissociation of thorium sulfate even in very dilute solution. The fact that sulfate also causes high results in the gravimetric determination of fluorine as thorium fluoride (*11*) suggests the formation of an insoluble compound of the type ThF_2SO_4. On the other hand, in titrations made in aqueous solution sulfate interference disappears almost entirely (Figure 3, *b*), and the small disturbing action that remains (error of 0.015 mg. of fluorine for 2 mg. of SO_4^{--}) appears to be independent of the volume.

The effects of a few other substances on the titration were studied briefly. In alcoholic solution (3.8 mg. of fluorine) the presence of 1 mg. of boron trioxide caused no trouble, and 5 mg. produced only a small increase in the titer, whereas 20 mg. were without effect in aqueous solution. With 1 mg. of fluorine in alcoholic solution 1.3 mg. of S^{--} had no effect, though 6.6 mg. lowered the titer about 0.1 ml. The titration of 3.8 mg. of fluorine in alcoholic solution was not affected by the presence of 10 mg. of AsO_3^{---}. The addition of 15 mg. of silicon dioxide, the largest amount tried, in the form of a solution of sodium silicate had no effect on the titration of 3.8 mg. of fluorine in 50 ml. of aqueous solution. Under the same conditions of titration 40 mg. of ClO_3^- added as the sodium salt were without effect. On the other hand, 2.5 mg. of ClO^- caused the indicator to fade rapidly. This fading of the indicator was not observed with solutions containing added hypochlorite that had been evaporated to 5 ml. and diluted to 50 ml. before titration. The interference of free chlorine has been noted by Lockwood (*18*).

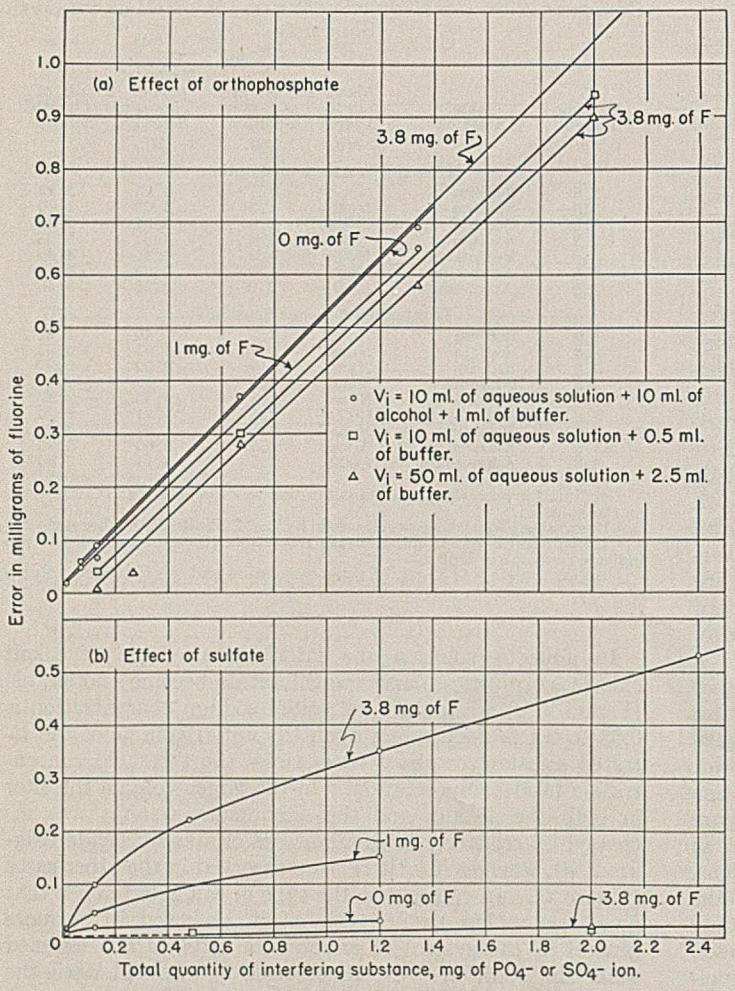


FIGURE 3. EFFECT OF ORTHOPHOSPHATE AND SULFATE IONS ON TITRATION OF SODIUM FLUORIDE WITH THORIUM NITRATE

Separation of Fluorine from Interfering Substances

Distillation with a nonvolatile acid is the most satisfactory method for isolating fluorine from natural phosphates. Phosphoric, sulfuric, and perchloric acids are available for this purpose. The effectiveness of these acids in the isolation of fluorine from various types of materials has been studied by Reynolds (*21*), Dahle and Wichman (*6*, *7*, *8*), and Churchill *et al.* (*3*).

CHOICE OF ACID FOR DISTILLATION. The use of phosphoric acid for the distillation of fluorine from phosphate materials has been frowned upon, because the distillates always contain phosphoric acid, in amount often sufficient to interfere in the subsequent titration (*21*). Phosphoric acid is useful, however, with materials that contain notable amounts of easily oxidizable organic matter, with which the use of perchloric acid would be unsafe. The phosphoric acid distillate may, where experience shows this course to be worth while, be redistilled with perchloric acid for complete separation of the phosphorus.

According to the experience of this laboratory, the use of sulfuric acid as a distilling agent for phosphate rock results in poor recovery of fluorine when the distillation temperature is maintained below 150° C. At a higher temperature complete expulsion of the fluorine from fused sodium carbonate samples is attainable (*15*) at the expense of contamination of the distillate with sulfuric acid.

On account of high solubility of its salts perchloric acid is the most satisfactory distilling acid, though considerable care should be exercised in its use directly on samples that contain notable amounts of organic matter. A hazard not always recognized resides in the use of rubber stoppers in the distilling flask. Phosphoric acid has not been found in the perchloric acid distillates of 0.1-gram samples of phosphate rock (*21*). With large samples of phosphate-rich material in the distilling flask the distillate does carry more or less orthophosphate (*3*, *21*). Furthermore, according to recent observations in this laboratory, perchloric acid distillates obtained with the aid of stills in which phosphoric acid had been used as a distilling agent also contain appreciable quantities of phosphate. Thus, it appears desirable to provide separate equipment for the use of phosphoric acid.

After distillation with perchloric acid the fluorine is accompanied by a small amount of the distilling acid, as well as a small amount of phosphoric acid under certain conditions, by practically all of the hydrochloric and nitric acids in the sample, and by sulfur compounds in the case of pyritiferous samples. Boron also distills in part, and arsenic may be expected under certain conditions. The distillate

(150 ml.) from 0.1 gram of phosphate rock and 0.05 gram of borax contained 5 mg. of boron trioxide. Although all these elements may be encountered in phosphatic materials, pyritic sulfur alone assumes importance in phosphate rock analysis, as the quantities of the other elements present in the sample are below the limits of interference shown above for titration in aqueous systems.

SUBSTANCES THAT RETARD THE DISTILLATION OF FLUORINE. Gelatinous silica (*28*) and large quantities of soluble aluminum salts (*7*) retard the rate of distillation of fluorine, but the quantities of these substances usually encountered in commercial phosphate rock are insufficient to interfere seriously. Silicates that are decomposed by acid also cause difficulty by forming on the interior of the flask a coating of precipitated silica, which is capable of retaining fluorine during the distillation of fluorine-rich samples only to give it up, at least in part, during subsequent distillations of samples less rich in fluorine, thereby vitiating the results in both instances (*21*). This coating of precipitated silica, which would ordinarily be mistaken for etching, is readily removed by treatment with hot concentrated alkali solution.

TABLE II. EFFECT OF EVAPORATION OF SODIUM FLUORIDE SOLUTION ON TITER WITH THORIUM NITRATE

(Solution was evaporated to 40 to 45 ml. V_i = 50 ml. of aqueous soln.)

Series No.	Added Fluorine[a]	Procedure	Approximate Volume of Solution at Beginning of Evaporation	Titers of Duplicate Experiments in Terms of 0.04 *N* Thorium Solution
	Mg.		*Ml.*	*Ml.*
1	1.0	Direct titration	Not evaporated	1.39, 1.41
		Plus water	150	1.40, ..
		Plus water + 0.05 mg. of SiO_2[b]	150	1.40, 1.40
		Distilled with $HClO_4$ to volume of 150 ml.	150	1.41, 1.42
2	3.8	Direct titration	Not evaporated	5.08, 5.10
		Plus water	300	5.08, 5.10
		Plus water + 1.9 mg.[c] of SiO_2[b]	150	5.02, 5.03
		Plus water + 3.8 mg. of SiO_2	150	5.01, 5.03
		Plus water + 7.6 mg. of SiO_2	150	4.98, 4.96[d]
3	3.8	Distilled with $HClO_4$ to volume of 150 ml.	150	4.98, 5.00
		Plus 150 ml. of $HClO_4$ distillate (blank) + 1.9 mg.[c] of SiO_2[b]	150	5.00, 5.00
4	10.0	Distilled with $HClO_4$ to volume of 150 ml., made up to 250 ml., and titrated 50-ml. aliquots (2 mg. of F)	Not evaporated	2.63, 2.72
			150	2.58, 2.68
5	20.0	Same as series 4. Aliquots = 4 mg. of F	Not evaporated	5.25, 5.30
			150	5.25, 5.23

[a] Aliquots of standard sodium fluoride solutions were used.
[b] Silica was added in the form of a clear solution of Na_2SiO_3.
[c] Approximately the SiO_2 equivalent of the fluorine as H_2SiF_6.
[d] Indistinct end point.

EVAPORATION OF FLUORINE-CONTAINING SOLUTIONS. In the analytical determination of fluorine it is frequently convenient, if not absolutely necessary, to reduce the relatively large volume of neutralized distillate by evaporation. In view of the limited size of sample (0.1 gram) heretofore considered practical in phosphate rock analysis concentration seemed desirable, in order to have as much as 3 to 4 mg. of fluorine for titration with thorium nitrate solution. Moreover, concentration seemed permissible on the basis of comparative results obtained on phosphate rock. More recently, as the result of efforts to locate the cause of low recovery of fluorine in the distillates of sodium fluoride, it has been found that under certain conditions, illustrated by typical data in Table II, evaporation of alkaline (phenolphthalein) fluorine-containing solutions leads to low titers with thorium nitrate solution.

When the involved quantity of fluorine was 1 mg., evaporation had no observable effect on the result (Table II, series 1). The lowered titers of larger quantities of fluorine seem to be traceable to the influence of soluble silica (series 2), although the presence of moderate amounts of soluble silica in unevaporated solutions does not affect the titer, and the effect of evaporation on the titer of aliquots of distillates (series 4 and 5) is attributable, at least in part, to the effect of the silica from the distilled fluosilicic acid. The reactions responsible for the lowered titer have not been determined. However, the addition of evaporated blank distillates from perchloric acid, which presumably carry only traces of soluble silica, also lowered the titer of standard sodium fluoride. The latter effect is briefly discussed in the following section.

TABLE III. EFFECT OF EVAPORATION OF DISTILLATES FROM PHOSPHATE ROCK ON TITER WITH THORIUM NITRATE

Sample No.	Type or Source of Phosphate	Titer of Solutions from 0.1 Gram of Sample[a] A	B	C
		Ml.	*Ml.*	*Ml.*
120[b]	Florida land pebble	4.94	4.90	4.94
		4.97	4.93	4.97
56a[b]	Tennessee brown rock	4.74	4.69	4.74
		4.76	4.71	4.71
930	Tennessee blue rock	4.61[c]	4.60[c]	4.58[c]
		4.63	4.57	4.58
948	Wyoming	4.63[c]	4.60[c]	4.63[c]
		4.62	4.60	4.65
1253	Idaho	4.31	4.27	4.34
		4.30	4.27	4.31

[a] In procedure A the 150-ml. perchloric acid distillate of a 1-gram sample was made up to 250 ml., from which a 25-ml. aliquot was taken, diluted to 50 ml., and titrated in aqueous solution. Procedure B is the same as A, except that the aliquot was diluted to 150 ml. and then evaporated to 45 to 50 ml., whereas in C the 150-ml. distillate of 0.1 gram of the rock was evaporated to 45 to 50 ml.
[b] National Bureau of Standards standard sample.
[c] Distilled in the presence of $KMnO_4$.

The titers (corresponding to 0.1-gram samples) of phosphate rock distillates show an observable lowering as a result of evaporation (Table III). The small differences (0.03 to 0.04 ml. of 0.04 *N* thorium solution), however, amount to only 0.02 to 0.03 per cent of the sample.

TABLE IV. THORIUM NITRATE CONSUMED BY BLANK DISTILLATES FROM PERCHLORIC ACID[a]

Series No.	Procedure[b]	Total Titers of Duplicate Experiments in Terms of 0.01 *N* Thorium Solution
		Ml.
1	Titration blank	0.11, 0.10
	150 ml. of distillate from water alone	0.10, 0.14
	150 ml. of distillate from $HClO_4$ No. 1	0.35, 0.33[c]
	150 ml. of distillate from $HClO_4$ No. 2	0.22, 0.20, 0.22[c,d]
2	150 ml. of a 300-ml. $HClO_4$ (No. 1) distillate	0.35, 0.35
	150 ml. of same distillate after evaporation and redistillation (150 ml.)	0.68, 0.67

[a] 10 ml. of 60 per cent perchloric acid and 5 ml. of water were added to distilling flask.
[b] All titrations were made in a volume of 10 ml. of aqueous solution. Neutralized distillates were evaporated to 5 to 10 ml.
[c] Results are for consecutive 150-ml. portions.
[d] When titration medium was 50 per cent ethanol (20 ml.) corresponding results were 0.13, 0.14, and 0.12 ml.

BLANK ON PERCHLORIC ACID. The distillate obtained from perchloric acid without added fluorine consumes more thorium nitrate than is required by the titration blank, and the amount varies with different lots of acid and with the volume of the distillate (Table IV). Eberz *et al.* (*10*) made similar observations and recommended that the acid be purified by continued distillation until the blank became zero. Noteworthy in this connection is the near constancy of the titers of three successive 150-ml. distillates from one lot of acid (series 1). Furthermore, the blank appears to accumulate in double distillation (series 2). On the other hand, by far the larger part of this blank is evidently due to something other than fluorine, because the addition of the evaporated blank distillate to a known amount of sodium fluoride solution, oddly enough, gives rise to a slightly lowered titer. This tendency towards a negative effect on the titration may also be noted by comparing the results in Table II (series 2 and 3).

RECOVERY OF FLUORINE BY DISTILLATION WITH PERCHLORIC ACID. The recovery of fluorine from solutions of sodium fluoride by distillation with perchloric acid and titration of unevaporated distillates was 100 per cent with amounts of fluorine ranging from 1 to about 15 mg. The apparent recovery shown by the titers of evaporated distillates was nearly constant (99 per cent) over the range 3 to about 15 mg. Below about 3 mg. of fluorine the effect of evaporation decreases (Figure 4, *a*) and becomes negligible at 1 mg., as is indicated in Table II. Above 15 mg. of fluorine the recovery was variable. In view of the fact that this behavior was not observed in the results for phosphate rock, the variable recovery of the larger quantities of fluorine from sodium fluoride was not investigated further.

TABLE V. FLUORINE IN PERCHLORIC ACID DISTILLATES OF TYPICAL PHOSPHATE ROCKS BY DIFFERENT METHODS OF ANALYSIS

(Weight of sample, 1 gram. Volume of distillate, 150 ml.)

Sample No.	Type or Source of Phosphate	Fluorine Found: Thorium nitrate titration[a]	Fluorine Found: Lead chlorofluoride method (*15*)
		%	%
120[b]	Florida land pebble	3.70	3.74
		3.71	3.72
56a[c]	Tennessee brown rock	3.54	3.47
		3.55	3.55
930	Tennessee blue rock	3.44[d]	3.53
		3.46	3.58
1253	Idaho rock	3.21	3.26
		3.20	3.29

[a] Aliquot of distillate was titrated directly in an initial volume of 50 ml. of aqueous solution.
[b] National Bureau of Standards standard sample No. 120. Certificate value for fluorine 3.76%.
[c] National Bureau of Standards standard sample No. 56a. Certificate value for fluorine 3.56%.
[d] Results obtained by distillation in presence of potassium permanganate.

That the recovery of fluorine from phosphate rocks is independent of the quantity of fluorine in the investigated range, 3 to about 40 mg., is shown by the linear relationship between the thorium nitrate titers of evaporated distillates (not aliquoted) and the weight of sample distilled (Figure 4, *b*). The results (Table V) obtained on perchloric acid distillates of typical phosphate rocks by titration with thorium nitrate and by the lead chlorofluoride method (*14*) agree very closely. That substantially complete recovery was realized is indicated by the fact that the results thus obtained on 1-gram samples of the National Bureau of Standards standard samples are only slightly different from the certified values for these samples. Perchloric acid distillation gave low results (0.2 to 0.3 per cent) on phosphate rock samples that had been fused with sodium carbonate. On the other hand, Hoffman and Lundell (*15*) found that a preliminary fusion with sodium carbonate improved the recovery when sulfuric acid was the distilling acid.

The entire distillate may also be titrated without resorting to evaporation. The blank correction to the titer, however, appears to vary with the type of phosphate. This condition is indicated by the intercepts of the curves with the zero ordinate in Figure 4, *c*, where only a part of the investigated range is shown.

ELIMINATION OF THE EFFECT OF PYRITIC SULFUR. As already indicated, perchloric acid distillates of pyritiferous phosphates, such as Tennessee blue rock, carry sulfur in some form. In the case of samples containing 3 to 5 per cent (as sulfur trioxide) of pyritic sulfur the determined quantity of total sulfur in 150 ml. of distillate from 0.1 gram of sample ranged from 1 to 3 mg. of sulfur trioxide. Approximately half of that distilled was in the sulfate condition after the distillate had been neutralized and evaporated to a volume of 10 ml. The milkiness of the distillates, which disappears upon neutralization and evaporation, is probably due to free sulfur. Only a trace of hydrogen sulfide could be detected at the condenser exit during distillation.

The quantities of sulfate sulfur found in the evaporated distillates of pyritiferous samples are sufficient to produce serious error in the results obtained by titration in an alcoholic solution (Figure 3, *b*), and the error, though greatly reduced, is not entirely eliminated by titration in an aqueous system. Separation of the sulfur from fluorine can be made much more complete in one distillation by adding permanganate to the distilling flask before starting the distillation, and its use in the absence of more than traces of chloride seems to be entirely unobjectionable. An excess of permanganate should be used. Although the amount needed will depend upon the quantity of oxidizable substance in the sample, the authors have found 5 ml. of a saturated solution of potassium permanganate to provide a sufficient excess for 1-gram samples of phosphate rock. Accordingly, the sample after transfer to the distilling flask is moistened with the permanganate solution, perchloric acid is then added, and the distillation is conducted in the usual manner. When an excess of permanganate is used, the residue from the distillation is black.

Results for fluorine in a number of pyritiferous and pyrite-free phosphates by distillation with and without permanganate and titration in alcoholic and aqueous solutions are

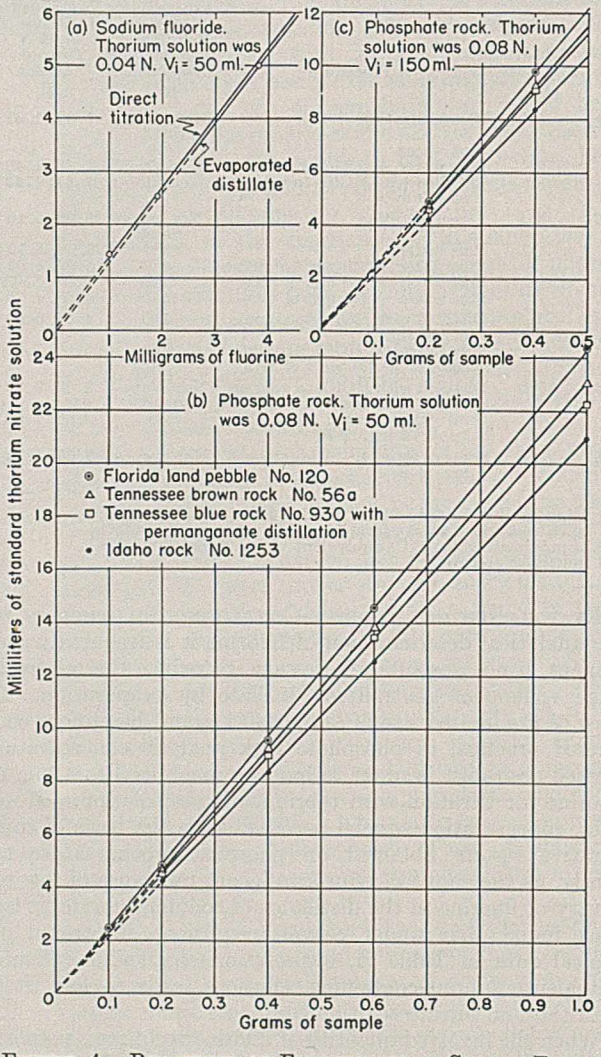


FIGURE 4. RECOVERY OF FLUORINE FROM SODIUM FLUORIDE AND PHOSPHATE ROCK

By distillation with perchloric acid and titration in aqueous solution with thorium nitrate. Volume of distillate, 150 ml.

TABLE VI. FLUORINE IN PYRITIFEROUS AND PYRITE-FREE PHOSPHATES

Sample No.	Type or Source of Phosphate	P_2O_5	Organic C[a]	Pyritic Sulfur as SO_3[a]	Fluorine Determined[b] D	E	F	G
		%	%	%	%	%	%	%
120[c]	Florida land pebble	35.25	0.32[d]	<0.02	3.71	3.70	3.71	3.69
..	Sample 120 + FeS_2	...	..	5.34	4.27	3.87	3.72	3.70
912	Florida land pebble	35.37	0.38	<0.02	3.71	3.68	3.69	3.69
56a[c]	Tennessee brown rock	32.82	0.26[d]	<0.02	3.53	3.53	3.56	3.54
56[c]	Tennessee brown rock	31.28	0.25	1.19	3.58	3.43	3.44	3.45
448	Tennessee blue rock	32.03	..	1.37	3.72	3.49	3.50	3.58
1049	Tennessee blue rock	31.22	1.46	2.02	3.23	3.12	3.03	3.06
772	Tennessee blue rock	30.45	0.36	2.71	3.51	3.27	3.25	3.22
449	Tennessee blue rock	33.65	..	3.19	4.17	3.82	3.76	3.75
930	Tennessee blue rock	30.97	0.20	5.21	3.98	3.51	3.42	3.49
1138	South Carolina land rock	27.85	0.51	0.46	3.63	3.55	3.53	3.49
948	Wyoming, Cokeville	30.19	2.69	1.30	3.60	3.45	3.46	3.47
1253	Idaho, Conda	32.13	>2	<0.02	3.30	3.23	3.22	3.23
1012	Montana, Garrison	36.07	<0.2	<0.02	4.54	4.42	4.42	4.42
1011	Montana, Garrison	27.63	>0.2	<0.02	6.93	6.79	6.83	6.84

[a] Unless indicated otherwise, results unaccompanied by inequality sign are those given by Jacob *et al.* (*17*).
[b] In procedure D a 150-ml. distillate of 0.1 gram of rock was evaporated to 10 ml. and titrated in 20 ml. of 50 per cent ethanol; in E a 150-ml. distillate of 0.1 gram of rock was evaporated to 45 to 50 ml. and titrated in this volume of aqueous solution; F is same as E with permanganate distillation; in G 0.5 gram of rock was distilled with permanganate, the 150-ml. distillate was made up to 250 ml., and fluorine was titrated in an unevaporated 50-ml. aliquot.
[c] Bureau of Standards standard sample of phosphate rock.
[d] Reported as organic matter by Hoffman and Lundell (*15*).

TABLE VII. FLUORINE IN IGNITED PHOSPHATE ROCKS

Sample No.	Type or Source of Phosphate	Organic C[a]	Pyritic Sulfur as SO_3[a]	Fluorine: Ingited sample[b]	Fluorine: Unignited sample[c]	Difference
		%	%	%	%	%
120[d]	Florida land pebble	0.32[e]	<0.02	3.71	3.71	±0.00
..	Sample 120 + FeS_2	..	5.34	3.31	3.72	−0.41
56a[d]	Tennessee brown rock	0.26[e]	<0.02	3.49	3.56	−0.07
56[d]	Tennessee brown rock	0.25	1.19	3.35	3.44	−0.09
449	Tennessee blue rock	..	3.19	3.55	3.76	−0.21
930	Tennessee blue rock	0.20	5.21	3.24	3.42	−0.18
948	Wyoming, Cokeville	2.69	1.30	3.40	3.46	−0.06
1253	Idaho, Conda	>2	<0.02	3.16	3.22	−0.06

[a] See footnote [a], Table VI.
[b] Sample was heated in a muffle furnace at 500° C. for 0.5 hour; its fluorine content was then determined by procedure E (Table VI).
[c] Fluorine was determined by procedure F (Table VI).
[d] Bureau of Standards standard sample of phosphate rock.
[e] Reported as organic matter by Hoffman and Lundell (*15*).

given in Table VI. At the time these analyses were made samples larger than 0.1 to 0.2 gram had not been shown to be permissible, which accounts for the small samples used. The effect of pyrite on the result for fluorine, as well as the usefulness of permanganate in its presence, can be most readily observed by comparing the results for Florida land pebble 120 with and without added pyrite.

Hoffman and Lundell (*15*) mention a collaborator's suggestion that the effect of pyrite can be eliminated by igniting the sample prior to distillation. Data obtained in this laboratory (Table VII) show that this treatment causes low results when the sample contains pyrite.

Other uses for permanganate distillation are worthy of mention in this connection. Organic substances have been observed in the distillate of certain research samples that contained cottonseed meal, in which cases the results for fluorine were low. With the use of permanganate, however, satisfactory results were obtained on these materials. Dahle (*4*) separated fluorine from large amounts of chloride by refluxing with sulfuric acid and permanganate prior to the distillation of the fluorine. The authors have used double distillation with perchloric acid and permanganate to separate fluorine from moderately large amounts of chloride.

Procedure for Determining Fluorine in Phosphate Rock

For accurate and consistent results the authors suggest the following procedure:

Distill 0.5 gram of the sample and 15 ml. of perchloric acid (2 + 1) at 125° to 150° C., preferably in a steam-distillation unit (*24*), until the volume of the distillate is 150 ml. If the material is pyritiferous, moisten the sample in the distilling flask with 2 to 3 ml. of a saturated solution of potassium permanganate and increase the concentration of the added perchloric acid accordingly. Neutralize (phenolphthalein) the distillate with 1 *M* sodium hydroxide and make it up to a volume of 250 ml. To a 50-ml. aliquot of this solution add 5 drops of alizarin indicator (0.1 per cent aqueous solution of sodium alizarin sulfonate) and 0.1 *M* hydrochloric acid until the pink of the alizarin is discharged. Now add 2.5 ml. of monochloroacetic acid (0.4 *M*)–sodium hydroxide (0.2 *M*) buffer solution and titrate with 0.04 *N* thorium nitrate solution. The end point is very sharp. About 1 hour is required for a determination.

Correct the titer by deducting the titration blank found by titrating a series of sodium fluoride solutions covering the range of the amounts of fluorine involved in the analysis. On account of the lowering effect of added blank perchloric acid distillates on the titer of sodium fluoride, this blank correction is slightly greater than the true blank.

For control work in which the highest attainable accuracy is not necessary the procedure can be shortened by distilling 1 gram of rock to a volume of 150 ml. and titrating the distilled fluorine directly in this volume with 0.08 *N* thorium solution, using 15 drops of indicator solution and 7.5 ml. of buffer solution. Since the end point is not sharp, a standard for comparison is desirable.

Literature Cited

(1) Armstrong, W. D., IND. ENG. CHEM., Anal. Ed., 8, 384 (1936).
(2) Armstrong, W. D., *J. Am. Chem. Soc.*, 55, 1741 (1933).
(3) Churchill, H. V., Bridges, R. W., and Rowley, R. J., IND. ENG. CHEM., Anal. Ed., 9, 222 (1937).
(4) Dahle, D., *J. Assoc. Official Agr. Chem.*, 20, 505 (1937).
(5) Dahle, D., Bonnar, R. U., and Wichman, H. J., *Ibid.*, 21, 459 (1938).
(6) Dahle, D., and Wichman, H. J., *Ibid.*, 19, 313 (1936).
(7) *Ibid.*, 19, 320 (1936).
(8) *Ibid.*, 20, 297 (1937).
(9) Dahle, D., Wichman, H. J., and Bonnar, R. U., *Ibid.*, 21, 468 (1938).
(10) Eberz, W. F., Lamb, F. C., and Lachele, C. E., IND. ENG. CHEM., Anal. Ed., 10, 259 (1938).
(11) Gooch, F. A., and Kobayashi, M., *Am. J. Sci.*, 45, 370 (1918).
(12) Hendricks, S. B., Hill, W. L., Jacob, K. D., and Jefferson, M. E., IND. ENG. CHEM., 23, 1413 (1931).
(13) Hillebrand, W. F., and Lundell, G. E. F., "Applied Inorganic Analysis," New York, John Wiley & Sons, 1929.
(14) Hoffman, J. I., and Lundell, G. E. F., *Bur. Standards J. Research*, 3, 581 (1929).
(15) Hoffman, J. I., and Lundell, G. E. F., *J. Research Natl. Bur. Standards*, 20, 607 (1938).
(16) Hoskins, W. M., and Ferris, C. A., IND. ENG. CHEM., Anal. Ed., 8, 6 (1936).
(17) Jacob, K. D., Hill, W. L., Marshall, H. L., and Reynolds, D. S., U. S. Dept. Agr., *Tech. Bull.* 364 (1933).
(18) Lockwood, H. C., *Analyst*, 62, 775 (1937).
(19) McAdam, Jr., D. J., and Smith, E. F., *J. Am. Chem. Soc.*, 34, 592 (1912).
(20) Reynolds, D. S., *J. Assoc. Official Agr. Chem.*, 17, 323 (1934).
(21) *Ibid.*, 18, 108 (1935).
(22) Reynolds, D. S., and Jacob, K. D., IND. ENG. CHEM., Anal. Ed., 3, 366 (1931).
(23) *Ibid.*, 3, 371 (1931).
(24) Reynolds, D. S., Kershaw, J. B., and Jacob, K. D., *J. Assoc. Official Agr. Chem.*, 19, 156 (1936).
(25) Reynolds, D. S., Ross, W. H., and Jacob, K. D., *Ibid.*, 11, 225 (1928).
(26) Rowley, R. J., and Churchill, H. V., IND. ENG. CHEM., Anal. Ed., 9, 551 (1937).
(27) Wagner, C. R., and Ross, W. H., J. IND. ENG. CHEM., 9, 1116 (1917).
(28) Willard, H. H., and Winter, O. B., *Ibid.*, Anal. Ed., 5, 7 (1933).

RECEIVED August 31, 1938.

Improvement of Vacuum Distillation

BOLESLAW LUDWIK DUNICZ, University, Lwów, Poland

OBTAINING substances of perfect purity is of the greatest importance in both chemical and physical investigations. When fractionating devices based on the Anschütz-Thiele apparatus are used for vacuum distillation, the purity of the fractions received is doubtful, because of the necessity of greasing the stopcock through which the distillate passes. Using other devices without this fault, distillation cannot be controlled without interrupting the process, which is inconvenient. This difficulty may be easily avoided by using the fractionating contrivance shown in Figure 1.

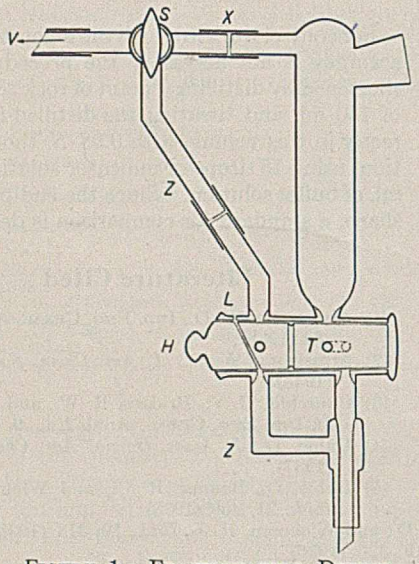


FIGURE 1. FRACTIONATING DEVICE

L. Hole to let in air
V. To vacuum pump

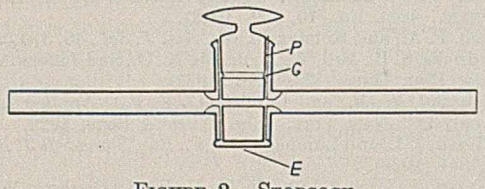


FIGURE 2. STOPCOCK

G. Groove
P. Greased part of stopcock
E. Sealed side of shell

A stopcock is fitted to this contrivance, the simplest form of which is shown in Figure 2. The plug of the stopcock has a groove, and its exterior is sealed at one side. The plug is greased only in the upper (broader) part of the groove, and the groove prevents dispersion of grease to its narrower part, which in the device described is greased by the distillate.

The manipulation of this device (Figure 1) is simple: The three-way stopcock, *S*, is so arranged that while the distillate is being collected it is evacuated with pump only through tubes *ZZ*, but during exchange of the receiving flask it is evacuated through connections *X*. The hole, *T*, of stopcock *H* is diagonal, for after exchange of the receiving flask it is possible, by suitably adjusting this stopcock and stopcock *S*, to remove air from the new receiver without disturbing the distillation.

The stopcock may also be applied to other apparatus, to avoid contamination usually caused by greasing whole plugs—in stopcocks which join tubes filled with mercury, etc. The

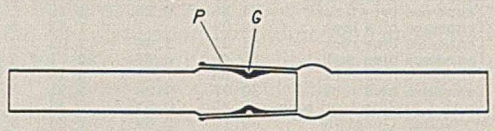


FIGURE 3. CONNECTION TUBES WITH GROUND JOINT

G. Groove
P. Greased part of joint

inner parts of connection tubes with ground joints should also be provided with grooves (Figure 3), as leaking of grease out of the joint is always undesirable.

RECEIVED September 3, 1938.

Direct Titration of Sulfate

Erythrosin as Internal Indicator

WALTER V. BURG, University of Toledo, Toledo, Ohio

DURING recent years several suggestions concerning the use of adsorption indicators for the volumetric determination of sulfate have been advanced.

Wellings (*6*) reported that, in the presence of magnesium or manganous ions, fluorescein can be used as an internal indicator for the direct titration of sulfate with barium hydroxide. His results indicate an average relative error of somewhat less than 0.5 per cent. However, according to Iyer (*2*), the end point of this titration is not very sharp. Moreover, nitrate ions were found to interfere with the operation of the indicator, a fact that is the more serious since a removal of these ions would render the determination very complicated. Essentially different from Wellings' method is the one suggested by Roy (*5*), who mentioned the possibility of using fluorescein as an external indicator for the indirect titration of sulfate with lead nitrate and potassium sulfate. Though, to the author's knowledge, no data concerning a practical application of this method have been presented, it appears certain that such a determination would be rather time-consuming. In 1936 Ricci (*4*) published a study of the direct titration of sulfate with lead nitrate in the presence of eosin as internal indicator, reporting an average relative error of 0.33 per cent in 65 analyses of sodium sulfate solutions. In a discussion of the effect of variations he stated that if the final volume of solution is much above 30 ml. it is difficult to detect the end-point change, and pointed out that efforts to sharpen the end point by the addition of alcohol did not meet with success. According to Ricci only small percentages of this diluent can be tolerated, while the presence of more alcohol delays the end point so much that the titration becomes impossible.

Erythrosin as Indicator

It was during a study of the properties of erythrosin (tetraiodofluorescein) that the very low solubility and characteristic violet-red color of its lead salt suggested to the author the possibility of using it as an internal indicator for the direct titration of sulfate with lead nitrate. However, the conditions under which this indicator works best are very different from those recommended for the eosin method. Preliminary experiments revealed that in the titration of sulfate with lead nitrate the replacement of eosin by erythrosin

causes the color change to start long before the equivalence point is reached. In order to render erythrosin useful as an indicator for this titration, it proved necessary to modify the relationship between the solubilities of lead sulfate and lead erythrosinate to a considerable extent. The influence of ethyl alcohol on the solubilities of these two compounds suggested that this diluent might be added to the solution to be titrated, to bring about a correct end point.

TABLE I. TITRATION OF SULFATE

No.	SO_4 Present	SO_4 Found	Error
	Gram	*Gram*	%
1	0.0482	0.0483	+0.2
2	0.0694	0.0694	0.0
3	0.0857	0.0860	+0.4
4	0.1089	0.1087	−0.2
5	0.1156	0.1159	+0.3
6	0.1349	0.1344	−0.4
7	0.1541	0.1536	−0.3
8	0.1782	0.1785	+0.2
9	0.1927	0.1925	−0.1

In order to study this question, a series of titrations of sodium sulfate solutions of varying strengths was carried out. These solutions were prepared from analytical grade salt and standardized gravimetrically either by evaporation and weighing of the residue or by precipitating and weighing as barium sulfate. Throughout the investigation a 0.1 *M* solution of lead nitrate was used. This solution, also prepared from analytical grade material, was standardized by various methods, both gravimetric and volumetric. The alcohol employed was absolute ethyl alcohol (95 per cent alcohol can also be used with success). The indicator solution was a 1 per cent solution of erythrosin B in water.

The investigation revealed that by adding adequate quantities of alcohol to the sulfate solution accurate results can easily be obtained with final volumes (not counting the alcohol) ranging from 20 to 70 ml. It was found advisable to keep the temperature of the solution below 30° C., in order to avoid a delay of the end point, and to adjust the solution to be titrated carefully so that it reacted just acid towards phenolphthalein. A distinctly basic character caused high results, while a certain degree of acidity (pH = 5) did not produce any harmful effects.

On the basis of these results a number of procedures were tested. In the procedure described below the amount of sulfate to be estimated is limited to approximately 0.19 gram and the final volume of aqueous solution to 70 ml. On exceeding these limits an increasing tendency towards low results is noticeable.

Procedure

MATERIALS AND REAGENTS. A 0.1 *M* lead nitrate solution, standardized gravimetrically, 1 per cent solution of erythrosin B in water, ethyl alcohol, phenolphthalein solution, and approximately 0.02 *N* nitric acid.

PROCEDURE. Transfer a 50-ml. sample, containing between 0.05 and 0.19 gram of sulfate, to a 250-ml. Erlenmeyer flask and render just acid to phenolphthalein by means of approximately 0.02 *N* nitric acid. Add 16 ml. of alcohol and 14 drops of indicator. Mix well, so that the color of the solution is a uniform orange-red. The temperature should not be over 30° C. Run the lead nitrate solution into the flask at a steady dropping rate and with constant swirling until the increasing persistence of the violet color, produced by each drop of standard, indicates the approach of the end point. Continue the titration very slowly and with vigorous agitation until the color of the whole mixture becomes a distinct violet.

Table I shows the results of a number of typical titrations of sodium sulfate solutions carried out according to the above procedure. These indicate that the method is satisfactory, the average relative error being less than 0.3 per cent. The same degree of accuracy was obtained in the titration of solutions containing potassium sulfate or mixtures of potassium and sodium sulfates.

In order to become well acquainted with the color change that is characteristic for this determination, it is best to titrate a few samples of known sulfate content according to the procedure just described. As soon as the end point has been reached, addition of a drop of lead nitrate solution will no longer cause the appearance of a dark spot on the surface of the mixture.

Successive Titration of Chloride and Sulfate

Owing to the low solubility of lead chloride, especially in an alcoholic medium, all but very small quantities of chloride ions interfere with the operation of the indicator. On the other hand, the presence of considerable quantities of nitrate has no appreciable influence on the end point. This fact suggested the use of silver nitrate for the removal of the chloride ions, thus presenting a method for the successive titration of chloride and sulfate.

A rapid and accurate method for the estimation of chloride, that can be combined with the sulfate determination discussed, is the direct titration with silver nitrate in the presence of fluorescein or dichlorofluorescein as adsorption indicators (*1*, *3*). A preliminary investigation was carried out with solutions containing varying quantities of sodium chloride and sodium sulfate, prepared from analytical grade salts and standardized by the usual gravimetric methods. A 0.1 *N* solution of silver nitrate, also prepared from analytical grade material and standardized gravimetrically, was used for the various chloride titrations. The indicator solution for the latter was a 0.1 per cent solution of sodium fluorescinate or sodium dichlorofluorescinate in water. The other reagents were those employed for the estimation of sulfate in the absence of chloride. The following procedure was used during the investigation:

Transfer a 50-ml. sample, containing between 0.04 and 0.13 gram of chloride and between 0.10 and 0.38 gram of sulfate, to a 250-ml. Erlenmeyer flask and render just acid to phenolphthalein by means of approximately 0.02 *N* nitric acid. Add 4 to 7 drops of the chloride indicator and titrate with silver nitrate in diffuse light. Run the standard solution into the flask at a steady dropping rate and with constant swirling until the silver chloride starts to flocculate. Continue the titration very slowly and with vigorous agitation until the precipitate turns reddish (end point of the chloride titration). Carefully transfer the contents of the vessel to a 100-ml. volumetric flask, make up to the mark with distilled water, and mix thoroughly. Filter into a dry beaker, after having discarded the first 5 or 10 ml. of the filtrate. Transfer 50 ml. of the clear solution to a 250-ml. Erlenmeyer flask and determine the sulfate according to the directions given above; no further adjustment of the acidity is necessary. Multiply the result of the sulfate titration by two.

TABLE II. SUCCESSIVE TITRATION OF CHLORIDE AND SULFATE

No.	Cl Present	Cl Found	Error	SO_4 Present	SO_4 Found	Error
	Gram	*Gram*	%	*Gram*	*Gram*	%
1	0.0464	0.0463	−0.2	0.0982	0.0985	+0.3
2	0.0928	0.0928	0.0	0.0982	0.0979	−0.3
3	0.1392	0.1390	−0.1	0.0982	0.0987	+0.5
4	0.0464	0.0463	−0.2	0.3851	0.3844	−0.2
5	0.0928	0.0930	+0.2	0.3851	0.3840	−0.3
6	0.1392	0.1393	+0.1	0.3851	0.3854	+0.1

Table II shows the results of a number of determinations carried out by this method. The results are satisfactory with regard to both the chloride and sulfate.

Conclusion

From 0.05 to 0.19 gram of sulfate, present in the form of sodium or potassium sulfate, can be estimated rapidly and accurately by means of the procedure described in this paper.

However, the applicability of the erythrosin method is not limited to the conditions set forth in that procedure. One way of extending the scope of the method is based upon the use of standard solutions that have concentrations other than 0.1 *M*. A few determinations carried out with 0.05 *M* and 0.2 *M* lead nitrate showed that with these solutions accurate results can easily be obtained, provided the conditions (quantities of alcohol and indicator) are adjusted adequately. It will be worth while to study the titration with these standards more closely with the purpose of working out analytical procedures for the estimation of amounts of sulfate that are either larger or smaller than those of the above range. Such an extension of the method would also broaden the applicability of the successive determination of chloride and sulfate that has been suggested in this paper. Another fertile field for further investigation is the replacement of ethyl alcohol by diluents that can be obtained without legal restrictions. Preliminary experiments revealed that both acetone and isopropyl alcohol give satisfactory results, though a somewhat smaller volume is to be used for a given titration as compared to ethyl alcohol.

Literature Cited

(1) Fajans, K., and Hassel, O., *Z. Elektrochem.*, 29, 495–500 (1923).
(2) Iyer, V., *J. Indian Chem. Soc.*, 12, 164–7 (1935).
(3) Kolthoff, I. M., Lauer, W. M., and Sunde, C. J., *J. Am. Chem. Soc.*, 51, 3273–7(1929).
(4) Ricci, J. E., Ind. Eng. Chem., Anal. Ed., 8, 130–2(1936).
(5) Roy, S. N., *J. Indian Chem. Soc.*, 12, 584–5 (1935).
(6) Wellings, A. W., *Trans. Faraday Soc.*, 28, 561–4 (1932).

Received September 9, 1938.

Glass Electrode for Determining Blood pH at 38° C.

M. K. HORWITT
Biochemical Research Laboratory, Elgin State Hospital, Elgin, Ill.

THE procedure for estimating the pH of blood under anaerobic conditions can be facilitated by building a glass electrode into the barrel of a hypodermic syringe. (This hypodermic electrode is now made by Rascher and Betzhold, Inc., Chicago, Ill.) The determination can then be made directly on blood drawn into the syringe within one minute after collection. Any size of barrel may be used, but the 1.5-cc. size has been found most convenient in this laboratory.

The plungers on the market are made of a heat-resisting glass, which will not fuse to Corning 015; therefore, it is necessary to grind a 7.5-cm. (3-inch) length of soft-glass tubing until it fits the barrel to be used. This is easily accomplished with the aid of a turning lathe, using fine silicon carbide powder as an abrasive. One end of this tube is closed off with a thin layer of Corning 015; the maximum thickness of this layer will depend on the measuring instruments employed. One of the author's electrodes, which has a membrane about 0.25 mm. thick, used in conjunction with a Beckman pH meter, has lasted for more than 5 months, during which time several hundred determinations have been made.

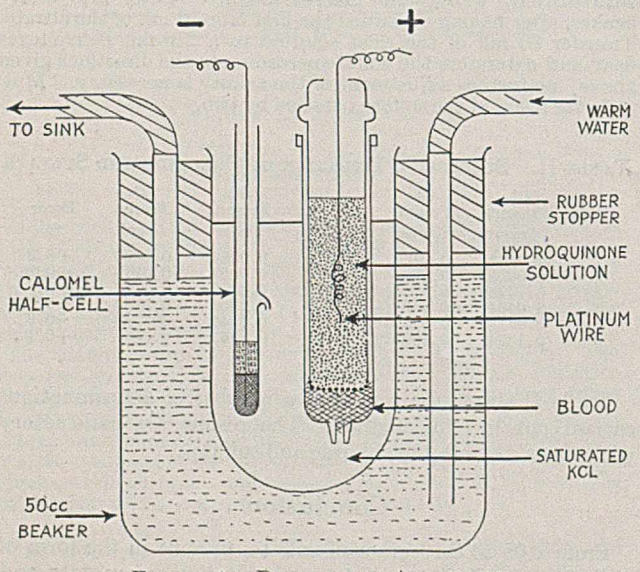


FIGURE 1. DIAGRAM OF APPARATUS
Corning 015 glass indicated by dotted line

The procedure for determining the pH of blood with this electrode is as follows:

The plunger (after a preliminary soaking in 0.1 *N* hydrochloric acid for 24 hours) is half filled with a solution of 0.1 *N* hydrochloric acid containing a slight excess of quinhydrone, and inserted into the barrel on which the metal clip for holding the plunger in place has been retained. Sufficient neutral sterile isotonic saline solution is then drawn into the syringe with needle attached to fill the air spaces in the needle and between the end of the plunger and the barrel. One drop of saline solution will fill all the air spaces in a well-constructed electrode. The syringe is then held in the hand for a few minutes to raise the temperature of the quinhydrone solution. About 1 cc. of blood is drawn into the syringe, all but about 0.2 cc. of which is immediately expelled, the needle is removed, and the syringe is half immersed in a saturated potassium chloride solution at 38° C. The potassium chloride solution serves as both the salt bridge and the constant-temperature bath as illustrated in Figure 1. A small calomel half-cell is kept in the potassium chloride bath during the procedure. A small thermometer (not shown in diagram) is also kept in the potassium chloride solution. Sufficient warm water at about 40° C. is siphoned to the 50-cc. beaker to keep the contents at 38° C. Placing the 50-cc. beaker in a 100-cc. beaker helps to insulate the contents.

A steady e. m. f. should be obtained within 2 minutes after immersion of the electrode in the potassium chloride solution, the time being dependent on the difference in temperature between the glass electrode and the calomel half-cell. Readings taken more than 5 minutes after withdrawal of the blood from the vein are not to be trusted because of an acid shift which becomes appreciable at that time. No acid shift is observed in blood within the first 3 minutes if the temperature is carefully controlled. Clotting does not have a measurable effect on the observed pH (*1*).

If one is careful to check each electrode with standardized buffers before and after each series of determinations, an accuracy of better than 0.02 pH unit may be obtained.

Literature Cited

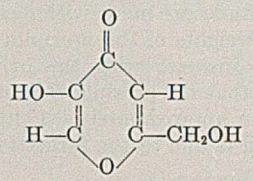
(1) Ferguson, J. H., and DuBois, D., *J. Lab. Clin. Med.*, 21, 663–9 (1936).

Received July 6, 1938. Demonstrated at Baltimore meeting of American Society of Biological Chemists, April, 1938.

Copper Precipitation Method for Kojic Acid Determination

H. N. BARHAM
Kansas State College, Manhattan, Kans.

KOJIC acid, 2-hydroxymethyl-5-hydroxy-γ-pyrone, may be produced in quantity by the proper fermentation of glucose and xylose solutions with members of the *Aspergillus flavus-oryzae* groups of molds. Interest in it has been shown because of its possible utilization for industrial purposes. Its accepted structural formula is:



Several methods have been employed for its quantitative estimation, the merits of which depend upon the quantity of the compound present and the nature of the investigation. Tamiya (*9*) and Corbellini and Gregorini (*6*) used a colorimetric method based upon the intense red coloration produced when kojic acid is treated with ferric chloride. Challenger, Klein, and Walker (*5*) repeatedly extracted culture media and washings with ether and weighed the product. Birkinshaw and Raistrick (*4*) developed a method of oxidizing kojic acid with an alkaline solution of iodine which is suitable in the presence of glucose, provided the analysis for glucose is made independently. In the absence of other acids, kojic acid may be determined with fair accuracy by titrating its solutions with dilute alkali, using alizarin orange R (*8*) or phenolphthalein (to full red color over a source of diffused light) (*3*) as indicators.

TABLE I. EFFECT OF VARIATION OF COPPER ACETATE CONCENTRATION

0.72 *N* Copper Acetate	No Alkali			Neutral			Equivalent Alkali		
	Copper kojate	CuO	Filtrate pH	Copper kojate	CuO	Filtrate pH	Copper kojate	CuO	Filtrate pH
Cc.	*Gram*	%		*Gram*	%		*Gram*	%	
2	0.1715	22.9	4.2	0.1740	22.7	5.9	0.1742	22.9	6.4
5	0.1647	22.8	5.0	0.1667	23.0	6.0	0.1706	23.8	6.0
10	0.1564	22.9	5.2	0.1566	23.6	5.7	0.1567	23.3	5.8
15	0.1459	23.3	5.2	0.1471	23.2	5.6	0.1467	23.0	5.6
20	0.1345	23.3	5.2	0.1353	23.1	5.5	0.1372	23.4	5.5
25	0.1175	23.2	5.2	0.1266	23.4	5.4	0.1275	23.4	5.5

For most purposes, the most convenient and accurate method is to precipitate the kojic acid from its neutralized solutions with dilute copper acetate and weigh the dried copper kojate. May, Moyer, Wells, and Herrick (*8*) used this method in their experiments; their assumption that the copper salt was the half-hydrate, $(C_6H_5O_4)_2Cu.{}^1/_2H_2O$, was based upon their value of 22.40 per cent of copper oxide in the salt. Maurer (*7*) found 22.12 per cent of copper oxide which is approximately midway between the values corresponding to the half-hydrate and monohydrate. The molecular formulas, $(C_6H_5O_4)_2Cu$ and $(C_6H_5O_4)_2Cu.H_2O$, have been reported by Yabuta (*11*) and Traetta-Mosca (*10*), respectively.

For several years, the author and others (*1*, *2*, *3*) have found it satisfactory to assume that copper kojate precipitates as the half-hydrate. In making the determination, no predetermined quantity of the copper acetate precipitant was added although it was common practice to add what was believed to be a small excess. More recent experience with the method, especially in the analysis of certain derivatives of kojic acid which retain the acidic character of the parent compound (*1*), gave the impression that the excess of precipitant is an important factor in the accuracy of the method. This raised a question as to the validity of the assumption of the half-hydrate. It was thought desirable, therefore, to investigate this factor as well as other conditions surrounding the precipitation of copper kojate and the treatment of the precipitate before weighing.

Experimental

PRECIPITATION AND COPPER OXIDE DETERMINATIONS. Unless otherwise stated, all precipitations were made in quadruplicate from solutions having a total volume of approximately 75 cc. and the data given are averages. The precipitates were filtered and washed in Gooch crucibles prepared with all the care required by the usual quantitative procedure. The accuracy of the work with Gooch crucibles was checked against that of fritted glass crucibles of the Gooch type with respect to both the precipitates themselves and the copper oxide derived from them. The copper oxide percentage was determined by igniting the precipitates to constant weight at ca. 525° C. Copper oxide percentages determined by ignition agreed closely with those determined by iodometry.

KOJIC ACID. The kojic acid used in these experiments was carefully purified by repeated crystallizations from water and alcohol, followed by extraction with chloroform. The chloroform-extracted kojic acid had a melting point of 152–3° C. In all cases, 10-cc. aliquots of 0.1 *N* kojic acid were precipitated and the weights of copper kojate were reported on that basis. The calculated weight of anhydrous copper kojate derivable from this quantity of kojic acid is 0.1729 gram; its calculated copper oxide percentage is 23.01 per cent.

SODIUM HYDROXIDE. It was necessary to titrate the solutions with standard alkali before precipitation to bring the pH within the required range and, more especially, to ascertain the maximum kojic acid concentration so that the proper excess of precipitant could be added. The 0.1 *N* sodium hydroxide solution used was freshly prepared, since solutions which have stood indefinitely give high results due to silicates dissolved from glass containers.

PRECIPITANT. The cupric salt to be used as the precipitant must be the salt of a weak acid such as copper acetate. Copper sulfate, for instance, lowers the pH prevailing at the time of precipitation, to the extent that an appreciable fraction of the copper kojate remains in solution. The standard stock solutions of copper acetate were filtered before using to avoid the addition of any basic salt which may have formed on standing. Five cubic centimeters of the precipitant (0.3 or 0.72 *N* copper acetate) were added in each experiment except those in which the concentration of copper acetate was varied.

EFFECT OF VARIATION OF COPPER ACETATE. The concentration of copper acetate was varied in solutions to which no alkali had been added, in those which had been made neutral with alkali (pink color of phenolphthalein), and in those to which the equivalent of alkali (full red color of phenolphthalein) had been added. The results of this variation are presented in Table I.

EFFECT OF BUFFERING WITH SODIUM ACETATE. For experiments involving the variation of sodium acetate concentrations, the two smaller copper acetate concentrations of Table I—2 cc. (ca. 5 cc. of 0.3 *N*) and 5 cc. of 0.72 *N*—were chosen; nothing was to be gained by using still greater concentrations. Sodium acetate solutions (10-cc. portions, or the equivalent) with the approximate normalities 0.1, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 6.0, and 8.0 were added to the solutions to be buffered after they had been titrated with 0.1 *N* sodium hydroxide to the pink color of phenolphthalein. pH measurements were made with a Coleman pH electrometer. The results are given in Table II.

SOLUBILITY OF COPPER KOJATE IN WATER. A quantity of copper kojate was prepared by adding a slight excess of copper acetate to a solution of kojic acid at a pH of about 4.0. The dry salt contained 22.8 per cent of copper oxide by ignition and by iodometry. Samples of this copper kojate were stirred with distilled water for 12 hours and the resulting suspensions filtered, dried, and weighed. There was no change in the weights of the samples nor had sufficient salt dissolved for the filtrate to give a perceptible color with ferric chloride (this test for kojic acid is sensitive to 1/200,000) or with ammonium hydroxide.

TABLE II. EFFECT OF BUFFERING WITH SODIUM ACETATE

Normality of Sodium Acetate	5 cc. of 0.3 *N* Copper Acetate			5 cc. of 0.72 *N* Copper Acetate		
	Copper kojate	CuO	Filtrate pH	Copper kojate	CuO	Filtrate pH
	Gram	%		*Gram*	%	
0.1	0.1739	22.9	5.9	0.1682	23.3	5.8
0.5	0.1742	23.0	6.3	0.1684	23.3	6.1
1.0	0.1742	22.7	6.6	0.1690	23.5	6.3
1.5	0.1742	22.8	6.7	0.1742	24.4	6.4
2.0	0.1738	22.7	6.8	0.1744	24.4	6.5
3.0	0.1742	22.8	7.0	0.1800	25.6	6.7
4.0	0.1740	22.8	7.2	0.1802	25.9	6.9
6.0	0.1739	22.7	7.4	0.1822	25.9	7.0
8.0	0.1743	22.8	7.6	0.1826	26.0	7.2

PRECIPITATION PERIOD. In order to determine the time required for complete precipitation of copper kojate without basic salt formation, kojic acid solutions, to which had been added the equivalent of 0.1 *N* sodium hydroxide, were precipitated by the addition of 5 cc. of 0.3 *N* copper acetate. The precipitates were filtered off at intervals, then dried, and weighed. The results are shown in Table III.

TABLE III. PRECIPITATION PERIOD

Hours	Copper Kojate *Gram*
2	0.1570
4	0.1634
6	0.1662
8	0.1669
24	0.1710
36	0.1732
48	0.1740
60	0.1741
72	0.1738

DRYING OF PRECIPITATES. Ten cubic centimeters of 0.1 *N* kojic acid should give 0.1729 gram of copper kojate on the basis of the anhydrous salt. Drying *in vacuo* over calcium chloride gave constant weights which averaged approximately 0.1740 gram. Drying in an air oven from 6 to 8 hours at 100° C. also gave weights which averaged approximately 0.1740 gram but with slightly more variation between individual weights. After drying in an air oven for 16 to 24 hours at 100° C. the weights averaged 0.1728 gram but the individual differences were still greater. Continued heating in an air oven at 100° C. or above showed that slow decomposition of the copper kojate occurs and that the resulting weights depend upon the temperature recorded by the oven and the period of heating. However, prolonged drying *in vacuo* at 100° C. gave weights which averaged 0.1736 gram. Heating later at 105° C. *in vacuo* showed no further change in the weights. Twelve samples, from which this average was calculated, weighed 0.1737, 0.1733, 0.1736, 0.1738, 0.1735, 0.1738, 0.1735, 0.1737, 0.1734, 0.1740, 0.1736, and 0.1733 gram, with a spread of 0.0007 gram. This serves to illustrate the distribution and maximum spread of weights which may be expected when the samples are dried without decomposition. Higher temperatures *in vacuo* which might have given constant weights corresponding to the anhydrous salt (0.1729 gram) were not used. If this could be done without decomposition, it might be expected that individual weights would check even more closely.

Copper kojate samples which have been dried *in vacuo* or in an air oven exhibit no tendency to absorb moisture while standing in air for 24 hours.

Discussion

For an adequate test of the suitability of this method for kojic acid determination, it is regarded as sufficient to establish conditions which permit the complete precipitation of copper kojate without basic salt formation. This information would also make it possible to estimate the extent of hydration of copper kojate.

Copper kojate is practically insoluble in distilled water and in relatively large concentrations of sodium acetate (Table II), since increasing quantities of sodium acetate have no effect on the quantity of copper kojate obtained from 10 cc. of 0.1 *N* kojic acid. However, copper acetate does exert a solvent action on copper kojate proportional to the excess of copper acetate in solution (Table I). Therefore, so far as these experiments are concerned, there is complete precipitation of kojic acid as copper kojate from solutions containing approximately 0.142 gram of kojic acid in 75 cc. and no more than 50 per cent excess of copper acetate.

An inspection of Table II will show also that, in experiments in which 10 cc. of 0.1 *N* kojic acid were precipitated by the addition of 5 cc. of 0.3 *N* copper acetate, the weights of the precipitates as well as the copper oxide percentages are constant within the pH range of 6.0 to 7.5. However, if similar precipitations are made with 5 cc. of 0.72 *N* copper acetate, both the weights of the precipitates and the copper oxide percentages increase with the pH. The conclusion follows, therefore, that the precipitation of weights of copper kojate greater than approximately 0.1740 gram from 10 cc. of 0.1 *N* kojic acid is due to the formation of basic salts of kojic or acetic acids.

TABLE IV. REPORTED FORMS OF COPPER KOJATE

Form of Copper Kojate	Copper Kojate *Gram*	Copper Oxide %
$(C_6H_5O_4)_2Cu$	0.1729	23.01
$(C_6H_5O_4)_2Cu.{}^1/_2H_2O$	0.1774	22.43
$(C_6H_5O_4)_2Cu.H_2O$	0.1819	21.87

Mention was made above of the different forms of copper kojate which have been reported. Which of these forms is the true one may be determined by the maximum weight of normal copper kojate obtainable from a given quantity of kojic acid. For purposes of comparison, the calculated weights of the different forms of copper kojate and corresponding copper oxide percentages equivalent to 10 cc. of 0.1 *N* kojic acid are given in Table IV. In every instance where weights of the order of 0.1774 or 0.1819 gram were obtained, there was evidence of basic salt formation. The experimental values, 0.1740 gram of copper kojate and 22.8 per cent of copper oxide, agree more closely with corresponding values of anhydrous copper kojate than with those of the half-hydrate or monohydrate. When it is recalled that copper kojate exhibits no tendency to form hydrates at room temperature and, also, that prolonged drying *in vacuo* at 100° to 105° C. reduces slightly the average copper kojate weights without decomposition, it appears a justifiable conclusion that, under the proper conditions, kojic acid is precipitated as anhydrous copper kojate containing a small quantity of strongly adsorbed water.

Summary

The copper precipitation method, when properly carried out, is an accurate method for the estimation of kojic acid. The solutions to be analyzed should be titrated first with standard alkali to the full red color of phenolphthalein, diluted until the kojic acid concentration is approximately 0.142 gram in 70 cc., and dilute copper acetate added in an excess which does not exceed 50 per cent of the amount determined by titration. At least 48 hours are required for complete precipitation, after which the precipitates are removed by filtration, washed, dried, and weighed as anhydrous copper kojate, $(C_6H_5O_4)_2Cu$. The precipitates may be dried without decomposition *in vacuo* over calcium chloride or in a vacuum oven at 100° to 105° C. The pH of the solution is not critical; it is sufficient to keep the filtrates within the pH range of 6.0 to 7.5.

Literature Cited

(1) Barham, H. N., and Reed, G. N., *J. Am. Chem. Soc.*, 60, 1541–5 (1938).
(2) Barham, H. N., and Smits, B. L., IND. ENG. CHEM., 28, 567–70 (1936).
(3) Barham, H. N., and Smits, B. L., *Trans. Kansas Acad. Sci.*, 37, 91–113 (1934).
(4) Birkinshaw, J. H., and Raistrick, H., *Trans. Roy. Soc.* (London), B220, 139–52 (1931).
(5) Challenger, F., Klein, L., and Walker, T. K., *J. Chem. Soc.*, 1929, 1498–1505.
(6) Corbellini, A., and Gregorini, B., *Gazz. chim. ital.*, 60, 244–56 (1930).
(7) Maurer, K., *Ber.*, 63B, 25–34 (1930).
(8) May, O. E., Moyer, A. J., Wells, P. A., and Herrick, H. T., *J. Am. Chem. Soc.*, 53, 774–82 (1931).
(9) Tamiya, I. H., *Acta Phytochim.* (Japan), 3, 51–173 (1927).
(10) Traetta-Mosca, F., *Ann. chim. applicata*, 1, 477–92 (1914).
(11) Yabuta, T., *J. Coll. Agr. Imp. Univ. Tokyo*, 5, No. 1, 51–8 (1912).

RECEIVED September 2, 1938. Contribution No. 230, Department of Chemistry.

Determination of Active Ingredients and Fatty Matter in Surface-Active Agents

RALPH HART
The Hart Products Corp., 1440 Broadway, New York, N. Y.

THE discovery that a sulfo group on a primary carbon of an aliphatic chain of the proper molecular weight, which may or may not be condensed with an aryl group, produces compounds that possess sudsing and scouring properties has led to a flood of patents on synthetic detergents. A good many such compounds are now on the market and their applications in the industries are already extensive and increasing. The synthetic surface-active agents are preferred to soap in numerous industrial operations, particularly in those processes where hard water is used or where the alkalinity due to the hydrolysis of soap is objectionable. Practically all the products available commercially contain considerable quantities of Glauber's salt, because of the process of manufacture or admixture where the product is marketed in the form of a powder. They are usually sold on an "as is" or performance basis, hardly ever on their content of active ingredients. No reliable method for estimating the effective ingredients in such products seems to have been described in the literature.

A method is here outlined for the determination of active ingredients in true sulfonic compounds and in sulfuric acid esters. It is applicable to such products as the sulfated fatty alcohols, sulfonated fatty acid amides or esters, sulfonated alkyl naphthalenes, sulfonated mineral oils, etc., and to the older type of sulfonated oils, such as sulfated castor or olive oil, sulfated oleic acid, sulfated tallow, etc. In the case of the latter type, the trade is accustomed to evaluate a given product by its content of fatty matter. The new method does not determine the fatty matter directly but it may readily be calculated from the active ingredients. The new method is not so convenient nor rapid, but the results are believed to be more accurate than those obtained by the usual method of acid hydrolysis and extraction; the fatty matter during hydrolysis may undergo various changes, such as loss of glycerol, formation of lactones and lactides, polymerization, re-esterification, etc., all of which affect the final weight of the fatty matter in both directions, the net effect depending upon the conditions of the hydrolysis and the nature of the sample. The new method consists essentially of extracting the active ingredients with solvents over a concentrated salt solution, evaporating the solvent, heating the residue to constant weight, and determining the loss in weight upon ashing the residue.

Procedure

RESIDUE BEFORE ASHING. The combined solvent layers from the determination of organically combined sulfuric anhydride by the ammonia method (*1*) are transferred to a tared 150-ml. beaker. The solvent is evaporated and the residue heated at 105° to 110° C. to constant weight.

In the case of sulfuric acid esters it is necessary to stabilize the oil with alkali before heating; otherwise the residue turns black because of decomposition. For ordinary sulfated oils, the addition of 2 ml. of 0.5 *N* alcoholic potash is sufficient to effect stabilization; with highly sulfated oils, double that quantity is required. The first sign of decomposition is when the residue begins to turn red, owing to the effect of the liberated sulfuric acid on the methyl orange present in the oil. With sulfonic compounds the use of alkali is not required.

A more rapid means of reaching constant weight is to heat the beaker, after practically all the solvent has been evaporated on a steam bath, in an oil bath at 135° C. with stirring for 15- to 20-minute periods. In that event the beaker should be provided with a tared glass rod. If the residue is very viscous or solid, an amount of oleic acid (previously heated for 10 minutes at 150° C.) approximately equal to the weight of the residue is added. This serves to liquefy the residue and hasten evaporation of the solvent.

RESIDUE AFTER ASHING. The residue is quantitatively transferred to a tared crucible, preferably platinum. Traces of the residue in the beaker are wiped clean with ashless filter paper moistened with solvents and finally with hot water, and the several pieces of filter paper are added to the crucible. The contents of the crucible are burned off and finally ignited until practically all the carbon is consumed; if necessary, the residue may be treated several times with small quantities of 30 per cent hydrogen peroxide. The ash is then treated with 2 ml. of concentrated sulfuric acid, the acid is evaporated, and the residue is ignited strongly until the weight is constant, preferably with a blast burner.

TOTAL ACTIVE INGREDIENTS. The difference in weight before and after ashing represents the loss of organic matter plus sulfur trioxide in the case of ester compounds or sulfur dioxide in the case of sulfonic compounds, in accordance with the following reactions:

$$\underset{\text{Active ingredients: ester compounds}}{2ROSO_3Na} = Na_2SO_4 + \underset{\text{Loss upon ignition}}{(SO_3 + CO_2, \text{ etc.})}$$

$$\underset{\text{Active ingredients: sulfonic compounds}}{2RSO_3Na} = Na_2SO_4 + \underset{\text{Loss upon ignition}}{(SO_2 + CO_2, \text{ etc.})}$$

TABLE I. TOTAL FATTY MATTER AND TOTAL ACTIVE INGREDIENTS IN SULFURIC ACID ESTERS

	Total Fatty Matter — New method			Total Fatty Matter — Acid-decomposition method			Total Active Ingredients, New Method		
	I	II	Av.	I	II	Av.	I	II	Av.
	%	%	%	%	%	%	%	%	%
Sulfated oleic acid	61.6	61.8	61.7	61.5	61.4	61.5	66.5	66.8	66.7
Sulfated castor oil	60.6	60.3	60.5	60.9	60.5	60.7	65.6	65.3	65.5
Sulfated tallow	83.4	83.1	83.3	82.9	83.0	83.0	86.6	86.3	86.5
Sulfated blended oil[a]	76.9	76.8	76.9	76.4	76.7	76.6	80.3	80.2	80.3
Highly sulfated castor oil	31.7	31.3	31.5	31.6	31.4	31.5	40.2	39.8	40.0
Sulfated fatty alcohol[b]	23.5	23.6	23.6	23.5	23.8	23.7	31.4	31.5	31.5

[a] Used in spinning rayon.
[b] Oleyl and cetyl alcohols.

TABLE II. LOSS UPON IGNITION OF PURIFIED SAMPLES OF SULFONIC COMPOUNDS AND TOTAL ACTIVE INGREDIENTS

	Loss upon Ignition, Purified Sample		Total Active Ingredients, Sample "As Is," New Method		
	New method, av.	Direct ignition, av.	I	II	Av.
	%	%	%	%	%
Fatty acid amide sodium sulfonate	85.8	85.0	27.6	27.3	27.5
Alkyl naphthalene sodium sulfonate	78.4	78.7	64.9	64.6	64.8
Alkyl aryl sodium sulfonate	80.2	79.9	34.6	34.8	34.7

Sulfuric acid is added to the ash in order to convert into sulfates the sulfides and sulfites which are formed upon ignition. The above reactions show that the total active ingredients for both types of compounds, represented by the right-hand side of the equations, are equal to the "loss upon ignition" plus one-half of the combined sulfuric anhydride as sodium sulfate. Hence, the total active ingredients may be calculated from the combined sulfuric anhydride and "loss upon ignition" (corrected as shown below) as follows:

1. Total active ingredients, per cent

$$= \frac{100 \times \text{loss upon ignition (corrected)}}{\text{weight of sample}} + \frac{Na_2SO_4}{2SO_3} \times \% \text{ combined } SO_3$$

$$= 0.8875 \times \% \text{ combined } SO_3 + 100 \times \frac{\text{loss upon ignition (corrected)}}{\text{weight of sample}}$$

Where alcoholic potassium hydroxide had been added, the loss in weight upon ignition is too high by an amount equal to (K − H) and too low by the corresponding amount of potassium sulfate. The corrections for these two items are made as follows:

Correction for (K − H), in grams

$$= -\left[\frac{(K - H)}{KOH} \times \frac{\text{mg. of KOH added}}{1{,}000}\right]$$

$$= -(0.0006774 \times \text{mg. of KOH added})$$

Correction for K_2SO_4, in grams

$$= \frac{K_2SO_4}{2KOH} \times \frac{\text{mg. of KOH added}}{1{,}000}$$

$$= 0.001552 \times \text{mg. of KOH added}$$

Total correction, grams

$$= -0.0006774 \times \text{mg. of KOH added} + 0.001552 \times \text{mg. of KOH added}$$

$$= +0.0008746 \times \text{mg. of KOH added}$$

Total Fatty Matter

In calculating the fatty matter from the active ingredients in samples of sulfuric acid esters, it may be assumed that the latter upon hydrolysis yield a hydroxy group for every combined sulfuric anhydride split off, as follows:

$$\underset{\text{Active ingredients}}{ROSO_3Na} + H_2O = \underset{\text{Fatty matter}}{ROH} + NaHSO_4$$

Hence

$$\underset{\text{Fatty matter}}{ROH} = \underset{\text{Active ingredients}}{ROSO_3Na} - NaSO_3' + H$$

Consequently the fatty matter is given by the following formula:

2. Fatty matter, per cent

$$= \% \text{ active ingredients} - \frac{(NaSO_3' - H)}{SO_3} \times \% \text{ combined } SO_3$$

$$= \% \text{ active ingredients} - 1.275 \times \% \text{ combined } SO_3$$

$$= 100 \times \frac{\text{loss upon ignition (corrected)}}{\text{weight of sample}} - 0.3875 \times \% \text{ combined } SO_3$$

From the last formula, it will be noted that an error of 1 per cent in the combined sulfur trioxide determination will affect the fatty matter by less than 0.4 per cent.

Experimental

SULFURIC ACID ESTERS. The fatty matter in sulfuric acid esters by the new method compared with the fatty matter obtained by the acid-decomposition method is given in Table I, in which also the total active ingredients are listed.

SULFONIC ACIDS. A number of different true sulfonic compounds were dissolved in a small quantity of water and acidified with sulfuric acid, and the solutions were evaporated to dryness. The residues were then dissolved in hot alcohol, filtered, and again evaporated to constant weights. A portion of each residue was then extracted according to the new method and the loss in weight upon ashing was determined. This was compared with the loss in weight upon direct ashing of the rest of the residue. The results are given in Table II which also includes the total active ingredients contained in the original samples.

It is evident that in the case of sulfonic compounds the loss of organic matter plus volatile sulfur (upon which the new method for active ingredients depends) may be determined directly by ashing the original sample, provided the moisture in the sample is known and there is no other salt present than sodium sulfate. This is also true of the sulfuric acid esters, but, in addition to the above, it is necessary to know the alkalinity of the sample and whether or not the alkali is sodium or potassium.

Summary

An accurate method for the determination of active ingredients in sulfuric acid esters and sulfonic compounds is outlined. This depends upon extracting the active ingredients, which may be contaminated with sodium sulfate but no other salts, and determining the loss in weight upon ignition. A method is also given for the determination of fatty matter in sulfuric acid esters, provided the organically combined sulfuric anhydride is known.

Acknowledgment

The writer is greatly indebted to Virginia Raison of this laboratory for assistance with the analytical work and to H. W. Elley, associate chemical director of E. I. du Pont de Nemours & Co., Inc., for a sample of 2-naphthalenesulfonic acid.

Literature Cited

(1) Hart, R., IND. ENG. CHEM., Anal. Ed., 10, 688 (1938).

RECEIVED August 13, 1938.

Viscometer for Routine Determination of Proteolytic Activity of Malts

JOHN R. KOCH, ORLANDO NELSON, AND LAWRENCE EHRNST
Marquette University, Milwaukee, Wis.

The apparatus is very simple to construct and use. One temperature (40° C.) is used for standardization, extraction, digestion, and viscosity determinations. Better timing visibility is obtained. Absolutely constant volume is assured during a series of readings.

No aliquot parts are taken from a changing substrate after digestion is started, no transfer of hot liquids to the viscometer is required as specified for the gelatin industry, there is no clogging due to evaporation at the tip, and intermediate cleaning is unnecessary between samples in a run.

The simple design of the viscometer permits three simultaneous runs in less than 2 hours. The filled viscometer can be inverted at once, making accurate extrapolations possible. No buffering is required. The proteolytic activity value increases with the amount of enzyme. One minute of digestion corresponds to one point of activity.

THE present paper is a continuation of work done at Marquette University on various materials containing proteolytic enzymes, as a result of which a paper was published on the use of gelatin as a substrate for measuring enzyme activity of commercial bating preparations (*6*). In this work the modified Bloom viscometer was used as standardized for the glue and gelatin industry.

As an outgrowth of this work, the viscometers as shown in Figure 1 were developed, for the purpose of eliminating as many sources of error as possible and making the operation extremely simple. During these experiments Ehrnst suggested that the viscometer could be nicely adapted to the determination of the proteolytic activity of malt.

Robert Wahl, basing his work on research done by Nilson (*4*), found that malt infusions prepared with water acidified with a small amount of bacterial lactic acid (0.1 to 2 per cent) would liquefy gelatin to a greater degree than did aqueous extracts. Commercial lactic acid and inorganic acids yielded no increase in proteolytic activity. Wahl used diluted solutions of pepsin (1 to 10,000 strength) as a standard for comparison, allowing them to react on the gelatin under the same conditions as the malt infusions. Later he modified this method of comparison (*12*), and more recently A. Wahl has introduced papain as a standard for comparison (*10*).

The authors' method of extraction followed the procedure of Wahl (*12*) except that no lactic acid was used. As an indication of proteolytic activity, the viscosity of gelatin was used instead of setting time. In 1937 Laufer (*3*) determined the proteolytic activity of malt by means of a gelatin viscosity method and an Ostwald pipet. Although the viscosity of gelatin has often been used to estimate proteolytic activity (*1*, *5*, *6*, *13*), Wahl (*12*) and Laufer (*3*) seem to have been the first to adapt these methods to malt.

An extensive bibliography on the determination of proteolytic activity in general is given by Orthmann, Surak, and Koch (*6*), and with the paper by Laufer which brings the literature on malt up to date (*3*) furnishes a rather complete survey of the literature.

The purpose of the present investigation has been to adapt the new viscometer to the routine determination of the proteolytic activity of malts.

Need for Simple Method of Determining Proteolytic Activity of Malts

The presence of nitrogenous or albuminoid substances has considerable effect on the finished product in regard to clarity (*7*), chill-proofing (*7*), body, and flavor (*11*). Because many of the substances which are added to beers to prevent haziness when chilled are actually enzymes, a knowledge of the proteolytic activity of a malt is important to the maltster as well as to the brewer. It is possible to determine the

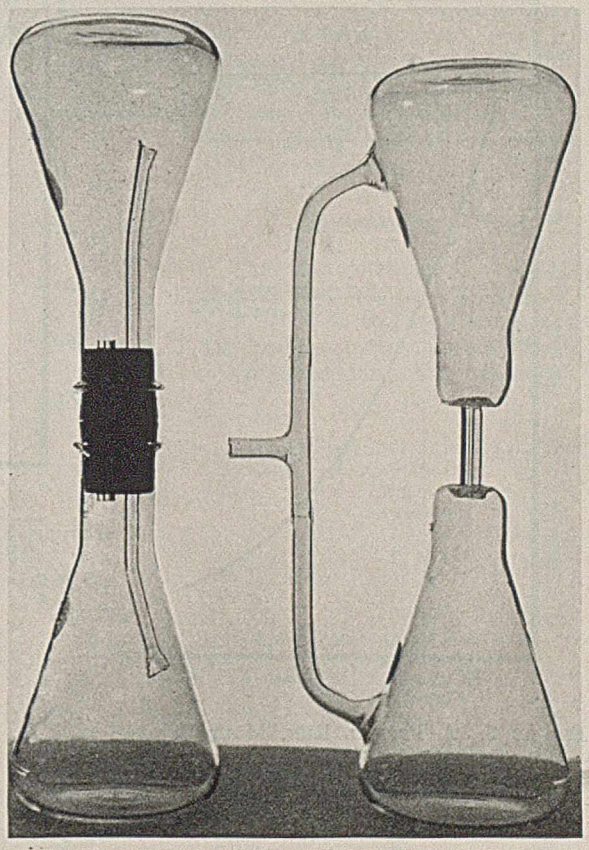


FIGURE 1. VISCOMETERS
Left. With rubber stopper
Right. All-glass type

proteolytic strength of malt and then to arrive at a clue as to its processing.

No method for determining proteolytic activity up to the present time has been simple or rapid enough to be generally adopted by malt or brewing laboratories. The viscometer presented herewith is as simple to operate as the ordinary kitchen egg-timer and the apparatus can be constructed in any laboratory without the aid of a glass blower. The determination is designed to meet the needs of a malting or brewing laboratory.

The method is based on the well-known principle that the viscosity of gelatin decreases as it is attacked by a proteolytic enzyme (*1, 3, 5, 6, 13*).

The viscometer consists of two Erlenmeyer flasks connected at the necks with a capillary tube. An air tube is provided so that no pressure will be built up in either flask as the viscometer is tilted back and forth. In the type made up with rubber stoppers the air tube is inside the flasks. If determinations are to be made regularly, the all-glass type can be made (Figure 1, right). In either case, the capillary should have a bore of about 1.5 mm. and be from 2.5 to 3.7 cm. in length. At room temperature 50 cc. of water should go through the capillary in the neighborhood of 35 or 36 seconds. This can be ascertained in advance and a different length or a different bore chosen, so that the finished viscometer will have a convenient and accurate time of flow.

The standardization is made at the same temperature as the experimental viscosity determinations and all factors such as volume, temperature, and pressure must necessarily remain constant throughout the entire series of determinations. If a number of viscometers are made from one piece of capillary tubing, their flow times will be found to be so close that check results or direct comparisons can be made. On the other hand, if the viscometers are not duplicated, the standardization takes care of all variations. Different laboratories can compare figures for proteolytic activities or the figures for proteolytic activity here given can be used as a standard, if reasonable care is taken to select a gelatin of approximately the same characteristics. Proteolytic values of several laboratories have been found to compare nicely, even with operators of very little training.

Comparison of the Proteolytic Activity of Malts

Preparation of 10 Per Cent Gelatin Solution. In the present experimental work a new gelatin solution was made for each determination. If extreme accuracy is not necessary, larger quantities can be made up and kept in the ice box for several days or even longer (*13*).

In order to prepare 250 cc. of 10 per cent gelatin, 25 grams of isinglass or other gelatin of good quality are sprinkled on top of about 125 cc. of distilled water at room temperature. The gelatin is stirred well and allowed to stand for a half hour. The beaker is now immersed in water held at a temperature of 60° to 65° C. and the gelatin stirred until dissolved. The contents of the beaker are transferred to a 250-cc. volumetric flask and the beaker is rinsed repeatedly with warm water. A 10 per cent solution is obtained by making up to the mark.

Preparation of Malt Infusion Containing Proteolytic Enzyme. A quantity of malt is finely ground in a Miag-Seck mill, 20 grams are transferred to a 250-cc. beaker, 100 cc. of distilled water at 40° C. are added, and the infusion is well stirred and placed in a water bath at 40° C. The infusion is stirred frequently for 0.5 hour, and then filtered. Thirty-five or 40 cc. are now placed in the water bath at 40° C. and allowed to stand for about 8 minutes. The following steps indicate the method of combining the malt infusion solution and the gelatin solution:

1. Twenty-five cubic centimeters of malt infusion at 40° C. are added to 50 cc. of 10 per cent gelatin solution at 40° C. and the time is noted. This is the so-called "zero" or initial time.
2. Fifty cubic centimeters of this infusion-gelatin mixture are placed in the viscometer (attempered at 40° C.) and a determination is made in 15 minutes from the zero time. The first run may be made sooner if desired. [The amount taken is actually 50 cc. plus the 1 or 2 cc. (accurately determined for each viscometer) trapped on the two sides of the viscometer because of the slight extension of the capillary. This extension of the capillary causes the gelatin to run freely from the tip without touching the sides of the Erlenmeyer.]
3. Subsequent determinations may be made every 15 minutes thereafter.
4. In practically all cases sufficient action has taken place in a 2-hour period to give a good graphic history.

Obviously, since all solutions are at 40° C. prior to and after mixing, temperature changes are held to an absolute minimum. A single temperature for extraction and di-

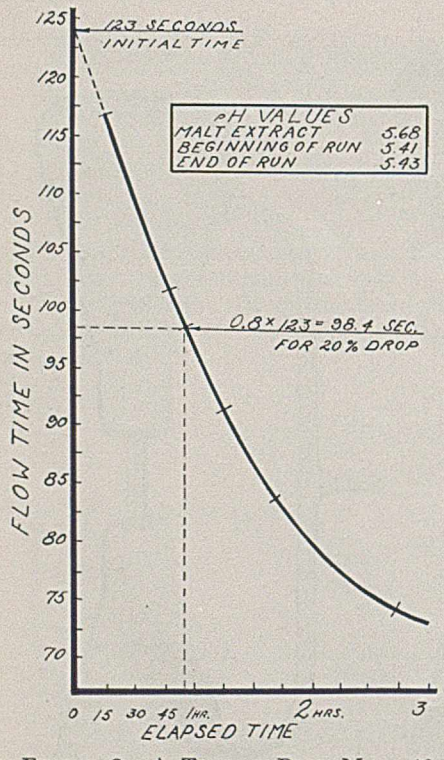


Figure 2. A Typical Run, Malt 10

pH at Beginning of Run, 5.41; at End of Run, 5.43. pH of Malt, 5.68. Viscometer 4

Run	Elapsed Time *Min.*	Flow Time *Sec.*
1	15	116.8
2	45	101.7
3	75	91.4
4	105	84.2
5	135	78.4
6	165	74.5

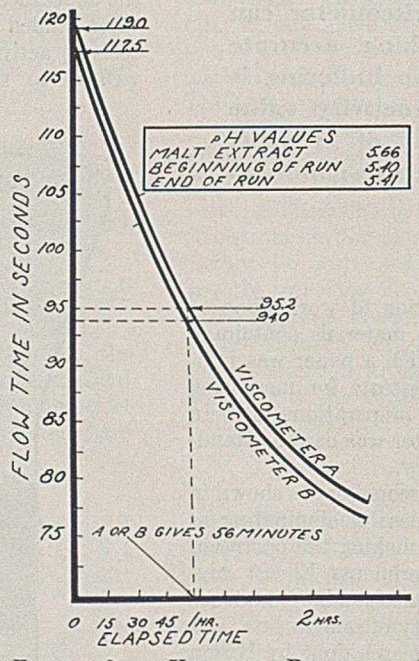
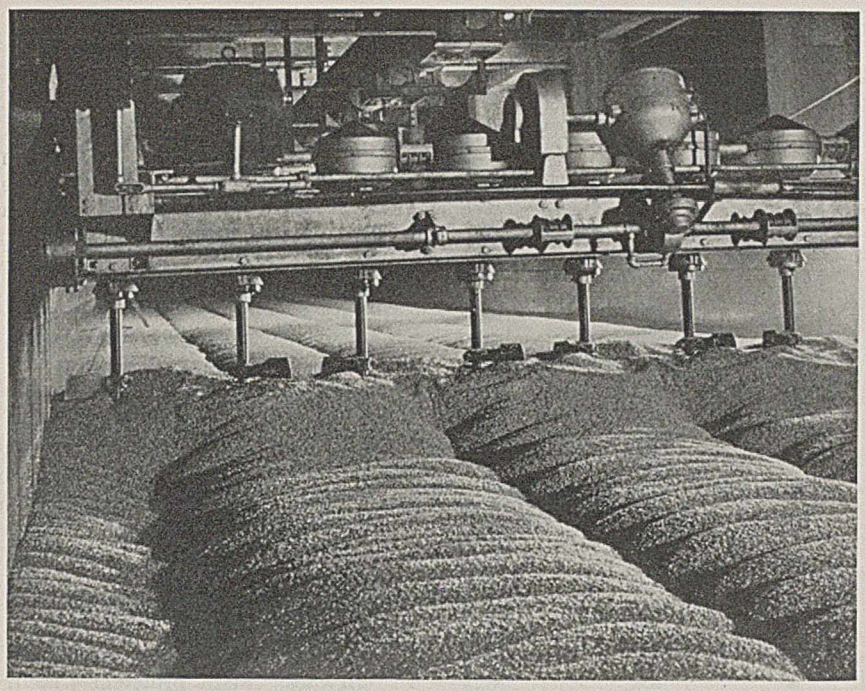


Figure 3. Viscosity Drop with Similar Viscometers

pH at Beginning, 5.40; at End, 5.41. pH of Malt, 5.66

Run	Elapsed Time *Min.*	Flow Time *Sec.*
	Viscometer A	
1	0	119.0
2	15	112.0
3	30	104.8
4	45	98.0
5	75	90.5
6	105	84.4
7	135	79.4
	Viscometer B	
1	0	117.5
2	15	109.6
3	30	102.2
4	45	97.2
5	75	89.8
6	105	82.5
7	135	78.0



GROWING FLOOR, SHOWING MECHANISM FOR TURNING GRAIN

gestion has proved very desirable, as it prevents error due to variation in temperature adjustment. The temperature should be high enough to hasten the action of the enzyme but should not exceed the temperature at which the enzyme is stable. The authors' experience with many hundreds of runs has placed this at 40° C.

A TYPICAL RUN. Although viscosities are best reported as kinematic viscosities, as outlined below, they can also be reported in terms of seconds for the 50-cc. flow through the viscometer. If viscometers of practically the same characteristics are made, the proteolytic activity of a series of enzymes can readily be compared without need for any standardization. Standardization and expression of results in kinematic viscosity are necessary only when using dissimilar viscometers, or when comparisons are to be made between different laboratories.

Figure 2 shows a typical run for a malt. Since the solution and viscometer are at 40° C., time of flow can be measured almost immediately after the viscometer has been put into the bath. As time elapses, the proteolytic enzymes of the malt break down the gelatin and its viscosity decreases (Figure 2). The dotted lines indicate the number of minutes required for a 20 per cent drop in viscosity. This is the number of minutes used to indicate the proteolytic strength of the malt in question.

Naturally the shorter the time taken to produce this 20 per cent drop in viscosity, the stronger the malt in proteolytic activity.

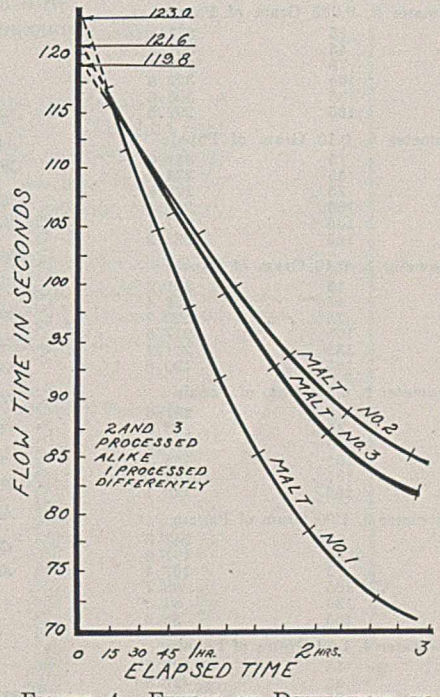


FIGURE 4. EFFECT OF DIFFERENCE IN PROCESSING
(See tables, *right*)

As indicated in Figure 2 (malt 10), initial time is obtained by extrapolating the graph. Numerous experiments have shown that this gives the same time of flow as a blank of gelatin and malt infusion boiled to kill the enzymes and therefore, in experimental runs, a blank determination is not necessary. The initial time gives a flow of 123 seconds, which multiplied by 0.8 gives 98.4 seconds as the time when the viscosity has decreased 20 per cent. Referring to the elapsed time on the horizontal axis, it required 55 minutes for this particular malt to produce a 20 per cent drop in viscosity.

Such figures will enable any purchaser of malts to arrange any number of samples in the order of their proteolytic activity.

MALT VALUES WITH LIKE VISCOMETERS. That the same lengths of capillary cut from the same piece will give very similar viscometers, and that these viscometers will give the same elapsed time for a 20 per cent drop in viscosity, are clearly indicated in Figure 3. The upper curve represents malt 8 in viscometer A, while the lower curve represents the same malt in viscometer B. In either case it required 56 minutes to produce a 20 per cent drop in viscosity.

EFFECT OF PROCESSING. In Figure 4 the curves for malts 2 and 3 are very similar. These malts were processed alike although they came from different sources. Malt 1 was made by a different process and has an entirely different slope to the curve. This set of curves shows that the graphic history of the digestion gives valuable information in addition to giving the minutes necessary for a 20 per cent drop.

Experimental Data

The maximum proteolytic activity of malt lies between pH of 5 and 6 (*3*, *13*).

In order to test the viscometer as to sensitivity, accuracy, and adaptability (it has been used for testing various gelatins

---

Run	Elapsed Time *Min.*	Flow Time *Sec.*
pH at Beginning, 5.36; at End, 5.12. Malt 1. Viscometer 3		
1	15	114.7
2	45	104.8
3	75	90.0
4	105	82.3
5	135	75.0
6	165	72.0
pH at Beginning, 5.39; at End, 5.38 Malt 2. Viscometer 2		
1	15	115.2
2	45	108.1
3	75	102.0
4	105	95.8
5	135	89.9
6	165	87.0
pH at Beginning, 5.41; at End, 5.48. Malt 3 Viscometer 4		
1	15	116.3
2	45	107.3
3	75	99.4
4	105	93.4
5	135	88.2
6	165	83.2

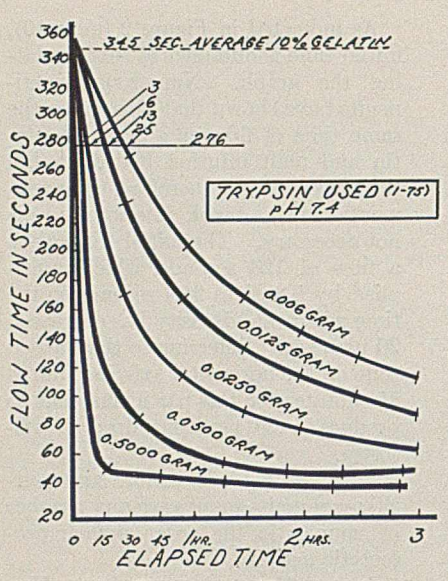


FIGURE 5. EFFECTS OF VARIOUS AMOUNTS OF TRYPSIN
(See tables, *right*)

1,000 Cc. of Substrate. 100 Grams of U. S. Gelatin 7A. pH of Gelatin, 7.4

Run	Elapsed Time *Min.*	Flow Time *Sec.*
Viscometer 4, 0.006 Gram of Trypsin		
1	15	320.0
2	45	231.8
3	75	185.6
4	105	163.4
5	135	147.5
6	165	134.3
Viscometer 2, 0.0125 Gram of Trypsin		
1	15	288.3
2	45	196.1
3	75	148.6
4	105	128.2
5	135	118.6
6	165	100.2
Viscometer 3, 0.0250 Gram of Trypsin		
1	15	228.6
2	45	137.8
3	75	105.6
4	105	92.1
5	135	82.6
6	165	78.2
Viscometer 2, 0.05000 Gram of Trypsin		
1	15	118.5
2	45	73.2
3	75	57.9
4	105	56.5
5	135	55.1
6	165	56.6
Viscometer 2, 0.5000 Gram of Trypsin		
1	15	46.8
2	45	44.3
3	75	42.8
4	105	41.8
5	135	42.0
6	165	42.8

and many types of proteolytic digestions), a large number of runs were made with pepsin, trypsin, and papain, chosen to cover a wide pH range. The series of curves for trypsin and papain (Figures 5 and 6) indicate that the viscometer gives very dependable results, since activity as determined corresponds to the amount of enzyme present. As a pure unbuffered gelatin was used, its viscosity was taken as initial viscosity and no extrapolation was required.

It is evident that a very satisfactory set of curves is obtained in each instance. Even though the amounts of enzyme differ but little, curves do not cross as they would if possible variables were not automatically kept constant by employing similar viscometers and method of making runs.

The extreme sensitivity is shown by the fact that the upper curve in Figure 5 contains 0.006 gram of trypsin per liter, representing an enzyme concentration of 6 parts per million of substrate.

CHOICE OF A 20 PER CENT VISCOSITY DROP AS THE STANDARD ENZYMATIC CHANGE. In working out a method of this sort it is exceedingly important to note for purposes of comparison the time necessary to produce a given change. As shown in Figures 5 and 6, it would be entirely unsatisfactory to compare the various amounts of activity produced in a given time. As the curves tend to become horizontal, there is very little change in viscosity for a considerable time. This use of comparative times necessary to produce a given change coincides with the views of Northrop and Hussey (*5*), Haldane (*2*), Tauber (*9*), Laufer (*3*), and others (*6*).

Figures 7 and 8, made from Figures 5 and 6, show very satisfactory agreement between observed and calculated time necessary to produce a 20 per cent drop in viscosity. It was found that a 10 per cent drop was too short a time for reaction, as slight variations in starting runs, transferring solutions, and temperature changes can produce some error. A 30 per cent viscosity drop is also very satisfactory, but there seems to be no justification for the extra time that would be required for runs.

CHOICE OF PH 5 TO 6 AS STANDARD FOR RUNS. In general the plant proteolytic enzymes seem to have a broader optimum activity curve than the animal proteolytic enzymes. Plant proteinases seem to center about an average pH of between 5 and 6 (*3*, *13*). These enzymes are all similar to papain and are often referred to as papainases. They have an optimum pH of from 4 to 7 (*9*). Laufer's work was done at a pH of 5 (*3*).

The authors' experience proved that the variation in activity for pH between 5 and 6 was within the magnitude of experimental error.

The pH at the beginning and end of a run varied only a few hundredths pH, showing that the gelatin was more than amply buffered for the determinations. These considerations simplify procedure to a great extent, as a gelatin with a pH of from 5 to 6 will surely give maximum activity, and buffering is entirely

1,000 Cc. of Substrate, 100 Grams of U. S. Gelatin 7A. pH of Gelatin 7.4

Run	Elapsed Time *Min.*	Flow Time *Sec.*
Viscometer 2, 0.050 Gram of Papain		
1	15	377.8
2	45	361.2
3	75	342.1
4	105	322.8
5	135	303.6
6	165	297.6
Viscometer 3, 0.10 Gram of Papain		
1	15	361.0
2	45	323.6
3	75	298.4
4	105	284.4
5	135	277.1
6	165	263.2
Viscometer 3, 0.40 Gram of Papain		
1	15	321.2
2	45	258.4
3	75	226.1
4	105	217.8
5	135	201.4
6	165	190.8
Viscometer 2, 0.50 Gram of Papain		
1	15	287.6
2	45	218.3
3	75	178.2
4	105	158.3
5	135	144.2
6	165	140.1
Viscometer 3, 1.00 Gram of Papain		
1	15	243.8
2	45	137.6
3	75	107.4
4	105	98.7
5	135	92.3
6	165	88.6
Viscometer 4, 1.50 Grams of Papain		
1	15	197.2
2	45	97.8
3	75	79.6
4	105	77.1
5	135	72.6
6	165	61.2

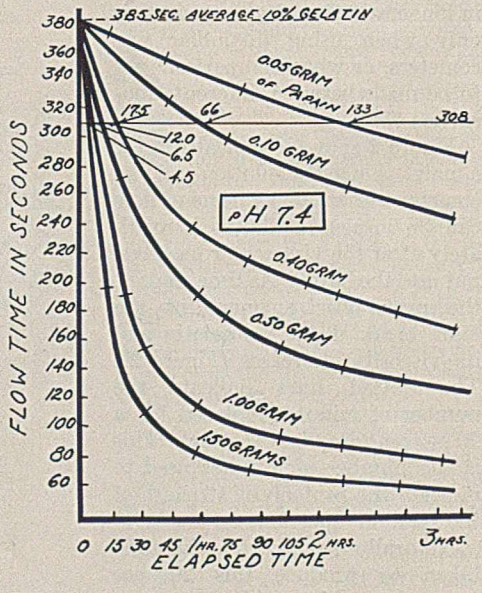


FIGURE 6. EFFECTS OF VARIOUS AMOUNTS OF PAPAIN
(See tables, *left*)

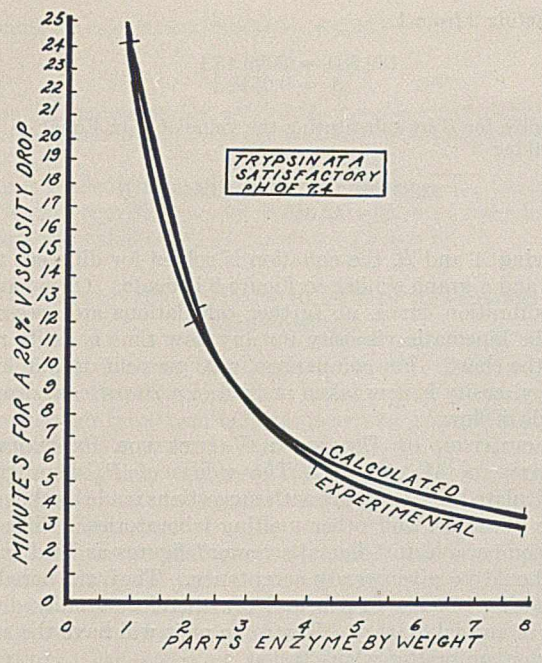


FIGURE 7. TIME REQUIRED FOR 20 PER CENT VISCOSITY DROP, USING TRYPSIN

20% Viscosity Drop

Parts by Weight of Enzyme	Calculated *Min.*	Observed *Min.*
1	25.0	25.0
2	12.5	13.0
4	6.25	6.0
8	3.12	3.0

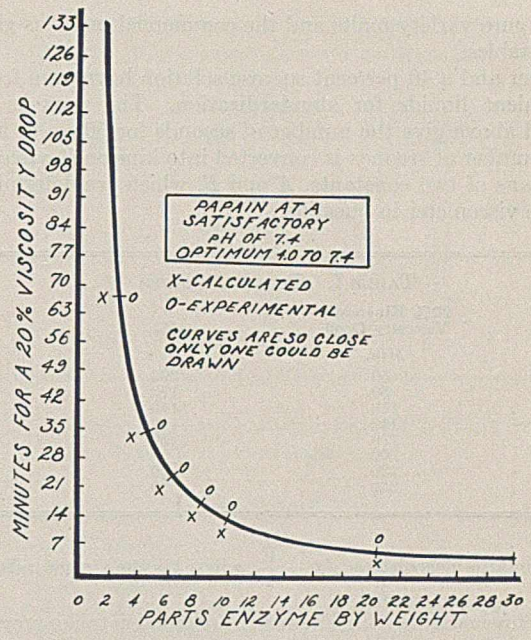


FIGURE 8. TIME REQUIRED FOR 20 PER CENT VISCOSITY DROP, USING PAPAIN

20% Viscosity Drop

Parts by Weight of Enzyme	Calculated *Min.*	Observed *Min.*
1	133.00	133.0
2	66.50	66.0
4	33.25	33.0
6	22.60	22.0
8	16.60	17.5
10	13.30	12.0
20	6.60	6.5

unnecessary. With the addition of no foreign agents whatever, retardation or activation of the enzymes in malt is out of the question.

Standardization of Viscometers in Kinematic Viscosity

In order to clarify the presentation, the standardization of viscometers has been postponed to this point. The fact that only one temperature is used simplifies the necessary calculations to a considerable extent. Only two liquids need be used and the following sample calculations give the necessary constants.

Undoubtedly one will use only kinematic viscosities as soon as he has become accustomed to making the determinations. The value for proteolytic activity, P_m, is calculated in terms of the time necessary for a 20 per cent drop in kinematic viscosity and comparisons can then be made with any laboratory. Graphs similar to Figure 9 allow the ready conversion of flow time to kinematic viscosity. Such conversions were made in calculating the proteolytic activities

Conversion of Time to Kinematic Viscosity, Viscometer 1

Time *Sec.*	Kinematic Viscosity *Millipoises*	Time *Sec.*	Kinematic Viscosity *Millipoises*
40	11.32	200	107.48
50	18.92	210	113.10
60	25.81	220	119.22
70	32.30	230	124.83
80	38.76	240	130.00
90	44.61	250	135.30
100	50.56	260	140.90
110	56.42	270	145.23
120	62.23	280	152.00
130	67.82	290	157.50
140	77.97	300	162.98
150	79.37	310	168.82
160	85.00	320	174.00
170	90.64	330	179.80
180	97.06	340	185.00
190	102.80	350	190.59

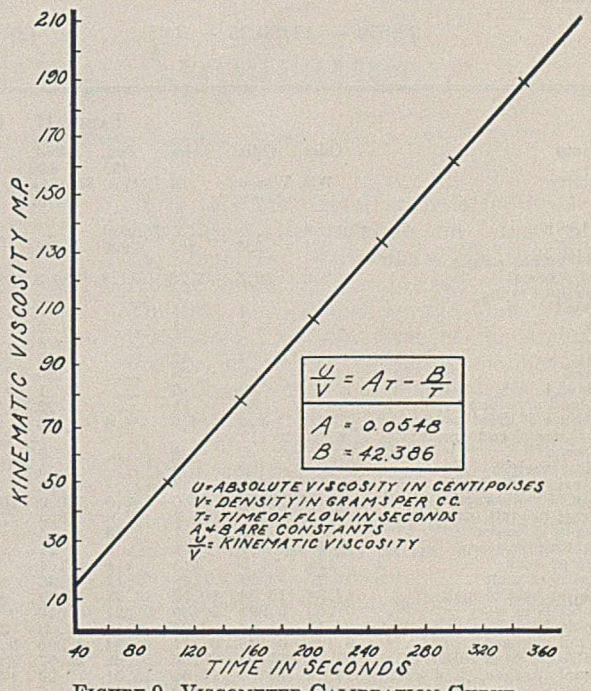


FIGURE 9. VISCOMETER CALIBRATION CURVE

(See table, *left*)

of the pure variety malts and the commercial malts as given in the tables.

Water and a 40 per cent sucrose solution have been found convenient liquids for standardization. The runs as described above give the number of seconds for 50 cc. to flow. This number of seconds is converted into kinematic viscosity by means of two constants, A and B, which are determined for the viscometer in question.

TABLE I. TYPICAL VALUES

20% Kinematic Viscosity Drop	P_m
Min.	
50	200
80	170
110	140
140	110
170	80
200	50
230	20
250	0

Kinematic viscosity $= At - \frac{B}{t}$, where t is time in seconds and A and B are constants.

The kinematic viscosities at 40° C. are found in tables prepared by Sheely (*8*).

Water at 40° C., 0.662
40% sucrose at 40° C., 2.94

It only remains to solve for A and B as follows:
Time for water at 40° C., 34.5 seconds
Time for 40 per cent sucrose at 40° C., 65.4 seconds
Then, for sucrose

$$2.94 = A65.4 - \frac{B}{65.4}$$

Clearing,

$$192.423 = A4283.7 - B \qquad (1)$$

For water,

$$0.662 = A34.5 - \frac{B}{34.5}$$

Clearing,

$$22.839 = A1190.25 - B \qquad (2)$$

Subtracting 2 from 1,

$$169.584 = 3093.45A$$
$$A = 0.0548$$

Now solve for B by substituting the value of A in Equation 1 or 2. Taking 2

$$22.839 = 1190.25 \times 0.0548 - B$$
$$B = 42.386$$

Having A and B, the equation is solved for different flow times and a graph similar to Figure 9 is made. Once having the calibration curve, no further calculations are necessary and the kinematic viscosity for any flow time is easily read from the chart. For comparison, a 20 per cent drop in kinematic viscosity is now taken instead of a 20 per cent drop in seconds of flow.

CALCULATION OF UNIVERSAL VALUES FOR PROTEOLYTIC ACTIVITY OF MALTS, P_m. The values of P_m here given are calculated in accordance with suggestions made by chemists in the Froedtert and other malting laboratories. They are very comparable to "diastatic power" figures as used today and should be given ready acceptance. They are based on kinematic viscosity figures and are therefore readily duplicated in any laboratory. The same malt will have the same P_m value, no matter where tested.

Diastatic power, proof of spirit, and other similar figures familiar to the brewing industry run to about 200 as a maximum value, the increase in numerical value meaning an increase in the property in question.

The proteolytic strength of malt varies inversely with the time required to effect a 20 per cent drop in kinematic viscosity. Thus a malt that produces a 20 per cent drop in viscosity in 50 minutes has a higher proteolytic value than a malt that produces a 20 per cent drop in 100 minutes. A proteolytic activity of 200 is given to a malt that produces a 20 per cent drop in 50 minutes. A proteolytic activity of 0 is given to a malt that produces a 20 per cent drop in 250 or more minutes. Thus we have a range of 200 minutes (250 − 50) in 20 per cent kinematic viscosity drop against a range of 200 points in terms of proteolytic activity. Thus a one-minute increase in the time required to effect a 20 per cent drop in viscosity is equivalent to a decrease of one point in proteolytic activity.

TABLE II. PURE VARIETY MALTS

Variety	Oder.	Oder.	Oder.	Ped. #38	Ped. #38	Ped. #38	Ped. #38	Velvet	Velvet	Velvet	Velvet	Manch.	Manch.	Manch.	Manch.	Peatland
Locality	Wis.	Waseca, Minn.	Ill.	Wis.	Waseca, Minn.	Ill.	Mont.	Madison, Wis.	Minn.	Ill.	Mont.	Wis.	Minn.	Ill.	Mont.	Wis.
Barley No.	Control	...	...	Control	...	...	...	...	...	...	...	...	...	...	...	...
Malt No.	934	958	881	920	876	887	857	933	930	879	872	939	957	890	830	932
1,000 kernel weight of malt (dry basis)	23.2	20.8	25.73	22.8	20.5	22.87	31.92	20.39	22.1	24.98	28.98	21.34	19.62	23.25	25.75	19.41
Growth of malt:																
Dead	...	4	1	...	7	5	3	1	0	1	0	2	4	1	0	0
0–1/4	...	1	1	...	0	2	11	1	1	1	2	6	0	0	0	0
1/4–1/2	...	2	8	...	8	9	19	4	18	20	26	11	2	3	8	34
1/2–3/4	...	63	62	...	58	61	46	35	50	62	49	45	26	72	58	45
3/4–1	...	30	28	...	26	23	21	59	30	15	23	35	66	24	33	21
Over 1	...	0	0	...	1	0	0	0	1	1	0	1	2	0	1	0
Exposed acrospires	...	10	11	...	22	4	3	5	8	11	14	1	17	6	12	6
Moisture of dried malt	4.5	4.5	4.0	4.4	4.0	4.4	5.2	4.6	4.4	4.4	5.0	4.4	5.0	4.9	6.2	4.5
Character of endosperm:																
Steely	...	0	0	...	0	0	0	0	0	0	0	0	0	0	0	0
Half steely	...	8	4	...	0	0	22	1	20	4	39	3	13	0	3	2
Mealy	...	92	96	...	100	100	78	99	80	96	61	97	87	100	97	98
Index of mellowness	98.0	96.0	98.0	100.0	100.0	100.0	89.0	99.5	90.0	98.0	80.5	98.5	93.5	100.0	98.5	99.0
Extract of malt (dry basis)	73.2	71.7	75.7	67.9	70.3	73.4	72.9	72.0	70.7	75.8	71.6	72.2	72.3	76.4	74.9	72.0
Time of inversion	7	>5	7	10	5	10	7–10	7	>5	5	5	>5	>5	5	>5	7–10
Filtration time	13	14	24	9	15	14	11	17	15	19	13	13	16	17	10	15
Color of wort	1.4	1.5	1.3	1.4	1.4	1.4	1.1	1.5	1.5	1.4	1.2	1.4	1.5	1.4	1.3	1.5
Total N of malt	1.97	2.49	1.68	2.12	2.36	1.54	2.30	2.02	2.56	1.76	2.30	2.10	2.56	1.73	2.25	2.16
Total protein of malt	12.34	15.53	10.52	13.22	14.70	9.64	14.34	12.63	15.96	11.01	14.37	13.13	16.00	10.83	14.02	13.50
Soluble N of wort	0.662	0.890	0.630	0.591	0.610	0.510	0.520	0.730	0.850	0.680	0.560	0.750	0.910	0.640	0.800	0.690
Soluble N as protein of wort	4.13	5.58	3.94	3.69	3.83	3.19	3.25	4.55	5.31	4.23	3.49	4.68	5.68	3.98	5.03	4.33
Formol nitrogen	0.130	0.178	0.111	0.094	0.098	0.089	0.081	0.154	0.175	0.135	0.089	0.154	0.188	0.118	0.155	...
Soluble N, % of total N	33.60	35.86	37.56	27.88	25.97	33.25	22.65	36.04	33.24	38.58	24.30	35.71	35.35	36.94	35.73	32.08
Formol nitrogen, % of wort N	19.64	19.93	17.59	15.91	15.99	17.38	15.55	21.15	20.56	19.88	15.92	20.53	20.77	18.47	19.28	...
Diastatic power	127	212	113	97	110	74	155	123	171	95	162	153	207	118	259	118
Proteolytic activity, P_m	149	157	141	88	99.5	111	53.5	169.5	167	134	60.5	153.5	172.5	154	141	179.5

Formula for calculating proteolytic activity, P_m:

$$P_m = 250 - t$$

where P_m represents the proteolytic activity of the malt and t the time in minutes for a 20 per cent drop in kinematic viscosity.

As is evident from the above expression, each minute required for the 20 per cent drop in kinematic viscosity decreases the value of P_m by one point (Table I).

Proteolytic Activity of Malts of Known Composition

Table II indicates constants ordinarily determined, together with the new proteolytic activity of malt figures, P_m. Even though these results have been carefully checked, they are significant only for these particular samples. Since they are pure varieties, they may differ widely from commercial samples and also from a pure variety grown under different climatic conditions.

Table II shows that one may expect more variation in proteolytic value of pure variety than in the ordinary run of commercial malts. Undoubtedly the smaller quantity of barley and small-scale processing would allow for more variation. The common practice of blending commercial malts would tend to make for some uniformity. Some of the extremely low proteolytic values in the pure varieties may have been caused by a dry season or a poor soil. Commercial malts naturally come from favorable localities.

Inspection of Table II will show proteolytic values between 53.5 and 179.5 for the pure varieties, while in Table III the values run between 172 and 204.

Acknowledgment

The pure variety malts and the major portion of data in Table II were furnished through the courtesy of J. G. Dickson of the University of Wisconsin Agricultural Experiment Station. The work is supported in part by a grant from the United States Maltsters Association.

Table III. Proteolytic Activity of Representative Commercial Malts

Malt	Time Required for 20% Kinematic Viscosity Drop	Proteolytic Activity $P_m = 250 - t$
	Min.	
1	46	204
2	78	172
3	76	174
4	52	198
5	72	178
6	77	173
7	76	174
8	52	198
9	50	200
10	46	204

Literature Cited

(1) Groer, F., *Biochem. Z.*, 38, 252 (1912).
(2) Haldane, J. B. S., "Enzymes," p. 6, New York, Longmans, Green & Co., 1930.
(3) Laufer, S., *J. Assoc. Official Agr. Chem.*, 20, 307 (1937).
(4) Nilson, A., *Am. Brewers Rev.*, 18, 294 (1904).
(5) Northrop, J. H., and Hussey, R. G., *J. Gen. Physiol.*, 5, 353 (1923).
(6) Orthmann, A. C., Surak, J., and Koch, J. R., *J. Am. Leather Chem. Assoc.*, 31, 484 (1936).
(7) Pozen, M. H., Ind. Eng. Chem., 26, 1127 (1934).
(8) Sheely, M. L., *Ibid.*, 15, 1109 (1923).
(9) Tauber, H., "Enzyme Chemistry," p. 95, New York, John Wiley & Sons, 1937.
(10) Wahl, A., *Am. Brewers Rev.*, 50, 21 (1936).
(11) Wahl, R., *Brewery Age*, 3, 45 (1935).
(12) Wahl, R., *Commun. Master Brewers Assoc. Am.*, 6, 9 (1935).
(13) Waksman, S., and Davison, W. C., "Enzymes," p. 205, Baltimore, Williams & Wilkins Co., 1926.

Received March 26, 1938. A contribution from the chemical laboratories of Marquette University and Froedtert Grain and Malting Company, Inc.

A Laboratory Mashing Apparatus

WESLEY M. CLARK, Columbia Breweries, Inc., Tacoma, Wash.

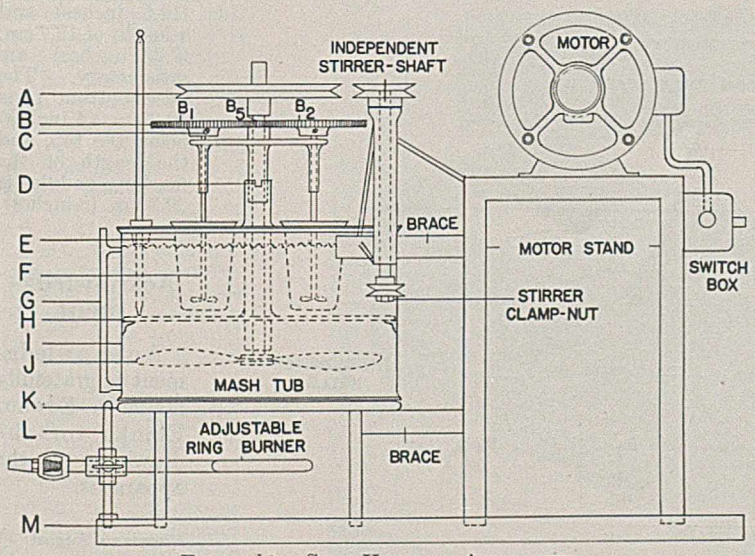


Figure 1. Side View of Apparatus

MALT and cereal analysis for total extract, the sugar-dextrin ratio, conversion time, and the color of the wort are a routine operation for brewery laboratories. The test, as described by the Malt Analysis Standardization Committee of the American Society of Brewing Chemists, specifies strict limitations of time and temperatures, as well as continuous stirring, held within narrow limits as to speed. Since the total time required for a malt analysis is 1 hour and 55 minutes, with an additional 10 minutes for cooling, it is obvious that some kind of mechanical assistance, with at least partial automatic temperature control, is needed.

There are a number of machines on the market for this purpose, but their high price militates against their general use, especially in the smaller commercial laboratories and those breweries where only one or two samples per week are required to be analyzed. A labora-

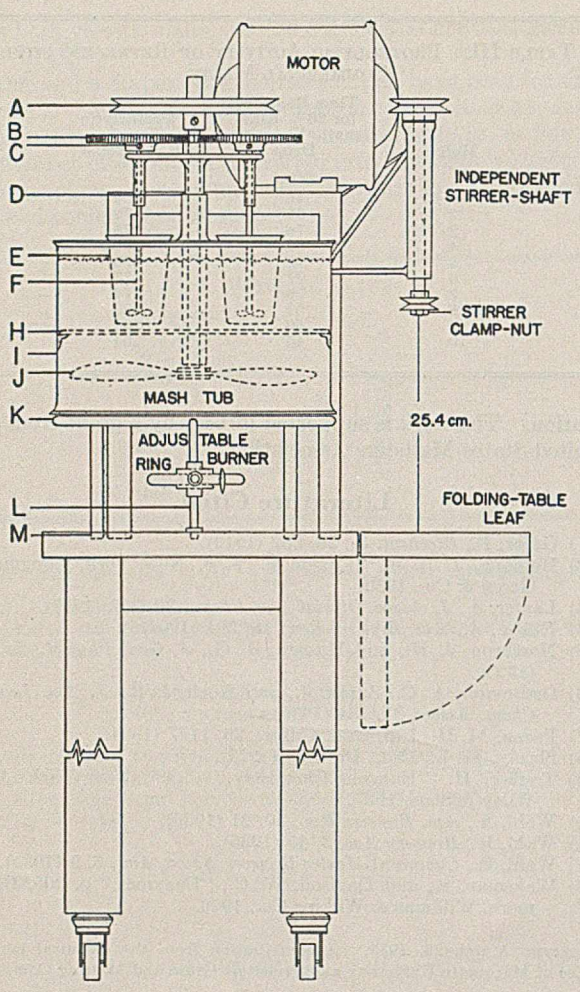


FIGURE 2. END VIEW OF APPARATUS

tory is usually unwilling to invest two to three hundred dollars in a piece of equipment that has such little and specialized use.

To meet the need for a low-cost mechanical mashing apparatus with semiautomatic temperature controls, the device described below was constructed. It is adaptable to a number of other uses besides that of mashing, and as such becomes a valuable piece of general laboratory equipment—for example, the introduction of an independent stirrer shaft serves, on the one hand, for occasional use as a stirrer and on the other as a motive source from which a ball mill or a shaking machine may be run. The pulleys are all interchangeable and may be run directly off the motor or through the mash-tub shaft, thus enabling the attainment of any desired speed. The four main brass mashing stirrers are easily removable and may be replaced by glass ones for use in other kinds of chemical reactions.

The cost of the entire machine, including labor of construction and the motor, did not exceed $50.00.

Figures 1, 2, and 3 show the side, end, and top views, respectively, of the apparatus.

In Figure 1, the large pulley, A, is run by belt from the motor and activates the gear system, B, through gear B_5. It is connected to the water paddle, J, through the loose slotted joint at D. The entire gear system and pulley may thus be lifted out to give access to the beakers, E. The brass stirrers, F, may be replaced by glass or other types by loosening the setscrew, C, beneath the gears, B_1, B_2, etc. G is a water-level tube. The perforated false bottom, H, and the stirrer, J, form a unit with the central shaft bearing and top of the mash tub. The top overlapping the tub slightly, and the false bottom, resting upon four brackets, I, give to this system the desired rigidity. The mash tub rests upon the frame, K, and is additionally supported and held in place by two braces. Two thermometer wells (Figure 3) are placed diametrically opposite each other in the top, and also serve during cooling, water being introduced through one and siphoned out through the other. Thermometers, which dip into the mash beakers for determination of mash temperatures, are held by buret clamps attached to the four stirrer-shaft housings. Tests have been run on the time required to cool the water bath. Running water at 15° C. into one thermometer well and siphoning out through the other, starting at 70° C. and using tubing 0.8 cm. in inside diameter, it required 4 minutes to bring the temperature down to that of the cooling fluid. The use of a larger or smaller siphon tube would decrease or increase this time.

The whole frame, including the motor stand, may be removed from the table by lifting the eight legs out of their drilled holes, M.

The 10-cm. (4-inch) ring burner is adjustable on its supporting stand, L, and is an adequate source of heat for all details of the analysis. Temperatures with variations not exceeding ±0.25° C. may be maintained for any desired length of time by carefully controlling the height of the burner and the flame.

Gears and pulleys of convenient size are obtained by use of a low-speed motor. In the present apparatus with a motor of 1165 r. p. m. and a pulley of 3.17 cm. (1.25 inches), an 18.41-cm. (7.25-inch) pulley, A, on the mash tub is needed. The gear ratio, B_5 to B_1 (diameters), is 5.71 cm. (2.25 inches) to 12.06 cm. (4.75 inches). This gives to the stirrers the satisfactory speed of 95 r. p. m., which, coupled with a rather high pitch of the blades, is sufficient to swirl the water gently throughout.

The mash tub is made of 22-gage copper and its size is governed by the number of beakers it is to accommodate. For four standard malt beakers a diameter of 32 cm. (12.5 inches) and a height of 19.7 cm. (7.25 inches) are satisfactory. The false bottom rests 10.2 cm. (4 inches) below the top, and the length of the mashing paddles is 20.3 cm. (8 inches).

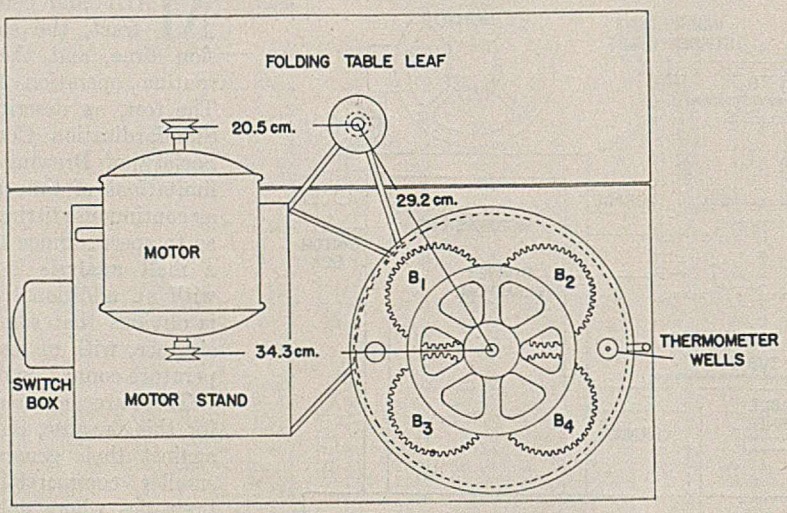


FIGURE 3. TOP VIEW OF APPARATUS

Acknowledgment

Acknowledgment is gratefully made to Edward Ehmke for the drawings of the apparatus.

RECEIVED August 30, 1938.

A Compact Field Laboratory for Sanitary Chemistry

JAMES G. WEART, Illinois Department of Public Health, Springfield, Ill.

THIS field laboratory was designed for the use of sanitary engineers engaged in the wide variety of problems encountered by the Department of Public Health and the State Sanitary Water Board. These problems include the supervision of all types of water-treatment plants and sewage plants, and the investigation of industrial wastes and stream pollution.

For these purposes, the kit was designed to permit the following tests: pH, dissolved oxygen, alkalinity, soap hardness, residual chlorine, carbon dioxide, and temperature. Sufficient extra capacity is provided so that it can be readily adapted to test for iron, nitrites, copper, or ammonia.

Apparatus and Methods

The case is substantial. Top, sides, and bottom are constructed of 1.25-cm. (0.5-inch) birch. The finish inside and out is acid- and alkali-resistant. A full-length piano hinge and trunk clasps support the cover. All corners are closed with a lock or pin box joint. Top and bottom corners are protected with trunk corners.

In the field, a clean work table is provided by the lid of the case, which is supported by two metal rods which screw into metal floor sockets. The inside of the lid is covered with white celluloid.

The buret support rod is screwed into another floor socket. The buret clamp is readily attached.

For burets, 10-ml. serological pipets are adapted by a modification of an old device, a bead in a rubber tube. The bead is located at the upper end of the pipet instead of at the bottom. This permits easy filling and excellent control during titrations. There are no stopcocks to break. Three of these pipet-burets, one for each of the three standard solutions, are held by clips in the removable tray.

The test most frequently made in this work is the determination of pH. The kit provides for the colorimetric determination of pH over the range of 4.0 to 11.0, in steps of 0.2 pH. For demonstration tests and approximations, a wide-range indicator is provided. In the range from pH 6.4 to 8.4, which is used most frequently, the two indicators required are supplied in 59-ml. (2-ounce) bottles. All other indicators are in 29.6-ml. (1-ounce) bottles. As but one or two drops of indicator are needed for each test, the amount of indicator supplied is ample. This type of pH equipment was designed about ten years ago at the laboratories of the Sanitary District of Chicago.

The regular Winkler method is used for dissolved oxygen. The reagents are in Pyrex dilution bottles of 180-ml. capacity, and are dispensed by a Pyrex pipet graduated at 0.5 and 1.0 ml., fitted in a rubber stopper, and operated by a rubber bulb. Two 118-ml. (4-ounce) ground-glass stoppered bottles, graduated at 100 ml., are provided for the collection of samples and for the test. Sulfuric acid is supplied in 50 per cent strength, rather than concentrated, so that 1 ml. can be added to fill the neck of the bottle. Fifty to sixty dissolved oxygen determinations can be made with the solutions provided.

Alkalinity and soap hardness are determined according to standard methods (*2*). For the measurement of samples there are a graduate and a calibrated bottle. Distilled water is available for dilution purposes.

Free carbon dioxide can be calculated from the alkalinity and pH, according to the formula of DeMartini (*1*):

$$\log CO_2 = 6.2874 + \log (HCO_3^- \text{ as } CaCO_3) - pH$$

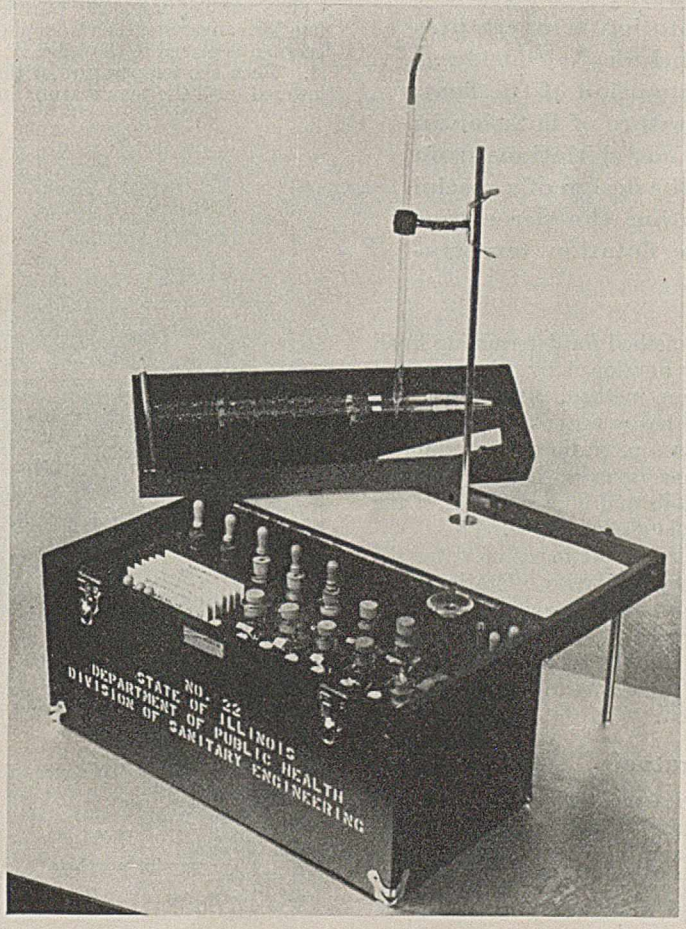
A slide rule or a log table is, of course, necessary.

For residual chlorine, standards prepared from Scott's buffered chromate-dichromate solutions are provided.

The *o*-tolidine furnished contains 20 per cent hydrochloric acid. Tests are made in 59-ml. (2-ounce) oil sample bottles.

For adaptions to special work, two dropping bottles, three 59-ml. (2-ounce) oil sample bottles, and one dilution bottle are provided as surplus. Two spare dosing pipets with bulb and rubber stopper are included.

The kits were prepared by Rascher & Betzold at a cost of $90 each in lots of ten. The weight is 13.6 kg. (30 pounds).



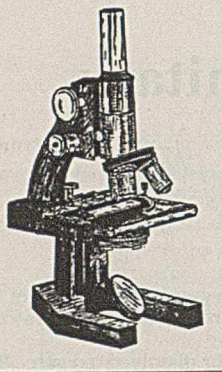
No claim for perfection is made, and suggestions for improvement are invited.

Literature Cited

(1) DeMartini, F. E., *J. Am. Water Works Assoc.*, 30, 105 (1938).

(2) "Standard Methods of Water Analysis," New York, American Public Health Assoc., 1936.

RECEIVED September 12, 1938. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 96th Meeting of the American Chemical Society, Milwaukee, Wis., September 5 to 9, 1938.



Microchemistry

Determination of Density Differences

By the Flotation Temperature Method

MERLE RANDALL AND BRUCE LONGTIN
University of California, Berkeley, Calif.

A description of the construction and manipulative details of a flotation temperature apparatus as used for analytical purposes is given. Of particular interest is the development of the flotation temperature determination as a density micromethod. The flotation temperature can be determined to within 0.005° C. in samples as small as 0.1 ml.

A method of calculating densities and compositions from flotation temperatures is discussed, which includes a consideration of the thermal expansion of the float, changes of the temperature of flotation in the reference sample, and deviations from ideal solution laws. The design of a special slide rule for calculating the percentage composition from the flotation temperature is indicated.

THE flotation temperature method for determining small differences in density was developed by Richards and co-workers (*8*, *9*) into a precision method. It is used regularly in the isotopic analysis of heavy water (*3*, *5*). In connection with a survey of the isotopic ratio of deuterium to hydrogen in water from various sources, Briscoe and coworkers (*1*) have described details and improvements of the method which make it more rapid and workable.

In the course of separation of isotopic forms of water the authors have found it necessary to devise "flotation temperature" apparatus which will handle very small samples of water. At the same time they have found certain methods of calculation to be time-saving in the treatment of results. This paper presents their conclusions as to these details of the flotation temperature method.

Apparatus

Figure 1 gives a diagrammatic view of the present apparatus as developed in this laboratory. The manual control of temperature is not proposed as any improvement over the automatic control described by Briscoe and others (*1*); the apparatus is easier to build, but the temperature control is somewhat less certain. The temperature readings are also made less certain, because the temperature of the sample itself cannot be determined directly, if it is desired to use small volumes of a sample. Nevertheless the flotation temperature as read from the Beckman thermometer is reproducible to within 0.005° C., which is sufficiently accurate for most purposes.

The electric buzzer, *L*, is used to agitate both the thermometer and the sample tube. This prevents sticking of the float and the mercury column of the Beckman thermometer. The copper wire, *O*, was originally used to dislodge the float when it became stuck, but with the buzzer it is not needed.

The sample, previously purified by distillation first over alkaline permanganate, then from phosphoric acid, and finally by outgassing, is placed in the tube, *A*, which contains the Pyrex float, *B*. Then the temperature of the bath is alternately raised and lowered until the temperature limits, above which the float sinks

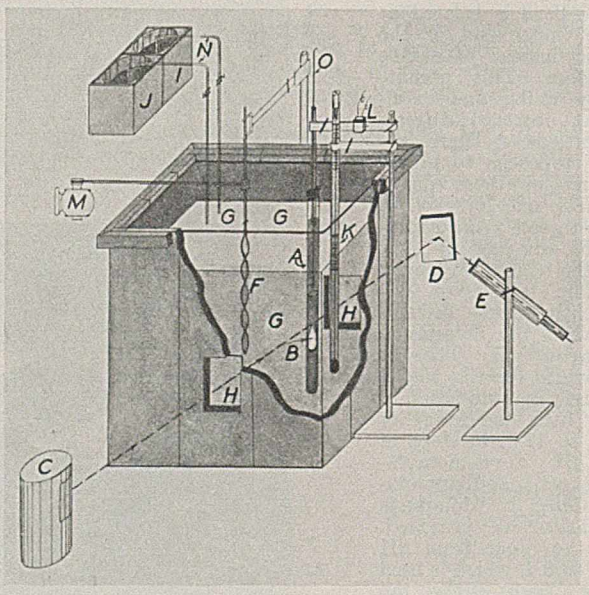


FIGURE 1. FLOTATION TEMPERATURE APPARATUS

A.	Sample test tube	*I.*	Thermostat control, cold
B.	Density float	*J.*	Thermostat control, hot
C.	Light	*K.*	Beckman thermometer
D.	Mirror	*L.*	Buzzer
E.	Telescope with cross hair	*M.*	Motor
F.	Stirrer	*N.*	Siphons
G.	Thermostat	*O.*	Float regulator
H.	Window		

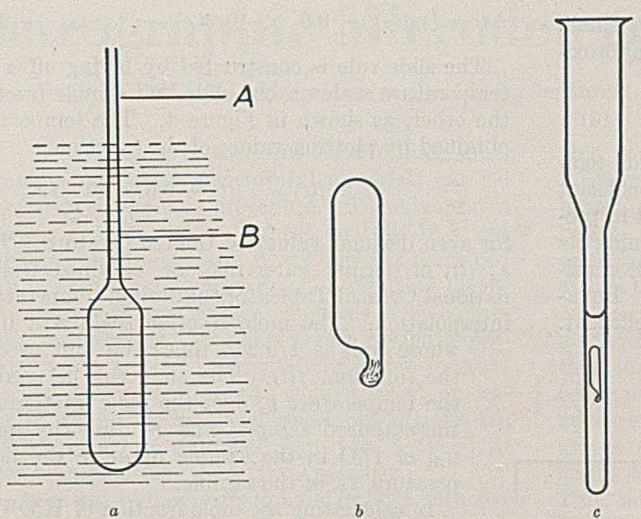


FIGURE 2. MICROFLOAT AND MICROFLOTATION TUBE

and below which it rises, are brought to within 0.005° C. In routine analysis for control purposes only, the distillation from phosphoric acid is dispensed with unless the ammonia content of the sample is known to be high.

In agreement with Briscoe and others (*1*) the authors have found that removal of dissolved carbon dioxide from the sample by heating it to 50° C. under vacuum with agitation materially alters the observed flotation temperature.

Microfloats

The microfloats are constructed from thin-walled tubing obtained by drawing out the central portion of a Pyrex test tube to about 2-mm. outside diameter. This tube is sealed at one end and then the other end is drawn out to a fine long capillary about 3 to 4 mm. away from the sealed end.

The most difficult problem is to adjust the density of the float so that it will just float in a standard reference sample—e. g., normal water—at a reasonable temperature. The uncompleted float is placed in a small quantity of the standard sample at the desired temperature. As shown in Figure 2*a*, it rides a little low. If the capillary is broken off at *A*, the float will rise until point *B* is at the level of the surface.

If the portion which projects above the surface is now melted down into a small drop very close to *B*, the float will still ride with *B* just at the surface. Further melting down of the capillary diminishes the volume of the float sufficiently that eventually it will just barely sink. With a little practice this can be done in such a way that the desired adjustment of flotation temperature in the standard sample is obtained in a short time. If the capillary is melted down too much, the bulb may be heated just to the softening point; the internal pressure will then cause the bulb to expand very slightly. Very fine adjustment may be obtained by scratching the glass drop very lightly with a file.

It is impossible to obtain sufficiently fine adjustment by using a mercury ballast, since sealing the float causes sufficient change in volume to destroy the adjustment entirely. For this reason the use of mercury ballast is of no value. The method described is the only one which has been found to give satisfactory adjustment without too much effort.

The completed float should preferably have the shape shown in Figure 2*b*. With this shape it will float stably in an upright position, owing to the extra weight of glass in the drop at the bottom. Otherwise it will tend to float diagonally and wedge in the sample tube. Floats have been made in this way which are about the size of a grain of wheat.

The sample tube is made as shown in Figure 2*c*. Its internal diameter is the smallest in which the float will move freely. By using the buzzer, *L*, the authors have been able to use extremely small clearances without materially affecting the accuracy of the determination. The only disadvantage of a small clearance which they have observed is that the float reacts more slowly to density changes, so that the total time of a determination is increased from the usual 10 minutes to about 15 minutes for the microfloats. Sample tubes have also been constructed which are directly connected to the microdistillation apparatus to avoid losses of material.

With microfloats and sample tubes constructed in this way, the authors have been able to determine the flotation temperature of samples as small as 0.1 ml. as accurately as with large samples in the usual way. This has been verified by control analyses in which the same sample was tested with different floats and sample tubes.

Calculation of Densities and Compositions

Both the density of the sample and the density of the float change with temperature. The flotation temperature is the temperature at which the two densities are the same.

In Figure 3, curve *B* represents the density of the sample as a function of temperature, while curve *F* represents that of the float. The intersection of the two curves corresponds to the temperature t_B. This is the temperature at which float and sample have the same densities, and hence is the flotation temperature. Curve *A* represents the density of another sample whose flotation temperature is t_A.

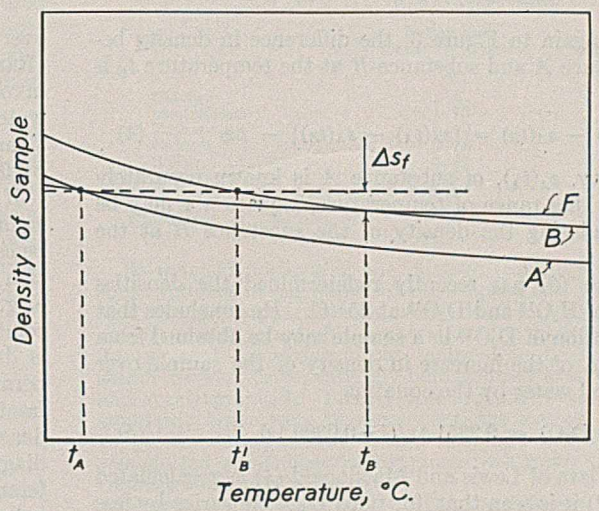


FIGURE 3. RELATION OF DENSITY TO FLOTATION TEMPERATURE

If the density of the float were constant, as represented by the horizontal dotted line, the flotation temperature of sample *B* would be t_B' instead of t_B. The flotation temperatures of a group of samples would then be the temperatures at which the samples all have the same density, equal to that of the float.

Actually, the density of sample *B* at its flotation temperature is less than that of sample *A* at its flotation temperature by the amount Δs_f. The ratio $\Delta s_f/(t_A - t_B)$ is the average thermal coefficient of the density of the float over the temperature interval (t_A, t_B). If the bob expands linearly with temperature according to the equation

$$V_f(t_B) = V_f(t_A)[1 + a(t_B - t_A)] \qquad (1)$$

where a is the coefficient of cubical expansion of the float, then the ratio, $s_f\ (t_B)/s_f\ (t_A)$, of densities of the float at the two temperatures is

$$s_f(t_B)/s_f(t_A) = V_f(t_A)/V_f(t_B) = \frac{1}{1 + a(t_B - t_A)} \qquad (2)$$

Since the coefficient of expansion, a, of glass is very small, this expression may be rewritten to a high degree of approximation as

$$\Delta s_f = s_f(t_A) - s_f(t_B) \cong s_f(t_A)\, a\, (t_B - t_A) \qquad (3)$$

Richards (*8*, *9*) has proposed the use of the flotation temperature method as a means of determining the coefficient of expansion of the float. The method would consist in preparing a float of the desired material and determining its flotation temperatures in two standard liquids whose densities are well known over a wide temperature range. Equation 3 may then be used to calculate a, the desired coefficient.

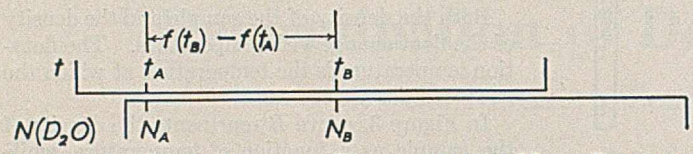


FIGURE 4. SLIDE RULE FOR CALCULATION OF MOLE FRACTION OF DEUTERIUM OXIDE FROM FLOTATION TEMPERATURE

Referring again to Figure 3, the difference in density between substance A and substance B at the temperature t_B is given as

$$s_B(t_B) - s_A(t_B) = \{s_A(t_A) - s_A(t_B)\} - \Delta s_f \qquad (4)$$

If the density, $s_A(t_A)$, of substance A is known accurately over the working range of temperature, Equation 4 may be used in calculating the density of the substance B at the temperature t_B.

Longsworth (*6*) has recently redetermined the densities of mixtures of H_2O^{16} and D_2O^{16} at 25° C. He concludes that the mole fraction of D_2O^{16} in a sample may be obtained from the value, Δs, of the increase in density of the sample over that of normal water by the equation

$$N(D_2O) = 9.2351\,\Delta s/(1-0.0309\,\Delta s) \qquad (5)$$

From the data of Lewis and Macdonald (*4*) as recalculated by Farkas (*2*) it is seen that, for pure D_2O, Δs varies by less than four parts per thousand over the range from 15° to 35° C., in which flotation temperatures of water are usually determined. In the more dilute solutions the percentage variation of Δs with temperature in this range should be about the same or less. Hence to within 0.5 per cent Equation 5 also holds for temperatures other than 25° C. in this interval.

For dilute solutions in which the density increment, Δs, is less than 0.05—i. e., solutions containing less than 0.50 mole fraction of D_2O—Equation 5 may be written to sufficient approximation as

$$N(D_2O) = 9.235\,\Delta s \qquad (6)$$

Furthermore, if substance A is taken as normal water, Equation 4 gives Δs for sample B at the temperature t_B which is ordinarily in the range from 15° to 35° C. The two equations may therefore be used to calculate the mole fraction $N(D_2O)$ of D_2O in the sample from the observed flotation temperatures if the difference is known to be due only to D_2O.

These calculations may be simplified by the use of a specially constructed slide rule. For Pyrex glass floats a is 9.6×10^{-6} per ° C. The density $s_f(t_A)$ is adjusted equal to that of normal water at some convenient temperature, t_A, preferably between 20° and 25° C. The term Δs_f is always relatively small, so that $s_f(t_A)$ may be taken with sufficient accuracy as unity for any temperature in this range (actually it lies between 0.997 and 0.998). Hence, $s_f \cong 9.6 \times 10^{-6}(t_B - t_A)$, and Δs for the sample at t_B is given as

$$\Delta s = [s_A(t_A) - 9.6 \times 10^{-6} t_A] - [s_A(t_A) - 9.6 \times 10^{-6} t_B$$

The slide rule is constructed by laying off a nonuniform temperature scale on one slide and a mole fraction scale on the other, as shown in Figure 4. The temperature scale is obtained by plotting values of the function

$$f(t) = s_A(t) - 9.6 \times 10^{-6}\, t$$

for even decimal values of the temperature. The densities, $s_A(t)$, of normal water may be obtained from the International Critical Tables for the desired temperatures, without interpolation. The mole fraction scale is a uniform scale whose unit is 1/9.235 times the unit used in plotting the function, $f(t)$. The slide rule is used by placing the temperature t_A over the mole fraction N_A of D_2O in the standard sample, and reading the mole fraction, N_B, of D_2O in the sample opposite the flotation temperature, t_B, of the sample.

In calculating the mole fraction of $H_2^1O^{18}$ in a sample from the flotation temperature, when the sample contains only $H_2^1O^{18}$ in amounts essentially different from normal water, the same method may be used. However, if we assume the density of pure $H_2^1O^{18}$ to be 1.111 [Randall and Longtin have found some slight evidence in favor of this value, from studies of the refractive index of water enriched in $H_2^1O^{18}$ (*7*)], the factor 9.235 for proportionality between mole fraction and density must be replaced by 9.00.

If the approximations assumed in analysis of heavy water cannot be applied, the calculations of compositions may still be carried out accurately by means of the graphical construction of Figure 3. For this purpose a series of density curves—e. g., A and B—is drawn, one for each mole fraction of solute. Then for a particular float the appropriate curve F is drawn. Corresponding to any particular flotation temperature, t_B, a point on the curve F is located. The mole fraction of solute in the sample is read from the solution density curve which passes through this point. The same diagram may be used for different floats by drawing in a different curve, F, for each float. This method does not involve any assumptions as to linear expansion of the float, or independence of the density increment of solutions and the temperature.

Acknowledgment

The authors wish to express their indebtedness to G. N. Lewis and R. T. Macdonald, who first used the flotation temperature method in this laboratory and out of whose technique the present work has developed. They also wish to thank Dale E. Callis, Merlin Reedy, and Forest J. Watson for their technical contributions, the Works Progress Administration (OP-465-03-3-147) for clerical and mechanical assistance, and the National Research Council for a grant made to the senior author for purchase of materials used in the study of heavy water.

Literature Cited

(1) Emeleus, James, King, Pearson, Purcell, and Briscoe, *J. Chem. Soc.*, 1934, 1207.
(2) Farkas, "Orthohydrogen, Parahydrogen, and Heavy Hydrogen," Cambridge, University Press, 1935.
(3) Lewis and Luten, *J. Am. Chem. Soc.*, 55, 5061 (1933).
(4) Lewis and Macdonald, *Ibid.*, 55, 3057 (1933).
(5) Lewis and Macdonald, *J. Chem. Phys.*, 1, 341 (1933).
(6) Longsworth, *J. Am. Chem. Soc.*, 59, 1483 (1937).
(7) Longtin, thesis, University of California, Berkeley, Calif., 1937.
(8) Richards and Harris, *J. Am. Chem. Soc.*, 38, 1000 (1916).
(9) Richards and Shipley, *Ibid.*, 34, 599 (1912); Richards and Lembert, 36, 1 (1914).

RECEIVED October 4, 1938. Mr. Longtin is Shell Fellow in Chemistry.

Spectrographic Microdetermination of Copper

LEWIS H. ROGERS,[1] University of Florida Agricultural Experiment Station, Gainesville, Fla.

THE need for a precise method for determining small proportions of copper in agricultural materials has led to the study of a spectrographic procedure. The advantages of spectrographic analysis over chemical analysis in speed and sensitivity are well known and in the method described below it has the additional advantage of eliminating all reagents except one. Microchemical methods for copper usually involve solution of the sample, one or more precipitations, and various other manipulations which increase the possibility of contamination with copper or of an appreciable loss of copper, when very small proportions are concerned. The procedure described here was designed to eliminate these manipulations in so far as possible.

There have been many determinations of copper with the spectrograph. Among those who have worked with biological materials are Gerlach and his co-workers (*4*, *5*, *9*), van Eyk (*1*), and Ramage and his co-workers (*2*, *10*), who have used the following elements as internal standards in one or more of their studies: cobalt, molybdenum, silver, sodium, and tin. Either tin or cadmium is used as the internal standard in the procedure described here.

Langstroth and McRae (*7*) have pointed out that a desirable internal standard element should behave in the discharge very much like the element being determined and that the two should have as nearly as possible the same ionization potential. When copper lines 3247 and 3273 are being used, tin line 3262 is convenient, and in addition tin has other characteristics which make its use as an internal standard appropriate (see Table I).

TABLE I. INTERNAL STANDARDS

Element	Ionization Potential *e-volts*	Boiling Point ° *C.*	Wave Length *Å.*
			3247
Cu	7.68	2310	3273
Sn	7.30	2270	3262
Cd	8.96	767	3261

Tin and copper have boiling points very nearly the same, and this should contribute to a similarity of behavior in the arc discharge, and hence increase the precision of the determination. Occasionally, however, tin is detected in the sample in the qualitative spectrographic analysis which is always made first; in this event, another internal standard must be chosen, which in this study has been cadmium. Table I indicates that cadmium is not as satisfactory as tin as an internal standard for the determination of copper, at least with regard to the characteristics discussed above.

Procedure

A large quartz Littrow spectrograph and nonrecording microphotometer have been used here, and essentially the internal standard procedure of Nitchie and Standen (*8*) has been followed. The magnified image of the direct-current arc source (220 volts, graphite electrodes, 10 amperes) was focused on the slit of the spectrograph with a condensing lens. The arc was always maintained until the sample was completely volatilized.

Since the purest commercial graphite electrodes available frequently contain detectable copper, all electrodes have been purified, following the solvent purification procedure of Standen and Kovach (*11*). As all C. P. chemicals examined at this laboratory have contained spectrographically detectable copper, some purification is necessary before a base mixture for the calibration curve can be prepared. This has been accomplished by the use of the basic magnesium carbonate procedure as proposed by Steinberg (*12*). As many as ten recrystallizations did not remove copper as effectively as one treatment with magnesium carbonate.

The calibration curve was prepared by making up a base mixture of purified salts which approximated in its composition the proportions of the macroconstituents known to occur in the material to be analyzed. For example, a base mixture for the analysis of orange leaves would contain 40 grams of calcium carbonate, 2 grams of magnesium oxide, 6 grams of potassium sulfate, and 2 grams of sodium chloride. This mixture approximates the proportions as given by Kelley and Cummins (*6*) as shown in Table II.

TABLE II. BASE MIXTURES

	Kelley and Cummins' Data %	Synthetic Mixture %
Calcium	31.4	32.0
Magnesium	1.73	2.4
Potassium	6.40	5.4
Sodium	0.78	1.6
Sulfur	0.97	2.2
Chlorine	0.95	2.4
Carbonate[a]	50.65	48.0

[a] Calculated (cf. Gaddum, *3*).

To weighed portions of the mixture (carefully homogenized) equal volumes of the standard tin solution and known volumes of a standard copper solution were added to give various standards over the range of concentrations (in this study 0.001 to 0.1 per cent) occurring in the material to be analyzed. The standards were dried, carefully homogenized in an agate mortar, and spectrographed. Twenty spectrograms were made of each standard; these were photometered, the average ratios of the copper-tin densities were determined, and a calibration curve was plotted on semilogarithmic paper with ratios as abscissa and concentration as ordinate.

Samples were ashed at 450° C., the ash was homogenized, and to weighed portions was added tin solution equivalent in volume to that added to the standards. These were dried, homogenized, spectrographed in quintuplicate, and photometered exactly as in the case of the standards.

Precision and Accuracy

Factors affecting precision are nonuniformity of the sample, contamination, variation of exposure conditions (wandering of the arc, change of line voltage), photometric errors, and perhaps others. Every effort has been made to reduce the effects of these variables. Solutions of the samples would, no doubt, increase the precision, but at the same time would introduce unnecessary manipulation and the possibility of contamination with acids; with the precision required this is an unnecessary risk.

As a measure of the precision of this procedure, the probable error of the mean result has been calculated for a large number of samples which were analyzed in quintuplicate. In general, this was found to be about 5 or 6 per cent, although it was sometimes less. For example, in one set of 22 samples, the greatest probable error was 9.6 per cent of the mean, and the smallest 1.1 per cent, with an average of 4.5 per cent.

Factors affecting the accuracy are incomplete burning, influence of varying major constituents on the volatility and "excitability" of the copper and internal standard atoms, and perhaps others. In this study, the sample has always been completely burned, and, since standards are prepared which simulate approximately the composition of the unknowns, the

[1] Present address, 222 University Ave., Ithaca, N. Y.

influence of this factor is minimized. Langstroth and McRae (7) advocate the use of a spectroscopic buffer that will prevent reasonable variations in the extraneous composition of the samples from materially altering the transport phenomena. No spectroscopic buffer has been employed in this study, but its use presents interesting possibilities. It has been found here that when a calibration curve is prepared with a base material consisting, for example, of potassium chloride only, the slope is appreciably different from that of the calibration curve prepared with a base mixture containing calcium, magnesium, sodium, and potassium in the proportions indicated above for a representative orange leaf ash. This effect is more pronounced with cadmium than with tin as the internal standard. Therefore, plant samples containing large proportions of potassium may require a different calibration curve from those containing large proportions of calcium. The use of a spectroscopic buffer may obviate this difficulty.

Discussion

This method may readily be extended to include both larger and smaller proportions of copper. The lower limit of spectrographic detectability of copper is less than 0.0001 per cent, and there is no upper limit. Above 0.1 per cent it would probably become desirable to utilize other copper lines than those used here, since their extreme sensitivity gives a plate blackening too great for convenient measurement.

The use of solutions of the samples has other objections than the one mentioned above. Of particular importance is the retention of copper in the insoluble residue. In addition, when solutions are dried on graphite electrodes, there is always some penetration, making it difficult to determine when the sample is completely volatilized. This penetration has been prevented by some workers by treating the electrodes with kerosene or paraffin, but it has been found that this introduces some copper contamination.

Acknowledgment

The author is indebted to Earle Peterson, R. C. Hughes, and L. L. Rusoff for assistance in the laboratory.

Summary

A procedure is described for the quantitative spectrographic determination of copper in biological materials in the range 0.001 to 0.1 per cent by direct arcing of the ash. The probable error of the method is about 5 per cent.

Literature Cited

(1) Eyk, B. J. van, "Quantitative Spectrographic Determination of Traces of Metals, Particularly of Copper, in Biological Materials," Amsterdam, N. V. Noord-Hollandsche Uitgeversmaatschappij, 1934.
(2) Fox, H. M., and Ramage, H., *Proc. Roy. Soc.* (London), B108, 157 (1931).
(3) Gaddum, L. W., *Proc. Florida Acad. Sci.*, 1, 128 (1936).
(4) Gerlach, Walter, and Gerlach, Werner, "Clinical and Pathological Applications of Spectrum Analysis," London, Adam Hilger, 1934.
(5) Gerlach, Werner, and Ruthardt, K., *Beitr. path. Anat.*, 92, 347 (1934).
(6) Kelley, W. P., and Cummins, A. B., *J. Agr. Research*, 20, 161 (1920).
(7) Langstroth, G. O., and McRae, D. R., *Can. J. Research*, A16, 61 (1938).
(8) Nitchie, C. C., and Standen, G. W., Ind. Eng. Chem., Anal. Ed., 4, 182 (1932).
(9) Ruthardt, K., *Arch. path. Anat.* (Virchow's), 294, 198 (1934).
(10) Sheldon, J. A., and Ramage, H., *Biochem. J.*, 25, 1608 (1931).
(11) Standen, G. W., and Kovach, L., Jr., *Proc. Am. Soc. Testing Materials*, 35, Part II, 33 (1935).
(12) Steinberg, R. A., *J. Agr. Research*, 51, 413 (1935).

Received September 24, 1938.

A Simplified Method of Preparing Microscopic Glass Spheres

KARL SOLLNER,[1] New York State College of Agriculture, Cornell University, Ithaca, N. Y.

WELL-defined microscopic spheres of glass (and similar high-melting substances) would be of considerable value for certain physico-chemical experiments if they could be prepared conveniently, but such material is not available commercially.

Sklarew (2) described in 1934 a method by which microscopic glass spheres may be produced by blowing glass powder through a blast lamp into a white-hot heat chamber which is connected to a steel pipe 300 cm. long and 90 cm. wide, leading to a 180 × 180 × 180 cm. cardboard settling chamber. The space required for this arrangement is not always available however, and the method is not very efficient as far as the quality of the product is concerned, many particles retaining more or less irregular shapes.

An attempt to use Sklarew's method in a moderately sized apparatus failed: It was difficult to keep the whole system sufficiently clean and the smallest particles, in which the author was most interested, did not settle down and thus were lost.

The method described below was finally found satisfactory for preparing the microscopic glass spheres needed for certain model experiments on colloids, adhesion experiments (now in progress) using Buzágh's method (1), but using geometrically well-defined bodies instead of irregularly shaped ones.

The underlying idea can easily be gathered from Figure 1.

Oxygen is passed through a moderately sized glass bottle, *A*, containing some glass powder. A suitable orifice, *B*, and, if necessary, a slight agitation of the bottle cause the oxygen stream to be loaded with glass powder. The oxygen may be passed through a small settling chamber, *C*, before reaching the torch, *E*, through the rubber tubing, *D*. Gas is fed to the torch through a side arm. The flame originating at the orifice, *F*, is directed by hand against the surface of the water which fills the dish, *G*, up to the rim.

The particles carried with the oxygen pass through the flame in which they are molten, forming spheres. These spheres are thrown into the water, probably by centrifugal forces originating in the curvature of the flame when it strikes the water surface.

On microscopic examination, the particles are seen to be perfect spheres, entirely independent of each other, the smaller ones, of course, showing vivid Brownian movement. Among thousands of particles usually not a single imperfect sphere is found. They seem, except perhaps for the very biggest ones prepared thus far, free from internal strain, when tested microscopically between crossed Nicol prisms.

The whole arrangement is so simple that usually the first attempt will be successful, if a few precautions are taken.

[1] Present address, University of Minnesota, Minneapolis, Minn.

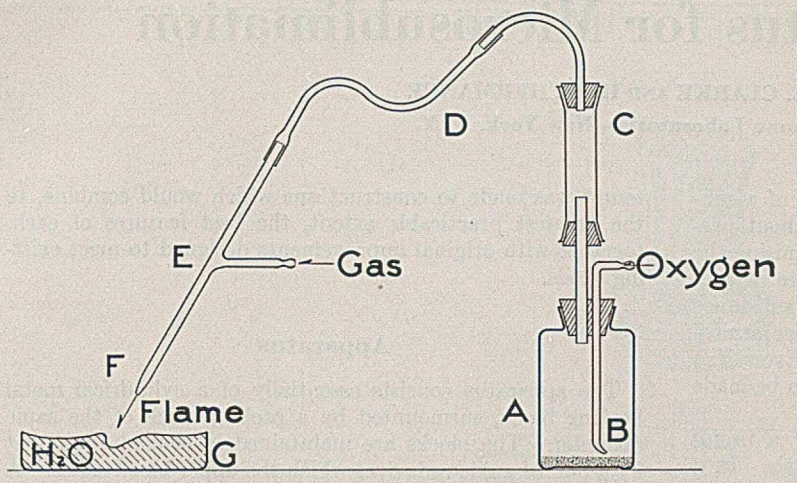


FIGURE 1. DIAGRAM OF APPARATUS

The gas and oxygen streams should be steady and properly adjusted; the quantity of glass powder carried by the oxygen should not be excessive and should be carried along uniformly and steadily. Thick-walled rubber tubing with a narrow bore should be used to secure high gas velocities; wider and thin-walled tubes lead to the formation of glass powder deposits owing to low oxygen velocities or kinks. Such deposits have a tendency to be blown out suddenly; then an excessive quantity of particles passes through the flame simultaneously and is not melted properly.

All containers, rubber tubes, etc., should be dry, and the glass powder should be carefully dried at increased temperature. If everything is dry each glass particle forms a single independent glass sphere; if the particles stick together because of moisture, these aggregates melt as units, forming big spheres that sometimes contain air bubbles.

Several commercial hand torches proved useful, particularly the type where the oxygen stream (carrying the powder) emerges at the orifice surrounded by a gas stream (Figure 2, upper). To avoid abrasion of metal by the sharp edges of the powder, the author used a simple quartz-glass torch (Figure 2, lower) to which a Pyrex glass tubing was fixed in the position indicated, below the torch, its constricted end being under the orifice of the torch a few millimeters back of it. Through the Pyrex tube some gas was fed, in order to surround the torch flame with combustible gas. In this manner every particle was sure to travel through a hot zone. Without this precaution, a few particles might occasionally slip through, without being melted completely.

The size and stiffness of the flame should be adjusted to the size and the melting point of the particles. A flame length of 5 to 10 cm. is sufficient for glass particles below 10μ diameter, but a hydrogen flame must be used for Pyrex. Small dishes—e. g., crystallizing—are suitable containers for the water.

The lower limit of particle size to which the method may be applied lies below that of microscopic visibility; the upper limit is probably determined by the flame size and the ability of the oxygen stream to carry big particles. Thus far the method has worked equally well with particles from below 0.5 up to 50μ diameter, no attempt being made to apply it to bigger particles.

It is advisable to prepare many small lots instead of one large one because of the possible appearance of nonspherical particles due to the sudden discharge of deposits, as mentioned above. Each small lot is examined microscopically before it is mixed with the others.

The use of hydrogen prevents the dissolution of carbon dioxide (and other impurities) in the water. Removal of such impurities can always easily be accomplished by repeated centrifuging out and redispersing of the particles in distilled water.

The simplicity of the method described allows in most cases the use of glass spheres prepared shortly beforehand, so that the time for a possible interaction between the glass and the water becomes greatly reduced. Even with soft glass such an interaction seems to be much less serious than might be expected—several samples of glass spheres prepared from soft glass (Williams and Hopkins, London, England) kept for a period of more than 2 years in water and aqueous solutions showed no detectable change, except that the distilled water showed a weakly alkaline reaction. But, of course, the particles are perfect spheres, absolutely independent of each other and showing lively Brownian movement when stirred up by shaking. When considering the possibility of a chemical interaction between the spheres and the water, one must always remember that one is dealing with smooth surfaces, probably rather free from microfissures as compared with the original glass powder.

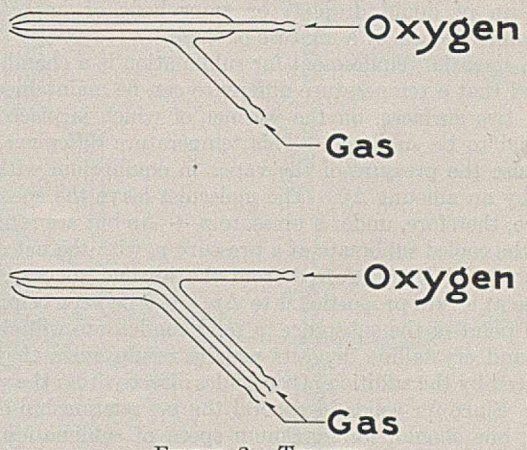


FIGURE 2. TORCHES

Though in the author's opinion the interaction between glass and water is not likely to go so far as to be a seriously disturbing factor when experimenting with the spheres, it is advisable to use freshly prepared spheres of resistant glass—e. g., Pyrex—or if possible of quartz.

An occasional attempt to prepare quartz spheres in a hydrogen-oxygen flame was not altogether successful; only the smallest particles were melted, often forming imperfect spheres. But there is no doubt that a more suitable torch and a bigger flame, or still better an acetylene-oxygen flame, would yield satisfactory results with quartz.

Acknowledgment

The author is greatly indebted to R. Bradfield, head of the Department of Agronomy, for generous hospitality in his department.

Literature Cited

(1) Buzágh, A. v., *Kolloid-Z.*, 47, 370 (1929); 51, 105, 230; 52, 46; 53, 294 (1930), etc.
(2) Sklarew, S., IND. ENG. CHEM., Anal. Ed., 6, 152 (1934).

RECEIVED August 17, 1938.

A New Apparatus for Microsublimation

BEVERLY L. CLARKE AND H. W. HERMANCE
Bell Telephone Laboratories, New York, N. Y.

THE term sublimation describes the transition of a substance between its vapor and solid states without passage through the intermediate liquid state. If on raising the temperature of a solid substance the vapor pressure reaches 760 mm. before the fusion point is attained, the substance will sublime when heated in an open vessel under atmospheric pressure (iodine, ammonium chloride). Even if a substance has its triple point below 760 mm., it can be made to undergo true sublimation by heating *in vacuo*.

Where sublimation is feasible, it is frequently a useful technique in analysis, particularly in microanalysis. In a suitable apparatus separations can be effected on microsamples, and it is often possible to produce sublimates that are readily identifiable under the microscope by their crystal form and habit. In synthetic work sublimation has been found useful in the purification of materials. In the authors' laboratory the apparatus to be described has also proved convenient for the separation, by simple distillation, of the volatile and condensable components of minute samples—e. g., dust particles. In such cases the condensate takes the form of liquid droplets or amorphous or imperfectly crystalline masses, or a mixture of these.

The essential requirement for sublimation is a chamber so divided that a temperature difference can be maintained between two surfaces, on the warmer of which is placed the material to be sublimed. This temperature difference, $\Delta\theta$, will raise the pressure of the vapor in equilibrium with the solid by an amount Δp. The molecules leave the specimen surface, therefore, under a pressure $p + \Delta p$ but are returned from the cooled sublimate at a pressure p, with the net result that material is transferred from the warmer to the cooler surface at a rate proportional to Δp. If θ be kept below the fusion point of the substance, a solid condensate will always form and crystalline deposits usually result, since they are produced by the addition of molecules directly from the vapor state. Since for solids in general the p-θ relationship is not linear, one should, for maximum speed of sublimation, operate at the steepest portion of the p-θ curve. The distance separating the hot and cold surfaces should be as small as practicable, since the speed of transfer is naturally affected by molecular collisions occurring in this space. These collisions can also be reduced by evacuating the sublimation chamber. It will be obvious also that heavy molecules will be transferred more slowly than lighter ones, since the velocity of molecules in a vapor is inversely proportional to their molecular weight.

Various methods have been used in carrying out microsublimation. For the simplest qualitative purposes the material may be heated on a microscope slide and condensed on a second slide held immediately above and cooled by a drop of water placed on its upper surface. Lack of temperature control and incomplete recovery of the volatilized material are obvious disadvantages of the method. Improvements consist in placing the slide on a heated aluminum block provided with a thermometer, a glass ring separating the two slides.

When the sublimation is to be continued for longer periods, however, and under more carefully controlled conditions, more permanent arrangements are desirable, which provide for continuous cooling by water or air circulation as well as for evacuation of the sublimation space.

With the limitations of existing devices in mind, an attempt was made to construct one which would combine, to the greatest practicable extent, the best features of each, together with original improvements designed to meet existing needs.

Apparatus

The apparatus consists essentially of a cylindrical metal heating block, surmounted by a cooling block of the same diameter. The blocks are maintained in coaxial alignment by a pair of guide rods over which the upper block slides. A glass ring, ground into grooves in the opposing faces of the blocks, separates them. Water or air, circulating through the upper block, cools the glass slip which receives the sublimate. The sublimation chamber is removable and fits into a plunger mechanism in the heater block. A spring, acting against this plunger, forces the chamber up against the cooled glass slip. Details are given in Figure 1.

The Duralumin heating block, A, is spool-shaped to accommodate the heater winding, Z, of Nichrome wire. This winding is center tapped and the two sections may be connected in series or parallel, giving two heat ranges. At the center of the block an appropriately shaped well, D, accommodates a snugly fitting plunger, E, also of Duralumin. The main body of the plunger is bored out to form a receptacle for holding the sublimation cup, F. Proper alignment of the plunger and well surfaces, necessary for smooth movement, is maintained by a rod extension which fits the lower, narrowed portion of the well. A light helical spring, S, seated in a recessed portion of this lower well serves to force the plunger upward against the cooling block.

The interchangeable sublimation cups are of standard outside dimensions but have a variety of inside shapes and sizes such as are shown in details F_1–F_4, suited to different uses. The cup is about 0.5 mm. higher than the accommodating receptacle in the plunger. This prevents the latter from touching the cooling unit, which would result in an undesirable transfer of heat with consequent loss of efficiency. The well is of sufficient depth to permit pressing the plunger completely into the block. Fine grooves, filed longitudinally into the sliding surface of the plunger, permit passage of air to and from the well. From points diametrically opposite on the upper spool flange, two 0.6-cm. (0.25-inch) holes, U, are drilled to a depth within 1 or 2 mm. of the well. Beyond the block, they are continued in the form of sleeves, about 2 cm. in length. One of these holes accommodates the thermometer for measuring the block temperature. The other holds the thermoregulator unit.

The vertical guide rods, I, which hold the upper block in alignment, are set in the upper face of the heater block at points 90° from the thermometer and thermoregulator holes and about 5 mm. from the edge. These rods are fluted to reduce heat conduction. The upper face of the heater block also contains a circular groove, J, 2 mm. deep and 3 mm. in breadth. The cooling block has an identical groove cut in its lower face. The glass ring, L, which separates the blocks has its edges ground into these grooves. If the apparatus is to stand on the table, short brass rods may be set into the bottom of the block to provide feet. For panel mounting, the block is supported by three 0.47-cm. (0.19-inch) steel rods threaded into the spool flanges at right angles to the thermometer and regulator. Two of these rods enter the top flange, and one enters the bottom. The metal surface of the spool is covered with thin asbestos paper, the heater coils are then put in place, and the space between the flanges is filled with Alundum cement. The heater coil leads are brought out through three holes in the bottom flange, each fitted with a ceramic insulating bushing.

The cooling block, B, is constructed of brass. On its lower face a central cylindrical extension, W, carries the metal slide, C, on which the glass slip is held by a tiny spring clip, T. The slide projects slightly above the retaining slot to prevent fouling the edges of the glass slip when it is removed from the block as well as to reduce unnecessary heat transmission. A stop pin, Y,

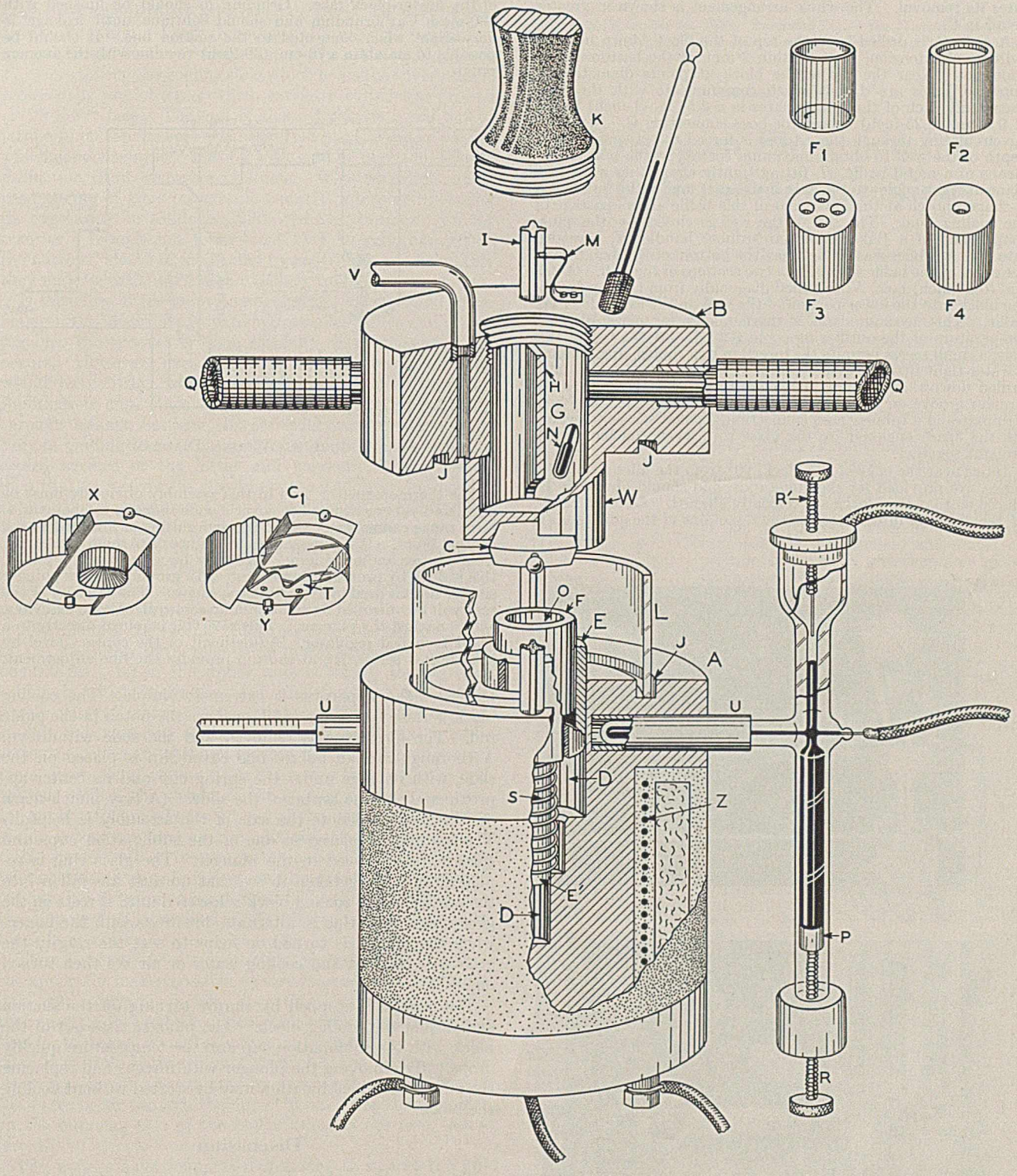


FIGURE 1. DIAGRAM OF SUBLIMATION APPARATUS SHOWING DETAILS OF CONSTRUCTION

fitting a small recess at the back end of the slide, prevents slipping past the center point. The slide may therefore be taken out for inspection and put back with assurance that the glass slip which it carries will be returned to its original position relative to the sublimation cup. A small knob at the front end of the slide facilitates its removal. The whole arrangement is shown in greater detail in C_1.

A well, G, is drilled from the top of the block, down into the cylindrical extension, W, to within 2 mm. of the bottom of the slide slot. Near the top of the block at points diametrically opposite, holes are drilled which communicate with the well. Outwardly each of these terminates in a 2.5-cm. (1-inch) length of 0.6-cm. (0.25-inch) tubing for hose connection Q. Water or air circulating through these tubes is forced to traverse the full depth of the well to obtain maximum cooling at the bottom, by means of a metal baffle, H, fitting tightly against its walls in a plane at right angles to the axis of the inlet and outlet tubes. A V-shaped notch at the lower end of this baffle allows passage of the cooling fluid. The top of the well is closed by the plug-shaped end of a Bakelite or hard-rubber handle, K, threaded into it. A rubber washer between the bottom of this handle and the edges of the baffle seals off the two sections of the well. A 0.6-cm. (0.25-inch) hole, N, is drilled diagonally from the top face of the block into the lower portion of the well on the exit side of the baffle. This accommodates a thermometer for measuring the temperature of the outflowing cooling fluid. At the top of this hole, a small recess permits the insertion of a rubber ring, making a water-tight fitting for the thermometer. A small hole is also drilled downward through the block to a point just inside the circular groove on the lower face. On the upper face, this hole terminates in a tubular hose connection, V, that serves to evacuate the space enclosed by the glass ring when the blocks are brought together.

Holes near the edge of the block, 90° from the inlet and outlet tubes, are provided for the guide rods, and should obviously be placed so that the blocks are coaxially aligned. A spring catch, M, which snaps into a notch at the top of one of the guide rods is mounted on the upper face of the cooling block and serves to hold the blocks apart during preparatory manipulations. The glass separating ring, L, should be of heavy-walled Pyrex tubing with the ends ground to parallel planes. Its height is such that when ground into the grooves, the cooling slide is held within 2 mm. of the heater-block face. Grinding in should be finished with 600-mesh Carborundum and should continue until leakage is very slight when connected to the suction line. It should be possible to maintain a 76-cm. (30-inch) vacuum with the average pump.

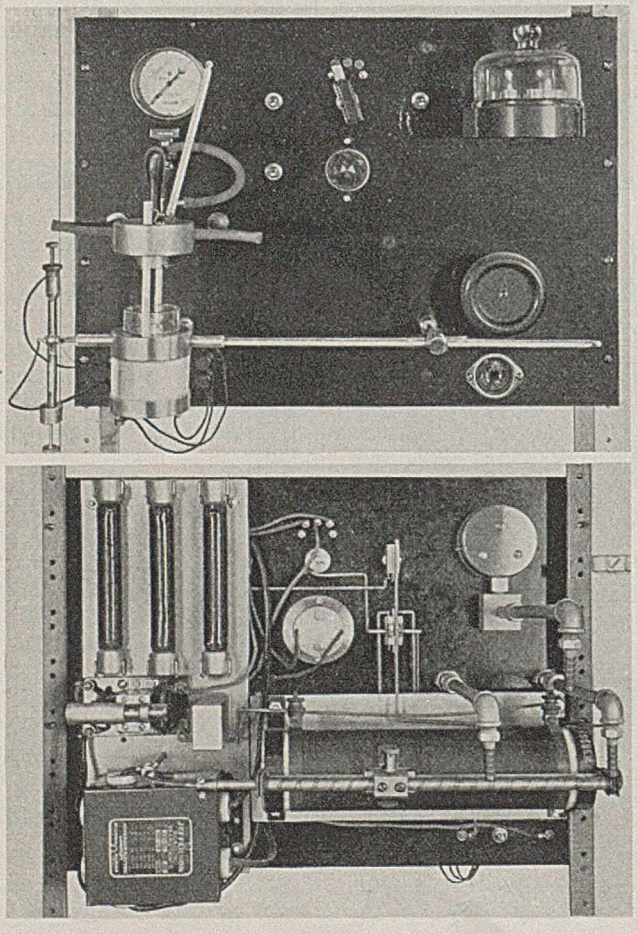


FIGURE 2. COMPLETE SUBLIMATION APPARATUS SHOWING DETAILS OF PANEL MOUNTING

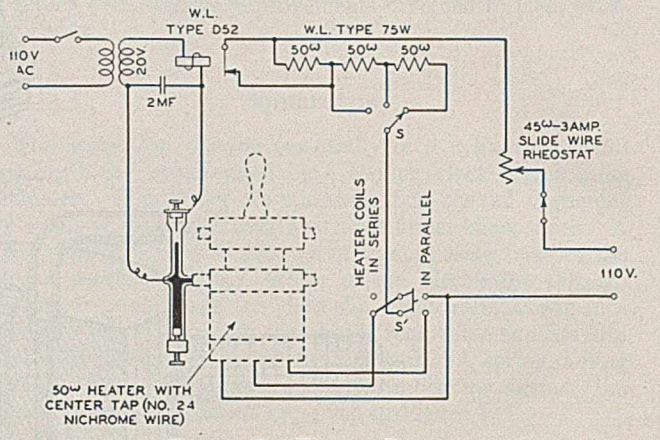


FIGURE 3. WIRING DIAGRAM

The thermoregulator used in this assembly obviously must be small and yet constructed to cover a wide range of temperatures. Such range cannot be obtained through raising or lowering of the contact point. It is necessary to introduce or to remove mercury from the expanding column. As may be seen in the drawing, this is done by providing a reservoir with ground-in glass plunger similar to that used in hypodermic syringes. The capacity of the reservoir is controlled by an aluminum screw, R, of large diameter, acting against the plunger. This reservoir is joined directly to a small L-shaped regulator. Adjustment of the contact level by the knurled screw, R', at the top provides the fine adjustment.

Use of the apparatus is extremely simple. The cooling block is raised until the catch engages the notch in the guide rod. The glass ring is removed and the slide withdrawn. A thoroughly clean microscope cover slip is placed on the slide, with its edge under the spring clip and its center approximately at the center of the slide. (A tiny punch mark on the slide to denote the axis of the assembly is helpful.) The material is placed in one of the sublimation cups and this, in turn, placed in the plunger. The glass ring is replaced, care being taken to see that no dust has fallen into the groove. The cooling block is lowered until it rests on the glass ring. Rotating in alternate directions with the fingers when the suction is turned on helps to seat the ring in the grooves. Current and cooling water or air are then turned on.

The process is stopped by simply turning off the suction and raising the cooling block. The plunger rises out of the block with the sublimation cup and the temperature quickly drops. By removing the plunger with forceps and replacing the cup a second sublimation may be started without cooling the block.

Discussion

The interchangeable cups provide convenient adaptation to varying types of specimens. The capacity of the subliming chamber may be thus reduced to a few cubic millimeters when dust particles or single crystals are dealt with. On the other hand, it may be large enough to accommodate small mechanical parts, the surface of which is to be examined for traces of waxy or oily matter as well as for volatile inorganic substances such as mercury or ammonium chloride.

Microdistillation of high-boiling substances under reduced pressure can also be carried out satisfactorily. When the quantity distilled is very small, or the viscosity of the distillate is high so that coalescence of the deposited droplets is prevented, the distillate is received on the cooled cover glass, as in sublimation. Larger quantities of more fluid substances are condensed on the arrangement shown in detail *X* (Figure 1). Here the regular cooling slide which holds the cover glass is replaced by one of silver which carries a cylindrical process on its lower face. The end of this cylinder is bored out to form a funnel-shaped reservoir inverted over the rising vapors which condense in it. Plating with gold or platinum affords protection from corrosive products. When a metal cup is used, a ring of glass or ceramic material interposed between its edge and the condenser slide reduces unnecessary heat transfer. Liquids not too viscous may be concentrated in the narrow "stem" of the funnel by centrifuging. From this they may be withdrawn with capillary tubes.

If the edges of the glass ring enclosing the evacuated space between the blocks are in perfectly parallel planes and grinding into the grooves is done carefully, little leakage of air occurs. However, even if this were considerable, it still would have little disturbing effect on the material in the sublimation cup, since communication is established only through leakage between the cup edge and the cover slip. Vapors tending to pass outward must therefore traverse the cooled surface of the latter and condense. As a result, quantitative recovery is closely approached, even in vacuum sublimation. Attainment of this goal is also furthered by the sharp temperature gradient maintained between the cup walls and the receiving slip. This facilitates the concentration of all the sublimate on a sharply defined area with practically no loss due to partial condensation on zones of intermediate temperature.

Alignment of the cooling block on guide rods and retention of the glass slip by a removable metal slide have distinct advantages. When the upper unit is raised, the slip and sublimate which it contains are lifted from the cup with a purely vertical motion, without interruption of the cooling. In this way smearing of the deposit and accidental volatilization of sublimate through leaving the uncooled slip, even for a short time, on the heated cup are both entirely prevented. When the weight of the cooling block is removed, the sublimation cup is forced out of the heater block by the spring acting on the plunger. Volatilization of material is thus arrested. This feature, combined with the slide, permitting quick removal of the glass slip, simplifies the problem of changing the slips at regular intervals when fractional sublimation or distillation is desired. No cooling of the heater block is necessary.

The use of metal for construction of the essential parts of the apparatus makes possible a more compact and less fragile unit and permits higher operating temperatures. The thermostatically controlled electrical heating makes it practicable to carry on sublimation or distillation over long periods of time with accurate control. The cooling of the receiving slip can be regulated by varying the rate of flow of the water or air through the upper block. The thermometer on the outgoing side of the baffle indicates the heat transferred.

The writers have found it convenient to mount the apparatus, together with electrical equipment, pressure gage, water outlets, etc., on a Bakelite panel which may be fastened to the wall or to a suitable rack, thus conserving table space. A complete portable unit is thereby provided, and the necessity of making flimsy connections between scattered pieces of equipment is eliminated. The photographs in Figure 2 show such an assembly. The electrical circuit is given in Figure 3.

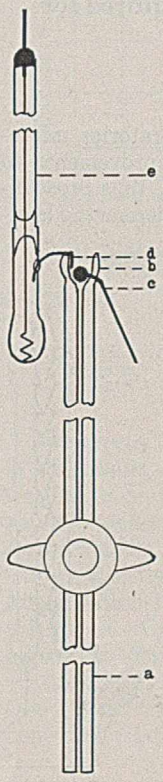
It is the authors' belief that an extension of the idea of panel mounting to other forms of microchemical equipment would distinctly improve both the efficiency and appearance of the laboratory.

RECEIVED September 30, 1938. Presented before the Microchemical Section at the 92nd Meeting of the American Chemical Society, Pittsburgh, Pa., September 7 to 11, 1936.

Hydrogen Electrode for pH Microdeterminations

H. A. FREDIANI
Louisiana State University, University, La.

THE apparatus illustrated has been found useful in this laboratory for determining pH on volumes ranging from 5 to 60 cu. mm., having the advantages (and disadvantages) of the hydrogen electrode but being more satisfactory with small volumes.



The electrode is constructed by cutting off the ends of a 1-mm. bore capillary stopcock, leaving approximately 8 cm. on each side of the cock. One end, *b*, is widened into a cup-shaped cell capable of holding a maximum of 0.1 ml. A small bead is formed on the end of a 3-cm. length of No. 20 platinum wire, flattened to a thin disk (1.5-mm. radius) and sealed in position as shown, *c*, with the thin edge in line with the capillary bore.

As calomel half cell the inner element, *e*, of the E. H. Sargent calomel electrode assembly, S-30,445, may be used without modification.

A satisfactory bridge is formed by soaking a piece of No. 50 cotton thread in saturated potassium chloride solution and then placing as shown, *d*. Natural and artificial silks, ramie, etc., are also satisfactory.

The electrode is plated by immersing the cell end in the ordinary plating (*1*) solutions and connecting as cathode. The electrode is washed by immersing in distilled water, the residual droplets being blown out by passing purified hydrogen through *a*.

After thorough cleansing, the electrode is inverted and connected to the calomel half cell as shown. If the cock is closed, when the solution is introduced into the cell by a micropipet the trapped gas in the capillary prevents the solution from dropping out of the cell. With a slight hydrogen pressure on *a*, turning the stopcock permits the gas to pass through the cell and form small bubbles, which are blown up to the mouth of the cell, coming in contact with both the blacked platinum disk and thread bridge. At the mouth the bubble breaks, the solution immediately flowing down the inside of the cell to the neck and forming a new bubble. Best results have been obtained when approximately 30 bubbles per minute formed. Equilibrium is reached very rapidly.

To determine the accuracy of this cell buffer solutions ranging in pH from 2.4 to 10.2 (in steps of 0.4 pH) were prepared and studied. The e. m. f. values recorded, using a type K-2 potentiometer, checked those obtained using a Hildebrand-type electrode on larger volumes of the same solutions.

Literature Cited

(1) Popoff, Kunz, and Snow, *J. Phys. Chem.*, 32, 1056–60 (1928).

RECEIVED November 7, 1938.

A Microdistillation Apparatus

With Receiver for Distilling under Reduced Pressure

S. A. SHRADER AND J. E. RITZER
The Dow Chemical Co., Midland, Mich.

An all-glass apparatus combining a receiver of new design with a microdistilling column for the distillation of high-boiling liquids is described. The receiver allows several fractions of the distillate to be collected without interrupting the pressure under which the distillation is performed.

Design and method of constructing the apparatus for 0.5 to 2.0 grams of material are given.

The apparatus is easily cleaned and assembled, and shortens the time required for a distillation.

SINCE their introduction in industrial laboratories, micro- procedures have constantly required improvements to reduce further the mechanical manipulations, thus broadening the field of application of some of the micromethods already familiar to industry.

Although several devices for microdistillation under reduced pressure (*2, 3*) have been reported, no attempt has been made to complete the distillation without interruption of the pressure under which the distillation is performed. This laboratory was confronted with the need for an apparatus for distilling small quantities of substituted benzene compounds. These compounds for the most part boiled at 225° to 325° C., and the apparatus here described seems an improvement justifying a communication at this time, although the work is still in progress.

Design of Apparatus

The flask and column of the apparatus are similar to that of Clarke and Hermance (*1*). The design of the side-arm delivery tube and that of the receiver for collecting the distillate were perfected in this laboratory during the past 2 years. The flask has a greatly flattened bottom; the size may be varied to suit special conditions or particular liquids. When a thin layer of 30-mesh silicon carbide or clean sea sand is used in place of boiling chips, as is customary in macrodistillations, evaporation takes place without active ebullition, thus eliminating bumping. An extremely small holdup becomes necessary, and this requirement can be fulfilled by using a Vigreux column. The internal projections made by punching indentations in the column act as baffles to arrest accidental spray and reduce the volume of the column to a minimum.

The receiver is constructed for easy removal of the fractions when the distillation is completed. The all-glass receiver has the advantage that no contamination from rubber stoppers is possible, and the desired amount of distillate can be estimated for each fraction before collecting the succeeding portion.

The apparatus shown in Figure 1, designed for volumes of 0.5 to 2.0 grams of material, is easily cleaned and assembled and relatively easy to manipulate. It has a holdup (weight of material in apparatus when the distilling flask has become dry) of approximately 0.08 to 0.12 gram of liquid, the column being 7 to 15 cm. in length and approximately 5 mm. in inside diameter. The receiver (Figure 1) contains small glass cups, each having a capacity of 0.10 ml. These cups are arranged in a circle of nine or more, so that each succeeding fraction distilled can be collected by rotating the entire receiver around joint *f*. The number of cups is variable with the thickness of the glass tubing used and the size of the glass joint, *m*. The details of the unassembled apparatus are shown in Figure 2. A condenser was not necessary for most of the liquids distilled in this laboratory. When low-boiling liquids are distilled, the side arm *e* may be wrapped with a cloth containing powdered solid carbon dioxide.

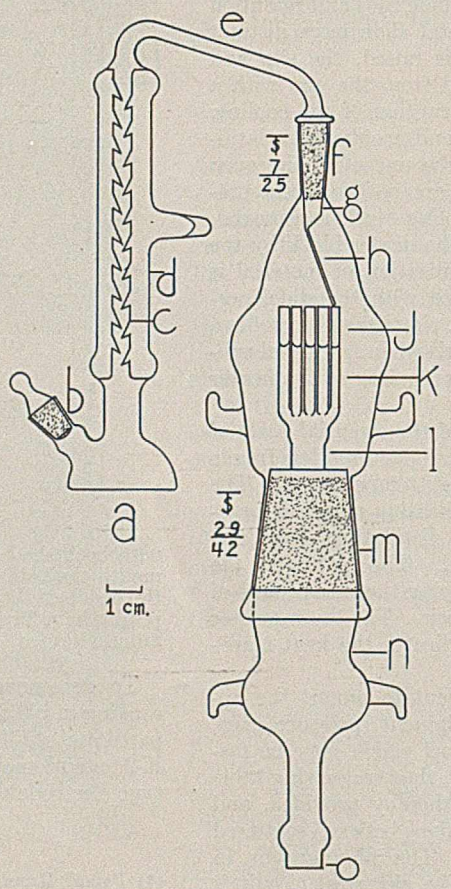


FIGURE 1. DIAGRAM OF APPARATUS

Constructional Details

The distilling flask, *a*, is a flat-bottomed bulb of 4-ml. capacity having neck with stopper to fit. The neck and stopper are made from a ⅋ 7/25 ground joint. Onto the top of the flask is sealed a 6.5-mm. tube, *c*, which is approximately 0.75 mm. in wall thickness and contains as many internal projections (4 to 5 mm. from center to center) as is convenient. The column has an outside jacket, *d*, 15 mm. in outside diameter, evacuated with a mercury vapor pump. The jacket is wrapped with aluminum foil further to insulate column *c*.

A 5-mm. tube is sealed to the top of the column and bent downward to form side arm *e*. The lower end of the tube has a ⅋ 7/25 glass joint to which is sealed a 5-mm. tubing, *g*. The latter is ground on a wheel to an angle, the long side being 9 mm. and the short side 4 mm. from the small end of the male part of the ground joint, *f*. To the long side of tube *g* is sealed a 1.0-mm. glass rod, tapering to 0.8 mm. The length of the glass rod varies with the distance the receiving cups, *j*, are placed from

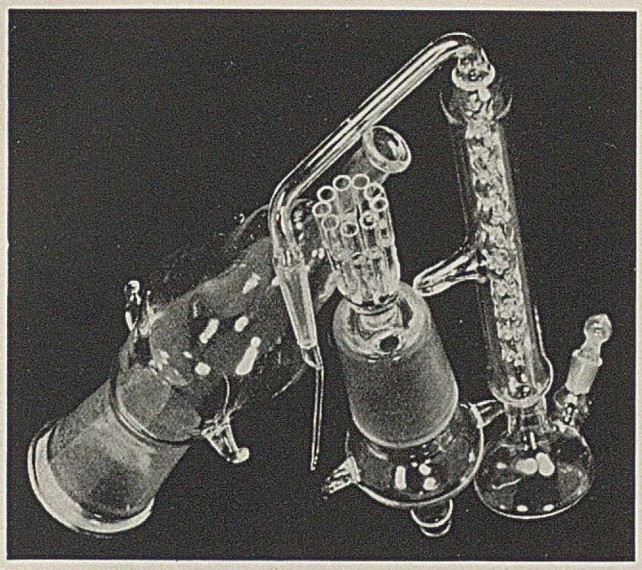


FIGURE 2. DETAILS OF UNASSEMBLED APPARATUS

the exit end of the side arm, the most convenient length being 225 to 290 mm.

Several different arrangements have been tried for conducting the drops of liquid from the side arm into the receiving cups, the one described above proving the most satisfactory. The only requirements for continuous transfer of the liquid from the side arm to the cups are: the glass rod, *h*, must be smoothly sealed to the lower end of the side arm with the end of the rod extending directly over the cups; and the apparatus must be entirely free from grease.

The receiving cups, *j*, for collecting the distillate are made from 4-mm. thin-walled glass tubing which is sealed to 4-mm. glass rod *k*. The rods with the cups are sealed to a 10-mm. glass rod, *l*, and the latter is made a part of the removal male glass joint, *n*. This latter operation is performed by closing the small end of the male joint and sealing the 10-mm. glass rod to the center of this closure. A 6-mm. hole (Figure 2) is then blown opposite this connection to permit evacuation of the apparatus by attaching tubing to vacuum pump at *o*.

The distilling flask is heated by means of an oil bath, which is stirred mechanically by a small air-driven stirrer. A thermometer in the oil bath is the only means of measuring the temperature.

A 1-mm. layer of clean sea sand or 30-mesh silicon carbide is placed on the bottom of the flask and the liquid is inserted with a pipet through neck *b*. The flask is connected to the receiver and the apparatus evacuated to the desired pressure. The temperature of the oil bath is then slowly raised until a steady reflux is maintained in the column. To do this it is necessary to adjust the temperature of the oil bath to ±1.0° C. to permit only one or two small drops of the liquid to be distilled during 3 minutes. If a large amount of liquid is driven over, the column floods and the efficiency of the apparatus is impaired. A uniform reflux is essential for best results.

Arbitrary fractions are collected by rotating the receiver containing the glass cups around joint *f*, rather than at *m*, there being less resistance, especially when a high vacuum is maintained. When the distillation is complete, air is allowed to enter the apparatus at *o*, and the lower part of receiver *n* is removed. The refractive index, boiling point, and chemical analysis, if desired, are determined on the separate fractions by well-known micromethods.

The receiver described here has been used with the Vigreux-type column, and the column described by Craig for high-boiling liquids. The latter was used in those cases where the liquid did not wet the glass surface. A short ground-glass joint was placed between the flat-bottomed flask and the column used by Craig to facilitate introduction of the resistance wire and the inner part of the column.

Tests on a Synthetic Mixture

Although the apparatus described has been used primarily for determining the boiling range of organic liquids obtained in small amounts, actual tests on the separation of synthetic mixtures were made to be sure of the value of the apparatus.

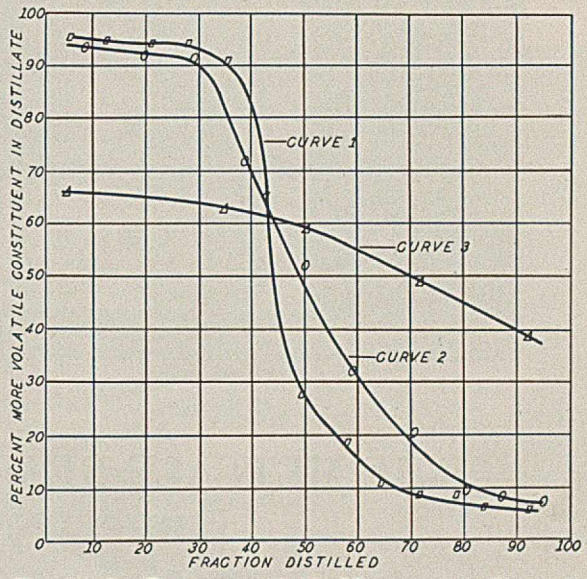


FIGURE 3. TESTS ON 50–50 MIXTURE OF ISOAMYL SALICYLATE AND CAPRYLIC ACID

□ Separation obtained by Craig's column
○ Vigreux column with evacuated jacket and receiver
△ Vigreux column without evacuated jacket but with receiver

The curves (Figure 3) represent graphically a comparison of the results obtained with a 50–50 mixture (per cent by weight) of caprylic acid and isoamyl salicylate. The analyses were made by the refractive index method. Curve 1 represents the separation given by the column described by Craig but without the receiver. Curve 2 is the separation obtained with a 15-cm. column and the receiver as described in this paper. Curve 3 represents the results obtained with an apparatus similar to the one described, but without the evacuated jacket surrounding the Vigreux column. In each case 1 gram of the mixture was used and the distillation was done under 1-mm. pressure.

Literature Cited

(1) Clarke, B. L., and Hermance, H. W., *Mikrochemie*, 18, 289 (1935).
(2) Craig, L. C., IND. ENG. CHEM., Anal. Ed., 9, 441 (1937).
(3) Peakes, L. V., Jr., *Mikrochemie*, 18, 100 (1935).

RECEIVED September 26, 1938. Presented before the Microchemical Section at the 96th Meeting of the American Chemical Society, Milwaukee, Wis., September 5 to 9, 1938.

THE METCALF RESEARCH LABORATORY AT BROWN UNIVERSITY

HARTLEY C. ECKSTROM
Brown University, Providence, R. I.

THE new Metcalf Research Laboratory, the construction of which was made possible by a gift of half a million dollars from former Senator Jesse H. Metcalf, stands on the Brown Campus adjacent to the Jesse Metcalf Memorial Laboratory, a gift from Mr. Metcalf in 1922. The architecture of the new laboratory, like that of the older structure, is Georgian and harmonizes with other nearby buildings. In addition to the building, Mr. Metcalf's gift provides for much new research equipment and endowment for research.

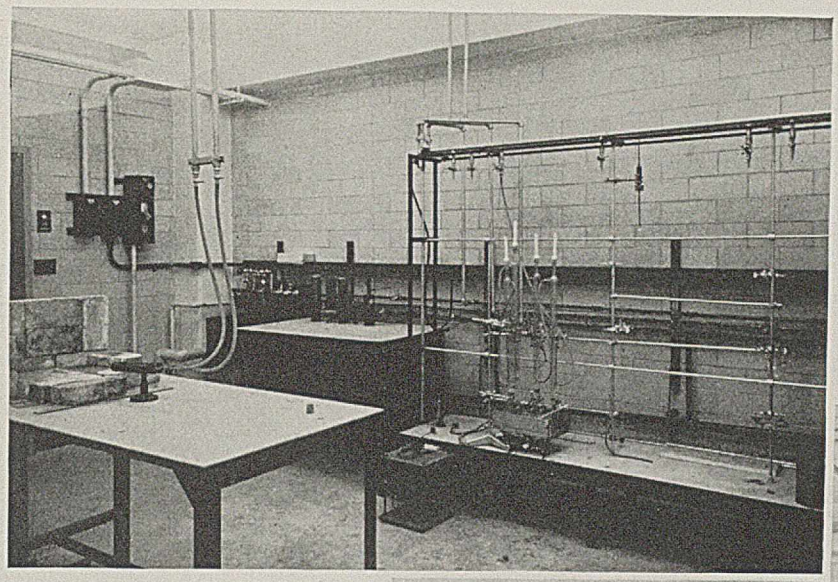
The new laboratory is a three-story structure, with basement, having a length of 130 feet and a width of 48 feet. Its primary purpose is to provide research facilities for the staff and students of the Department of Chemistry. It also houses the laboratories of undergraduate physical chemistry and the combined libraries of the Departments of Chemistry, Physics, and Mathematics.

The arrangement of laboratories and service rooms will be evident from the floor plans. The corridor walls divide the building so that the laboratories on either side have a depth of 19 feet. The corridor ends at a transverse partition wall at the west side in order to provide some larger rooms, 30 × 45 feet, which may be used intact or divided suitably to meet the need for laboratories of unusual size and shape.

In the basement are laboratories for photochemical and spectroscopic research, the machine shop, generator and switchboard room, storerooms, and the air-conditioning unit. Undergraduate physical chemistry is provided with a large laboratory on the west end of the first floor, as well as several small laboratories, a dark room, and a storeroom. Except for one office, the remaining space on the first floor has been divided into small laboratories, all equipped with light-tight blinds. On the second floor are located offices, a conference room, research rooms, and service rooms which include a storeroom, an instrument room, a balance room, and a conductance room. Altogether, there are twenty-two research laboratories capable of accommodating thirty-five laboratory workers very comfortably.

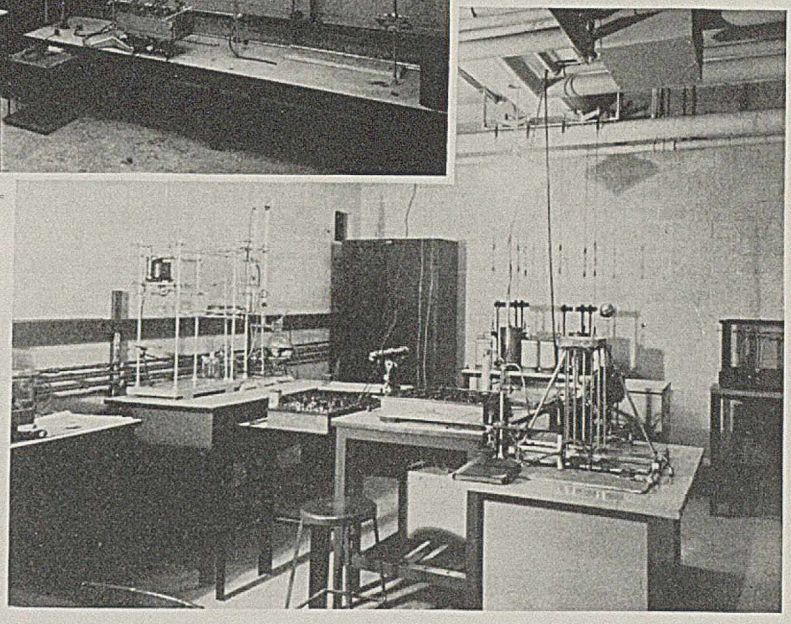
Numerous rooms are provided for special purposes; they include the microphotometer room, grating room, spark room, special spectroscopic laboratories, two darkrooms, and computing room. The combined chemistry, mathematics, and physics libraries are housed on the third floor, where there are two levels of stacks accommodating 60,000 volumes. In addition, there are a reading room, three offices, and a small conference room. Additional reading room is provided by means of carrells along the south and north walls at the end of the stacks. A small freight elevator connects all three floors and the basement. It is located next to the stock rooms, thus providing an easy means of transporting heavy equipment and stock from one floor to another.

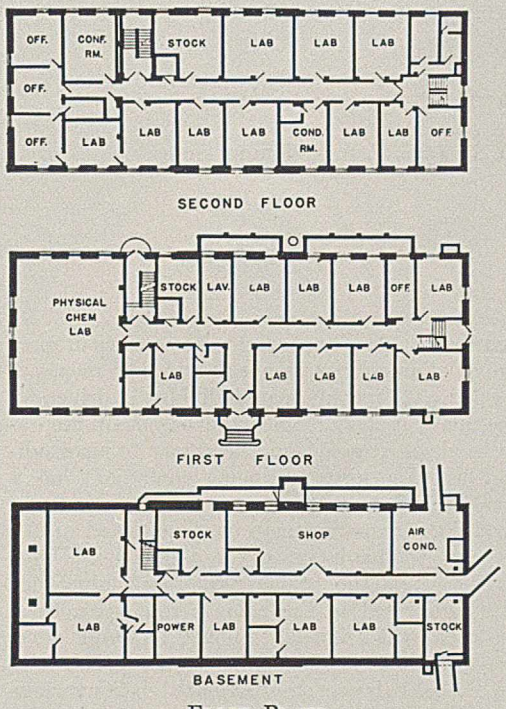
The entire building was designed so that it may easily be adapted to any type of research. The only permanent floor fixture in any laboratory is the sink. All sinks are Karcite and are provided with steam and steam mixers. All chemical desks and tables are constructed of steel with Transite tops and are portable. Around the walls of all laboratories, pipes for gas, water, and air are attached to racks by means of small brackets and a special pipe for water drainage is hung below these. This arrangement permits the moving of tables, desks, ammonia benches, and special apparatus to any



Above. LAYOUT OF LABORATORY 213

Below. LAYOUT OF LABORATORY 5
Setup of freezing point apparatus





FLOOR PLANS

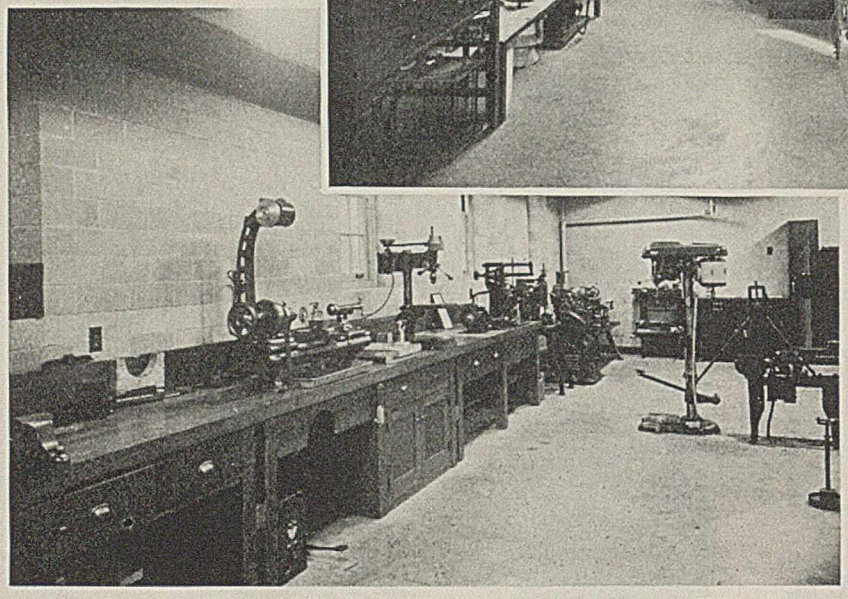
part of a laboratory with the necessary services always available. All the services—water, gas, air, and steam—that supply a laboratory may be shut off in that laboratory, so that any necessary changes may be made in a laboratory without disrupting the work in any other part of the building. Since all pipes and electrical conduits are exposed, changes may be easily made.

Each laboratory is also provided with 110- and 220-volt alternating current, 110-volt direct current of 35 amperes capacity, and two special circuits with a carrying capacity up to 100 amperes. These circuits run directly to the switchboard in the basement. In all laboratories, the 110-volt alternating current circuit is run along the walls in a 4 × 4 inch steel trough with hinged front, fastened to the wall racks above the pipes for water, gas, air, and drain. Whenever it becomes necessary to add other electrical services, the conductors may be laid in this trough. All laboratory circuits, except special circuits, are provided with individual circuit breakers. The special circuits terminate in safety switches. This, again, permits changes to be made in the wiring of any laboratory without inconvenience to workers in the rest of the building.

The photographs illustrate the flexibility of the arrangement adopted. The steel trough conduit, the water, gas, and air pipes, and the water drain are clearly visible. A unit of two circuit breakers and a special circuit safety switch is visible in Laboratory 213. The design and construction of the ammonia benches and the manner in which they are connected to the services may also be seen in Laboratories 204 and 213.

Since the building is fire-proof throughout, with the interior walls and facing of vitrified tile, it was necessary to provide an easy means of hanging pipes, conduits, and wires, and of suspending special apparatus, such as galvanometer suspensions. This was accomplished by means of ceiling inserts which are regularly spaced at 4-foot intervals in all laboratories, starting 1 foot from all walls. By means of special hangers, any type of apparatus or pipe may be readily hung without boring holes in either the walls or the ceiling. In Laboratory 213 the pipes for gas and air are run across the ceiling to the middle of the

Right. LAYOUT OF LABORATORY 204
New parallel high-resistance bridge and thermostat on right



Left. MACHINE SHOP

room for use with a blast lamp and two galvanometer suspensions and numerous wires are shown hung from the inserts in Laboratory 5.

The undergraduate physical chemistry laboratory and several other laboratories are equipped with hoods which are constructed of black composition stone with glass doors. Each hood is provided with a sink, and with water, gas, air, steam, and electrical services. The table tops in the hoods are removable, so that racks, similar to those of the ammonia benches, may be set up inside the hoods. Each hood is provided with an individual exhaust fan. All other laboratories are provided with ducts for fume ventilation. Not more than two laboratories are connected to one exhaust fan and all fans have a capacity of 900 cubic feet per minute. The ducts are constructed of Transite pipe. The fans are placed just under the roof, and each fan has its own exhaust to the atmosphere, so that there is no danger of a down draft returning the exhausted fumes to another laboratory.

Near the south wall in the basement of the building provision has been made for hanging a 110-foot absorption tube for spectroscopic work. On the west side, in the basement, a special thermally insulated room has been provided for a 21-foot grating which will be used with a modified Eagle mounting, and has been so arranged that the grating may be used in conjunction with the absorption tube. The machine shop, which is 50 feet long and 18 feet wide, provides ample facilities for machine work and apparatus construction required for research purposes. In one corner of the shop, a small student shop has been provided and equipped with a small lathe, drill press, and other tools. The shop is lighted by means of mercury vapor lamps. Fume ventilation is provided by means of an open-faced hood. All machines are individually driven by means of three-phase motors. Since the basement laboratories have no windows, it was found necessary to air-condition the basement. The air-conditioning equipment has a capacity of 2,000 cubic feet per minute.

On the second floor, a special room has been fitted up for conductance work. In this laboratory is a shielded, soundproof room which holds the bridge used for conductance measurements. Connected to the balance room is a thermally insulated room which is used to house a microbalance. The balance room itself is used only for special balances of high sensitivity; other balances are distributed in the various laboratories as needed.

Every effort has been made to ensure adequate lighting in all parts of the building. Each research laboratory, depending upon size, has from two to six ceiling fixtures, each of 350-watt capacity. In addition, a special ceiling receptacle with its own switch is provided to supply additional lights as required.

Each research laboratory is furnished with a chemical desk which has three drawers, plain tables, a glass-blowing table, an ammonia bench, a storage cabinet, a clothes locker, and a desk with lamp and chair and a bookcase. Each ammonia bench is furnished with gas, water, air, and electricity. The chemical desks are open underneath and have no lockers for storage; adequate storage space is provided in 72 × 36 × 18 inch cabinets.

Subscription Rates

American Chemical Society Publications

1.	Journal American Chemical Society	$ 8.50
2.	Chemical Abstracts	12.00
3.	**Industrial and Engineering Chemistry.**	
	a. Industrial Edition	$3.00
	b. Analytical Edition	2.50
	c. News Edition	1.50
	3a and 3b together	5.00
	3a, 3b and 3c (i. e., complete journal)	6.00

10% discount for combinations of 1, 2 and (or) 3 (complete). Postage to foreign countries outside the Pan American Postal Union extra as follows: 1, $1.50; 2, $2.10; 3a, $1.20; 3b and 3c, $0.60 each; 3 complete, $2.40. Canadian postage one-third these rates.
Single copies of current volumes, 75 cents each, except 3b ($.50) and 3c ($.10).

BACK NUMBERS AND VOLUMES

Jour. Am. Chem. Soc., Vols. 28–60 (only ones available), each		$ 9.00
Index to Vols. 1–20		1.00
Single copies, some prior to Vol. 28, each		.80
Chemical Abstracts, Vols. 1–32, including 1st and 2nd Decennial Indexes		645.00
Vols. 9–15, each		20.00
Vols. 16–32, each		15.00
Single copies, except Index Nos., each		.80
Annual Index, each year		2.50
2nd Decennial Index, 5 Volumes		50.00
Ordered with 3rd Decennial Index before June 1, 1939, or for replacement		25.00
3rd Decennial Index, 5 Volumes		100.00
Contingent discount of 50% to individual members, contributing firms, educational institutions and public libraries in the United States.		
Industrial and Engineering Chemistry		
Industrial Edition,	Vols. 1–30	270.00
	Vols. 9–30, each	9.00
	Single copies, each	.80
Analytical Edition,	Vols. 1–10	40.00
	Vols. 4, 5, 7, 9, 10, each	4.00
	Single copies, when available, through Vol. 8, each	.60
	Single copies, Vols. 9–10, each	.50
News Edition,	Vols. 1–16, each	2.00
	Single copies	.10

Volumes not priced singly, available only in complete sets.
Members, for personal use, 20% discount from above prices, except complete sets, Decennial Indexes, and single copies of the News Edition.

Advance payment is required in all cases and must be made by postal order or check payable in U. S. currency on a bank in the United States.

DOMESTIC SHIPMENTS. Single copies are sent by mail. Full volumes and sets are sent in the United States and Canada express collect.

FOREIGN SHIPMENTS. Additional charge for postage. Foreign shipments will be sent by mail either at purchaser's risk or by registered mail at postage cost plus 5% of invoice additional for registry; minimum charge, 75 cents. Large shipments will be delivered free, if desired, to responsible forwarding agents in New York, further charges to be paid by the purchaser on receipt.

The Society will not be responsible for loss due to change of address unless notification is received ten days in advance of issue. Claims for non-receipt must be made within 60 days of date of issue. "Missing from files" cannot be accepted as evidence of non-receipt. If change of address means a change of position, please indicate its nature.

Subscribers desiring their journals forwarded from an old address should always notify their Postmaster and leave necessary postage.

The names of members and subscribers, whose journals cannot be delivered by the Post-Office Department, will be cut off the mailing list at once, and will not be restored until correct addresses have been furnished.

In the absence of other information, the notices of change of address received from the Post-Office Department will be considered as correct, and the mailing list changed accordingly.

Address communications relating to the foregoing to
CHARLES L. PARSONS, Business Manager, Mills Building, Washington, D.C.