ANALYTICAL CHEMISTRY

Walter J. Murphy, Editor

Second Summer Symposium

ORGANIC Reagents" is the subject of the second summer symposium cosponsored by the Division of Analytical and Micro Chemistry and the publication ANALYTICAL CHEMISTRY. The place is the Wesleyan University campus, Middletown, Conn., and the time, Friday and Saturday, June 24 and 25.

The general chairman, S. E. Q. Ashley, General Electric Co., has assembled an outstanding group of speakers. Through the courtesy of the Minister of Agriculture of the Brazilian Government, Fritz Feigl will lecture at the Saturday morning session on the broad topic, "The Role of Organic Reagents in the Chemistry of Specific, Selective, and Sensitive Reactions." The opportunity to hear Professor Feigl has been eagerly awaited by the analytical chemists of the United States.

I. M. Kolthoff of the University of Minnesota, recently honored by the presentation of the Nichols Medal, will discuss the use of organic reagents in amperometric titrations; Philip W. West of Louisiana State University will deliver a paper on "Interferences with Reactions between Organic Reagents and Metal Ions"; and Earl H. Winslow and H. A. Liebhafsky of the General Electric Laboratories will report on "The Spectrophotometric Evaluation of Spot Tests."

N. H. Furman, the 1948 Fisher medalist, and W. B. Mason and J. S. Pekola are scheduled to present a paper on "The Extraction of Cupferrates." A second paper from the Princeton University laboratories will be presented by C. E. Bricker and K. H. Roberts.

G. Frederick Smith, in cooperation with Warren W. Brandt, will present a paper on "Polysubstituted 1,10-Phenanthroline and Bipyridine Derivatives as Multiple Range Redox Indicators. Further Applications in Their Use as Specific Reagents for Anion Analysis."

A partial list of other well known research workers who will present papers includes Mary L. Willard, H. H. Willard, Louis A. Gordon, C. Vanselow, Charles E. White, Gordon H. Ellis, E. M. Zook, and Oskar Baudisch.

One of the highlights of the two-day affair will be the dinner on Friday evening. The main speaker will be William E. Kappauf, Jr., of Princeton University, whose subject will be "Applied Aspects of the Psychology of Vision"—a challenging topic to an audience composed of chemical analysts.

The toastmaster at the dinner will be A. B. Lamb, editor of the *Journal of the American Chemical Society*, who is retiring as active head of the *Journal* at the end of this year. The occasion will afford friends and associates an opportunity of honoring a scientist and editor who has served in a most distinguished manner the science of chemistry both in contributions of important original research and as editor-in-chief of the world's leading journal recording the progress of fundamental chemistry. Dr. Lamb has served as editor of the *Journal of the American Chemical Society* since 1918 and in that 31-year period the *Journal* has grown in influence to its present position of international pre-eminence.

The program of the second summer symposium is printed in this issue and will appear also in *Chemical and Engineering News*. Local arrangements are under the general direction of M. Gilbert Burford of Wesleyan University. Accommodations at the university are limited and we urge that those planning to attend use the coupon on page 648 of this issue to signify intention to attend. Wesleyan University has very kindly placed all its facilities at the disposal of those attending and it is imperative that a definite indication be made, at least by June 9, of the number who plan to be present.

The idea of summer symposia sponsored jointly by the Division of Analytical and Micro Chemistry and this publication is no longer experimental. The first, held last year at Northwestern, demonstrated the practicability of holding meetings on specialized subjects at a time other than national meetings of the Society. The subject of the 1950 symposium, "Analytical Separations," was selected at a recent meeting of the Executive Committee of the division. Analysts, we believe, will find this program as interesting as "Analytical Chemistry and Nucleonics" and "Organic Reagents." And in closing, it is our pleasant duty to report that the papers presented at Wesleyan, June 24 and 25, will be published in the November issue of ANALYTICAL CHEMISTRY.

Divisional Membership Climbs

THE suggestion of a membership of 1000 for the Division of Analytical and Micro Chemistry by the end of the present year may have sounded to some as slightly on the fantastic side when it was made originally in January, but with nearly 700 now on the rolls, it would appear that the original goal will be exceeded by several hundred, a gain by the way of more than 200 per cent in less than a year.

The division, presenting an active and interesting program, deserves the whole-hearted support of every analyst. If you are not a member already, may we suggest that you give moral and financial endorsement by joining this concerted and constructive effort to provide analytical chemists with a program that they can well be proud of, and from which they individually and collectively will be sure to derive a great many benefits.

Dues, one dollar a year, should be sent to William G. Batt, Biochemical Research Foundation, Newark, Del.

Microwave Spectra and Chemical Analysis

B. P. DAILEY, *Columbia University, New York, N. Y.*

Absorption spectroscopy in the microwave region offers a new and useful tool in chemical analysis and process control. Molecular absorption spectra in the microwave frequency range are usually due to molecular rotation. To aid in understanding these spectra the relevant principles of molecular dynamics are discussed. The microwave spectrograph possesses extreme resolution, permitting actual absorption line shapes to be observed. The use of a single resolved molecular rotation line for quantitative analysis of an organic molecule in a complex mixture is proposed. The limitations of this analytical technique due to low intensities, the presence of only a small permanent electric dipole moment, excessive chemical reactivity of the absorption cells, etc., have been explored. The advantages and disadvantages of microwave spectroscopy in various applications are contrasted with those of the mass spectrometer and the infrared instruments. Molecular rotational spectra are characteristic of the molecule as a whole and do not possess features, as do vibrational spectra, characteristic of individual groups of atoms within the molecule. The extreme resolution available suggests that microwave techniques might be suitable for isotopic analyses in some instances.

MODERN analysts, who have made good use of molecular spectroscopy in the infrared and Raman regions, have shown considerable interest in the recent development of spectroscopy in the microwave frequency range. Just as the electronic spectra of molecules occur largely in the visible and ultraviolet and vibrational spectra in the infrared, transitions between the rotational energy states of molecules are to be observed most conveniently in the frequency range from 0.3 to 20 cm.$^{-1}$ Little purely analytical work has been done in this field as yet, but such applications of microwave techniques should find increasing importance in the near future. Workers in the field of microwave spectra preparing very small samples of organic molecules containing enriched isotopes find the microwave spectrograph the most convenient analytical tool available.

A considerable number of laboratories are now equipped with microwave spectrographs with which research groups are studying problems of molecular structure and the determination of the spins and moments of various nuclei. As a result of this work understanding of the basic principles underlying molecular rotational spectra has been much improved. This article presents certain of these principles briefly, in order that analysts searching for new instrumental methods may be able to evaluate the possibilities and limitations of chemical analysis with the microwave spectrometer.

This new technique offers attractive possibilities. Although the occurrence of a sharply resonant line spectra in this frequency region is limited to dilute gases, any compound having a vapor pressure of as much as 10^{-4} mm. may be worked with if as much as 10^{-8} mole is available. The resolution of the microwave spectrometer is so great that in the microwave region so far investigated there is room for 5,000,000 noninterfering rotational lines. In principle, at least, 1000 or more different complex organic molecules could be quantitatively determined from a sample smaller than 1 microgram without harming the sample in any way. Such performance cannot be expected of equipment in use at the present time, but is possible in principle and indicates why this field should be of interest to analysts. Furthermore, rotational spectra when observed at such high resolution are extremely sensitive to the over-all structure of molecules in a way that is different in important respects from infrared and mass spectra. On the other hand, microwave spectra have certain fundamental limitations which prevent detection of whole classes of molecules.

MOLECULAR DYNAMICS

Rotational spectra have in the past several years been observed by microwave techniques over the frequency range from 0.2 to 2 cm.$^{-1}$, although for the most part any given investigator has been able to work in only a portion of that band. It is convenient in discussing spectra in this region to express frequencies in megacycles (1 Mc. = 10^6 cycles; 29,978 Mc. = 1 cm.$^{-1}$). It is possible with not very elaborate equipment to measure the frequency of a rotational line to 0.01 Mc. (*6*), which for a line falling at 30,000 Mc. is better than one part in 10^6. Lines separated by no more than 0.1 Mc. clearly have been resolved by microwave spectrographs (*11*). The pattern of the rotational spectrum of a molecule depends on the molecular symmetry. Spectra for a representative group of molecules are shown in Figure 1. In the absence of perturbing effects the frequency spacing of the rotational lines of linear and symmetric rotor molecules is linear. This can be seen to be true for all the molecules in Figure 1 except sulfur dioxide. This asymmetric rotor has a complex rotational spectrum rich in lines with no obvious pattern of frequencies. The figure would be more representative if all but one of the molecules were asymmetric rotors, as this is the class of molecules met most frequently in analytical work.

A line occurs in the rotational spectrum of a molecule when a transition is made between two stationary energy states in such a manner as to interact with electromagnetic radiation. The frequency of the emitted or absorbed line is related to the difference in energy of the rotational energy states by the equation

$$\nu = (W_2 - W_1)/h \qquad (1)$$

where h is Planck's constant.

A solution of the quantum-mechanical problem of the energy levels of a rigid symmetric rotor gives the following expression for the rotational energy

$$\frac{W_r}{hc} = F(J, K) = BJ(J + 1) + (A - B)K^2 \qquad (2)$$

where W_r = rotational energy in ergs
c = velocity of light
$F(J, K)$ = rotational energy in cm.$^{-1}$
$Jh/2\pi$ = total angular momentum
$Kh/2\pi$ = the component of the angular momentum parallel to the axis of symmetry of the molecule

$$A = \frac{h}{8\pi^2 c I_A} \qquad B = \frac{h}{8\pi^2 c I_B}$$

I_B = moment of inertia of the molecule about an axis through its center of gravity and perpendicular to the molecular symmetry axis

I_A = moment of inertia of the molecule about its axis of symmetry

Microwave spectra are obtained as absorption spectra, by noting the amount of microwave radiation transmitted through a gas sample as a function of frequency. The quantum-mechanical selection rules for transitions between the rotational energy levels of a symmetric rotor are

$$\Delta J = +1 \quad \Delta K = 0 \tag{3}$$

A molecule which is only accidentally a symmetric rotor can have in addition transitions for which $\Delta K = +1$ if there is a component of the dipole moment perpendicular to the symmetry axis of the molecule.

With the selection rule given in Equation 3 a very simple formula is obtained for the frequencies of the rotational transitions

$$\nu \text{ cm.}^{-1} = 2B(J + 1) \tag{4}$$

where J is the angular momentum quantum number for the lower rotational state.

For a linear molecule in the ground vibrational state $K = 0$, so that the expression for the rotational energy reduces to

$$F(J, K) = BJ(J + 1) \tag{5}$$

The expression for the frequencies of the rotational transitions has the same form as Equation 4.

The calculation of the rotational energy levels of an asymmetric molecule is a somewhat more complicated problem although techniques have been worked out for the lower rotational energy levels which are normally of chief interest (*4*, *5*, *9*). Equations of the following form are encountered in these calculations

$$F(J_\tau) = {}^1/_2(B + C)J(J + 1) + [A - {}^1/_2(B + C)]W_\tau \tag{6a}$$

or
$$F(J_\tau) = {}^1/_2(A + C)J(J + 1) + {}^1/_2(A - C)E_\tau \tag{6b}$$

$$A > B > C$$
$$I_A < I_B < I_C$$

W_τ and E_τ are closely related quantities which depend in a complicated manner on A, B, C, and J, and for a given J assume $2J + 1$ different values.

These formulas and the sample spectra shown in Figure 1 indicate the considerable increase in complexity of rotational spectra with increasing asymmetry of the molecule. For a linear molecule or for a symmetric rotor it is possible to obtain the moment of inertia of the molecule directly from the frequency of a single identified line. The relation used is

$$I_B = \frac{16{,}774(J + 1) \times 10^2}{\nu\, mc} \times 10^{-40} \text{ g. sq. cm.} \tag{7}$$

As an example, as the molecule $O^{16}C^{12}S^{32}$ has a spectral line occurring at 24,325.92 Mc. corresponding to the rotational transition $J = 1 \longrightarrow J = 2$, its moment of inertia is 137.9×10^{-40} g. sq. cm.

The moment of inertia of a molecule is defined as $\Sigma m_i r_i^2$ where the m_i are the masses of the individual atoms and the r_i are the perpendicular distances to the axis running through the center of gravity of the molecule. For a specific molecule this can be transformed into an expression involving the atomic weights of the various atoms making up the molecule and the internuclear distances. In the case of OCS this expression has the form

$$I_B = m_c r^2_{c-s} + m_o(r_{o-c} + r_{c-s})^2 - \frac{[m_c r_{c-s} + m_o(r_{o-c} + r_{c-s})]^2}{M}$$

of the $J = 1 \longrightarrow J = 2$ transition

where J is the rotational quantum number. The frequencies and derived moments of inertia have been obtained for several of the isotopic forms of the OCS molecule (Table I).

Table I. Moments of Inertia for OCS

Molecule	ν 1 ⟶ 2, Mc.	$I_B \times 10^{-40}$ G. Sq. Cm.
$O^{16}C^{12}S^{32}$	24,325.92	138.0
$O^{16}C^{12}S^{33}$	24,020.3	139.7
$O^{16}C^{12}S^{34}$	23,731.33	141.4
$O^{16}C^{13}S^{32}$	24,247.82	138.4
$O^{16}C^{14}S^{32}$	24,173.0	138.8

If it is assumed that the internuclear distances are the same for these molecules, a set of simultaneous linear equations may be set up, any two of which are sufficient to determine the molecular parameters. The internal consistency of such data indicates that internuclear distances accurate to 0.01 Å. may be determined in this manner.

Equation 7, relating the frequency of rotational transitions to the moment of inertia, serves to point out one of the limitations of microwave spectroscopy as an analytical method. Symmetric rotor and linear molecules with small moments of inertia will have widely spaced spectral lines and for molecules with moments less than about 30×10^{-40} g. sq. cm. will have no rotational transitions falling within an accessible portion of the microwave frequency range. This limitation does not hold, however, for asymmetric molecules obeying a different set of selection rules.

It may also be seen from the simple relation between the moment of inertia and the frequencies of the rotational transitions that the rotational spectrum is a function solely of the overall structure of the molecule and does not contain, as does the infrared vibrational spectrum, features characteristic of groups within the molecule. Thus in analysis the two techniques, micro-

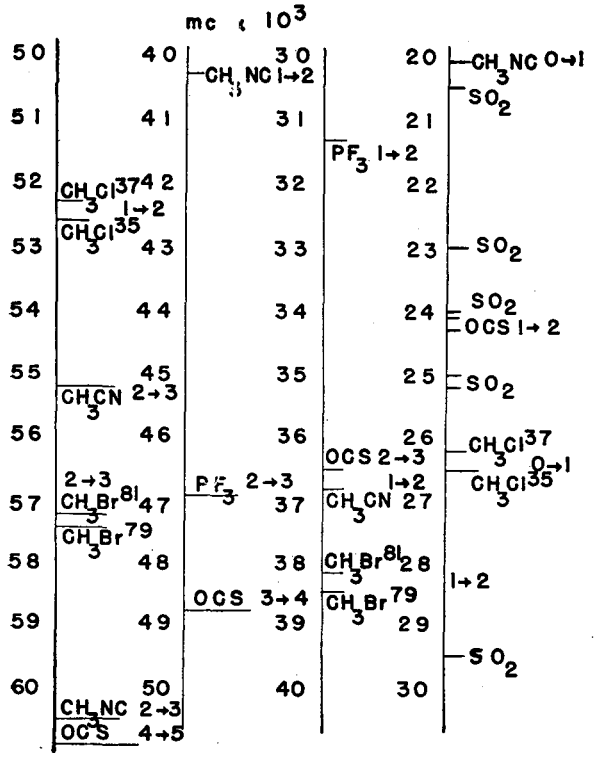

Figure 1. Sample Microwave Rotational Spectra

wave and infrared, are in many cases natural complements rather than competitors. From the infrared spectrum the presence of characteristic groups may be determined and from the microwave spectrum their arrangement within the molecule.

The foregoing treatment of the rotational spectra of molecules has given an exaggerated impression of their simplicity. Actual rotational spectra are frequently complicated by various types of fine structure, some of which have been encountered for the first time in the microwave region because of the extreme resolving power available. In some instances, when there is no specific interest in the fine structure, it may be neglected by operating the spectrometer at less than maximum resolving power. In many cases this is not practical and the fine structure serves to decrease the intensity of the observed spectral line. For a molecule whose total intensity for a given rotational transition is small fine structure, splitting may reduce the intensity of the individual lines below the observable limit.

In discussing OCS the occurrence of individual rotational transitions for each isotopic variety of the molecule was pointed out. This type of fine structure should have little effect in reducing the intensity of a line in the rotational spectrum for atoms which have only a single abundant stable isotope such as C^{12}, H^1, O^{16}, S^{32}, etc. However, for a molecule involving bromine the intensity of each individual line would be only half that of the total intensity of the rotational transition.

An important type of fine structure, first observed in the microwave spectrum of ammonia (*2*, *3*), is due to nuclear quadrupole coupling. This perturbation of the rotational energy of a molecule occurs if atoms possessing nuclear quadrupole electric moments and nuclear spins greater than $^1/_2$ are present. Commonly occurring nuclei having these properties are N^{14}, Cl^{37}, Cl^{35}, Br^{81}, Br^{79}, I^{127}, and S^{33}. The expression for the change in rotational energy due to nuclear quadrupole coupling (*1*) has the form

$$\Delta W = eQqF(J, K, I)$$

where e is the electronic charge, Q is the nuclear quadrupole moment, q is the gradient of electrostatic potential produced by all charges in the molecule except those inside a small sphere surrounding the nucleus of interest, and $F(J, K, I)$ is a function of the angular momentum and nuclear spin quantum numbers. This type of fine structure splitting may have a very pronounced effect on the spectrum, because for a molecule containing more than one chlorine, bromine, or iodine the intensity of the strongest component may be less than 0.1 of the total intensity for the rotational transition. This coupling of the molecular and nuclear properties of molecules is of great interest to physicists, for in many cases it provides the best method of determining the nuclear spin and quadrupole moment of some nucleus of interest.

Although the foregoing discussion has been based on the assumption of a rigid nonvibrating molecule, at best we can deal with molecules in the ground vibrational state in which they still possess 0.5 quantum of vibrational energy for each normal vibrational mode. Furthermore, at ordinary temperatures excited vibrational states will be appreciably populated. Because for an actual molecule the rotational constants have a dependence on the vibrational quantum numbers of the following form (*7*)

$$B_v = B_e - \Sigma_i \alpha_i^B (v_i + d_i/2)$$

where the α_i are constants small in comparison to B_e, which is the rotational constant for the molecule in its equilibrium position, and d_i is the degree of degeneracy of the vibration, there will be a separate rotational spectrum for each vibrational state which is sufficiently populated. For a molecule with a number of low-lying vibrations observed at higher temperatures, the vibrational fine structure may appreciably reduce the intensity of the strongest line in the group corresponding to a single rotational transition.

One of the lowest lying vibrations of a number of common molecules is of a special type. These are the torsional oscillations possible in molecules such as methanol, which have internal rotating groups. The presence of such groups in a molecule not only gives rise to a rotational spectrum having a complicated fine structure but if there is a component of the dipole moment along an appropriate axis can give rise to new series of lines corresponding to free rotation and to the interaction of the rotation of internal groups and of the molecule as a whole.

The rotational transitions of rigid symmetric rotors are degenerate because of the existence of separate energy levels corresponding to the $2J+1$ different values of K for each J value. The actual molecule is not rigid and undergoes an amount of centrifugal distortion which is proportional to the speed of molecular rotation. As a result, the K degeneracy is removed to some extent. This effect is not large for the lower rotational states of symmetric rotor molecules and can usually be neglected. Effects due to centrifugal distortion play a much more important role in the higher rotational states of asymmetric molecules. For a molecule that is not quite an accidentally symmetric rotor the K degeneracy may also be imperfect. In treating a molecule which is even moderately asymmetric K is no longer a proper quantum number and there are $2J+1$ sublevels of different energy for each value of J. Naturally the intensities of transitions involving these discrete sublevels will be less than for the corresponding transition between degenerate levels in a symmetric rotor.

In the absence of external electric and magnetic fields, each rotational energy level J, K is made up of $2J+1$ degenerate sublevels. The removal of these degeneracies in an external field gives rise to the Stark and Zeeman effects in molecular spectroscopy. For symmetric rotor molecules the Stark splitting of the rotational levels can be large. These effects have proved useful in the interpretation of microwave spectra and have served as the basis of modulation techniques which have increased the available sensitivity of microwave spectrometers.

SPECTRAL INTENSITIES

The analytical applications of microwave spectroscopy depend strongly on the intensity of the available spectra and the sensitivity of the available spectrometer. These factors determine the class of molecules which may be detected, the size of sample required, and the maximum possible dilution ratio. A formula for the intensity of a line in the rotational spectrum of a molecule has been obtained as follows:

$$\gamma = \frac{4\pi}{3ckT} |\mu_{ij}|^2 \nu^2 S(\nu_o, \nu)\, n$$

where γ = absorption coefficient in cm.$^{-1}$
$|\mu_{ij}|$ = quantum-mechanical matrix element for the absorption transition averaged over all values of the magnetic quantum number, m
$S(\nu_0, \nu)$ = a shape factor for the spectral line with ν the working frequency and ν_o the resonant frequency for the transition
n = number of molecules per cubic centimeter in the lower state of the transition $i \longrightarrow j$
c, k, and T = velocity of light, Boltzmann constant, and absolute temperature of the gas, respectively

$$S(\nu_o, \nu) = \frac{1}{\tau}\left[\frac{1}{(\nu - \nu_o)^2 + \left(\frac{1}{2\pi\tau}\right)^2} + \frac{1}{(\nu + \nu_o)^2 + \left(\frac{1}{2\pi\tau}\right)^2}\right]$$

τ = mean time between molecular collisions

$$\tau = \frac{1}{2\pi \Delta\nu}$$

$\Delta\nu$ = half-width of the spectral line

$$n = \frac{Nge^{-W/kT}}{Z}$$

N = total number of molecules per cc.
g = statistical weight of the lower state
W = energy of the lower state
Z = rotational partition function for the molecule

When the working frequency is exactly equal to the resonant frequency and the second term in the expression for $S(\nu_o, \nu)$ is neglected, as is permissible at pressures below a few millimeters of mercury, the shape factor becomes simply

$$S(\nu_o, \nu_o) = 4\pi^2\tau$$

Making the appropriate substitutions, the following expression for $\gamma_{max.}$ results

$$\gamma_{max.} = \frac{8\pi^2 |\mu_{ij}|^2 \nu^2}{3ckT\ \Delta\nu} \quad \frac{Nge^{-W/kT}}{Z}$$

For a linear molecule this expression can be put in a particularly simple form. Substituting as follows:

$$|\mu_{ij}|^2 = \mu^2 \frac{J+1}{2J+1}$$

$$Z_{rot.} = \frac{kT}{B} + \frac{1}{45}\frac{B}{kT} + \frac{4}{315}\left[\frac{B}{kT}\right]^2 \pm \cdots$$

$$N = 0.9658 \times 10^{19} \frac{P_{mm.}}{T}$$

$$\frac{1}{\Delta\nu} = \frac{7.1 \times 10^{-8} M^{1/2} T^{1/2}}{\sigma^2 P_{mm.}}$$

$$\gamma_{max.} = 2.09 \times 10^8 \frac{\mu^2 \nu^3 M^{1/2}}{T^{5/2}\sigma^2}$$

Table II. Intensity of Rotational Transitions for Carbonyl Sulfide

Transition	ν, Mc.	γ Calcd., Cm.$^{-1}$	T, ° K.
$J = 1 \rightarrow 2$	24326	6.8×10^{-5}	300
$J = 2 \rightarrow 3$	36489	23.0	300
$J = 3 \rightarrow 4$	48652	54.4	300
$J = 4 \rightarrow 5$	60814	106.2	300
$J = 1 \rightarrow 2$	24326	18.8	200
$J = 4 \rightarrow 5$	60814	293.3	200

The significance of this equation can perhaps best be understood by means of a specific example. In the case of the OCS molecule $\mu = 0.75$ Debye unit, $\mu^2 = 0.52 \times 10^{-36}$ in c.g.s. units, and $M^{1/2} = 7.75$. The observed experimental value of Δ is 12 Mc., which corresponds to a molecular diameter σ of 10.7 Å., so that σ^2 is 115.0. The $\Delta\nu$'s observed for molecules with appreciable dipole moments are usually considerably larger than the values calculated from molecular diameters obtained from electron diffraction, viscosity measurements, etc.

The calculated intensity of several rotational transitions of OCS are given in Table II. It may be readily seen that a weak spectral line can be made much more easily observable by cooling the gas or by working with a higher rotational transition at a higher frequency. Unfortunately, at present experimental difficulties encountered at the higher frequencies make the advantages of working at these frequencies somewhat less obvious.

As the formula indicates, a molecule with zero dipole moment has rotational transitions with zero intensity. Thus symmetric molecules such as carbon dioxide and methane cannot be detected with the microwave spectrometer and in general hydrocarbons and other classes of molecules with dipole moments of less than 0.1 Debye unit will offer serious difficulties. Because the intensity varies inversely with the molecular diameter, large molecules will have weak absorptions.

Calculations for symmetric rotors are slightly more complex but still straightforward. The following expressions may be used for the dipole moment matrix element and the partition function

$$|\mu_{ij}|^2 = \mu^2 \frac{(J+1)^2 - K^2}{J+1}$$

$$Z_{rot.} = \frac{5.4 \times 10^6}{p}\left[\frac{T^3}{AB^2}\right]^{1/2}$$

p = degree of symmetry of the p-fold axis of symmetry of the molecule
A and B = the rotational constants in Mc.

For a molecule with a threefold axis of symmetry—e.g., CH_3Cl, at 300 °K.—the partition function reduces to

$$Z_{rot.} = 1.8 \times 10^3 \left[\frac{1}{AB^2}\right]^{1/2}$$

with A and B now expressed in cm.$^{-1}$

From this relation it may be seen that the intensity of the rotational transitions of nonlinear molecules (as the expression for the partition function of an asymmetric molecule has a similar form) is inversely proportional to the moments of inertia. There are, then, a number of factors that serve to reduce the strength of the rotational absorption spectra of large molecules: an effect due to the large molecular diameter, one due to the large moments of inertia, and frequently most important of all the effect of fine structure due to quadrupole coupling, excited vibrational states, hindered internal rotation, etc. At present the most complex molecule for which a fairly intense microwave absorption spectrum has been obtained is pyridine.

It may be worth while to obtain an idea of the range of intensities of practical interest.

The most intense molecular absorption so far observed in the microwave region is probably the $J = 3$, $K = 3$ line in the ammonia inversion spectrum, having a γ of approximately 10^{-3} cm.$^{-1}$ Substituting this value in the fundamental absorption equation

$$I = I_o e^{-\gamma x}$$

it may be seen that this represents an absorption of only approximately 40% of the incident power in a 10-meter absorption path length. The weakest absorption so far observed corresponds to a γ at room temperature of approximately 10^{-9} cm.$^{-1}$ This sets a value of 10^6 as the maximum dilution ratio possible with equipment now available.

Considering the short period of time in which intensive development of microwave spectroscopy has been under way, it seems unduly pessimistic to consider the 10^{-9} cm.$^{-1}$ figure an ultimate limit. A calculation has been made, however, of the theoretical limiting sensitivity of a microwave spectrometer (*10*) resulting in the following equation

$$\gamma_{g\ min.} = 2e\gamma_e \sqrt{\frac{2kTN\,\Delta f}{P_o}}$$

$\gamma_{g\ min.}$ = minimum detectable absorption coefficient of the gas
γ_c = attenuation coefficient in cm.$^{-1}$ of the wave guide
e = base of natural logarithms
P_o = power introduced into wave guide before absorption takes place
N = noise figure of the receiver
Δf = band width of the receiver

The assumption is made in deriving this equation that the optimum length of guide ($2\gamma_c^{-1}$) has been used. If the following data are substituted in this equation

$\gamma_c = 8 \times 10^{-4}$ cm.$^{-1}$
P_o = 1 milliwatt
Δf = 30 cycles
N = 1
Guide length = 25 meters
$T = 300°$ K.

the minimum detectable absorption coefficient is seen to be 6.8×10^{-11} cm.$^{-1}$

Thus dilution ratios of more than 10^7 are possible. This means that the microwave spectrometer could detect the presence of as little as 10^{-15} mole of either $N^{14}H_3$ or $N^{15}H_3$ and distinguish between them.

ABSORPTION CELLS

Little has been said about experimental techniques, which might properly form the basis of an independent discussion. However, one feature of the equipment in use at present is likely to serve as a serious limitation on the applicability of microwave spectroscopy to problems of chemical analysis. Most spectrometers which have been constructed to date use wave guides or resonant cavities as absorption cells. These must be constructed so that highly conducting metal surfaces (copper, brass, silver, gold) are exposed to the microwave radiation. Any material placed in front of these surfaces must have a very small attenuation coefficient. Ordinary glass attenuates the radiation too strongly, although special low-loss glasses have been developed. An absorption cell with a vacuum-tight liner of quartz surrounded by the metal surfaces of the wave guide or resonant cavity would be practicable but because of fabrication difficulties most absorption cells now in use expose metal surfaces to direct contact with the gas sample. In the most sensitive spectrometers some plastic insulation, usually polystyrene or Teflon (polyfluoroethylene), is also exposed. The difficulties encountered with corrosive samples are obvious but because of the very small samples used difficulty is frequently experienced with adsorption on the exposed metal and plastic surfaces as well.

CONCLUSIONS

If other than purely qualitative results are to be obtained in an analysis using the microwave spectrometer it will be necessary to make accurate measurement of the intensity of lines in the rotational absorption spectra. Unfortunately, with most present-day microwave spectrometers these measurements are difficult. Particularly with the instruments using various modulation techniques (such as the Stark modulation technique of Hughes and Wilson, *8*) is it difficult to make even accurate relative intensity measurements, as the detected output signal is not simply related to the absorption coefficient. However, using straight detection techniques it has proved possible to measure absorption coefficients of the magnitude of 10^{-6} cm.$^{-1}$ to an accuracy of 10%. There should be no insurmountable difficulties in making the necessary intensity measurements using instruments specially designed for analytical work. The intensity of microwave spectral lines observed with low gas pressures and high incident power levels is influenced by saturation effects involving the displacement of the thermal equilibrium between adjacent rotational states. Although these effects are now fairly well understood, it is possible to reach erroneous conclusions concerning the relative intensities of very strong and very weak lines unless these effects are carefully guarded against.

Equipment for microwave spectroscopy is still in an early stage of development and it seems probable that the microwave spectrometer is not yet ready to compete on even terms with infrared spectrometers or mass spectrographs in the solution of problems in miscellaneous general analysis. The microwave instruments so far developed have the following serious limitations:

They are unsuitable for the analysis of material in the solid or liquid state or even, in many applications, gases at pressures greater than 1 mm.

They are unsuitable for use with either very small molecules or large complex ones.

Molecules that do not possess a permanent dipole moment may not be detected.

Corrosive samples may not be used.

Difficulties are experienced with the absorption of small samples on the extensive metal and plastic surfaces of the absorption cells.

However, the microwave spectrometer does have the following important advantages:

Any compound having a vapor pressure of as much as 10^{-4} mm. may be worked with if as much as 10^{-8} mole is available.

Resolution available is so great that interferences from overlapping spectra are almost completely eliminated.

Microwave spectra when observed at such high resolution are extremely sensitive to the over-all structure of molecules in a way that is different in important respects from the way infrared and mass spectra are influenced by structure.

Frequency measurements may be made so accurately in the microwave region that in most cases a compound can be identified by a single line. Catalogs of spectra can be tables of numbers rather than collections of graphs.

Although these advantages do not indicate a general utility of the microwave spectrometer in chemical analysis at this time, they should lead to application to experimental problems of a special nature.

An example of such an application might arise in the use of a stable isotope as a tracer in a biochemical system. There the microwave spectrometer's ability to locate the tracer isotope not only within a certain molecule but at a specific place within that molecule, using a sample of less than 1 microgram, might be highly valuable. This location of the tracer isotope would not be interfered with even if the isotope were distributed among dozens of complex molecules. Furthermore, the analytical sample could be recovered in its original form, unchanged in any way, and would be available for further tests and experiments. In the elucidation of the structure of some naturally occurring compound available only in minute quantities, the microwave spectrometer could be used to determine the arrangement of various reactive groups within the molecule after their presence had been inferred or demonstrated from other data.

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Direct Determination of Oxygen in Petroleum Products

Adaptation of Schuetze-Unterzaucher Method

R. A. DINERSTEIN AND R. W. KLIPP
Standard Oil Company (Indiana), Whiting, Ind.

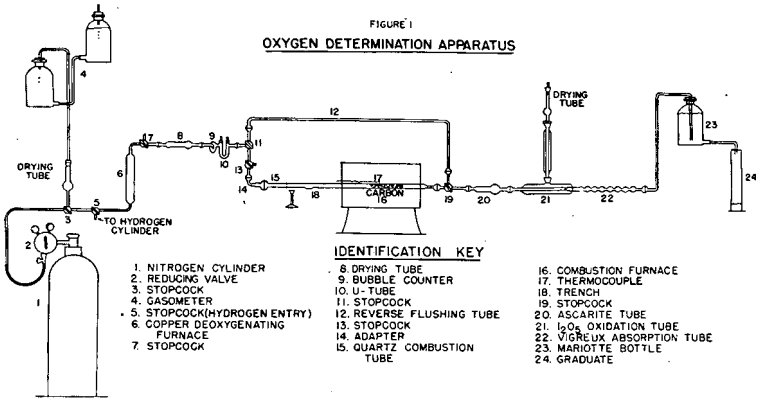
Adaptation of the Schuetze-Unterzaucher method to the direct determination of oxygen in petroleum products is described. Modifications of the apparatus include enlargement of the combustion tube to permit the use of larger samples, elimination of the conventional side arm on the combustion tube, and use of an inexpensive commercially available furnace in place of special equipment previously described in the literature. Results are given for known and unknown compounds containing from 0.15 to 26% oxygen.

OXYGEN in organic compounds has usually been determined by difference in conjunction with carbon and hydrogen determinations. This method has attributed to the oxygen value the sum of all the errors of carbon and hydrogen measurement, and, when constituents other than carbon, hydrogen, and oxygen are present, has necessitated additional analyses for such components. The methods for direct determination of oxygen in use before 1939 were based on either complete oxidation of the compound with measurement of the oxygen consumed, or catalytic hydrogenation to form water. The complete oxidation method requires very accurate determination of hydrogen, carbon, and consumed oxygen, and if sulfur or nitrogen is present in the compound under investigation, an additional determination must be made. The catalytic hydrogenation method determines oxygen directly, but other elements interfere and sulfur or halogen compounds poison the catalyst (*2*).

In 1939 Schuetze (*5*) proposed a new semimicromethod involving passage of the decomposition vapors of a pyrolyzed sample over carbon at 1000° C. and oxidation of the resultant carbon monoxide to the dioxide with iodine pentoxide. Either the carbon dioxide or the iodine could be determined. In 1940 Unterzaucher (*6*) adapted the method to the microchemical scale by making various improvements in the apparatus. A recent publication by Aluise *et al.* (*1*) describes an adaptation of the Unterzaucher method to American equipment and reagents. There are also references to a similar method in the recent Russian literature (*3*, *4*) as well as in work by the National Bureau of Standards on the analysis of rubber polymers (*7*).

The present paper describes the adaptation of the Schuetze-Unterzaucher method to the direct determination of oxygen in petroleum products. The apparatus has been modified to permit the use of larger samples and thus minimize titration errors in cases where the oxygen content is low. The conventional side arm of the combustion tube has been eliminated by the use of a special adapter assembly which permits more efficient forward and backward nitrogen sweeping. In addition, an inexpensive commercially available furnace has been satisfactorily substituted for the special furnace referred to in previous publications.

FIGURE 1
OXYGEN DETERMINATION APPARATUS



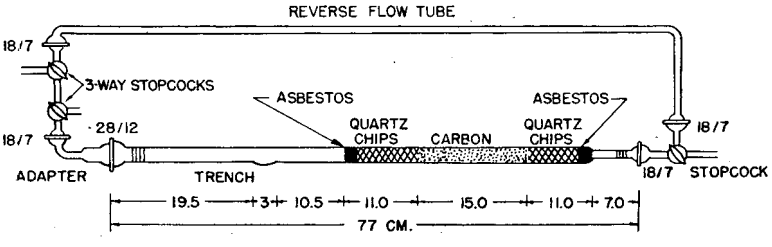


Figure 2. Combustion Tube Assembly

APPARATUS

A diagram of the apparatus is shown in Figure 1.

The nitrogen tank, 1, is equipped with a reducing valve, 2, connected to a 3-way stopcock, 3, by Tygon tubing. One arm of this stopcock leads to the gasometer, 4, in which nitrogen is stored for use in maintaining an inert atmosphere in the apparatus when it is idle for prolonged periods. The other arm of the stopcock leads through a 3-way stopcock, 5, to nitrogen-purification tube, 6, which is a vertical 22-cm. length of heavy-walled 18-mm. Pyrex tubing filled with 40- to 60-mesh copper grits and wound with 300 cm. (10 feet) of Nichrome ribbon (1.206 ohms per foot) under asbestos tape. The extra arms of stopcocks 5 and 7 permit introduction of hydrogen for reduction of the copper in place.

The effluent end of the nitrogen-purification tube is joined through a 2-mm. stopcock, 7, and an 18/7 ball-and-socket joint to drying tube 8, which is filled with porous barium oxide. This tube is connected by means of a second 18/7 ball-and-socket joint to bubble counter 9 and U-tube 10. The bubble counter is filled with concentrated sulfuric acid, the inlet arm of the U-tube

is filled with porous barium oxide, and the outlet arm with phosphorus pentoxide and glass wool. A 2-mm. three-way stopcock, 11, permits the purified and dried nitrogen to pass to the combustion tube, 15, either through the reverse-flushing tube, 12, or through stopcock 13 and adapter 14.

The combustion tube, detailed in Figure 2, is made of clear quartz (13 mm. in inside diameter) with Pyrex-to-quartz graded seals at either end leading to ball-and-socket joints. A trench, 18, at the bottom of the tube holds the sample and is designed to prevent liquid or melted samples from flowing to the unheated adapter end of the tube. The tube is filled with 15 cm. of carbon held in place on either side by quartz chips and asbestos fibers.

The combustion tube is placed in an electric furnace, 16, Hoskins Type 303A, regulated by a rheostat. (This furnace has been found adequate for maintenance of 1120° C. in the central 16- to 18-cm. portion which is sufficient for the 15-cm. carbon filling. The present furnace has been in operation for 11 months with no significant change in operating characteristics.) A chromel-alumel thermocouple, 17, is used with a portable potentiometer for temperature measurements. The furnace entrance and exit are covered with Transite drilled to admit the combustion tube and thermocouple. The tube has a 10-cm. Nichrome-gauze roll covering the portion preceding the furnace where the sample is heated by a blast Meker burner. The forward portion of the system is shielded from the heat by the asbestos sheeting indicated to the left of the burner.

Three-way stopcock 19 and drying tube 20—filled with Ascarite to remove nitrogen, sulfur, or halogen compounds—transfer the exit gases from the combustion tube into the oxidation tube, 21. This tube (8 mm. in inside diameter) is filled with granular iodine pentoxide and is surrounded by a jacket containing boiling glacial acetic acid to maintain a temperature of 118° C. The jacket is heated by Nichrome ribbon (1.206 ohms per foot) and is equipped with a water-cooled reflux condenser. Connected to the oxidation tube by a 19/38 standard-taper joint within the acetic acid jacket is the indented Vigreux absorption tube, 22, the walls of which are moistened with 20% sodium hydroxide for collection of iodine vapors. The absorption tube is joined to a Mariotte bottle, 23, which is used to measure the volume of gas passing through the system.

This assembly includes several changes from the Unterzaucher apparatus. The chief improvement lies in the substitution of the straight combustion tube for Unterzaucher's quartz tube with side arm, and the elimination thereby of a pocket not completely swept out by the passage of nitrogen into the combustion tube. More efficient nitrogen flushing and less danger of sample loss behind the flame result.

In addition, leakage has been minimized by eliminating all rubber connections. Except for the Tygon tubing joining the nitrogen cylinder to the apparatus, all connections are of glass—either ball-and-socket joints, where flexibility is required, or standard-taper joints. Silicone lubricants are employed for the glass joints.

REAGENTS

Nitrogen, Linde, high purity, dry (oxygen content 0.001%).

Barium oxide, porous grade, Barium & Chemicals Company, Inc.

Carbon, Wyex Compact Black, pelleted amorphous, J. M. Huber, Inc.

Iodine pentoxide, Baker's C.P.

Formic acid, 98 to 100%, Eastman Kodak Company.

Phosphorus pentoxide, Baker's C.P.

Ascarite.

Sodium hydroxide, 20% solution of Baker's C.P. in distilled water.

Starch, 0.5% solution in water.

Bromine, Merck's C.P.

Sodium thiosulfate, 0.02 N solution of Baker's C.P.

Potassium iodide, 6% solution of Baker's C.P.

Potassium acetate, 10% solution of Baker's C.P. in glacial acetic acid.

Sodium acetate, 20% solution of Baker's C.P. in distilled water.

PROCEDURE

The sample (weighed on the analytical balance) will vary in size from 200 to 400 mg. for materials containing less than 0.5% oxygen to 15 to 25 mg. for samples with about 25% oxygen. For crystalline materials, a platinum or porcelain boat has been found a satisfactory sample vessel. For liquid samples, short lengths of quartz tubing 4 to 5 mm. in inside diameter are sealed at one end and drawn to a constriction at the other end with the opening flared. The sample is introduced through the constriction with a hypodermic needle attached to a 2-ml. syringe. If the sample is volatile the flared end of the tube is filled with paraffin wax immediately after weighing to prevent loss of the sample. When this sample tube is inserted in the combustion tube, the wax-filled end is placed facing the furnace.

Newly assembled apparatus is swept out with nitrogen for 24 hours with the various heating units (6, 16, 21) operating. To ensure maximum activity of the deoxygenation tube, the copper is reduced at 400° C. with hydrogen at the start of each day's work. The entire apparatus is swept out with nitrogen for about an hour while the furnace is allowed to come to 1120° C. The nitrogen rate is set at 10 to 15 ml. per minute.

Stopcock 11 is set to pass nitrogen through tube 12 and then back into the combustion tube in reverse flow via stopcock 19, stopcock 13 being set to permit the gas to leave the system. The adapter, 14, is opened, and the sample is introduced against the nitrogen stream and placed in the trench, 18, by means of a glass rod with a platinum-wire hook. The adapter, 14, is replaced and the combustion tube and adapter are swept out in reverse flow for an additional 30 minutes. The walls of the absorption tube are thoroughly moistened with 20% sodium hydroxide, and the tube is placed in position. At the end of the sweeping-out period the nitrogen flow is changed to the forward direction, through the combustion tube to the Mariotte bottle, by closing stopcock 13 to the air and shutting off side arm 12 by stopcocks 11 and 19. The Mariotte bottle side arm is lowered to a horizontal position above a 1000-ml. graduated cylinder.

Pyrolysis of the sample is then begun. In the case of a liquid sample, the wax at the end of the sample tube is first melted by the application of a small flame. The Meker burner, adjusted to provide a low flame, is then placed about 3 cm. to the left (Figure 1) of the sample, and the initial evaporation of the sample is begun slowly, so that the back pressure does not exceed the forward nitrogen pressure. After the sample starts to volatilize, the burner is moved in increments of about 1 cm. toward the furnace at such a rate as to reach the furnace in about 20 minutes. The burner is then returned to a position about 10 cm. to the left of the sample and the flame adjusted to bring the combustion tube to white heat. The burner is again moved toward the furnace over a period of about 10 minutes to sweep any remaining portions of the sample into the furnace. Following the second sweeping, nitrogen is passed through the system for 10 minutes more.

The absorption tube, 22, is removed and its contents are rinsed with about 125 ml. of distilled water into a 250-ml. Erlenmeyer flask containing 10 drops of bromine (to oxidize all iodine to iodate) and 10 ml. of a 10% solution of potassium acetate in glacial acetic acid. The contents of the flask are stirred, 10 ml. of a 20% solution of sodium acetate are added, and formic acid is added dropwise until the excess bromine is destroyed. After 4 or 5 minutes, 5 ml. of 6% potassium iodide solution and 5 ml. of 10% sulfuric acid are introduced, and the liberated iodine is titrated with 0.02 N thiosulfate using a starch indicator.

A blank run is made by introducing an empty sample vessel into the combustion tube and carrying out the complete procedure. The blank usually requires about 0.5 to 1.0 ml. of 0.02 N thiosulfate except that, when paraffin wax is used to seal the quartz tubes containing volatile samples, about 1 ml. additional is required.

The per cent oxygen is calculated as follows:

$$\frac{(Y - b) \times \text{normality of } Na_2S_2O_3 \times 6.667 \times 100}{\text{milligrams of sample}} = \% \text{ oxygen}$$

where Y = ml. of sodium thiosulfate required for sample, b = ml. of sodium thiosulfate required for blank, and 6.667 = milligrams of oxygen equivalent to 1 ml. of 1 N sodium thiosulfate.

The total time required for a determination is about 70 minutes. In practice, either five analyses and one blank or four analyses and two blanks may be run per day, depending on the stability of the blank value for the particular apparatus and the accuracy desired.

Carbon deposition on the combustion tube occurs in the vicinity of the sample. It has been found convenient to remove this carbon, which obscures the view of the sample, by introducing a fine stream of air at low pressure into the tube against a reverse flow of nitrogen while a hot flame is applied to the tube. Care must be taken to avoid the entrance of air into the filled portion of the tube; hence, the reverse nitrogen flow is continued after the stream of air is withdrawn.

Table I. Analyses of Pure Compounds

	Benzoic Acid	Benzoic Acid in Xylene
Oxygen calculated, %	26.20	1.20
Sample size, mg.	18–28	290–395
0.02 *N* thiosulfate used, ml.	35–55	34–36
Oxygen found, %	26.10, 26.52, 26.34	1.17, 1.23
	26.00, 26.32, 26.07	1.19
Average, %	26.23	1.20
Average deviation from known, %	0.17	0.03

Table II. Analyses of Sulfur and Nitrogen Compounds

	Thio-*tert*-butoxy-propionic Acid Methyl Ester	*n*-Heptadec-anoamide
Oxygen calculated, %	18.15	5.94
Sample size, mg.	15–30	45–70
0.02 *N* thiosulfate used, ml.	20–40	20–30
Oxygen found, %	17.65	5.91
	17.96	5.90
	18.11	6.01
Average, %	17.91	5.94
Average deviation from known, %	0.24	0.05

Table III. Typical Analyses of Fischer-Tropsch Product

	A	B	C	D
Sample size, mg.	230–310	110–135	215–250	210–235
0.02 *N* thiosulfate used, ml.	45–75	15–18	11–13	2.5–2.6
Oxygen found, %	2.75	1.78	0.69	0.14
	2.68	1.81	0.62	0.16
	2.75	1.77	0.73	
Average, %	2.73	1.79	0.68	0.15

Carbon also is deposited on the quartz chips preceding the carbon filling of the combustion tube. This deposition cannot be removed by heating in the presence of air because of the proximity of the carbon filling. It has been found advisable to refill the combustion tube after about 80 analyses of samples containing 1 to 10% oxygen. If allowed to accumulate further, the carbon deposition will interfere with the passage of gas through the tube and become increasingly difficult to remove.

It is good practice to check the fillings of the combustion and oxidation tubes to avoid losses due to channeling and also the drying agents to ensure complete dehydration of nitrogen.

RESULTS AND DISCUSSION

The analyses of benzoic acid and of a dilute xylene solution of benzoic acid are shown in Table I. Table II gives the results of oxygen determination of pure compounds containing nitrogen or sulfur to demonstrate that these elements do not interfere with the method. Table III shows results of typical analyses of hydrocarbon samples from Fischer-Tropsch synthesis. The accuracy of the method with the known samples is about 1% of the oxygen content. The precision in the determination of unknown samples containing over 1% oxygen averaged about 2% of the amount present; samples with lower oxygen content show poorer precision.

The precision of the method is dependent on the reproducibility of the blank titer, which varies from day to day by about 0.3 ml. of 0.02 *N* thiosulfate. This variation is equivalent to 0.4% oxygen for a 10-mg. sample or 0.02% oxygen for a 200-mg. sample. By mass spectrometer analysis, the nitrogen has been found to contain about 0.03% oxygen by the time it reaches the copper deoxygenating tube and, because the copper does not remove all this oxygen, a positive blank value is obtained. Air adsorbed on the sample vessel or the walls of the combustion tube must be removed; the efficient sweeping technique described above minimizes errors from this source.

CONCLUSIONS

The Schuetze-Unterzaucher method for the direct determination of oxygen has been adapted to the semimicroanalysis of petroleum products. The modifications include a redesigned combustion tube which permits more efficient sweeping of gases to reduce the blank value and the use of an inexpensive, commercially available furnace.

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Analysis of Gaseous Hydrocarbons

Combining Infrared and Mass Spectra

DANIEL MILSOM, W. R. JACOBY, AND A. R. RESCORLA
Cities Service Refining Corporation, Lake Charles, La.

WITH the advent of cracking petroleum stocks, the complexity of samples received for light hydrocarbon analysis has necessitated a search for faster methods of evaluation without sacrificing the accuracy of the results. The chemical similarity and the difficulty of separating compounds of isomeric composition by distillation or chemical methods have led to the use of other physical properties for their detection and estimation.

Two instruments, the mass spectrometer and the infrared spectrometer, have been accepted for analyzing hydrocarbon samples. These instruments are faster and at least as accurate as low temperature fractionation and other accepted methods of gas analysis. Each instrument, however, has definite limitations. The mass spectrometer is accurate for compounds that have no isomers, but as the number of isomers increases the degree of accuracy rapidly decreases, owing to the similarity of ionization patterns for isomeric compounds. The infrared spectrometer is faster and more accurate for isomeric compounds than the mass spectrometer. However, its use is limited to the number of spectral positions at which the absorptions of different compounds do not interfere sufficiently to affect the accuracy.

In analyzing samples of complex mixtures of hydrocarbons, it is customary to determine the composition of distillation frac-

A highly accurate method of gas analysis combining infrared and mass spectrometer techniques is described. This method can be applied to any gaseous mixture and is based on the fact that infrared analysis of isomeric compounds is faster and more accurate than mass spectrometer analysis and that the mass spectrometer is faster as well as more efficient in analyzing samples in which an isomeric breakdown is not necessary. Instruments may be calibrated in the normal way and used following standard procedures. Calculations are combined by placing infrared calibration coefficients and mass spectrometer sensitivities in the same reciprocal matrix. Tables indicating the accuracy of proposed method for analysis of gaseous hydrocarbons as compared to other methods are presented.

tions by the mass spectrometer, the infrared spectrometer, or both. Results thus separately obtained are then calculated to yield the most probable analysis of the sample. Necessity for these separate analyses has made the mass spectrometer and the infrared spectrometer competitive instruments. The proposed method of calculation combines mass spectrometer data and infrared data in one computation, thus making the two instruments complementary rather than competitive.

It is possible, from mass spectrometer data, to calculate the mole fraction for any component in a gas mixture from the peak heights in divisions per micron and the sensitivity coefficients of the compounds according to the following equation:

$$M_i = \sum_{j=1}^{n} S_{ij} X_j$$

where M_i are the mass spectrometer mixture peak heights in divisions per micron, S_{ij} are the mass spectrometer sensitivity coefficients, and X_j are mole fractions.

This equation states that the mixture peak heights in divisions per micron at any ratio of mass to charge is the sum of the products of the sensitivity coefficients at any ratio of mass to charge and the mole fractions of the respective compounds.

It is also possible to determine the mole fraction for any component in a gas sample from infrared optical density measurements using the following equation:

$$D_i = \sum_{j=1}^{n} A_{ij} X_j$$

where D_i are infrared optical densities at some standard pressure and temperature, A_{ij} are infrared calibration coefficients, and X_j are mole fractions.

This equation as used assumes the increase in optical density to be a linear function of the pressure of the hydrocarbon. This is not exactly true. For purposes of this report, this equation is used to obtain the approximate mole fraction. The optical density as measured is then corrected from this approximate analysis and the results are again calculated. A detailed discussion of this method of calculation is given in (*5*).

This equation states that the optical density of a gas mixture at any particular spectral position and at some standard pressure and temperature is the sum of the products of the calibration coefficients and the mole fractions of the respective compounds.

Given complete data from both the mass spectrometer and the infrared spectrometer, there are $2n$ equations in n variables. Because only n equations are required to solve a system of simultaneous equations in n variables, any legitimate means of obtaining the required values may be employed. Among these methods would be: (1) least squares treatment; and (2) from supplementary data, selecting equations that will yield more accurate results. In most cases, the latter method will be more attractive for treatment of mass spectrometer and infrared spectrometer data, because equations giving a greater degree of accuracy for any particular component can be selected.

SCOPE

This method of calculation is intended for use in the analysis of light hydrocarbon mixtures with the infrared spectrometer and the mass spectrometer complementing each other. The optical densities obtained on the infrared spectrometer are used to determine one or more isomeric components of a sample, and the sensitivity coefficients from the mass spectrometer are used to determine the remaining compounds in the mixture of gases.

DEFINITIONS

Spectral Position. A given angular position of the prism which allows radiation in a narrow wave-length range to traverse the spectrometer and strike the radiation measurement device.

Optical Density. The logarithm to the base 10 of the ratio of energy incident on the sample to the energy transmitted by the sample; both energy measurements are determined at the same wave-length setting and the same slit widths.

Mono Peak. In a mass spectrum of a hydrocarbon in each C group—i.e., CH_4, C_2H_6, C_3H_8, etc.—it is possible to compute the amount of any peak resulting from ions containing one or more heavy isotopes. When the portions of a peak attributable to heavy isotopes C^{13} and H^2 are subtracted from the peak at which they appear, the remaining peak is due solely to ions containing the more abundant light isotopes C^{12} and H^1. The peak thus obtained is referred to as a "mono peak" (*1*).

APPARATUS AND REAGENTS

Infrared spectrometer, Beckman Model IR-1.

Mass spectrometer, Consolidated Engineering Corporation Model 102.

Thermometer, graduated to 0.2° C. for measuring the base plate temperature of the infrared spectrometer.

Ascarite, for use in drying samples.

Liquid nitrogen.

Hydrocarbon-insoluble stopcock lubricant.

Standards. Research grade hydrocarbon samples as supplied by Phillips Petroleum Company, Bartlesville, Okla., and certified by the National Bureau of Standards.

METHOD

From comparative accuracy data as released by Rubber Reserve (*4*), the mass spectrometer or the infrared spectrometer was selected for use in determining those components in a mixture of gases which would yield the most probable results. Equations containing the infrared optical density measurement from the infrared spectrometer and the sensitivity coefficients at the mass-to-charge ratio selected from the mass spectrum together with calibration information from each instrument are solved simultaneously using a reciprocal matrix method of solution. Reciprocal matrix as used throughout this report is defined in (*3*).

CALIBRATION

The infrared spectrometer is calibrated for components that have greater accuracy of analysis by infrared methods. The instrument is calibrated at those wave lengths at which one component has a high absorption and the other components have low absorption. The optical densities for all gases are determined at these preselected spectral positions at a standard temperature and a series of pressures from zero to twice the

standard pressure to be used for analysis. Each pressure is corrected for gas imperfection—i.e., doubling the pressure of hydrocarbon in the absorption cell more than doubles the amount of hydrocarbon vapor in the cell. Consequently, it is necessary to add a correction to the pressure as read by the manometer. Each pressure is also corrected to standard base plate temperature from the following equation:

$$\text{Pressure correction} = \frac{(t_0 - t)p}{273 + t_0}$$

where p = the observed pressure corrected for gas imperfection; t_0 = the standard base-plate temperature, ° C.; and t = the base-plate temperature, ° C., at the time the pressure was read.

Because the mole fraction of a compound in a mixture of gases is equal to the partial pressure divided by the total pressure, the mole fractions corresponding to the observed pressure readings may be calculated by dividing the corrected pressure by the standard pressure selected for analysis. The optical density of the gas at each of the observed pressures is divided by the corresponding calculated mole fraction. These values are plotted against the optical density. The line is extended through the ordinate, and the point at which it intercepts the ordinate is tabulated as the A value (*5*). The slope of the line is calculated and tabulated and is used for correction of the observed optical densities.

Spectra of the research grade gases are determined on the mass spectrometer. The sensitivity coefficients at the mass-to-charge ratio selected to give the most accurate results from the mass spectrometer are determined by dividing the total heights of the peak by the observed pressure (*1*).

A reciprocal matrix using the A values calculated from the infrared spectrometer data and the mass spectrometer sensitivity coefficients is calculated using any approved method (*2, 5, 6*).

PROCEDURE FOR ANALYZING

Before any sample is analyzed on the mass spectrometer, a sensitivity check is made on the instrument.

Research grade n-butane is made to enter the gas inlet system and the spectrum is recorded. The sensitivity coefficients at a mass-to-charge ratio of 58, 38, 28, and 26 are determined, and compared to the sensitivity coefficients obtained on the day of calibration. A ratio of the sensitivity coefficients of the day of calibration and the current day's operation is determined at each mass-to-charge ratio and an average is obtained. This ratio is used to correct the observed pressure reading on the mass spectrometer to the pressure it would have been, had the same peak heights been obtained on the day of calibration.

$$P_i = P\frac{S}{S_1}$$

where P_i is the corrected pressure, P is the observed pressure, S_1 is the sensitivity coefficient of the current operation, and S is the sensitivity coefficient obtained at the time of calibration.

The mass spectrum of the gas mixture is obtained and the observed pressure is corrected according to the preceding equation.

The mono peaks for hydrogen, methane, ethane, and propane at a mass-to-charge ratio of 1, 16, 30, and 44 are calculated. These mono peak heights are divided by the corrected mono sensitivity coefficients of their respective standard samples. The partial pressures thus obtained are divided by the corrected observed pressure to obtain the mole fractions of these components in the total sample.

The contributions of the methane, ethane, and propane to those peaks below their respective mass-to-charge ratio are subtracted from the gross peak heights. These corrected peaks are divided by the corrected observed pressure. The sensitivity coefficients

Table I. Analysis of Research Grade Hydrocarbons

Sample No.	1		2		3		4	
Method	IR-MS[a]	Bureau of Standards	IR-MS	Bureau of Standards	IR-MS	Bureau of Standards	IR-MS	Bureau of Standards
Component, mole %								
2-Methylpropane	99.92	99.88 ± 0.06	0.12	...	0.05	...	...	...
n-Butane	0.08	...	99.86	99.78 ± 0.08	0.28	...	0.03	...
2-Methylpropene	...	...	0.02	...	99.41	99.30 ± 0.20	0.28	...
n-Butenes	...	...	...	...	0.26	...	99.69	99.60 ± 0.20

[a] Infrared, mass spectrometer.

Table II. Analysis of Synthetic Blends

Sample No.	1			2			3			4		
Method	IR-MS	MS	Syn	IR-MS	MS	Syn	IR-MS	MS	Syn	IR-MS	MS	Phillips[a]
Component Liquid, vol. %												
Propane	5.0	...	4.9	15.5	15.4	15.8	3.7	3.9	3.7	...	...	...
2-Methylpropane	21.8	...	21.9	71.7	70.0	71.5	26.4	25.1	26.6	5.4	5.2	5.2
n-Butane	25.3	...	25.8	10.5	11.9	10.2	13.4	13.8	12.4	5.1	4.8	4.9
2-Methylpropene	21.0	...	20.7	2.3	2.7	2.5	23.5	24.9	23.5	46.8	47.1	46.6
n-Butenes	26.9	...	26.7	...	...	...	33.0	32.3	33.8	42.7	42.9	43.4

Sample No.	5			6			7		
Method	IR-MS	MS	Phillips[a]	IR-MS	MS	Phillips[a]	IR-MS	MS	Phillips[a]
Component Liquid, vol. %									
Propane	...	...	...	...	...	...	...	0.4	...
2-Methylpropane	45.1	44.9	44.6	16.3	...	16.4	54.4	54.4	54.4
n-Butane	33.2	32.0	33.7	83.4	...	83.6	45.6	45.1	45.6
2-Methylpropene	10.3	11.3	10.3	...	...	...	...	0.1	...
n-Butenes	11.4	11.8	11.4	0.3	...	...	...	...	...

[a] Samples blended by Phillips Petroleum Company for Rubber Reserve. Results listed under Phillips are calculated from purity of compounds and volume of each used in making blend.

Table III. Analysis of Plant Stream Sample

Sample No.	1		2		3		4		5	
Method	IR-MS	MS	IR-MS	MS	IR-MS	MS	IR-MS	MS	IR-MS	MS
Component Liquid, vol. %										
Propene	...	...	...	...	...	...	...	...	...	1.6
Propane	6.3	6.8	4.4	4.4	0.1	0.1	0.1	0.1	17.6	16.9
2-Methylpropane	90.5	90.9	65.9	66.5	69.0	68.9	68.7	68.9	66.3	64.8
n-Butane	3.0	2.3	29.7	29.1	30.9	31.0	30.9	31.0	16.1	16.5
2-Methylpropene	0.1	...	...	...	...	...	...	...	...	...
n-Butenes	0.1	...	...	...	...	...	...	...	...	...

Sample No.	6		7	
Method	IR-MS	MS	IR-MS	MS
Component Liquid, vol. %				
Propene	...	1.9	...	...
Propane	...	...	...	...
2-Methylpropane	...	0.8	...	2.5
n-Butane	1.2	...	3.7	1.6
2-Methylpropene	...	...	...	...
n-Butenes	...	...	...	...
2-Methylbutane	94.2	94.0	90.2	92.3
n-Pentane	4.6	3.0	6.1	3.3
Pentenes	...	0.3	...	0.3

thus obtained are used in the reciprocal matrix to calculate the remaining components.

The optical density of the sample is determined at the preselected wave lengths. The observed optical densities are corrected for pressure deviation from standard pressure; pressure deviation from ideal gas law; temperature deviation from standard base plate temperature; false energy contribution; and the mole fraction of the components previously determined from the mono peaks of the mass spectrum. These optical density corrections are calculated from the following equation:

$$D_i = X_i A_i + \Delta D_i$$

where D_i is the optical density of component i, X_i is the mole fraction of i, A_i is the A value for component i at wave length involved, and ΔD_i is the correction of the optical density of component i due to failure to observe Beer's law.

These corrected optical densities are then used in the calculation of the sample by using the reciprocal matrix.

Solution of the reciprocal matrix will give the mole fraction of each component. The mole fraction thus determined plus those previously determined from the mono peaks of the mass spectrum for hydrogen, methane, ethane, and propane multiplied by 100 should total 100.0%. If the results deviate from 100.0%, they are normalized in the following manner:

(*a*) Add to or subtract from each original value $1/n$ of the difference between the sum and 1.000, where n is the number of components in the sample.

(*b*) Add to or subtract from each original value its own percentage of the difference between the sum and 1.000.

(*c*) Take the averages of the mole fractions determined in (*a*) and (*b*) as final values.

Note. The normal lack of accuracy may cause the calculated percentages of components present to less than 0.5% to be slightly negative. These are reported as zero. Negative values larger than 0.7% indicate an error either in calculation or in the experimental data.

If the deviation of the mole percentages from 100.0% is greater than 0.5 times the number of components, check the calculation and experimental data for errors.

DISCUSSION

With the use of this method of calculation, it is necessary to obtain for each sample both the infrared optical densities at preselected wave lengths and the mass spectrum. The equations to be used to calculate the concentration of any particular component are selected from the method that gives the greater accuracy. In general, one or more isomers in a homologous series will be more accurate by the infrared method of analysis; others, when determined by the mass spectrometers.

A sample of butanes and butenes contaminated by a small amount of propane may be used to illustrate this method.

From a study of the mass spectra and infrared spectra of the components, it was noted that the propane and *n*-butane had high interference with *each other* on the infrared spectrometer and very little interference on the mass spectrometer. *It was therefore* decided to use the data from the mass spectrometer to analyze for propane and *n*-butane. Because there is little interference with the determination of 2-methylpropane (isobutane) with the infrared spectrometer, data from the infrared spectrometer were used to determine the 2-methylpropane content.

In like manner, 2-methylpropene and 2-butene were selected to be analyzed from infrared spectrometer data and 1-butene from mass spectrometer data.

Analytical data obtained from this method are presented in Tables I and II. These analyses are in agreement with the sample composition known from the synthesis of the mixtures which were analyzed. Table III compares the results of analyses of plant stream samples obtained by complementary infrared mass spectrometer analysis with those determined by the mass spectrometer. In samples 6 and 7, the mass spectrometer results show propylene and 2-methylpropane in the 2-methylbutane samples, whereas the infared–mass spectrometer (IR-MS) analyses gave no propylene or 2-methylpropane. From a knowledge of the history and flow of the sample through the refinery, it is unlikely that either sample contains 2-methylpropane and definitely should contain no propylene. It would seem therefore that the combined analyses for these two samples are more accurate than the mass spectrometer.

This method of calculation can be applied to any gaseous mixture. The method is not restricted to the wave lengths and sensitivity coefficients presented in this paper but it is possible to use any combination of infrared optical density measurements and sensitivity coefficients to calculate the analysis of the sample.

ACKNOWLEDGMENT

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Ultraviolet Absorption Analysis for Naphthalenes

NORMAN D. COGGESHALL AND ALVIN S. GLESSNER, JR.
Gulf Research & Development Company, Pittsburgh, Pa.

THE present report describes analytical methods based on ultraviolet absorption spectra, developed for the determination of naphthalene, α-methylnaphthalene, and β-methylnaphthalene in hydrocarbon mixtures boiling in the kerosene range. Despite the rather close similarity and proximity of the absorption bands of these compounds, it has been found practical to utilize them for quantitative analysis work. Such a method is feasible because of the nature of the ultraviolet absorption of the other types of compounds found in such samples. The semiempirical theory of electronic oscillations (*2*, *3*), together with the rather wide range of data now available for various classes of hydrocarbons, allows a reliable prediction to be made of the ultraviolet absorption of definite classes of hydrocarbons in the different spectral regions.

Paraffins, naphthenes, mono-olefins, and nonconjugated diolefins are known to possess no appreciable absorption at wave lengths longer than 200 mμ (*3*). The onset of absorption for conjugated diolefins is near 230 mμ and is continuous for shorter wave lengths. Alkyl benzenes and polycyclic aromatics possessing only one benzene ring—Tetralin, for example—have strong absorption in the characteristic benzene ring region, 250 to 280 mμ. Mononuclear aromatics with unsaturated side chains—styrene, for example—may possess additional bands around 290 mμ if the benzene ring and an olefin group are conjugated. For all these classes, the intensity of absorption is generally decreasing very rapidly with increasing wave lengths in the vicinity of 300 mμ. Thus they may contribute relatively little to the absorption in the region of the characteristic naphthalene

A method, based on the ultraviolet absorption of the naphthalenes, is described for the analysis of hydrocarbon mixtures boiling in the kerosene range for naphthalene, α-methylnaphthalene, and β-methylnaphthalene. For the lower boiling cuts a method of analyzing for naphthalene alone is described. This utilizes a system of correcting for the background absorption due to other unsaturated compounds present. For the higher boiling cuts containing all three naphthalenes the method is based on data taken at three separate wave lengths. The accuracy obtainable under routine conditions is satisfactory; the average errors are less than 0.3% of total sample. For proper utilization the cuts must be made between definite temperature limits. Results of accuracy tests and tests made on synthetic samples are given.

bands, 300 to 330 mμ. Certain polycyclic compounds such as acenaphthene and fluorene possess appreciable absorption in this region but fortunately have boiling points outside the range of the samples considered here.

The method is a straightforward one based on Beer's law of absorption given in Equations 1 and 2:

$$I = I_0 \times 10^{-ac} \quad (1)$$

$$D = \log (I_0/I) = ac \quad (2)$$

where a is a constant depending upon the absorbing material, the wave length at which data are being taken, and the thickness of the cell; and c is the concentration of the absorbing material in the cell. a is known as the calibration coefficient. When several absorbing compounds are present in the sample, all of which obey Beer's law, it is known that the resulting optical density is linearly dependent on each (*1*)

$$D = a_1c_1 + a_2c_2 + a_3c_3 \cdots \quad (3)$$

where a_1 is the calibration coefficient for the first compound, c_1 is the concentration of the first compound, etc. This allows different wave lengths to be used when several different components are being sought; the individual concentrations are then obtained as solutions of simultaneous equations of the type illustrated by Equation 3.

EXPERIMENTAL DETAILS

The instrument used throughout was the quartz spectrophotometer equipped for ultraviolet work as manufactured by the National Technical Laboratories, South Pasadena, Calif. The naphthalene and β-methylnaphthalene were obtained from Eastman Kodak Company and the α-methylnaphthalene was obtained from J. E. Nickels of Mellon Institute. The solvent used throughout was iso-octane (2,2,4-trimethylpentane) obtained from Rohm & Haas Company, Philadelphia, Pa. All dilutions in both the calibration and analytical work were by weight, using an analytical balance. Glass-stoppered bottles were used throughout. Between uses both bottles and stoppers were thoroughly washed in a Drene solution and given a subsequent oven drying.

In some cases the solutions containing the calibration and unknown samples were given an alkaline permanganate treatment to remove olefinic materials. This treatment is widely used for the treatment of samples prior to an ultraviolet analysis for the C_3 and lighter aromatics. It consists of agitating the solution of sample in iso-octane in a strong aqueous solution of potassium permanganate and potassium hydroxide for some 10 to 20 minutes at room temperature.

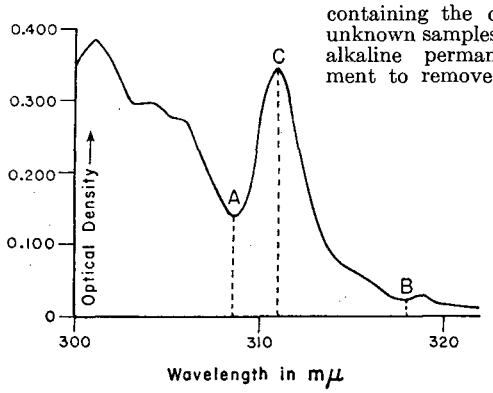

Figure 1. Ultraviolet Absorption Spectrum of Naphthalene

NAPHTHALENE ANALYSIS

It is often desired to determine the naphthalene content of hydrocarbon fractions that have boiling point ranges sufficiently below those of the α- and β-methylnaphthalenes that they do not contain these latter compounds in appreciable quantities. Low concentrations of the latter may be appraised from the appearance of the absorption bands. On the other hand, kerosene fractions having low initial boiling points may include high percentages of mononuclear aromatics. Although the region of principal absorption of this latter class of compounds is around 260 mμ, they may produce an appreciable background absorption in the 300- to 320-mμ range due to their heavy concentrations. A method of correcting for this must therefore be used.

In Figure 1 may be seen the absorption spectrum for naphthalene in the 300- to 320-mμ region. The wave length designated as C, where naphthalene possesses a maximum of absorption, is chosen for the calculation of the naphthalene concentration. In a sample containing a heavy concentration of compounds that give rise to background absorption in this region, the appearance of the curve will be altered. The left-hand portion will generally be elevated relative to the right-hand portion as the absorption of the interfering materials will be decreasing with increasing wave length. To achieve a background correction wave lengths A and B were chosen to be used with C.

Method of Correction. For pure naphthalene, the following ratios were determined:

$$R_1 = D_c/D_a \text{ and } R_2 = D_c/D_b$$

where D_a, D_c, and D_b are the optical densities at wave lengths A, C, and B, which are 308.5, 311, and 318 mμ, respectively. The corresponding optical densities, $D_{a,s}$, $D_{c,s}$, and $D_{b,s}$, are then determined for the sample. Assuming an average correction, d_1, to apply between the 308.5- and 311-mμ points and d_2 to apply between the 311- and 318-mμ points, we may solve for these quantities by means of the following equations:

$$R_1 = (D_{c,s} - d_1)/(D_{a,s} - d_1) \quad (4)$$

$$R_2 = (D_{c,s} - d_2)/(D_{b,s} - d_2) \quad (5)$$

Next a mean value between d_1 and d_2, which is designated as d, is determined. This is used for wave length C. The true optical density at C, due to the naphthalene alone, is then $(D_{c,s} - d)$. To obtain the weight percentage of naphthalene in the solution, C_1, we merely use

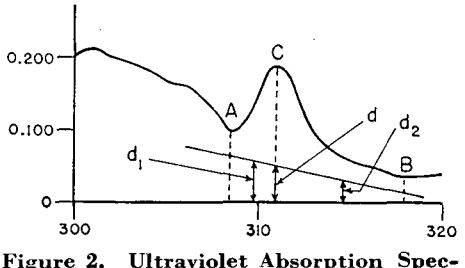

Figure 2. Ultraviolet Absorption Spectrum of Naphthalene

Sample possesses large background correction near 310 mμ

Table I. Comparison between Known and Analyzed Concentrations of Naphthalenes in Synthetic Samples

Sample No.	Known % of Naphthalene	Calculated % of Naphthalene	% Difference
1	8.28	8.07	−0.21
2	6.16	6.05	−0.11
3	3.22	3.33	0.11
4	2.40	2.33	−0.07
5	3.27	3.30	0.03
6	1.02	1.03	0.01

Average error = 0.09%

Table II. Comparisons between Known Increases of Naphthalene Concentrations in an Actual Sample and Calculated Increases

Sample No.	Increased % of Naphthalene	Calculated Increase of Naphthalene, %	% Difference
1	0.81	0.77	−0.04
2	1.92	1.90	−0.02
3	3.24	3.25	0.01
4	4.31	4.26	−0.05
5	5.26	5.32	0.06
6	6.80	6.53	−0.27

Average error = 0.08%

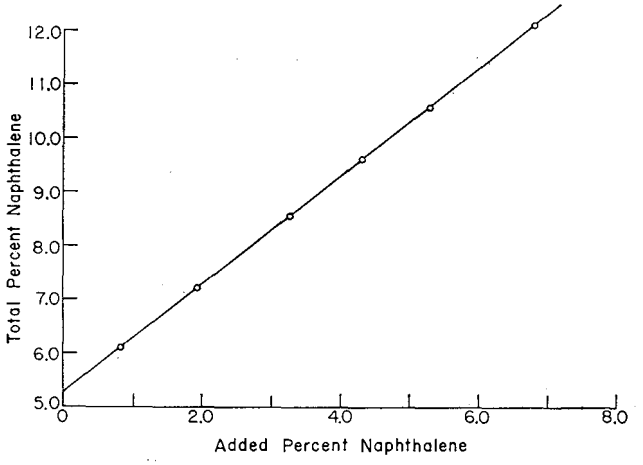

Figure 3. Observed, Total Naphthalene Concentration in Sample
Plotted against known amounts of naphthalene added to sample

$$C_1 = (D_{c,s} - d)/a_1 \qquad (6)$$

where a_1 is the calibration coefficient for naphthalene at wave length C determined by using the pure material. In Figure 2 may be seen a schematic plot of the data for an actual unknown sample. This illustrates the general relationship of d_1, d_2, and d.

To test the effectiveness and accuracy of this method, three types of tests were made: Synthetic samples containing large amounts of interfering compounds were analyzed, known amounts of naphthalene were added to submitted samples possessing appreciable background corrections with subsequent re-examinations, and an extrapolation procedure was used. In Table I may be seen the results obtained when synthetic samples were prepared. These samples were made to contain varying amounts of interfering compounds (up to 30% by volume) and were analyzed by the above procedure. The average error in terms of total sample is only 0.09%.

Further tests of the accuracy were made by adding known amounts of naphthalene to actual submitted samples which were then re-examined. If the calculated naphthalene concentrations in the original unknown samples were in error because of improper corrections for background, the calculated increase in concentration would also be expected to be in error. The agreement between added and calculated naphthalene concentrations seen in Table II gives further assurance as to the effectiveness of the method. The average error is of the same order of magnitude as given in Table I.

A further test of the method is to make such a series of increases of naphthalene concentrations to a single sample, plot total observed naphthalene concentration against added concentration, and extrapolate back to zero added material. If the method is correct, the extrapolated concentration should be close to the concentration observed for the original material. This has been found true for all samples thus tested. In Figure 3 may be seen a plot for such an example. Here are plotted the observed, total naphthalene concentrations against the known, added concentrations. The extrapolation of the curve to zero added material yields 5.25% naphthalene for the original sample. The analysis of the original sample, using wave lengths A, B, and C by the procedure described above, yields a naphthalene concentration of 5.28%. This agreement for the naphthalene concentration obtained by the two procedures adds further validity to the methods used on routine samples.

A routine analysis of a submitted sample may be carried out in about 1 hour, including the necessary time for dilutions and calculations. The complete spectrum between 300 and 320 mμ is always obtained and inspected to determine whether either of the monomethylnaphthalenes is present. They may be detected by the resultant alteration in the shape of the spectrum. When the sample is given an alkaline permanganate treatment to remove some of the interfering compounds, the naphthalene concentrations are always the same as the untreated sample to within a few hundredths per cent. Tests have shown that this treatment leaves the naphthalene concentration essentially unchanged.

Of the many unknown samples examined, the background correction was frequently low. It could actually have been neglected in some cases with a maximum resultant error of only a few tenths per cent (based on total sample) of naphthalene. However, for the most reliable accuracy it should be corrected for in all cases.

Two alternative methods of calculating the background correction, d, were tested.

In one of these a correction, d, was assumed for wave length C, a correction, $d + \Delta d$, was assumed for wave length A, and a correction, $d - \Delta d$, was assumed for wave length B. Using equations similar to 4 and 5 it is possible to eliminate Δd and to solve for d in terms of R_1, R_2, $D_{a,s}$, $D_{c,s}$, and $D_{b,s}$. In the other method it was assumed that the change of background optical density is linear through this region. Then with the assumption of a correction, d, for wave length C, the correction for wave length A would be $d + 2.5\Delta d$ and the correction for B would be $d - 7\Delta d$ where Δd is now the change in background optical density per mμ. Using similar equations a solution for d may also be obtained in terms of the above quantities.

Neither of these two methods gave as good agreement for the synthetic samples as the one used and both were more involved in application.

ANALYSIS FOR NAPHTHALENE, α-METHYLNAPHTHALENE, AND β-METHYLNAPHTHALENE

When the absorption spectra for naphthalene, α-methylnaphthalene, and β-methylnaphthalene are viewed individually they are seen to possess some close similarities which at first would seem to rule out the possibility of a simultaneous analysis. However, when they are plotted together as in Figure 4, there are enough distinct differences to allow such an analysis. The absorption peaks chosen for analysis are those designated by arrows in the figure and they lie at 311, 314, and 319 mμ. They are representative of naphthalene, α-methylnaphthalene, and β-methylnaphthalene, respectively. The α-methylnaphthalene used for the data of Figure 4 was not so pure as that used for calibration and shows a small concentration of β-methylnaphthalene.

If we designate by D_1, D_2, and D_3 the observed optical densities at wave lengths 311, 314, and 319 mμ, respectively, and let C_1, C_2, and C_3 represent the weight percentages of naphthalene, α-meth-

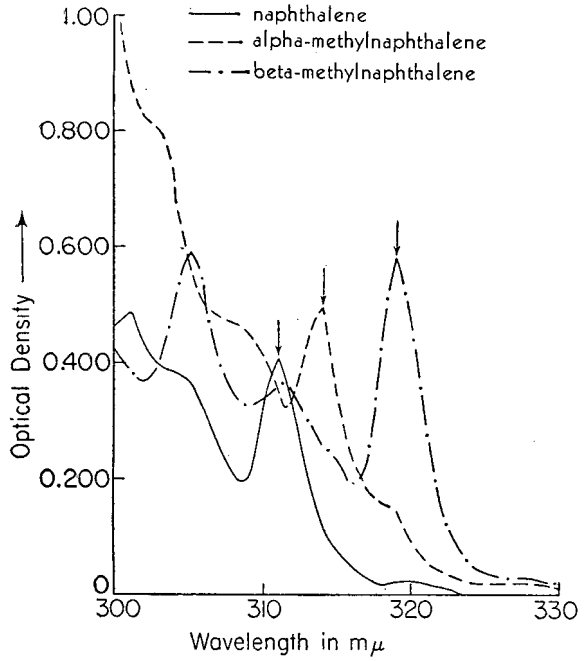

Figure 4. Ultraviolet Absorption Spectra
Arrows indicate wave lengths used for analysis

ylnaphthalene, and β-methylnaphthalene in the solution as examined, we have:

$$D_1 = 1.338\ C_1 + 1.138\ C_2 + 1.326\ C_3$$
$$D_2 = 0.335\ C_1 + 1.580\ C_2 + 0.990\ C_3 \qquad (6)$$
$$D_3 = 0.107\ C_1 + 0.446\ C_2 + 2.152\ C_3$$

where the calibration coefficients obtained with the pure compounds have been used. These calibration coefficients are unique to the absorption cells and slit widths used and are representative of concentrations expressed in grams per kilogram of solution in the absorption cells. For optimum accuracy in an absorption spectroscopic method, it is important that the optical density at each wave length be dominated by one compound and that each compound be represented by such a wave length. These conditions are not exactly fulfilled in Equations 6. The largest coefficient for D_1 comes from naphthalene, the largest for D_2 comes from α-methylnaphthalene, and the largest for D_3 comes from β-methylnaphthalene. However, the calibration coefficient for β-methylnaphthalene at 311 mμ is almost as large as that for naphthalene. Although this is a departure from the ideal conditions suitable for best accuracy, the equations can be solved with very satisfactory results.

In the simultaneous analysis for the three naphthalenes no correction was made for background, for several reasons. In the work on samples containing only naphthalene and using the method of the previous section the background correction was often small enough to be neglected with relatively small error. In the samples containing naphthalene plus the α and β isomers, the total naphthalene was generally high, making the errors caused by neglecting the background small. The distillation cuts were sharper; this actually eliminated many of the lower boiling point materials that contribute to the background. Those that remained were in some cases eliminated by the alkaline permanganate treatment. A consideration of the source of the samples also indicated that few if any interfering compounds would be present.

In Table III may be seen the results of analyses of a series of synthetic samples of mixtures containing up to about 30% naphthalenes by weight. As the accuracy is in general less than that for the analysis for naphthalene alone, the concentrations are reported only to the nearest 0.1%. The same degree of absolute accuracy is obtainable for higher concentrations.

An application of the analysis may be seen in Table IV, which gives the calculated concentrations for several of a series of sharp distillation cuts from an aromatic-rich hydrocarbon sample. When such a series is analyzed, the various naphthalene concentrations are readily obtained and a complete naphthalene analysis for the material boiling below about 248° C. is possible. Cuts boiling in this region and above cannot in general be accurately analyzed because of the presence of interfering compounds of higher boiling points. The time per analysis is about 1.25 hours. This includes the dilutions, reading the data, making the calculations, and plotting the curves. The spectra through the naphthalene range are plotted for all samples, to determine the presence of any possible interfering compounds.

In addition to the tests of the analysis displayed by the results on the synthetic samples, material balance calculations have been carried out for several complete distillation and concentration processes. For the necessary data the initial material, the intermediate products, and the final products were all analyzed for the three naphthalenes. The results were combined with the yield data for the process in the material balance calculations. The results were consistent to a few tenths per cent of total sample.

Table III. Comparison between Known and Calculated Concentrations for Naphthalene, α-Methylnaphthalene, and β-Methylnaphthalene in Synthetic Samples

Compound	Known, %	Calculated, %	% Error
Naphthalene	4.7	4.7	0.0
α-Methylnaphthalene	9.5	9.5	0.0
β-Methylnaphthalene	2.4	2.3	−0.1
Naphthalene	0.6	0.6	0.0
α-Methylnaphthalene	4.0	4.0	0.0
β-Methylnaphthalene	7.4	7.3	−0.1
Naphthalene	1.4	1.0	−0.4
α-Methylnaphthalene	24.0	24.0	0.0
β-Methylnaphthalene	2.8	2.6	−0.2
Naphthalene	6.2	6.0	−0.2
α-Methylnaphthalene	4.7	4.5	−0.2
β-Methylnaphthalene	10.7	10.4	−0.3
Naphthalene	5.7	6.1	0.4
α-Methylnaphthalene	0.0	0.0	0.0
β-Methylnaphthalene	10.0	9.6	−0.4
Naphthalene	3.6	3.9	0.3
α-Methylnaphthalene	3.9	3.9	0.0
β-Methylnaphthalene	4.4	4.3	−0.1
	Average error = 0.2%		

Table IV. Naphthalenes in Distillation Cuts from an Aromatic-Rich Hydrocarbon Sample

Boiling Point Range, ° C.	Naphthalene, %	α-Methyl-naphthalene, %	β-Methyl-naphthalene, %
210–215	9.4	0.0	0.0
215–220	17.1	0.0	0.0
220–225	18.2	0.0	0.0
225–230	8.2	0.3	2.1
230–235	0.3	0.9	8.9
235–240	0.0	4.2	27.3
240–245	0.0	13.5	45.0

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Determination of Total Olefins and Total Aromatics

In Hydrocarbon Mixtures by Raman Spectrometry

J. J. HEIGL, J. F. BLACK, AND B. F. DUDENBOSTEL, JR.
Esso Laboratories, Standard Oil Development Company, Elizabeth, N. J.

RAMAN spectrometric data obtained at the Esso Laboratories of the Standard Oil Development Company show that the total aromatic and total olefin content of complex hydrocarbon samples can be determined by a fast, simple procedure. This analysis is performed with a spectrograph equipped with a photoelectric detecting device and a high speed pen recorder. The data are obtained by recording the scattering intensity in a narrow spectral region which includes a peak characteristic of the olefins and another peak characteristic of the aromatics. The exact spectral positions at which these peaks occur vary somewhat among the individual compounds in each series and, therefore, it is not possible to base the method on absolute peak height measurements. The recorded area under each peak, however, gives a relationship between scattering intensity and the concentration of the olefin double bond and of the aromatic carbon-carbon bond.

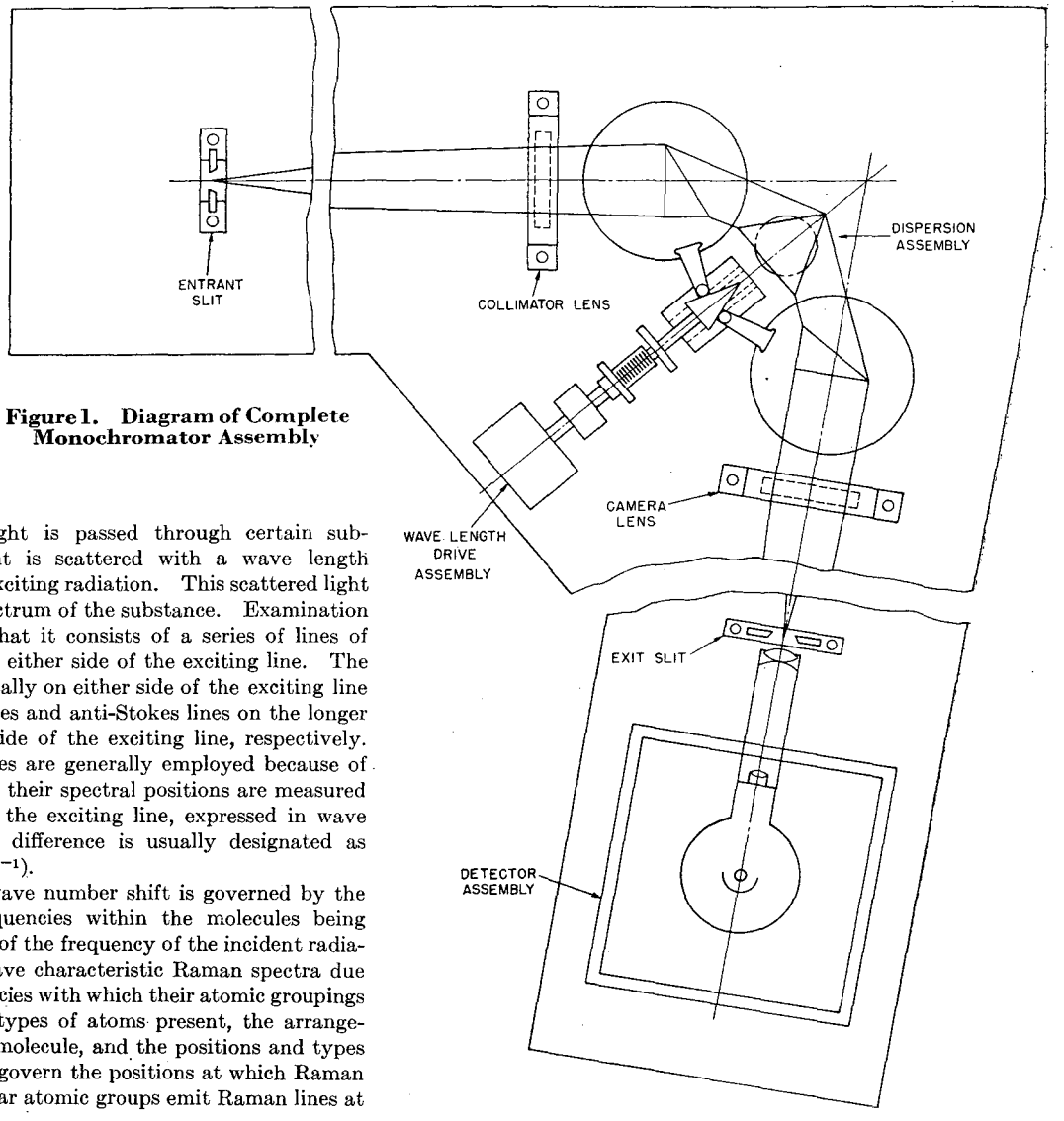

Figure 1. Diagram of Complete Monochromator Assembly

BASIS OF METHOD

The Raman effect, discovered only 20 years ago (*4*), is based on the fact that when a beam of light is passed through certain substances, part of the light is scattered with a wave length different from that of the exciting radiation. This scattered light constitutes the Raman spectrum of the substance. Examination of this spectrum reveals that it consists of a series of lines of extremely low intensity on either side of the exciting line. The lines are located symmetrically on either side of the exciting line and are designated as Stokes and anti-Stokes lines on the longer and shorter wave length side of the exciting line, respectively. In practice, the Stokes lines are generally employed because of their greater intensity, and their spectral positions are measured in terms of distance from the exciting line, expressed in wave numbers. This frequency difference is usually designated as wave number shift ($\Delta\tilde{\nu}$ cm.$^{-1}$).

The magnitude of the wave number shift is governed by the interatomic vibration frequencies within the molecules being excited and is independent of the frequency of the incident radiation. All hydrocarbons have characteristic Raman spectra due to differences in the frequencies with which their atomic groupings vibrate and rotate. The types of atoms present, the arrangement of atoms within the molecule, and the positions and types of interatomic linkages all govern the positions at which Raman spectral lines occur. Similar atomic groups emit Raman lines at approximately the same displacement frequency. For example, the olefin carbon-carbon double bond stretching vibration emits Raman lines in the 1640 to 1680 $\Delta\tilde{\nu}$ cm.$^{-1}$ region (*2*), and the stretching vibration between the carbon-carbon bond in the aromatic ring gives rise to a line in the 1590 to 1615 $\Delta\tilde{\nu}$ cm.$^{-1}$ region (*3*). The exact positions of the peak locations within these regions are governed by the structure of the molecules. In addition to affecting the position of the peak, the remainder of the molecule acts in a manner similar to a diluent, thereby affecting the relative intensity of the Raman line. The fact that this effect is directly proportional to molecular volume has been

The Raman lines characteristic of the olefin and aromatic carbon-carbon bond vibrations are employed in the determination of total unsaturation and total aromaticity. The analyses are performed by scanning the spectral region with a Raman displacement of 1590 to 1680 $\Delta\tilde{\nu}$ cm.$^{-1}$ from the exciting line. Functions of the areas under the recorded peaks rather than peak heights are employed in both analyses, as the positions of the peaks shift slightly with different olefin or aromatic compounds. Results from both analyses may be obtained with an accuracy of approximately ±10% of the correct value.

established in investigations of the analytical applications of the Raman effect at the Esso Laboratories.

APPARATUS

A complete description of the Raman spectrometer employed in the development of this analysis will be the subject of an additional publication. A brief description of this apparatus is presented below.

The monochromator follows conventional lines and consists of a lens and prism assembly mounted in accordance with a modified Young-Thallon design (*6*). The design of the light source and sample cell follows that previously described by Fenske *et al.* (*1*). The mercury lines around 4358 Å. are employed as the exciting frequencies. A diagram of the complete assembly is shown in Figure 1. A photograph of the instrument is given in Figure 2.

The most important feature of the equipment is the detecting, amplifying, and recording system, which was designed at the Research Division of the Esso Laboratories. A photomultiplier, mounted in accordance with the design shown in Figure 3, is employed as the detecting element. The photomultiplier is cooled with dry ice. The output from the photomultiplier is fed to a direct current amplifier whose output is recorded on a two-recorder system. The recorders operate with a sensitivity ratio of 1 to 3, so that peaks with a wide range in intensity can be recorded with maximum accuracy. A view of the amplifying and recording system is given in Figure 4.

MEASUREMENT OF RAMAN LINE INTENSITIES

Pure Compounds. For the quantitative applications of Raman spectrometry, a reproducible method for expressing scattering intensities is required. Because of slow changes in instrument sensitivity, absolute scattering intensities are not comparable over an extended period. This limitation is overcome by employing a standard reference procedure (*1*), which involves scanning the 459 $\Delta\tilde{\nu}$ cm.$^{-1}$ line of carbon tetrachloride before and after the spectral trace of each sample. Scattering intensities are then converted to scattering coefficients by dividing the recorded height of the sample peak by the average of the heights of the two carbon tetrachloride peaks. Both the carbon tetrachloride standard and the hydrocarbon sample must be measured in cells of the same dimension.

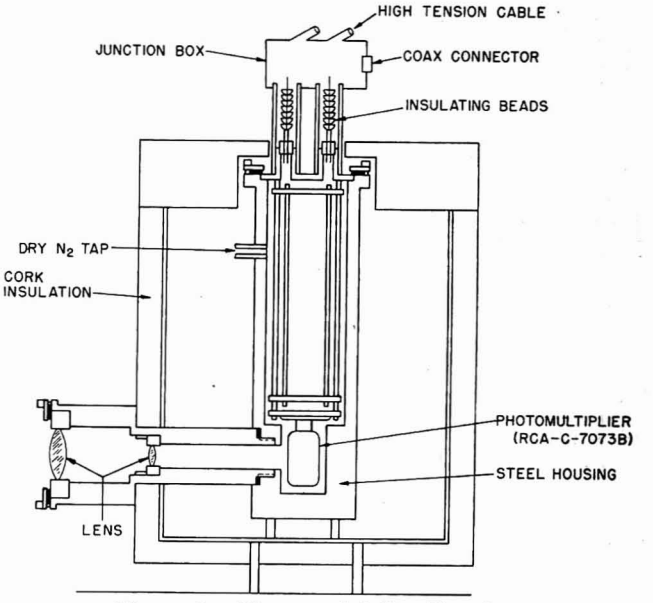

Figure 3. Photomultiplier Housing

In the analysis of hydrocarbon mixtures for individual isomers, the Raman peaks selected are due to single constituents (*1*, *5*). For these samples, scattering coefficients based on peak height alone are employed. However, in the analysis of complex hydrocarbon mixtures for total aromatic and total olefin content, the Raman peaks characteristic of the aromatic and olefinic carbon-carbon bonds are the result of a large number of individual compounds. Because these Raman displacements are found to vary among the various compounds, a broad band is recorded at the position characteristic of each of these bond types. Scattering coefficients based on recorded peak height cannot be employed under these conditions.

It has been established at this laboratory that the area under the recorded peak can be employed as a measurement of scattering intensity. The procedure that has been developed for calculating the scattering intensity from the recorded peak area is illustrated in Figure 5. The peak height (*PB*, Figure 5) is divided by the height of the 459 $\Delta\tilde{\nu}$ cm.$^{-1}$ carbon tetrachloride peak to give the scattering coefficient previously described.

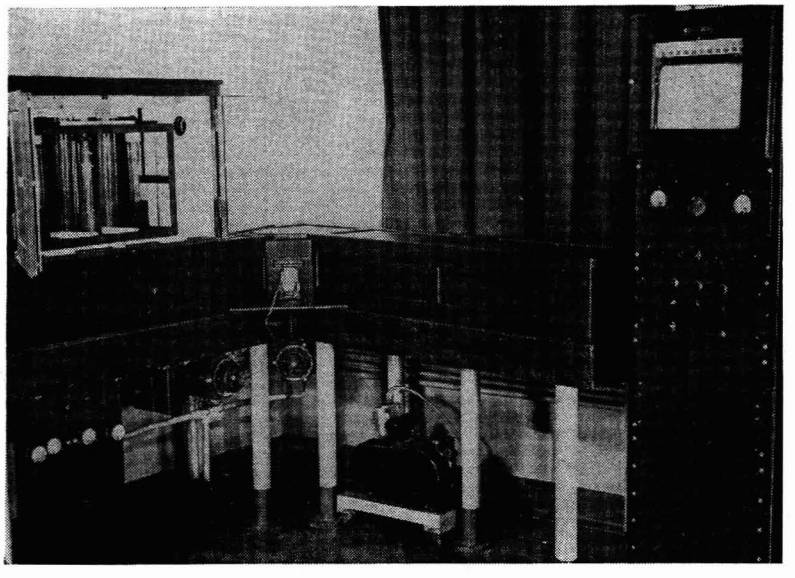

Figure 2. Photoelectric Recording Raman Spectrograph

Table I. Raman Data Used in Determination of Total Mono-olefins by Measurement of Raman Line Characteristic of —C=C— Stretching Vibration

Olefin Hydrocarbon	Olefin Type	Raman Shift, Cm.$^{-1}$	Scattering Coefficient	Scattering Coefficient × Mol. Vol.	Peak Base Width, Mm.
3-Methyl-1-pentene	I	1640	0.294	36.9	25.0
4-Methyl-1-pentene	I	1643	0.332	41.8	24.5
cis-4-Methyl-2-pentene	II	1663	0.338	42.3	23.0
2,3-Dimethyl-1-butene	III	1647	0.265	32.8	23.5
trans-4-Methyl-2-pentene	II	1647	0.260	32.5	23.5
2-Methyl-1-pentene	III	1650	0.261	32.1	23.5
1-Hexene	I	1650	0.338	42.2	24.0
trans-3-Hexene	II	1670	0.314	38.9	23.5
cis-2-Hexene	II	1660	0.288	35.3	23.5
2,3-Dimethyl-2-butene	V	1680	0.323	38.3	23.5
Average for hexenes			0.301 ± 0.028	37.3 ± 3.4	
2,4-Dimethyl-2-pentene	IV	1675	0.298	41.9	24.5
4,4-Dimethyl-1-pentene	I	1643	0.216	30.2	27.0
1-Heptene	I	1645	0.306	43.0	23.0
3-Ethyl-2-pentene	IV	1665	0.317	43.0	25.0
trans-2-Heptene	II	1660	0.226	31.5	27.0
cis-2-Heptene	II	1660	0.253	35.0	25.5
3-Heptene	II	1660	0.255	35.7	27.0
Average for heptenes			0.267 ± 0.034	37.2 ± 4.7	
2,4,4-Trimethyl-1-pentene	III	1647	0.212	33.1	25.0
2,4,4-Trimethyl-2-pentene	IV	1675	0.230	35.2	24.5
6-Methyl-1-heptene	I	1643	0.235	36.9	24.0
2-Methyl-1-heptene	III	1650	0.277	43.0	24.0
2-Ethyl-1-hexene	III	1647	0.230	35.5	24.0
1-Octene	I	1640	0.293	45.9	25.0
4-Methyl-3-heptene	IV	1665	0.297	45.8	24.0
trans-2-Octene	II	1670	0.198	30.9	25.0
cis-2-Octene	II	1670	0.192	29.7	28.0
Average for octenes			0.240 ± 0.031	37.3 ± 5.0	
3,4,4,5-Tetramethyl-2-hexene (L.B.)[a]	IV	1655	0.225	42.6	23.0
3,4,4,5-Tetramethyl-2-hexene (H.B.)[a]	IV	1655	0.190	35.9	23.0
1-Decene	I	1643	0.178	33.7	24.5
Average for decenes			0.198 ± 0.018	37.4 ± 3.5	
Over-all average				37.3 ± 4.2	23.8 ± 1.0

[a] Distinguished as low boiling and high boiling isomers.

The base width of the peak is then measured on a line, *DBE*, drawn perpendicular to the peak height, *PB*. The limits of the base width (points *D* and *E*) are defined by the intersection of line *DBE* with the linear extrapolation of the sides of the peak. The base width observed for the sample is divided by the average base width calculated from the spectra of pure compounds. The observed scattering coefficient is then multiplied by this quotient to correct for the width of the peak.

The use of relative base width to correct the scattering coefficients of the Raman lines employed for the total olefin and total aromatic analyses is justified by the constant base width observed for pure compound data. The average base width of the olefinic double bond peak, calculated from Raman data on 29 pure olefins, is 23.8 ± 1.0 mm. and is independent of molecular weight or double bond position. The average base width of the Raman line characteristic of the conjugated carbon-carbon bond in the aromatic nucleus is 15.3 ± 1.5 mm. This observation is based upon the Raman spectra of 22 pure aromatic hydrocarbons.

OLEFIN ANALYSIS

Calibration. The total olefin analysis presented in this paper was developed from data obtained in the examination of the Raman spectra of 29 pure mono-olefins, which ranged from hexenes to decenes and included all olefin types as defined by the classification system of Schmidt and Boord (*7*). The Raman scattering characteristic of the carbon-carbon double bond vibration in the mono-olefins examined at the Esso Laboratories is presented in Table I.

The data in Table I reveal that the magnitude of the scattering coefficient characteristic of the olefinic double bond decreases with increasing molecular weight of the pure compound being examined. Experiments at these laboratories have established that this behavior is due to the fact that the reported scattering coefficients are directly proportional to the concentration of olefinic double bonds in the sample. The linear relationship between the scattering coefficients of the pure mono-olefins and the concentration of olefinic double bonds per unit volume is indicated in Figure 6, where the average of the scattering coefficients for the mono-olefins of each molecular weight is plotted against the average concentration of mono-olefins expressed as moles per milliliter.

A coefficient independent of molecular weight is obtained by multiplying the observed scattering coefficient of each individual olefin by the molecular volume of the pure hydrocarbon. The product from this calculation is termed the molal scattering coefficient. The average value of this term (37.3) is the slope of the line presented in Figure 6 and is constant over the entire molecular weight range as indicated in Table II.

The use of the molal scattering coefficient provides a simple and direct method for converting the measured scattering coefficient into moles of unsaturates per milliliter. The conversion procedure and its validity are indicated by the following considerations.

The line in Figure 6 must, by definition, pass through zero scattering coefficient at zero moles of unsaturates per milliliter of sample. Inspection of Figure 6 indicates that, within experimental error, this behavior is observed. According to this curve, a scattering coefficient is therefore equal to the moles of unsaturates per milliliter times the slope of the line—i.e., moles of unsaturates per milliliter times 37.3. It is conversely true that an observed scattering coefficient divided by 37.3 (the average molal scattering coefficient) is equal to the moles of unsaturates per

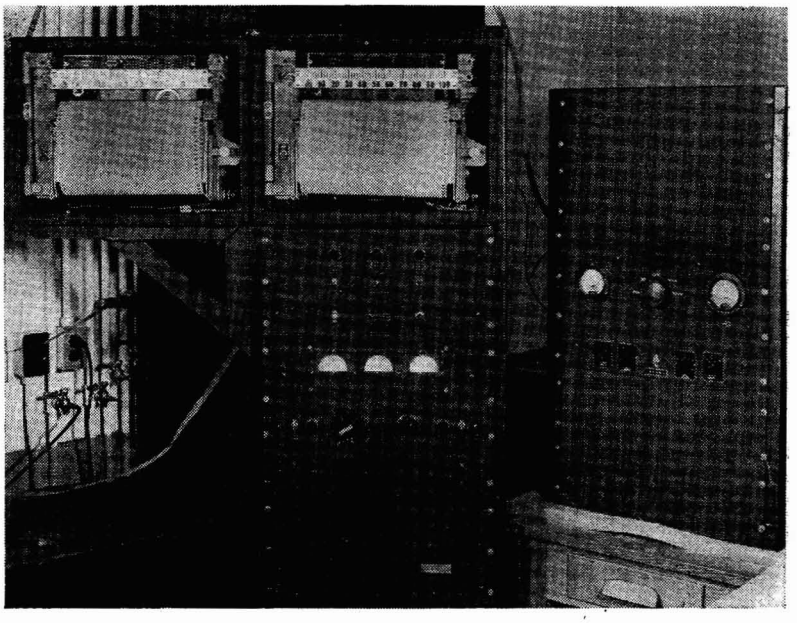

Figure 4. Amplifying and Recording System

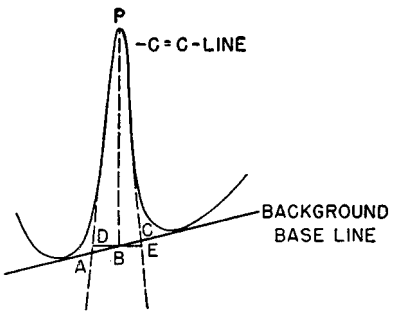

Figure 5. Method Employed in Measuring Area under Recorded Peak

Peak height = *PB*

Scattering coefficient = $\frac{PB}{\text{height of } CCl_4 \text{ peak}}$

True peak area corrected for time delay in recording = triangle *PDE*

Peak base width = *DBE*

Scattering area = scattering coefficient x base width

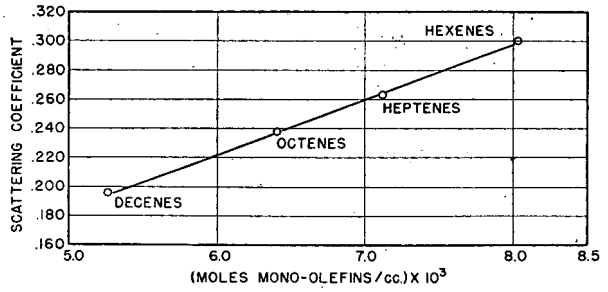

Figure 6. Relation between Scattering Coefficient at 1640 to 1680 $\Delta\bar{\nu}$ Cm.$^{-1}$, and Moles of Mono-olefins per Milliliter

milliliter. This relationship, the one employed for analyses, is valid regardless of the molecular weight range of the mono-olefins in the sample.

The data presented in the previous paragraphs lead to the following equation for calculating the concentration of olefins from the 1640 to 1680 $\Delta\bar{\nu}$ cm.$^{-1}$ Raman band.

$$\text{Moles of mono-olefin per ml.} = \frac{K \times b}{37.3 \times 23.8} \qquad (1)$$

where K = observed scattering coefficient for olefin peak; b = observed base width of olefin peak, mm.; 37.3 = molal scattering coefficient; and 23.8 = average base width from pure compound data, mm.

In Equation 1 millimeters must be the units employed for measurement of the base width of the olefin peak, as millimeters are the units employed for the average base width (23.8) from pure compound data. The scattering coefficient is dimensionless.

ANALYTICAL RESULTS

Analytical procedures established from consideration of pure compound spectra must first be evaluated by the analysis of synthetic samples of known composition. If satisfactory accuracy and precision are indicated, the procedure may be extended to routine samples.

Table II. Constancy of Molal Scattering Coefficient with Molecular Weight

Molecular Weight Range	No. of Isomers Studied	Molal Scattering Coefficient
Hexenes	10	37.3
Heptenes	9	37.2
Octenes	7	37.3
Decenes	3	37.4
	Av.	37.3

Table III. Determination of Total Mono-olefins by Raman Spectrometry

(Blends of olefins of all types [a] diluted with 2,2,4-trimethylpentane)

	Sample A, 100% Olefins by Volume		Sample B, 76.9% Olefins by Volume		Sample C, 51.2% Olefins by Volume	
	Olefin, millimoles/ml.	% deviation	Olefin, millimoles/ml.	% deviation	Olefin, millimoles/ml.	% deviation
Blended composition	7.06	...	5.43	...	3.61	...
Found						
Run 1	7.07	0.1	5.30	2.4	3.45	4.4
Run 2	6.60	6.5	...	...	3.32	8.0

[a] 1-Heptene, 1-octene; 3 ethyl-1-pentene, 2 methyl-1-pentene; *cis*-4-methyl-2-pentene; 2,3-dimethyl-2-butene; 2,4,4-trimethyl-2-pentene.

Application of the total olefin analysis to a series of synthetic samples containing olefins of all types is illustrated in Table III. In samples containing less than 100% olefins, 2,2,4-trimethylpentane is employed as a diluent. Data in this table indicate that total olefin content may be determined with a maximum deviation of 8% of the constituent and an average deviation of 4.5% of the reported value.

Application of the analysis in the presence of paraffins, naphthenes, and aromatics is demonstrated by the data in Table IV. These results show a deviation of 5.2% between the reported value and the known concentration of olefins in the synthetic blend.

Table IV. Determination of Total Olefins and Aromatics by Raman Spectrometry

(Sample blend of 23.7% C_9 aromatics, 46.3% mono-olefins, 25% naphthenes, and 5% paraffins)

Molecular Type	Composition Known	Composition Found	% Deviation from Reported Value
Olefins, millimoles/ml.	0.327	0.310	5.2
Aromatics, vol. %	23.7	24.5	3.4

Table V. Determination of Total Olefins in a Hydrocarbon Synthesis Naphtha

Sample	Analytical Method: Raman	Bromine Addition	Infrared
	Mono-olefins, millimoles per ml.		
Total naphtha	4.36	5.06	4.62
135–250° F. fraction	5.45	5.28	5.73
250–350° F. fraction	3.16	3.78	2.75

Results in Table V illustrate the application of the total olefin analysis to routine samples. These data, on fractions from a hydrocarbon synthesis naphtha, reveal satisfactory agreement among the total olefin contents as determined by Raman spectrometry, bromine number, and a summation of the infrared analyses for the olefin types. These data show that the Raman method is satisfactory for the determination of the total olefin content of hydrocarbon samples.

AROMATIC ANALYSIS

Calibration. The Raman peak characteristic of the conjugated carbon-carbon stretching vibration in the aromatic ring is observed at a displacement of 1590 to 1615 cm.$^{-1}$ Data on 22 pure aromatic hydrocarbons which were examined in establishing this analysis are presented in Table VI. The scattering coefficients for aromatic hydrocarbons presented in this table do not exhibit the pronounced drift with molecular weight which was encountered in the carbon-carbon double bond stretching vibration for mono-olefins. The more regular behavior may be a reflection of the fact that the alkyl side chains do not represent a large proportion of the molecule in the molecular weight range investigated. Aromatic hydrocarbons much beyond this molecular weight range are not analyzable by the Raman technique, for the fluorescence of materials in this range will interfere with obtaining a satisfactory Raman spectrum. Because the scatter-

Table VI. Raman Spectral Data in the 1590 to 1615 $\Delta\tilde{\nu}$ Cm.$^{-1}$ Region for Pure Aromatic Hydrocarbons

(Raman peak characteristic of conjugated carbon-carbon vibration in aromatic ring)

Aromatic Hydrocarbon	Raman Shift, Cm.$^{-1}$	Scattering Coefficient	Peak Base Width, Mm.
Benzene	1590	0.291	17.3
Toluene	1600	0.297	17.0
Ethylbenzene	1600	0.288	15.0
m-Xylene	1595	0.187	16.2
p-Xylene	1615	0.315	10.5
o-Xylene	1600	0.235	17.0
Isopropylbenzene	1605	0.248	15.8
n-Propylbenzene	1600	0.249	16.0
m-Ethyltoluene	1610	0.198	15.8
p-Ethyltoluene	1605	0.279	13.0
1,3,5-Trimethylbenzene	1600	0.223	16.8
o-Ethyltoluene	1595	0.239	17.6
1,2,4-Trimethylbenzene	1615	0.261	11.2
1,2,3-Trimethylbenzene	1590	0.215	13.8
Hydrindene	1600	0.217	15.5
tert-Butyl benzene	1595	0.227	16.0
Isobutylbenzene	1600	0.235	15.5
sec-Butyl benzene	1600	0.244	16.0
m-Cymene	1600	0.203	15.5
p-Cymene	1615	0.370	13.2
o-Cymene	1605	0.223	17.7
n-Butylbenzene	1590	0.228	14.5
Av.		0.249 ± 0.031	15.3 ± 1.5
% deviation from average		12.4	9.8

ing coefficients for the aromatic peak do not vary over the analyzable range of molecular weights, a molecular volume correction, such as applied in the total olefin analysis, is not required for the determination of total aromatics. The average scattering coefficient for the aromatic analysis as determined from the data in Table VI is 0.249 ± 0.031. The equation employed to calculate per cent total aromatics is as follows:

$$\text{Volume \% aromatics} = \frac{K \times b}{0.249 \times 15.3} \times 100 \qquad (2)$$

where K = observed scattering coefficient; b = observed base width of aromatic peak, mm.; 0.249 = average scattering coefficient from pure compound data; and 15.3 = average base width from pure compound data, mm.

The calculation of total aromatic content is, therefore, based upon measurement of the scattering coefficient and base width of the 1590 to 1610 $\Delta\tilde{\nu}$ cm.$^{-1}$ Raman peak. These quantities are divided by their average values determined from pure compound data.

Table VII. Raman Analyses of Synthetic Blends for Total Aromatics

Blend No.	Components Present	Volume % Aromatics Present	Volume % Aromatics Found	% Deviation from Reported Value
1	Xylenes	96	95	1.0
2	Xylenes + 40% 2,2,4-trimethylpentane	58	53	8.6
3	Solvesso 100[a]	95	93	2.1
4	Solvesso 100 + 40% 2,2,4-trimethylpentane	56	54	3.6
5	Solvesso 100 + 80% 2,2,4-trimethylpentane	18.6	16.5	11.3
6	Solvesso 100 + 92% 2,2,4-trimethylpentane	7.4	7.5	1.0
7	Solvesso 100 + 20% 2,2,4-trimethylpentane + 40% *trans*-3-heptene	37	34	8.1
			Average deviation	5.1

[a] Commercial solvent naphtha boiling between 300° and 365° F.

ANALYTICAL RESULTS

A maximum deviation of 11.3% and an average deviation of 5.1% of the constituent are obtained in an evaluation of the total aromatic analysis with the synthetic blends shown in Table VII. In this table samples 3 to 7 were prepared from Solvesso 100, a commercial solvent naphtha, the aromatic content of which has been determined by a number of analytical methods. Raman analysis for the total aromatic content in the presence of paraffins, naphthenes, and olefins is demonstrated by the data in Table IV, in which the reported aromatic content is 3.4% greater than the blended value. Determination of the total olefins in this same sample has been previously discussed.

The total aromatic analysis is frequently applied to routine samples to provide an independent check upon the summation of the individual aromatic constituents. In Table VIII, results from the analysis of the total sample of an aromatic concentrate are compared with data obtained from the analysis of blends from a 200-plate distillation of the same material. Raman analyses for the individual isomers as well as for total aromatics were performed on these samples. These data show that, in the analysis of the distillation fractions, the maximum deviation between the total aromatic determination and the summation of results for the individual isomers is 9.9%. The summation of total aromatic analyses on the individual blends is 69.8 volume % which compares favorably with the 70.0% aromatics determined from the total sample.

Tables IX and X present data obtained by Raman analysis for the aromatics present in a number of refinery naphthas. For each distillation blend presented in these tables, data from the Raman analysis for total aromatic content are compared with the summation of analytical results for the individual aromatic isomers. The deviation between the total aromatic analysis and the summation of individual isomers is greater than 10% in only 4 of 25 blends presented in these tables. The blend that exhibits the greatest deviation (25%) consists of only a single aromatic isomer which is present in very low concentration. The average deviation for all blends in these tables is 6.5%.

APPRAISAL OF METHOD

Total olefin and aromatic content may be determined by a number of procedures which do not involve Raman spectrometry. The Raman technique, however, provides results that may be obtained rapidly and are generally independent of the other constituents in the sample.

Conjugated olefins are the only class of hydrocarbons that interfere with the Raman determination of the total concentration of aromatics. The conjugated olefins, as well as organic acids and imides, interfere with Raman determination of the total concentration of mono-olefins. Unconjugated diolefins appear as two unsaturated molecules in the olefin determination. The presence of conjugated olefins may be determined by ultraviolet spectrometry and a suitable correction applied to the Raman analysis. Organic acids and

Table VIII. Raman Analysis of an Aromatic Concentrate

(312.7° to 338.8° F. fraction from 40-plate distillation of catalytically cracked naphtha)

Constituents	Distillation Fractions 1	2	3–12	13–21	22–28	29–33	34–R12	Bottoms	Summation of Blend Analyses	Total Sample Analysis
o-Xylene	3	..	...	..	...	..	...	...	0.1	..
Isopropylbenzene	...	...	...	..	...	..	...	...	...	..
n-Propylbenzene	13	8.5	0	..	...	...	...	...	0.5	..
m-Ethyltoluene	20	39	50	5	...	..	...	...	15.1	16.8
p-Ethyltoluene	7	8	20	21.5	...	..	...	...	10.3	10.9
1,3,5-Trimethylbenzene	...	..	0	31	60	20	0	...	20.0	16.8
o-Ethyltoluene	...	..	...	8.5	28	12.5	0	...	8.4	6.2
1,2,4-Trimethylbenzene	...	..	...	..	...	23	60	76	14.4	14.5
Summation	43	55.5	70	66	88	55.5	60	76	68.8	65.2
Total aromatics (from 1600 cm.$^{-1}$ Raman line)	44	60	76	71	85	50	65	81	69.8	70.0
Percentage deviation	2.3	8.2	8.6	7.6	3.4	9.9	8.3	6.6	1.5	7.4

Table IX. Raman Analysis

Distillation fractions	Solvent Naphtha 29–45	46–51	52–61	62–80	81–85	86–89	Heavy Catalytic Naphtha 18–25	26–49	50–58	59–62	63–65	66–69
No. of aromatics present	3	5	5	3	1	3	2	5	1	2	2	3
Summation of % aromatics by Raman analysis of isomers	100	98	100	100	95	82	37	74	76	73	60	53
Total aromatics by Raman, %	105	93	92	93	100	92	40	69	78	76	64	52
% deviation	5	5	8	7	5	12	8	7	3	4	7	2

Table X. Raman Analysis of Aromatic Concentrates

Distillation fractions	Virgin Naphtha 54–55	56–57	58–60	61–65	66–68	69–70	Thermal Naphtha 9–16	17–21	25–29	30–35	36–41	42–47	48–54
No. of aromatics present	5	5	5	5	3	4	1	3	4	4	4	3	2
Summation of % aromatics by Raman analysis of isomers	62	78	86	100	84	87	8	7	47	59	41	53	32
Total aromatics by Raman, %	72	71	86	95	85	89	6	7	48	59	44	46	35
% deviation	16	9	0	5	1	2	25	0	2	0	7	13	9

imides are not normally present in petroleum products but, if present, can be removed by chemical methods.

For analyses by Raman spectrometry at the Esso Laboratories, 4 ml. of liquid sample are required, all of which is recovered at the end of the measurements. With this sample size, the minimum detectable aromatic content is approximately 5 volume % and the minimum detectable olefin content corresponds to the unsaturation present in a sample containing 5 volume % of hexenes (0.4 millimole per ml.).

Total mono-olefin and aromatic content may be determined on the same sample; 15 minutes are required for the analysis. Approximately the same time is required if only one of these hydrocarbon classes is to be determined. The time requirement for the Raman technique compares favorably with that of other analytical methods of comparable accuracy.

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pH Response of Glass Electrodes

GEORGE A. PERLEY
Leeds & Northrup Company, Philadelphia, Pa.

The newer lithia-silica types of glasses show very rapid response to rapid and wide changes of pH in buffered solutions. The speed of response of the newer types of glass electrodes to changes of pH in buffered solutions is such that it is consistent to use the newer types of high speed electronic recorders and controllers in connection with these systems. In solution changes from a buffered to an unbuffered condition, the response of these glass electrodes to actual pH changes is much slower than when the change is from one buffer to another of different pH. Considerable errors may result unless thorough washing is employed when glass electrodes are used for measurements in unbuffered solutions after the electrode has been used in buffers, as in a prestandardization of the entire electrode-instrument assembly. In making measurements in sparingly buffered solutions by means of glass electrodes, vigorous agitation should always be maintained at the glass-solution interface. The lithia-silica types of glasses are not as susceptible to drying influences as are the Corning 015 types.

IN THESE days of recording or automatic control of a wide variety of industrial processes, the speed of response of the primary elements is of considerable importance.

Relatively rapid temperature measurements have been possible for some time. However, until recently the continuous measurement of pH in processes where sudden changes in hydrogen ion activity occur has not been the cause of too great concern. With the newer electronic recorders and the resultant high speed response, it seemed desirable to know more concerning the pH-response characteristics of modern glass electrodes.

GLASS ELECTRODE RESPONSE TO pH CHANGES

There is little published information concerning the rate of response of glass electrodes to pH changes, although it is known that in many industrial operations, such as the neutralization type of reactions, the pH changes at the inflection point are extremely rapid. The facts on the response characteristics, particularly of the newer types of glass electrodes, seemed desirable.

Regular production pH electrodes of the older Leeds & Northrup 1199-12 type constructed of Corning 015 glass, consisting of a sodium oxide–calcium oxide–silica glass, of the Leeds & Northrup glass 1199-30, consisting of a lithium oxide–cesium oxide–barium oxide–lanthanum oxide–silica glass, and an industrially available lithia-baria-silica type of glass electrode were used with a regular Leeds & Northrup 1199-31 calomel–salt bridge assembly as reference electrode. A Leeds & Northrup Speedomax recorder was used for recording the performance of these electrodes. The electrodes were transferred from a buffer solution in one beaker to another buffer solution in another beaker at 25° C. directly without washing. The buffer solutions were stirred mechanically by a motor-driven glass stirrer.

Table I. Response of pH Glasses in Buffer Solutions

[Rapid mechanical agitation, no intermediate washing, 25° C. Reading in pH 6.86 (by standardization)]

Time after Immersion, Sec.	L. & N. 1199-12 Corning 015 Glass, pH	B Glass, Lithia-Silica, pH	L. & N. 1199-30 Lithia Glass, pH
In pH 9.18 buffer			
2	9.03	9.00	9.06
10	9.11	9.13	9.14
24	9.13	9.13	9.14
In pH 12.90 (2 *N* sodium)			
2	....	11.86	12.51
10	....	12.38	12.70
24	....	12.53	12.76
30	....	12.59	12.78
4 min.	....	12.75	12.85
In pH 9.18 buffer			
2	....	9.80	9.20
10	....	9.21	9.17
24	....	9.15	9.14
In pH 6.86 buffer			
2	6.86	6.89	6.70
10	6.86	6.87	6.80
24	6.84	6.86	6.84
In pH 4.01 buffer			
2	4.08	4.10	4.01
10	4.05	4.10	4.01
24	4.05	4.11	4.04
In pH 1.07 solution			
2	1.15	1.34	1.17
10	1.10	1.20	1.10
24	1.08	1.16	1.09
In pH 4.01 buffer			
2	4.08	1.27	4.14
10	4.08	4.24	4.11
24	4.07	4.25	4.05
In pH 6.86 buffer			
2	6.87	6.87	6.88
10	6.86	6.90	6.88
24	6.86	6.90	5.88
In pH 9.18 buffer			
2	9.02	9.13	9.11
10	9.10	9.14	9.14
24	9.12	9.15	9.14
In pH 12.90 (2 *N* sodium)			
2	11.18	11.91	12.41
10	11.26	12.29	12.63
24	11.26	12.49	12.73
30	11.25	12.53	12.75
1 min.	11.21	12.61	12.78
In pH 9.18 buffer			
2	9.33	9.35	9.27
10	9.15	9.32	9.14
24	9.09	9.13	9.14

The data of Table I give the results as transcribed from the recording charts. Table I indicates that the newer lithia-silica glasses as well as the soda-lime-silica glass are relatively fast in their response to pH when dealing with changes involving typical buffer solutions. It may be concluded that these glasses respond within about pH 0.10 of the equilibrium value within 2 seconds for changes from pH 1.0 to 6.86 as well as from pH 6.86 to 9.18. It appears that the limiting feature in the response characteristics is involved with the concentration changes in the film of liquid in contact with the glass surface.

Because of the sodium error of the Corning 015 glass the change from a pH 9.18 to a pH 12.90 solution containing 2 *N* sodium salts is of a smaller magnitude than both the other glasses. The response of the Leeds & Northrup 1199-30 glass electrode for a change from a pH 9.18 buffer solution to a pH 12.90 buffer solution (containing 2 *N* sodium salts) of within pH 0.15 of the final value within a 30-second period might be considered as rather good performance. The rapid response from pH 12.90 to 9.18 is also worthy of comment.

The problem as applied to changes from well buffered solutions directly to unbuffered solutions is another story. Glass surfaces are excellent ionic sorption materials. The influence of the sorption of specific ions on a glass surface may be important in some applications where the efficiency of washing is being controlled.

In order to simulate industrial practice, where continuous measurements are essential in the automatic control of the pH of a process, a small Pyrex flow cell of 75-ml. capacity was used as a container for the glass-calomel–salt bridge electrode assembly. Figure 1 represents the general equipment. The glass electrode pH-responsive bulb was located within the slightly enlarged bottom inlet to the flow cell. The flow cell intake was closed and 75 ml. of a chosen buffer were placed in the cell. pH was measured after the electrode had stood in the buffer for 5 minutes and then distilled water was allowed to flow through the electrode cell at 375 ml. per minute. The pH readings were taken until fairly stable readings were obtained.

It is recognized that the response time includes the wash time of the lower section of the electrode container or flow cell. However, this was relatively small, as the pH-responsive glass bulb was located in the narrow intake at the bottom inlet of the flow cell.

The presence or absence of streaming potentials in this specific electrode arrangement may be debatable. It is the author's feeling that the magnitude of this effect is small as compared to the time required to secure the same composition at the glass interface as in the body of the test solution. In other words, any glass surface is not rapidly cleaned from sorption products. The time depends on the type of glass and the nature of the products.

Table II summarizes the results when glass electrodes are subjected to a buffer solution and then followed by a continuous washing with distilled water. A study of the data of Table II indicates that the response of glass electrodes to changes from buffer solutions to wash water is far slower than the response to changes involving only buffer solutions.

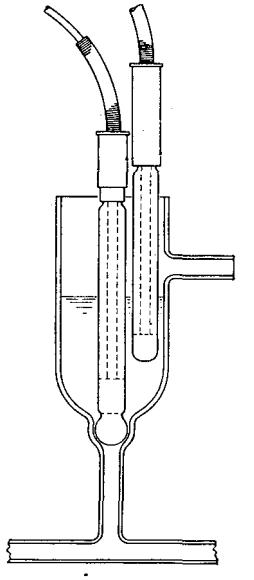

Figure 1. Flow Channel for pH Response Tests

The data of Table II were obtained at 25° C. The author has many data for the temperature range of 0° to 80° C. The response of glass electrodes to changes in pH is considerably slower at 5° C. than at 25° C. The higher the temperature the more rapid is the response.

The data of Table II have a bearing on those industrial applications where pH control is used to establish the completion of any process involving the use of either acid or alkali treatment and then subsequent washing out of this excess acid or alkali by city water. It appears that a glass electrode measurement in the wash water may lag considerably behind the actual pH of this water. Possibly a correction factor might be obtained for this time-pH relationship for any specific washing operation, yet this must be carried out with great care.

INDICATING MEASUREMENTS IN UNBUFFERED SOLUTIONS

If a glass electrode has been used in buffer solutions, such as over-all electrode standardization, and is to be subsequently used for pH measurements in unbuffered solutions, a considerable amount of thorough washing must be provided even before accurate indicator pH measurements can be obtained. Failure to wash the electrodes completely after a standardization, and prior to measurements in sparingly buffered solutions, has been a common practice.

Indicating measurements in sparingly buffered solutions by

means of the lithia type of glass electrodes must be carried out with considerable care if any reasonable limit of error is to be obtained. Simple dip type measurements should not be employed. This is a confirmation of the work by Ellis and Kiehl (*2*), who used the sodium oxide–calcium oxide–silica type of glass.

Measurements in unstirred sparingly buffered solutions are generally in error, because the pH of the thin layer of the solution at the glass solution interface tends towards that of the resultant solution of the particular kind of pH-responsive glass. Any method of continuous disturbance of the solution layer close to the surface of the pH-responsive bulb will favor more accurate pH measurements. The pH measurement by glass electrode systems of certain types of soil extracts is a typical case. False conclusions have resulted from failure to keep a vigorous agitation of the solution during the measurement. The Corning 015 glass is a relatively highly soluble type of glass. In general, the use of this glass in the measurement of unbuffered solutions over the range of pH 4 to 9 tends to give too high pH values.

Table III illustrates the response of several types of commercial glass electrodes in measurements on typical soil extracts.

There is no type of pH-responsive glass available today which does not require the use of vigorous agitation of the solution, either mechanically or by rapid flow, if rapid and accurate pH measurements are to be obtained in poorly buffered solutions.

The Corning 015 type of glass electrode gives abnormally high pH values in sparingly buffered solutions. The lag in obtaining a constant pH value is evident if the solution is not thoroughly agitated. The importance of stirring such solutions is obvious from the data of Table III.

Glass electrodes give unreliable pH values when measurements are made with an electrode that has been left standing for a long period in distilled water and no flow or stirring of the solution is employed.

Table II. Response of Glass Electrodes in Flow Cell Buffer to Distilled Water

(Flow rate of 350 ml. per min. Glass electrode compartment volume 3 ml. 25° C.)

Time after Starting Water	L. & N. 1199-12 Corning 015 Glass, pH	B Glass, Lithia-Silica, pH	L. & N. 1199-30, Lithia Glass, pH
5 Minutes in pH 4.00			
Sec.			
3	3.82	3.79	3.77
30	4.36	4.53	4.89
Min.			
1	4.96	4.86	5.47
3	6.55	6.56	6.42
5	6.59	6.68	6.61
10	6.59	6.70	6.64
5 Minutes in pH 1.06			
Sec.			
10	1.89	1.99	2.31
30	2.32	2.36	2.94
Min.			
1	3.04	3.16	3.87
3	6.15	6.51	6.44
5	6.52	6.67	6.62
10	6.57	6.70	6.66
5 Minutes in pH 9.18			
Sec.			
10	8.64	8.45	7.98
30	8.50	7.92	7.40
Min.			
1	8.07	7.77	7.17
3	6.85	6.99	6.74
5	6.65	6.73	6.68
10	6.57	6.70	6.67
5 Minutes in pH 12.8 (2 *N* Sodium)			
Sec.			
0	11.06	12.54	12.68
1	11.43	13.15	12.76
10	11.40	11.11	10.55
30	10.71	9.91	9.65
Min.			
1	9.55	9.44	8.68
3	7.68	7.58	7.33
5	7.11	7.02	6.95
10	6.70	6.78	6.78
15	6.64	6.75	6.71

Table III. Time Response of pH Electrodes at 25° C.

(Extract of 15 grams of soil in 150 ml. of water. All electrodes standardized in pH 6.86 buffer and washed to water equilibrium prior to use. Solution of extract not agitated. Reference electrode L. & N. 1199-31)

Time after Electrode Placed in Solution	L. & N. 1199 A Thin Bulb Corning 015, pH	L. & N. 1199-12 Thick Bulb Corning 015, pH	Macbeth A-1 Corning 015, pH	L. & N. 1199-30, pH
Sec.				
15	7.62	8.00	6.62	6.80
30	7.80	8.12	6.88	7.00
45	7.92	8.17	7.00	7.13
Min.				
1	7.99	8.20	7.13	7.22
2	8.13	8.28	7.39	7.51
3	8.20	8.33	7.56	7.69
4	8.24	8.40	7.70	7.80
5	8.25	8.42	7.83	7.90
10	8.30	8.45	8.50	8.08
Stirred by motor	8.18	8.18	8.18	8.08
New soil extracts of above composition, motor stirring equipment with glass stirrer				
Sec.				
15	8.20	8.30	7.80	7.75
30	8.20	8.28	7.94	7.84
45	8.20	8.26	8.01	8.00
Min.				
1	8.20	8.26	8.07	8.06
3	8.20	8.22	8.15	8.08

A Corning 015 glass electrode was permitted to stand for 15 hours in 75 ml. of city water contained in the flow cell after certain wash tests had been completed. The pH of the Philadelphia city water under flowing conditions averaged about 7.1 at 25° C. when equilibrium had been established. After standing for 15 hours, the electrode indicated pH 7.6 at the glass interface. This was the value at the solution-glass interface and not of the entire water solution. When flow conditions were re-established after the 15-hour immersion, the original pH 7.1 reading was obtained within less than 5 minutes of continuous city water flow.

This is not surprising when one notes that if 1 gram of Corning 015 glass is ground to a 100- to 200-mesh powder and then added to 20 ml. of water a pH 10.8 solution results.

AGING OF pH GLASSES

Glass electrodes are shipped by the manufacturer in containers which allow the outer glass surface to be exposed to the atmosphere. There is considerable contradictory information as to what pretreatment a pH glass electrode should receive prior to use. This probably is related to the glass composition. The influence of drying of the glass membrane may also be another variable.

There is considerable published information on the importance of the water content of the glass surface.

Haber and Klemensiewicz (*3*) steamed out glass bulbs with wall thickness of about 0.1 mm. for an hour, then soaked them in water until they were used. When the bulbs dried out in air irregular results were obtained. Thus a soda-rich, relatively low-silica type of glass which gave 0.6-volt differential between a given acid and base solution, gave a differential of from 0.3 to 0.5 volt after drying. A Jena glass which had no hydrogen electrode function was converted to an imperfect pH membrane by treating with superheated water at 250° C. in an autoclave.

Kerridge (*5*) cleaned freshly blown electrodes with cleaning solution, steamed them out 2 hours, and soaked them in water for 24 hours before use.

Hughes (*4*) observed that the hydrogen electrode function disappeared when a glass electrode was dried at a high temperature.

Elder (*1*) annealed his glass electrodes for 15 to 20 hours at 120° C. to reduce the asymmetry potential, but actually the asymmetry potential increased. The change varied with the nature of the glass.

MacInnes and Belcher (*7*) studied the increase in resistance of glass electrodes fabricated from glass similar to Corning 015. They noted that an electrode having initially a resistance of 32 megohms developed a resistance of 40,000 megohms on heating to 50° C. in vacuum over phosphorus pentoxide, and that the dried membrane slowly returned to the original resistance after immersion in water.

Laug (*6*) found that short periods of drying had no effect on the asymmetry potential. He observed that it required about 3

hours for the electrode to reach its normal condition at 38° C. after drying.

Yoshimura (*8*) observed that the asymmetry potential of glass electrodes, the errors in alkaline solution, and the relative rate of corrosion decline on standing in water, although the ability to act as a hydrogen electrode improves with time.

Many of the published data up to this time have been obtained on the Corning 015 type of glass: 21.39 mole % sodium oxide, 6.44 mole % calcium oxide, and 72.17 mole % silica. Some of the data have been obtained on the very thin glass membrane type of electrode.

Newer robust types of lithia-silica glasses are now available, such as the National Technical Laboratory 1190-E or the Leeds & Northrup 1199-30. It seemed desirable to learn something about the aging properties of these newer pH-responsive glasses.

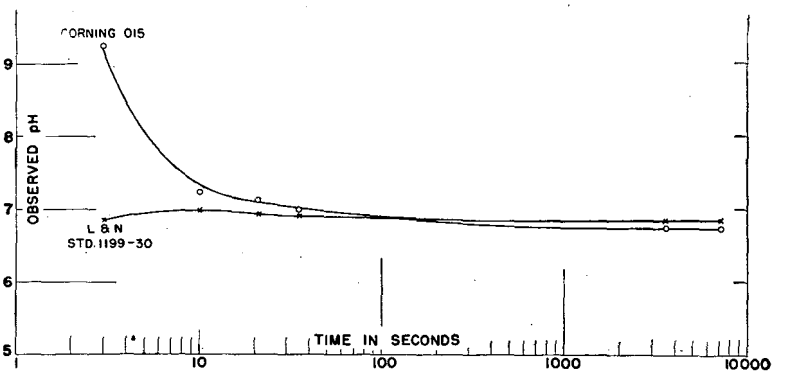

Figure 2. Speed of Response of Freshly Blown pH Glasses

No pretreatment. In pH 6.86 buffer at 25° C. L. & N. standard 1199-31 saturated calomel reference

Glass electrodes were blown from the Corning 015 glass as used in the Leeds & Northrup 1190-12 type, as well as from a glass of the new 1199-30 type. These electrodes were filled with a suitable 7.0 pH buffer. An internal reference calomel electrode was employed. A regular Leeds & Northrup 1199-31 electrode–salt bridge unit was used as the reference half-cell system. The pH-responsive bulb of the 1199-30 electrodes has an outside diameter of about 9.5 mm., the weight of glass averages about 0.1 gram, and the wall thickness of the bulb is about 0.1 mm. The electrode was placed immediately in a 6.86 buffer solution. (The buffer recommended for use in A.S.T.M. Designation E70–46T was employed.) The time interval between blowing and use was of the order of 5 minutes. No pretreatment was employed.

A Leeds & Northrup Speedomax voltage recorder was used to follow the changes which took place and a permanent record of these changes was thereby obtained. The results are summarized in Table IV and Figure 2.

Table IV indicates that the newer types of glasses require less pretreatment than the Corning 015 glass. It is the author's experience that the asymmetry correction of the newer glasses is less than for the Corning 015 type of glass.

It is interesting to note in Table IV that the Corning 015 glass gradually changes from a higher pH value to a lower value. However, the Leeds & Northrup 1199-30 type of glass rapidly reaches a small maximum, but within 30 seconds a reading within pH 0.05 of the final equilibrium value is obtained. Figure 2 indicates the relative magnitude of these differences.

Table IV. Speed of Response of Freshly Blown pH Glasses at 25° C.

Time after Immersion in pH 6.86 Buffer, Sec.	pH Indicated	
	Corning 015	L. & N. 1199-30
3	9.24	6.86
10	7.24	7.00
21	7.14	6.94
35	7.00	6.91
1 hour	6.76	6.87
2 hours	6.73	6.86

INFLUENCE OF ABNORMAL DRYING

In view of the results obtained by MacInnes and Belcher (*7*) on the influence of drying upon the glass membrane, it seemed desirable to obtain similar information on the newer types of glasses now on the market.

Freshly blown Haber type bulbs of Corning 015 and Leeds & Northrup 1199-30 glasses were made. The internal buffer and reference electrode were sealed within the glass electrode. The pH response and electrical resistance of these electrodes were then determined. These electrodes were placed in a vacuum desiccator over phosphorus pentoxide at 25° C. for 14 days, then in 6.86 pH buffer, and a Leeds & Northrup 1199-31 calomel–salt bridge system was used as reference. The measurements were made on a Leeds & Northrup Speedomax recorder with high chart speed in order to secure a permanent record of the behavior of these electrodes.

Table V. Effect of Vacuum Drying of Glass Electrodes at 25° C.

Time after Immersion in pH 6.86 Buffer	Corning 015 Glass, pH Reading		L. & N. 1199-30 Glass, pH Reading	
	After making	After vacuum drying 14 days	After making	After vacuum drying 14 days
Min.				
1	7.20	7.29	6.96	6.77
3	7.08	7.29	7.00	6.77
30	6.92		6.98	
Hours				
1	6.87	7.23	6.96	6.88
2	6.83		6.93	
4	6.83	7.00	6.92	6.92
Characteristics before and after Drying				
	After Making	After Drying	After Making	After Drying
Resistance, 25° C. megohms	136	145	51	53
ΔpH response, pH 4.0 to 6.85 (ΔpH 2.86 by H_2-calomel electrode)	2.85	2.86	2.85	2.85
ΔpH response, pH 6.86 to 12.88 (2 *N* Na) (ΔpH 6.02 by H_2-calomel electrode)	4.53	4.54	5.89	5.89

Table V summarizes the data as transcribed from the recorder chart, and shows that the bulb type of glass electrode performs somewhat differently on vacuum drying than the thin membrane types used by MacInnes and Belcher (*7*). In general, the newer types of lithia-silica pH glasses are less influenced when exposed to drying agents than the Corning 015 type of glass.

Results of a similar series of tests, carried out in vacuum drying at 50° C. for 4 days, were qualitatively the same as with the 25° C. tests.

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Polarographic Study of Molybdiphosphoric and Molybdisilicic Acids

D. F. BOLTZ[1] WITH THOS. DE VRIES AND M. G. MELLON
Purdue University, Lafayette, Ind.

Dilute ammonium molybdate solutions gave satisfactory polarograms in a buffered solution containing sodium phosphate, potassium chloride, and citric acid. Two stages of reduction were observed. Molybdiphosphoric and molybdisilicic acids gave polarographic waves influenced considerably by the nature of the supporting electrolyte. Two stages of reduction exist, but the half-wave potentials are not well established.

IN AN investigation of certain heteropoly complexes (*1*), it was necessary to determine the concentration of dilute molybdenum solutions. It also seemed feasible to obtain information concerning the oxidation-reduction potentials of some complexes, such as molybdiphosphoric and molybdisilicic acids. A polarographic study of those compounds was undertaken, involving molybdate ions as the coordinating group and phosphorus or silicon as the central atom.

Souchay (*8*) had used the polarograph in studying heteropoly tungstic acids. No similar information concerning the heteropoly compounds of other elements such as molybdenum was found. Very little information was available about the polarographic determination of molybdate ions.

Table I. Supporting Electrolytes

	pH	KCl	Sodium Acetate	Acetic Acid
	Concentration, Moles per Liter			
I	4.55	0.5	0.40	0.40
II	4.6	0.1	1.00	1.00
III	3.5	0.1	0.10	1.00

Uhl (*11*) obtained a double wave for the reduction of molybdate with half-wave potentials at −0.35 and −0.5 volt against a saturated calomel electrode in a supporting electrolyte of dilute nitric acid solution containing lactic and oxalic acids. Stern (*10*) reported a half-wave potential of the molybdate ion in 2 *N* ammonium nitrate solution containing 3 grams of methylcellulose per liter as being −0.82 volt against a normal calomel electrode, the space requirements of the wave being rather large. Stackelberg (*9*) reported that no wave was obtained in neutral or alkaline solutions but a well defined wave was obtained in 18 *N* sulfuric acid at −0.26 volt. Kanevskiĭ and Shvartsburd (*6*) obtained two waves for the reduction of molybdate in a phosphoric acid solution but they did not report half-wave potentials.

APPARATUS AND REAGENTS

A Fisher Elecdropode was used to obtain the polarograms. A Sargent, Model XII polarograph was available for only a few experiments. Provision was made to keep the solutions at 25° ± 0.5° C. A saturated calomel electrode was used as a reference electrode with the type of salt bridge suggested by Hume and Harris (*4*). The reliability of the reference electrode was checked using thallous ion as a pilot ion. The value of $m^{2/3}t^{1/6}$ for the capillary used with the Elecdropode was 0.87 (t = 10 seconds) and for the capillary used with the Sargent polarograph it was 2.42 (t = 1.9 seconds). Air was removed by bubbling nitrogen through the solutions for 15 minutes.

Molybdiphosphoric acid was prepared from molybdic oxide and phosphoric acid according to the procedure of Linz (*7*) and also from sodium molybdate and phosphoric acid according to the procedure of Wu (*12*). Potassium molybdiphosphate was made from molybdic oxide and potassium phosphate (*3*). Molybdisilicic acid was made from sodium molybdate and sodium silicate according to the procedure of North and Haney (*2*). Ammonium molybdate solutions were prepared from a C.P. quality reagent.

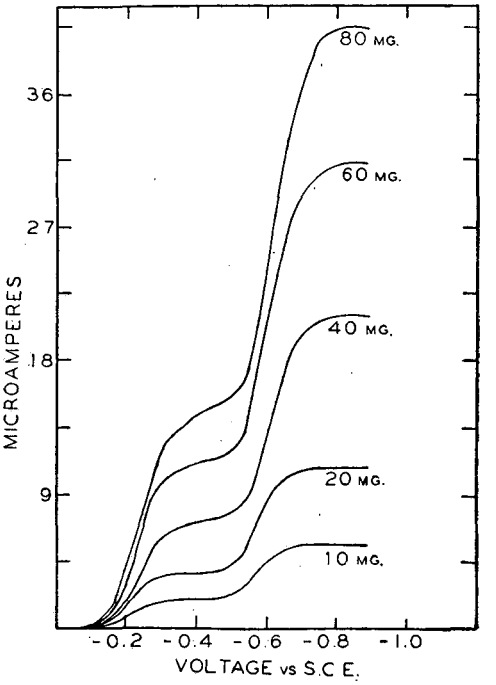

Figure 1. Effect of Ammonium Molybdate Concentration in 50 Ml. of Supporting Electrolyte

For the polarographic study of molybdiphosphoric acid and molybdisilicic acid, various solutions were used as supporting electrolytes, but only those listed in Table I were used for work reported in this paper.

RESULTS

Ammonium Molybdate. From 10 to 80 mg. of ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, were weighed into 50 ml. of the supporting electrolyte. An electrolyte of potassium chloride and hydrochloric acid which had a pH of 1.9 did not have sufficient buffer capacity to give satisfactory results. Satisfactory polarograms were obtained with a supporting electrolyte made by mixing 150 ml. of 0.2 *M* disodium hydrogen phosphate, 850 ml. of 0.1 *M* citric acid, and 0.1 mole of potassium chloride. This solution has a pH of 2.8. The two waves were well defined (Figure 1), and

[1] Present address, Wayne University, Detroit, Mich.

the wave heights were proportional to the concentration within close limits. The half-wave potentials were −0.23 and −0.58. The values of n, the number of equivalents per reduction step, obtained from the plots of potential *vs.* log $(i_d - i)/i$ were not plausible. Values of 0.7 and 0.45 were obtained for the first and the second wave. Likewise, the values of n obtained by using the Ilkovič equation and Jander's value (*5*) of 2.8×10^{-6} for the diffusion coefficient of the ionic species $(Mo_6O_{21})^{-6}$ were 8.4 for the first wave and 16.8 for the second wave.

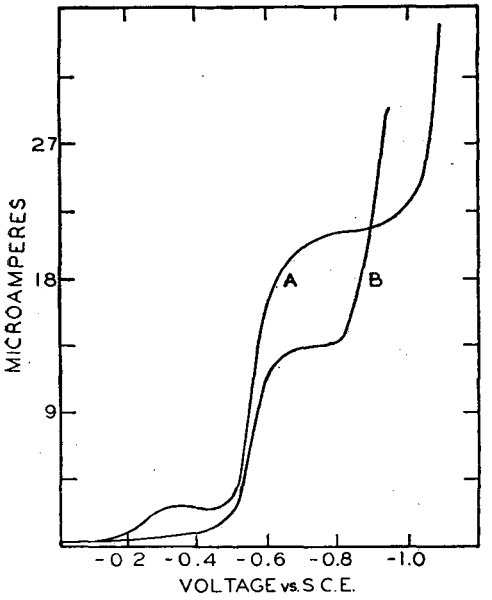

Figure 2. Effect of Potassium Chloride on Wave Heights for Molybdiphosphoric Acid

A. **125 mg. in electrolyte I**
B. **125 mg. in electrolyte II**

It was noted that the height of the second wave was twice that of the first wave. From the known chemistry of molybdenum this might suggest a reduction from 6 to 5 for the first step and from 5 to 3 for the second step. Another possibility is that only two of the molybdenum atoms in the complex anion are reduced from 6 to 5 in the first step and the remaining four are reduced similarly in the second step.

Molybdiphosphoric Acid. The polarograms of molybdiphosphoric acid in supporting electrolyte I with a pH of 4.55 had a single wave with a half-wave potential of −0.57 volt. The wave heights were only approximately proportional to the concentration. This may have been due to the difficulty in measuring wave heights because of the appearance of a small wave at −0.35 as the concentration increased beyond 100 to 150 mg. per 50 ml. When supporting electrolyte II with a pH of 4.6 was used, the height of the main wave was only 0.66 as much and the small wave at −0.35 did not appear (see Figure 2). Inasmuch as the pH of the solutions were nearly the same, the marked influence of the potassium chloride concentration was indicated.

In supporting electrolyte III with a pH of 3.50, a double wave was obtained with 10 to 60 mg. of molybdiphosphoric acid in 50 ml. of solution. At the selected voltages of −0.6 and −0.9 the wave heights were proportional to the concentration but were not well defined (see Figure 3). The results indicate that two stages of reduction can exist for molybdiphosphoric acid but no satisfactory half-wave potential could be assigned.

Molybdisilicic Acid. In a similar study of molybdisilicic acid with supporting electrolytes in which the hydrogen ion concentration was varied, the polarograms at the smaller pH values consisted of two waves. Thus in supporting electrolyte III with a pH of 3.5 it was found that the wave heights measured at

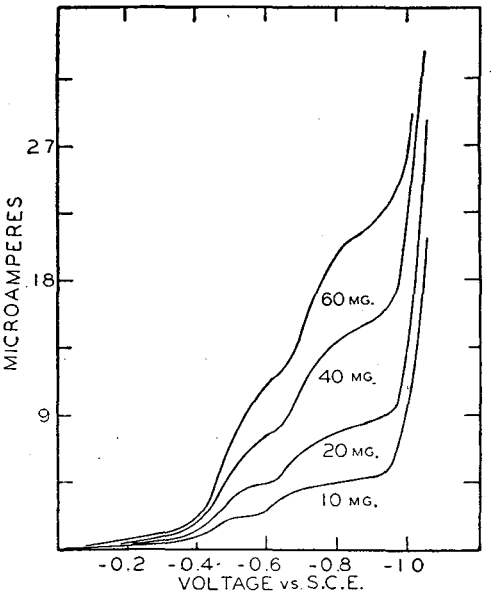

Figure 3. Effect of Concentration of Molybdiphosphoric Acid in Electrolyte III

−0.35 and −0.85 volt were proportional to the concentration (see Figure 4). With solution I of pH 4.55 only one wave of greatly diminished height was obtained. The fairly large space requirements of the waves indicate that the reduction is irreversible. It is believed that the double wave obtained with low pH solutions is characteristic of the heteropoly compound and that in less acid solutions the heteropoly complex is unstable, giving a curve that is characteristic of molybdate ions. The evidence to substantiate this belief is the observation that fading of the yellow color of the molybdisilicic acid complex was appreciable at pH 3.5, about 3% every 5 minutes. The rate of fading increased rapidly as the pH was increased but in the pH range from 0.9 to 2.7 no fading of the yellow color was detectable. The change in transmittancy of the solutions was followed with a General Electric spectrophotometer. The buffered solu-

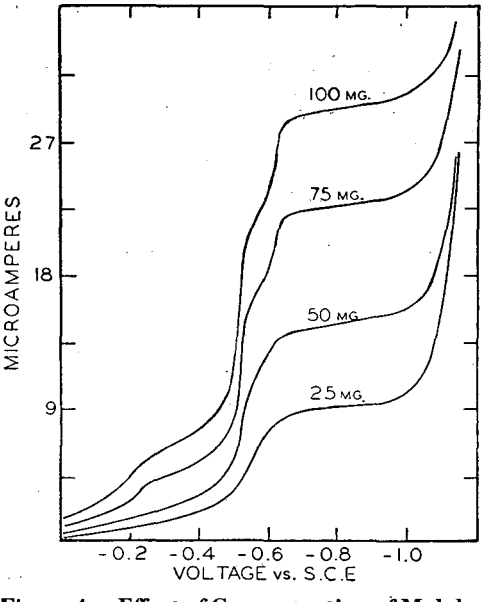

Figure 4. Effect of Concentration of Molybdisilicic Acid in Electrolyte III

tions contained potassium chloride, hydrochloric acid, sodium acetate, and acetic acid in varying proportions.

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Amperometric Titration with Diazotized Aromatic Amines

R. M. ELOFSON AND PATRICIA A. MECHERLY

General Aniline & Film Corporation, Easton, Pa.

The amperometric titration of a coupler such as a pyrazolone or a naphthol with diazotized aromatic amines in well buffered solutions is described. The method depends upon the amperometric measurement of the excess diazo compound present after the end point is reached. A dropping mercury electrode *vs.* a saturated calomel electrode with an applied potential of 0.2 to 0.3 volt is used. Techniques are given for the estimation of diazotized amines and of couplers. The importance of temperature and pH control and the selection of diazo compound for the estimation of couplers are outlined.

DIAZOTIZED aromatic amines have been found in this laboratory to give well defined polarograms in acid, neutral, and slightly alkaline media. Although the behavior of diazo solutions at the dropping mercury electrode is complex, a wave always occurs at a potential less negative than that due to azo compounds in the pH range 4 to 9. This wave has now been made the basis of an amperometric titration wherein phenols and related compounds in buffered solutions are titrated with diazotized aromatic amines. The titration is performed in a typical amperometric titration cell (*3*) with an applied voltage across the dropping mercury cathode and calomel half-cell of 0.2 to 0.3 volt, at which potentials the diazo is reduced through the first stage. Under these conditions the azo dye produced is not reduced. Therefore no current flows until the equivalence point is reached, whereupon the current increases linearly with concentration of the excess diazo. Because the coupling reaction is not instantaneous, the mixtures are allowed to react for a standard interval of time, usually 1 minute after each addition of diazo solution before readings are taken.

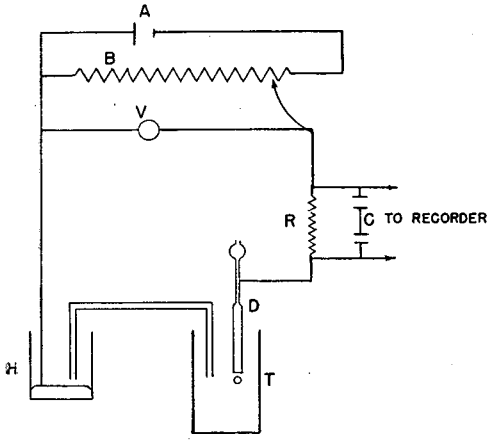

Figure 1. Amperometric Titration Assembly

A. 2-volt battery
B. Slide-wire potentiometer
C. Electrolytic condensers
D. Dropping mercury electrode
H. Saturated calomel electrode
R. 1500-ohm resistor
T. Titration cell
V. Voltmeter

APPARATUS

The titration cell was similar to that described by Kolthoff and Langer (*2*), except that both the cell and buret were jacketed and cold water was circulated through both, preferably at 0° to 5° C. A large-area calomel half-cell connected by a saturated potassium chloride–agar bridge was usually employed as the anode. Satisfactory results may be obtained with a mercury pool anode, but the volume of mercury used is considerable. A dropping mercury electrode fabricated from marine barometer tubing with a drop rate of approximately 3 seconds at −0.3 volt in the buffer solutions was used as the cathode. A voltage of 0.3 volt was applied across the electrode, and the resulting current was recorded automatically on a Leeds & Northrup electronic recorder according to the circuit illustrated in Figure 1. A microammeter or galvanometer may be used with satisfactory, although less accurate, results.

DETERMINATION OF DIAZO CONCENTRATION

Procedure. Fifty milliliters of buffer solution (pH 8.0) prepared according to the directions of Clark and Lubs, and 5 ml. of a 0.01 *M* solution of 3-methyl-1-phenyl-5-pyrazolone are introduced into the water-jacketed amperometric titration cell. Oxygen-free nitrogen is then passed through the cell until all the oxygen has been removed and the cell contents have reached a temperature of 0° to 5° C. With 0.3 volt applied across the cell, the initial current reading is taken, and an approximately 0.01 *M* diazo *p*-toluidine solution is then titrated into the cell. [It has been the practice in this laboratory to use a recorder that records only positive current. Strictly a slight negative (anodic) current is usually observed at the beginning, but the error resulting from this approximation is very small. However, if much more dilute solutions were used, this could hardly be true. No appreciable differences were detected when the anodic current was measured and considered in the calculations. This consideration is eliminated

in the determination of unknown coupler concentration because it is canceled by the standardization of the diazo compound against the methylphenylpyrazolone.]

At the beginning 1 or 2 ml. of solution may be added at a time, nitrogen passed in for 1 minute to ensure mixing of the solution and removal of oxygen, and the current recorded, preferably for 1 minute, to ensure an accurate measurement. As the end point is approached, the volume of diazo solution added at each 2-minute interval is decreased to 0.25 or 0.50 ml. Addition of diazo solution is continued until 1.0- to 2.0-ml. excess has been added. Once an excess of diazo compound is present, the current increases linearly with concentration.

In Figure 2 is depicted an actual recording of 3-methyl-1-phenyl-5-pyrazolone titrated with diazo-*p*-toluidine. Figure 3 is a graphical presentation of the data. In this case the end point is 5.22 ml., the point where the plot of chart readings *vs.* milliliters of diazo solution intersects the abscissa. The molarity of the diazo solution is therefore 0.00958.

The linearity of the relationship between concentration of diazo compound and current as measured by chart readings has been found to be good, provided diazo solutions of the order of 0.01 *M* are used for titration. The current appears to fall off a little if much more concentrated solutions are used. In practice this is not a significant factor and leads to no error unless coupling is so slow that it is necessary to go far beyond the end point to ensure complete coupling. In such cases the pH may be adjusted to bring about a faster reaction and hence a sharper end point.

Discussion. The method outlined can be used to determine the concentration of a solution of diazotized aromatic amine. For this purpose, a pure sample of 3-methyl-1-phenyl-5-pyrazolone (melting point, 130–131° C.; nitrogen found, 16.06%; calculated, 16.08%) has been used as a primary standard. This compound was selected because it is a very rapid coupler, it couples only once, it does not undergo side reactions, and it is easy to obtain in a highly purified state.

In order to check the results by an independent standard method, diazo solutions were analyzed by decomposing them with cuprous chloride and measuring the evolved nitrogen in a nitrometer.

Table I. Determination of Diazo Concentration

Amine Diazotized	Molarity of Diazonium Solution: By coupling with methylphenyl-pyrazolone	Molarity of Diazonium Solution: By nitrogen evolution
Sulfanilic acid	0.0501	0.0495
p-Anisidine	0.0495	0.0497
m-Nitroaniline	0.0485	0.0479
m-Toluidine	0.0430	0.0430
2,5-Dichloroaniline	0.0709	0.0706
	0.0357	0.0352
	0.0291	0.0287

In Table I the results obtained by the two methods for a number of diazotized amines are compared. The methods appear to be in excellent agreement and to indicate that diazotized amines can be estimated with an error of not more than 1 or 2% if it is assumed that the nitrogen evolution technique has an absolute accuracy of this order.

Incompletely diazotized amines could not in general be analyzed accurately by the coupling technique. This would follow from the fact that the diazotized amine would react with free amine when the titration solution was run into the buffered solution, and so the results would be somewhat low. On the other hand, as a measure of the coupling power of the diazotized solution, the results would be of practical value.

The results listed in Table I were obtained by direct titration. However, if the diazotized amine couples too slowly to give a satisfactory end point, the method may be modified by indirect titration. By adding an excess of the 3-methyl-1-phenyl-5-pyrazolone at a suitable pH, the coupling can be driven to completion, and the excess of methylphenylpyrazolone can be back-titrated with a standardized solution of a suitable diazo compound.

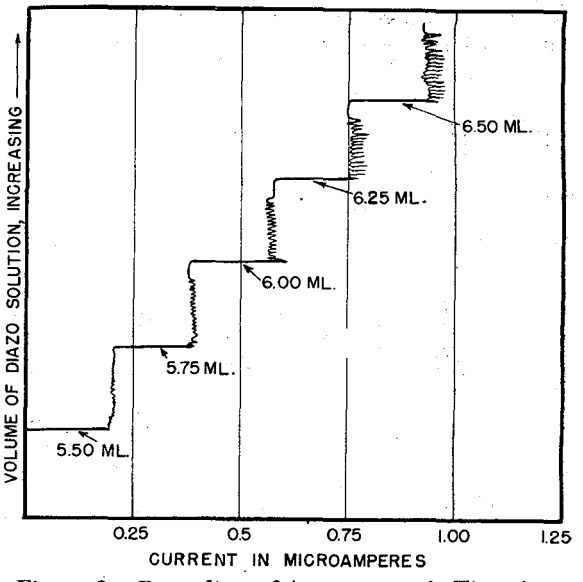

Figure 2. Recording of Amperometric Titration

0.0005 mole of 1-phenyl-3-methyl-5-pyrazolone titrated with approximately 0.01 *M* *p*-toluenediazonium chloride. Applied voltage 0.3 volt dropping mercury electrode *vs.* saturated calomel electrode. Temp., 1° C.

DETERMINATION OF COUPLERS

The coupling values of phenols, naphthols, and similar compounds with diazotized amines have been determined either by making spot tests for excess diazo and coupler or by following optically the formation of the dye. The amperometric method described in this paper has the advantage that much more dilute solutions and smaller volumes can be titrated than where spot tests are used. The chief advantage of the new method over the optical method lies in the fact that it is not necessary to arrange for the formation of soluble dyes, and so the method is distinctly more versatile.

In Table II are listed the results of titrating a number of pure or nearly pure couplers with various diazotized amines. In all cases, the diazotized amines were standardized by amperometric titration with 3-methyl-1-phenyl-5-pyrazolone which was used as a primary standard. As the table shows, different conditions have been used with each coupler. In the case of substances such as the pyrazolones which couple only once and do so with ease, vir-

Table II. Determination of Couplers

Coupler	Diazo	Temp., ° C.	pH	% Found	Remarks
Acetoacetanilide	Sulfanilic acid	Room	8	99.9	
3-Methyl-5-pyrazolone	*p*-Toluidine	Room	8	99.9	
		0	8	98.5	
1-Naphthol-5-sulfonamide	*p*-Toluidine	0	9	100.1	
	m-Nitroaniline	Room	6	99.3	
	Sulfanilic acid	Room	9	98.7	
1-(4′-Sulfophenyl)-3-methyl-5-pyrazolone	*p*-Toluidine	0	8	94.7	Known to contain 5 to 6% H_2O of crystallization
		Room	6	94.6	
	Sulfanilic acid	Room	6	95.2	
		Room	9	95.4	
2-Naphthol-6-sulfonamide	*p*-Toluidine	Room	9	97.0	
	m-Nitroaniline	Room	6	99.3	
	Sulfanilic acid	Room	9	98.7	
2,3-Dihydroxynaphthalene	*m*-Nitroaniline	15	5.4	100.1	
6,7-Dihydroxynaphthalene-2-sulfonic acid	2,5-Dichloroaniline	0	7.4	98.1	
Resorcinol	*p*-Toluidine	25	9	97.9	Based on double coupling
β-Naphthol	*p*-Toluidine	15	8	98.9	

tually any condition recorded in the table could be used—i.e., any pH 5 to 9, any of the more active diazos, and apparently any temperature up to room temperature.

With other substances such as acetoacetanilide, the only condition necessary is to maintain the pH high enough to ensure rapid enough coupling to provide a reasonably sharp end point. If the coupling is so slow that an excess of diazo is present for a considerable time before the end point is reached, the results tend to be inaccurate and are in general low because of the difficulty of drawing the true tangent to which may indeed be a considerably rounded curve instead of a straight line.

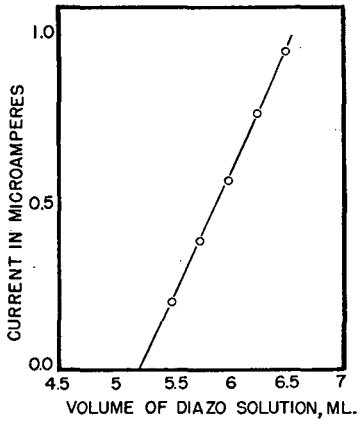

Figure 3. Amperometric Curve of Titration Recorded in Figure 2

End point 5.22 ml.

Some couplers, on the other hand, require careful control of temperature, pH, and selection of diazo in order to obtain a satisfactory titration. This situation is not unique to this particular method, as definite conditions must be specified when the older methods are used. The fact that it also shows whether the diazo is still reacting or taking part in side reactions clearly indicates false end points. Thereupon, intelligent steps may be taken to improve the titration conditions.

Table III. Effect of Temperature on Titration of 1-Phenyl-3-methyl-5-pyrazolone with Diazo Sulfanilic Acid

(pH 8)

Temp., ° C.	Normality of Diazo Found Amperometrically	Temp., ° C.	Normality of Diazo Found Optically
41	0.01012	20	0.01019
18	0.01009	20	0.01031
1	0.01011	27	0.01022
1	0.01005		

TEMPERATURE CONTROL

Many titrations can be carried out at room temperature. Thus in Table III are listed the results of titrating 1-phenyl-3-methyl-5-pyrazolone with diazo sulfanilic acid at widely different temperatures.

Excellent agreement was found at various temperatures. These particular solutions were simultaneously analyzed by following the formation of dye by optical means. These checks, together with those presented in Table I, can be regarded as conclusive proof that the method provides a true analysis of such systems.

Couplers such as 2-naphthol-3,6-disulfonic acid (R acid), 2-naphthol-6,8-disulfonic acid (G acid), and particularly 1-amino-8-naphthol-3,6-disulfonic acid (H acid), should be titrated at a low temperature—0° to 5° C. The reason for this is not known. Sometimes this merely prevents multiple coupling, but in other cases other factors appear to be involved. Thus, with H acid at pH 8, a perfectly satisfactory titration can be made using diazo-*p*-toluidine if the temperature of the solution is kept at 0° to 5°. At room temperature the diazo seems to be consumed almost indefinitely, and no end point is obtained.

EFFECT OF pH

Conant and Peterson (*1*) have shown that the rate of coupling reactions may be expressed by Equation 1:

$$\log k = \log k_0 + \text{pH} \qquad (1)$$

where k is the measured reaction velocity constant, and k_0 is the reaction velocity constant at pH 0. According to this equation, the velocity of the reaction increases tenfold for a pH change of 1 unit.

A coupler such as 3-methyl-1-phenyl-5-pyrazolone reacts fast enough to be titrated with diazo-*p*-toluidine, a relatively slow-acting diazo, at a pH as low as 6.0. On the other hand, G acid must be titrated with a relatively fast acting diazo such as diazo-*m*-nitroaniline at a pH not lower than 8 in order to get a reasonably sharp end point. When β-naphthol is titrated with diazo-*m*-nitroaniline, at pH 6 an end point is obtained which corresponds to single coupling; at pH 9 the end point corresponds to consumption of 2 moles of diazo. Because it is unlikely that a bisazo dye is formed, some other reaction must be taking place. Conversely, caution must sometimes be exercised, for frequently a coupler such as 2-naphthol-6-sulfonamide, which is readily titrated at pH 6 with diazo-*m*-nitroaniline at room temperature, cannot be titrated at all at pH 9 under the same conditions.

An important limitation of the amperometric method is that in general the low break disappears at a pH of about 10 and higher, so that titrations much above pH 9 are not practical. It might be feasible at still higher pH's, where the lower break of the diazo has disappeared completely, to measure the amount of dye formed and take as the end point the point where the maximum concentration of dye develops. However, it has been found possible to titrate all the couplers so far studied in the pH range 5 to 9.

SELECTION OF DIAZO

Diazo-*p*-toluidine has been found the most generally useful of the various diazotized amines. In general, a higher pH is required with diazo-*p*-toluidine than with diazo sulfanilic acid, which in turn requires a higher pH than diazo-*m*-nitroaniline. Thus, acetoacetanilide can be titrated at pH 7 or 8 with diazo-sulfanilic acid, but at pH 8 diazo-*p*-toluidine reacts too slowly. On the other hand, 1-naphthol-5-sulfonamide at 0° C. is readily titrated with diazo-*p*-toluidine at a pH of 9, but with *m*-nitroaniline under the same conditions no diazo can be detected, even when well past the end point. However, diazo-*m*-nitroaniline can be used with very satisfactory results if the pH is reduced to 6.0 with this coupler

When *m*-nitroaniline is used in the lower pH range, it is generally necessary to reduce the applied voltage from 0.3 to about 0.20 to 0.25 volt because the nitro groups in the coupled dye may interfere. This, of course, is not a serious limitation, but it should not be ignored when using diazos containing one or more nitro groups. If the coupler contains a nitro group to begin with, this interference might be observed with all diazos and should be treated accordingly.

ACKNOWLEDGMENT

The authors wish to express appreciation to L. J. Lohr wh made the diazo determinations based on nitrogen evolution, an to C. H. Benbrook and Miss E. Aiken who were responsible for the determinations by optical means and aided the investigation by supplying some of the chemicals and making many helpful suggestions. Appreciation is also expressed to L. T. Hallett, under whose direction this work was performed.

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Stability Test for Additive-Treated Motor Oils

S. A. McKEE AND ANN ROBINSON FRITZ, *National Bureau of Standards, Washington, D. C.*

The National Bureau of Standards has developed a laboratory test for rating lubricating oils, which simulates the characteristic engine deposit formation significant in the engine testing of motor oils. In the apparatus used, oil is made to flow in a thin film at a regular rate and is recirculated for a definite period over a steel strip which is maintained at an elevated temperature. The strip is weighed before and after the test to obtain a numerical as well as a visual indication of the amount of deposit formed. A method was developed for washing the strip with precipitation naphtha to remove the oil film on the strip without removing the deposit. The oils tested were straight mineral motor oils and additive motor oils containing oxidation inhibitors, detergents, and combinations of both. The additive oils include both premium and heavy-duty types. The data obtained provide a reasonably sensitive measure of the effectiveness of inhibitors and detergents and their combinations. The conditions used in the tests tend to accentuate the effectiveness of full heavy-duty oils. The correlation with engine performance is of sufficient promise to justify further work with the method described in this paper.

IN THE lubrication of automotive engines the present trends are toward the use of well-refined base oils, with which additives are compounded to give the desired characteristics as regards oil stability (*2*). This paper describes an investigation at the National Bureau of Standards of the effectiveness of some typical additive-treated crankcase oils when tested in a laboratory apparatus in which the conditions of operation simulate those present in certain parts of the engine. Because the rating of crankcase oils at present is based primarily upon engine deposits, the objective in the design of the apparatus was the formation of characteristic deposits rather than the study of the changes of the oil in bulk.

APPARATUS

The method consists essentially of circulating the oil under test over a heated steel strip. The oil on the strip is in the form of a relatively thin film similar to the oil film on the cylinder walls of an engine. A mechanical lubricator pump delivers the oil from a small glass beaker to the upper end of the thin steel strip, which is held in an inclined position and maintained at the test temperature. The oil leaving the lower end of the plate drops into the beaker and is recirculated.

Two such test units are shown in Figure 1. The circulating pumps of each unit are driven by a common camshaft, but otherwise are entirely separate. The complete setup is enclosed in a hood with restricted air inlet, so that fumes are removed from the room, but no forced draft is used.

A 200-watt electric strip heater (see unit on right in Figure 1) is mounted by means of studs to a fixture supported on a ring stand in such a manner that the upper surface of the heater may be inclined at any desired angle toward the beaker containing the oil under test. An adjustment is also provided to level the heater in a transverse direction. A copper bar 7 inches (17.8 cm.) long, 1.5 inches (3.81 cm.) wide, and 0.5 inch (1.27 cm.) thick is fastened on top of the heater. The test specimen, a steel strip 9 inches long, 1.75 inches wide, and $^1/_{32}$ inch thick, is fastened to the top of the bar by eight steel machine screws, four along each side. At the lower end, the center of the strip extends beyond the sides, forming a point from which the oil may drop. A steel overstrip 3 inches long, 1.75 inches wide, and $^1/_{32}$ inch thick is fastened at the upper end and overlaps the test strip 2.5 inches. A piece of doubled 20-mesh steel wire screen 1.25 inches long and 0.625 inch wide is placed on the overstrip to assist in spreading the oil evenly on the test strip. The heater assembly is positioned so that the oil dripping from the point at the lower end of the test strip drops into the beaker containing the test oil and the suction line of the pump.

The mechanical lubricator pump is operated by a camshaft driven by a 0.125-hp. electric motor through a 100-to-1 gear speed reducer. The camshaft, turning at 18 r.p.m., has two cams for each pump, so that each positive displacement pump is operated 36 displacements a minute. The suction line of the pump is fitted with a fine wire mesh strainer which is immersed in the test oil in the beaker. The discharge from the pump is through 0.125-inch copper tubing, which can be adjusted to conduct the oil to the overstrip during a test run or off to one side for cleaning or calibrating operations. A special head, made from 0.25-inch copper tubing, is slipped over the 0.125-inch tubing to deliver the oil to the overstrip. The end of the head resting on the overstrip has been compressed to provide a slit $^1/_{32}$ by 0.5 inch, and beginning 0.25 inch above the slit a hole is notched in the tube.

Temperatures are measured by a thermocouple inserted in the side of the copper bar at midpoint. The test temperature is controlled manually by a variable transformer in the line to the heater. Draft guards made of 0.25-inch Transite board 8 inches long and 3.5 inches wide are fastened on each side of the heater assembly. In Figure 1, the front guard has been removed in the unit on the right.

This arrangement provides for a considerable degree of flexibility. The temperature of the strip may be changed by adjusting the transformer. Changes to the film of oil flowing down the strip may be made by adjusting the stroke of the pump to change the rate of circulation and also by changing the slope of the strip.

In preliminary tests in flowing oil at relatively low rates down a heated strip, it was found that when either sight-feed oilers or mechanical lubricators were used to discharge the oil on the strip, most of the oil flowed down the center of the strip in a series of surges. These conditions did not provide a reproducible or significant pattern of deposit on the strip. Accordingly, a number of methods were tried to improve this condition. The present arrangement, described above, is reasonably satisfactory in providing an even film of oil across the strip. The pulsations from the pump are reduced by the notched hole and the slit in the discharge head. A further reduction of these pulsations is obtained by pointing the head "up-hill," so that the oil comes to rest before starting to flow down the strip. The piece of folded wire screen lying flat on the strip just below the discharge head is used for distributing the oil across the strip. The oil fills the spaces between the wires and flows out from the lower edge in a relatively even film the full width of the screen.

The overstrip is used in order to remove from the test results extraneous deposits formed while the oil is being distributed. Thus the actual test strip contains only those deposits that are formed when the oil is flowing in an even thin stream.

TEST PROCEDURE

Usually tests are run on the two units simultaneously. The test strip and overstrip are prepared for the test by polishing with No. 0 emery cloth followed by No. 0 polishing paper, and then washing with precipitation naphtha. The test strip is weighed before it is attached to the copper bar. Before each run, the rate of delivery of the oil from the pumps is checked and adjusted when necessary by changing the stroke of the pumps. This adjustment is conveniently checked by the use of a dial indicator touching the top of the plunger.

After the system has been flushed with test oil and the rate of delivery adjusted, 150 ml. of the test oil are placed in a 250-

ml. beaker and the weight of the sample is determined on a balance. The beaker is placed in position under the drip point of the test strip and the pump intake tube is connected with its screen near the bottom of the beaker. The delivery tube is positioned with the delivery slit parallel to and about 0.625 inch below the top of the overstrip. The steel screen is placed on the overstrip with the folded edge down and the upper edge about 1 inch below the delivery slit. A few strokes of the pump are made by hand to produce a film of oil on the strip and then the pump motor is started and the heater is turned on. Usually the test temperature is reached in about 0.5 hour and the apparatus is then held at that temperature for a 6-hour run.

At the end of the 6-hour run, the test strip is removed and hung in a vertical position to drain overnight. The back of the strip is cleaned with a naphtha-moistened cloth and the strip is weighed. Then it is secured in test position again, with the copper bar, screws, and steel screen cleaned, and a second 6-hour run is made. After this run the test is complete and the strip is removed and allowed to drain at least 24 hours before cleaning the back and weighing.

The difference in the weight of the strip before and after the test provides a numerical indication of the amount of deposit formed. However, these values are influenced by the amount of oil remaining on the deposit. Ordinary methods for removing this oil film, such as dipping the strip in solvent or wiping with a cloth, were not suitable because they also removed some of the deposit. In the later tests a method reasonably satisfactory was used.

The strip is supported over a pan in a slightly inclined position. A piece of cotton gauze is placed across the strip near the top, and a beaker of precipitation naphtha is placed slightly higher than the strip. A wick of gauze from the beaker feeds naphtha to the gauze on the strip. This provides an even gentle flow of naphtha down the strip which does not disturb the deposit. When the naphtha dripping from the strip is colorless, the gauzes are removed and the strip is dried and weighed.

After the test the weight of the oil remaining in the beaker is determined; the loss in weight of the sample provides an approximate indication of the evaporation loss. The viscosities at 100° F. are also determined before and after heating.

Duplicate tests were run with each oil, one on each unit. The strip from one test was washed with naphtha. The other strip was drained but not washed, and held as permanent record.

LUBRICANTS TESTED

In general, the oils tested are in commercial production and have a considerable background of service performance. These include oils with no additives, premium type additive oils (*5*) containing inhibitors and/or detergents, and full heavy-duty oils containing additives having U. S. Army Ordnance 2-104B (*4*) and Navy 9000 series approval (*3*).

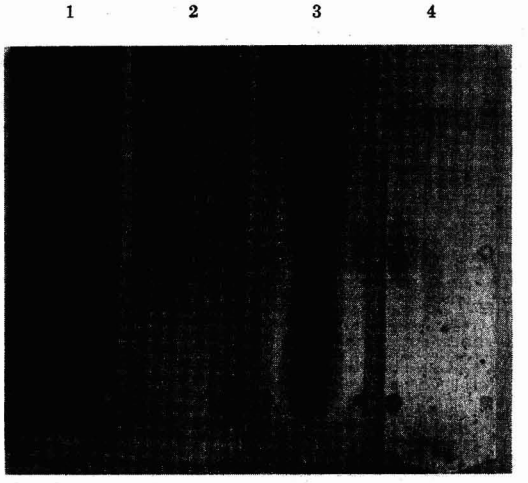

Figure 2. Deposits Formed Using Mid-continent Conventionally Refined Base Oil and Various Additives

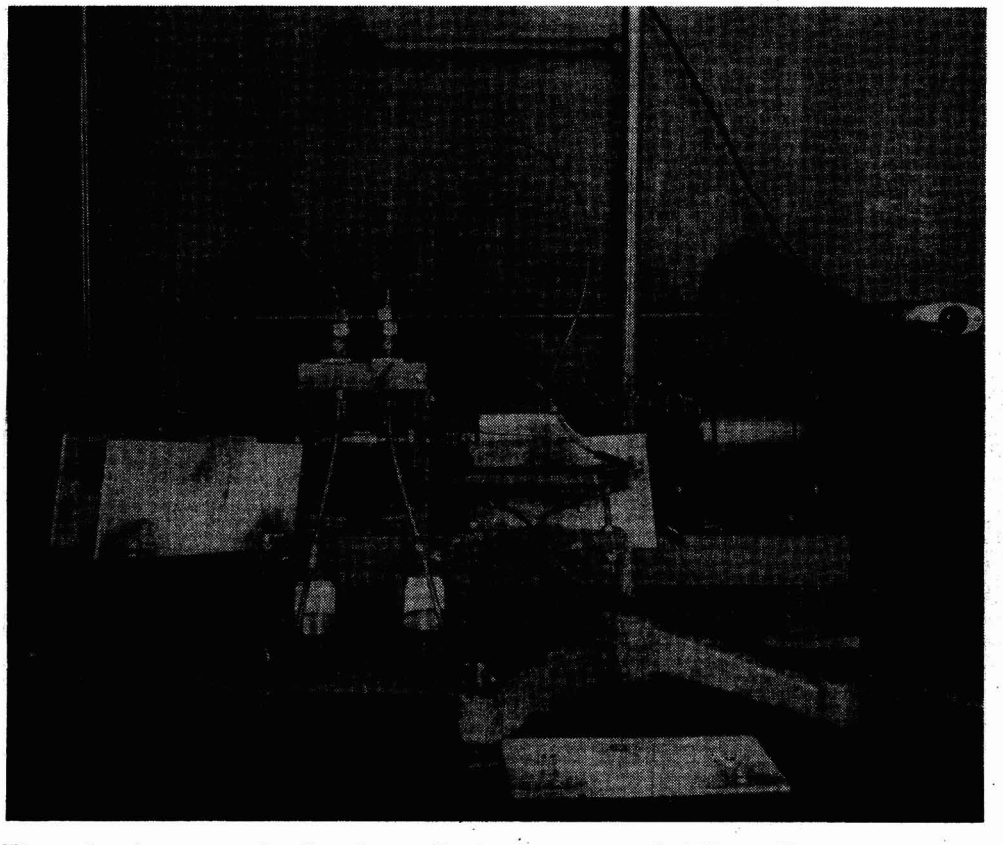

Figure 1. Apparatus for Simulating Engine Deposits with Additive-Treated Crankcase Oils

TEST RESULTS

The tests with this apparatus were made under the following conditions: temperature, 250° C. (as measured by thermocouple in copper bar); oil delivery, approximately 0.7 gram per minute; and slope of strip, 8.5° ($\sin^{-1} = 0.15$) from the horizontal.

The above temperature possibly approximates the high temperature regions in the engine under full power operation.

Photographs of the deposits obtained in test under these conditions with some typical additive and nonadditive oils are shown in Figures 2, 3, 4, and 5. In these photographs the strips had been drained but not washed with precipitation naphtha. The strips in each figure show the results of a particular series of tests.

Sample 1 (Figure 2) is a conventionally refined mid-continent oil of 55 viscosity index and SAE 30 grade, used as a base oil for samples 2, 3, and 4. Sample 2 is treated with a premium-grade additive of the combined detergent–oxidation inhibitor type. Sample 3 contains a different premium-duty type additive, and 4 has the prescribed amount of a full heavy-duty additive having both U. S. Army Ordnance 2-104B and U. S. Navy 9000 series approval.

The base oil used with all the samples shown in Figure 3 is a solvent-extracted mid-continent oil of 95 viscosity index and SAE 30 grade. Sample 5 is the straight oil with no additives, 6 contains an oxidation inhibitor and no detergent, 7 has the same premium additive as was used in 3 (Figure 2), 8 contains a full-strength 2-104B additive, different from 4, and 9 has a detergent only without oxidation inhibitor.

Table I. Identification and Test Data for Oils

Sample No.	Base Oil	V.I.	SAE No.	Additives: Inhibitor	Additives: Detergent	Additives: Grade[a]	Weight of Strip Deposit, Grams: Drained	Weight of Strip Deposit, Grams: Drained and washed	Viscosity Increase, %	Evaporation Loss, %
1	Mid-continent	55	30	No	No	...	1.01	0.417	378.5	63.2
2	conventionally	55	30	Yes	Yes	P	0.104	0.038	77.7	47.6
3	refined	55	30	Yes	Yes	P	0.089	0.032	76.1	47.6
4		55	30	Yes	Yes	H	0.095	0.022	89.7	50.0
5	Mid-continent	95	30	No	No	...	0.791	0.222	198.9	38.6
6	solvent-	95	30	Yes	No	P	0.170	0.090	68.3	33.1
7	extracted	95	30	Yes	Yes	P	0.058	0.022	66.9	33.3
8		95	30	Yes	Yes	H	0.073	0.016	58.7	34.1
9		95	30	No	Yes	...	0.329	0.116	234.6	55.4
10	Mid-continent	95	30	Yes	No	...	0.119	0.048	94.3	39.0
11	solvent-	95	30	Yes	Yes	...	0.521	0.110	59.7	30.6
12	extracted	95	30	Yes	No	...	0.364	0.152	157.8	39.6
13		95	30	Yes	Yes	H	0.083	0.018	89.5	36.2
14		95	30	Yes	No	...	0.352	0.093	79.4	36.6
15		95	30	Yes	Yes	...	0.058	0.019	81.9	38.3
16	Pennsylvania	102.6	30	Yes	No	...	0.142	0.032	41.8	25.4
17	solvent-	104.2	10	Yes	Yes	H	0.067	0.024	55.9	61.8
18	extracted	101.0	30	Yes	Yes	H	0.064	0.020	32.8	27.6
19	and	114.1	10	Yes	Yes	H	0.079	0.017	799.3	77.7
20	dewaxed	105.3	30	Yes	Yes	H	0.055	0.013	91.4	44.1
21		116.3	10	Yes	Yes	...	0.230	0.102	824.6	75.6
22		102.8	30	Yes	Yes	...	0.124	0.064	67.3	28.5
23		115.3	10	Yes	Yes	...	0.099	0.033	958.1	77.1

[a] P = premium. H = heavy duty, 2-104B.

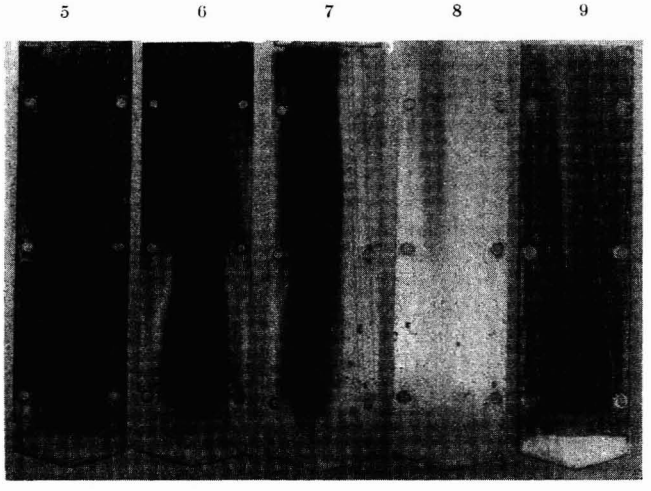

Figure 3. Deposits Formed Using Mid-continent, Solvent-Extracted Base Oil and Various Additives

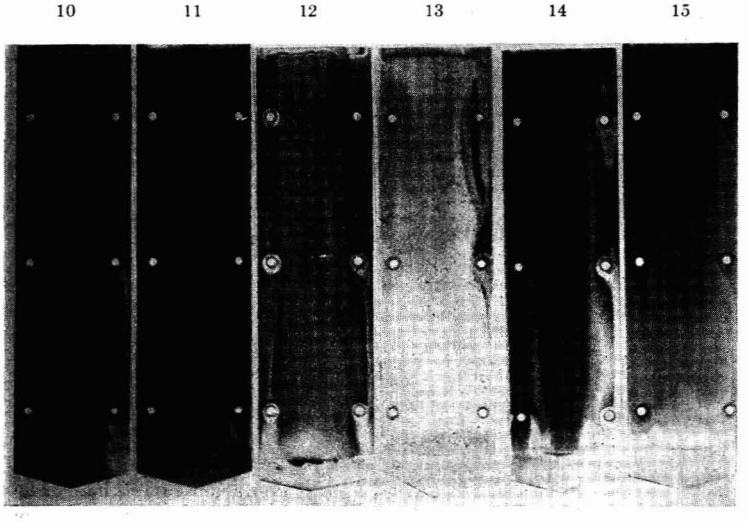

Figure 4. Deposits Formed Using Mid-continent, Solvent-Extracted Oil with Various Additives

In Figure 4, the base oil used is also an SAE 30 grade solvent-extracted mid-continent oil of 95 viscosity index. Sample 10 contains an inhibitor, 11 is 10 plus a small amount of detergent, 12 has a different type of inhibitor, 13 is 12 plus full-strength detergent and has 2-104B approval, 14 contains a different inhibitor of the same type as 10, and 15 is 14 plus partial-strength (about one-third the amount used in a full heavy-duty oil) detergent.

Solvent-extracted, dewaxed Pennsylvania oils were used as the base oils in the samples shown in Figure 5. Samples 16, 18, 20, and 22 were SAE 30 grade and 17, 19, 21, and 23 were SAE 10. All had a viscosity index over 100. All contained inhibitors of the same type. There was no detergent in sample 16. All the rest contained detergents of the same type.

Numerical data obtained in the tests of these samples, given in Table I, include the weight of the strip deposit before and after washing with naphtha, the percentage increase of the viscosity of the sample, and the weight per cent loss of oil during the test (approximate evaporation loss).

The figures show that under the conditions covered in these tests the commercially used additives have marked effects upon the deposits formed, especially when the full 2-104B heavy-duty oils are compared with the respective base oils. A number of heavy-duty oils have been run in the apparatus, and in all cases where the additive met with 2-104B approval very little deposit was formed on the strip, whereas with the base oil the strip was covered with a relatively heavy deposit. Comparisons of strips 1 with 4 in Figure 2 and 5 with 8 in Figure 3 are typical examples.

In considering the relative performance of the base oils without additives the photographs do not provide as significant a differentiation as the actual strips. Sample 1 was of recognized poor stability and the deposit formed was considerably heavier than with sample 5. This is shown in Table I, where the weight of deposit (after being washed with naphtha) with sample 1 was nearly twice that obtained with sample 5.

Sample 9 in Figure 3 indicates that under the test conditions a detergent, when used alone, is not especially effective. However, the detergent does tend to reduce deposits, especially when used in appreciable amounts in conjunction with an oxidation inhibitor. This is shown in Figure 4. The addition of a detergent in the amount prescribed for a 2-104B oil to sample 12 gave results shown on strip 13 and a partial-strength detergent added to 14 gave results shown on 15.

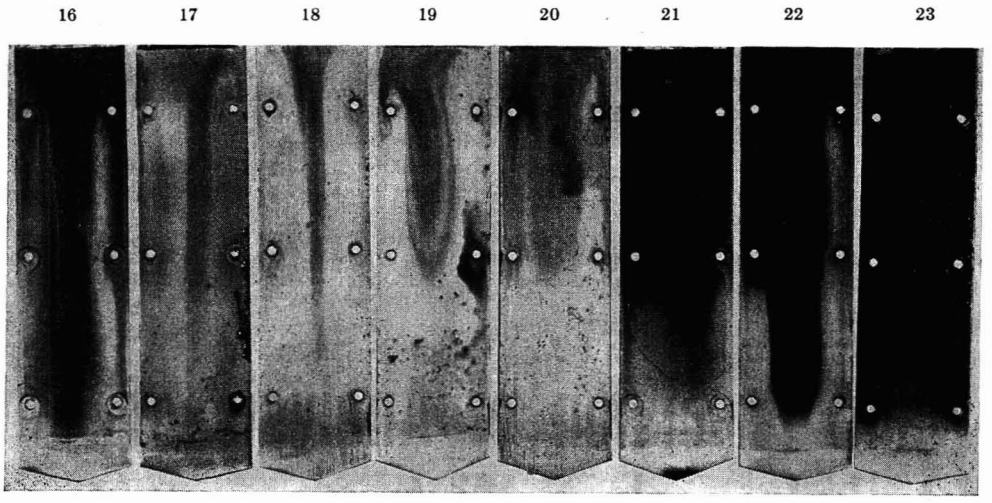

Figure 5. Deposits Formed Using Pennsylvania, Solvent-Extracted and Dewaxed Oils with Various Additives

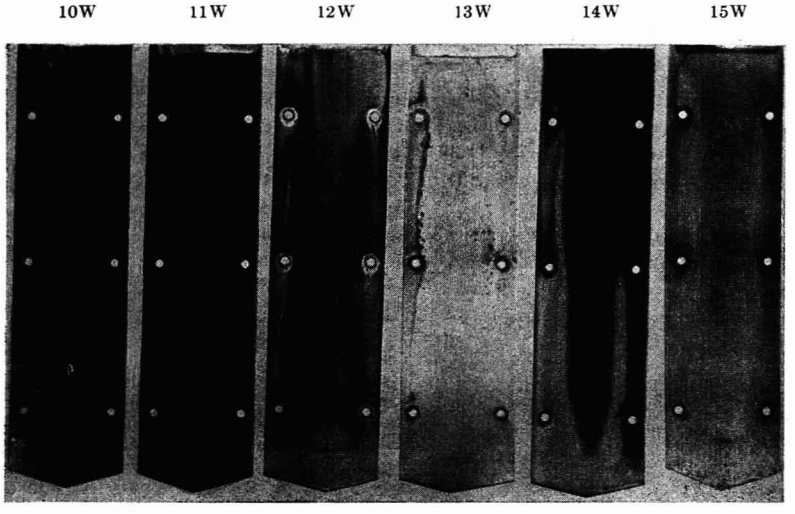

Figure 6. Deposits Shown in Figure 4 Washed with Precipitation Naphtha

Of the numerical ratings given in Table I, it is believed that the weights of the deposits obtained after the strips were washed with naphtha are more representative, especially with the nonadditive oils and the heavy-duty oils. The weights of the deposits formed with the 2-104B oils are usually not over 0.02 gram, whereas those for the mid-continent base oils run 0.20 gram or greater; the partial-strength additive oils in general fall in between. The most marked differences between the appearance of the strips and the measured weights of the deposits are found with some of the partial-strength additive oils. Some of these differences may be due to accidental deposits which formed along the edges of the strip in a few of the tests. This condition is probably aggravated by the screw heads holding down the strip, and possibly could be improved by using some other method of fastening.

All the samples were run on each of the test units but not on both at the same time. In general, the strips from the two units for a given sample were reasonably alike in appearance. After draining, one strip was washed while the other was held as a permanent record. The washed strips usually do not photograph well because of lack of contrast between deposit and strip; the steel sometimes becomes discolored in places where there is practically no deposit. Photographs of the washed strips obtained with samples 10 through 15 are given in Figure 6. These strips appear to be in general relative agreement with those shown in Figure 4, which are the unwashed strips for the same oils using the other test unit.

Engine tests of these oils were not run at the National Bureau of Standards. However, engine data on some of the samples were furnished by the suppliers. In this connection, the strips shown in Figure 5 are of interest. Ratings obtained in 2-104B engine tests were furnished for all the samples shown in the figure. Of these samples, 17, 18, 19, and 20 were listed as passing, whereas samples 16, 21, 22, and 23 did not pass. The oils that passed the engine tests gave definitely cleaner strips. It is believed that, in general, the differentiation between passing and nonpassing is more marked in the laboratory test than in the engine test. For example, the 2-104B ratings of samples 21 and 22 were "not passing but nearly acceptable," whereas the deposits on the strips were markedly heavier than those that passed. Another deviation was noted with the strips that passed. The engine test rating for 17 was "superior," while 18, 19, and 20 were rated as "average to superior" and this differentiation is not indicated by the strips. However, the ratings by the laboratory method are based on a single operating condition, whereas the engine performance ratings are based on a number of factors involving a multiplicity of conditions.

CRC-L-4-545 (*1*) engine test results were furnished also for samples 1, 2, 3, and 4 shown in Figure 2. The total varnish ratings for these oils were 11.5, 32.5, 40.5, and 43.0, respectively, and the corresponding combined sludge and varnish ratings were 34.5, 68.5, 80.5, and 85.5. The most marked deviation observed between the available L-4 engine data and the laboratory data has been with the solvent-extracted mid-continent base oils without additives. Usually the engine ratings reported for these oils have been higher than would be expected from the nature of the strip deposits.

The data given in Table I on the changes in viscosity and the evaporation loss provide an indication of the changes that occurred to the bulk oil during the test. Comparison of these data with reported L-4 engine test drain analysis data indicates that the changes in the oil in the laboratory test were of the same order of magnitude but consistently greater than the changes occurring in the L-4 engine test. Some of this increase may be due to the small size of the sample used in the laboratory test.

CONCLUSION

The data obtained provide a reasonably sensitive indication of the effectiveness of inhibitors and detergents and their combinations. The particular conditions present in these tests tend to accentuate the effectiveness of full heavy-duty additive oils. Possibly other operating conditions might be found which would be more suitable for the premium grade oils or would give additional information on the over-all effectiveness of a given oil-additive combination. The apparatus is sufficiently flexible to cover a fairly wide range of conditions.

The correlation with engine performance, although limited in

extent, is of sufficient promise to justify further work with the method. Plans are being made to provide automatic temperature control, so that the test may be run overnight and hence reduce the time of test in terms of work days.

ACKNOWLEDGMENT

Acknowledgment is made to the laboratories which assisted in this investigation by supplying the oils tested.

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(3) Navy Bureau of Ships, *Pamphlet N.B.S.* **431** (Aug. 14, 1945); Specification **14-0-13A** (Dec. 1, 1944).
(4) U. S. Army Specification **2-104B** (May 6, 1943).
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Accuracy and Precision of Analysis of Light Hydrocarbon Mixtures

C. E. STARR, JR., AND TRENT LANE

Esso Laboratories, Esso Standard Oil Company, Louisiana Division, Baton Rouge, La.

Comprehensive testing of analytical methods for light hydrocarbons has been conducted by the Rubber Reserve Committee on Butadiene Specifications and Methods of Analysis. About 70 laboratories performed 8000 tests employing such analytical tools as the mass spectrometer, infrared and ultraviolet spectrophotometers, low temperature fractional distillation, and a variety of chemical procedures. Study of the test data, obtained under standardized conditions, reveals that each procedure has some unique advantage, and that by employing the most suitable methods high degrees of accuracy and precision may be obtained for the analysis of most of the common light hydrocarbons.

THE establishment of a synthetic rubber industry, rapidly brought about by the exigencies of war, included among its many technological phases the problem of formulating accurate and precise analytical methods for light hydrocarbons. The interrelated operations of the petroleum, chemical, and rubber industries in cooperation with the United States Government, agencies of which financed and owned the plants of the new industry, required proper assays of feed stocks and products. This paper relates in summary form the evaluation of analytical methods employed in the control and assay of the feed stocks and products involved in the production of butadiene. The formulation of the test methods and their evaluation were conducted by the Committee on Butadiene Specifications and Methods of Analysis, organized under the sponsorship of the Reconstruction Finance Corporation's Office of Rubber Reserve and composed of members of this governmental agency along with industrial concerns which were feed stock suppliers or producers of butadiene.

PURPOSES OF ANALYTICAL PROGRAM

At the outset of the butadiene production program it was necessary to collate and supply the various analytical methods made available by the industrial concerns involved in the program. The numerous methods available, the variations of claims made for them, and the frequent lack of concordance of test results necessitated careful review by the Committee on Butadiene Specifications and Methods of Analysis. This review, as well as preliminary but extensive selection, refinement, and evaluation of the available methods, the introduction of new spectroscopic methods, and the establishment of specifications, logically led to the committee's formulation of a comprehensive analytical test program to provide an evaluation of the methods and a basis for adoption of control and referee methods. The objects of this program are to determine:

How well a given laboratory checks its own analyses. Such information is useful in ascertaining the precision of analytical control.

How well various laboratories check each other. This information is necessary to provide measures of limitations that would be reasonable to impose on any contractual arrangements for sale of feed stocks or product.

How accurately the various light hydrocarbon components can be measured. Such data are useful for process and equipment design, and for determining the actual effects of plant operation.

The best analytical methods for the various light hydrocarbon compounds. With a wide variety of methods available from which to choose, it was felt necessary by the committee to bring factual data to bear upon this phase of the problem and, on the basis of such test data, to designate standard control and standard referee procedures.

The summarized results of this program related herein cover the more general analytical methods and pertain to the main C_3 to C_5 hydrocarbons. The testing of other methods and the application to other gas components, as well as full descriptions of all the analytical methods employed and the complete data regarding their evaluation, will appear in a book (*8*). The complete information is needed by those engaged in this field of analytical work in order to answer properly and fully the questions posed by the stated objectives of the program. The summarized results are presented to provide generalized answers to the questions, to stimulate interest in further study of the committee's work, to inspire similar evaluations in other analytical fields, and to provide a basis for critical evaluation of the current analytical methods for light hydrocarbons with the object of furthering improvements in this field.

SAMPLES ANALYZED AND TEST METHODS

To accomplish the objectives of the program a number of synthetic mixtures of light hydrocarbons were prepared and analyzed by the various methods in use in the laboratories of the industrial

Table I. Laboratories Participating in Butadiene Analytical Committee Test Program

Company	Location	Company	Location
Atlantic Refining Co.	Port Arthur, Tex.	Lion Oil Refining Co.	El Dorado, Ark.
California Research Corp.	San Francisco, Calif.	Magnolia Petroleum Co.	Beaumont, Tex.
Canadian Synthetic Rubber, Ltd.	Sarnia, Ontario	National Bureau of Standards	Washington, D. C.
Carbide and Carbon Chemicals Corp.	Louisville, Ky.	National Synthetic Rubber Corp.	Louisville, Ky.
Carbide and Carbon Chemicals Corp.	Institute, W. Va.	Neches Butane Products Co.	Port Neches, Tex.
Carbide and Carbon Chemicals Corp.	South Charleston, W. Va.	Pan-American Refining Corp.	Texas City, Tex.
Cities Service Refining Co.	Lake Charles, La.	Phillips Petroleum Co.	Bartlesville, Okla.
Consolidated Engineering Corp.	Pasadena, Calif.	Phillips Petroleum Co.	Borger, Tex.
Copolymer Corp.	Baton Rouge, La.	Polymer Corp., Ltd.	Sarnia, Ontario
Crown Central Petroleum Corp.	Houston, Tex.	Pure Oil Co.	Winnetka, Ill.
Dow Chemical Co.	Midland, Mich.	Pure Oil Co.	Nederland, Tex.
Esso Standard Oil Co., La. Div. (CPL)	Baton Rouge, La.	Richfield Oil Corp.	Los Angeles, Calif.
Esso Standard Oil Co., La. Div. (EL)	Baton Rouge, La.	Saint Clair Process Corp.	Sarnia, Ontario
Esso Standard Oil Co., La. Div. (P. 152)	Baton Rouge, La.	Saybolt and Co., E. W.	Wilmington, Calif.
Firestone Tire and Rubber Co.	Lake Charles, La.	Saybolt and Co., E. W.	Houston, Tex.
Firestone Tire and Rubber Co.	Akron, Ohio	Shell Chemical Corp.	Torrance, Calif.
Firestone Tire and Rubber Co.	Port Neches, Tex.	Shell Chemical Corp.	Houston, Tex.
General Petroleum Corp. of California	Los Angeles, Calif.	Shell Oil Co., Inc.	Wood River, Ill.
General Tire and Rubber Co.	Louisville, Ky.	Sinclair Refining Co.	East Chicago, Ind.
General Tire and Rubber Co.	Baytown, Tex.	Sinclair Refining Co.	Houston, Tex.
Goodrich Co., B. F.	Akron, Ohio	Sinclair Rubber, Inc.	Houston, Tex.
Goodrich Co., B. F.	Louisville, Ky.	Socony Vacuum Oil Co., Inc.	Paulsboro, N. J.
Goodrich Co., B. F.	Borger, Tex.	Southern California Gas Co.	Los Angeles, Calif.
Goodrich Chemical Co., B. F.	Port Neches, Tex.	Standard Oil Co. of California	El Segundo, Calif.
Goodyear Rubber Co.	Houston, Tex.	Standard Oil Dev. Co., Res. Div.	Bayway, N. J.
Goodyear Synthetic Rubber Corp.	Akron, Ohio	Standard Oil Co. (Indiana)	Whiting, Ind.
Goodyear Synthetic Rubber Corp.	Torrance, Calif.	Standard Oil Co. of Ohio	Cleveland, Ohio
Goodyear Synthetic Rubber Corp.	Houston, Tex.	Sun Oil Co.	Toledo, Ohio
Gulf Oil Corp.	Port Arthur, Tex.	Taylor Refining Co.	Corpus Christi, Tex.
Humble Oil and Refining Co.	Ingleside, Tex.	Texas Co.	Port Arthur, Tex.
Humble Oil and Refining Co.	Baytown, Tex.	Tidewater Associated Oil Co.	Associated, Calif.
Houdry Process Corp. of Pennsylvania	Marcus Hook, Pa.	Universal Oil Products Corp.	Chicago, Ill.
Imperial Oil, Ltd.	Sarnia, Ontario	U. S. Rubber Co.	Naugatuck, Conn.
Kellogg Co., M. W.	Jersey City, N. J.	U. S. Rubber Co.	Los Angeles, Calif.
Koppers Co., Inc.	Kobuta, Pa.	U. S. Rubber Co.	Institute, W. Va.

concerns involved in the production of butadiene. A sufficiently large number of laboratories (Table I) and analytical determinations (about 8000 total for all methods) was involved so that the results obtained could be considered representative of what might normally be expected of the various analytical methods.

The synthetic mixtures were analyzed by the mass spectrometer, by infrared and ultraviolet spectrophotometric procedures, and by low temperature distillation plus chemical and spectroscopic tests on segregated fractions. The committee's work in the testing of analytical methods was made possible by the cooperation and assistance of the Phillips Petroleum Company, which undertook the responsibility of preparing the synthetic mixtures to very exacting specifications, and by the cooperation of the participating laboratories. Summarized data regarding the composition of the synthetic samples are given in Table II. The compositions of the synthetic mixtures were known to ±0.05% based on the total sample. The methods of analysis are briefly outlined in subsequent sections.

Table II. Composition of Synthetic Mixtures Used in Test Program

Component	Concentration Range, Mole % From	To	No. of Mixtures
Propene	3	16	5
Propane	0.2	11	9
Total C_3	0.2	18	8
Isobutane	Trace	45	16
n-Butane	Trace	99	16
Total butanes	Trace	99	16
1-Butene	0.1	95	16
2-Butenes	Trace	41	15
Total *n*-butenes	0.1	99	16
Isobutylene	0	46	13
Total butenes	9	90	13
Butadiene	0.2	86	10
Total C_4	6	100	16
Pentenes	3	3	1
Isopentane	0.3	8	8
n-Pentane	Trace	10	6
Total C_5	Trace	18	11
Butadiene dimer	0.1	0.2	3

METHODS OF DATA ANALYSIS

The analytical methods were prepared in a tentative standardized form and along with formalized data sheets were submitted to the laboratories participating in the program. The test results were collated in a manner exemplified by Table III. Standard statistical evaluations of the test data were employed. Accuracy was gaged by the difference between the arithmetic average of a given series of values for a given component and the synthesis value; precision was judged by the determination of probable error.

In deriving values for accuracy and precision the data were first examined for the purpose of eliminating questionable values. The criterion of rejection of Pierce and Chauvenet (*3*), modified by Jeffreys (*7*), was used. The procedure was repeated until no further rejections were indicated; in most instances sufficiently divergent results were eliminated in one or two trials.

The probable error, r, used as a criterion of precision, is a value of precision such that one half of all the measurements fall between the limits of $a \pm r$ where a is the arithmetic mean. The probable error determines the degree of confidence we may have in using the mean as the best representative value of a series of observations.

In applying the standard statistical measures and deriving probable error the Gaussian distribution function was assumed (*2*). Although the test data did not conform in all cases to the normal distribution curve, typical data shown in Figure 1 substantiate the belief that the assumption was reasonable. Various limitations, particularly such as the number of tests reported by a single laboratory with a given method for a specific component, indicated that the compilation and analysis of data exemplified by Table III were reasonable procedures for placing all data on a comparative basis. More detailed analysis can be obtained by close examination of the complete data, to be reported in tabular and graphical form (*8*). The theory of errors, including discussions of probable error, are given in standard texts (*1*, *4–6*).

Other statistical evaluations are described in subsequent sections dealing with the testing of the various methods.

ANALYSES BY MASS SPECTROMETER

Analytical Method. The general method of applying the mass spectrometer to the analysis of light hydrocarbons has been sufficiently described in the literature (*13*, *14*), as have applications to gas analysis. A high degree of standardization was

achieved in that all laboratories that conducted analyses by this method employed one type of instrument (Consolidated Engineering Corporation) (*13*, *14*), and followed the procedures for calibrating, operating, and computing prescribed in the manuals issued by this concern. In addition, circulars were issued by the committee to the cooperating laboratories to furnish specific methods for sampling, calibrating, and computing; and for the latter function specific peaks were suggested for each type of sample.

Test Results. Fifteen laboratories reported 3042 values by the mass spectrometer, 2842 of which values have been summarized in Table IV. This table includes one mixture (No. 20) that was obtained from plant operations, and is included only for the value of precision measurements. The difference between the above figures represents values obtained on other components not included in the scope of this article and values rejected (approximately 9%).

Table IV shows the summarized test results for each component according to the mixture containing the component. This permits ready observation of any change in accuracy and precision as affected by concentration of the component or presence of other components. A final summary of all analyses for a given component is shown and this includes the following measures:

$\Sigma\bar{r}/N$. The average probable error for an individual component occurring in various mixtures. This value was selected as most representative of a summarized measure of over-all precision, as approximately the same magnitude of precision was observed regardless of concentration of the component in the various mixtures.

$\Sigma|a-a_s|/N$. The average of the deviations from the synthetic value for a given component in the various mixtures. This is a summarized measure of over-all accuracy for all mixtures tested.

$\Sigma(a-a_s)/N$. The average of the deviations from the synthetic value for a given component in the various mixtures, giving weight to the sign, positive or negative with respect to the synthetic value. This indicates whether or not the method tends to report values greater or less than the *synthetic value.*

With regard to precision, the summarized results of Table IV for the mass spectrometer method show values of $\Sigma\bar{r}/N$ of 0.2 to 0.5 mole % for all components listed with the exception of isobutylene (2-methylpropene) and total *n*-butenes, in which cases the values are on the order of 1.0%. Although many laboratories reported values for 1-butene and 2-butenes, these are not included in Table IV, as it is generally known that the mass spectrometric method is not normally a suitable means for effecting such analyses.

With regard to accuracy, the values for $\Sigma|a-a_s|/N$ range from 0.1 to 0.7%. The accuracy of analysis for paraffins appears to be

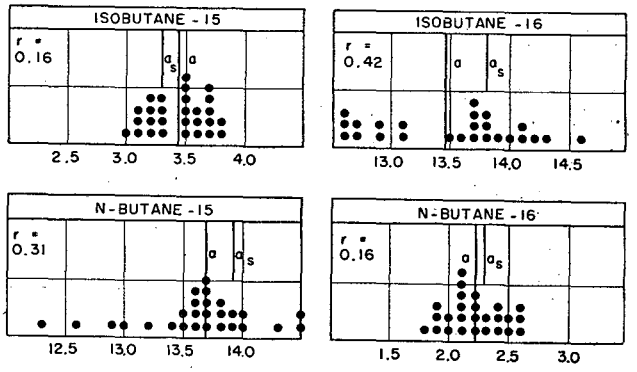

Figure 1. Distribution Plots of Individual Measurements by Mass Spectrometer Analysis

r. Probable error
a_s. Synthetic value
a. Average of all values
Number following component identifies mixture

Table III. Mass Spectrometer Analysis, Mixture 16

Laboratory No.	Isobutane	*n*-Butane	Total Butanes	1-Butene	2-Butenes	Total *n*-Butenes	Isobutylene	Total Butenes	Butadiene	Total C_4
1	14.1	1.8	15.9	50.1	20.5	70.6	11.7	82.3	1.8	100.0
	12.9	2.1	15.0	46.8	24.7	71.5	11.7	83.2	1.8	100.0
	12.5	2.1	14.6	45.6	27.6[a]	73.2	10.4	83.6	1.8	100.0
2	12.6	2.4	15.0	55.7	21.5	77.2	6.0	83.2	1.8	100.0
	12.7	2.5	15.2	55.4	21.7	77.1	6.0	83.1	1.7	100.0
	12.6	2.4	15.0	55.1	21.0	76.1	7.2	83.3	1.7	100.0
4	13.1	2.4	15.5	53.3	24.1	77.4	5.1	82.5	2.1	100.1[a]
	12.7	2.5	15.2	54.5	22.2	76.7	5.9	82.6	2.2	100.0
	12.6	2.6	15.2	54.0	23.3	77.3	5.4	82.7	2.2	100.1[a]
6	13.1	1.9	15.0	45.9	22.2	68.1	14.9	83.0	2.0	100.0
	12.9	2.0	14.9	47.8	22.3	70.1	13.0	83.1	2.0	100.0
7	14.3	2.1	16.4	45.1	33.7[a]	78.8	3.0	81.8	1.6	99.8[a]
	13.7	2.2	15.9	43.3	32.9[a]	76.2	6.0	82.2	1.7	99.8[a]
	13.8	2.2	16.0	42.8	34.1[a]	76.9	5.3	82.2	1.6	99.8[a]
8	13.9	2.3	16.2	51.7	22.8	74.5	7.5	82.0	1.8	100.0
	13.7	1.9	15.6	51.6	22.6	74.2	8.4	82.6	1.8	100.0
	13.7	2.0	15.7	55.1	17.2[a]	72.3	10.2	82.5	1.8	100.0
11	13.8	2.2	16.0	56.0	15.1[a]	71.1	10.9	82.0	2.0	100.0
	14.0	2.1	16.1	51.7	23.3	75.0	6.9	81.9	1.9	99.9[a]
	13.7	2.1	15.8	52.5	19.0[a]	71.5	10.6	82.1	2.0	99.9[a]
12	14.2	2.6	16.8	53.8	20.0	73.8	7.6	81.4	1.8	100.0
	14.6	2.6	17.2[a]	50.6	22.5	73.1	8.0	81.1	1.7	100.0
	14.1	2.2	16.3	51.3	23.0	74.3	7.5	81.8	1.9	100.0
13	13.6	2.1	15.7	46.9	23.5	70.4	11.8	82.2	1.8	99.7[a]
	13.5	2.3	15.8	47.9	24.2	72.1	10.3	82.4	1.8	100.0
	13.8	1.9	15.7	46.7	22.2	68.9	13.6	82.5	1.8	100.0
Synthetic value, mole %	13.80	2.29	16.09	52.34	21.79	74.13	7.98	82.11	1.80	100.00
Average value, mole %	13.47	2.21	15.62	50.43	22.51	73.78	8.65	82.43	1.85	100.00
Average minus synthetic	−0.33	−0.08	−0.47	−1.91	+0.72	−0.35	+0.67	+0.32	+0.05	0.00
Standard deviation	0.61	0.23	0.54	4.02	1.20	2.91	3.00	0.60	0.16	0.00
Probable error	0.42	0.16	0.42	2.76	0.83	2.00	2.06	0.41	0.11	0.00
No. of analyses used	26	26	25	26	19	26	26	26	26	18
No. of analyses rejected	0	0	1	0	7	0	0	0	0	8
No. of laboratories	9	9	9	9	9	9	9	9	9	9

[a] Values rejected in calculating average according to the Pierce-Chauvenet criterion.
Laboratory 7 reports 0.1% isopentane in each of two runs, 0.1% *n*-pentane in one run, and 0.1% propane in each of three runs.
Laboratory 11 reports 0.1% propane in each of two runs.
Laboratory 13 reports 0.3% propane in one run.

better than for olefins, except that very high accuracy was found for total butenes and for butadiene.

The lower degree of precision encountered with individual olefins as contrasted with the paraffins is the result of greater interferences on the mass spectrum peaks used for olefins. Mutual interference of individual butenes yields a compensating effect that results in more precise measurement of total butenes than is possible for individual butenes.

Lower degree of accuracy for olefins compared to paraffins, excepting total butenes and butadiene, is probably due in large part to greater effects of calibration drift for olefins.

Accuracy and precision values shown in Table IV apply only for the particular set of conditions chosen for the analyses. It is possible to obtain greater accuracy and precision for some components than indicated in Table IV by choosing selective systems of spectra, as is the case for most spectrographic procedures.

Table IV. Accuracy and Precision of Analyses by Mass Spectrometer Method

Component		Mixture Number 4	5	6	12	13	14	15	16	17	18	19	20	21	Summary	
Propene	n	....	9	....	....	23	....	....	....	....	....	....	21	21	N	74
	a_s	....	15.85	....	....	6.81	....	....	....	....	....	....	..	7.00	Range	7.0–15.8
	a	....	14.86	....	....	6.14	....	....	....	....	....	....	4.72	6.70	$\Sigma\lvert a-a_s\rvert/N$	0.6
	$a-a_s$	....	−0.99	....	....	−0.67	....	....	....	....	....	....	..	−0.30	$\Sigma(a-a_s)/N$	−0.6
	r	....	0.56	....	....	0.37	....	....	....	....	....	....	0.33	0.77	$\Sigma\bar{r}/N$	0.5
Propane	n	20	9	....	17	18	23	....	....	....	....	....	16	21	N	124
	a_s	2.54	2.01	....	0.74	10.39	6.62	....	....	....	....	....	..	10.55	Range	0.7–10.6
	a	2.57	2.13	....	0.95	10.12	6.25	....	....	....	....	....	0.16	10.18	$\Sigma\lvert a-a_s\rvert/N$	0.2
	$a-a_s$	+0.03	+0.12	....	+0.21	−0.27	−0.37	....	....	....	....	....	..	−0.37	$\Sigma(a-a_s)/N$	−0.2
	r	0.07	0.07	....	0.41	0.24	0.25	....	....	....	....	....	0.03	0.17	$\Sigma\bar{r}/N$	0.2
Total C_3	n	....	9	....	....	23	26	....	....	....	....	....	21	21	N	100
	a_s	....	17.86	....	....	17.20	6.62	....	....	....	....	....	..	17.55	Range	6.6–17.9
	a	....	16.99	....	....	16.06	6.40	....	....	....	....	....	4.95	16.88	$\Sigma\lvert a-a_s\rvert/N$	0.7
	$a-a_s$	....	−0.87	....	....	−1.14	−0.22	....	....	....	....	....	..	−0.67	$\Sigma(a-a_s)/N$	−0.7
	r	....	0.51	....	....	0.76	0.41	....	....	....	....	....	0.39	0.73	$\Sigma\bar{r}/N$	0.5
Isobutane	n	20	7	4	8	24	22	28	26	18	31	28	18	19	N	253
	a_s	11.55	18.00	1.04	0.00	14.10	40.75	3.30	13.80	5.26	44.62	5.22	..	13.25	Range	0.0–44.6
	a	11.17	18.58	0.84	0.19	14.49	40.95	3.44	13.47	5.26	44.80	5.02	0.94	14.00	$\Sigma\lvert a-a_s\rvert/N$	0.3
	$a-a_s$	−0.38	+0.58	−0.20	+0.19	+0.39	+0.20	+0.14	−0.33	0.00	+0.18	−0.20	..	+0.75	$\Sigma(a-a_s)/N$	+0.1
	r	0.25	0.33	0.19	....	0.93	0.44	0.16	0.42	0.36	0.49	0.23	0.07	0.36	$\Sigma\bar{r}/N$	0.4
n-Butane	n	18	9	4	6	21	26	26	26	19	31	27	16	21	N	251
	a_s	11.57	18.03	1.05	Trace	29.77	5.12	13.92	2.29	84.42	33.68	4.93	..	29.88	Range	1.0–84.4
	a	11.84	17.86	1.16	0.18	29.83	5.05	13.68	2.21	84.28	33.33	5.04	0.69	29.59	$\Sigma\lvert a-a_s\rvert/N$	0.2
	$a-a_s$	+0.27	−0.17	+0.11	+0.18	+0.06	−0.07	−0.24	−0.08	−0.14	−0.35	+0.11	..	−0.29	$\Sigma(a-a_s)/N$	−0.1
	r	0.14	0.20	0.09	....	0.52	0.18	0.31	0.16	0.34	0.45	0.21	0.04	0.24	$\Sigma\bar{r}/N$	0.3
Total butanes	n	18	7	4	14	22	25	24	25	16	30	28	21	21	N	255
	a_s	23.12	36.03	2.09	Trace	43.87	45.87	17.22	16.09	89.68	78.30	10.15	..	43.13	Range	0.0–89.7
	a	23.09	36.54	2.00	0.19	44.22	45.82	16.92	15.62	89.53	78.17	9.99	1.69	43.59	$\Sigma\lvert a-a_s\rvert/N$	0.2
	$a-a_s$	−0.03	+0.51	−0.09	+0.19	+0.35	−0.05	−0.30	−0.47	−0.15	−0.13	−0.16	..	+0.46	$\Sigma(a-a_s)/N$	0.0
	r	0.14	0.26	0.17	0.07	0.38	0.57	0.22	0.42	0.09	0.29	0.43	0.21	0.33	$\Sigma\bar{r}/N$	0.3
Total n-butenes	n	20	9	4	16	24	28	27	26	20	28	28	16	18	N	264
	a_s	24.27	14.16	0.08	98.76	14.51	32.45	57.44	74.13	8.50	11.36	43.28	..	14.52	Range	0.0–98.8
	a	22.55	14.86	0.00	98.26	14.56	32.60	56.02	73.78	8.35	10.86	42.72	2.82	14.29	$\Sigma\lvert a-a_s\rvert/N$	0.6
	$a-a_s$	−1.72	+0.70	−0.08	−0.50	+0.05	+0.15	−1.42	−0.35	−0.15	−0.50	−0.56	..	−0.23	$\Sigma(a-a_s)/N$	−0.5
	r	0.70	0.50	0.00	0.32	0.69	1.29	2.28	2.00	0.32	0.54	1.19	0.14	1.67	$\Sigma\bar{r}/N$	1.1
Isobutene	n	20	9	4	....	24	28	25	26	20	28	28	..	18	N	230
	a_s	44.52	7.91	10.96	....	6.13	5.23	7.06	7.98	0.89	10.34	46.57	..	6.10	Range	0.9–46.6
	a	46.47	7.80	11.16	....	6.29	4.73	8.12	8.65	1.17	10.98	47.21	..	6.48	$\Sigma\lvert a-a_s\rvert/N$	0.7
	$a-a_s$	+1.95	−0.11	+0.20	....	+0.16	−0.50	+1.06	+0.67	+0.28	+0.64	+0.64	..	+0.38	$\Sigma(a-a_s)/N$	+0.5
	r	0.75	0.50	0.18	....	0.70	0.90	1.53	2.06	0.38	0.52	1.42	..	1.32	$\Sigma\bar{r}/N$	1.0
Total butenes	n	18	9	4	17	20	24	25	26	17	30	27	..	21	N	238
	a_s	68.79	22.07	11.04	98.76	20.64	37.68	64.50	82.11	9.39	21.70	89.85	..	20.62	Range	9.4–98.8
	a	68.89	22.66	11.16	98.30	20.87	37.55	64.48	82.43	0.54	21.72	89.98	..	20.66	$\Sigma\lvert a-a_s\rvert/N$	0.2
	$a-a_s$	+0.10	+0.59	+0.12	−0.46	+0.23	−0.13	−0.02	+0.32	+0.15	+0.02	+0.13	..	+0.04	$\Sigma(a-a_s)/N$	0.0
	r	0.12	0.49	0.18	0.33	0.22	0.40	0.39	0.41	0.09	0.35	0.35	..	0.31	$\Sigma\bar{r}/N$	0.3
Butadiene	n	19	9	4	9	....	....	28	26	20	....	....	16	....	N	131
	a_s	2.47	20.06	85.79	0.20	....	....	18.28	1.80	0.93	....	....	..	....	Range	0.2–85.8
	a	2.44	20.04	85.59	0.14	....	....	18.16	1.85	0.92	....	....	1.56	....	$\Sigma\lvert a-a_s\rvert/N$	0.1
	$a-a_s$	−0.03	−0.02	−0.20	−0.06	....	....	−0.12	+0.05	−0.01	....	....	..	....	$\Sigma(a-a_s)/N$	0.0
	r	0.04	0.59	0.18	....	....	....	0.49	0.11	0.05	....	....	0.18	....	$\Sigma\bar{r}/N$	0.2
Total C_4	n	20	9	4	17	20	25	25	18	17	30	21	19	20	N	245
	a_s	94.39	78.16	98.92	98.96	64.51	83.55	100.00	100.00	100.00	100.00	100.00	..	63.75	Range	64–100
	a	94.34	78.48	98.76	98.53	65.27	83.50	99.99	100.00	100.00	99.93	100.00	5.78	64.31	$\Sigma\lvert a-a_s\rvert/N$	0.2
	$a-a_s$	−0.05	+0.32	−0.16	−0.43	+0.76	−0.05	−0.01	0.00	0.00	−0.07	0.00	..	+0.56	$\Sigma(a-a_s)/N$	+0.3
	r	0.18	0.56	0.23	0.38	0.30	0.60	0.04	0.00	0.00	0.23	0.00	0.51	0.32	$\Sigma\bar{r}/N$	0.1
Isopentane	n	15	9	3	17	22	23	....	....	....	....	....	..	18	N	107
	a_s	1.53	1.99	0.54	0.30	8.75	4.84	....	....	....	....	....	..	6.48	Range	0.3–8.6
	a	1.68	2.57	0.87	0.21	8.65	4.97	....	....	....	....	....	..	6.63	$\Sigma\lvert a-a_s\rvert/N$	0.2
	$a-a_s$	+0.15	+0.58	+0.33	−0.09	−0.10	+0.13	....	....	....	....	....	..	+0.15	$\Sigma(a-a_s)/N$	+0.1
	r	0.05	0.78	0.23	0.09	0.31	0.17	....	....	....	....	....	..	0.12	$\Sigma\bar{r}/N$	0.2
n-Pentane	n	14	9	3	6	22	24	....	....	....	....	....	..	20	N	98
	a_s	1.54	1.99	0.54	Trace	9.48	4.95	....	....	....	....	....	..	8.88	Range	0.0–9.5
	a	1.31	1.71	0.35	0.20	9.61	4.93	....	....	....	....	....	..	8.93	$\Sigma\lvert a-a_s\rvert/N$	0.1
	$a-a_s$	−0.23	−0.28	+0.19	+0.20	+0.13	−0.02	....	....	....	....	....	..	+0.05	$\Sigma(a-a_s)/N$	0.0
	r	0.03	0.21	0.22	....	0.38	0.30	....	....	....	....	....	..	0.19	$\Sigma\bar{r}/N$	0.2
Total C_5	n	20	9	4	17	22	22	....	....	....	....	....	..	18	N	112
	a_s	3.07	3.98	1.08	0.30	18.23	9.79	....	....	....	....	....	..	18.70	Range	0.3–18.3
	a	3.09	4.28	1.14	0.28	18.27	9.86	....	....	....	....	....	..	19.14	$\Sigma\lvert a-a_s\rvert/N$	0.1
	$a-a_s$	+0.02	+0.30	+0.06	−0.02	+0.04	+0.07	....	....	....	....	....	..	+0.44	$\Sigma(a-a_s)/N$	+0.1
	r	0.17	0.91	0.19	0.09	0.64	0.30	....	....	....	....	....	..	0.27	$\Sigma\bar{r}/N$	0.4

n = Number of all analyses included in statistical computations for a given component in individual mixtures.
N = Number of all analyses included in statistical computations for an individual component for all mixtures.
a = Grand average of all analyses included for a given component in individual mixtures (mole % except for samples 4, 5, 6, which are given in wt. %).
a_s = Synthetic value of component in a given mixture (mole % except for samples 4, 5, 6, which are given in wt. %).
$a-a_s$ = Grand average minus synthetic value for a given component.
r = Bessel's probable error.
$\Sigma\bar{r}/N$ = Average probable error for an individual component occurring in various mixtures.
$\Sigma\lvert a-a_s\rvert/N$ = Average of deviations from synthetic value for a given component in various mixtures.
$\Sigma(a-a_s)/N$ = Average of deviations from synthetic value for a given component in various mixtures giving weight to sign.

Table V. Accuracy and Precision of Analyses by Distillation Method

Method of Analysis	Mixture No.	N	Total C_3 a_s	a	$a - a_s$	r
2.1.81						
Without chaser or antecedent	12	30	0.74	0.13	−0.61	0.12
	13	31	17.20	16.54	−0.66	0.67
	14	29	6.62	6.06	−0.56	0.38
With chaser	12	25	0.74	0.02	−0.72	0.03
	13	32	17.20	16.41	−0.79	0.65
With antecedent	12	26	0.74	0.45	−0.29	0.20
	13	17	17.20	16.87	−0.33	0.44
With chaser and antecedent	12	29	0.74	0.52	−0.22	0.19
	13	24	17.20	16.53	−0.67	0.66
2.1.51.1	13	26	17.20	16.27	−0.92	0.50
	14	22	6.62	5.92	−0.70	0.41
2.1.51[a]	1	46	5.01	4.5	−0.5	0.4
	2	24	8.08	7.5	−0.6	0.3
	4	40	2.54	1.9	−0.6	0.2
2.1.51.1[a]	5	31	17.86	17.4	−0.5	0.3
2.1.81[a]	5	32	17.86	16.6	−1.3	0.7

Summary of Total C_3

		Range	$\Sigma\lvert a - a_s\rvert/N$	$\Sigma(a - a_s)/N$	$\Sigma\bar{r}/N$
2.1.81					
Without chaser or antecedent	90	0.7–17	0.6	−0.6	0.4
With chaser	57	0.7–17	0.8	−0.8	0.4
With antecedent	43	0.7–17	0.3	−0.3	0.3
With chaser and antecedent	53	0.7–17	0.4	−0.4	0.4
2.1.51.1	48	6.6–17	0.8	−0.8	0.5
2.1.51[a]	110	2.5–8	0.3	−0.3	0.3
2.1.51.1[a]	31	18	0.5	−0.5	0.3
2.1.81[a]	32	18	1.3	−1.3	0.7

[a] Values reported on wt. % basis.

Table VI. Accuracy and Precision of Analyses by Distillation Method

Method of Analysis	Mixture No.	N	Total C_4 a_s	a	$a - a_s$	r
2.1.81						
Without chaser or antecedent	12	30	98.96	99.44	+0.48	0.17
	13	31	64.51	64.99	+0.48	0.61
	14	29	83.55	84.15	+0.60	0.32
With chaser	12	30	98.96	99.52	+0.56	0.21
	13	30	64.51	64.92	+0.41	0.32
With antecedent	12	26	98.96	99.04	+0.08	0.24
	13	18	64.51	64.86	+0.35	0.47
With chaser and antecedent	12	29	98.96	99.05	+0.09	0.28
	13	21	64.51	64.82	+0.31	0.44
2.1.51.1	13	25	64.51	65.06	+0.55	0.50
	14	22	83.55	84.22	+0.67	0.49
2.1.51[a]	1	46	89.95	90.6	+0.7	0.5
	2	24	87.89	88.5	+0.6	0.4
2.1.51.1[a]	4	47	94.39	95.0	+0.6	0.5
	5	31	78.16	78.9	+0.7	0.7
2.1.81[a]	4	41	94.39	95.2	+0.8	0.4
	5	32	78.16	79.4	+1.2	0.7

Summary of Total C_4

		Range	$\Sigma\lvert a - a_s\rvert/N$	$\Sigma(a - a_s)/N$	$\Sigma\bar{r}/N$
2.1.81					
Without chaser or antecedent	90	64–99	0.5	+0.5	0.4
With chaser	60	64–99	0.5	+0.5	0.3
With antecedent	44	64–99	0.2	+0.2	0.3
With chaser and antecedent	50	64–99	0.2	+0.2	0.4
2.1.51.1	47	64–84	0.6	+0.6	0.5
2.1.51[a]	70	88–90	0.7	+0.7	0.5
2.1.51.1[a]	78	78–94	0.6	+0.6	0.6
2.1.81[a]	73	78–94	1.0	+1.0	0.5

[a] Values reported on wt. % basis.

Developments in instrumentation, since the time of the test program, will permit of analyses with less error.

ANALYSES BY DISTILLATION

Analytical Methods. The Podbielniak Hyd-Robot distillation column (*9*) was used for all low temperature fractional distillations. Depending upon the sample mixture and further analysis of the distilled fractions, variations in the distillation procedure were employed and are referred to by the Office of Rubber Reserve butadiene laboratory manual designation.

METHOD 2.1.51.1. Analysis of selected fractions of hydrocarbon mixtures consisting principally of C_4 hydrocarbons. The C_4 fraction is isolated from the lower and higher boiling contaminants and is separated in such a manner that isobutane (2-methylpropane) and *n*-butane will be collected in separate fractions. A chaser, *n*-heptane, cyclohexane, or *n*-hexane, is employed in this procedure.

In this method the cut point between C_3 and C_4 is taken at −27° C., between the isobutane-containing and the *n*-butane-containing C_4 fractions at about −5.5° C., and between C_4 and C_5 at −10° C. (at 300 mm. distillation pressure).

METHOD 2.1.51 is the same as 2.1.51.1 except that an ethyl alcohol chaser is used.

METHOD 2.1.81 is a modification of 2.1.51.1, particularly to provide a C_4 cut free of C_3 and C_5 impurities, so that subsequent spectrophotometric methods can be applied. In this case, C_3 is separated from C_4 at −17.5° C. to prevent the inclusion in the C_4 fraction of any methylacetylene present. The C_4 fraction is taken overhead at a faster rate than in method 2.1.51.1. The C_4-C_5 cut is made at −10° C. at 300 mm. In order to determine the effect of a chaser and/or an antecedent upon the distillation, various combinations were employed with this method.

Test Results. Thirty-two laboratories reported 1716 values by straight distillation analysis, 1655 of which values have been summarized in Tables V, VI, and VII; 61 values were rejected (approximately 4%).

Table V lists the analyses for total C_3. One of the most obvious conclusions is that all of the distillation procedures employed tend to yield low results; the accuracy averages about −0.6 mole %. Precision is good; the probable error averages ±0.4%. There is a trend of magnitude of probable error with concentration of the component.

Analyses for total C_4, listed in Table VI, show that the distillation procedures tend to yield high results; the accuracy averages about +0.4 mole %. Precision is also good for the total C_4 determination, with the probable error averaging ±0.4%. No trend of magnitude of accuracy or precision is noted with concentration changes, but there were not any low C_4-content samples prepared as synthetic mixtures.

In Table VII the data for isopentane (2-methylbutane) show that the results are slightly high, about +0.2 mole %, compared with the synthesis values, whereas for *n*-pentane the synthetic values are checked very closely, on the average. Accordingly, the total C_5, sum of the iso- and *n*-pentanes, would be expected to be high by +0.2%.

The actual results confirm this. Thus the distillation procedures are in error for C_4 and C_5 on the high side (+0.4 and +0.2%, respectively) in an amount equal to the error for C_3, on the low side (−0.6%). This is a generalized conclusion; variations of the distillation procedures employed in the test program

indicated some slightly beneficial effect upon accuracy for the use of an antecedent, as would be expected, but otherwise the various modifications of procedures did not effect significant improvements.

Precision of analysis for isopentane, *n*-pentane, and total C_5 is very good, the average probable error being $\pm 0.4\%$; one case involving the use of method 2.1.81 (no chaser or antecedent) showed a value for $\Sigma\bar{r}/N$ of $\pm 0.6\%$.

Subsequent to this test program Starr, Anderson, and Davidson (*10*, *11*) found that higher charging and distillation rates than specified by the butadiene laboratory manual could be employed with no sacrifice in accuracy. It was also found from a study of contamination of distilled fractions that cut points should be raised (*11*). Such modifications should result in greater accuracy for the distillation method than was obtained in the test program reported herein.

ANALYSES BY CHEMICAL METHODS

Analytical Methods. A variety of chemical methods was employed to analyze the synthetic test mixtures, either directly or by application to fractions segregated by distillation. In the latter case the errors of analysis are due to both the chemical and the distillation methods. It was unfortunate that only a small number of the methods were employed by a sufficient number of laboratories to yield enough data to warrant statistical treatment and inclusion in this study for comparative purposes.

The methods that warranted study were applied directly to samples that were not segregated by distillation, and the errors determined represent those attributable only to the specific chemical method under discussion.

METHOD 2.1.52. Direct determination of isobutene (2-methylpropene) by hydrochlorination when this hydrocarbon is present with paraffin, olefin, diolefin, and acetylene hydrocarbons.

METHOD 2.1.53.2. Determination of total unsaturates in any concentration in C_4 hydrocarbon fractions (but may be applied to a large number of other gas mixtures). The gas mixture is passed into 65% sulfuric acid until almost constant residual volume is obtained (this provides an analysis for isobutene); then the mixture is passed into 87% sulfuric acid until constant absorption per pass is obtained. The higher concentration acid removes the *n*-butenes.

METHOD 2.1.54T is another method for the determination of isobutene, and was applied to samples that contained essentially all C_4 hydrocarbons. Isobutene reacts with a mercuric nitrate solution of controlled pH. The complex formed is rendered insoluble by heating to 90° C.; after removal from the solution this complex is dissolved in nitric acid, and the mercury in solution is determined by titration with potassium thiocyanate.

METHOD 2.1.53.3. Determination of total unsaturates in C_4 hydrocarbon mixtures by selective absorption of the unsaturates in a slightly acidic solution of silver and mercuric nitrates.

METHOD 2.1.1.1. Reaction of 1,3-butadiene with molten maleic anhydride, employing gravimetric technique.

METHOD 2.1.1.2. Reaction of 1,3-butadiene with molten maleic anhydride, employing volumetric measurement of residual gas (impurities in the butadiene).

METHOD 2.1.1.9. Reaction of 1,3-butadiene with molten maleic anhydride and volumetric measurement of residual gas. This method differs from 2.1.1.2 in that after the maleic anhydride is brought into contact with the butadiene-containing gas, the maleic anhydride is flushed with carbon dioxide to remove the physically adsorbed unreacted gases. The carbon dioxide is removed by potassium hydroxide before the residual gas is measured. This method utilizes the Koppers-Hinckley apparatus described in the butadiene laboratory manual.

KOPPERS-HINCKLEY-TORRANCE modification of method 2.1.1.9 with respect to apparatus.

Test Results. In Tables VIII, IX, and X are reported 582 analyses which are representative of the eight chemical methods that were considered to have been sufficiently tested. Results

Table VII. Accuracy and Precision of Analyses by Distillation Method

Isopentane

Method of Analysis	Mixture No.	N	a_s	a	$a - a_s$	r
2.1.51.1	13	22	8.75	8.95	+0.20	0.39
	14	21	4.84	5.05	+0.21	0.25
2.1.81	13	33	8.75	9.08	+0.33	0.56
	14	26	4.84	4.77	−0.07	0.28

Summary of Isopentane

		Range	$\Sigma\lvert a - a_s\rvert/N$	$\Sigma(a - a_s)/N$	$\Sigma\bar{r}/N$
2.1.51.1	43	4–9	0.2	+0.2	0.3
2.1.81	59	4–9	0.2	+0.2	0.4

n-Pentane

			a_s	a	$a - a_s$	r
2.1.51.1	13	21	9.48	9.67	+0.19	0.32
	14	24	4.95	4.83	−0.12	0.36
2.1.81	13	33	9.48	9.57	+0.09	0.65
	14	26	4.95	4.88	−0.07	0.25

Summary of *n*-Pentane

		Range	$\Sigma\lvert a - a_s\rvert/N$	$\Sigma(a - a_s)/N$	$\Sigma\bar{r}/N$
2.1.51.1	45	5–10	0.2	0.0	0.3
2.1.81	59	5–10	0.1	0.0	0.5

Total C_5

			a_s	a	$a - a_s$	r
2.1.81						
Without chaser or antecedent	12	30	0.30	0.38	+0.08	0.15
	13	32	18.23	18.54	+0.31	1.00
With chaser	12	30	0.30	0.34	+0.04	0.14
	13	31	18.23	18.73	+0.50	0.59
With antecedent	12	26	0.30	0.48	+0.18	0.17
	13	17	18.23	18.38	+0.15	0.50
With chaser and antecedent	12	29	0.30	0.38	+0.08	0.16
	13	18	18.23	18.57	+0.34	0.21
2.1.51.1	12	16	0.30	0.27	−0.30	0.09
	13	22	18.23	19.01	+0.78	0.33
2.1.51[a]	1	46	5.04	4.9	−0.1	0.4
	2	24	4.03	4.0	0.0	0.3
2.1.51.1[a]	4	44	3.07	3.1	0.0	0.5
	5	31	3.98	3.8	−0.2	0.4
2.1.81[a]	5	32	3.98	4.0	0.0	0.3
	6	35	1.08	0.9	−0.2	0.3

Summary of Total C_5

		Range	$\Sigma\lvert a - a_s\rvert/N$	$\Sigma(a - a_s)/N$	$\Sigma\bar{r}/N$
2.1.81					
Without chaser or antecedent	62	0.3–18	0.2	+0.2	0.6
With chaser	61	0.3–18	0.3	+0.3	0.4
With antecedent	43	0.3–18	0.2	+0.2	0.3
With chaser and antecedent	57	0.3–18	0.2	+0.2	0.2
2.1.51.1	38	0.3–18	0.6	+0.3	0.2
2.1.51[a]	70	4–5	0.1	−0.1	0.4
2.1.51.1[a]	75	3–4	0.1	−0.1	0.5
2.1.81[a]	67	1–4	0.1	−0.1	0.3

[a] Values reported on wt. % basis.

by three methods for isobutene are summarized in Table VIII. The data appear erratic, although in general all methods tend to give high results for isobutene. The most consistent data were furnished by method 2.1.52; and it appears that this method could be depended upon to give an accuracy of about 0.5 mole %, and a probable error of ±0.5%.

Table IX furnishes data for the determination of total unsaturates by only one method. This method, when applied in the first phase of the program (mixtures 5 and 6), gave results that averaged about 1% low, and a precision of ±0.7%. It is considered that in the last phase of the program (mixtures 13 to 20) the additional experience of the laboratories yielded a more representative evaluation of the method. In this case the results averaged about 0.2% high, although there was still a lack of consistency in accuracy. Precision measurements were more consistent, and the probable error averaged ±0.4%.

Data given in Table X for the analysis of 1,3-butadiene show that the early methods (both gravimetric method 2.1.1.1 and volumetric method 2.1.1.2) reported values too high (0.7 to 1.4%). This was attributed to retention of hydrocarbons other than 1,3-butadiene on the maleic anhydride reagent. In the later methods (2.1.1.9 and its modifications), this factor was minimized by flushing the unreacted but retained hydrocarbons from the maleic anhydride. In both these methods the accuracy (−0.2%) and precision (±0.3%) were excellent. The data reported are for concentrations of 1,3-butadiene from 1 to 18 mole %. Starr and Ratcliff (*12*) reported a high degree of accuracy for the gas flushing methods on samples containing 98% 1,3-butadiene, as evidenced by the concordance of results with values obtained at the National Bureau of Standards by the freezing point method.

Table VIII. Accuracy and Precision of Analyses by Chemical Methods

Method of Analysis	Mixture No.	N	a_s	a	$a - a_s$	r
			Isobutene			
2.1.52 (HCl)	15	16	7.06	7.65	+0.59	0.57
	16	15	7.98	8.38	+0.40	0.31
	17	14	0.89	1.18	+0.29	0.28
	18	13	10.34	10.49	+0.15	0.15
	19	14	46.57	46.08	−0.49	0.47
2.1.53.2 (65% H_2SO_4)	15	20	7.06	8.28	+1.22	0.47
	16	25	7.98	8.62	+0.64	0.76
	17	23	0.89	1.18	+0.29	0.24
	18	17	10.34	10.22	−0.12	0.13
	19	24	46.57	46.67	+0.10	0.90
2.1.54T [$Hg(NO_3)_2$]	15	11	7.06	5.21	−1.85	1.94
	16	10	7.98	7.31	−0.67	0.96
	17	9	0.89	1.16	+0.27	0.07
	18	10	10.34	10.42	+0.08	0.50
	19	8	46.57	46.61	+0.04	0.83

Summary of Isobutene

	Range	$\Sigma\lvert a - a_s\rvert/N$	$\Sigma(a - a_s)/N$	$\Sigma r/N$
2.1.52 (72)	0.9–47	0.4	+0.2	0.4
2.1.53.2 (109)	0.9–47	0.5	+0.4	0.5
2.1.54T (48)	0.9–47	0.6	−0.5	0.9

Table IX. Accuracy and Precision of Analyses by Chemical Methods

Method of Analysis	Mixture No.	N	a_s	a	$a - a_s$	r
			Total Unsaturates			
2.1.53.3	13	28	27.45	28.44	+0.99	0.82
	14	30	37.68	37.87	+0.19	0.35
	15	28	82.78	82.66	−0.12	0.40
	16	31	83.91	83.62	−0.29	0.52
	17	28	10.32	10.81	+0.49	0.27
	18	26	21.70	21.64	−0.06	0.28
	19	32	89.85	89.81	−0.04	0.45
	20	15	...	5.55	....	0.15
2.1.53.3[a]	5	37	57.98	59.4	−1.4	1.0
	6	38	96.83	97.5	−0.7	0.5

Summary of Total Unsaturates

	Range	$\Sigma\lvert a - a_s\rvert/N$	$\Sigma(a - a_s)/N$	$\Sigma r/N$
2.1.53.3 (218)	10–90	0.3	+0.2	0.4
2.1.53.3[a] (75)	58–97	1.0	−1.0	0.7

[a] Wt. % basis.

Table X. Accuracy and Precision of Analyses by Chemical Methods

Method of Analysis	Mixture No.	N	a_s	a	$a - a_s$	r
			Butadiene			
2.1.1.9	15	11	18.28	18.16	−0.12	0.34
	16	9	1.80	1.69	−0.11	0.24
	17	9	0.93	0.71	−0.22	0.33
2.1.1.9 (Torrance modification)	15	6	18.28	18.07	−0.21	0.04
	16	9	1.80	1.69	−0.11	0.14
	17	9	0.93	0.68	−0.25	0.28
2.1.1.1[a]	3	18	77.62	78.3	+0.7	0.5
2.1.1.2[a]	3	19	77.62	79.0	+1.4	0.7

Summary of Butadiene

	Range	$\Sigma\lvert a - a_s\rvert/N$	$\Sigma(a - a_s)/N$	$\Sigma r/N$
2.1.1.9 (29)	0.9–18	0.2	−0.2	0.3
2.1.1.9 (Torrance modification) (24)	0.9–18	0.2	−0.2	0.2
2.1.1.1[a] (18)	78	0.7	+0.7	0.5
2.1.1.2[a] (19)	78	1.4	+1.4	0.7

[a] Wt. % basis.

ANALYSES BY INFRARED SPECTROSCOPIC METHOD

Analytical Method. Where infrared analyses were made alone, and not in combination with other procedures, only one analytical procedure was employed, butadiene laboratory manual method 2.1.94T. This is a procedure for analyzing a seven-component C_4 fraction consisting of *n*-butane, isobutane, 1-butene, *cis*-2-butene, *trans*-2-butene, isobutene, and 1,3-butadiene. This procedure gives complete analyses but suffers a lack of precision and accuracy for some of the components in the C_4 fraction.

Test Results. In Table XI are given summarized accuracy and precision measurements representing 888 analyses for seven C_4 hydrocarbon components contained in a variety of mixtures. A total of 922 analyses was reported in the program but 4% of them were rejected.

These results show a lack of resolution of iso- and *n*-butane when they occur in relatively high concentrations. Values for isobutane are indicated to be as much as 0.9% high, whereas values for *n*-butane are as much as 1.3% low. A corresponding lack of precision, 0.5 to 1.5% probable error, is indicated for these components. This is an example of what might be expected in the analysis of a complex mixture by infrared absorptiometry. Unavoidable interferences often occur between compounds, with the result that the absorption due to the particular component being determined will emerge as a relatively small difference between large values. This, of course, means that those random

errors due to readings, etc., will have a more pronounced effect and thus a lower precision will be found in the analysis. Likewise deviations from linearity and drifts in calibration will be less easily eliminated and these will lead to greater systematic errors, $\Sigma(a-a_s)/N$. For example, it will be observed that the analysis for *n*-butane shows rather large systematic and probable errors. This is unavoidable in a system which includes all the C_4's, for *n*-butane must then be determined at a spectral position where its absorption is not very intense. It does not follow that *n*-butane must always suffer from such poor precision and accuracy. For example, in a system of isobutane and *n*-butane the spectral position 10.4 microns would be chosen for the latter rather than 13.3 microns as used in the total C_4 scheme. In this case *n*-butane would show a stronger absorption with consequently greater precision and accuracy.

The summarized results for the other components listed in Table XI show that this infrared procedure provides on the average a reasonably satisfactory degree of accuracy (within 0.5% of the true value). However, observation of the values for the various mixtures leads to the conclusion that there was considerable individual variation in accuracy experienced. The same can be said for the precision values. The precision, on the average, was from ±0.4 to ±1.3% probable error. Some trend of accuracy and precision with concentration changes may be noted in the results for certain of the C_4 components.

ANALYSES BY ULTRAVIOLET SPECTROSCOPIC METHOD

Analytical Method. The ultraviolet absorption spectra measurement procedure, butadiene laboratory manual method 2.1.85, is intended for the determination of 1,3-butadiene in mixtures of C_4 and lighter hydrocarbons that contain less than 0.5 to 2.0 mole % vinyl acetylene and 1,2-butadiene.

Test Results. Table XII lists 182 analyses for 1,3-butadiene in a variety of mixtures containing this hydrocarbon in concentrations up to 86%. Analyses are reported for some synthetic mixtures known to be free of 1,3-butadiene. In this special case the ultraviolet procedure indicates traces of 1,3-butadiene (less than 0.1%). Accuracy of analysis for mixtures containing from 1 to 86% 1,3-butadiene is excellent (+0.1% on the average). Precision of analysis is dependent upon concentration of 1,3-butadiene, varying from ±0.1% probable error for a 1% concentration of this hydrocarbon, to ±1.2% for 86% concentration.

ANALYSES BY COMBINATION METHODS

Infrared Plus Ultraviolet. Method 2.1.90 is intended for the analysis of C_4 fraction components; iso- and *n*-butane and individual butenes are determined by infrared, while 1,3-butadiene is determined by ultraviolet. Reference to Table XIII shows that accuracy for both iso- and *n*-butane is improved, as expected. For the samples containing the largest amounts of total butanes, the accuracy was lower, as was also the case when method 2.1.94T was used. However, contrary to expectations, the accuracy of analysis for the individual C_4 unsaturates was not so good as experienced with method 2.1.94T. The precision of analysis, on the average, was about the same with the straight infrared (2.1.94T) as with the combination infrared and ultraviolet (2.1.90) methods.

Distillation Plus Chemical. Data are given in Tables XIV and XV for combinations of distillation and various chemical methods of analysis. In addition to method 2.1.53.3, previously described, methods 2.1.57T and 2.1.53 were utilized in the chemical test phase of this part of the program. Method 2.1.57T involves the determination of unsaturates by blending the sample with air and removing the unsaturates with a saturated bromine water solution. Method 2.1.53 measures unsaturates by reaction with Hofmann solution, a mixture of mercuric and potassium nitrates and nitric acid.

Because distillation yields low values for total C_3 and high values for total C_4 and C_5, the distillation procedure exerts an important influence on the combination analysis. It was shown that total C_3 averages about 0.6 mole % low by distillation. When a C_3 fraction is analyzed for unsaturates by chemical methods (Table XIV) the values found for both propene and pro-

Table XI. Accuracy and Precision of Analyses by Infrared Method

(Procedure 2.1.94T)

Mixture No.	N	a_s	a	$a-a_s$	r	Mixture No.	N	a_s	a	$a-a_s$	r
		Isobutane						Total *n*-Butenes			
15	17	3.30	3.18	−0.12	0.55	16	19	74.13	73.85	−0.28	1.37
16	19	13.80	14.23	+0.43	0.96	17	17	8.50	9.01	+0.51	0.59
17	18	5.26	5.41	+0.15	0.61	19	16	43.28	43.49	+0.21	0.88
18	20	44.62	45.48	+0.86	1.54						
19	16	5.22	5.16	−0.06	0.53						
		n-Butane						Isobutene			
15	18	13.92	13.68	−0.24	0.36	15	16	7.06	7.74	+0.68	0.71
16	18	2.29	1.77	−0.52	0.24	16	19	7.98	8.02	+0.04	0.71
17	19	84.42	83.38	−1.04	1.00	17	18	0.89	0.93	+0.04	0.31
18	20	33.68	32.35	−1.33	1.45	18	20	10.34	10.15	−0.19	0.44
19	14	4.93	4.71	−0.22	0.16	19	16	46.57	46.59	+0.02	0.62
		Total Butanes						Total Butenes			
15	16	17.22	16.99	−0.23	0.66	15	15	64.50	65.01	+0.51	1.44
16	19	16.09	16.13	+0.04	1.04	16	19	82.11	81.87	−0.24	1.07
17	17	89.68	89.18	−0.50	0.51	17	19	9.39	10.35	+0.96	0.85
18	20	78.30	77.83	−0.47	0.58	18	18	21.70	21.99	+0.29	0.62
19	16	10.15	9.81	−0.34	0.67	19	16	89.85	90.14	+0.29	0.69
		1-Butene						Butadiene			
15	18	16.72	17.33	+0.61	0.68	15	22	18.28	18.12	−0.16	0.89
16	19	52.34	51.93	−0.41	0.77	16	22	1.80	2.04	+0.24	0.35
17	19	6.23	6.63	+0.40	0.40	17	22	0.93	0.96	+0.03	0.26
18	20	6.23	6.65	+0.42	0.60	19	12	0.00	0.02	+0.02	0.03
19	14	33.86	34.03	+0.17	0.34						
		cis-2-Butene						Total Unsaturates			
15	16	...	39.31	....	4.02	15	15	82.78	82.94	+0.16	0.66
16	16	...	20.87	....	1.49	16	15	83.91	83.84	−0.07	1.16
17	16	...	2.29	....	0.31	17	13	10.32	11.04	+0.72	0.40
18	20	...	5.00	....	0.26	18	14	21.70	22.01	+0.31	0.64
19	16	...	9.03	....	0.68	19	15	89.85	90.12	+0.27	0.66
		trans-2-Butene									
15	16	...	1.20	....	1.31						
16	16	...	0.88	....	0.92						
17	9	...	0.00	....	0.00						
18	12	...	0.00	....	0.00						
19	16	...	0.45	....	0.51						

Summary by Component

	N	Range	$\Sigma\lvert a-a_s\rvert/N$	$\Sigma(a-a_s)/N$	$\Sigma r/N$
Isobutane	90	3-45	0.3	+0.3	0.9
n-Butane	89	2-84	0.7	−0.7	0.7
Total butanes	88	10-90	0.3	−0.3	0.7
1-Butene	90	6-52	0.4	+0.2	0.6
cis-2-Butene	84	...	...	...	1.3
trans-2-Butene	69	...	...	...	0.6
Total *n*-butenes	52	8-74	0.3	+0.1	1.0
Isobutene	89	1-46	0.2	+0.1	0.6
Total butenes	87	9-90	0.5	+0.4	0.9
Butadiene	78	0-18	0.1	0.0	0.4
Total unsaturates	72	10-90	0.3	+0.3	0.7

pane are also low; those for propane (a difference figure) are the lowest (−0.6 mole %). This would be expected because propane, which boils higher than propene, acts as a chaser for propene. There were no significant differences in accuracy and precision for the three chemical methods tested.

Table XII. Accuracy and Precision of Analyses by Ultraviolet Method

(Procedure 2.1.85)

Mixture No.	N	a_s	a	$a - a_s$	r
		Butadiene			
15	25	18.28	18.62	+0.34	0.91
16	25	1.80	1.95	+0.15	0.16
17	24	0.93	0.87	−0.06	0.08
18	15	0.00	0.02	+0.02	0.03
19	15	0.00	0.07	+0.07	0.03
4	27[a]	2.47	2.6	+0.1	0.1
5	19[a]	20.06	20.4	+0.3	0.4
6	30[a]	85.79	85.5	−0.3	1.2

Summary of Butadiene

	Range	$\Sigma\lvert a - a_s\rvert/N$	$\Sigma(a - a_s)/N$	$\Sigma\bar{r}/N$
104	0–18	0.1	+0.1	0.3
76[a]	2–86	0.2	0.0	0.6

[a] Wt. % basis.

Table XIII. Accuracy and Precision of Analyses by Infrared Plus Ultraviolet Methods

(Procedure 2.1.90)

Mixture No.	N	a_s	a	$a - a_s$	r	Mixture No.	N	a_s	a	$a - a_s$	r
		Isobutene						*trans*-2-Butene			
15	15	3.30	3.13	−0.17	0.34	15	15	...	0.93	....	0.84
16	17	13.80	13.81	+0.01	0.37	16	15	...	0.43	....	0.31
17	15	5.26	5.17	−0.09	0.38	17	15	...	0.66	....	0.63
18	14	44.62	45.22	+0.60	1.02	18	14	...	0.21	....	0.21
19	15	5.22	5.13	−0.09	0.34	19	15	...	0.65	....	0.55
		n-Butane						*n*-Butenes			
15	15	13.92	13.75	−0.17	0.33	16	18	74.13	73.49	−0.64	1.32
16	18	2.29	2.22	−0.08	0.58	17	15	8.50	9.23	+0.73	0.90
17	15	84.42	83.57	−0.85	1.11	19	15	43.28	41.91	−1.37	1.19
18	14	33.68	32.69	−0.99	1.68						
19	15	4.93	5.07	+0.14	0.28						
		Total Butanes						Isobutene			
15	15	17.22	16.87	−0.35	0.39	15	15	7.06	6.98	−0.08	0.52
16	18	16.09	16.15	+0.06	0.97	16	18	7.98	8.44	+0.46	0.32
17	15	89.68	88.74	−0.94	0.96	17	12	0.89	0.98	+0.09	0.15
18	14	78.30	77.91	−0.39	0.93	18	14	10.34	10.49	+0.15	0.30
19	15	10.15	10.20	+0.05	0.57	19	15	46.57	47.69	+1.12	0.66
						4[a]	6	44.52	45.4	+0.9	0.6
						5[a]	2	7.91	6.7	−1.2	..
						6[a]	9	10.96	9.3	−1.7	1.8
		1-Butene						Total Butenes			
15	14	16.72	17.36	+0.64	0.44	15	15	64.50	64.70	+0.20	0.48
16	18	52.34	51.59	−0.75	1.50	16	18	82.11	82.01	−0.10	1.14
17	15	6.23	6.28	+0.05	0.42	17	15	9.39	10.44	+1.05	0.98
18	14	6.23	6.16	−0.07	0.43	18	14	21.70	21.51	−0.19	1.28
19	15	33.86	32.53	−1.33	1.14	19	15	89.85	89.74	−0.11	0.54
		cis-2-Butene						Total Unsaturates			
15	14	...	39.09	....	3.02	15	15	82.78	83.14	+0.36	0.42
16	17	...	21.51	....	0.50	16	15	83.91	83.54	−0.37	0.90
17	15	...	2.31	....	0.32	17	15	10.32	11.26	+0.94	0.96
18	14	...	5.15	....	0.47	18	14	21.70	22.02	+0.32	0.94
19	15	...	8.73	....	0.76	19	15	89.85	89.80	−0.05	0.56

Summarized Results by Component

	N	Range	$\Sigma\lvert a - a_s\rvert/N$	$\Sigma(a - a_s)/N$	$\Sigma\bar{r}/N$
Isobutane	76	3–45	0.2	0.0	0.5
n-Butane	77	2–84	0.4	−0.4	0.8
Total butanes	77	10–90	0.4	−0.3	0.8
1-Butene	76	6–52	0.6	−0.3	0.8
cis-2-Butene	75	2–39	...	...	1.0
trans-2-Butene	74	0.2–0.9	...	...	0.5
n-Butenes	48	9–73	0.9	−0.4	1.1
Isobutene	74	1–48	0.4	+0.4	0.4
Isobutene[a]	17	7–45	1.4	−0.7	1.3
Total butenes	77	10–90	0.3	+0.2	0.9
Total unsaturates	74	11–90	0.5	+0.2	0.8

[a] Wt. % basis.

In analyzing C_4 components by distillation and chemical methods the procedure involves, first, segregating the C_4 fraction into two cuts by distillation. The lower boiling cut is analyzed by chemical methods for total unsaturates; the residue is isobutane. The higher boiling C_4 cut is also analyzed for total unsaturates to yield *n*-butane by difference. The difference between total unsaturates and isobutene, analyzing both C_4 cuts, represents *n*-butenes, except where butadiene is present. Obviously, there are numerous variables involved in obtaining the individual C_4 components by the combination of distillation and chemical methods, including the influence of butadiene on the precise segregation of cuts to provide the assay for iso- and *n*-butane (1,3-butadiene boils close to the cut point employed to segregate the two C_4 fractions).

In Table XV, the results of analyses for iso- and *n*-butane are shown. Where C_3 is present, the results for both iso- and *n*-butane tend to be high compared to synthetic values, in line with the influence of the distillation procedure (Table VI) and the lesser influence of the chemical test (Table IX). As was expected, the data for the lower boiling isobutane showed somewhat higher results than for the higher boiling *n*-butane. For such samples that contained no C_3, the iso- and *n*-butane values are somewhat low and reflect the influence of the high values that are obtained for the total unsaturates analyses. In this case, with the influence of C_3 lacking, the concordance of accuracy values for iso- and *n*-butane indicates that the cut point employed in the distillation procedure (2.1.51.1) is satisfactory. In the case of sample 17, which contains the highest content of total butanes, the lowest degrees of accuracy and precision were obtained; this is attributed to absorption of the saturates in the chemical reagent (silver–mercuric nitrate), and this is in line with the tendency of this chemical method to yield high results for unsaturates (Table IX). The reproducibility of the determinations for both iso- and *n*-butane is on the order of ±0.7 mole %. The influence of 1,3-butadiene in concentrations up to 20% on the separation of iso- and *n*-butane is not marked.

The test program of the Committee on Butadiene Specifications and Methods of Analysis involved numerous other analytical tests, but the data presented herein reflect the salient objectives and accomplishments of the program.

CONCLUSIONS

Although in this paper no attempt has been made to show the individual results of the more than 8000 analyses obtained in the test program, the individual laboratories were able to check their own analyses with excellent precision, by any of the standard methods employed. On the average, a given laboratory can be expected to make determinations for most light hydrocarbon components of a gas within a probable error of ±0.2 to 0.3 mole %. Furthermore, the extent to which laboratories check each other has been

found to be within values two to three times the probable error for a given laboratory.

The data presented in this article show that most of the standard methods have certain unique advantages. The mass spectrometer method appears to be best for the determination of individual paraffin hydrocarbons, total butenes, and butadiene in high concentrations. The ultraviolet absorption spectra method is advantageous for the analysis of butadiene in low concentrations. Infrared absorption spectra measurements are best for the analysis of isobutene and the individual *n*-butenes. Distillation and mass spectrometer methods show about the same accuracy and precision for the analysis of total C_3, total C_4, and total C_5. The distillation method is a necessity when it is desired to separate a complex mixture so that the infrared method can be applied to the analysis of the individual butenes. Chemical methods evidenced little, if any, advantage for the analysis of specific olefin hydrocarbons; the chemical method for total unsaturates has advantage mainly for speed.

In general, methods are available for determination of the main light hydrocarbon components of gas mixtures with an accuracy of 0.3 mole %, and a precision of 0.3 mole % expressed as probable error. Improvements in several of the methods and apparatus since the time of the test program, and variations of methods to apply more specifically to a desired component, indicate that the above values of accuracy and precision can be bettered.

The test program conducted by the Committee on Butadiene Specifications and Methods of Analysis has proved of inestimable value in standardizing methods of analysis for light hydrocarbons, and for bringing factual data to bear on the accuracy and precision of such analyses. This latter information should be of great value to all engaged in the design and operation of plants utilizing these hydrocarbons.

Table XIV. Accuracy and Precision of Analyses by Distillation Plus Chemical Methods

Method of Analysis: Dist. + Chem. Method No.	Mixture No.	N	a_s	a	$a - a_s$	r
Propane						
2.1.53.3 (Ag and Hg nitrates)	13	40	10.39	9.50	−0.89	0.54
	20	11	...	0.35	....	0.13
	5[a]	32	2.01	1.8	−0.2	0.2
2.1.57T (Br_2-air)	20	16	...	0.49	....	0.16
2.1.53 (Hofmann solution)	2[a]	19	5.12	4.6	−0.5	0.3
Summary of Propane						
			Range	$\Sigma\|a - a_s\|/N$	$\Sigma(a - a_s)/N$	$\Sigma r/N$
2.1.53.3		83	0.4–10	0.7	−0.7	0.4
2.1.57T		16	0.5	...	....	0.2
2.1.53		19	5	0.5	−0.5	0.3
Propene						
			a_s	a	$a - a_s$	r
2.1.53.3	13	35	6.81	6.69	−0.12	0.34
	20	17	...	4.65	....	0.22
	5[a]	31	15.85	15.6	−0.3	0.4
2.1.57T	13	11	6.81	6.92	+0.11	0.12
	20	5	...	5.06	....	0.13
2.1.53	2[a]	9	2.96	2.8	−0.2	0.1
Summary of Propene						
			Range	$\Sigma\|a - a_s\|/N$	$\Sigma(a - a_s)/N$	$\Sigma r/N$
2.1.53.3		83	5–16	0.2	−0.2	0.4
2.1.57T		16	5–7	0.1	+0.1	0.1
2.1.53		9	3	0.2	−0.2	0.1

[a] Wt. % basis.

Table XV. Accuracy and Precision of Analyses by Distillation Plus Chemical Methods

Method of Analysis: Dist. + Chem. Method No.	Mixture No.	N	a_s	a	$a - a_s$	r
Isobutane						
Containing C_3						
2.1.53.3 (Ag and Hg nitrates)	13	18	14.10	14.62	+0.52	0.55
	14	17	40.75	41.25	+0.50	0.63
	4[a]	40	11.55	12.8	+1.3	1.1
	5[a]	30	18.00	18.5	+0.5	0.4
2.1.53 (Hofmann solution)	1[a]	30	17.15	17.9	+0.8	0.6
	2[a]	13	12.04	12.3	+0.3	0.6
Containing no C_3						
2.1.53.3	15	17	3.30	3.37	+0.07	0.37
	16	17	13.80	12.95	−0.85	0.84
	17	15	5.26	5.30	+0.04	0.65
	18	14	44.62	44.59	−0.03	0.46
	19	15	5.22	4.61	−0.61	0.44
Summary of Isobutane						
			Range	$\Sigma\|a - a_s\|/N$	$\Sigma(a - a_s)/N$	$\Sigma r/N$
2.1.53.3 containing C_3		105	11–41	0.8	+0.8	0.7
2.1.53 containing C_3		43	12–18	0.6	+0.6	0.6
2.1.53.3 no C_3		78	3–45	0.4	−0.3	0.6
***n*-Butane**						
			a_s	a	$a - a_s$	r
Containing C_3						
2.1.53.3	13	16	29.77	29.88	+0.11	0.36
	14	17	5.12	5.68	+0.56	0.35
	4[a]	41	11.57	11.8	+0.2	0.7
	5[a]	30	18.03	17.7	−0.3	0.7
2.1.53	1[a]	28	24.93	25.1	+0.2	0.8
	2[a]	12	16.00	16.5	+0.5	0.6
	3[a]	9	3.96	4.6	+0.6	0.4
Containing no C_3						
2.1.53.3	15	17	13.92	14.04	+0.12	0.40
	16	13	2.29	2.91	+0.62	0.22
	17	15	84.42	82.93	−1.49	1.02
	18	13	33.68	33.49	−0.19	0.23
	19	17	4.93	5.72	+0.79	0.65
Summary of *n*-Butane						
			Range	$\Sigma\|a - a_s\|/N$	$\Sigma(a - a_s)/N$	$\Sigma r/N$
2.1.53.3 containing C_3		104	5–30	0.3	+0.2	0.6
2.1.53 containing C_3		49	4–25	0.3	+0.3	0.7
2.1.53.3 no C_3		75	2–85	0.6	0.0	0.5

[a] Wt. % basis.

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Influence of pH on Lead Chlorofluoride Precipitation

SAMUEL KAUFMAN[1], *National Bureau of Standards, Washington, D. C.*

THE lead chlorofluoride method for determining fluorine in silicates depends on the precipitation of lead chlorofluoride (PbClF) from the buffered filtrate following the separation of silica as zinc silicate. From a subsequent Volhard determination of the chloride in the precipitate, the fluorine may be calculated. This has been investigated by Hoffman and Lundell (*3*), whose procedure was used in the present work. They reported their method as reliable for samples containing between 0.01 and 0.1 gram of fluorine.

In analyses of materials containing approximately 50% of silica and 0.5% of fluorine, it was necessary to use samples of at least 2 grams to supply the minimum quantity of fluorine. Larger samples were objectionable because their high silica content would introduce bulky precipitates in the separations of fluorine from silica, and they would require excessive and interfering (*3*) quantities of alkali carbonate flux. Consequently, the samples analyzed contained the very minimum recommended quantity of fluorine.

The fluorine, after separation from the silica, is precipitated from a solution buffered by hydrochloric acid and sodium acetate. The proper pH of this solution is said to have values between 3.6 and 5.6 (*1, 2, 3*). This range of 2 pH units suggests a need for only moderate precision in buffering. Because small variations in buffering led to erratic results, experimental analyses were conducted to investigate the effect of pH on the precipitation of lead chlorofluoride.

Solutions were prepared simulating the composition of the filtrate following the removal of silica. Known amounts of fluorine were added volumetrically as standard sodium fluoride solution. With the exceptions mentioned below, the procedure of Hoffman and Lundell (*3*) was followed to the conclusion of the analyses. In order to prepare solutions of different pH values, varying amounts of hydrochloric acid were used with simultaneous variation of amounts of sodium chloride solution to keep the chloride ion concentration identical in all cases.

Three series of solutions were analyzed containing, respectively, 0.0100, 0.0200, and 0.0000 gram of fluorine. After removal of the lead chlorofluoride by filtration, the pH of its mother liquor, excluding any washings, was determined with a Beckman glass electrode pH meter.

Results of the experiments are represented graphically in Figure 1. No blank corrections were made in plotting these curves.

The data show that when 0.0100 gram of fluorine was present, precipitation was incomplete at pH values up to and including 4.80. Above pH 4.84, the results are scattered, and indicate more fluorine than was present. When 0.0200 gram of fluorine was present, results were in error (after subtraction of blanks) by less than 1%, and consistent up to and including pH 4.83; above pH 4.83, results were erratic. When no fluorine was present, results were consistent up to and including pH 4.72. At higher pH values, analyses indicated considerable quantities of fluorine, and yielded erratic results.

In the analyses of solutions containing no fluorine (the blanks) little or no precipitation was observed at pH values of 4.72 and less, but precipitates did form at higher pH values. Visual observation revealed no dissimilarity among the various precipitates. However, that precipitates formed at the higher pH values

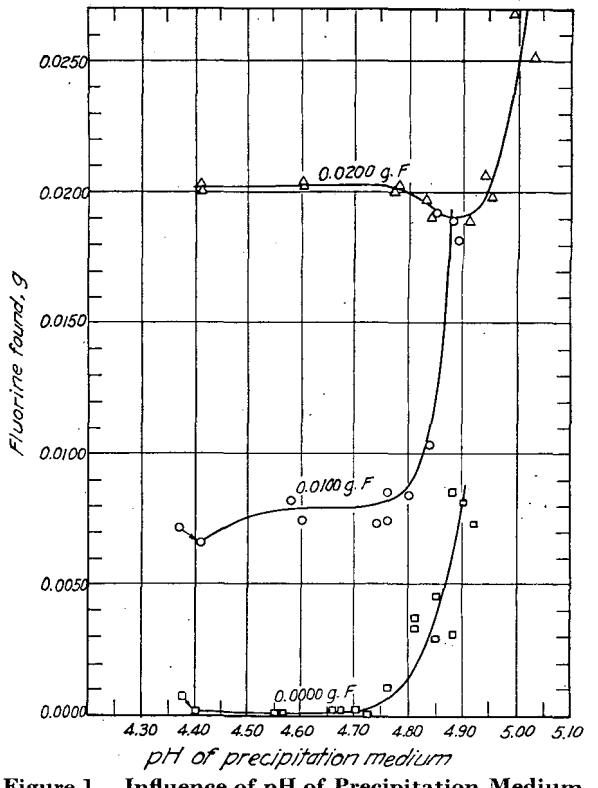

Figure 1. Influence of pH of Precipitation Medium on Analyses of Solutions

Solutions containing: ○ 0.0100 gram, △ 0.0200 gram, □ no fluorine

[1] Present address, Naval Research Laboratory, Washington, D. C.

contained chlorine in excess of the amount required for the precipitation of all the fluorine as lead chlorofluoride is illustrated by the fact that analyses indicated considerable amounts of fluorine present, when none was introduced. As the determination is indirect and the calculation of the fluorine present is derived from the amount of chloride found in the precipitate, it is possible to calculate greater amounts of fluorine than are present.

DISCUSSION

It is concluded that the lower satisfactory limit of the method lies somewhere between 0.01 and 0.02 gram of fluorine. The pH of the precipitation medium must be controlled within limits narrower than previously supposed, especially with the quantities of fluorine studied here.

Rigorous execution of the directions of Hoffman and Lundell (*3*) will lead to a precipitation medium in the safe pH range. However, perhaps more than the usual degree of precision in buffering is required, since the tolerable variation of the pH is so slight. Variations in strength, purity, or measurement of reagents may lead to pH values outside the safe pH range. Consequently, when conducting an analysis, one should determine the pH of the mother liquor, exclusive of washings. The pH should fall between 4.60 and 4.70. The validity of the result should be questioned if the pH is outside this range, especially if it is high. Readjustment of the pH, if high, will not correct matters once the precipitation has taken place.

When a sample containing less than 0.020 gram of fluorine must be used, it is recommended that enough fluorine be added as standard sodium fluoride solution to bring the total fluorine content to at least 0.0200 gram. This should be introduced into the filtrate after the separation of the silica. The quantity thus added should be subtracted in calculating the result.

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Determination of Levulose

Colorimetric Determination in Presence of Dextrose

D. T. ENGLIS AND JAMES W. MILES[1], *University of Illinois, Urbana, Ill.*

The establishment of the conditions under which levulose has a pronounced reducing action upon the Folin-Denis phosphotungstate-phosphomolybdate reagent while dextrose has a very slight action has been made the basis for a rapid colorimetric estimation of the former in the presence of the latter.

IN THE course of an examination of the official method (*1*) for the determination of vanillin, an interesting observation was made concerning the conduct of dextrose and levulose with the Folin-Denis phosphotungstic-phosphomolybdate reagent used in this connection. A slight modification of the official procedure involved the substitution of trisodium phosphate for sodium carbonate as the basic reagent. However, the reaction was so slow at room temperature that it was necessary to heat the mixture for 10 to 15 minutes to develop the desired color. Furthermore, when the procedure was applied to commercial extracts, the results for vanillin were always high (*6*). In order to seek out the sources of error, two probable interfering substances, dextrose and levulose, were treated with the reagent under the prescribed conditions. It was then noted that dextrose gave practically no color, even when present in concentrations up to 2%, whereas small quantities of levulose produced considerable color under these conditions. These observations suggested a method whereby levulose might be determined in the presence of dextrose.

Some of the methods and factors concerned with the selective oxidation of levulose with other reagents have been discussed (*4*). In many instances the available procedures are involved and time-consuming. It is believed a quicker colorimetric procedure has advantages for certain types of work.

EXPERIMENTAL

Equipment for Colorimetric Analysis. First, it was necessary to determine the nature of the color developed by the reagent. Accordingly, the reduction product was examined (*6*) with a Cenco spectrophotelometer and the color curve was constructed. No sharp change in absorption occurred at any point. There was a maximum transmittance near 420 mμ and a gradual reduction in transmittance down through 650 mμ. Hence, it was evident that a simple filter photometer would be adequate for the colorimetric work and a red filter would be desirable to limit the source of illumination to a more effective region. A Cenco-Sheard photelometer equipped with a red filter was selected as the instrument to be used.

Determination of Optimum Time of Heating. The reagents used were the Folin-Denis phenol reagent (*5*) and a 20% solution of trisodium phosphate in water. Six 5-ml. portions of a 2% solution of levulose were placed in six 100-ml. volumetric flasks and 5 ml. of Folin-Denis reagent were added to each. After 4 minutes, 10 ml. of the trisodium phosphate solution were added to each. The flasks were placed in a water bath at 100° C. The first was removed after 2 minutes and made to volume with water; the second was allowed to heat for 5 minutes, the third for 10 minutes, etc. Each flask was made to volume and the colored solutions were compared in a cell of 1-cm. depth against water in the photelometer.

The results are shown in Table I. From this experiment, it was determined that the color value was near its maximum after heating 10 minutes and this period was selected as the optimum time of heating.

Preparation of Working Curves. Solutions containing 0.1, 1.0, 2.0, 4.0, and 8.0% of levulose were prepared; 5-ml. portions of each solution were placed in separate 100-ml. flasks, and a 5-ml. portion of the Folin-Denis reagent was added to each. After 4 minutes, each was neutralized with 10 ml. of 20% trisodium phosphate solution. All flasks were placed in boiling water and heated for 10 minutes, then made to volume with water, and the solutions were examined in the photelometer. The resulting colored solutions were compared with a blank treated in the same way. Color values are expressed as log 100/% T or E for the solution at 1-cm. cell depth.

[1] Present address, College of Pharmacy, University of Kentucky, Louisville, Ky.

To avoid the limitation of the volume of sugar solution taken for analysis to 5 ml. as in the previous experiments, the procedure was altered slightly in a second series of experiments to test the use of volumes up to 15 ml. The desired quantity of sugar solution was placed in the 100-ml. graduated flask, the volume was brought to a total of 15 ml. with water, then 5 ml. of Folin-Denis reagent were added. Beyond this point, all the steps were as in the previous experiments. The results are given in Table II.

The series of tests employed for the study of levulose was repeated, using solutions of dextrose instead of levulose (Table III). In all respects, the operations were identical.

The data for the B series for both dextrose and levulose are plotted in Figure 1. These curves emphasize the differences in the reducing ability of the two sugars for the reagent and furnish the information necessary for calculation of the amount of each in a mixture of the two. Although the E values obtained are not directly proportional to concentration of levulose, carrying out the reaction under carefully specified conditions gives data that make possible a satisfactory working curve.

Analysis of Mixtures of Dextrose and Levulose. A measured quantity of each dextrose and levulose solution was placed in a 100-ml. volumetric flask and enough water was added to make the volume 15 ml. The reduction was then carried out in the prescribed manner. The quantities of dextrose and levulose contained in the mixtures taken for analysis are given in Table IV. The E values were calculated from the per cent transmittance of each solution.

In order to use the working curve (Figure 1) for the determination of levulose, the quantity of total sugars in the mixture must be known. For an unknown solution, the total reducing sugars may be determined by some other method—for example, the Lane and Eynon (*2*) or Munson and Walker (*3*) procedures.

The E value for a given solution is referred to the levulose curve and from this the approximate amount of levulose is determined (here it is assumed that all the color is due to the levulose). This quantity is subtracted from the quantity of total sugars to obtain the approximate quantity of dextrose present. The quantity of dextrose found by this method is referred to the dextrose curve to obtain the E value for the dextrose; thus, the amount of color resulting from the dextrose is estimated. The dextrose E value so obtained is subtracted from the experimental E value to obtain the corrected E value for the levulose. More exact calculation could be made, using this result as a first approximation and proceeding further, as is indicated in the previous article (*4*). The amount of levulose present is determined finally by referring this levulose E value to the levulose curve.

The results calculated by the above method are given in the last column in Table IV. The method is convenient and rapid.

Deviations from the curves that are given may characterize the use of equipment, reagents, and conditions not exactly identical to those employed here. It is recommended that each observer prepare similar working curves for conditions under which the operations are to be performed. Slight changes in temperature and time of heating may make possible a better utilization of the reaction for determination in the low concentration range for levulose.

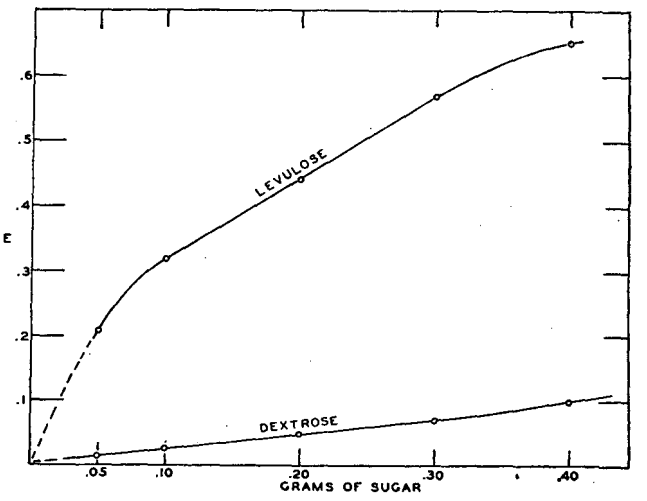

Figure 1. Relation of Color Value and Sugar Concentration

Table I. Effect of Period of Heating on Color Value

Solution	Time of Heating, Minutes	% Trans-mittance
1	2	75.5
2	5	59.5
3	10	53.0
4	15	52.0
5	20	50.0
6	30	49.0

5 ml. of 2% levulose, 5 ml. of Folin-Denis reagent, and 10 ml. of 20% Na_3PO_4 solution. Final dilution to 100 ml.

Table II. Relation of Color Value and Concentration of Sugar

	Concn. of Levulose, %	Levulose, Gram	T, %	E
A	1.0	0.05	63.0	0.201
	2.0	0.10	54.0	0.268
	4.0	0.20	40.8	0.389
	8.0	0.40	24.8	0.605
B	1.0	0.05	61.9	0.207
	2.0	0.10	48.0	0.319
	4.0	0.20	36.0	0.444
	6.0	0.30	27.0	0.569
	8.0	0.40	22.5	0.648

A. 5 ml. of sugar solution, 5 ml. of Folin-Denis reagent, and 10 ml. of 20% Na_3PO_4. Final dilution to 100 ml., after heating 10 min.
B. Same as A except 10 ml. of water added with 5 ml. of sugar solution.

Table III. Relation of Color Values and Concentration

	Concn. of Dextrose, %	Dextrose, Gram	T, %	E
A	1.0	0.05	97.5	0.011
	2.0	0.10	96.0	0.016
	4.0	0.20	87.0	0.060
	8.0	0.40	83.5	0.078
B	1.0	0.05	96.5	0.015
	2.0	0.10	94.5	0.025
	4.0	0.20	89.8	0.047
	6.0	0.30	85.5	0.068
	8.0	0.40	79.5	0.100

A and B as in Table II except that dextrose is sugar present.

Table IV. Determination of Levulose in Presence of Dextrose

Sugar Taken, Gram		Total			Levulose Found,
Levulose	Dextrose	Sugar, Gram	T, %	E	Gram
0.20	0.20	0.40	32.5	0.488	0.200
			32.8	0.484	0.197
0.10	0.10	0.20	45.0	0.347	0.106
			45.2	0.345	0.105
0.20	0.10	0.30	32.5	0.488	0.222
			33.0	0.481	0.212
			33.8	0.471	0.205
0.10	0.05	0.15	46.0	0.337	0.105
			46.0	0.337	0.105
0.10	0.20	0.30	45.5	0.342	0.090
			45.0	0.347	0.094
			45.0	0.347	0.094
0.20	0.40	0.60	29.7	0.527	0.203
			30.0	0.523	0.202

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Determination of Boron in Borine Compounds

ANNE L. CONRAD AND M. S. VIGLER, *Standard Oil Company (Ohio), Cleveland 6, Ohio*

A rapid method for the analysis of organic borine compounds is accurate to within ±0.04% and requires but 3 hours' total analysis time and a working time of 1 hour. The oxidation is accomplished through use of the Parr oxygen bomb and hot permanganate solution.

A SURVEY of the literature revealed but two methods of practical value for the determination of boron in borine compounds. Snyder, Kuch, and Johnson (*4*) describe a method of oxidation with hydrogen peroxide and a second method of fusion with sodium peroxide in a Parr bomb. The first is very time-consuming; the second may be dangerous when used with low boiling borines.

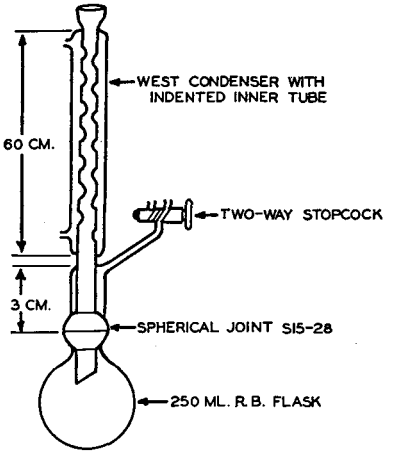

Figure 1. Detail of Reflux Apparatus

The method described here is an adaptation of that used by Burke (*1*) for determining boron in organic borates. The sample is carefully weighed in a gelatin capsule in an atmosphere of nitrogen and is burned in the bomb in oxygen under pressure. Sodium carbonate solution serves as the absorbent. To complete the oxidation, the acidified bomb washings are boiled with potassium permanganate solution until the purple color remains. The resulting boric acid is determined by the standard procedure of removing carbonate and titrating with sodium hydroxide in the presence of mannitol. The total working time of analysis is typically about 1 hour.

EQUIPMENT AND REAGENTS

Parr oxygen bomb, oxygen, and gelatin capsule (*2*). Nitrogen or other inert gas supply. Potassium permanganate solution, 1.5%. Sodium carbonate solution, approximately 5%.

Boron-free distilling flask. West condenser fitted with an entry tube and 2-way stopcock (see Figure 1).

Hydrochloric acid solution, approximately 5%. Sodium sulfite solution, saturated. Mannitol, reagent grade. Standardized sodium hydroxide solution.

PROCEDURE

Sampling. A fusion wire, about 10 cm., is looped into the capsule, leaving protruding ends. Capsule and fusion wire are weighed accurately and flushed with nitrogen.

The pipet is filled with nitrogen. The sample bottle is opened while flooding with nitrogen. An approximately 0.2-gram sample is drawn into the pipet and transferred into the weighed gelatin capsule. The capsule lid is placed quickly over the looped fusion wire and capsule (*2*), and capsule and contents are weighed.

Combustion. The protruding ends of the fusion wire are attached to the bomb electrodes. A 10-ml. vial is filled with 5% sodium carbonate solution and placed upright against the wall in the clean dry base of the bomb. The bomb is assembled and oxygen is admitted equal to 500 pounds per square inch.

While immersed in a water bath, the contents of the bomb are ignited electrically. After a 5-minute cooling period the bomb is tipped to allow the sodium carbonate in the vial to come in contact with the combustion gases. The bomb is left in the cooling bath for 0.5 hour.

Preparation of Solution. Pressure is released from the bomb slowly to avoid loss of liquid. The bomb contents are washed carefully into a 250-ml. boron-free round-bottomed flask. The solution is adjusted to a pH of 1 to 4 with hydrochloric acid. The West condenser is connected to the flask and nitrogen is entered through the 2-way stopcock (Figure 1).

The flask contents are heated to boiling under a constant stream of nitrogen, and potassium permanganate solution is added dropwise to the boiling solution until a permanent purple color is maintained after several minutes of boiling; this indicates that oxidation is complete. The saturated sodium sulfite solution is added dropwise until the solution becomes colorless. Boiling and refluxing are continued for 5 minutes.

Titration. The flask and contents are cooled to room temperature and the condenser is rinsed with distilled water. The wash water is collected in the distilling flask. Contents of the distilling flask are washed into a boron-free titrating beaker. The solution is titrated with standardized sodium hydroxide in the presence of mannitol; a pH meter is used to determine the end point.

Calculation

$$\% \text{ boron} = \frac{\text{ml. of NaOH} \times N \times 0.1082}{\text{weight of sample}}$$

Table I shows results obtained for boron determination by the above procedure as compared with the hydrogen peroxide digestion method. In all cases the normality of the sodium hydroxide was checked against recrystallized A.C.S. standard sodium tetraborate as described by Hurley (*3*). Purity of the borine was checked by boiling point and molecular weight determinations.

Table I. Tri-*n*-butylborine

(Theoretical % B, 5.94)

Bomb Oxidation		H_2O_2 Digestion (*1*)	
Sample, gram	B, %	Sample, Gram	B, %
0.2010	5.95	0.0471	5.92
0.2172	6.01	0.0674	5.97
0.0372	5.98		
0.1363	5.92		
0.1514	5.91		
Av.	5.95		

ACKNOWLEDGMENT

The authors wish to thank E. C. Hughes for suggesting this problem and for many helpful suggestions in the course of this work.

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Determination of Sugars in Plant Materials

Use of Decolorizing Carbon in the Ferricyanide Method

ARTHUR BEVENUE, *Western Regional Research Laboratory, Albany, Calif.*

Experimental data are presented on the sugar adsorption properties of some commercially available charcoals, as they may be used in the clarification process of plant extracts for quantitative sugar analyses. Percentage of sugar adsorption by charcoals varies with different sugars, type of carbon, and concentrations of sugar and carbon.

IN THE preparation of some plant extracts for sugar analysis, clarification is necessary for the removal of nonsugar-reducing substances. In many cases, the use of neutral lead acetate, and removal of excess lead with disodium phosphate, will not wholly accomplish this purpose. Unless the extract is water-clear, the organic coloring matter present may be oxidized, giving high sugar values.

Hassid (*3*) using Carboraffin, a charcoal of European origin, and Forsee (*2*), using the charcoal Norite, obtained 100% recovery of dextrose but presented no data on the recovery of levulose or sucrose from carbon-treated pure sugar solutions. Hiscox (*5*) stated that charcoal treatment lowered the reducing-sugar content of silage and root crops but gave no data. Lott (*6*) and Morris and Wesp (*7*) treated plant extracts with Baker & Adamson Code 1551 decolorizing carbon and found no measurable loss of dextrose.

In the course of experiments on methods for the determination of sugars in plant materials, it was necessary to find the sugar-adsorptive properties of some commercially available decolorizing carbons. Solutions of dextrose, sucrose (both obtained from the National Bureau of Standards), and levulose (Eastman Kodak Company) were used separately with and without the lead clarification process. The selection of the carbons was based primarily upon a study of the origin and the properties of decolorizing carbons as outlined by Deitz (*1*).

REAGENTS

Saturated solution of neutral lead acetate.

Saturated solution of disodium phosphate.

Ceric sulfate, alkaline potassium ferricyanide, and setopaline C indicator solutions prepared as directed by Hassid (*3*).

Dextrose, National Bureau of Standards sample 41. Sucrose, National Bureau of Standards sample 17. Levulose (Eastman Kodak Company).

Acetic acid, 10% solution. Invertase. Carbons as listed in Table I.

PROCEDURE

Twenty-five milliliters of a dextrose solution, containing 0.2 gram of dextrose, were pipetted into a 100-ml. volumetric flask, 50 ml. of distilled water were added to dilute the sugar solution, and 0.5 gram of decolorizing carbon was added. The volume was made to 100 ml. with distilled water, the contents of the flask were mixed thoroughly, and the mixture was allowed to stand at room temperature for 10 minutes with occasional shaking. (Previous experiments indicated that adsorption was no greater if time of standing was 30 or 60 minutes.) The mixture was filtered through a fluted filter paper of analytical quality. After the first 25 ml. of filtrate were discarded, 25 ml. of the filtrate were diluted to 100 ml. and used for analysis.

The same procedure was followed with levulose solutions.

Sucrose solutions (0.1 gram per 100 ml.) were treated with carbon as described for dextrose and levulose. After the carbon treatment, the solutions were adjusted to pH 4.8 to 5.1 with a 10% solution of acetic acid. Invertase was added and hydrolysis was allowed to take place at 25° C. overnight.

Similar experiments were conducted in which the amount of carbon was varied. In another series, the sugar concentration was varied.

The sugar analyses were determined by the Hassid method (*4*), and the values given in the tables are the averages of several determinations, with a maximum variation of ±2%.

RESULTS

The data in Table I show that there was no adsorption of dextrose or levulose by ten of the twelve decolorizing carbons studied. The five animal charcoals did not adsorb sucrose. However, sucrose recovery from the other charcoals varied from 43 to 87%.

To simulate conditions of actual analysis, neutral lead acetate was added to dextrose, levulose, and sucrose solutions; the lead was removed with a slight excess of disodium phosphate and the solutions were filtered. The filtrates were treated with carbon under the conditions of procedure described above. Six of the twelve carbons described in Table I were used in this experiment—the three Darco varieties, Baker & Adamson Code 1551, animal charcoals 325-mesh and No. 2. The absorption of sugars by the carbons from these filtrates was the same, within the limits of error (±2%), as from the distilled-water solutions.

In the experiments in which the carbon concentration was varied (Table II), Baker & Adamson Code 1551 carbon adsorbed no dextrose or levulose at the lower carbon concentrations. However, at the higher carbon concentrations a slight adsorption of these two sugars was indicated. The adsorption of sucrose increased with added increments of B. & A. Code 1551 carbon. Animal charcoal, 325-mesh, did not adsorb dextrose, levulose, nor sucrose at the carbon concentrations studied.

When the sugar concentration was varied (Table III), none of the carbons tested adsorbed a measur-

Table I. Recovery of Dextrose and Levulose from 0.2% Solutions and of Sucrose from a 0.1% Solution

(After treatment of 100 ml. of sugar solution with 500 mg. of decolorizing carbon)

Carbon	Dextrose, %	Levulose, %	Sucrose, %
Norit SG (American Norit Co., Jacksonville, Fla.)	93.6	92.0	44.4
Norit A (Pfanstiehl Chemical Co., Waukegan, Ill.)	94.0	92.8	43.2
Nuchar (Eastman Kodak Co., Rochester, N. Y.)	99.6	97.2	71.2
Darco G60 (Darco Corp., New York, N. Y.)	99.2	100.8	80.4
Darco S51 (Darco Corp., New York, N. Y.)	98.3	102.0	82.6
Darco KB (Darco Corp., New York, N. Y.)	99.1	99.2	75.4
Baker & Adamson Code 1551 (General Chemical Co., New York, N. Y.)	100.0	100.2	86.6
Animal charcoal, 8/24-mesh (Consolidated Chemical Industries, Inc., San Francisco, Calif.)	100.4	100.8	99.6
Animal charcoal, 325-mesh (Consolidated Chemical Industries, Inc., San Francisco, Calif.)	101.0	100.8	98.8
Animal charcoal, No. 1 (American Agricultural Chemical Co., Detroit, Mich.)	101.2	102.8	102.0
Animal charcoal, No. 2 (American Agricultural Chemical Co., Detroit, Mich.)	101.8	101.2	99.6
Bone black, HL (Baugh & Sons Co., Philadelphia, Pa.)	101.2	101.6	102.0

Table II. Recovery of Dextrose and Levulose from 0.2% Solutions and of Sucrose from 0.1% Solution

(After treatment of 100 ml. of sugar solution with varied amounts of decolorizing carbon)

Carbon, Mg.	B. & A. Code 1551 Carbon			Animal Charcoal, 325-Mesh		
	Dextrose, %	Levulose, %	Sucrose, %	Dextrose, %	Levulose %	Sucrose, %
100	99.6	98.5	98.3	100.8	99.0	100.8
200	99.6	99.3	96.0	100.8	100.1	100.0
300	99.6	98.5	92.8	100.0	98.2	100.0
500	98.8	98.4	88.8	100.0	99.0	100.3
700	98.4	97.3	84.4	100.8	98.0	99.6
1000	96.4	97.3	77.6	100.4	98.4	98.4

Table III. Recovery of Dextrose, Levulose, and Sucrose from Solutions of Varied Sugar Concentration

(After treatment of 100 ml. of sugar solution with 500 mg. of decolorizing carbon)

Sugar, %	B. & A. Code 1551 Carbon			Animal Charcoal, 325-Mesh		
	Dextrose, %	Levulose, %	Sucrose, %	Dextrose, %	Levulose, %	Sucrose, %
0.05	98.4	96.0	80.0	100.0	99.6	96.0
0.10	...	...	88.0	...	...	98.4
0.20	98.8	98.9	92.4	98.8	100.9	98.4
0.30	...	...	93.2	...	...	99.2
0.50	98.8	98.2	95.6	100.0	98.1	98.4
1.00	98.8	99.5	97.2	99.6	98.5	98.8

able quantity of dextrose. Only at the lowest sugar concentration was there evidence of levulose adsorption by B. & A. Code 1551 carbon. The adsorption of sucrose by this carbon was appreciable at all concentrations. Animal charcoal, 325-mesh, adsorbed no sucrose except at the lowest sugar concentration studied.

The data show that it is necessary to determine the adsorption of sucrose as well as dextrose and levulose when a carbon is selected for the decolorization of plant extracts for sugar analysis. Sugar concentration and the quantity of carbon must also be taken into consideration.

As solutions of dextrose and levulose can be treated with selected carbons without appreciable loss, it is advisable to carry out hydrolysis after lead clarification but prior to treatment with carbon and thereby avoid the adsorption of sucrose.

SUMMARY

The percentages of recovery of dextrose, levulose, and sucrose from water solutions after treatment with commercially available decolorizing carbons have been determined. Animal charcoals did not adsorb any measurable quantity of the three sugars, except sucrose at the lowest sugar concentration studied. Sucrose recovery from the other carbons varied from 43 to 87%. Within certain useful limits of carbon and sugar concentrations, ten of the twelve carbons studied did not absorb levulose or dextrose. Sugar solutions were also treated with neutral lead acetate and dibasic sodium phosphate prior to the carbon treatment, and it was found that the adsorption of the sugars by the carbons was the same as from the water solutions.

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STUDIES ON RESINS

Specific Color Reaction for Dehydroabietic Acid and Its Application in Analysis of Technical Resins

WILHELM SANDERMANN

Zentralinstitut fur Forst-und Holzwirtschaft, Hamburg-Reinbek, Germany (British Zone)

This paper describes a new specific intensive blue-violet color reaction which has been used to detect dehydroabietic acid in various resin products. A resin containing dehydroabietic acid is sulfonated in the cold, and after standing 12 hours at room temperature is neutralized with concentrated sodium hydroxide or potassium hydroxide. A blue-violet color appears; the intensity varies with the amount of dehydroabietic acid in the sample.

THE simplest test for resinic acids is the color reaction with acetic anhydride and sulfuric acid according to Storch and Morawski (*1*, *3*). However, this reaction is not specific because other compounds such as terpenoids give the same color. The Halphen-Grimaldi reaction with phenol and bromine (*4*) is known to have the same disadvantages. Both of these identification tests show good results with *l*-pimaric acid, abietic acid, and proabietic acid, but not with hydrogenated resinic acids, dehydroabietic acid, *d*-pimaric acid, and the compound of *l*-pimaric acid with maleic anhydride. A new specific color reaction for dehydroabietic acid has been found.

PROCEDURE

In an ice-cooled test tube 0.05 to 0.1 gram of fine powdered resin is added in small portions to 2 ml. of sulfuric acid (density 1.84). After standing for about 12 hours at room temperature the test tube is placed in a test tube clamp, and 3 ml. of water are added. Then slowly with a pipet a 50% solution of sodium hydroxide in water is added until the mixture shows an alkaline reaction. The reaction is extremely violent and every precaution must be taken. If the sample contains dehydroabietic acid a blue-violet color appears, which is stable for days and often for weeks. If the sample is acidified the color disappears but will reappear to a lesser degree if sodium hydroxide is added. If ammonia or amines are substituted for alkali hydroxide no color is produced, nor does any color appear if the neutralization with sodium hydroxide takes place in the cold.

Apparently a sulfonic acid is transformed into a phenolic compound under the influence of heat and concentrated alkali hydroxide. If the pure sulfonic acid II is neutralized with concentrated sodium hydroxide there is no color reaction, but a very intensive one if II is first treated with sulfuric acid in the same

way as described for dehydroabietic acid. Therefore it may be supposed that the color is caused by a polyphenolic compound—e.g., V—which has been formed from a polysulfonic acid like IV. The polyphenol V may be transformed into an oxyquinone VI which forms blue-violet sodium salts, analogous to quinones with hydroxyl groups.

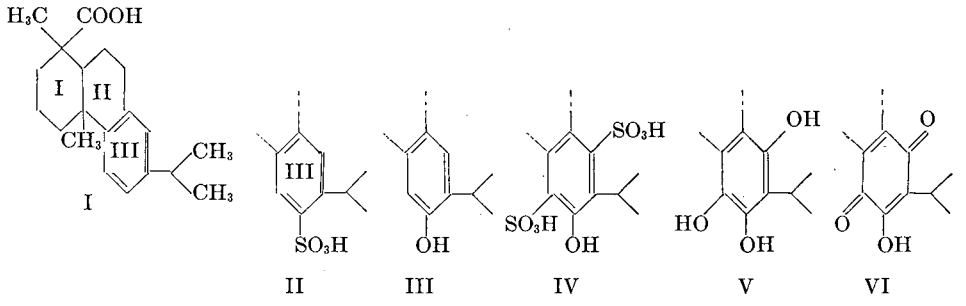
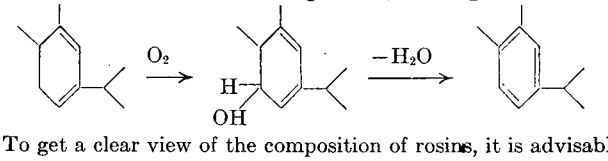


Table I shows that this color reaction is really specific for dehydroabietic acid.

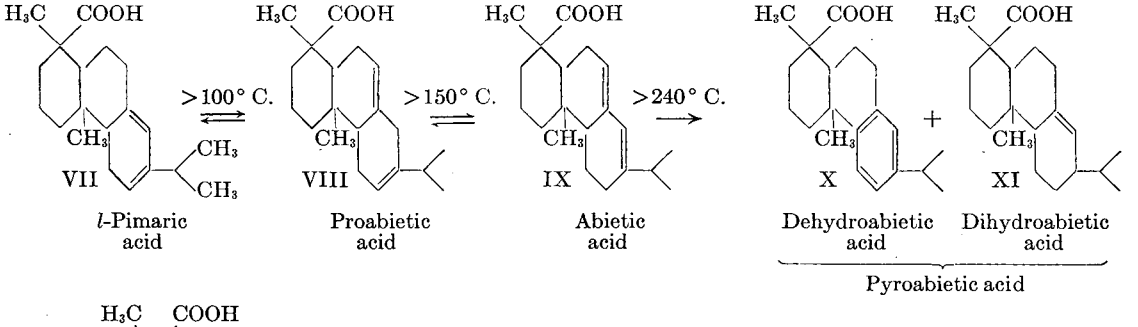
As many technical resins are characterized by the presence of dehydroabietic acid, this new color reaction is very useful in the analysis of technical resins.

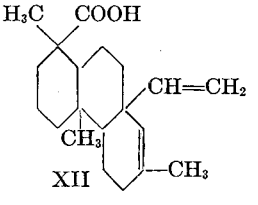
Technical resins contain several resinic acid isomerides. The varieties and amounts of these isomerides depend on the heat treatment they have undergone. The amount of *d*-pimaric acid (XII) is nearly constant up to temperatures of about 230° C.

But the resinic acids of the type of *l*-pimaric acid change their structure with the temperature, as shown in VII to XI. According to this scheme a rosin obtained from gum by distillation up to 180° to 200° C., should not give a positive reaction in the new test, as it contains no dehydroabietic acid. Indeed Table II shows that such rosins contain none or only traces of dehydroabietic acid. But in agreement with the scheme all resinic acids that have been heated to over 240° C.—e.g., resinic acids from distilled tall oil—give a dark blue-violet color. Not only the common wood rosins but also the hydrogenated product Staybelite and the polymerized rosin Polypale contain considerable amounts of dehydroabietic acid. It was found by diene titration (*2*) that a wood rosin obtained by low temperature extraction of stumps contained a large amount of pyroabietic acids which did not react with maleic anhydride. Probably the dehydroabietic acid of such rosins obtained by extraction has been formed by autoxidation according to the following scheme:



To get a clear view of the composition of rosins, it is advisable





d-Pimaric acid

Table I. Results of Color Reaction Test

l-Pimaric acid	−	Cholesterol	−
Abietic acid	−	Oxycholesterol	−
Dihydroabietic acid	−	Cholestanone	−
d-Pimaric acid	−	Phytosterol	−
Compounds of maleic anhydride or quinone with *l*-pimaric acid	−	Ergosterol	−
		Digitonin	−
Dehydroabietic acid	+	Copal	−
Dehydroabietic-sulfonic acid	+	Dammar gum	−
		Sandarac	−
		Copaiva gum	−
		Shellac	−
		Turpentine oil	−

[a] − = negative color reaction; + = positive color reaction.

Table II. Tests of Technical Resins for Dehydroabietic Acid and Comparison of Color with Solution of Sodium Permanganate

Resins	Concentration of Permanganate Solution with Same Shade as Test, %
American gum rosin	0.0
Greek rosin, WC Spanish rosin, AAA Portuguese rosin, WC	0.05
French rosin, Special Greek rosin, H/S Mexican rosin, H/S Spanish rosin, Exelsior German rosin, Stäcker	About 0.1
Hercules rosins Wood rosin FF Wood rosin N Wood rosin K Staybelite (hydrogenated rosin) Polypale (polymerized rosin)	About 0.5
Distilled rosins and special products	
Rosin, heated 5 hours at 270° C.	0.7
Distilled resinic acids from tall oil	1.2
Pyroabietic acid from rosin + palladium catalyst at 250° C.	1.5
Dehydroabietic acid (crude) from rosin + sulfur at 280° C.	2

Table III. Examination of Technical Rosins by Storch-Morawski Reaction, New Color Reaction on Dehydroabietic Acid, and Diene Titration

Resin	Storch-Morawski Reaction	Color Reaction on Dehydroabietic Acid	Diene Titration	Composition of Rosins: *d*-Pimaric acid	*l*-Pimaric acid	Pro-abietic acid	Abietic acid	Dihydro-abietic acid	Dehydro-abietic acid
Original resinic acids from gum	+	−	+	+	++	+	−	−	−
Rosin from gum	+	−(+)	+	+	−(+)	++	+	−	−
Resin acids from distilled tall oil	+	+	+	+	−	+	+	+	+
Hercules wood rosin	+	+	+	+	−	+	+	+	+
Staybelite (hydrogenated wood rosin)	−	+	−	−	−	−	−	+++	+
Polypale (polymerized wood rosin)	−	+		+	−	?	?	?	+

to combine the new color test with the reaction of Storch-Morawski and the diene titration. This is shown in Table III.

ACKNOWLEDGMENT

The author is indebted to the Hercules Powder Company Wilmington, Del., for the samples of wood rosin products and to H. Hanner, Hamburg-Reinbek, Germany, for assistance in the experiments.

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Colorimetric Determination of Silicon in Low-Alloy and Carbon Steels

UNO T. HILL, *Inland Steel Company, East Chicago, Ind.*

The colorimetric determination of silicon in steels, based on the yellow silicomolybdate color, is improved in accuracy and increased in range by the utilization of a decolorized blank containing all the reagents used to produce the color. Simplicity of procedure obtained by the use of ammonium persulfate with resulting increase in speed makes the method suitable for routine analytical work.

COLORIMETRIC methods for silicon in steels generally depend on the formation of a yellow heteropoly complex of silicon and molybdate ions (*11*). The percentage of silicon may be determined either by measuring the intensity of the yellow color in a weak acid solution (*3, 10, 12–16, 19*), or by reducing the bound molybdenum to the blue color, the intensity being proportional to the silicon present (*1, 2, 4, 5, 7–9*).

The earlier methods (*3, 6, 12, 15*) depend on a preliminary separation of iron and silicon based on the method of Thayer (*18*); later Pinsl (*13, 14*) found that the interference caused by both iron and phosphorus could be avoided by the use of a fluoride.

Pinsl's method has been modified by Weihrich and Schwarz (*19*), and a procedure described by them has been proposed for routine analysis by Rozental and Campbell (*16*).

The purpose of the work reported here was to develop a method for the colorimetric determination of silicon in steel that would be more accurate and rapid than those described in the literature, and would meet the exacting demands of the industry for the routine analysis of very large numbers of samples.

EQUIPMENT

The Coleman Model 11 spectrophotometer and the Fisher Model A C. electrophotometer were used.

EXPERIMENTAL

The method of Pinsl (*13*) as modified by Weihrich and Schwarz (*19*), based on the yellow color, seemed to offer the greatest possibilities, but because of the many small details to be taken into account, it was not adaptable to simultaneous routine analysis in a large steel laboratory.

The parallel reference curves formed with different types of steels indicated that the molybdate ion, which was absent in the blank, formed colored complexes with varying constituents of steels. These complexes were not destroyed or prevented from forming by the fluoride ion.

By inclusion of the same reagents in the blank as in the sample, yet without forming the silicomolybdate color, two advantages conducive to greater accuracy may be gained. The complexes produced by varying constituents of the steel are compensated for in the blank, and the inception of the reference curve will be at the origin, where the smaller percentages of silicon are measured with greater sensitivity; thus the full scale of the instrument is utilized. This can be accomplished, in the procedure described, by reversing the order of addition of the reagents.

By oxidizing the sample with ammonium persulfate instead of potassium permanganate, the time and the number of manipulations were reduced sufficiently to make the procedure applicable to routine analysis on a large scale.

A spectral transmittance curve obtained with the Coleman spectrophotometer showed that the silicomolybdate complex has a broad absorption band with a maximum at 380 mμ. Schwartz and Morris (*17*) have indicated that the most sensitive band for the measurement of the yellow silicomolybdate complex is at 410 mμ, based on the fact that deviations from Beer's law were observed for bands of less than 410 mμ. Conformity to Beer's law is not a requirement for an accurate colorimetric procedure and reproducible reference curves for the yellow silicomolybdate color, more sensitive than those at 410 mμ, may be constructed below 410 mμ. Practical considerations, caused by a blank that may have to compensate for varying alloying elements, influenced

the choice of 400 mμ as the most desirable wave length in this procedure, although accurate measurements may be made even at 390 mμ. With a flexible instrument for selecting wave lengths reference curves may be constructed at two or more wave lengths, and the range of the procedure may be increased without dilution of the sample. However, a large number of points is necessary to establish a reference curve where Beer's law is not followed. The author has found it advisable to check all colorimetric curves used by numerous reference curve points, even when they approach straight lines, to be assured of the greatest accuracy possible.

The reference curves were constructed from National Bureau of Standards steel samples and checked with solutions of pure iron to which known amounts of silicate were added. The fact that the curve had its inception at the origin demonstrated that the reagents used were free of silicon.

Numerous acids, including sulfuric, nitric, and hydrochloric, are interchangeable on the same reference curve. When sulfuric acid alone is used, the amount of ammonium persulfate normally added must be doubled in order to oxidize all the iron. When only the specified amount of persulfate is added the silicomolybdate complex is reduced to the blue color with the addition of the fluoride. Silicon may be determined on the basis of this color if a reference curve is constructed at 470 mμ. The curve will have its inception at the origin. In adapting the method to the Fisher Electrophotometer a filter having a maximum absorption at 410 mμ was used.

PROCEDURE

Solutions Required. Nitric acid, 3 *N*. Dilute 208 ml. of concentrated nitric acid to 1 liter.

Ammonium Persulfate, 12%. Dissolve 120 grams of ammonium persulfate in water and dilute to 1 liter.

Ammonium Molybdate, 8.0%. Dissolve 80 grams of ammonium molybdate in 1 liter of warm water, cool, let settle, and filter or siphon off.

Sodium Fluoride, 2.4%. Dissolve 24.0 grams of sodium fluoride in water and dilute to 1 liter.

Hydrochloric Acid, 3 *N*. Dilute 249 ml. of concentrated hydrochloric acid to 1 liter.

Nitric Acid, 0.6 *N*. Dilute 50 ml. of 3 *N* nitric acid to 250 ml.

Procedure. Weigh 0.5 gram of sample into a 250-ml. Erlenmeyer flask, add 50 ml. of 3 *N* nitric acid, and put in solution on hot plate. Add 5 ml. of 12% ammonium persulfate, boil until clear (about 1 minute), remove, and cool slightly. Make up to 250 ml. and mix. Pipet two 25-ml. aliquots into two dry beakers or flasks. To one flask add 5 ml. of 8% ammonium molybdate solution with mixing and allow to react 6 minutes (longer standing does no harm), and to the blank add 10 ml. of 2.4% sodium fluoride. At the end of 6 minutes add 10 ml. of 2.4% sodium fluoride to the sample and 5 ml. of the 8% molybdate solution to the blank. Obtain transmittancy at 400 to 410 mμ against the blank. From a previously prepared curve of silicon *vs.* transmittancy obtain per cent of silicon.

Alloy Steels. If the sample does not go into solution with 3 *N* nitric acid, use 25 ml. of 3 *N* hydrochloric acid and 25 ml. of 3 *N* nitric acid and proceed as above.

High Silicon. Should the silicon be in excess of that shown on the silicon *vs.* transmittancy curve, dilute 100 ml. of the original sample with 100 ml. of 0.6 *N* nitric acid, and develop color on a 25-ml. aliquot as before.

RESULTS

Table I shows the values obtained with the method on National Bureau of Standards samples.

EFFECT OF VARIABLES

Acid Concentration. For the most accurate results the acid concentration must be maintained within 10% of the amount specified.

Temperature. The intensity of the color increases with temperature, but the blank will compensate for color changes caused by fluctuations of room temperatures up to about 0.5% silicon; above this value solutions must be maintained within a few degrees of the temperature at which the reference curve was made.

Table I. Determination of Silicon

N.B.S. Standard Sample	Certificate Value	Colorimetric Value
14 b	0.009	0.009
129 a	0.021	0.019
14 c	0.058	0.060
100	0.191	0.192
130	0.237	0.236
13 d	0.265	0.270
12 e	0.278	0.280
65 b	0.341	0.344
65 c	0.440	0.440
19 e	0.171	0.171

Time. The maximum color intensity will form within 5 or 6 minutes after addition of the molybdate, but longer standing, even for several hours, does not increase the color. Heating, on the other hand, will accelerate the color formation. After the addition of fluoride, however, time becomes an important factor.

Interfering Elements. No interference from elements commonly present in low-alloy steels have been observed. Excessive carbon, such as is present in cast iron, may be removed by filtration.

Molybdate Concentration. The actual amount of molybdate present is not critical, but the same quantity must be added to the sample and blank. Because the addition is dilution to volume, it must be made from a buret or pipet.

Fluoride Concentration. The amount of fluoride added must be measured from a pipet or buret. The actual concentration of the fluoride is not critical.

Persulfate Concentration. The amount of persulfate may be varied within wide limits without influencing the accuracy of the method. With only half of the specified amount of persulfate, the blank is lighter than when normal or double the normal amounts are used, and the intensity of the color is greater.

Silicon Concentration. Samples of steels higher than 3.0% silicon have not been analyzed by this method. Unsatisfactory results due to insolubility of the sample were obtained with a steel of over 5.0% silicon.

Stability of Color. With low silicon contents both the sample and blank will remain constant for 15 minutes or longer, but for the higher silicon contents the blank will begin gaining color in a few minutes while the sample will begin fading. For these samples transmittancy values must be obtained within a few minutes after the addition of the fluoride. The blank may be stabilized by the addition of 0.1% citrate in the fluoride.

DISCUSSION

In analyzing steels of similar specifications the same blank may be used for a series of samples, and the blank may be stabilized by the addition of a small amount of citrate with the fluoride. The citrate should not be added to the sample, as it will cause rapid fading of the yellow color.

Single samples may be analyzed in 15 minutes or less; a larger number of samples require about the same amount of time as the usual gravimetric procedure. For routine work this colorimetric procedure has been preferred to the gravimetric method by the routine analyst because there is less chance for error.

Over four thousand samples of various specifications of steels have been analyzed by this method and checked against gravimetric values. The results have been in good agreement.

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Oxidation of Vanillin to Vanillic Acid

Significance to Determination of Vanillin

D. T. ENGLIS AND MERLE MANCHESTER[1]

University of Illinois, Urbana, Ill.

By means of ultraviolet absorption studies, it is shown that a dilute solution of vanillin in air is slowly oxidized to vanillic acid. Ethyl vanillin shows the same type of change. This change is responsible for low results when either of the vanillins is determined by a direct ultraviolet examination. Confirmation is also given for the high results by the official Folin-Denis colorimetric method following atmospheric oxidation. Fairly complete oxidation of the vanillin compounds by air requires several weeks for the very dilute aqueous solution at room temperature. Neither coumarin nor vanillic acid shows appreciable change under the same conditions. Prompt examination is necessary to avoid serious errors in the quantitative estimation of vanillin in flavoring extracts.

IN 1944 Englis and Hanahan (*3*) described a method for determining vanillin (4-hydroxy-3-methoxybenzaldehyde) in flavoring extracts, which was based upon the absorption characteristics of vanillin in the ultraviolet region. Since that time it has been found that samples which have been allowed to stand for some time yield low results by this method. Under similar conditions, the official colorimetric method (*4*) based upon the reduction of the Folin-Denis phosphomolybdate-phosphotungstate reagent gives high results. These high values have been attributed to the formation of 4-hydroxy-3-methoxybenzoic acid (vanillic acid), which is reported to have a greater reducing power for the reagent than the corresponding aldehyde, vanillin. Therefore, it seemed important to study the effect of standing and exposure to air, to determine the nature and rate of change which is characteristic of vanillin, and to learn whether coumarin would undergo any adverse change under the same conditions.

There has long been a discussion as to the reaction that takes place when a dilute solution of vanillin is allowed to stand. Tiemann (*7*) in 1875 stated that he had obtained traces of vanillic acid by subjecting the vanillin to the action of moist air for a long period of time. Hubbard (*5*) said that it was likely that the vanillin was slowly oxidized to pyrocatechuic acid. Ciamician and Silber (*1*) obtained vanillic acid by exposing vanillin to sunlight in the presence of nitrobenzene. Pearl (*6*) worked out a direct method for the preparation of vanillic acid from vanillin based on the classical oxidation of aldehyde by means of silver oxide. He found that with an excess of alkali and 0.5 mole of silver oxide with 1.0 mole of vanillin the reaction gave quantitative results.

In the colorimetric procedures (*4, 5*) for the quantitative determination of vanillin Hubbard (*5*) and Curl and Nelson (*2*) noticed that the standard vanillin solution tended to increase in apparent strength on standing in a partially filled bottle. Curl and Nelson (*2*) believed that this was due to the oxidation of vanillin, as a full bottle of standard solution kept in the refrigerator checked with a freshly prepared solution. A partially filled bottle kept several months at room temperature gave a color increase of 19% over a freshly prepared standard solution. They also compared the color formed by standard solutions of vanillin and vanillic acid. Vanillic acid gave about 50% more color than did the vanillin solution of the same concentration. The colorimetric results obtained were higher than those from the gravimetric analysis. A colorimetric determination made on the residue from the extraction of the vanillin in the gravimetric method showed the substance was definitely not vanillin.

The official colorimetric method (*4*) for the determination of vanillin has been modified slightly by Wilson (*8*) in regard to the quantity of the sodium carbonate reagent and the instrument employed to measure the color value.

The ultraviolet method (*3*) was designed for quantitative determination of vanillin and coumarin when present together and depends upon their differences in chemical structure. Vanillin has a maximum absorption where coumarin shows only slight absorption. This greatest difference occurs at 2313 Å., whereas at 2875 Å. the extinction value for equal weights of either constituent is the same. Thus, by determining the extinction value at 2875 Å. the total concentration for the mixture of the two may be determined, and the amount of each individual constituent may be calculated by a simple equation from the extinction value at 2313 Å. When the measurements are made immediately after separation of the constituents or dilution of the sample, the results are good; if the solutions are allowed to stand, there is a marked reduction in the absorption at 2313 Å., leading to low results for apparent vanillin.

EXPERIMENTAL

Equipment. A Beckman Model D.U. spectrophotometer employing 1-cm. cells was used in the absorption studies.

Procedure. Solutions of vanillin, coumarin, and vanillic acid were prepared in concentrations of 10 mg. per liter of water containing about 10% of ethyl alcohol. A mixture containing 2.5 mg. per liter each of vanillin and coumarin was prepared by taking 250 ml. of each of the primary solutions and diluting to 1 liter. The solutions were sampled after 5 months and the absorption of each was determined with the spectrophotometer.

A marked change took place in the vanillin curve as a result of allowing the solution to stand. There was a pronounced decrease

[1] Present address, Firestone Tire & Rubber Co., Pottstown, Pa.

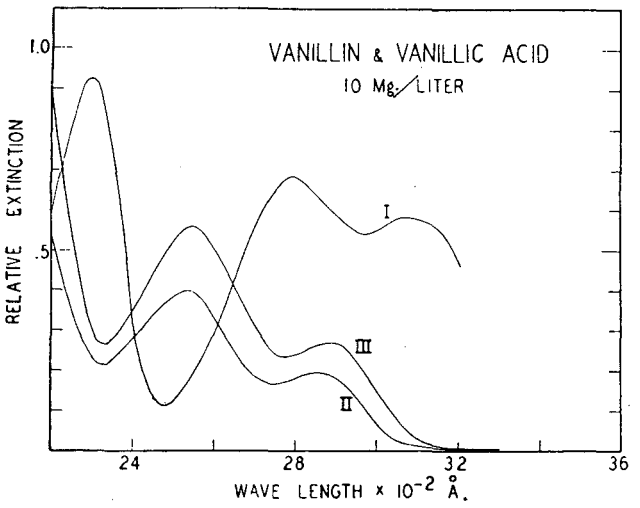

Figure 1. Ultraviolet Absorption Curves

I. Freshly prepared vanillin solution
II. Vanillin solution after standing 5 months
III. Vanillic acid

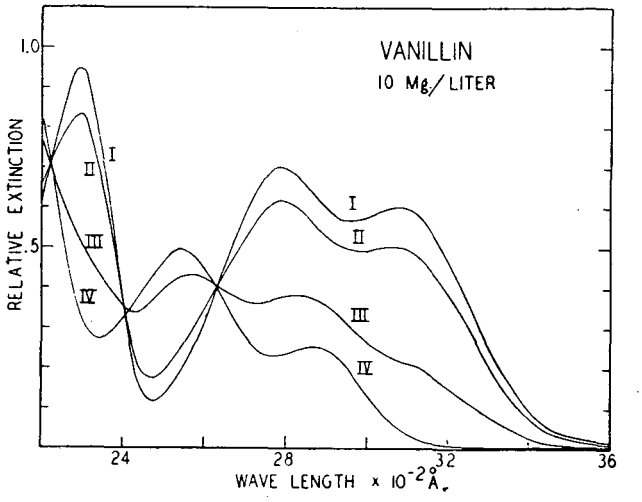

Figure 2. Changes in Ultraviolet Absorption Spectrum of Vanillin on Standing

I. 1 week
II. 2 weeks
III. 3 weeks
IV. 4 weeks

in the peaks for vanillin near 2300 and 2800 Å. (curve I, Figure 1) for the freshly prepared solution when compared to curve II for the solution allowed to stand. Such a change causes a tremendous error in the apparent vanillin by the ultraviolet method. In curve II a peak has developed near 2540 Å. and its whole nature conforms closely to that shown for vanillic acid (curve III).

The vanillic acid alone and solution of coumarin showed no measurable change upon standing. The absorption curve for the latter is available in a previous article (*3*). The change in absorption characteristics of the vanillin-coumarin mixture upon standing appeared to be solely due to a change in the vanillin.

Inasmuch as 10 mg. of vanillin should yield about 11 mg. of vanillic acid, one would anticipate the peak at 2540 in curve II of the exposed vanillin to exceed that of curve III. Because it is slightly lower one must conclude that the oxidation of the vanillin was not complete even after 5 months.

Stronger solutions of vanillin in 95% alcohol appeared to change less rapidly than did the dilute aqueous solution. In regular extracts the solvents and extraneous materials present may exert some protective action.

The vanillin solution of Figure 1 had been allowed to stand in a container which had a considerable air space above the surface of the solution and was opened frequently to the air.

In order to determine whether the conditions had accelerated the oxidation, a second solution containing 10 mg. of vanillin per liter was prepared. No special treatment was given the distilled water to expel dissolved oxygen. The absorption data were determined immediately on the fresh solution; then part of the remaining solution was placed in glass-stoppered bottles which were filled so that there was no air space remaining above the solution, then sealed with paraffin wax. These solutions were allowed to stand at room temperature in the laboratory. Once a week, one of the solutions was examined with the spectrophotometer.

There was a marked change in the shape of the curve over a period of a few weeks (Figure 2). At the end of a month (curve IV) the general characteristics of the vanillic acid curve are evident. It is apparent that the additional precautions to exclude oxygen, after the solutions were once prepared, had little benefit for this concentration of vanillin.

For the oxidation of vanillin to vanillic acid, 152 parts of the former would require 16 parts of oxygen. Assuming the water used in the preparation of the solutions was about half-saturated with oxygen and contained about 4 parts per million, this would be sufficient for the oxidation of 38 mg. per liter of vanillin—a quantity much greater than the 10 mg. actually present.

In ordinary flavoring extracts the concentration of vanillin is about 2000 mg. per liter. Although a certain amount of oxidation may take place in the stored extract, it is not likely under ordinary conditions to be a significant amount in proportion to the total vanillin present. However, when a tremendous dilution has been made for the purpose of the colorimetric determinations and the solutions are allowed to stand, the effect upon the analytical results may be very serious.

Study of Ethyl Vanillin. Ethyl vanillin (ethyl protocatechuic aldehyde) has a higher flavoring ability than regular vanillin. It has come into wide use as a constituent of imitation vanilla extracts and sometimes as an adulterant of extracts represented to be genuine. Therefore, it was desirable to subject this material to the same type of study as had been accorded the vanillin. A solution containing 10 mg. of ethyl vanillin in approximately 10% ethyl alcohol was prepared and its absorption curve evaluated. Curve I, Figure 3, is very similar to the vanil-

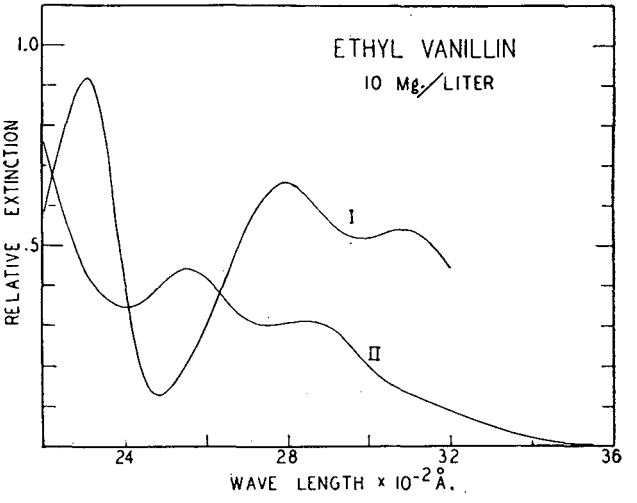

Figure 3. Changes in Ultraviolet Absorption Spectrum of Ethyl Vanillin on Standing

I. Freshly prepared solution
II. After 5 months

lin curve. Substitution of the ethoxy for the methoxy group produces little change in the absorption. The effect of standing for 5 months (curve II) is of the same nature as for vanillin. There is a conversion to the corresponding acid. The extent of conversion appears to be a little less than that for vanillin in the same period of time. It appears safe to conclude that errors in its estimation would be affected to about the same extent.

COLORIMETRIC ANALYSIS WITH FOLIN-DENIS REAGENT

While the work on the ultraviolet method was in progress, it seemed advantageous to include experiments in which the official method, as modified by Wilson (*8*), was utilized.

The procedure followed was essentially as Wilson has outlined, except that the solutions were examined at the specified wave lengths (6100 and 6500 Å.) with the Beckman instrument in 1-cm. cells in place of the wedge photometer.

The solutions were prepared in concentrations such that 10 ml. at the stage of analysis contained the quantity of material shown in Table I. To each portion analyzed, 5 ml. of the Folin-Denis reagent and 10 ml. of 20% sodium carbonate were added. The solutions were thoroughly mixed, allowed to stand 10 to 15 minutes, and made up to 100 ml. Then the color values were read.

The data of Table I supplement the findings of Curl and Nelson (*2*). Vanillic acid has a much stronger reducing action than freshly prepared vanillin, and the samples of vanillin and ethyl vanillin which have been allowed to stand have greatly increased color values, approaching those of the vanillic acid.

If one plots the E values against concentration for the freshly prepared vanillin and vanillic acid (series A), Beer's law is observed up to a concentration of 1 mg. per 10 ml. of solution analyzed. Beyond this point, it is apparent that the concentration of the oxidant (Folin-Denis reagent) is not sufficient to give a linear response. It makes little difference which wave length is selected; both ranges give linear response if the quantity of material is in the specified range.

Table I. Color Values with Folin-Denis Reagent

	Mg. per 10 Ml. Portion of Solution Analyzed	E at 6100 Å.		E at 6500 Å.	
		Vanillin	Vanillic acid	Vanillin	Vanillic acid
Series A	0.2	0.057	0.147	0.062	0.159
	0.4	0.098	0.264	0.105	0.276
	0.6	...	0.353	...	0.376
Freshly prepared solutions	1.0	0.213	0.574	0.225	0.593
	1.4	0.227	...	0.237	...
	2.0	0.248	...	0.260	...
			Ethyl vanillin		Ethyl vanillin
Series B	0.2	0.114[a]		0.122[a]	
		0.117[b]	0.118	0.125[b]	0.122
		0.129[c]		0.137[c]	
Solutions allowed to stand several weeks	0.5	0.212[a]		0.219[a]	
		0.247[b]	0.247	0.254[b]	0.257
		0.285[c]		0.295[c]	

[a], [b], [c]. Slightly different times of standing and different solutions.

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Vitamin A in Mixed Feeds

Chromatographic Separation and Estimation

MAXWELL L. COOLEY, *Larrowe Division, Rossford, Ohio*, JAMES B. CHRISTIANSEN, *Larro Research Farm, Detroit, Mich.*, AND RAY C. KOEHN, *General Mills, Inc., Minneapolis, Minn.*

A method for determining vitamin A in mixed feeds is improved by extracting the sample with a hot solvent and passing the extract through a chromatographic column which serves to remove plant pigments. The column is packed with equal parts of magnesia and diatomaceous earth. Vitamin A esters are eluted free from significant amounts of carotene and carotenoids. Carotene is, however, eluted together with the vitamin A alcohol from saponification mixtures.

IN A previous publication, Cooley, Christiansen, and Schroeder (*2*) advocated the determination of vitamin A in mixed feeds by extraction, partial purification of the extract by chromatographic adsorption on sodium carbonate, and measurement of total antimony trichloride color. Vitamin A content was obtained by correcting total color for that produced by carotene also present in the eluate, following a separate determination of the latter pigment. Although this method has been used successfully several years, certain improvements have been developed.

When the sodium carbonate adsorbent is used, some pigments such as lycopene are difficult to separate, the application of the carotene correction is cumbersome and a source of error, and the sodium carbonate must be a particular type and usually must be dried and ground before use.

More recently, Brew and Scott (*1*) have proposed a somewhat different technique for vitamin A determination in mixed feeds, which also involves partial chromatographic purification of feed extracts and correction of the total antimony trichloride color for that formed by nonvitamin substances present. This method has some of the same drawbacks as that of Cooley, Christiansen, and Schroeder.

Objectionable features of the earlier methods can be overcome by modification of the adsorption step in the determination. The activated magnesia–Hyflo Super Cel mixture suggested by Strain (*6*) and by Wall and Kelley (*7*) for chromatographic isolation of carotene is an effective agent in vitamin A determination and incidentally is more convenient to use than the special sodium carbonate recommended by Cooley *et al.*

The Waring Blendor originally suggested for extraction is effective, particularly when large samples of feeds are used. However, when it is employed with the magnesia–Super Cel mixture, an additional filtration is required. The hot solvent extraction technique suggested here has been found more convenient.

The proposed method affords quanftitative separation o-

Table I. Recovery of Vitamin A from Solution with and without Added Carotene after Chromatography

Vitamin A Added	Carotene Added	Eluting Volume	Vitamin A Found	
I.U.	γ	*Ml.*	*I.U.*	%
50	0	50	56	112
100	0	50	106	106
150	0	50	148	99
50	100	30–35[a]	55	110
100	100	30–35[a]	100	100
150	100	30–35[a]	154	101

[a] Eluating reagent added until carotene band reached bottom of adsorption column.

Table II. Recovery of Vitamin A from Mixed Feeds after Chromatography

Alfalfa Meal in Formula	Vitamin A, I.U./Pound Calcd.	Found	Carotene by Chromatograph
%			*I.U. of A/lb.*
0	4000	4000	600
6	7700	7600	3600
50	2000	2200	26,500

vitamin A from carotene, either as an isolated pigment or incorporated in feeds, and from lycopene.

To check on the completeness of the separation from carotene, three increments of vitamin A oil of known content were dissolved in petroleum ether. Then to each of three duplicate portions of oil was added a known quantity of (General Biochemicals, Inc., Chagrin Falls, Ohio) carotene (90% beta–10% alpha). All solutions were passed through chromatographic columns containing the recommended magnesia–Super Cel adsorbent. The columns containing vitamin A alone were eluted with a sufficient volume of 10% acetone in petroleum ether (more than 50 ml.) to be certain that all of the vitamin A was washed out. The second group was treated with the same eluting reagent only until the carotene band reached the bottom of the column. Vitamin A was then determined in the eluate by the antimony trichloride reaction.

Vitamin A is recovered quantitatively by this method and carotene is effectively removed by the adsorption column (Table I).

To confirm these findings when the method was applied to feeds, three feeds containing varying amounts of alfalfa meal, and therefore carotene, were analyzed by the proposed technique. Recovery of added vitamin A was excellent, as shown in Table II, even when ten times the amount of true vitamin A as carotene equivalent was present.

Thus with this technique, there is an effective separation of carotene from vitamin A and no need for the supplementary determination of carotene and application of a correction term.

When sodium carbonate was used as an adsorbent in the original procedure, lycopene was difficult to separate. The magnesia–Super Cel mixture effectively removes this pigment as shown in Table III reporting recovery of known amounts of vitamin A in the presence of tomato pomace.

Table III. Recovery of Vitamin A in Presence of Lycopene Separated by Chromatography

(Known amounts added to tomato pomace)

Added	Found
I.U.	*I.U.*
50	50
100	104

Similarly, many samples of fish meal contained a brownish pigment which the sodium carbonate adsorbent did not separate completely from vitamin A. This pigment reduced the accuracy of the assay unless saponification was used. This pigment has given no difficulty when the magnesia–Super Cel mixture was used. However, a colorless substance is extracted in varying amounts, both from liver meal and from certain samples of fish meal, which is not separated from added vitamin A by the magnesia–Super Cel adsorbent. The reaction product of this substance with antimony trichloride appears to be identical to that formed with true vitamin A. Both fresh liver and fish body oils may contain appreciable amounts of preformed vitamin A. Hence this chromagenic substance is tentatively assumed to be true vitamin A pending development of direct biologic evidence. Chromatographed wheat germ extracts caused brownish discoloration in the Carr-Price reaction. As vitamin E is not retained by the adsorbent, this discoloration is probably due to vitamin E.

Discrepancies were previously noted in certain samples of fish oil where saponification caused an increase in apparent vitamin A determined by the Carr-Price reaction. This is in contrast to normal behavior where a small percentage of vitamin A is usually lost through saponification (Table IV). Of a number of fish oils examined at this time, a sample of cod liver oil was located showing a 6.7% increase in apparent vitamin A after saponification (Table V). However, chromatographed preparations of the saponified and unsaponified oil agreed within 3.5% in apparent vitamin A content, both being about 10% lower than results from the unpurified saponified oil. Apparently in this case saponification released a substance separable from vitamin A by chromatography which caused an erroneously high figure for apparent vitamin A content.

Table IV. Comparison of Cod Liver Oil Sample with other Oils with Respect to Saponification

Oil Sample	Direct Assay	Saponified Oil	Recovery
	I.U./g.	*I.U./g.*	%
U.S.P. cod liver oil	1,500	1,600	107
Vitamin A acetate in cottonseed oil	10,250	10,000	98
6000 Å. feeding oil	6,200	6,000	97
10,000 Å. feeding oil	10,300	10,000	97

Table V. Anomalous Behavior of Cod Liver Oil Sample on Saponification

Treatment of Sample	Direct Assay[a]	Chromatographic[a]
	I.U./g.	*I.U./g.*
Unsaponified	1500	1450
Saponified	1600	1400

[a] Petroleum ether and 10% acetone in petroleum ether were used as solvent and eluant in each case.

The procedure of Koehn and Sherman (*4*) was used for saponification in all cases.

Separation of vitamin A alcohol from the carotene of saponification mixtures was unsuccessful under the conditions outlined (Table VI). Only about 30% of the vitamin A was eluted before the carotene. An additional 60% was eluted together with the bulk of the carotene. After saponification, carotene appeared to have slightly less affinity for the adsorbent, being eluted by a smaller volume of solvent, and vitamin A alcohol was more strongly adsorbed than the natural esters.

While vitamin A alcohol can be estimated using a predetermined correction for the amount of carotene present, as suggested in the previous method there is an over-all loss of vitamin A upwards to 10%. This is in substantial agreement with the data of Narod and Verhagen (*5*) who recorded recoveries after saponification ranging from 78 to 103% of the recoveries prior to saponification.

Generally saponification is inadvisable because of the potential inaccuracies introduced by the procedure. The presence of any appreciable amount of vitamin A alcohol in a feed mixture is unusual. Most natural fish oils and distilled concentrates contain only 0 to 1% of their vitamin A in alcohol form with tuna and dogfish liver oils containing 3 and 4% vitamin A alcohol (*3*). The presence of appreciable amounts of vitamin A alcohol such as might be provided by a saponified fish oil concentrate, can be detected readily by comparison of the apparent vitamin A content after complete elution of the carotene with the amount of vitamin A ester eluted prior to the carotene.

Table VI. Recovery of Vitamin A in Presence of Carotene after Chromatography

Vitamin A Added	Form	Carotene Added	Treatment	Eluting Volume	Vitamin A Found
I.U.		γ		*Ml.*	*I.U.*
2000	Vitamin A acetate in cottonseed oil	200	None	35	1940
2000	10,000 Å. feeding oil	200	None	35	1920
2000	10,000 Å. feeding oil	200	Saponified	20	600
2000	10,000 Å. feeding oil	200	Saponified	45[a]	1800
2000	10,000 Å. feeding oil	200	Oxidized	35	1220

[a] Also eluted carotene.

Table VII. Agreement between Laboratories Using Modified Method on Feed Mixtures

Feed Type[a]	Vitamin A Content, I.U./Pound Calcd.	Found, Lab. 1	Found, Lab. 2	Difference between Labs., %
Chick starter	2700	2700	2900	7
Chick starter	3600	3800	3600	5
Chick starter	4600	4900	4900	0
Chick starter	7200	7000	7000	0
Laying mash	6100	6400[b]	6200[c]	3
Pig feed	4600	4880[d]	4600[c]	6
Pig feed	1800	1900	1700	11
Breeder mash	6100	6250	6000	4
Turkey grower	6900	7150	6950	3
Breeder mash	6900	6800	6800	0
Feed concentrate	5900	5600	6050	8
Feed concentrate	8000	8900	8600	3

[a] Feeds used represent variety of commercial livestock feeds likely to contain true vitamin A.
[b] Average of 3 determinations.
[c] Average of 2 replicate determinations.
[d] Average of 4 determinations.

In agreement with Narod and Verhagen (*5*) oxidation products of vitamin A are retained by magnesia (Table VI).

The carotene–vitamin A mixture was oxidized at 90° C. Carotene and vitamin A were partially oxidized. The recovery of 61% of the initial vitamin A content indicates an appreciable retention of oxidation products derived from this vitamin.

Furthermore, it is unlikely that oxidation products from carotene were determined as vitamin A after the adsorption procedure. Additional studies using pure carotene subjected to oxidation by 10% hydrogen peroxide 2 hours at 130° C. showed that oxidation products of carotene were more strongly adsorbed by the column than was carotene and, hence, were readily separable from carotene and vitamin A esters. The oxidation products were less strongly adsorbed than chlorophyll and xanthophylls.

Similar work using peroxide-treated 10,000 Å. feeding oil indicated that oxidation products of vitamin A produced a brownish purple color when subjected to the Carr-Price reaction, and that these compounds were likewise effectively retained by the column. The same type of color is produced by extracts of feeds after prolonged storage unless adsorption procedures are used to separate vitamin A from oxidation products.

PROPOSED METHOD

Apparatus. Colorimeter. Coleman Model II Universal spectrophotometer was used in this work.

Chromatographic tubes, cylinder 23 × 200 mm., sealed to 4 × 80 mm. tube. Pass the stem of this tube through a two-hole stopper of proper size to fit in the top of a lipless, graduated cylinder. Through the other hole in the stopper insert a bent tube and connect this to a source of vacuum. Ordinarily an efficient water pump will be sufficient.

Place a small amount of cotton or glass wool at the bottom of the cylinder and pack tightly to a depth of 100 mm. with a well blended mixture of equal parts by weight of Hyflo Super Cel and magnesia. In order to assure a homogeneous blend of these two components, mix by rubbing out lumps by hand and rolling on paper at least fifty times. Add the mixture in several portions, tamping well with a stopper or similar device. Keep suction on the column during packing. Add a 1-cm. layer of anhydrous sodium sulfate to the top of the column.

Graduated cylinder, 100-ml. lipless.

Fat-extraction apparatus.

Automatic pipet, 10 ml. This pipet should deliver rapidly.

Reagents. Petroleum ether, boiling point 60° to 71° C. (Skellysolve B).

Skellysolve-acetone mixture, 450 ml. of Skellysolve B plus 50 ml. of acetone.

Johns-Manville Hyflo Super Cel.

Magnesia (Micron Brand 2641).

Anhydrous sodium sulfate.

Chloroform, C.P.

Antimony trichloride reagent (Carr-Price). Weigh 150 grams of C.P. antimony trichloride crystals into a 1000-ml. beaker and add 500 ml. of C.P. chloroform. Heat beaker and contents on hot plate. When solution is complete, cool and add 2% C.P. acetic anhydride. Centrifuge or filter solution if cloudy. Store solution in brown bottle.

Procedure. Weigh 10 grams of feed directly into fat-extraction flask. Add 100 ml. of Skellysolve B and digest 15 minutes, using fat extractor as a reflux condenser. [Longer periods of digestion (30, 45, and 60 minutes) were tried without any improvement in the efficiency of extraction of vitamin A, although carotene extraction is sometimes incomplete.] Remove flask from extractor, cover with watch glass to prevent evaporation, and allow solids to settle. Loss of solvent in this operation is generally negligible. A mark on the extraction flask showing the original liquid level may be used to show whether loss has been excessive. After 10 or 15 minutes pipet 50 ml. of the supernatant liquid onto an adsorption column, apply suction, and draw liquid through the column. Add approximately 35 ml. of 10% acetone in Skellysolve, using only enough of this reagent so that the first portion of the carotene band passes through the column. A trace of carotene is eluted from the column at this point to ensure complete removal of vitamin A. Disconnect the suction line from the column, which should stop the passage of the acetone and Skellysolve reagent. Dilute the solution containing the vitamin A to 50 ml. with Skellysolve. Pipet 25 ml. of solution into a 125-ml. Erlenmeyer flask and evaporate the solvents, using mild heat and reduced pressure. Transfer vitamin A from flask to colorimeter tube with small amounts of ethyl ether, and again evaporate using water bath and reduced pressure. Dissolve vitamin A residue from sample extract in 1 ml. of chloroform.

Set colorimeter at zero, using a blank comprised of 1 ml. of chloroform and 10 ml. of Carr-Price reagent. Place the assay tube in the colorimeter and add rapidly (automatic pipet) 10 ml. of Carr-Price reagent.

Take the maximum reading (color starts to fade rapidly). Determine units of A in tube from standard curve and calculate units of A per pound of feed.

The modified method gives good recovery values when known quantities of vitamin A are added to small laboratory-prepared feed samples, and results are in line with calculated figures for vitamin A content of commercially prepared feeds. Typical values given in Table VII show that the proposed method gives a good agreement between two different laboratories.

SUMMARY

A method for determining vitamin A in mixed feeds has been modified by substituting a mixture of activated magnesia and diatomaceous earth for the sodium carbonate. Carotene and lycopene, even in large quantities, do not interfere with determination of vitamin A esters. Carotene is not readily separated from vitamin A alcohol after saponification.

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Separation of Calcium from Magnesium

Preliminary Precipitation of Magnesium Hydroxide

J. A. GREEAR AND E. R. WRIGHT
Texas Division, The Dow Chemical Company, Freeport, Texas

In the analysis of magnesites or other magnesium compounds containing little calcium, 95% of the magnesium can be precipitated as the hydroxide without appreciable error due to precipitation of calcium. Traces of carbonate do not interfere, nor does the addition of sugar or mannitol aid the separation under the conditions studied.

A METHOD of analysis for calcium (*1*, *5*) used for many years in industrial laboratories depends upon the precipitation of most of the magnesium as magnesium hydroxide followed by filtration and precipitation of the calcium in the filtrate as calcium oxalate by standard procedures. This method was devised by Prutton (*4*) in the summer of 1925 for the analysis of magnesium chloride brines low in calcium. No systematic study of the method has been published, although a modification has been proposed by Hazel and Eglof (*2*).

The method is useful chiefly in two cases, (1) where the ratio of magnesium to calcium is so high that a separation cannot be made by direct oxalate precipitation, and (2) where a rapid method is desired involving only a single rather than a double oxalate precipitation. In the first classification fall most magnesites and magnesium chloride brines containing magnesium-calcium weight ratios of 20 to 1 or greater. Such materials are difficult or impossible to analyze by direct oxalate precipitation.

An example of a magnesite difficult to analyze by direct precipitation is Bureau of Standards sample 104 which has a certificate value of 85.67% magnesium oxide and 3.35% calcium oxide, or a magnesium-calcium ratio of 21.6 by weight. This sample was analyzed by careful triple precipitation of calcium oxalate with results shown in Table I. The average value obtained for calcium (3.31% CaO) is reasonable, as no correction was made for error due to the solubility of calcium oxalate. The error from this source amounts to about 0.1 mg. of calcium per precipitation (*3*), or 0.07% calcium oxide on the 0.6-gram sample taken for analysis.

In the method herein described, most of the magnesium (usually 95%) is removed as magnesium hydroxide in order to lower the magnesium-calcium ratio sufficiently to allow a direct oxalate precipitation to be made conveniently.

REAGENTS

A 16.0% magnesium chloride solution and standard calcium chloride solutions were prepared by the methods used by Wright and Delaune (*6*).

Potassium permanganate solutions were standardized against Bureau of Standards sodium oxalate.

Carbonate-free sodium hydroxide solution was made by filtration of a 50% solution made from C.P. material. Analysis showed less than 0.1% sodium carbonate present in the 50% sodium hydroxide.

All reagents were examined spectrographically, and were found to contain negligible amounts of calcium or strontium.

PROCEDURE

A sample is taken of sufficient size to contain 1.0 to 2.5 grams of magnesium. In the case of magnesites the sample is dissolved in hydrochloric acid, and the silica is removed by customary dehydration procedures. Iron and aluminum must also be removed if present to the extent of 30 mg. or more. The neutral solution from which ammonium salts have been removed is placed in a 500-ml. volumetric flask and diluted to about 200 ml. and an amount of 1 *N* sodium hydroxide is added equivalent to 95% of the magnesium. The solution is then made to volume, mixed thoroughly, and allowed to stand (usually 1 to 3 hours) until 250 ml. of nearly clear supernatant liquid can be siphoned off. A slight cloudiness at this point can be disregarded. (A permissible alternative procedure is to filter the magnesium hydroxide slurry through a 24-cm. Whatman No. 12 paper. However, in this case a correction may be necessary for traces of calcium in the filter paper.)

The 250-ml. aliquot portion is placed in a 400-ml. beaker and acidified with 5 ml. of 6 *N* hydrochloric acid. Ten milliliters of 5% ammonium oxalate solution are added, and the solution is heated nearly to boiling and is made alkaline to methyl red by dropwise addition of 6 *N* ammonium hydroxide. After digestion for about 2 minutes, 5 grams of solid ammonium oxalate are added and the solution is heated to boiling again. The precipitate is digested 1 hour, and is then allowed to stand for several hours or preferably overnight.

The calcium oxalate is filtered on a fritted Pyrex filter and washed four times with small portions of cool 0.1% ammonium oxalate solution. The precipitate is then dissolved in 75 ml. of hot 2% hydrochloric acid, 1 ml. of 5% ammonium oxalate solution is added, and the hot solution is made slightly alkaline with 6 *N* ammonium hydroxide. After digestion for 5 minutes, an additional 5-ml. portion of 5% ammonium oxalate solution is added and the precipitate is digested for 0.5 hour, then allowed to cool with occasional stirring for at least 3 hours.

The precipitate is finally filtered on a Pyrex filter, washed four times with 0.1% ammonium oxalate solution and then four times with distilled water, and after solution in 100 ml. of hot 2% sulfuric acid, the oxalate is titrated with 0.05 *N* potassium permanganate.

RESULTS

Effect of Sugar. The method as originally devised involved the addition of sugar as an aid in preventing loss of calcium through inadvertent addition of too much sodium hydroxide. Mannitol has also been recommended (*2*). In order to show whether such additive agents are necessary, a series of known mixtures were analyzed (Table II). It is apparent from these results that neither sugar nor mannitol is required, so long as not more than 95% of the magnesium is removed, but with removal of 100%, or in the presence of excess sodium hydroxide, the results are invariably low.

Effects of Carbonate. In order to find out what quantity of carbonate can be tolerated, a series of determinations was made

Table I. Analysis of Bureau of Standards Sample 104

	% CaO Found	
By triple oxalate precipitation	3.29	3.31
	3.28	3.32
	3.34	Av. 3.31
By recommended procedure without removal of iron	3.20[a]	3.09[b]
	3.20[a]	3.10[b]
	3.20[a]	
By recommended procedure with removal of iron	3.33[a]	3.32[b]
	3.34[a]	3.34[b]
	3.35[a]	3.30[b]
	3.36[a]	3.30[b]
	Av. 3.35[a]	3.32[b]

[a] Analyst A.
[b] Analyst B.

Table II. Effect of Sugar and Mannitol with Varying Amounts of Sodium Hydroxide

Magnesium Removed	Calcium Present[a]	Calcium Found: Without sugar or mannitol	Calcium Found: With sugar[b]	Calcium Found: With mannitol[b]
%	*Mg.*	*Mg.*	*Mg.*	*Mg.*
90	10.0	..	9.8	..
95	10.0	9.8	9.8	9.8
98	10.0	9.8	9.8	9.8
100	10.0	9.2	9.4	9.2
102	10.0	8.0	8.6	8.6
80	50.0	50.2	50.1	50.1
90	50.0	49.7	49.7	50.0
95	50.0	49.9	49.7	49.9
100	50.0	49.2	49.2	49.4
105	50.0	43.4	45.6	45.0

[a] Total weight of calcium taken.
[b] 20 grams used per determination. All figures are average of duplicate determinations.

Table III. Effect of Carbonate

Magnesium Removed	Na_2CO_3 Present	Calcium Present[a]	Calcium Found
%	*Mg.*	*Mg.*	*Mg.*
95	15	10.0	9.7
102	15	10.0	8.4
95	15	50.0	49.9
102	15	50.0	46.2
95	150	10.0	9.4
102	150	10.0	7.8
95	150	50.0	48.2
102	150	50.0	26.4
95	270	10.0	8.6
102	270	10.0	8.1
95	270	50.0	35.6
102	270	50.0	12.3

[a] Total weight of calcium taken.

with sodium hydroxide containing known amounts of sodium carbonate (Table III). As could be expected, the results show that the error due to the presence of carbonate increases with the amount of calcium present, and with the proportion of magnesium removed. In general, the small amount of carbonate normally left in 50% sodium hydroxide and the traces picked up during handling are not sufficient to cause appreciable error.

Effect of Impurities. As shown in Table I, low results were consistently obtained on Bureau of Standards sample 104 unless iron and aluminum were removed by a double precipitation with ammonia. This is not unexpected (*3*). In order to show the magnitude of the effect, a few determinations were made with known amounts of impurities (Table IV). It is apparent that even comparatively small amounts of phosphate cause serious error, but that the error from iron is serious only when 50 mg. or more are present.

Other Applications. Results with three other samples are shown in Table V. Because the spectrographic method may be in error by 10 to 15% of the quantity of calcium present, the results in the case of the magnesite sample agree somewhat fortuitously. However, the authors believe that the chemical method gives acceptable accuracy on such materials.

The published rapid method (*1*, *5*), which consists of removal of 95% of the magnesium, followed by a single hot precipitation of calcium oxalate, tends to give slightly high results. Thus by this procedure the authors found 5.2 and 51.7 mg. of calcium when 5.0 and 50.0 were taken, respectively. Apparently the negative error to be expected from hot filtration and washing is more than offset by the positive error due to coprecipitation of magnesium oxalate and failure to make a blank correction.

Table IV. Effect of Impurities

Impurity Present	Calcium Present[a]	Calcium Found
Mg.	*Mg.*	*Mg.*
10 Fe	50.0	49.8
50 Fe	50.0	49.2
100 Fe	50.0	47.4
10 PO_4	50.0	49.0
50 PO_4	50.0	43.8

[a] Total weight of calcium taken. 95% of magnesium removed in every case.

DISCUSSION

Results by this procedure are consistently low by 0.1 to 0.3 mg. of calcium because of solubility errors which are inherent in all oxalate methods for calcium. In the most accurate work, this error can be corrected by recovery of the traces of calcium precipitated along with the magnesium ammonium phosphate according to the method of Hillebrand and Lundell (*3*). However in ordinary work, the magnitude of the error is small enough to be neglected, or a fixed correction may be applied. It is better to make such corrections than to depend on a procedure that involves compensating errors (*3*). In Tables II, III, and IV, these solubility errors have been doubled, as the results are calculated to the original sample basis.

In the presence of magnesium ion, hydrolysis of carbonate would be expected to take place, resulting in the formation of magnesium hydroxide and bicarbonate ion. Such hydrolysis is in part responsible for the fact that small amounts of carbonate can be tolerated without significant loss of calcium. It appears also that part of the carbonate present is precipitated with the magnesium hydroxide, and consequently the error caused by carbonate is smaller than expected.

Table V. Other Applications

Description	Mg-Ca Ratio by Weight	Calcium Spectrographic Method	Calcium Chemical Method
		%	%
Crude 34% $MgCl_2$ liquor	140:1	0.075	0.064
			0.063
			0.063
Synthetic magnesite A	110:1	0.48	0.48
			0.48
			0.48
			0.48
Synthetic magnesite B	170:1	0.36	0.34
			0.33
			0.34
			0.34

The elimination of iron by double precipitation with ammonia is time-consuming, as ammonium salts must also be removed before precipitation of magnesium hydroxide. A faster procedure would be to remove the iron by electrolysis with a mercury cathode or by extraction with ether. However, most of the materials with which the authors have dealt have not required removal of iron and aluminum.

Many sources of sodium hydroxide contain traces of strontium compounds. Possible error from this cause must be avoided by analysis of the sodium hydroxide or by use of a carefully determined blank correction.

The authors know of no procedure by which the magnesium can be precipitated completely as hydroxide without some loss of calcium. It is possible that adsorption errors become significant as the equivalence point is passed.

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Determination of Copper by Dithio-oxamide in Magnesium and Magnesium Alloys

H. H. WILLARD, *University of Michigan, Ann Arbor, Mich.*, AND ROBERT E. MOSHER AND A. J. BOYLE, *Wayne University, Detroit, Mich.*

A rapid, accurate, and direct colorimetric procedure for the estimation of copper in refined magnesium and magnesium alloys is presented. The color reagent employed is rubeanic acid (dithio-oxamide) in combination with a buffer complex composed of acetate and malonic acid. No separation or concentration techniques are required.

THE initial study of rubeanic acid (dithio-oxamide) appears to have been made by Wöhler (*7*), who observed that this compound precipitated copper, silver, mercury, and lead. Rubeanic acid was first reported as a reagent for the quantitative precipitation of copper by Rây and Rây (*5*), and was subsequently used for detecting copper by a spot test technique (*3*). Later Allport and Skrimshire (*1*) employed rubeanic acid in the colorimetric estimation of copper in certain drug materials following an extraction procedure. Willard and Diehl (*6*) state that rubeanic acid may be used as a color reagent for copper in the presence of manganese and zinc but not cobalt and nickel. Center and MacIntosh (*2*) introduced the use of rubeanic acid for the determination of copper in potable water supplies.

The selection of rubeanic acid as the reagent for the colorimetric estimation of copper in magnesium and magnesium alloys appears to offer several advantages. The method is rapid, accurate, and direct, and requires only a fraction of a gram to determine copper in refined and alloy magnesium.

REAGENTS

Nitric acid, concentrated, C.P.
Ammonium hydroxide, concentrated, C.P.
Glacial acetic acid, C.P.
Sodium acetate trihydrate, C.P.
Rubeanic acid, Eastman Kodak Company.
Malonic acid, Paragon Testing Laboratories.
Cupric sulfate pentahydrate, C.P.
Gum arabic.
Methyl orange.

Buffer Color Reagent. Weigh out 300 grams of sodium acetate into 1-liter beaker, and add 300 ml. of distilled water to dissolve the salt. Filter the solution with suction through a properly prepared Gooch crucible. Add 280 ml. of glacial acetic acid to the filtrate.

Dissolve 0.200 gram of finely powdered gum arabic in 20 ml. of distilled water in a 50-ml. beaker. In a separate 50-ml. beaker dissolve 0.100 gram of rubeanic acid in 20 ml. of alcohol. Both the gum arabic and the rubeanic acid may require slight heating. Add the gum arabic and rubeanic acid solutions to the acetic acid–acetate mixture, cool, and dilute to 1 liter with distilled water.

Malonic Acid Solution. Dissolve 200 grams of malonic acid in 500 ml. of distilled water. Neutralize with concentrated ammonium hydroxide to a faint odor of ammonia, cool, and dilute to 1 liter with distilled water.

Methyl Orange Solution. Dissolve 1.0 gram of the indicator in water and dilute to 1 liter with distilled water.

Standard Copper Solution. Dissolve 393 mg. of cupric sulfate pentahydrate in 1 liter of distilled water. This solution represents approximately 0.1 mg. of copper per ml. Two 100-ml. portions of this solution are taken for standardization. Suitable dilutions of the standard copper solution are then used for the preparation of the standard curve.

PROCEDURE

Copper in Magnesium Alloys. Weigh a 2.0-gram sample of alloy into a 400-ml. beaker, and add 50 ml. of distilled water followed by just enough concentrated nitric acid to dissolve the metal. Boil vigorously for 5 minutes after solution is complete to remove the oxides of nitrogen, cool, and transfer to a 250-ml. volumetric flask. Dilute to the mark with distilled water. Pipet one 25-ml. aliquot into a 100-ml. beaker, and a similar aliquot into a 100-ml. volumetric flask. Add 3 drops of methyl orange to the beaker and neutralize by dropwise addition of concentrated ammonium hydroxide until color changes. Add the same number of drops of concentrated ammonium hydroxide to the aliquot in the 100-ml. volumetric flask. Add 5 ml. of a 20% solution of malonic acid followed by 25 ml. of buffer color reagent. Dilute to the mark with distilled water. Mix thoroughly after each addition listed above. Permit the sample to stand for 30 minutes, then compare in a suitable photoelectric colorimeter using a blue filter.

Copper in Refined Magnesium. This procedure is identical with that for magnesium alloys, except that no malonic acid reagent is added and only 5 ml. of buffer color reagent are used. It is advisable to permit a development time of 60 minutes for these very low concentrations of copper, before comparison with standards.

RESULTS AND DISCUSSION

To reduce the error due to segregation common in light metal alloys a 2.0-gram sample weight is advocated initially, from which an aliquot containing 200 mg. of metal is finally taken for analysis. Nitric acid serves best as the solvent for the metal, as it is important that all copper be present as cupric ion. A Cenco photelometer equipped with 50-mm. cells was used to estimate copper in the normal range for magnesium alloys as listed by the American Society for Testing Materials. For the lower concentrations present in refined magnesium use was made of a Lumetron Model 402E employing 100-mm. comparison cells.

Table I shows the results for copper in the presence of the elements common to magnesium alloys. As will be noted, the concentrations of these elements are maximum or in excess of that normally encountered. The standard copper curve may be prepared with the addition of purified magnesium nitrate or distilled magnesium. Results are the same within the limits of experimental error, however, using only standard copper solution.

Table I. Determination of Copper by Rubeanic Acid

(In solutions containing magnesium, aluminum, zinc, manganese, iron, cadmium, and nickel)

Cu Present	Mg.	Al	Zn	Mn	Fe	Cd	Ni	Cu Found A	Cu Found B	Cu Found Av.
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
0.0408	200	..	16	..	...	..	...	0.0409	0.0404	0.0407
0.184	200	..	..	..	...	..	...	0.181	0.178	0.180
0.0408	200	20	..	..	...	..	...	0.0405	0.0410	0.0408
0.184	200	20	..	..	...	..	...	0.184	0.184	0.184
0.0408	200	..	16	..	...	..	...	0.0404	0.0405	0.0405
0.184	200	..	16	..	...	..	...	0.184	0.181	0.183
0.0408	200	..	..	4	...	..	...	0.0414	0.0412	0.0413
0.184	200	..	..	4	...	..	...	0.188	0.174	0.183
0.0408	200	..	..	..	0.02	..	...	0.0409	0.0404	0.0407
0.184	200	..	..	..	0.02	..	...	0.178	0.181	0.180
0.0408	200	..	..	..	...	10	...	0.0410	0.0412	0.0411
0.184	200	..	..	..	...	10	...	0.181	0.178	0.180
0.0408	200	..	..	..	...	..	0.02	0.0411	0.0407	0.0408
0.184	200	..	..	..	...	..	0.02	0.178	0.178	0.178
0.0408	200	20	16	4	0.02	10	0.02	0.0408	0.0407	0.0408
0.184	200	20	16	4	0.02	10	0.02	0.181	0.181	0.181

Table II. Influence of Certain Cations on Color Intensity of Copper Rubeanate

(In presence of Al, Bi, and Th)

Cu	Al	Bi	Th	Malonic Acid	Transmittance
Mg.	*Mg.*	*Mg.*	*Mg.*	*Gram*	%
0.102	..	..	..	..	24.5
0.102	..	..	..	..	24.5
0.102	..	..	..	1.0	19.9
0.102	..	..	..	1.0	19.6
0.102	10	..	..	..	23.0
0.102	10	..	..	..	24.6
0.102	10	..	..	1.0	19.6
0.102	10	..	..	1.0	19.8
0.102	..	10	..	..	23.3
0.102	..	10	..	..	22.6
0.102	..	10	..	1.0	21.4
0.102	..	10	..	1.0	20.6
0.102	..	..	10	..	24.3
0.102	..	..	10	..	23.7
0.102	..	..	10	1.0	20.6
0.102	..	..	10	1.0	20.3

Although aluminum does not produce a color reaction with rubeanic acid, it decidedly affects the color intensity of copper rubeanate. Attempts at complexing aluminum with fluoride, tartrate, and citrate were without success. Results for copper in these circumstances were always high. Malonic acid, however, served to eliminate this error in the presence of as much as 100 mg. of aluminum per aliquot. Employment of a boric acid–borax-citrate buffer complex (pH 7) appeared to eliminate the aluminum error, but precision and color quality were unacceptable. The manner of mixing color reagent with standard copper solutions caused significant deviation in duplicate standards.

Certain other multivalent cations shown in Table II, although failing to produce a color reaction with rubeanic acid, influence the colloidal properties of copper rubeanate. Thorium and bismuth decrease color intensity. In the absence of malonic acid, copper standards show a lower color intensity.

Iron interferes in this method if present in the ferrous state (*4*). Solution of the sample in nitric acid precludes this possibility. The yellow color of ferric citrate is also a source of error. As malonic acid both decolorizes and complexes ferric iron, this factor is conveniently eliminated.

The presence of ammonium phosphate, sulfate, perchlorate, and chloride in 1-gram quantities had no effect on the results.

The full development of the olive green copper rubeanate is complete within 30 minutes in the range common to magnesium alloys. For refined magnesium in which copper concentrations are extremely low it is advisable to permit a 60-minute development period before comparison. When the log of the transmittance was plotted against amounts of copper from 0.010 to 0.002 mg., a straight line was obtained, showing that the results are equally good for these very small amounts of copper. In samples requiring malonic acid (alloys), retardation of color development occurs if this substance is present in concentrations exceeding 1%. All fully developed colors are stable for several hours.

The application of this method to ferrous and other nonferrous alloys as well as biological materials is being investigated.

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Metallic Contaminants in Fluid Cracking Catalyst

Determination by Emission Spectrograph

E. L. GUNN, *Humble Oil & Refining Company, Baytown, Tex.*

A method has been developed for the routine analysis of fluid cracking catalyst for trace metal contaminants by means of the emission spectrograph, employing the internal standard technique with direct current arc excitation. As applied to typical plant samples, the precision of the method in the respective concentration ranges involved is expressed by a standard deviation of approximately 8% for iron, 16% for sodium and calcium, 12% for nickel, and 5% for chromium and vanadium. Results obtained by the spectrographic method are in fair agreement with those obtained by chemical methods. The influence on the method of changes in the alumina content of the catalyst is discussed.

IN FLUID catalytic cracking operations, quantitative analyses of the catalyst are usually desired at periodic intervals as an aid in controlling operations and in interpreting results. The analyses required usually are not for the major components, alumina and silica, but for trace contaminants which can accumulate on the catalyst either through metal erosion in the system or the deposition of inorganic components imparted to the catalyst from the feed stocks during cracking operations. The tedious and time-consuming nature of chemical methods of analysis makes such methods practically prohibitive for routine control use. The emission spectrograph has been used in this laboratory for the routine determination of catalyst contaminants for about 3 years, and it has proved capable of providing results of adequate precision and accuracy which compare favorably with those obtainable by the more difficult chemical methods. Furthermore, only 2 to 2.5 hours are required for the complete spectrographic analysis of a catalyst sample for iron, nickel, chromium, vanadium, sodium, and calcium contaminants.

Spectrographic methods have been applied (*3*, *5*, *6*) to the analysis of various minerals and ores. A method has been described (*1*) for the analysis of silica-alumina catalyst for contaminants in which lines of silicon and aluminum are used for reference; empirical factors are introduced to compensate for the differences of film emulsion response of the separate spectral regions of the film. The method of catalyst analysis employed in this laboratory differs from that described (*1*) in several significant respects: (1) the present method uses added internal standards as references against the sought elements; (2) the ex-

Table I. Spectral Line Pairs Used in Analysis of Fluid Cracking Catalyst (4)

Element Sought	Wave Length, Å.	Internal Standard	Wave Length, Å
Fe	3407.5	Co	3405.1
Ni	3483.7	Co	3474.0
Cr	4254.3	W	4294.6
V	3184.0	Co	3405.1
Na	3302.3	Co	3405.1
Ca	3179.3	Sr	3464.6

citation source and procedural steps are different; and (3) the group of metal contaminants determined is different in that calcium rather than copper is determined. At the start of the experimental studies in this laboratory it was contemplated that suitable spectral lines of a major catalyst constituent, silicon or aluminum, might be used as references for comparison with appropriate metal contaminant lines. However, the relative paucity of aluminum and silicon lines, as well as their remoteness from lines of the sought elements and unsuitability for density measurements with the source of excitation employed, precluded their use and suggested the addition of internal standards. Three internal standards, cobalt, tungsten, and strontium, are added to the sample prior to analysis. The spectral lines used for measurements are shown in Table I.

REAGENTS AND CALIBRATION STANDARDS

Internal Standard Reagents. Standard Cobalt Solution. C.P. Baker's analyzed cobaltous nitrate is added to distilled water to prepare a solution containing 1 mg. of cobalt per ml.

Standard Tungsten Solution. C.P. Eimer & Amend analyzed para-ammonium tungstate is added to distilled water to prepare a solution containing 20 mg. of tungsten per ml.

Standard Strontium Solution. C.P. Baker's analyzed strontium nitrate is added to distilled water to prepare a solution containing 80 mg. of strontium per ml. (Cobalt and strontium reagents may be prepared as one standard solution, but ammonium tungstate must be prepared separately, as it is incompatible with the other two reagents.)

Standard Catalyst Blend. A blend for spectrographic calibration is prepared by adding a known amount of the metal contaminant, or contaminants, in solution form to a portion of fresh catalyst. It is necessary to detect the presence and establish the concentration of each sought element initially present in the fresh catalyst before the blend is made. The contaminants most likely to be found are iron, sodium, and calcium, and account is taken of the amount of each that is present. The fresh catalyst is preignited for 4 hours in a muffle furnace at 539° C. (1000° F.) before the contaminants are added. Sodium is introduced as the chloride or sulfate, vanadium as ammonium vanadate, and iron, nickel, chromium, and calcium as the nitrates. To impregnate the catalyst uniformly with the contaminants, water is cautiously evaporated from the mixture during stirring, and this is followed by ignition in a muffle furnace at 1000° F. for 8 hours. Internal standards are added and the calibration blends are analyzed in the manner described below.

By plotting concentration in per cent against intensity ratio of the selected analytical line pair for each contaminant, a set of calibration curves similar to those of Figure 1 is obtained.

ANALYTICAL PROCEDURE

Sample Preparation. A 10-gram portion of the catalyst sample is weighed to the nearest hundredth gram into a tared 100-ml. beaker. Exactly 1 ml. of cobalt internal standard reagent is added by means of a pipet for the determination of iron, nickel, vanadium, and sodium; 1 ml. of ammonium tungstate reagent is added for the determination of chromium; and 1 ml. of strontium nitrate is added for the determination of calcium. The beaker is covered with a watch glass and heated on an electric hot plate at 450° to 500° C. Although the fluid nature of the catalyst is of considerable aid in mixing, the contents should be stirred initially with a glass rod and occasionally during heating to ensure complete sample homogeneity. Heating is continued for 30 minutes after the water apparently has evaporated. A working time of 5 to 7 minutes is normally required to introduce the internal standards for an analysis. Tests with plant-regenerated catalyst samples have shown that the weight of the sample mixture thus prepared for spectrographic analysis is within 0.7% of the weight of the original catalyst sample plus that of the evaporated internal standards before they are mixed.

Spectrographic Technique. A portion of the prepared sample is inserted into the sample electrode by forcing the electrode into the catalyst, so that the crater may be fully packed. Three electrodes are prepared in this manner for each spectrogram. The arcing process is carried out immediately under the standard conditions outlined in Table II. In rare instances the sudden heat of the initial arcing may result in expulsion of the sample from the electrode crater. The operator can detect this occurrence, both by the observed over-all decrease in density compared with other exposures and by the size of the residual fused bead left in the electrode crater, so that this exposure may be rejected and another made. Use of the rotating step sector with four levels of exposure provides for density measurements of the several line pairs in the more favorable regions of the emulsion calibration curve. Film measurements, calculation of intensity ratios, and conversion to percentage of the sought components by reference to the respective analytical calibration curves are carried out in a conventional manner (2).

Table II. Equipment and Standard Conditions Used in Analysis of Fluid Cracking Catalyst

Spectrograph. A.R.L. grating spectrograph, 1.5-meter, 2460 to 4580 Å. region
Densitometer. A.R.L. projector—comparator with voltage regulator
Source. D.C. full-wave rectifier, 250 volts open circuit, 12.0 ± 0.2 ampere excitation current
Grating Aperture. Full opening
Slit Width. 10 microns
Aperture. Rotating sector disk, 18 cm. from slit
Lens. 5-inch focal length cylindrical quartz, 31 cm. from slit.
Electrodes. Carbon rods 3 inches in length, 0.25 inch in diameter. Lower, positive, having sample crater with depth and diameter of 0.125 inch; upper, negative, with 20° conical trim to 0.125 inch diameter,
Analytical Gap. 7.0-mm., optical axis at center of gap
Film. 35-mm., Eastman Spectrum Analysis No. 1
Exposure. For complete arcing time of 30 seconds
Development. 3 minutes at 70° F., Eastman Formula D-19.
Film Emulsion Calibration. Iron spectrum with rotating sector disk, four steps, factor of 2. Calibrations established for 3200 to 3400 and 4200 to 4300 Å. regions

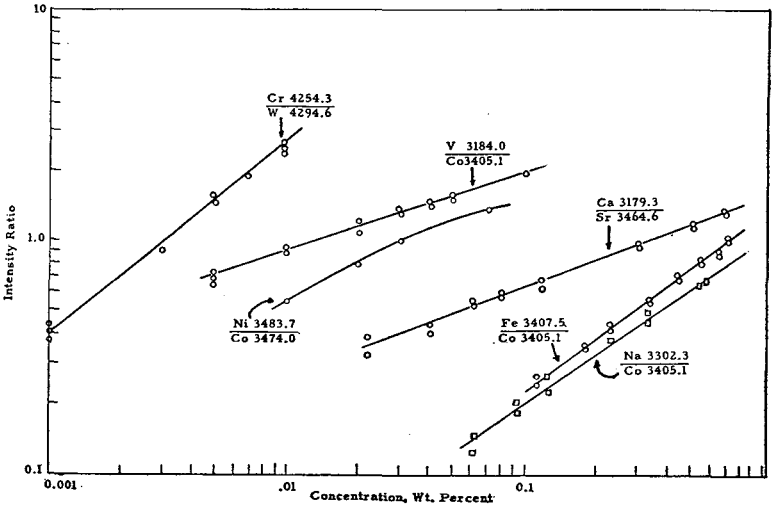

Figure 1. Analytical Calibration Curves for Metal Contaminants in Fluid Cracking Catalyst

Table III. Determination of Iron in Fluid Cracking Catalyst

Sample	Iron, % Chemical analysis	Iron, % Spectrographic analysis	Per Cent Deviation Based on sample	Per Cent Deviation Based on component
1	0.21	0.18	−0.03	−14.3
2	0.26	0.22	−0.04	−15.4
3	0.27	0.30	+0.03	+11.1
4	0.28	0.24	−0.04	−14.3
5	0.30	0.31	+0.01	+ 3.3
6	0.32	0.32	0.00	0.0
7	0.39	0.42	+0.03	+ 7.7
8	0.42	0.39	−0.03	− 7.1
		Av.	±0.026	9.1

Replicate Spectrographic Determinations

Detn.	Sample 1[a]	Sample 2[b]
1	0.45	0.20
2	0.46	0.24
3	0.41	0.19
4	0.41	0.24
5	0.39	0.20
6	0.39	0.24
7	0.42	0.24
8	0.43	
9	0.45	
Av.	0.42	0.22
Standard deviation (based on component), %[c]	5.9	10.4
Range (based on component), %	16.6	22.7

[a] By average of several chemical determinations, % iron = 0.42.
[b] By average of several chemical determinations, % iron = 0.22.
[c] Calculated from standard deviation = $\sqrt{\frac{\Sigma d^2}{n-1}}$, where Σd^2 = sum of squares of deviations of each result from their average.

Table IV. Determination of Calcium in Fluid Cracking Catalyst

Sample	Detn.	Calcium, % Chemical analysis	Calcium, % Spectrographic analysis	Per Cent Deviation Based on sample	Per Cent Deviation Based on component
1	1	0.04	0.04	0.00	0.0
	2		0.02	0.02	−50.0
	3		0.02	0.02	−50.0
2	1	0.24	0.21	0.03	−12.5
	2		0.19	0.05	−20.8
	3		0.23	0.01	−4.2
	4		0.24	0.00	0.0
3	1	0.53	0.49	0.04	−7.5
	2		0.55	0.02	3.8
			Av.	0.02	16.5

CHEMICAL METHODS

Chemical methods (*7*, *8*) of analysis of fluid cracking catalyst also have been empolyed to obtain data for comparison with results from the spectrographic method. The chemical methods used are briefly as follows:

Iron. Solution of the catalyst is effected by sodium carbonate fusion, followed by the addition of water and hydrochloric acid. The thiocyanate color complex is developed with an aliquot of the solution and the color intensity is measured with a Klett-Summerson photoelectric colorimeter to determine iron.

Calcium. Solution of the sample is effected in the same manner as for iron, and after separation of interfering elements calcium is determined as the oxalate.

Sodium. The sample is decomposed by sulfuric-hydrofluoric acid treatment, then dissolved in hydrochloric acid. Sodium is precipitated with zinc uranyl acetate reagent for the gravimetric determination.

Nickel. The sample is put into solution by the procedure used for iron and calcium. By the addition of sodium hydroxide and sodium peroxide to a solution aliquot, nickel is separated as the hydroxide from vanadium and chromium, and these latter are converted to the vanadate and chromate, respectively. Nickel is separated from other insoluble hydroxides, such as iron and titanium, by the use of sodium citrate, ammonium hydroxide, and dimethylglyoxime. The nickelous dimethylglyoxime is extracted with chloroform, then decomposed with hydrochloric acid. Bromine is added to oxidize nickel to the nickelic form, ammonium hydroxide and dimethylglyoxime are added to develop a brown color complex, and the color intensity is measured with the photoelectric colorimeter to determine nickel.

Chromium. A portion of the solution from the nickel separation is made acid and the chromium determined by photoelectric measurement of the red color produced by the addition of diphenylcarbozide reagent.

Vanadium. The phosphotungstovanadic acid complex is developed in a portion of solution from the nickel separation and the vanadium determined by measurement of the yellow color intensity with the photoelectric colorimeter.

EVALUATION OF METHOD

Indications of the reliability of the present spectrographic method as applied to routine plant samples are furnished by the data shown in Tables III to VI, where the results of chemical and

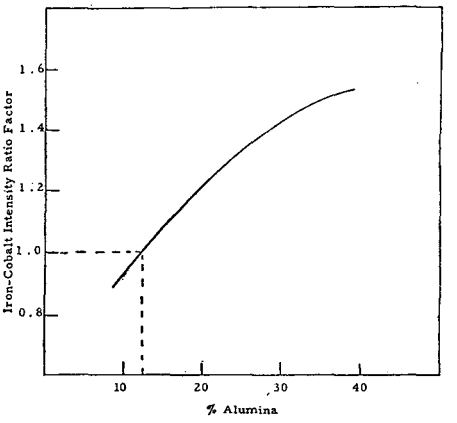

Figure 2. Relation of Iron-Cobalt Intensity Ratio to Alumina Content

Table V. Determination of Sodium in Fluid Cracking Catalyst

Detn.	Sodium, % Chemical analysis	Sodium, % Spectrographic analysis
1	0.14	0.16
2	0.16	0.16
3		0.15
4		0.22
5		0.18
Av.		0.17
Standard deviation (based on component), %[a]		16.5
Range (based on component), %		41.2

[a] Calculated from standard deviation = $\sqrt{\frac{\Sigma d^2}{n-1}}$, where Σd^2 = sum of squares of deviations of each result.

Table VI. Determination of Nickel, Chromium, and Vanadium in Fluid Cracking Catalyst

Sample	Nickel, % Chemical	Nickel, % Spectrographic	Chromium, % Chemical	Chromium, % Spectrographic	Vanadium, % Chemical	Vanadium, % Spectrographic
1	0.013	0.012	0.004	0.004	0.007	0.011
2	0.009	0.015	0.003	0.003	0.005	0.005
3	0.008	0.009	0.004	0.0045	0.002	0.003
4	0.011	0.011	0.004	0.0037	...	...

Replicate Spectrographic Determinations

Detn.	Nickel, %	Chromium, %	Vanadium, %
1	0.012	0.003	0.0039
2	0.010	0.003	0.0044
3	0.009	0.002	0.0044
4	0.009	0.003	0.0042
5	0.010	0.003	0.0044
Av.	0.010	0.028	0.0043
Standard deviation (based on component), %[a]	12.0	5.3	5.11
Range (based on component), %	30.0	33.3	11.6

[a] Calculated from standard deviation = $\sqrt{\frac{\Sigma d^2}{n-1}}$, where Σd^2 = sum of squares of deviation of each result from their average.

Table VII. Spectrographic Analysis of Fluid Cracking Catalyst in Absence and Presence of Strontium

Sample	Iron, %		Nickel, %		Chromium, %		Vanadium, %		Sodium, %		Calcium, %
	No Sr	0.3% Sr	No Sr	0.8% Sr	No Sr	0.8% Sr	No Sr	0.8% Sr	No Sr	0.8% Sr	0.8% Sr
1	0.41	0.43	0.012	0.013	0.0037	0.0047	0.012	0.012	....	....	0.03
2	0.26	0.26	0.0092	0.011	0.0043	0.0041	0.0040	0.0035	< 0.05	< 0.05	0.02
3	0.73	0.70	0.0075	0.0070	0.0023	0.0023	0.013	0.012	0.35	0.32	0.52
4	0.32	0.32	0.0098	0.011	0.0025	0.0030	0.0074	0.0078	0.17	0.17	0.03

spectrographic analyses of the same samples are compared; sets of replicate spectrographic determinations provide measures of the precision of these determinations. These data indicate for the spectrographic method an approximate precision based on the component of 5% for vanadium and chromium, 8% for iron, 12% for nickel, and 16% for calcium and sodium, whereas the deviations of spectrographic from chemical results are approximately 9% for iron; 5% for chromium, 16% for calcium and sodium, 22% for nickel, and 30% for vanadium.

During development of the present spectrographic method the use of several spectral line pair combinations of the internal standards and sought elements were investigated. Cobalt, for instance, was found unsatisfactory as an internal standard for calcium because of erratic intensity ratios among the various measured lines of these two elements. The addition of strontium provides a satisfactory reference for calcium; but this element was found unsuitable for sodium. In the development of the method it was considered highly desirable that all contaminants be determined on the same spectrogram; but because the quantity of strontium added (0.8%) is much greater than the amounts of the other internal standards, its possible interference in the determination of other elements was suspected. To clarify this point, plant samples were analyzed with and without strontium. The results shown in Table VII are typical, and reflect no significant influence of strontium on determinations of the other elements.

Fluid cracking catalysts supplied by commercial manufacturers vary in alumina content from 10 to 20%, according to type. For a given type of catalyst this variation is probably never greater than 1 or 2%. The influence of alumina content on the determination of one element (iron) was investigated by spectrographic analysis of blends containing various known amounts of alumina and iron. Changes in iron-cobalt intensity ratio with alumina concentration were calculated and plotted (Figure 2) to show that intensity ratio increases with alumina content. Thus, for two catalyst samples of the same iron content, one sample having 10% alumina and the other 20%, an intensity ratio increase of about 20% is noted. For a given type of catalyst, where the changes in alumina concentration are small, the indicated effect is negligible.

ACKNOWLEDGMENTS

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Determination of Saponification Number

D. T. ENGLIS AND JAMES E. REINSCHREIBER
University of Illinois, Urbana, Ill.

THE method for determining the saponification number of fats and oils, proposed by Koettstorfer (*5*) in 1879, which is the basis for the official methods, has been retained with slight modification through the years. This, in itself, indicates a reasonable degree of satisfaction with and reliability for the method. However, in many cases a good agreement in values obtained may have been the result of close duplication of conditions for each analysis and may not necessarily represent real theoretical values. Experience with the performance of students in a course in food analysis, in which the determination of the saponification number was one of the exercises, has shown that the values reported for the same sample have varied considerably, even when the reagents were from the same stock solutions. It was of some concern to try to discover the causes of these variations.

Commonly recognized factors which may affect the determination are the composition of the ethanol-water mixture at the completion of the titration, and the absorption of carbon dioxide during the determination. Less well considered is the nature of the solvent effect upon the titration curve and the indicator response.

The first factor, composition of the ethanol-water mixture, is a function of loss of alcohol during the saponification, concentration of reagents, and weight and nature of the glyceride. The last two factors affect the amount of aqueous hydrochloric acid in the back-titration and hence the proportion of waters in the final solution. The official method of the American Oil Chemists' Society (*1*) is more specific on these points than is that of the Association of Official Agricultural Chemists (*2*). In the first the length of air condenser, nature of heating, and magnitude of the back titration are carefully designated.

For the most part, organic neutralization indicators have been employed in the saponification procedures for the analyses of fats and oils. However, in 1931, Demarest and Rieman (*3*) used the potentiometric method for determining the saponification number of mixtures of asphalt and drying oils in alcohol-anisole solutions. In this way the difficulty of the end-point detection by the usual indicator method was overcome. Snell (*9*) employed the potentiometric technique in a somewhat similar connection for samples of tall oils in which the natural color was so high that evidence of the color change of phenolphthalein was very uncer-

The reaction of potassium hydroxide with hydrochloric acid in solutions of varied proportions of ethanol and water, and in the presence and absence of soap, has been followed potentiometrically with special reference to its significance to the determination of the saponification number of oils and fats. In the usual saponification procedure the final ethanol content of the solution may be as low as 35%, yet the hydrolysis of the soap does not interfere seriously with the end-point detection at the proper stage of the reaction. The change in the pK value for phenolphthalein with change in solvent composition does not detract from the use of this indicator for the determination. The directions in the official method are properly prescribed. A series of analyses showing the effect of absorption of carbon dioxide under ordinary operating conditions was performed and results are reported.

tain. Another article of allied interest is that of Frampton and Martin (*4*) on the lipides of the cottonseed.

REAGENTS

The reagents for the present work were prepared essentially as specified in the official method (*1*).

Ethanol (2.4 liters) for the potassium solution was refluxed with potassium hydroxide (20 grams) and powdered aluminum (12 grams) for 30 minutes. The alcohol was then distilled off and the first 100 ml. were discarded. In 2 liters of the remaining distillate, potassium hydroxide (80 grams) was dissolved and finally filtered to obtain a clear solution, free of carbonate.

Hydrochloric acid in 0.5 *N* concentration was made from Du Pont C.P. reagent quality. It was standardized against Merck recrystallized and dried sodium carbonate.

The oil examined was a commercial sample represented as virgin pure olive oil, Ariston Brand.

The phenolphthalein indicator was made by dissolving 1 gram of the reagent in 50 ml. of 95% ethanol and 50 ml. of water.

EQUIPMENT

A Beckman Industrial Model pH meter equipped with a blue-tipped (alkali range) glass electrode was calibrated over the pH range 4 to 10, using Clark and Lubs standard buffer solutions. All values of pH are corrected to these standard values. Corrections for values outside the calibrated range were secured by extrapolation.

Because the glass electrode is subject to an appreciable error in aqueous solutions containing a high proportion of alcohol, the readings of the pH meter should be termed apparent pH. This situation does not detract from the use of the instrument for analytical work of the nature reported here.

PROCEDURE

Except for specified variations, the official saponification procedure was followed. All solutions were cooled after the saponification and the titrations were carried out at room temperature (about 27° C.).

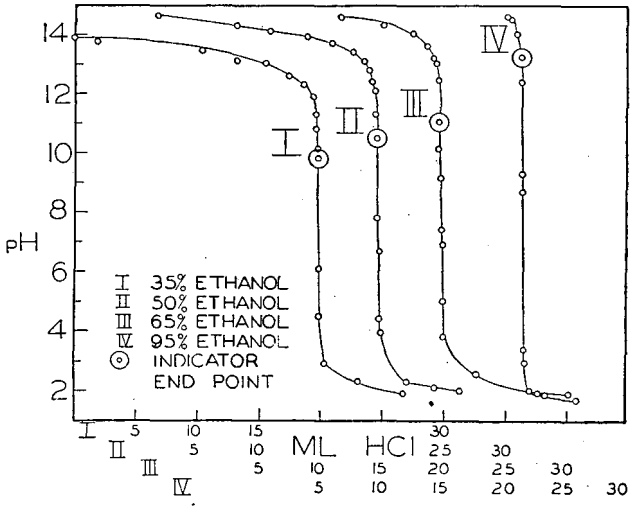

Figure 1. Titration Curves of Blank and Sample in a Saponification Determination

TITRATION CURVES

Sample and Blank in Saponification Number Determination. As the first phase of the study, a blank and a saponified sample were titrated in the regular way with aqueous hydrochloric acid. The pH changes during the process were followed with the pH meter. These solutions were about 90% in ethanol at the start of the titration. The sample contained about 63% ethanol at the stage of completion of the titration of excess potassium hydroxide, and the solutions of blank and sample were each about 40% in ethanol at the final stage of the titrations. The data obtained are shown graphically in Figure 1.

The slight rise in pH in the early stages of the titrations appears somewhat disconcerting. In the case of the blank, the increase in activity of the hydroxyl ion as a result of the change in the solvent is greater than the reduction of hydroxyl ion by neutralization and dilution. In the case of the sample, the added effect of the increase in hydroxyl ion from the hydrolysis of the soap accentuates this initial rise in pH. The first break in the titration curve for the sample is sharp under the conditions prevailing here. The second break, representing the titration of the soap after the excess alkali has been neutralized, is not particularly sharp. The total alkali equivalence of the blank is attained near pH 4. This and other experiments in which the ethanol content was kept near 65% have shown that a determination of the saponification number is possible with the single solution that contains the treated oil. The value for the so-called blank is established by continuation of the titration to the electrometric end point for the second break in the titration curve. Demarest and Rieman (*3*) had made this observation in their work on the asphalt–linseed oil mixtures. In later work, Rieman (*8*) studied the matter further and proposed the use of a double indicator method which may be substituted for the potentiometric method in the elimination of a supplementary blank determination.

Potassium Hydroxide–Hydrochloric Acid. In Solutions of Varying Ethanol Content. The interesting features of the titration curves shown in Figure 1 gave rise to an investigation of the nature of the curves for the reagents when the ethanol content was carefully controlled. Included as a part of this study was the determination of the pH value for the phenolphthalein indicator change when the ethanol in the solvent mixture varied from 90 to 35%. To maintain a constant proportion of ethanol during the titration, both potassium hydroxide and hydrochloric acid were prepared in a solvent mixture of the same composition. Graphical representation of the data is given in Figure 2.

In order to simplify the drawing of the curves and to avoid complications in superimposition of certain portions, the zero value for the abscissa is changed for each curve, and the titration values are expressed in terms of equivalent volumes of hydrochloric acid of the highest concentration used, instead of the actual titration value.

The pH value at which the phenolphthalein end point is observed is of major interest. Fortunately, in all cases the color change takes place at a pH in the nearly vertical section of the curve. Hence, a negligible experimental difference from the proper value is to be encountered when this indicator is used for these solvent mixtures.

Kolthoff and Rosenblum (*6*) have called attention to the effect of ethanol in mixtures with water upon the pK values of a number of indicators. The effect upon phenolphthalein is very pronounced; for this indicator the pK value, 9.3 in water, reaches 15.3 in ethanol solution.

In Presence of Soaps and in Solutions of Varying Ethanol Content. In the next series of experiments soap was present in the solution. In each experiment, 5 grams of pure Castile soap were added to 25 ml. of alcoholic potassium hydroxide prior to each titration. The resulting data have been organized as for the other series and are shown graphically in Figure 3.

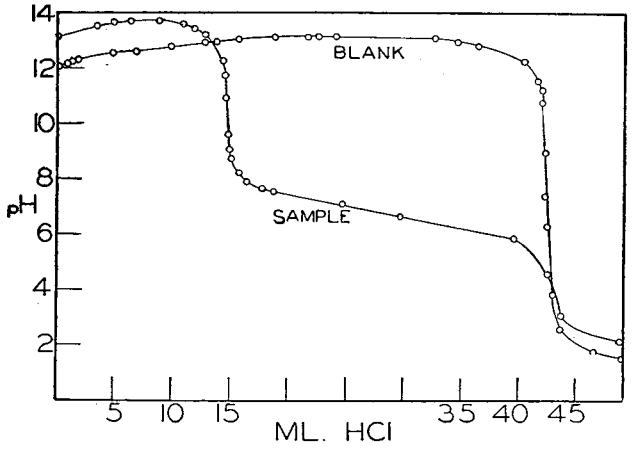

Figure 2. Titration Curves of Potassium Hydroxide *vs.* Hydrochloric Acid in Ethanol-Water Mixtures

The pH trend for titration curve V, Figure 3 (soap and potassium hydroxide in 95% ethanol *vs.* hydrochloric acid in 90% ethanol) has the same general characteristics as that for the sample in Figure 1. When the proportion of ethanol is reduced to 65%, a similar but less marked rise in pH in the initial stages of neutralization (curve IV) is noted. This feature was unexpected. As there was no change in the proportion of ethanol and water during the titration, one cannot attribute the pH rise to the same causes assigned for the sample in Figure 1. McBain, Laurent, and John (*7*) have studied the hydrolysis of soaps in aqueous solution and found that the pH value for potassium palmitate shows an increase on dilution up to a maximum in about 0.01 *M* solution. This value then decreases as the dilution is increased. Perhaps a similar phenomenon is characteristic at a higher concentration of soap when ethanol is present in the solution.

Table I. Saponification Values of Olive Oil
(% ethanol in solution varied)

Sample	Olive Oil	Ethanol in Final Solution	Saponification No.
	Grams	%	
1	4.0087	72	190.9
2	4.7090	72	188.1
3	4.1827	72	188.4
4	3.9973	72	187.0
5	4.0918	70	189.8
6	3.9277	69	188.6
7	4.1014	68	188.6
8	4.0108	67	189.8
9	3.9975	67	187.0
10	3.9888	67	188 8
			Av. 188.8
11	4.1542	67	189.8
12	4.2092	63	189.2
13	3.8392	64	189.6
14	3.7060	60	190.4
15	4.3019	57	189.7
16	4.0302	53	188.9
17	4.0769	48	189.7
18	4.0515	47	188.5
19	3.8881	42	186.0
20	4.1672	39	190.2
21	4.1477	34	189.1
			Av. 189.2
22	3.5002	26	191.3
23	4.2392	23	191.6
			Av. 191.5

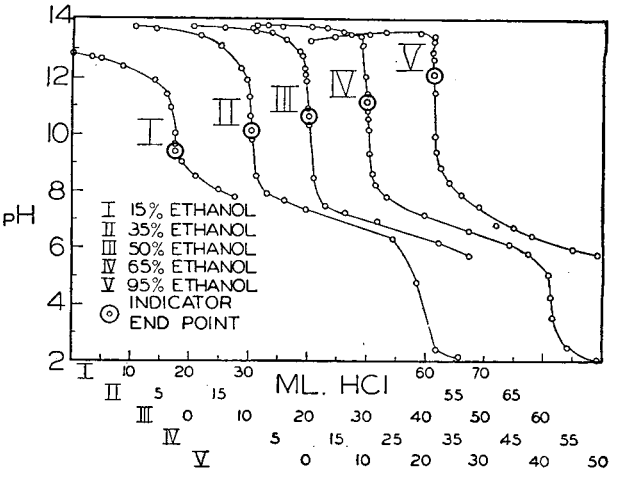

Figure 3. Titration Curves of Potassium Hydroxide plus Soap *vs.* Hydrochloric Acid in Ethanol-Water Mixtures

Table II. Effect of Exposure to Atmosphere upon Determination of Saponification Values of Olive Oil

Series	Conditions	% Ethanol in Final Solution A[a]	% Ethanol in Final Solution B[b]	Saponification No. A[a]	Saponification No. B[b]
1	Flasks stoppered and cooled and solutions immediately titrated	59 56 53	53 53 52 53	190.6 189.7 190	189.3 189.5 189.3 189.8
2	Exposed to atmosphere 1 hour before titrating	40 35	56 53 50	189.9 190.0	190.8 190.3 190.6
3	Exposed to atmosphere 2 hours before titration	59 59 52 36	57 53 53 52	191.3 191.5 190.6 190.2	190.4 190.4 190.2 190.6
4	As for series 3, then air blown over solution 0.5 hour	56 55 35 34		207 198.8 203.4 196.0	
5	Exposed to atmospher 5 hours before titration		56 53 50		190.8 190.3 190.6

[a] Blanks titrated immediately after saponification process.
[b] Blanks treated exactly like samples.

The nature of these curves and the pH at which the phenolphthalein end point is observed show that in determining a saponification number successful titrations of excess alkali may be made in solutions of the soap in which the ethanol content is 35% or more.

SAPONIFICATION VALUES

Determination by Official Procedure. As a test of the procedure in actual practice, a series of determinations of the saponification value of olive oil was made by the official method (*2*). The specified 650-mm. air condenser was employed for each sample. The flasks containing the oil samples and 50 ml. of alcoholic potash were first weighed, then heated for the 30-minute period, and weighed again so that the alcohol loss was determined. The solution at the final titration was always well above 35% in ethanol content, provided care was taken to see that the vapor ring never got beyond the end of the air condenser tube. In many cases the alcohol was intentionally reduced beyond a normal loss by removing the condenser, so that the proportion of water resulting from the titration with the aqueous hydrochloric acid could be correspondingly increased.

The series of results given in Table I was not so consistent as was desired and expected. When the water content was above

65%, increased hydrolysis of the soap gave, as was anticipated, higher saponification values.

Effect of Exposure of Samples to Air. Although usual precautions had been observed to minimize exposure to the atmosphere during the analysis of the samples reported in Table I, it was believed that the lack of close agreement might have been due to variations in carbon dioxide absorbed.

To study this factor, a series of analyses was made in which the opportunity for absorption of carbon dioxide was varied. The conditions of the determinations and the results are recorded in Table II. In the A series, the blanks were titrated immediately after the saponification period. Accordingly, absorption of carbon dioxide by samples allowed to stand longer was not subject to compensation by blanks handled similarly. In the B series, blanks were included in each set of determinations where the treatment was different.

The differences resulting from exposure of samples to the air for 1 hour, even when the blank was not subject to this additional exposure, are no greater than those resulting from other experimental errors. Exposure for 2 hours gave only slightly higher values. When the blank as well as the sample was exposed, exposure to the air for 5 hours gave essentially the same values as after the 2-hour exposure and only slightly higher than those for the samples titrated immediately.

The potentiometric titrations have confirmed the correctness of the conditions of the official procedure for the determination of the saponification number and have furnished additional information on the procedure. However, the reasons for lack of close agreement in determinations upon the same sample are still not clear. The errors resulting from absorption of carbon dioxide and from variations in the ethanol content are slight under usual operating conditions. Some other experimental errors are of greater significance to consistency of results in repeated determinations.

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VANADIUM AS PHOSPHOTUNGSTOVANADATE

A Spectrophotometric Method

M. D. COOPER AND PAUL K. WINTER
General Motors Corporation, Research Laboratories Division, Detroit, Mich.

The formation of a complex by the interaction of vanadate, phosphate, and tungstate ions in an acid medium, and the measurement of its absorbancy using the Beckman spectrophotometer, are common to these procedures for the determination of vanadium in low-alloy steels. Four procedures are described. Two involve a preliminary separation by means of sodium bicarbonate; in one case a sulfuric acid medium and in the other a perchloric acid medium is employed. Either procedure, in which electrolysis over the mercury cathode constitutes a final separation of all interfering elements from the vanadium, is recommended where high precision is required. Two alternative procedures, in which the preliminary separation is avoided, are recommended for routine analysis. Their precision as indicated by a standard deviation is approximately 1%, while that of the others is of the order of 0.5 to 0.6%.

THE increasing popularity of the spectrographic method for the routine analysis of steels has caused the chemical method to be subjected to greater scrutiny. Routine chemical methods which were popular in the past, although sufficiently accurate from the standpoint of control work, have proved in some cases to be inadequate for the analysis of steels to be used as spectrographic standards. Speed, precision, and high sensitivity are inherent in the spectrographic method, but its accuracy depends upon the reliability of chemically analyzed standards. Furthermore, because the spectrographic method is capable of high sensitivity without sacrifice of speed, there has resulted an increased interest in residual and trace elements, and chemistry is required to establish accurate values in a concentration range which received little attention in the past.

The work reported in this paper was prompted by the conviction that vanadium values for a series of spectrographic standards should be known within 1% of the amount present in the range of approximately 0.20% to less than 0.01%. It was realized from the start of the investigation that to analyze for low percentages a spectrophotometric method was more likely to succeed than a titrimetric method. However, a few titrimetric methods were given some consideration.

Methods based upon the oxidation of vanadium by nitric acid followed by potentiometric titration were found inadequate for the analysis of low-vanadium steels—i.e., less than 0.03%—as deviations were approximately 5% of the amount present. In the higher percentage range the precision becomes acceptable, but the accuracy in all cases is subject to the hazard of incomplete oxidation of vanadium by nitric acid.

Some methods which involve the use of potassium permanganate are recommended in the literature. It was found that among the limitations of these methods is the fact that they are not well suited to low vanadium concentrations.

A volumetric method proposed by Smith and Getz (*1*) was given some consideration. In this procedure mixtures of ferrous and vanadyl perchlorates in the same solution may be titrated potentiometrically by virtue of the high oxidation potential available in strong perchloric acid medium, by means of perchlorato-ceric acid. The method failed in practice, because chromic ions inevitably present apparently lowered the oxidation potential of the ceric-cerous system below that required for the oxidation of the vanadyl ions with a detectable inflection.

The work of Wright and Mellon (*2*) yielded valuable information on the phosphotungstate complex of vanadium. As an

introduction they mentioned that the phosphotungstovanadates were first studied in 1883 but their use in colorimetric analysis did not begin until 1928 when the complex was utilized to determine traces of vanadium contaminating tungstic acid residues. They stated that the exact chemical nature of the complex is somewhat obscure, but suggested the likelihood that it is a coordinated compound of the so-called heteropoly type, in which V_2O_6 groups replace part of the W_2O_7 groups of phosphotungstic acid.

Since the time that Wright and Mellon did their work (1937) rapid advances in technique and design of equipment have occurred in the field of spectrophotometry.

By modifying the procedure to take full advantage of the increased accuracy in the measurement of absorbancy with the most modern equipment, an improved method for vanadium has been developed.

Table I. Calibration Data for 1.000-Cm. Cells

Vanadium, Mg./100 Ml.	Absorbancy	Vanadium, Mg./A	Weighted Average, Mg./A
0.2521	0.086	2.930	
0.5032	0.171	2.945	
0.7573	0.259	2.925	2.925
1.008	0.346	2.915	
1.258	0.431	2.920	

SPECIAL APPARATUS

A Beckman Model DU spectrophotometer equipped to accommodate cells of lengths up to 10 cm., and a mercury cathode unit were used.

The cell used for the mercury cathode separation was the Bolger mercury vessel recommended by Slomin available through E. H. Sargent and Company, Chicago, Ill. The cathode consisted of about 400 grams of mercury and the anode was a perforated platinum electrode of the type used for electrolytic deposition. An air-driven stirrer, prepared with a downward thrust propeller which was adjusted to dip just below the surface of the mercury, served to agitate the pool of mercury. The source of the current was a motor-driven generator of the type used in an automobile, the output of which was stabilized by two 6-volt storage batteries connected in parallel. As the energy requirements may be as much as 5 or 6 ampere-hours per sample, the inconvenience of operating directly from storage batteries is obvious.

After the electrolysis the mercury was removed by way of the side arm, leaving only enough to cover the platinum lead to the cathode. The solution was removed by means of suction into the 300-ml. Erlenmeyer flask used previously for the sample preparation. For this purpose a short length of glass tubing extending just below the level of a two-hole stopper was connected to the vacuum line. Through the other hole an inlet tube was provided, one end of which extended well below the stopper; the other end extended horizontally a few centimeters beyond the mouth of the flask, then downward parallel to the wall of the flask, a distance slightly greater than the depth of the mercury cathode vessel. A T-tube in the vacuum line near the flask was provided with a short length of rubber tubing which, when partially constricted, served to regulate the rate of flow of solution into the flask.

As the solution was removed from the cell, rinsing was accomplished by means of a fine stream of water from a wash bottle. The cell was finally rinsed thoroughly. During removal of the solution the current was left on, thus minimizing the dissolution of deposited metals from the mercury.

REAGENTS

Perchloric acid (30%), 300 ml. of perchloric acid (70%) diluted to 1 liter with water.

Nitric acid, specific gravity 1.42.

Nitric acid (1 to 1), 1 volume of nitric acid (specific gravity 1.42) diluted with 1 volume of water.

Phosphoric acid (3 to 2), 3 volumes of phosphoric acid (85%) diluted with 2 volumes of water.

Sodium tungstate solution, 0.2 molar, 66 grams of sodium tungstate dihydrate dissolved in water and diluted to 1 liter.

Sodium bicarbonate solution (8%), 80 grams of C.P. sodium bicarbonate dissolved in water and diluted to 1 liter.

Sulfuric acid (specific gravity 1.84).

Sulfuric acid (1 to 1), 1 volume of sulfuric acid (specific gravity 1.84) diluted to 1 liter with water.

Sulfuric acid (10%), 100 ml. of sulfuric acid (specific gravity 1.84) diluted to 1 liter with water.

Hydrofluoric acid (48%).

Standard vanadium solution, which may be prepared in the following manner.

After a solution of ammonium vanadate had been boiled with excess sodium hydroxide to remove ammonia, an excess of perchloric acid was added followed by fuming to ensure complete oxidation of vanadium to vanadate. Aliquots of this stock solution were titrated potentiometrically to determine the exact vanadium concentration. By using weight burets to dispense potassium dichromate and ferrous sulfate solutions and a microburet in the back-titration of excess ferrous sulfate, the error in the standardization was held within 0.1%.

CALIBRATION OF SPECTROPHOTOMETER

Transfer aliquots of the standard solution (see Tables I and II) to 100-ml. Pyrex volumetric flasks. Add 10 ml. of nitric acid (1 to 1), 7 ml. of perchloric acid (70%), 5 ml. of dilute phosphoric acid (3 to 2), and exactly 5.00 ml. of 0.2 molar sodium tungstate solution. Rinse down the neck of the flask and dilute to about 75 ml. with water. Prepare a reference solution similarly but omit the aliquot of standard vanadium solution. Heat the solutions to boiling, then digest on the steam plate for at least 30 minutes. Cool, dilute to volume, and mix the solutions thoroughly. Measure the transmittancy (T) of the colored solutions against the prepared reference solution at 410 millimicrons, using the recommended "sensitivity" setting and the corresponding slit setting, and then calculate the absorbancy (optical density) as $\log 1/T$. (The work reported in this paper was based upon a slit setting of 0.055 mm., resulting in a band width of approximately 0.75 millimicrons.)

The data obtained in this manner are shown in Tables I and II.

In regard to Table I attention is called to the method of utilizing the calibration data. In the third column the ratio of concentration to absorbancy at each level of concentration is shown. As it may be assumed that the deviations from constancy are due to experimental error, an average factor has been calculated by weighting the individual values according to the magnitude of the corresponding absorbancy.

In Table II (column 3) the concentration-absorbancy ratio at the lower concentrations is not constant. However, when concentration of vanadium is plotted against absorbancy the points fall on a straight line represented by the equation mg. of $V = 0.5860\ A + 0.0040$. The validity of the equation may be noted by comparing the calculated values of vanadium concentration shown in column 4 with the known values in the first column.

It was found that 0.01 molar sodium tungstate assured maximum complex formation with vanadium in the highest concentration—i.e., 1.258 mg. per 100 ml. Because 0.025 molar sodium tungstate, recommended by Wright and Mellon, caused the factors for the 1.000-cm. cells to deviate from constancy in a pattern similar to that shown in Table II, it may be assumed that the high ratio of tungstate to vanadate is responsible for the deviations shown in the 5.000-cm. cell data. For obvious reasons it would be impractical to adjust the tungstate to correspond to the vanadium concentration.

RECOMMENDED ANALYTICAL PROCEDURES

I. The sample size may be varied from 2.5 grams for vanadium concentration of approximately 0.2% to 10.0 grams for less than 0.01%. Transfer the sample to a 300-ml. Erlenmeyer flask and treat with dilute sulfuric acid (10% by volume) adding 10 ml. for each gram of sample and 10 ml. excess. Invert a 100-ml. beaker over the flask to prevent excessive oxidation of iron and digest the sample on the steam plate until action ceases. Add 100 ml. of

Table II. Calibration Data for 5.000-Cm. Cells

Vanadium, Mg./100 Ml.	Absorbancy	Vanadium, Mg./A	Vanadium Calculated,[a] Mg./100 Ml.
0.0504	0.079	0.638	0.0507
0.0756	0.121	0.625	0.0749
0.1258	0.207	0.608	0.1263
0.1515	0.252	0.601	0.1517
0.2016	0.339	0.595	0.2026
0.2520	0.422	0.597	0.2513

[a] Values in column 4 based on equation: Mg. V = 0.5860 A + 0.0040.

water heated to boiling, place the covered flask on the hot plate, and boil the solution for about 1 minute. Remove the flask from the plate, and immediately on removing the cover from the flask, add sodium bicarbonate solution (8%) from a buret until a permanent precipitate forms, then continue the addition until 5 to 6 ml. excess has been provided. Cover the flask again, and, after allowing 5 or 10 minutes for the precipitate to settle, filter the warm solution through a No. 41 Whatman paper, or its equivalent, with the aid of pulp, using a glass rod to facilitate the quantitative handling of the sample. Rinse the flask and wash the filter a few times with water containing a little sodium bicarbonate. Place the paper and precipitate in the flask and wipe the lip of the flask with a piece of moistened filter paper and put it in the flask. The glass rod to which an appreciable amount of precipitate clings may be left in the flask until later.

This procedure has been found to precipitate vanadium, chromium, and tin quantitatively; molybdenum nearly quantitatively; and from 10 to 15% of the nickel. From 200 to 300 mg. of iron, which becomes oxidized during filtration, is precipitated and carries with it some elements such as manganese and copper. Because most of these elements would interfere in the vanadium determination they are removed in the following manner.

Transfer 5 ml. of sulfuric acid (specific gravity 1.84) to the flask containing the precipitate, and heat to char the paper. Add approximately 20 ml. of nitric acid (specific gravity 1.42) and digest the sample to remove most of the organic matter. Swirl the flask while heating rather strongly and add nitric acid in small increments by means of a medicine dropper until all organic matter is destroyed. Fume the sulfuric acid strongly for not more than 1 minute to expel all but traces of nitric acid. (Prolonged fuming, even though mild, causes the formation of difficultly soluble chromium salts.)

After cooling, rinse down the neck of the flask with water and heat again to fumes to remove the remaining nitric acid. Add approximately 50 ml. of water and heat until the salts are dissolved. After cooling add sodium hydroxide to neutralize about one half of the sulfuric acid, remove the stirring rod, and transfer the solution to the mercury cathode cell.

Dilute the solution to approximately 125 ml., cover the cell with a split cover glass, and electrolyze with a current of 5 to 6 amperes while stirring the mercury pool. Deposition may be considered to be complete when the solution becomes nearly colorless; however, allow an additional 15 minutes to ensure complete deposition of molybdenum. At intervals during the electrolysis rinse the cover glass and walls of the vessel with distilled water.

After removing the solution from the mercury cathode cell, evaporate it to approximately 50 ml., cool, transfer to a 100-ml. volumetric flask, and dilute to volume.

Transfer an aliquot of suitable size to a 125-ml. Erlenmeyer flask, add 10 ml. of perchloric acid (70%), evaporate the solution, and fume strongly for about 5 minutes to oxidize the vanadium. Cool the solution, add about 1 ml. of hydrofluoric acid (48%), and remove silica by fuming, leaving approximately 7 ml. of perchloric acid in the flask. Dissolve the salts by adding about 25 ml. of water and transfer the solution to a 100-ml. volumetric flask, which should be Pyrex in order to withstand subsequent heating. Then add 10 ml. of nitric acid (1 to 1), 5 ml. of phosphoric acid (3 to 2), and 5.00 ml. of 0.2 *M* sodium tungstate solution, and rinse down the neck of the flask with water. Dilute the solution to about 75 ml. and mix.

Prepare a reference solution by transferring 50 ml. of water, 7 ml. of perchloric acid, 10 ml. of nitric acid (1 to 1), 5 ml. of phosphoric acid (3 to 2), and 5.00 ml. of 0.2 *M* sodium tungstate solution to a 100-ml. Pyrex volumetric flask. Boil the sample and reference solutions for about 1 minute, then digest on the steam plate for not less than 30 minutes. After cooling and diluting to volume, determine the absorbancy by means of the spectrophotometer with wave-length and slit settings the same as in the calibration and using the appropriate cells.

II. Prepare the sample for the bicarbonate separation according to Procedure I, using perchloric acid (30%) instead of sulfuric acid (10%). Perform the bicarbonate separation as described previously.

After transferring the paper and precipitate to the original flask add 30 ml. of nitric acid (specific gravity 1.42) and 10 ml. of perchloric acid (70%). Evaporate the solution at a moderate rate until the perchloric acid fumes, then fume strongly. When the volume of perchloric acid is reduced to about 5 ml. cool the solution, add about 50 ml. of water, swirl the flask to dissolve the salts, then transfer the solution to the mercury cathode cell and electrolyze.

Perform the remaining steps of this procedure according to Procedure I.

Table III. Analytical Results

Procedure	Sample No.	No. of Detns.	Average % Vanadium	Standard Deviation, %	Maximum Deviation, % V
1	5-1	10	0.222	0.6	0.003
	3-5	5	0.0344	0.6	0.0003
	N.B.S. 30C	2	0.239	....	....
2	3-1	10	0.221	0.5	0.002
3	3-1	2	0.223	....	....
	3-5	2	0.0348	....	....
	N.B.S. 30C	2	0.240	....	....
4	3-1	10	0.225	0.6	0.002
	3-5	10	0.0343	1.1	0.0007

	Composition								
Sample No.	Mn	Si	Ni	Cr	Mo	Cu	Sn	V	As
3-1	0.48	0.13	0.92	0.32	0.03	0.10	0.008	...	...
3-5	0.76	0.28	1.71	0.87	0.10	0.06	0.006	...	...
30C	0.707	0.237	0.080	0.977	0.010	0.099	...	0.235	0.016

ALTERNATIVE ANALYTICAL PROCEDURES

III. Transfer the sample, not to exceed 500 mg., to a 200-ml. Erlenmeyer flask, add 10 ml. of sulfuric acid (10%), and heat until the sample is dissolved. Add a few milliliters of nitric acid (specific gravity 1.42) and 10 ml. of sulfuric acid (1 to 1). Remove the nitric acid by fuming, observing the precautions cited in Procedure I. Cool, add about 50 ml. of water, and digest to dissolve the salts. Cool, neutralize about half of the sulfuric acid with sodium hydroxide, transfer the solution to the mercury cathode cell, and electrolyze.

Perform the remaining steps of this procedure according to Procedure I.

IV. Transfer the sample, not to exceed 500 mg., to a 200-ml. Erlenmeyer flask, add 10 ml. of nitric acid (1 to 1) and 10 ml. of perchloric acid (70%). Heat to fumes and continue until the perchloric acid is evaporated to a volume of about 5 ml. Cool, add about 50 ml. of water, swirl the flask to dissolve the salts, then transfer the solution to the mercury cathode cell and electrolyze.

Perform the remaining steps of this procedure according to Procedure I.

ANALYTICAL RESULTS

The analytical results as well as the calculated standard and maximum deviations are shown in Table III. The standard deviation in each case was calculated according to the equation $\sigma = \sqrt{\frac{\Sigma D^2}{n-1}}$. Results obtained on two samples selected from a series of spectrographic standard steels, all of which were analyzed by Procedure I, are shown in Table III. Results on a National Bureau of Standards sample are also included.

Table IV. Interferences

Element	Concentration Mg./100 Ml.	Absorbancy, Ion	Absorbancy, Ion + Na_2WO_4
Fe	10	0.007	0.028
Ni	10	0.046	0.046
Cr	10	0.247	0.247
Mn	2.5	0	0
Al	20	0	0
Ti[a]	....	0	0
Sn[b]	....	Not measured	
Mo	2.0	0	0.138

[a] Titanium caused precipitation in acid medium before sodium tungstate was added. The solution was filtered and interference of any titanium that stayed in solution was measured.
[b] Tin formed insoluble salts on fuming with perchloric acid.

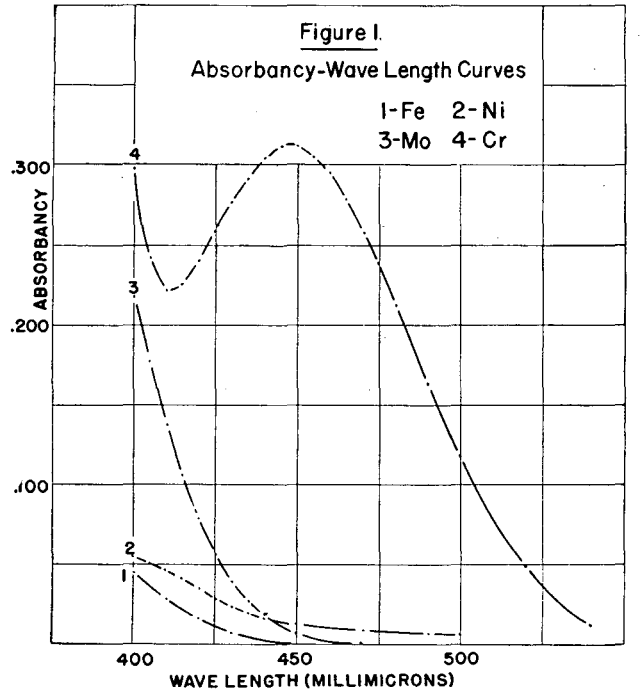
STABILITY OF COMPLEX

The absorbancy of the phosphotungstovanadate complex formed according to this procedure has been found to remain constant for at least 3 weeks.

INTERFERENCES

An investigation of possible interferences corroborated the findings of Wright and Mellon with the exception of iron, which was found to form a complex of slight absorbancy with the reagent. High purity metals procured from the Adam Hilger

Company were used for the purpose of this study. Solutions of the metals were prepared after fuming with perchloric acid to bring them to the same oxidation state which they would have if carried along with vanadium. Data are shown in Table IV.



The transmittancy of the solution of the metal was first measured against the acid medium as a reference and the corresponding absorbancy is shown in column 3. In another experiment (data in column 4) the effect of treating the element with the sodium tungstate reagent was observed by measuring the transmittancy against a reference containing the reagent in an identical medium. All transmittancy measurements were made at 410 millimicrons, slit setting 0.055 mm., in 5 cm. cells with the exception of chromium which was measured in 1-cm. cells.

Absorbancy–wave-length curves for solutions of the elements which furnished the data shown in column 4, Table IV, are shown in Figure 1.

Where the interference of elements corresponds to that of nickel and chromium it may be compensated by measuring the absorbancy of the solution of the "untreated" sample and applying a correction to the observed absorbancy of the "treated" sample. The type of interference exhibited by iron and molybdenum, however, is more difficult to compensate, because information regarding the concentration of the element is required and the ratio of concentration to absorbancy must be evaluated. Such an approach to the problem presented by iron without a preliminary separation to reduce its concentration would not be feasible. Data indicating that the degree of interference of molybdenum is difficult to evaluate accurately were obtained in the course of this investigation.

In some colored systems the interference of a component may be avoided by the judicious selection of the wave length at which the transmittancy of the system is measured. A study of Figures 1 and 2 reveals that the spectral region of high absorbancy is common to the interfering elements and the vanadium complex; hence this latter technique cannot be employed.

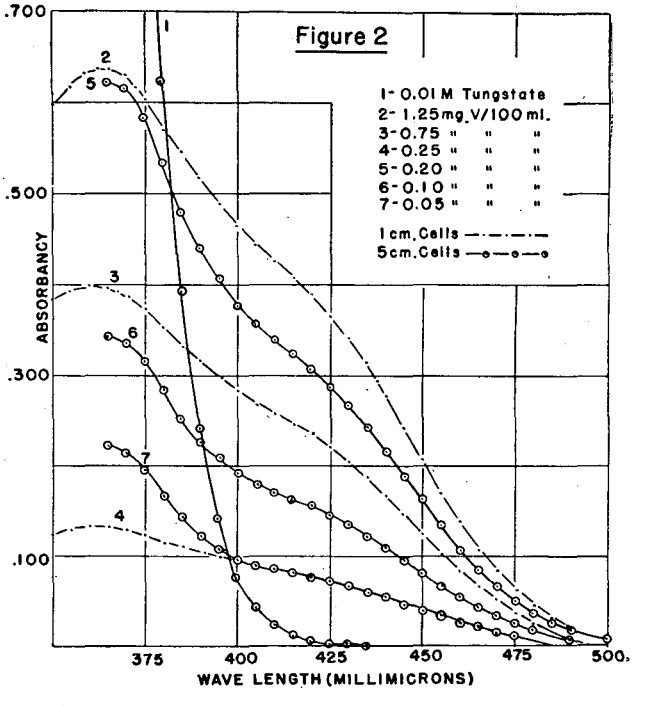
In the light of the above information it is apparent that the aims of this investigation as outlined early in this paper are best realized by utilizing the mercury cathode to remove the interfering elements.

SELECTION OF WAVE LENGTH

In Figure 2 are shown absorbancy–wave length curves for the phosphotungstovanadate complex, covering a range of vanadium concentrations, as measured against a reference solution 0.01 *M* in tungstate ions. The curve for 0.01 *M* tungstate, also shown, was based upon measurements against a reference solution consisting of a comparable acid medium. Curve 1 indicates that 0.01 *M* tungstate, in the presence of phosphoric acid, exhibits a pronounced absorbancy below 400 millimicrons; the absorbancy is approximately 2.000 in the 5-cm. cells at 365 millimicrons. Because this latter solution was used as a reference solution to obtain the data for the other curves shown in Figure 2 it was necessary to open the slits of the spectrophotometer appreciably in order to balance the instrument at 100% transmittancy, especially at the shorter wave lengths and when using the 5-cm. cells. In fact, it was not possible to obtain readings for curves 5, 6, and 7 (5-cm. cells) below 365 millimicrons.

Curves 2, 3, and 4 in Figure 2 indicate a maximum absorbancy of the vanadium complex at approximately 365 millimicrons, but other considerations led to the choice of 410 millimicrons for absorbancy measurements. It was found that the absorbancy was not reproducible in the wave-length region below 410 millimicrons. This was attributed chiefly to inadvertent variations in concentration of tungstate ions in the sample and reference solutions. It was also found that variations in solution temperature could lead to error. When the sample solution was cooled to a temperature below that of the reference solution a decrease in absorbancy was observed at 365 millimicrons, while at 410 millimicrons the absorbancy increased slightly and approximately in proportion to the resultant increase in concentration.

The error due to the variables just cited is more serious, of course, at low vanadium concentrations (0.05 to 0.25 mg. of vanadium per 100 ml.), as toward wave lengths below 410 millimicrons the absorbancy due to the vanadium complex becomes a progressively smaller part of the total absorbancy of the medium in which it is measured. However, appreciable error, approximately 5%, may occur in the values found for the absorbancy of the vanadium complex in the highest concentration used—i.e., 1.25 mg. of vanadium per 100 ml., when measurements are made at 365 millimicrons.



Reasons for avoiding wave lengths below 410 millimicrons have been shown. To avoid entirely the tungstate ion interference would require selecting a wave length of approximately 435 millimicrons and result in a serious sacrifice of sensitivity. In this sense the selection of 410 millimicrons was the result of a compromise.

SUMMARY

The demand for a precise method for the determination of vanadium in the low concentration ranges characteristic of low-alloy steels has been fulfilled by this investigation. Two methods have been demonstrated from the standpoint of precision to be comparable with well established methods for the determination of the more common alloying elements in this type of steel. Two alternative procedures for routine analysis have been shown to have a precision far more satisfactory than routine methods which were known in the past; their adaptability to routine application in laboratories faced with the problem of handling large numbers of these determinations is immediately suggested.

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Colorimetric Determination of Aluminum in Steel

Use of 8-Hydroxyquinoline

STEPHEN E. WIBERLEY AND LEWIS G. BASSETT, *Rensselaer Polytechnic Institute, Troy, N. Y.*

The development of a simple, rapid, and accurate oclorimetric method for the determination of small quantities of aluminum in steels is described. The sample is dissolved in nitric and perchloric acids, fumed, cooled, diluted, and electrolyzed in a water-jacketed mercury cathode cell until iron-free. The aluminum salt of 8-hydroxyquinoline (8-quinolinol) is formed in a buffered acetic acid solution at a pH of 6.0 ± 1.0. The salt is extracted with chloroform and the color intensity of the resulting solution is measured with a suitable colorimeter or spectrophotometer. The application of the method to various types of samples is described. The effects of interfering elements and of such variables as wave length, pH, and amount of reagent are evaluated.

At present there is a recognized need for a simple, rapid, and accurate method for the determination of small amounts of aluminum in steels. The generally used gravimetric procedure (*3*) is tedious and of doubtful accuracy when used for samples containing less than 0.1% aluminum. The small amounts of aluminum under consideration, and the need for simplicity and rapidity of measurement, indicate the desirability of a colorimetric method.

A survey of the literature shows several possibilities. Aluminon (*5, 12*), alizarin red S (*4*), and hematoxylin (*11*) form colored lakes with aluminum hydroxide. These reagents have the disadvantage common to many lake-forming compounds, relative instability of the lakes over a period of time. Fluorometric methods using morin (*10, 19*) and pontachrome blue black R (*18*) have been developed. However, common anions such as phosphate, fluoride, and sulfate cause marked interference with morin, and pontachrome blue black R, although extremely sensitive, requires approximately 1 hour before full intensity of fluorescence is attained. 8-Hydroxyquinoline (8-quinolinol), has been used extensively as a precipitant for many metals, including aluminum. Colorimetric methods (*2, 8*) based on solution of the quinolate in acid with subsequent conversion to an azo dye, require the separation of the precipitate. Alexander (*1*), Moeller (*16*), and Gentry and Sherrington (*6*) have determined aluminum directly by measuring the color intensity of the yellow solution obtained by the extraction of the aluminum quinolate with chloroform. This method appeared most promising to the authors and has been used with certain modifications, as the basis of the method described.

The determination of aluminum in steel poses a particular problem, because iron interferes with both the formation and extraction of the quinolate. Electrolysis with a mercury cathode has been chosen as the means of removing most of the interfering elements including iron. The cell used is a modification of that of Melaven (*15*).

REAGENTS AND ERUIPMENS

Solution A, 2% 8-Hydroxyquinoline in 1 *N* Acetic Acid. Dissolve 20 grams of 8-hydroxyquinoline (Mallinckrodt reagent grade) in 1 liter of 1 *N* acetic acid (60 ml. of glacial acetic acid diluted to 1 liter).

Solution B, Buffer Solution. Dissolve 200 grams of ammonium acetate and 70 ml. of concentrated ammonium hydroxide (approximately 15 *M*) in a total volume of 1 liter.

Solution C, Standard Aluminum Solution. Weigh 13.9 grams of reagent grade $Al(NO_3)_3 \cdot 9H_2O$ or 17.6 grams of $Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$, dissolve in water, make up the volume to 1 liter, and standardize by ammonia precipitation and ignition to the oxide. (Solution should contain 1.000 mg. of aluminum per ml.)

Solution D. Pipet 20 ml. of the above solution and dilute to 500 ml. in a volumetric flask. This solution now contains 0.040 mg. (40 micrograms) of aluminum per ml.

Reagent grade chloroform.

Beckman quartz spectrophotometer, Model DU. All measurements were made in 1-cm. cells.

Beckman pH meter, laboratory Model G.

Mercury cathode cells (see Figure 1).

DEVELOPMENT OF PROCEDURE

Previous investigators of the extraction colorimetric method for aluminum have added a chloroform solution of the 8-hydroxyquinoline reagent to a buffered aqueous solution of an aluminum salt, and then agitated the mixture. The aluminum quinolate formed remains in the chloroform layer on settling. The yellow chloroform layer is then separated, and diluted to a definite volume with chloroform, and its color intensity is measured. There is some disagreement concerning the proper conditions for the extraction. Alexander (*1*) found complete extraction at pH 3.5,

Moeller (*16*) only in the pH interval of 4.3 to 4.6, and Gentry and Sherrington (*6*) in a pH range of 4.5 to 11.5 except between 6.5 to 8 where incomplete extraction was reported.

An alternative procedure to that given above is first to form the quinolate by adding an acetic acid solution of the reagent to the buffered aluminum salt solution, then to adjust the pH, and extract with chloroform. This should extend the permissible range of pH, as complete extraction should be obtained at any pH at which the quinolate is normally insoluble in the aqueous layer. The conditions for this latter procedure have been investigated.

pH. Solutions containing 4.00 ml. of the standard aluminum solution (Solution D) in 50 ml. of water were treated with 10 ml. of a buffer solution (30 grams of ammonium acetate and 30 ml. of glacial acetic acid in 650 ml. of water), 2 ml. of 2% 8-hydroxyquinoline (Solution A), and sufficient ammonium hydroxide or acetic acid to attain the desired pH. Three extractions were made on each sample with 10- to 15-ml. portions of chloroform. The chloroform layers were combined and made up to a total volume of 50 ml. The optical density was determined on the Beckman spectrophotometer at 390 millimicrons versus chloroform. Samples containing the same amounts of the reagents except for the aluminum were run in a similar manner.

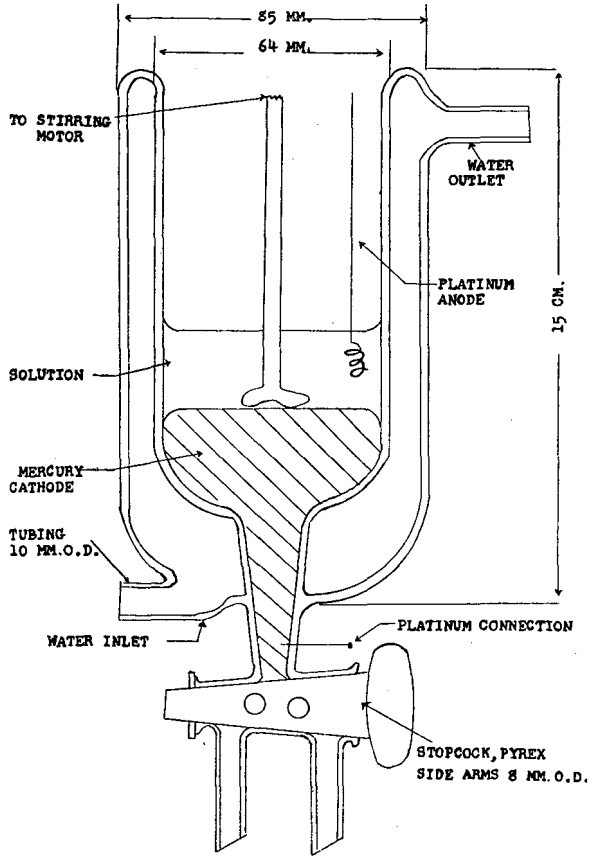

Figure 1. Water-Jacketed Mercury Cathode Cell

The results obtained are shown in Figure 2. Extractions are seen to be complete over a pH range of 4.9 to 9.4. These results check reasonably well with those of Goto (*7*), who found in working with macroamounts of aluminum that precipitation was complete over the pH range 4.2 to 9.8. The amount of reagent extracted increases more rapidly at the higher pH values, resulting in higher blanks. The blanks are reasonably constant in the pH range 5.0 to 7.0 which has therefore been chosen as the optimum range for the method.

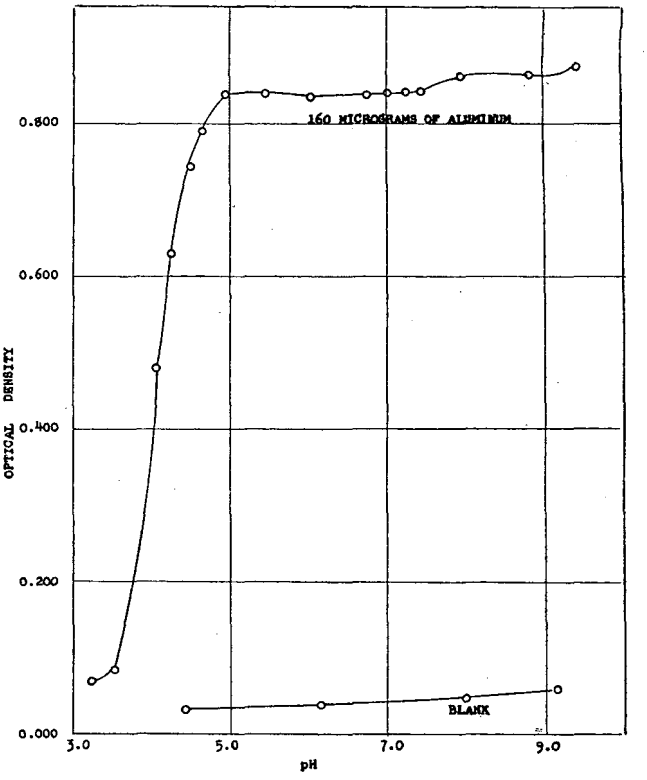

Figure 2. Effect of pH on Extraction of Aluminum Quinolate

Table I. Effect of Reagent on Optical Density

8-Hydroxyquinoline, Ml.	Optical Density	Optical Density (Corrected for Blank)
1 (Blank)	0.038	...
1	0.838	0.800
2 (Blank)	0.038	...
2	0.840	0.802
3 (Blank)	0.039	...
3	0.838	0.799
4 (Blank)	0.049	...
4	0.847	0.798
5 (Blank)	0.058	...
5	0.848	0.790
6 (Blank)	0.081	...
6	0.879	0.798

Wave Length. Solutions containing 2 ml. of reagent Solution A, 2 ml. of buffer Solution B, and 0, 1, and 2 ml. of Solution D corresponding to 0, 40, and 80 micrograms of aluminum, respectively, were extracted with chloroform, and diluted to 50 ml., and optical densities were measured over a wave length range of 360 to 430 millimicrons. The data obtained are shown in Figure 3. Although there is a relatively broad absorption band, the curve for 80 micrograms shows a slight maximum at 390 millimicrons. Accordingly, this wave length has been chosen for the method.

Amount of Reagent. Solutions containing 4 ml. of Solution D (160 micrograms of aluminum), 2 ml. of buffer Solution B, and 1, 2, 3, 4, 5, and 6 ml. of 2% 8-hydroxyquinoline (Solution A), respectively, were extracted at a pH of 6.3 and the optical densities determined. A similar set but with no aluminum present was also run. The results are shown in Table I.

The optical densities, after correction for the blank readings, are constant over the whole range of reagent concentration. Two milliliters of reagent Solution A have been selected as furnishing both a sufficient excess of reagent and a low blank.

Stability. Optical densities of the chloroform extracts obtained during the investigation of the effect of pH were measured over a period of 24 hours. No variations were observed, regardless of the pH at which the extractions were made.

Preparation of Calibration Curve. Based on the above study of conditions the following procedure was used for the preparation of a calibration curve.

Standard solution samples containing 0, 40, 80, 120, and 160 micrograms of aluminum were each treated with 2 ml. of reagent Solution A and 2 ml. of buffer Solution B, made up to a total volume of approximately 60 ml. with distilled water, and extracted in a separatory funnel with three 10- to 15-ml. portions of chloroform. The chloroform layers were drawn off through a 7-cm. No. 40 Whatman filter into a 50-ml. volumetric flask, and diluted to the mark with chloroform. Optical densities were then measured on the Beckman spectrophotometer at 390 millimicrons.

The results corrected for the blank (see Table I) are shown in Figure 4. The curve is linear over the entire range measured. The slope of the curve indicates excellent sensitivity.

The same chloroform solutions were measured in a Klett filter photometer using a 420-millimicron Corning filter. A linear relationship was obtained except for a slight tapering off at higher concentrations.

Separation of Interfering Elements. Elements which interfere with this extraction colorimetric procedure have been extensively studied by Gentry and Sherrington (*6*). Of the elements that may be found in steel, zirconium, molybdenum, vanadium, manganese, antimony, cobalt, copper, iron, nickel, tin, titanium, and uranium might be expected to interfere. Of these elements all but zirconium, vanadium, titanium, and uranium are simply and rapidly removed to a sufficient degree by electrolysis with the mercury cathode (*13*). Zirconium and uranium are used but rarely in a few special steels and their removal has not been investigated further. Titanium and vanadium interfere if present in amounts equal to or greater than the aluminum, but can be removed by precipitation in dilute acid solution with cupferron (*14*). Some work done by the authors indicates that a cupferron precipitation from dilute sulfuric acid solution immediately after a mercury cathode electrolysis will eliminate the titanium and vanadium. This procedure would materially add to the time required for the aluminum analysis, because the excess cupferron must be destroyed by fuming with nitric and perchloric acids before the colorimetric procedure may be applied. The final procedure given below then does not provide for the interference of titanium and vanadium.

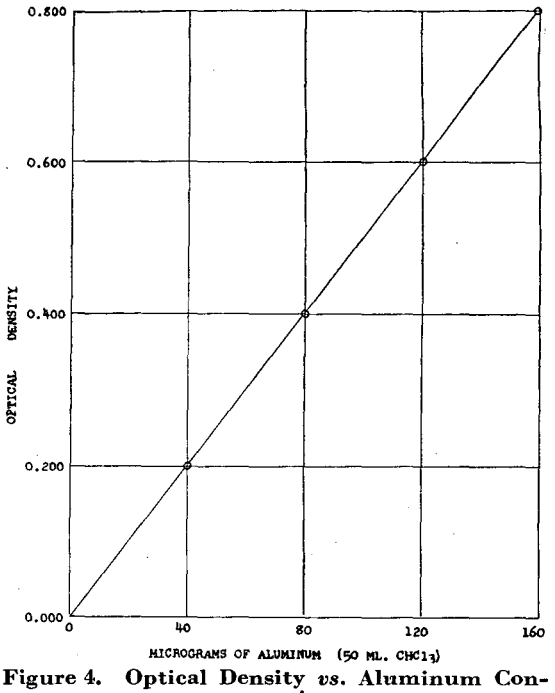

Figure 4. Optical Density *vs.* Aluminum Concentration

Beckman spectrophotometer, 390 millimicrons

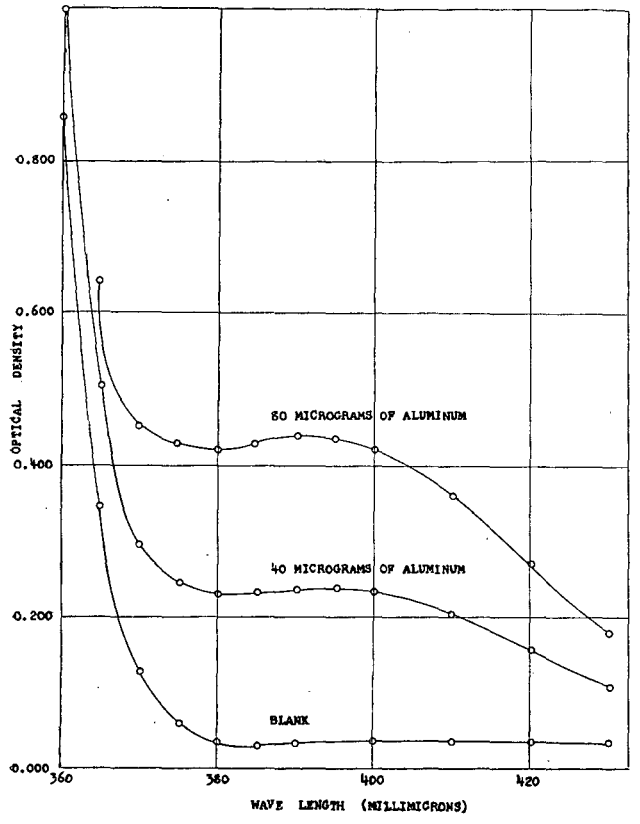

Figure 3. Effect of Wave Length

Gentry and Sherrington (*6*) have shown that large amounts of acetate, chloride, nitrate, and sulfate do not interfere. It was necessary to investigate the interference of perchlorates, as the procedure below was developed originally for determining aluminum in high-silicon steels, and fuming the sample with nitric and perchloric acids was chosen as the simplest method of eliminating the silica. The authors have found that 100% recovery of aluminum is obtained with the extraction colorimetric procedure from a solution which is 1 *M* in perchlorate ion and contains 80 micrograms of aluminum.

As a result of the above considerations, electrolysis with a mercury cathode cell was chosen as the means of eliminating interfering elements. Figure 1 illustrates the cell used. It is essentially the Melaven cell (*15*) with the addition of a water jacket and a mechanical stirring device. The water jacket permits the use of the relatively high current (5 to 8 amperes) necessary for the rapid removal of the elements without heating of the solution which causes appreciable solution of the mercury. Stirring the top of the mercury layer so that a fresh surface is constantly exposed also promotes rapid deposition and was found to be essential if large amounts of iron (0.5 to 1 gram) are to be removed. Clean mercury is also an aid to rapid deposition. The mercury can easily be cleaned by covering it with nitric acid (3 to 100) and bubbling air through it until the aqueous solution after several changes remains clear. Finally, the mercury should be run through a small column containing nitric acid (40 to 60).

Another critical factor of the electrolysis is the acidity of the solution. Low acidity reduces the conductivity of the solution and high acidity promotes the solution of the metals from the mercury pool. A solution approximately 1 *N* in acid was found most suitable. Use can be made of acetic acid (*9*), sulfuric acid (*13*), or perchloric acid (*17*). In the procedure below perchloric

Table II. Size of Aliquot and Amount of Sulfuric Acid Used in Preparation of Solution for Electrolysis

Suspected Aluminum, %	Aliquot, Ml.	6 N H_2SO_4 Required, Ml
0.01	50	None
0.05	25	5
0.25	5	10
0.50	3	10
1.00	2	10

Table III. Analysis of Bureau of Standards Steels

Sample Designation	Silicon, %	No. of Detn.	Deviation from Mean, % Av.	Deviation from Mean, % Max.	Aluminum Found	Accepted Value
BS—125	4.97	6	2	3	0.259	0.261
BS—106a	0.25	4	2	4	1.06	1.07

Table IV. Analysis of Low Aluminum Synthetic Samples

Synthetic	Aluminum, %	Aluminum Found, %
1	0.0124	0.0122–0.0124
2	0.0268	0.0263–0.0271
3	0.0434	0.0423–0.0434
4	0.0851	0.0867–0.0878

acid is present and if necessary the acidity is adjusted to approximately 1 N with sulfuric acid.

If the above conditions for the electrolysis are followed, 0.5 gram of iron can be quantitatively removed in about an hour.

PROCEDURE FOR STEELS

Acid-Soluble Aluminum. A 2-gram sample of the steel is dissolved in a mixture of 10 ml. of water, 10 ml. of concentrated nitric acid, and 20 ml. of 72% perchloric acid. The solution is heated until perchloric acid fumes begin to appear and then fumed for approximately 5 minutes, cooled, diluted to 150 ml., and filtered through a 12.5-cm. No. 40 Whatman filter paper into a 250-ml. volumetric flask. The residue on the paper is washed with water, and the washings are collected in the volumetric flask. The solution in the flask is diluted to the mark with water, and an aliquot is taken for electrolysis as indicated in Table II. The acidity of the aliquot is adjusted by adding the amount of 6 N sulfuric acid indicated in Table II. The adjusted solution is diluted to approximately 50 ml. and electrolyzed at a current of 5 amperes until free of iron. The solution is then removed from the cell, and treated with 2 ml. of Solution A and 2 ml. of Solution B, and the pH is adjusted to 6.0 ± 1.0 with 6 N ammonium hydroxide. The adjusted solution is transferred to a 125-ml. separatory funnel and extracted and measured according to the procedure described under preparation of the calibration curve.

The main source of error is failure to remove practically all the iron. Amounts of iron exceeding 50 micrograms cause noticeable interference. A simple spot test to be used before removing the solution from the electrolysis cell is as follows:

A drop of a standard solution containing 1 microgram of ferrous iron per ml. and a drop of the solution in the cell are placed on a white spot plate. To each of these one drop of 10% hydroxylamine hydrochloride is added. After waiting about a minute 2 drops of 20% ammonium acetate are added, followed by 1 drop of a 5% ethanol solution of *o*-phenanthroline. If the solution shows less iron than the known by comparison of the red colors formed, it may be removed from the electrolytic cell.

Acid-Insoluble Aluminum. The residue from the perchloric acid treatment above is washed once with 5% sulfuric acid, ignited, treated with a few milliliters of hydrofluoric acid and a few drops of sulfuric acid, taken to dryness, and again ignited. The remaining residue is fused with 0.50 gram of potassium bisulfate; the fused mass is dissolved in water; the resulting solution is made 1 N with sulfuric acid, electrolyzed, extracted, and measured as before.

Blanks should be carried through the entire procedures. In the acid-insoluble determination it is necessary to add a fixed weight of potassium bisulfate because of its marked effect on the blank. The optical density of the blank solution should be subtracted from that of the sample before readings are made from the curve (Figure 4).

DATA

Two Bureau of Standards steels of high aluminum content were run. The results are shown in Table III.

To indicate the accuracy of the method in the lower range of aluminum content, synthetic samples were made by mixing aliquots of solutions prepared from known weights of Bureau of Standards Samples 125 and 55 (ingot iron of 0.002% aluminum), and analyzed (Table IV). Two samples were run in each case.

As a further indication of precision and of the order of magnitude of the acid-insoluble aluminum obtained by the method, three commercial samples known to be of low aluminum content were analyzed (Table V).

SUMMARY AND CONCLUSIONS

A modification of Moeller's extraction colorimetric method may be used to determine small quantities of aluminum in steel over a broad range of pH. Interfering elements except for titanium and vanadium may be simply removed by mercury cathode electrolysis in a perchloric–sulfuric acid solution in a modified Melaven cell. A precision of better than 5% can be readily obtained on samples of high-silicon steel of aluminum content from 0.005 to 0.10%.

Table V. Comparison of Results for Acid-Soluble and Acid-Insoluble Aluminum in Commercial Steel Samples

Sample No.		Aluminum, % Acid-soluble	Aluminum, % Acid-insoluble	Aluminum, % Total
1-A		0.0012	0.0000	
		0.0021	0.0001	
		0.0014	0.0001	
	Av.	0.0016	0.0001	0.0017
1-B		0.0040	0.0018	
		0.0037	0.0011	
		0.0042	0.0019	
	Av.	0.0040	0.0016	0.0056
1-C		0.0396	0.0014	
		0.0388	0.0019	
		0.0386	0.0014	
	Av.	0.0390	0.0016	0.0406

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Tungsten in Low-Grade Ores

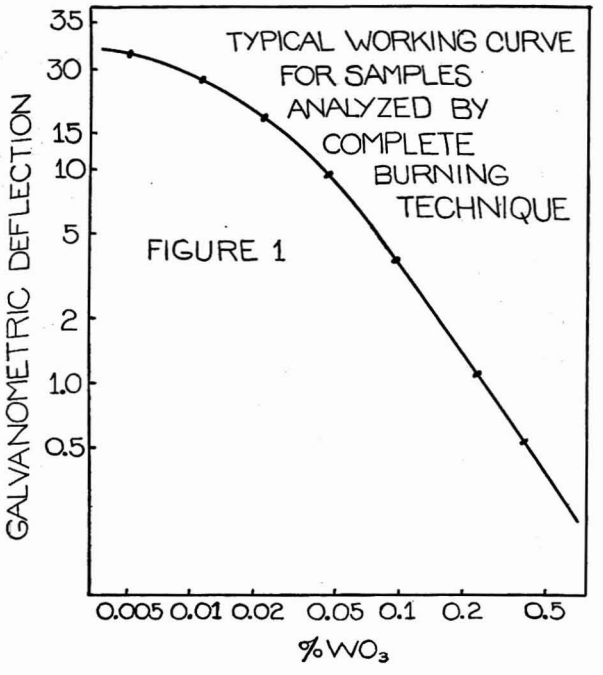
Quantitative Spectrographic Determination

DAVID KAUFMAN, *Massachusetts Institute of Technology, Cambridge, Mass.*, AND S. K. DERDERIAN, *Metal Hydrides Incorporated, Beverly, Mass.*

A method is described for the determination of tungsten in ores and products from ore treatment. This method is applicable from 0.001 to 0.3% tungstic oxide and as much as 50% ferric oxide can be tolerated. Direct burning of ore samples in a direct current arc in graphite electrodes does not provide good results. By diluting samples with silica so that the concentration of tungstic oxide was less than 0.05% and then mixing samples 1 to 1 or 1 to 2 with silver chloride, satisfactory results could be obtained. The precision is good and can be improved. In routine operation a probable error of 5% is realized.

THE problem of determining tungsten spectrographically in ores and ore products has been studied by a number of workers (*1*, *4–7*, *10*) and for specific problems satisfactory methods have been developed. Some of these methods are direct, and some require chemical concentration. The problem at hand concerned the determination of tungsten in siliceous ores and ore products which contained from 0.001 to 0.3% tungstic oxide and from 0.01 to 50% ferric oxide. No direct spectrographic method reported in the literature would give quantitative results at a concentration of tungsten as low as 0.001%, and all the direct methods list iron as a serious interference. Wilson and Fieldes (*10*) and Scobie (*7*) developed combined chemical and spectrographic methods applicable to the problem, but the chemical separations are too involved for rapid control analyses on a large scale.

Ahrens (*1*) has suggested a relatively simple procedure for the direct determination of tungsten in siliceous ores, but the limit of sensitivity is about 0.02% tungstic oxide. In Ahrens' procedure finely ground samples are placed in a graphite cup, and volatilized in a direct current arc, and the spectrum is photographed. The tungsten concentration is then determined by densitometry of the photographic plates. Silicon is used as an internal standard. Apparently the ores studied by Ahrens contained little iron.



DEVELOPMENT OF ANALYTICAL METHOD

Preparation of Standards. Three samples of gravity concentrates from the ores under investigation had been analyzed chemically in the laboratories of the Climax Molybdenum Company. The gravity tailing was primarily silica; therefore, dilution of these concentrates with pure silica reconstituted the original ore and provided a rapid method for the preparation of standards.

The three gravity concentrates contained 0.396, 0.227, and 0.093% tungstic oxide, respectively. A series of standards ranging from 0.396 to 0.001% tungstic oxide was obtained by using the three chemically analyzed concentrates for the highest points and diluting the 0.093% concentrate with quartz crystals to obtain the others. All grinding was done by hand in an agate mortar. An investigation of the spectrum of the standards showed that the only tungsten line that did not have either an iron or titanium line coincident with it was 4924.61 Å. (*2*). (There is a very strong iron line only 0.5 Å. away, 4294.13 Å.)

The spectrograph employed (located at Metal Hydrides Incorporated, Beverly, Mass.) was a Paschen mounted grating instrument designed by the senior author. It has a dispersion of 4.0 Å. per mm. in the first order and uses a 10-cm. (4-inch), 4.1-meter focal length, 15,000 line per inch original grating. By adjusting the exposure conditions and using a 10-micron slit, the tungsten 4294.61 and the iron 4294.13 Å. lines were not only resolved but sufficiently separated to allow densitometry of the tungsten line if the iron concentration was not too high. All plates were densitometered on an Adam Hilger densitometer equipped with a Tinsley galvanometer and galvanoscope. A variable opening disk was rotated in front of the slit to obtain the correct exposure. The spectra were photographed on Eastman 40 plates and after development were densitometered without calibration.

At first an attempt was made to analyze for tungsten by simply burning a weighed sample directly in a direct current graphite arc. When 20-mg. samples were burned completely (2 minutes) at 10 amperes (400 volts applied), consistent results were not obtained, although the working curve (Figure 1) was reproducible. The blackening of tungsten 4294.61 Å. was measured and referred to standards exposed on the same plate. Normally four standards were burned in addition to the samples and a working curve was constructed for each plate. All observations were made in triplicate. Some improvement might have been obtained by using an internal standard. However, the technique of Ahrens (silicon as an internal standard) could not be applied because of the wide variation in sample composition. Fortunately, the necessity for an internal standard was eliminated by use of a new technique which is described below.

Silver Chloride Volatilization. Some experiments were conducted to determine whether or not tungsten could be volatilized selectively. The senior author (*3*) had found that silver chloride

Table I. Effect of Dilution with Silica in Assay of Typical Concentrate by Silver Chloride Volatilization

Mixture[a], Mg.	Assay of Mixture, % WO_3	Dilution Factor	Assay of Sample, % WO_3	Av. % WO_3	Probable[b] Error, % WO_3	P.E. %
1. No dilution	0.10	1	0.10[c]	...	...	...
2. 200 sample 100 silica	0.055	1.5	0.083			
3. 200 sample 200 silica	0.038	2	0.076			
4. 200 sample 300 silica	0.031	2.5	0.078	0.080	0.002	2.5
5. 200 sample 400 silica	0.027	3	0.081			
6. 200 No. 5 200 silica	0.014	6	0.084			
7. 200 No. 6 200 silica	0.009	12	0.108[c]	...	...	...

[a] 100 mg. of each mixture ground with 200 mg. of AgCl.
[b] Probable error of individual determination (*9*).

$$\text{P.E.} = 0.67\sqrt{\frac{d_1^2 + d_2^2 + d_3^2 \ldots\ldots d_n^2}{n - 1}}$$

d = deviation from mean of individual value
n = number of values

[c] Values omitted in calculations.

assisted the volatilization of a large number of otherwise refractory elements. The principle of the method is similar to that of the pyroelectric concentration procedure described by Scribner and Mullin (*8*).

One concentrate and one tailing were selected for test work. Each was ground with silver chloride (Mallinckrodt analytical reagent) in the following ratios: 2 parts of sample to 1 part of silver chloride, 1 part of sample to 1 part of silver chloride, and 1 part of sample to 2 parts of silver chloride. Twenty milligrams of each of these mixtures were burned in graphite electrodes and moving plate studies were made by racking the plate every 10 seconds. It was found that all of the tungsten from an 0.02% tungstic oxide sample was volatilized from the 1 part of sample to 1 part of silver chloride mixture in 30 seconds. The iron was volatilized as well, but nevertheless, because of the shorter burning time and lower arc temperature, the background on the plates was greatly decreased. It was found with a 20-mg. sample that a 0.6-cm. (0.25-inch) graphite electrode drilled to a depth of $^3/_{32}$ inch with a $^7/_{32}$ inch drill gave best results. With a 1 to 2 ratio of sample to silver chloride, all the tungsten from the 0.046% standard could be volatilized in 40 seconds.

Because the majority of concentrates analyzed about 0.1% tungstic oxide, a dilution of 1 part of sample to 3 parts of silica was employed. One part of the diluted sample was then ground with 2 parts of silver chloride, weighed into electrodes, and burned. If the dilution was insufficient to bring the concentration below 0.05%, the results were generally high rather than low, although a low result was expected.

A series of different dilutions was made on one concentrate to determine just how critical the dilution factor was. The data are presented in Table I.

It is apparent that consistent results can be obtained as long as the dilution factor is large enough to bring the tungstic oxide concentration of the mixture below 0.05%. The poor result obtained with mixture 7 probably can be attributed to bad sampling because of the high dilution.

Most of the tailing samples contained less than 0.02% tungstic oxide so that dilution with silica was unnecessary. A ratio of 1 part of sample to 1 part of silver chloride gave complete volatilization of all the tungsten in the tailings and gave better sensitivity than the 1 part of sample to 2 parts of silver chloride employed for concentrates.

When concentrates and tailings were both analyzed by the partial burning technique, satisfactory checks were obtained between calculated feed values and actual assay of feed, and the spectrographic results showed reasonably good agreement with chemical determinations (Table II).

Detailed Description of Analytical Procedure. Original samples must be dry and preferably finer than 200-mesh. If there is any question of sample uniformity, a representative portion of approximately 5 grams should be ground in an agate mortar until no grittiness is apparent.

For concentrates 200 mg. of the sample were ground with 600 mg. of powdered quartz crystals; 100 mg. of the sample-quartz mixture were then ground with 200 mg. of silver chloride. For the actual analysis 20-mg. portions of the silver chloride mixture were weighed out in triplicate. Four standards containing 0.006, 0.012, 0.023, and 0.046% tungstic oxide, respectively, were run with each set of concentrates. The standards were also weighed out in triplicate.

For tailing samples no initial dilution with quartz was required, and a 100-mg. portion of the original sample was ground directly with 100 mg. of silver chloride. From this point on the procedure was the same as for the concentrates, except that the standards contained 0.002, 0.006, 0.012, and 0.023% tungstic oxide, respectively.

All concentrates were burned for 40 seconds at 10 amperes. Tailings were burned for only 30 seconds. A rotating disk with a 180° opening decreased the background sufficiently for both tailings and concentrates, so that no background corrections had to be made.

Normally 8 samples and 4 standards (36 burnings) were taken on one plate. Some time could have been saved by calibrating plates and burning fewer standards, but a calibration procedure was not available above 4000 Å. on the spectrograph used. Without calibration it was necessary to draw a new working curve for each plate.

Reproducibility of Analysis. In order to obtain some idea of the reproducibility of the spectrographic method, eight typical samples were chosen and analyzed repeatedly on seven different plates. For each analysis a separate portion of the original sample was weighed out and ground with silica. On two of the plates, all the samples were treated as tailings and after dilution were ground with an equal weight of silver chloride. On the other five plates, the samples were treated as concentrates and

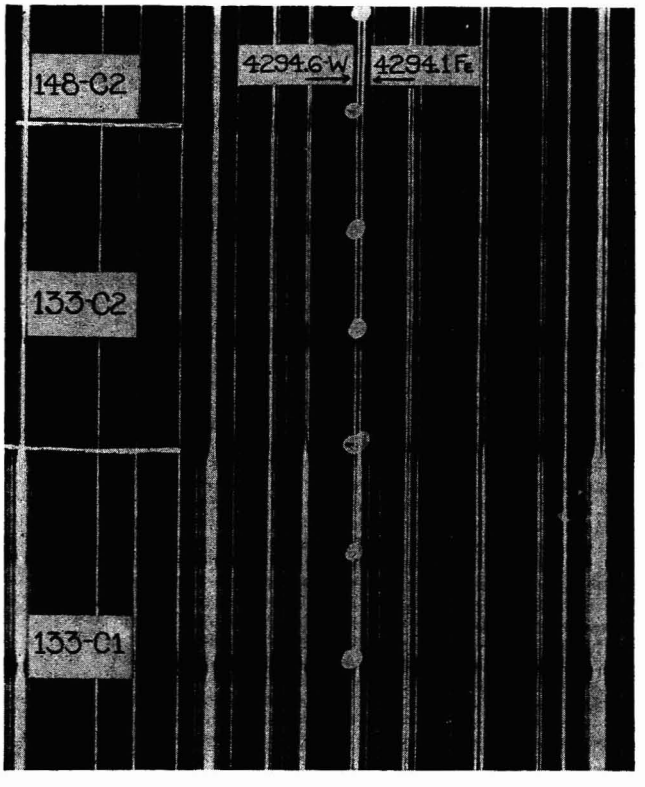
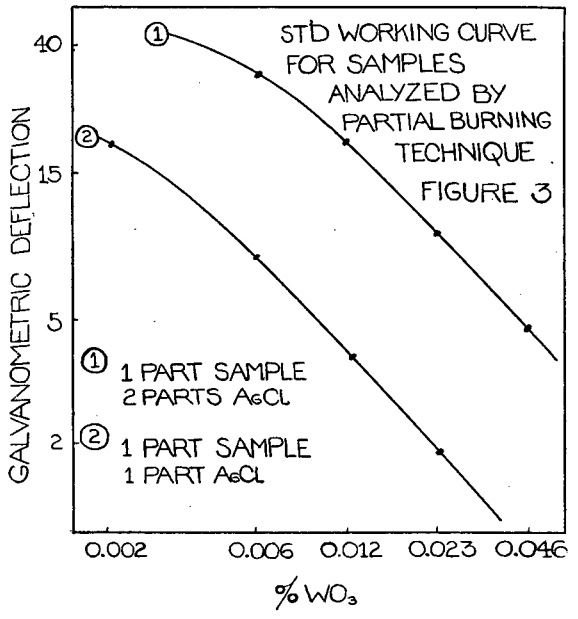


Figure 2

Table II. Results of Seven Separate Analyses of Eight Typical Samples by Silver Chloride Volatilization Method

Sample No.	Per Cent Tungstic Oxide: Chem. values[a]	Plate T-4, 2:1[b]	Plate T-5, 2:1	Plate T-6, 2:1	Plate T-9, 1:1	Plate T-10, 2:1	Plate T-11, 2:1	Plate T-12, 1:1	Av.	Probable Error[c]	Probable Error, %
27C	0.077	0.056	0.066	0.068	0.065	0.080	0.066	0.064	0.067	0.004	6.0
133-C1	0.08	0.070	0.076	0.092	0.086	0.088	0.080	0.092	0.083	0.006	7.2
133-C2	0.17	0.172	....	0.176	0.160	0.164	0.144	0.176	0.165	0.008	4.8
148-C2	0.19	0.180	0.188	0.172	0.172	0.180	0.172	0.164	0.175	0.005	2.8
165C	0.12	0.096	0.122	0.126	0.114	0.100	0.098	0.128	0.111	0.007	6.3
169-CT	0.09	0.064	0.075	0.076	0.062	0.076	0.064	0.062	0.068	0.005	7.3
169-T1	0.01	0.0090	0.0078	0.0094	0.0094	0.0093	0.0092	0.0082	0.0089	0.0004	4.5
1107	0.007	0.0057	0.0058	0.0053	0.0052	0.0058	....	0.0050	0.0055	0.0002	3.6

[a] Chemical analyses made by Donald Guernsey, Department of Metallurgy, Massachusetts Institute of Technology.
[b] 2:1—2 parts AgCl, 1 part sample. 1:1—1 part AgCl, 1 part sample.
[c] Probable error formula, refer to Table I. Mean probable error, 5.3%.



after dilution were ground with double their weight of silver chloride. From each sample–silver chloride mixture, 20-mg. samples were weighed into the electrodes in triplicate. In Table II each figure represents the mean of three burnings.

An enlargement of the region of the 4294.6 Å. tungsten line is shown in Figure 2, which gives a good indication of how the lines appear on the viewing screen of the densitometer. In spite of the high iron concentration in sample 133 C-1, the tungsten line can be adequately resolved. Typical working curves for concentrates and tailings are demonstrated in Figure 3.

Sources of Error. The probable error for a single determination (mean of three burnings) is approximately 5%. Part of this error is inherent in the burning; part may be attributed to sampling both from the original material and from the mixtures after grinding; and part may be the result of variation in the working curves on the individual plates. The error involved in the burning step can be determined by multiple analyses from a single grinding made on one plate with one set of standards. To determine this error a concentrate (27C) and a tailing (1107) were treated as follows:

A 200-mg. portion of sample 27C was ground with 600 mg. of silica. Two hundred milligrams of this mixture were then ground with 400 mg. of silver chloride. Fifteen duplicate samples of 20 mg. each were taken from the silver chloride–sample mixture and burned on one plate against one set of standards (in triplicate), and the results were arbitrarily divided into groups of three. Each group was then considered as a separate analysis, and the mean and probable errors for the five analyses were determined. The probable error determined in this manner was compared with the probable error for this same sample given in Table II. In Table II the probable error was obtained from seven analyses comprising three samples each, but each group of three samples was taken from a separate mixture of sample, silica, and silver chloride rather than from the mixture described above and each of the seven analyses was made on seven different plates with seven different sets of standards.

A similar determination was carried out with sample 1107, but no dilution with silica was required, and 200 mg. of the original sample were mixed directly with 200 mg. of silver chloride. Fifteen 20-mg. portions were burned, compared with standards, and treated as above. The data are presented in Table III.

The probable error for a number of determinations made from a single grinding and compared with a single set of standards is much smaller than that obtained from different grindings compared with different sets of standards. This indicates that a considerable increase in precision could be obtained by more careful attention to sampling and grinding and by better control of development conditions.

Effect of Iron Concentration. As noted above, most direct methods for the determination of low concentrations of tungsten (below 0.1%) are applicable only when the iron concentration is low. However, some of the ore products contained large amounts of pyrite. High iron causes difficulty chiefly because of the interference of iron with most of the high intensity tungsten lines. At high concentrations iron line 4294.13 Å. becomes very broad and has a dark background in its immediate neighborhood. If tungsten line 4294.61 is weak, it may be completely lost in the background. In order to determine how much iron can be tolerated at various concentrations of tungsten, a concentrate which previously had been analyzed at 0.066% tungstic oxide was diluted with different amounts of silica and analyzed. These same diluted samples were then further diluted with ferric oxide and analyzed. The results are presented in Table IV.

Table III. Comparison of Probable Error for Single and Multiple Grindings

	Sample 27C, % WO_3		Sample 1107, % WO_3	
	Single grinding	Multiple grinding from Table II	Single grinding	Multiple grinding from Table II
	0.070	...	0.0055	....
	0.076	...	0.0054	....
	0.064	...	0.0052	....
	0.068	...	0.0051	....
	0.066	...	0.0050	....
Mean % WO_3	0.069	0.067	0.0052	0.0055
Probable error	0.003	0.004	0.0001	0.0002
P.E., %	4.4	6.0	1.9	3.6

Table IV. Effect of Added Iron on Tungsten Assay at Various Concentrations of Tungsten

Sample[a]	Fe_2O_3 Added, %	WO_3 Calculated, %	WO_3 Determined, %
1. 1 part sample 2 parts silica	..	0.022	0.022
2. 3 parts No. 1 1 part Fe_2O_3	25	0.016	0.016
3. 1 part sample 3 parts silica	..	0.0165	0.0165
4. 3 parts No. 3 1 part Fe_2O_3	25	0.0124	0.0135
5. 1 part No. 3 1 part Fe_2O_3	50	0.0083	0.0105

[a] All samples mixed with 2 parts of AgCl after noted dilution.

It is apparent that as much as 25% ferric oxide can be tolerated with little loss of precision, provided the tungsten concentration is at least 0.01%, although 50% ferric oxide partially obscures the tungsten line and leads to high results. Fortunately, with the exception of pyrite concentrates, when the iron is high, the tungsten is also high, and dilution with silica is effective in decreasing the concentration of both elements to a point where the tungsten can be determined.

CONCLUSIONS

The silver chloride volatilization technique has several advantages over other methods for the determination of tungsten in ores.

The method is very sensitive and can determine concentrations as low as 0.0005% tungstic oxide without difficulty. By increasing the size of sample, it should be possible to increase this sensitivity still further.

The method is reasonably precise even in the absence of an internal standard. A probable error of 5% can be obtained routinely.

The method is rapid and is readily adaptable to routine operation. Burning time per sample is only 30 to 40 seconds.

The method is almost independent of changes in matrix composition. The presence of a large amount of silver chloride ensures that the volatilization conditions will be controlled by this compound.

The method can be employed over a wide range of concentration. In actual practice it has given satisfactory results with tungsten concentrations between 0.3 and 0.0005%.

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Determination of Isopropyl Alcohol, Diacetone Alcohol, and 2-Methyl-2,4-pentanediol

In the Presence of Each Other

F. J. FRERE AND J. J. BUSZ, *Publicker Industries, Inc., Philadelphia, Pa.*

A rapid method, based on the work of Barbaudy, has been developed for the determination of isopropyl alcohol, 4-hydroxy-4-methyl-2-pentanone, and 2-methyl-2,4-pentanediol in the presence of each other. Results with a reasonably high degree of accuracy can be obtained in 15 minutes.

IN THE process of hydrogenating diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) there is formed in addition to the main product, 2-methyl-2,4-pentanediol, a small amount of isopropyl alcohol (2-propanol). This results from the degradation of diacetone alcohol to acetone, which in turn is reduced to isopropyl alcohol. In order to follow the rate of hydrogenation and ascertain the activity of the catalyst, it is essential to know the composition of the reaction mixture at any given instant. Fractional distillation is time-consuming and cannot be used for the rapid analysis of spot samples.

A rapid method has been developed which requires an expenditure of time not exceeding 15 minutes. Its principle is not new, but rather is based on the work of Barbaudy (*1*), who first applied it to the analysis of the mixture: benzene–ethyl alcohol–water. More recently, Campbell and Miller (*2*) applied the method to the analysis of the mixture: benzene–ethyl alcohol–carbon tetrachloride. Both authors claim an accuracy of approximately 0.25%.

PRINCIPLE OF THE METHOD

A survey of the literature reveals that the method has found only limited use among analytical chemists, although undoubtedly there are many systems to which it may be successfully applied. One of the great advantages to be gained by its use is that of time.

Just as one physical or chemical property is sufficient to fix the composition of a binary system, two will fix the composition of a ternary system. Therefore, the composition of a ternary liquid system may be determined if any combination of two pairs of components possesses some chemical or physical property that is nearly identical for members of a given pair but is not possessed by, or is different from, that for members of the other pair. In many cases it is necessary to consider only a single pair of components, providing one member of the pair possesses some chemical property that is not common to the other two components.

To illustrate the principle more specifically, let us consider a system composed of components A, B, and C. Now, the compo-

sition may be ascertained if A and B possess some nearly identical physical or chemical property that differs from that of C, or if A and C or B and C possess some other nearly identical physical or chemical property that differs from that of components B and A, respectively. When only one pair of components such as A and B is under consideration, it is only necessary that either A or B possess some chemical property that is not common to the other two components. In each of the above cases of component pairs it is assumed that the third component is present without materially altering the relative values of the properties common to the pair.

A method of obtaining data in ternary systems, afforded by the use of pseudobinary curves, consists simply of adding to a fixed binary mixture varying amounts of the third component. If the binary mixture is treated as unicomponent, it is possible to plot any property against composition on rectangular coordinates. From several such plots one is able to select ternary solutions of variable composition but with fixed chemical or physical property. The values of these properties may be plotted on triangular coordinates, with the result that there are formed two series of nearly parallel lines intersecting at an angle approximating 60°. The accuracy of the method depends to a very great extent on the similarity of properties exhibited by the component pairs.

Any physical property which is, or is approximately, a linear function of composition may be used. In general, specific gravity and refractive index satisfy this requirement. Chemical properties appear to be somewhat more numerous: bromine, hydroxyl, carbonyl, and acid number, and oxidation value. Oxidation reaction offers a choice of reagents which may be selective for certain types of compounds, in which case it can be used in conjunction with an oxidant that is capable of completely oxidizing all the components.

The method fails when the system is composed of more than three components. However, if these extraneous materials are present in low concentration, one may obtain a reasonably good approximation as to the composition of a given system.

MATERIALS AND REAGENTS

Diacetone Alcohol. A reagent grade material was fractionated under reduced pressure on a Podbielniak column. The center cut was selected for use.

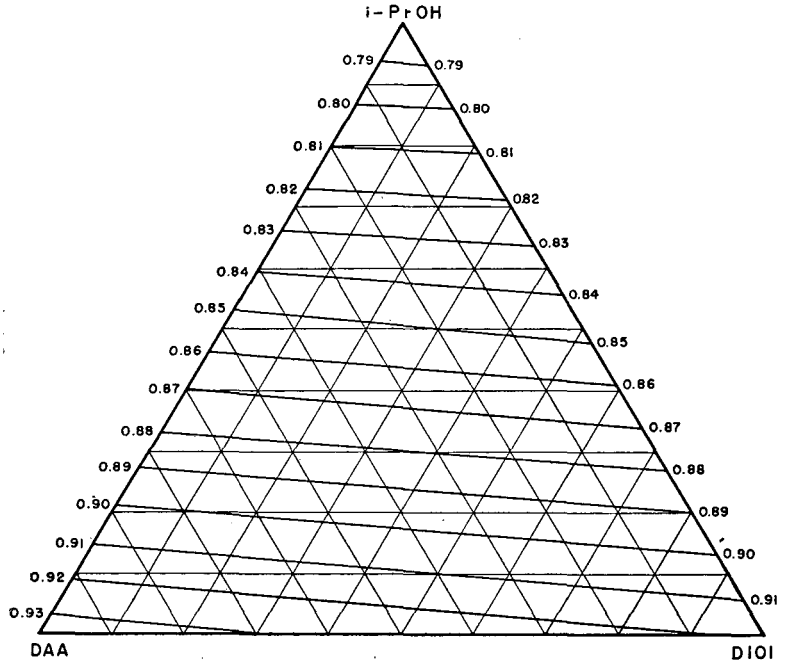

Figure 1. Gravities (25/25) in System: Isopropyl Alcohol–Diacetone Alcohol–2-Methyl-2,4-pentanediol

Table I. Specific Gravities in Ternary System: Isopropyl Alcohol–Diacetone Alcohol–2-Methyl-2,4-pentanediol

Sp. Gr., 25°/25° C.	Iso-PrOH	DAA[a]	Diol	Iso-PrOH	DAA	Diol	Iso-PrOH	DAA	Diol
	Weight Per Cent								
0.7900	93.6	0.6	5.8	93.5	3.2	3.3	93.4	5.9	0.7
0.8000	86.0	1.4	12.6	86.3	6.8	6.9	86.6	12.1	1.3
0.8100	78.7	2.1	19.2	79.1	10.4	10.5	79.6	18.4	2.0
0.8200	71.1	2.9	26.0	71.9	14.0	14.1	72.8	24.5	2.7
0.8300	63.7	3.6	32.7	64.7	17.6	17.7	65.7	30.9	3.4
0.8400	55.0	4.5	40.5	57.5	21.2	21.3	59.0	36.9	4.1
0.8500	48.4	5.2	46.4	50.5	24.7	24.8	52.5	42.7	4.8
0.8600	41.5	5.9	52.6	43.6	28.2	28.2	45.7	48.9	5.4
0.8700	34.4	6.6	59.0	36.9	31.5	31.6	39.2	54.7	6.1
0.8800	27.4	7.3	65.3	30.0	35.0	35.0	32.6	60.7	6.7
0.8900	20.5	8.0	71.5	23.5	38.2	38.3	26.4	66.2	7.4
0.9000	13.6	8.6	77.8	16.9	41.5	41.6	20.0	72.0	8.0
0.9100	6.5	9.4	84.1	10.1	44.9	45.0	13.7	77.7	8.6
0.9200	4.1	47.9	48.0	5.7	64.3	30.0	7.9	82.9	9.2
0.9300	1.2	78.8	20.0	1.9	88.3	9.8	2.3	92.7	5.0

[a] DAA, diacetone alcohol; diol, 2-methyl-2,4-pentanediol.

Isopropyl Alcohol. A reagent grade material was refluxed for several hours with freshly calcined calcium oxide, after which it was fractionated at atmospheric pressure on a Podbielniak column. The center cut was selected for use.

2-Methyl-2,4-pentanediol. Every grade of diol tested was found to contain varying amounts of a carbonyl compound which could not be removed by repeated fractionation, but could be removed by first azeotroping with benzene at atmospheric pressure. The diol was then fractionated under reduced pressure on a Podbielniak column. The center cut was selected for use.

2 *N* Solution of Hydroxylamine Hydrochloride, made by dissolving 139 grams of the salt in distilled water and diluting to 1 liter.

0.5 *N* Sodium Hydroxide. Twenty grams of carbonate-free sodium hydroxide are dissolved in freshly boiled distilled water, diluted to 1 liter, and standardized against pure diacetone alcohol as described in procedure.

Bromophenol Blue, 0.1 gram dissolved in 100 ml. of water.

PROCEDURE

Diacetone Alcohol. Add 20 ml. of 2 *N* hydroxylamine hydrochloride and 2 to 3 drops of bromophenol blue to 150 ml. of distilled water contained in a 250-ml. Erlenmeyer flask and neutralize with 0.5 *N* sodium hydroxide to the appearance of a faint greenish blue coloration. Weigh out 1 to 2 grams of sample in a weighing pipet and transfer to the flask containing the solution. Thoroughly mix and allow to stand for several minutes. Titrate with 0.5 *N* sodium hydroxide, comparing the color change with that of a blank containing the same volume of solution, indicator, and hydroxylamine hydrochloride. The color change is from yellow to greenish blue.

Specific Gravity. Determine the specific gravity of the sample at 25° C. using a 25-ml. pycnometer.

Locate, on the diagram, the point of intersection of the diacetone alcohol and specific gravity lines. Determine the composition of the solution, corresponding to this point, according to the method of Gibbs or Roozeboom as outlined in Findlay's text on the phase rule (*3*).

RESULTS AND DISCUSSION

Lines of constant specific gravity were constructed as outlined under Principle of the Method. The results shown in Table I are plotted in Figure 1.

Solutions containing known varying amounts of diacetone alcohol, isopropyl alcohol, and 2-methyl-2,4-pentanediol were prepared and analyzed according to the above procedure. The gravities were determined in duplicate and the diacetone alcohol in triplicate. These results are shown in Table II.

Table II. Analysis of Synthetic Mixtures

Added			Found		
Iso-PrOH	DAA	Diol	Iso-PrOH	DAA	Diol
Weight Per Cent			Weight Per Cent		
49.7	50.3	0.0	49.8	50.2	0.0
0.0	47.8	52.2	0.0	47.6	52.4
50.0	0.0	50.0	50.3	0.0	49.7
5.0	90.0	5.0	4.8	90.1	5.1
90.1	5.3	4.6	90.1	5.4	4.5
10.0	5.3	84.7	9.8	5.2	85.0
50.9	23.3	25.8	51.0	23.4	25.6
25.1	49.8	25.1	25.2	49.6	25.4
25.2	25.0	49.8	25.0	25.1	49.9
10.0	45.0	45.0	9.8	44.8	45.4
42.3	48.0	9.7	42.1	48.2	9.7

It is seen that the method is capable of giving results with a reasonably high degree of accuracy, but that an error in one determination, gravity or diacetone alcohol, will cause a piling up of errors on one or more of the components. This is especially true in the case of diacetone alcohol because of its large equivalent weight. However, despite these shortcomings, results of sufficient accuracy may be obtained to permit one to follow the course of the hydrogenation reaction and to evaluate the activities of various types of catalysts. When reasonably pure diacetone alcohol is used as a starting material, nothing will be gained by resorting to the more lengthy procedure of fractional distillation. An examination of the hydrogenated products showed negligible amounts of acetone.

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MAGNESIUM

Rapid Alkalimetric Determination in Calcium and Magnesium Carbonate Ores

S. C. SANE AND M. S. TELANG, *Laxminarayan Institute of Technology, Nagpur University, Nagpur, India*

SOME of the volumetric methods employed for determining the magnesium content of carbonates have been reviewed by Williams (*5*). Kolthoff and Stenger (*2*) have discussed the application of acid-base displacement titration methods for magnesium salts. Some of the existing methods are applicable in the presence of calcium salts under appropriate limiting conditions. An acid-alkali method employing calcium hydroxide (lime water) in place of sodium hydroxide for the volumetric determination of magnesium in the presence of calcium (*4*) is of particular interest on account of its extreme simplicity, rapidity, and accuracy. Although this method usually has been employed for water analysis, it could be safely utilized for the determination of magnesium in hydrochloric acid solution of calcium and magnesium carbonates, provided iron and aluminum, which are likely to be precipitated in alkaline medium, are not present.

Table I. Alkalimetric Determination of Magnesium in Prepared Mixtures of Carbonates of Calcium and Magnesium

Mixture No.	$MgCO_3$ in Mixture	$MgCO_3$ Present	$MgCO_3$ Found
	%	*Gram*	*Gram*
1	1.96	0.02	0.0204
2	4.74	0.05	0.0502
3	9.09	0.10	0.1012
4	13.04	0.15	0.1521
5	16.67	0.20	0.2014
6	25.00	0.15	0.1525
7	33.34	0.10	0.1200
8	50.00	0.02	0.0202
9	66.67	0.20	0.2031
10	80.00	0.20	0.2042

The authors' principal objective was to develop a rapid method for the determination of magnesium in the presence of interfering elements like iron and aluminum without sacrificing accuracy, and at the same time to employ easily available and less expensive reagents. The calcium hydroxide method (*4*) appeared very promising in these respects, provided due modifications could be made, so that it could be applied in the presence of iron and aluminum. Experience showed that the method outlined in the present paper fills the requirements.

Williams (*5*) used sulfuric acid to dissolve the carbonate ore, with the obvious intention of preventing calcium from going into solution. It is likely that the digestion may not be complete unless a vigorous agitation is carried out during the digestion, as the calcium sulfate formed produces a resistant coating on the undigested particles, and prevents the inner core of the carbonate ore from coming into contact with the acid. Furthermore, on account of the slight solubility of calcium sulfate, the solution will contain a little calcium which will be precipitated as the carbonate if the sodium hydroxide used contains carbonate. This point appears to have been overlooked by Williams.

PREPARATION OF SAMPLES AND REAGENTS

The purity of Merck's precipitated calcium carbonate (*proanalysi*) and magnesium carbonate was established by analysis in this laboratory. In order to check the reliability of the proposed method, three sets of experiments were carried out as illustrated in the tables. Errors may arise from inefficiency of mixing, sampling, etc., if a large quantity of a mixture of calcium carbonate and magnesium carbonate is prepared and if a representative sample of the mixture for further analysis is then chosen. It was, therefore, thought advisable to prepare the required mixtures by directly weighing out actual quantities of calcium carbonate and magnesium carbonate.

To obtain a 1-gram mixture containing 20% magnesium carbonate, 0.2 gram of magnesium carbonate and 0.8 gram of calcium carbonate were weighed out separately and mixed, and the whole mixture of 1-gram weight was employed for analysis. Similarly, to determine the accuracy of the method in the presence of iron and aluminum, the mixtures of calcium and magnesium carbonates were prepared by actual weighing and then a few milliliters of solutions of aluminum chloride and ferric chloride, the iron and aluminum contents of which per milliliter were determined by previous analysis, were added. Sodium hydroxide solution was standardized against pure succinic acid (analytical reagent quality, British Drug Houses) and checked by titrating with hydrochloric acid standardized against a known weight of a carefully selected piece of calcite crystal; both methods gave concordant values of the strength of the sodium hydroxide solution. Calcium hydroxide was also standardized against the same hydrochloric acid.

After its accuracy had been tested with known artificial mixtures of calcium and magnesium carbonates with and without iron and aluminum, the method was applied to some samples of calcium and magnesium carbonate ores. To establish that the proposed method gives accurate results even for ores, the usual gravimetric pyrophosphate method (*3*) for magnesium was resorted to as shown in Table III. The samples of magnesium carbonate ore were free from manganese.

Table II. Alkalimetric Determination of Magnesium in Presence of Iron, Aluminum, and Calcium

Mixture No.	% Composition of Mixture				$MgCO_3$ Present	$MgCO_3$ Found
	$CaCO_3$	$MgCO_3$	Al_2O_3	Fe_2O_3	*Gram*	*Gram*
1	95.19	1.90	1.72	1.19	0.02	0.0204
2	92.54	4.63	1.67	1.16	0.05	0.0503
3	19.30	77.16	2.09	1.45	0.20	0.2043

Table III. Determination of Magnesium in Carbonate Ores

Ore Sample No.	Per Cent MgO	
	Gravimetric pyrophosphate method	Alkalimetric method
1	6.38	6.38
2	3.49	3.48
3	2.33	2.33
4	2.40	2.39
5	5.57	5.57
6	1.42	1.42
7	8.86	8.85

EXPERIMENTAL PROCEDURE IN ABSENCE OF MANGANESE

To obtain the results in Table I, weigh out separately pure calcium carbonate and magnesium carbonate into one 500-ml. Erlenmeyer flask so as to obtain a mixture of the two substances in the requisite proportions. Cover the mixture with about 25 ml. of distilled water. Slowly add 50 ml. of 0.5 *N* hydrochloric acid, heat to ensure complete decomposition of the carbonates, and allow to cool. Make the solution to a known volume in a volumetric flask by adding water. Divide the solution into two equal parts. To one part, add a few milliliters of a concentrated solution of ammonium chloride, then titrate the solution with 0.5 *N* sodium hydroxide to the methyl red end point. Note the volume of sodium hydroxide required for the titration, which indicates the amount of free acid present.

To the second part of the solution add exactly the same volume of 0.5 *N* sodium hydroxide required in the above titration, without the addition of ammonium chloride and methyl red, so that excess acid is neutralized. Mix the contents of the flask well by shaking, then add as quickly as possible a known volume of standard calcium hydroxide solution in moderate excess to precipitate magnesium. Close the flask with a rubber stopper bearing a Bunsen valve to exclude the atmospheric carbon dioxide and boil for a minute or two. Cool under a running tap. Transfer the mixture after cooling to a 250-ml. volumetric flask and make up the volume to the 250-ml. mark by adding fresh distilled water. Shake the contents of the flask well. Quickly filter through a dry quantitative filter paper into a dry receiver. Reject a few milliliters of the first filtrate. Titrate the excess calcium hydroxide present in an aliquot of the subsequent filtrate with 0.05 *N* hydrochloric acid to the phenolphthalein end point. Calculate the amount of 0.05 *N* acid that would be required for the whole of the calcium hydroxide excess present in 250 ml. of the mixture. Hence, calculate the quantity of calcium hydroxide actually consumed for the precipitation of magnesium, as the volume added in the beginning is known. It is thus possible to calculate the amount of magnesium present in the original mixture of the carbonates.

For obtaining the results in Table II, repeat exactly the same procedure by adding known quantities of iron and aluminum chloride solutions to the Erlenmeyer flask before adding hydrochloric acid to decompose the carbonates.

Adopt the following procedure to determine the magnesium contents of actual carbonate ores (see Table III).

Weigh out in an Erlenmeyer flask the required weight of the carbonate ore and carry out the decomposition of the carbonates with known volumes of standard hydrochloric acid in the same manner as before. Filter and wash the acid-insoluble residue consisting of silica and silicates four or five times with hot water. Treat the filtrate and washings consisting of iron, aluminum, calcium, and magnesium as before. Determine the magnesium content also by the usual gravimetric pyrophosphate method for comparison (*3*).

The first titration is merely to determine the quantity of sodium hydroxide required to neutralize the excess acid and to precipitate iron and aluminum, whereas the actual calculation of magnesium is based on the titer value of calcium hydroxide with the second part of the solution.

DISCUSSION

From the titration of the excess acid with 0.5 *N* sodium hydroxide using the first part of the ore solution, the quantity of 0.5 *N* hydrochloric acid actually consumed for the decomposition can be calculated, and from this the carbonate content of the ore can be estimated, provided other constituents capable of reacting with hydrochloric acid are absent. Usually, such constituents are negligible in quantity and, therefore, this method can give a reasonable idea of the carbonate content of the ore. Similarly, after the acid taken up by magnesium carbonate has been determined, it is possible to calculate the acid that would be required for dissolving calcium carbonate, from which a rough idea of the calcium content of the ore can be had. In the absence of iron, aluminum, etc., which may be attacked by hydrochloric acid, this method can even give the exact value of the calcium content.

Iron and aluminum if present will be precipitated by sodium hydroxide in the titration of the excess hydrochloric acid with methyl red indicator (pH 4.4 to 6.2). At the methyl red end point in presence of the added ammonium chloride solution, iron and aluminum are precipitated, while calcium and magnesium are not precipitated (*1*). The sodium hydroxide used up by iron and aluminum will not appear in the determination of magnesium in the subsequent operation using calcium hydroxide. The fact that the proposed method is applicable even in the presence of iron and aluminum is a distinct advantage over the existing volumetric methods of determination of magnesium, which are otherwise applicable in presence of calcium. Iron, if present in large quantities, obscures the color change of methyl red indicator during the titration with sodium hydroxide. Addition of water to the titer mixture so as to reduce the ferric oxide content to 0.1 gram per 100 ml. of the mixture facilitates the titration. Adopting the experimental procedure given above, the volume of the titre solution consisting of the filtrate and washings from the acid treatment of the ore may be expected to be not less than 100 ml. It is, therefore, permissible to carry out the titration in presence of iron, employing a 1-gram sample of the ore with 10% ferric oxide content without further dilution.

Thus, the quantitative determination of magnesium and approximate determinations of calcium and carbonate content can be carried out in about 2.5 hours. This method proved to be of great assistance for limestone prospecting work for portland cement manufacture, where the magnesium content is the deciding factor in the choice of a suitable limestone. The reagents are cheap and readily available. Sodium hydroxide (0.5 *N*) need not be necessarily free from carbonate when methyl red indicator is used (*5*). Finally, the error obtained is within reasonable limits, considering the fact that it has been multiplied ten times by taking a tenth portion of the mixture as the aliquot for the titration.

PROCEDURE IN PRESENCE OF MANGANESE

If manganese is present in the ore, it is necessary to remove it by the peroxide method used by Williams (*5*) with some modification.

Prepare a solution of the ore employing nitric acid instead of hydrochloric acid. The filtrate and washings consist of iron, aluminum, manganese, calcium, and magnesium. Neutralize the solution with dilute sodium hydroxide and add about 0.5 gram of sodium peroxide with stirring. Boil until excess sodium peroxide is removed. Acidify with dilute nitric acid and boil for a few

minutes to dissolve the soluble salts. Add a few drops of phenolphthalein indicator (pH 8 to 10) and then slowly add 0.5 N sodium hydroxide until the red color appears. Carefully add 0.1 N nitric acid until the red color of the supernatant liquid is just discharged. Boil for a few minutes and filter, washing the residue with hot water. The residue will consist of the insoluble hydroxides of iron, aluminum, etc., and manganese dioxide, and the filtrate will consist of calcium and magnesium salts.

Because the filtrate is neutral (pH × 8) and free from interfering radicals, the earlier portion of the original procedure given in the present paper should be omitted. The rest of the procedure, commencing with the addition of a known volume of standard calcium hydroxide solution in moderate excess to precipitate magnesium, is followed.

Hydrochloric acid is objectionable in the presence of the manganese dioxide to be precipitated and sulfuric acid interferes with calcium hydroxide. Hence, nitric acid is recommended in this procedure.

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Determination of Pentosans in Cellulose

Simplification of TAPPI Standard T 450 m 44 Method

PIETER HENDRIK TEUNISSEN, *N. V. Onderzoekingsinstituut Research (A.K.U. and Affiliated Companies), Arnhem, Holland*

A determination of pentosan by an abbreviated form of TAPPI standard T 450 m 44 method is discussed. The method is shortened by not adding fresh hydrochloric acid during distillation. A change in the calculation formula is required. A correction factor for the presence of hydroxymethylfurfural is presented.

IN THE analysis of straw cellulose the author has used for a long time the method of Gierisch (*1*) for the determination of pentosans. According to this method a quantity of cellulose containing 150 to 200 mg. of pentosan is put with 210 ml. of 12% hydrochloric acid in a 500-ml. round-bottomed flask (Figure 1). The flask stands on a tripod with an asbestos ring in order to prevent superheating of the walls. In the cases of cellulose samples with a very low pentosan content, a large quantity of cellulose must be used for the experiment and consequently more 12% hydrochloric acid—e.g., 250 ml. for 10 grams of cellulose. The velocity of the distillation must be accurately adjusted at 12 ml. per 5 minutes. In this way 180 ml. are distilled off in 75 minutes. The volume is not kept constant by supplying fresh 12% hydrochloric acid as is the case with other methods. The furfural that distills over is determined by precipitation with barbituric acid. This has an advantage over the phloroglucinol method of Kröber (*2*) because the barbituric acid does not precipitate hydroxymethylfurfural.

Recently the bromide-bromate method of TAPPI (T 450 m 44) has been used by the author. This TAPPI standard prescribes distillation while the volume is kept constant by adding fresh hydrochloric acid. The author found that the distillation can be shortened, when no fresh 12% hydrochloric is supplied during distillation. This requires a change in the calculation formula as described below.

TAPPI STANDARD AND ABBREVIATED DISTILLATION METHODS

The two distillation methods were compared by applying them to Kahlbaum's "xylose-reinst." From this substance only furfural is formed and no hydroxymethylfurfural, so that a strict comparison of the determinations of furfural is possible (Table I). For the titration by means of bromate both the distillation according to the TAPPI standard and that according to the abbreviated method were applied. For the barbituric acid test only the abbreviated method was used, because when a more prolonged distillation is applied no additional furfural distills over.

When for the bromate titration of the furfural V_1 ml. of thiosulfate are used (normality N) and for the blank test V_2 ml., this corresponds with $N(V_2 - V_1) \times 0.048$ gram of furfural. The quantity of pentosan is then $1.58 \times N(V_2 - V_1) \times 0.048$ gram and the pentosan content when W grams of dry cellulose had been used is

$$\frac{1.58 \times N(V_2 - V_1) \times 0.048 \times 100}{W}\% = \frac{7.57 \times N(V_2 - V_1)}{W}\%$$

In the TAPPI standard, the following formula is given for the pentosan content in cellulose:

$$\frac{7.5 \times N(V_2 - V_1)}{W} - 1.0\%$$

The correction −1.0 is due to the presence of hydroxymethylfurfural which is formed from cellulose. This is not formed from

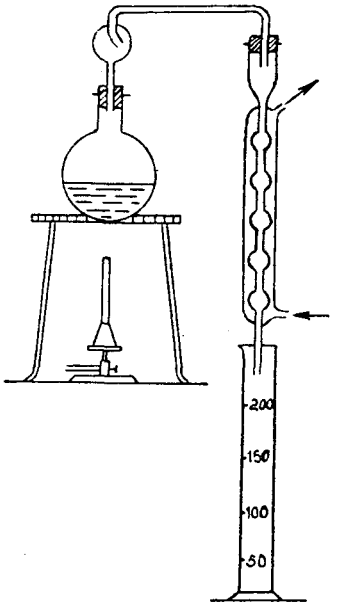

Figure 1. Apparatus Used in Gierisch's Distillation Method

Table I. Comparison of TAPPI and Abbreviated Distillation Method on Xylose

Distillation Method		Furfural Determination Using	Calculated Content, %
TAPPI	300 ml.	$KBrO_3$	101.2
TAPPI	300 ml.	$KBrO_3$	100.6
Abbreviated	180 ml.	$KBrO_3$	99.0
	180 ml.	$KBrO_3$	100.4
	180 ml.	$KBrO_3$	99.7
	180 ml.	$KBrO_3$	100.4
	180 ml.	Barbituric acid	99.2
	180 ml.	Barbituric acid	100.1

xylose, so in that case no correction is necessary. As a consequence of this the formula is equal to that used by the author except that 7.5 is mentioned instead of 7.57 in this author's formula. In this special case, where the monomer xylose has been used, the result has to be multiplied by

$$\frac{\text{Molecular weight of xylose}}{\text{molecular weight of xylans}} = \frac{150}{132} = 1.136$$

This factor is valid for both the barbituric acid and the bromate method.

Table I shows that, when the bromate method is applied to xylose, the difference between the TAPPI distillation method (300 ml.), the abbreviated method (180 ml.), and the barbituric acid method remains within the experimental error. This corresponds with the remark made above, that for xylose no correction for hydroxymethylfurfural is required.

After this the bromate and barbituric acid methods were applied on straw cellulose. Here a correction for hydroxymethylfurfural can be expected. In these determinations the abbreviated distillation method (180 ml.) was applied in all cases. The results of a number of determinations have been collected in Table II.

For the calculation of the pentosan content the previously mentioned formula was used:

$$\frac{7.57 \times N(V_2 - V_1)}{W} \%$$

The pentosan contents calculated by means of this formula are given in the third column of Table II. In the fourth column the pentosan content is shown when the furfural was determined by means of barbituric acid.

In the furfural determination with barbituric acid, the distillate is transferred into a 500-ml. beaker, after which the measuring cylinder is rinsed twice, each time with 10 ml. of 12% hydrochloric acid.

In the meantime 0.75 gram of barbituric acid has been dissolved by heating in 100 ml. of 12% hydrochloric acid; this solution is added to the furfural solution. A yellow color is immediately formed, and after heating to about 60° C. the yellow furfural-barbituric acid double compound is separated. During the first hour, when the liquid is cooling, it is stirred frequently. The next day the liquid is filtered through a Jena glass filter G 3 and the precipitate is washed free of acid by means of a saturated solution originating from an acid-free precipitate of a former determination. After drying 4 hours at 100° C. the precipitate is weighed. The calculation takes place as follows

$$\begin{array}{ccccccc} \text{Furfural} & + & \text{barbituric acid} & \longrightarrow & \text{double compound} & + & H_2O \\ 96 & + & 128 & \longrightarrow & 206 & + & 18 \end{array}$$

When the weight of the double compound amounts to P grams, the quantity of furfural is $96/206 \times P = 0.466\ P$. A small correction is, however, still required because of the solubility of the double compound, which is 1.22 mg. per 100 ml. of 12% hydrochloric acid. The precipitate has been formed in 300 ml. (180 ml. of distillate, 20 ml. with which the measuring cylinder has been rinsed, and 100 ml., in which the barbituric acid has been dissolved). The quantity of furfural becomes

$$\begin{aligned} F &= 0.466\ (P + 3 \times 0.00122) \\ &= 0.466\ (P + 0.0037) \end{aligned}$$

The calculation of the pentosan content from the quantity of furfural found takes place by means of an empirical factor. The theoretical factor—i.e., the ratio of the molecular weights of xylans and furfural—132/96 = 1.38, was found to be too low. According to Kröber 1.56, according to Schmidt (*3*) 1.58 must be taken. This means that the furfural yield is $1.38/1.58 \times 100 = 87.5\%$ of the theoretical one. This is also mentioned in the TAPPI standard. The quantity of pentosans *then becomes*

$$1.58 \times 0.466\ (P + 0.0037) = 0.735\ (P + 0.0037)$$

When W grams of dry cellulose are used, the pentosans-content becomes:

$$\frac{0.735\ (P + 0.0037) \times 100}{W} \%$$

Table II shows that the bromate titration always gives too high a value, which points to the presence of hydroxymethylfurfural. On an average this value is 0.6%, so that we shall have to correct our formula by this amount. Thus, the pentosan content in cellulose becomes

$$\frac{7.57 \times N(V_2 - V_1)}{W} - 0.6\%$$

Table II. Furfural Determination with Potassium Bromate and Barbituric Acid

Sample	Quantity of Substance, G.	Pentosan Content, % Using $KBrO_3$	Pentosan Content, % Using barbituric acid	Difference
K 97	1.5	11.3	10.8	0.5
K 119	0.6	21.6	21.3	0.3
K 66	1.0	18.7	18.1	0.6
K 121	1.0	24.0	23.4	0.6
K 122	1.0	25.6	25.2	0.4
K 123	1.0	25.4		
K 123	0.6	25.4	24.4	1.0
K 124 A	0.6	26.1	25.4	0.7
K 124 A	1.0	26.2		0.8
K 124 B	0.6	25.0	24.6	0.4
K 126 A	1.0	26.6		
K 126 A	0.6	26.6	25.9	0.7
α cake K 126 A	1.2	7.1	6.5	0.6
K 126	0.8	27.0	26.4	0.6
α cake K 126 B	1.0	8.5	7.9	0.6

Table I showed that for xylose the same pentosan content is found when the TAPPI distillation (300 ml.) or the abbreviated method (180 ml.) is applied—viz., in both cases 100%. Table III gives the pentosan content of some samples of straw cellulose, determined according to three methods—viz., TAPPI (calculated with the TAPPI formula), the shortened method (calculated with the author's formula), and the shortened method in which the pentosans are determined by means of barbituric acid. From the results obtained (Table III) it follows that with the shortened distillation method the furfural has distilled over quantitatively just as when the TAPPI method is applied.

Table III. Pentosan Content in Cellulose Samples

	Straw Cellulose 97	Straw Cellulose 119	Straw Cellulose 66
Author's formula, %	10.7	21.0	18.1
Using barbituric acid, %	10.8	21.3	18.1
TAPPI formula, %	10.8	21.2	18.4

Some check experiments were performed to prove the correctness of the abbreviated method and to demonstrate the essential difference between this method and the TAPPI method. In the first experiment, after 180 ml. had distilled off according to the shortened method, 210 ml. of 12% hydrochloric acid were added again and distilled (without supplying fresh 12% hydrochloric acid during distillation). This second distillate (180 ml.) was divided into two parts, one part was used for the furfural deter-

Table IV. Continued Distillation without Supplying Fresh 12% Hydrochloric Acid during Distillation

Sample	Pentosans, % First 180 ml.	Second 180 Ml. Bromide-bromate	Second 180 Ml. Barbituric acid
146	27.5	0.3	No precipitate
151	25.8	0.3	No precipitate
154	17.5	0.2	No precipitate
158	10.8	0.1	No precipitate
174	27.5	0.3	No precipitate
175	28.5	0.3	No precipitate

mination with bromide-bromate, the other for that with barbituric acid. In all cases there was no flocculation at all with barbituric acid, thus, no more furfural distills over after the first 180 ml. With bromide-bromate a slight amount of oxidizable materials was found (Table IV); this result was expected because of the continued decomposition of the cellulose when boiled for a second time.

The same amounts of oxidizable materials, which do not precipitate with barbituric acid, are found when, after 300 ml. according to the TAPPI method have distilled over, the distillation is continued and the following 180 ml. are collected.

	% Pentosans, TAPPI Method In 300 ml.	In following 180 ml.
Sample 174	27.5	0.3

Applying the TAPPI distillation method the 300 ml. of distillate were divided into the first 180 ml. and the following 120 ml. In both fractions the furfural was determined by means of bromide-bromate. For the calculation of pentosans the correction term 1.0 was divided into $\frac{180}{300} \times 1.0 = 0.6$ for the first 180 ml. and $\frac{120}{300} \times 1.0 = 0.4$ for the second (120 ml.) fraction.

The results were:

Sample 174	In 180 ml.	26.2 % Pentosans
	In 120 ml.	1.25% Pentosans
Total	In 300 ml.	27.45% Pentosans

It follows from these figures that, when distilling according to TAPPI, the furfural is not distilled over quantitatively with 180 ml., but that 300 ml. are necessary.

But by applying the shortened method, 180 ml. are sufficient for quantitative distillation of the furfural. The essential difference between the TAPPI method and the shortened method is not the volume of distillate, but the fact that in the abbreviated method the distilling proceeds without supplying fresh 12% hydrochloric acid, so that the hydrochloric acid concentration and the temperature increase during distillation. Because of this, less time or less distillate is required to distill the furfural quantitatively. Continued distillation gives in both cases a little amount of oxidizable materials but no additional furfural. Thus the conclusion is justified, that when distilling 180 ml. without supplying fresh 12% hydrochloric acid during distillation, the furfural is distilled over quantitatively.

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Volumetric Determination of Nitrate Ion

By Reduction with Chromous Ion

JAMES J. LINGANE AND ROBERT L. PECSOK
Harvard University, Cambridge 38, Mass.

A method is described for the determination of nitrate ion based on reduction to ammonium ion by chromous ion in dilute sulfuric acid solution. With amounts of nitrate ion of the order of 20 to 50 mg. the method is precise and accurate to ±0.2%, and the accuracy is about ±2% with 2 to 5 mg. of nitrate ion. Large amounts of chloride do not interfere. Nitrite ion undergoes the same reduction.

OF THE various volumetric methods that have been proposed for the determination of nitrate ion the best known is that of Devarda (*3*), based on reduction to ammonia in strongly alkaline solution by an aluminum-zinc-copper alloy.

$$3NO_3^- + 8Al + 5OH^- + 2H_2O = 3NH_3 + 8AlO_2^-$$

The ammonia is distilled and finally determined by acidimetric titration. As improved by Arndt (*1*), who recommended a copper-magnesium alloy and reduction and distillation from saturated magnesium hydroxide solution, this is probably the most reliable of existing methods.

Knecht and Hibbert (*4*) described a distillation method based on reduction of nitrate ion to ammonia by titanous hydroxide in strongly alkaline solution.

Methods based on acidimetric titration of the ammonia produced by electrolytic reduction of nitrate ion at a copper cathode have been described by Vortmann (*12*), Böttger (*2*), and Szebelledy and Schall (*10*).

Szebelledy (*9*) developed a more or less empirical method involving direct titration in concentrated sulfuric acid with ferrous ion. The nitrate ion undergoes a 2-electron reduction to nitrosyl sulfuric acid,

$$2Fe^{++} + NO_3^- + 3H^+ + H_2SO_4 = 2Fe^{+++} + HSO_5NO_2 + 2H_2O$$

and the end point is indicated by the red compound formed between the nitrosyl sulfuric acid and the first excess of ferrous ion.

The method of Kolthoff, Sandell, and Moskovitz (*6*) utilizes the fact that nitrate ion is reduced quantitatively to nitric oxide by ferrous ion in hot hydrochloric acid medium.

$$3Fe^{++} + NO_3^- + 4H^+ = 3Fe^{+++} + NO + 2H_2O$$

A measured excess of standard ferrous solution is added to the nitrate solution in 10 N hydrochloric acid, ammonium molybdate is added as a catalyst, the reaction is driven to completion by boiling, and the excess ferrous ion is finally back-titrated with standard dichromate solution using diphenylamine sulfonate as indicator. All operations must be conducted with exclusion of atmospheric oxygen, and the titer of the ferrous solution is determined in a blank experiment.

Wellings (*13*) employed titanous chloride to reduce nitrate ion to nitric oxide in nearly neutral solution, according to

$$3Ti^{+++} + NO_3^- + 4H_2O = 3TiO_2 + NO + 8H^+$$

The titration is performed in a boiling solution with alizarin indicator, which is adsorbed on the precipitated hydrous titanic oxide and undergoes a color change from red to grayish green at the end point.

In a study of the reducing properties of chromous ion, Traube and Passarge (*11*) found that in acidic solutions nitrates were reduced to ammonium ion, but could not obtain quantitative results. They stated that the reduction is quantitative to ammonia in alkaline solution, and described an analytical method based on subsequent distillation of the ammonia with results about 2% lower than the theoretical. The same method is applicable to hydroxylamine. They reported that nitrite ion is not reduced to ammonia by chromous ion in either acidic or basic media.

The reduction by chromous ion was later studied by Wiercinski (*14*), who concluded that in a solution containing about 0.2 N sulfuric acid at 60° C., and with an excess of chromous ion, the reduction proceeds according to

$$6\ Cr^{++} + NO_3^- + 8\ H^+ = 6\ Cr^{+++} + NH_3OH^+ + 2\ H_2O$$

The present paper describes an investigation of the reduction of nitrate ion by chromous ion under various conditions, which has led to new methods for the determination of nitrate. Contrary to Wiercinski's conclusion, the authors found that reduction under these conditions does not stop at hydroxylamine but proceeds quantitatively to ammonium ion.

$$8Cr^{++} + NO_3^- + 10H^+ = 8Cr^{+++} + NH_4^+ + 3H_2O$$

Practically complete reduction to ammonia is also obtained in alkaline solutions, provided tartrate ion is present to prevent precipitation of chromous and chromic ions. Nitrite ion is similarly reduced. Because in either acid or alkaline medium the reaction is too slow to permit direct titration, an excess of chromous ion is added and, after time is allowed for complete reduction, the excess is titrated back with standard ferric solution potentiometrically. The ammonia produced can also be determined by distillation and acidimetric titration as in the Devarda method.

EXPERIMENTAL

Standard solutions of chromous sulfate in 0.1 N and 1 N sulfuric acid were prepared determinately as described in a previous paper (*8*).

An approximately 0.1 M solution of titanic sulfate in 4 N sulfuric acid was prepared by air-oxidation of a titanous sulfate solution. This solution was used as a catalyst and its exact concentration need not be known.

Standard solutions of potassium nitrate were prepared determinately from dried samples of the pure salt.

The ferric ion solution used for back-titrations was prepared from ferric alum and standardized by potentiometric titration with standard chromous solution under the conditions extant in the nitrate determination.

Titrations were performed in a closed beaker and air was excluded by purified nitrogen. A magnetic stirrer was employed. A bright platinum wire served as indicator electrode, and its potential was measured against a saturated calomel electrode in the usual manner.

RESULTS AND DISCUSSION

Reduction in Alkaline Medium. The complete reduction of nitrate ion to ammonia by Cr(II) in alkaline medium was first established by the distillation method. Tartrate was added to complex chromic and chromous ions to prevent their precipitation. The potential of the couple involving the tartrate complexes of chromic and chromous ions in alkaline medium is considerably more negative (more reducing) than the half reaction involving the simple ions, which favors complete reduction of nitrate ion.

Known volumes (usually 10 ml.) of 0.0400 M potassium nitrate solution were added to 50 ml. of the alkaline tartrate solution in a Kjeldahl flask, air was removed with nitrogen, and an excess of chromous sulfate solution was added. The ammonia was then distilled in the usual way into an excess of standard acid and back-titration was made with carbonate-free sodium hydroxide using methyl red indicator. The correctness of the methyl red end point was verified by titration curves obtained with the glass electrode. Blank determinations were run and proper corrections were applied.

Systematic experiments showed that a large concentration of sodium tartrate (1.5 M) and a relatively small concentration of sodium hydroxide (0.2 M) led to best results. Under these conditions the amount of ammonia produced was uniformly 99.0 ± 0.3% of the theoretical. Varying the amount of excess chromous sulfate from 15 to 50% had no effect, and the results were also independent of the time of standing before distillation between 1 minute and 1 hour. When the concentration of tartrate ion is so small, or the concentration of sodium hydroxide so large, that precipitation of chromous hydroxide occurs, the reduction is incomplete.

The fact that even under optimum conditions the amount of ammonia produced is 1% less than the theoretical indicates that there is some formation of intermediate nitrogen compounds that are either not reducible by chromous ion, or are gaseous and escape from the solution. Likely gaseous intermediates are nitrous oxide and elemental nitrogen. Because the transient formation of small amounts of hydroxylamine and/or hydrazine is also probable, special experiments were made to determine whether these substances are reduced by chromous ion in an alkaline tartrate medium. It was found that hydrazine is not reducible at all, and the reduction of hydroxylamine was only 97% complete under the optimum conditions mentioned above. The incomplete reduction of hydroxylamine is doubtless due to its partial disproportionation into nonreducible hydrazine and nitrogen in alkaline solution. Thus, the small negative error in the nitrate reduction is understandable if appreciable amounts of either hydrazine or hydroxylamine are formed transiently.

Experiments were then made under the above optimum conditions in which the amount of chromous ion consumed was determined by potentiometric back-titration of the excess with ferric ion. As the titration with ferric ion cannot be performed in alkaline medium, the solution was acidified with air-free sulfuric acid before the back-titration. The ferric solution was also freed from dissolved air with nitrogen. The excess chromous sulfate used varied from 12 to 25%, and the time of standing at room temperature between the addition of the chromous solution and acidification was 3 to 5 minutes. The amount of chromous ion consumed was reproducibly 101.0 to 101.5% of the theoretical. The positive error in this method may be attributed to a small amount of extraneous oxidation of chromous ion.

The results of amperometric titrations were in agreement with the distillation—i.e., they confirmed the fact that the reduction is about 99% complete. Inasmuch as neither nitrate ion nor chromic ion gives a polarographic wave in alkaline tartrate solution, and chromous ion gives an anodic wave, the diffusion current remains practically zero during the titration and increases negatively after the equivalence point.

The dropping mercury electrode was maintained at −0.4 volt versus the saturated calomel electrode, and measurements were made according to the usual technique (*5*). In separate experiments it was shown that the diffusion current of chromous ion

remains proportional to concentration up to an amount corresponding to a 15% excess in the titration.

Under conditions similar to those used in the distillation method, the error was consistently negative, averaging about −1%.

The reduction of nitrite by chromous ion under the same conditions and followed by distillation and the determination of the ammonia yielded results also about 1% low.

Reduction in Acid Medium. A 25-ml. sample of 0.04000 *M* potassium nitrate solution was placed in a Kjeldahl flask, heated to 70° C., and freed from dissolved air with nitrogen. An excess of 0.25 *M* chromous sulfate solution in 1 *N* sulfuric acid was then added. After 5 minutes standing, an excess of sodium tartrate–sodium hydroxide solution was added, and the ammonia was distilled and titrated. In three experiments with 10, 20, and 35% excess chromous sulfate solution the amount of ammonia found was 100.1, 100.1, and 100.2% of the theoretical. The reduction is thus stoichiometrically exact.

Attempts were made to titrate nitrate ion directly with chromous ion in acid medium by the potentiometric technique, but the reaction was much too slow to be feasible.

After many preliminary experiments the following procedure based on addition of excess chromous ion and back-titration with ferric ion was adopted.

A 25-ml. sample of the nitrate solution was placed in the titration beaker, heated to about 70°, and freed from air with nitrogen. An excess of chromous sulfate solution in 0.1 *N* sulfuric acid was then added. After 5 minutes, 25 ml. of air-free ferric solution (an excess) were pipetted into the solution, a platinum indicator electrode was introduced, and the titration with chromous ion was completed. The ferric solution was standardized against the chromous solution in blank experiments. The difference between the volumes of chromous solution in the actual determinations and the blank corresponds to the nitrate ion reduced.

Figure 1 shows the results obtained by this procedure using 25-ml. portions of 0.04000 *M* potassium nitrate, 0.2 *M* ferric alum solution, and various excesses of 0.2500 *M* chromous sulfate. Points indicated by circles were obtained with solutions containing approximately 0.1 *N* sulfuric acid, and the points indicated by crosses were obtained with solutions 2 *N* in sulfuric acid. With 0.1 *N* sulfuric acid and 7 to 60% excess chromous ion the average precision and accuracy are both about ±0.5%.

The high values obtained with a larger excess of chromous ion probably reflect a significant amount of reduction of chromous ion by hydrogen ion, and the low results when only a small excess of chromous solution was used appear to be due to incomplete reduction during the 5-minute reduction interval used. The use of 2 *N* sulfuric acid requires a larger excess of chromous ion than 0.1 *N* acid, apparently because of a slower reduction rate with increasing hydrogen ion concentration.

With more dilute potassium nitrate (0.01 *M*) and chromous sulfate solutions (0.1 *M*) the amount of chromous ion consumed was even more dependent on the amount of chromous solution added in excess.

Final Procedure with Titanic Ion as Catalyst. It seemed likely from the foregoing experiments that the slowest step in the nitrate chromous ion reaction is the initial reaction of nitrate and chromous ions, and that subsequent stages of the reduction probably proceeded rapidly. Because the rate of reduction of nitrate ion to nitric oxide by titanous ion is much greater than the reduction rate with chromous ion, and titanic ion is reduced very rapidly by chromous ion (*7*), it was expected that titanic (or titanous) ion should act as a catalyst in the nitrate-chromous reaction. This was found to be true. In the presence of a relatively small amount of titanium the nitrate-chromous reaction proceeds so much faster that a lower temperature (50°) may be used, which very greatly minimizes the oxidation of chromous ion by hydrogen ion, and excellent results are obtained independent of the amount of excess chromous ion used between 10 and 100%.

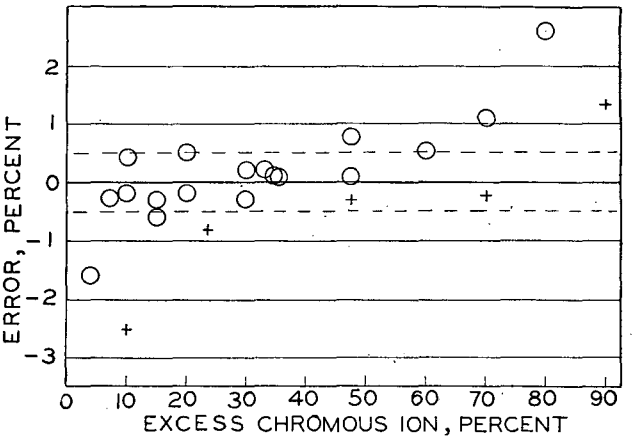

Figure 1. Determination of Nitrate Ion

The titanium catalyst is added as titanic ion. As the titanous ion formed is reoxidized by the ferric ion added later, and the final potentiometric titration with chromous ion is stopped at the completion of the reduction of the ferric ion without reducing titanic ion, the amount of titanic sulfate solution used need not be known accurately and no correction for it is required.

Add about 5 ml. of approximately 0.1 *M* titanic sulfate solution to a 25-ml. sample of the 0.01 to 0.02 *M* nitrate solution in the titration vessel, and adjust the acidity to between 0.5 and 1 *N* in sulfuric acid. Heat to 50° ± 3° C. and remove dissolved air with nitrogen or carbon dioxide. Add rapidly from a buret a 10 to 100% excess of 0.1 *M* chromous sulfate solution in 0.1 to 1 *N* sulfuric acid. After 3 to 5 minutes (not longer) add a measured excess of air-free, 0.1 *M* ferric alum solution. Insert a platinum indicator electrode and titrate the excess ferric ion with the chromous solution to an equivalence point potential of +0.10 volt against the saturated calomel electrode.

Run a blank experiment with the same volume of ferric alum solution used above. Subtract this blank from the total volume of chromous solution to obtain the volume equivalent to the nitrate ion.

Results obtained in eleven titrations by this procedure, with 10 to 100% excess chromous ion, ranged from 99.9 to 100.3% of the theoretical. The average was 100.1% and the average deviation was ±0.13%.

The procedure described above for 0.01 *M* nitrate solutions applied to 0.001 *M* solutions requires a considerably larger excess of chromous ion, approximately 200%, and a 10-minute reduction period. Because the result is calculated in terms of the difference of two larger quantities, less precise results are obtained. Several titrations of 25 ml. of 0.00125 *M* potassium nitrate (3.090 mg.) yielded results about 98% of the theoretical.

The titration of ferric ion with chromous ion in the presence of titanic ion has been described in detail (*7*). The potential is established quickly, and the break at the equivalence point is so large that the end point may be taken at any potential between +0.2 and 0 volt versus the saturated calomel electrode. A complete determination requires only about 20 minutes, from the time the sample is pipetted into the titration vessel until the final titration is completed.

The ferric alum solution must be free from dissolved oxygen before it is added to the reaction mixture.

The volume of 0.1 *M* titanic sulfate solution used is not critical, and identical results are obtained with 3 to 7 ml. Because titanic ion is very rapidly reduced by chromous ion, and titanous ion reduces nitrate ion only to nitric oxide, the volume of chromous solution added initially obviously must be in excess of that required to reduce both the nitrate and titanic ions.

Chloride ion, added as sodium chloride, in a 400 to 1 excess over nitrate ion has no significant effect.

Nitrite ion also undergoes complete reduction to ammonium ion in the above procedure. However, the method is not suitable

for the determination of nitrite, because in the warm acid medium used the nitrous acid disproportionates rapidly into nitrate ion and nitric oxide and it is difficult to prevent the escape of the latter from the solution. The reaction between nitrous acid and ammonium ion to produce elemental nitrogen is another prohibitive factor.

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Microdetermination of Sulfur in Organic Compounds

A Simplified Gravimetric Method

G. L. STRAGAND AND H. W. SAFFORD
The University of Pittsburgh, Pittsburgh, Pa.

A modified gravimetric method has been devised by which the sulfur content in organic compounds may be determined quantitatively on a micro scale. Nitrogen and the halogens (except fluorine) do not interfere. The sample is burned in an atmosphere of oxygen using a platinum catalyst; the sulfur trioxide formed is absorbed by a silver gauze with the quantitative formation of silver sulfate. When halogens other than fluorine are present, the silver sulfate is extracted in water and the percentage of sulfur is calculated from the loss in weight of the gauze. In the absence of halogens, the gain in weight of the gauze (as sulfate) may be used to estimate the amount of sulfur. Samples of sulfur content from less than 10 up to 100% (pure sulfur) have been analyzed by this method.

THE conventional quantitative microanalysis of sulfur in organic compounds is considered essentially to be the conversion of "organic" sulfur to the sulfate ion. Wet and dry combustion methods are employed in carrying out this oxidation and the final sulfate estimation may be volumetric or gravimetric (*11*, *13*). Although the well-known Carius determination has many staunch supporters, the time consumed in this and most other gravimetric microprocedures has prompted many investigators to propose modified titrimetric methods of sulfur analysis (*1*, *3*, *6*, *12*, *15*, *17*).

No existing procedure seemed to be without one or more attendant difficulties or objections. The requirements for speed, simplicity, and accuracy that are to be found in a modern microanalytical service laboratory led to the search for fundamental reactions upon which might be based a new or improved method incorporating these and other advantages.

The combustion of the sulfur in an organic compound at atmospheric pressure and in the presence of oxygen yields for the most part sulfur dioxide and sulfur trioxide, the relative amounts of which depend largely upon temperature, the amount of oxygen present, and the presence or absence of a catalyst. Uhl (*16*) has indicated that metallic silver heated in a stream of sulfur dioxide forms silver sulfate and silver sulfide, together with small amounts of sulfur trioxide. Dennstedt (*5*) was perhaps the first to employ silver to retain sulfur trioxide quantitatively in his elemental organic analyses.

Kirner (*8*) almost 40 years later recognized the importance of Dennstedt's pioneering work, and proposed the silver–sulfur trioxide reaction as the basis for a quantitative determination of sulfur. Huffman (*7*) applied the suggestions of Kirner by establishing a method for the determination of sulfur in which the oxides of sulfur formed during a combustion reaction with metallic silver, yielded silver sulfate quantitatively; the electrodeposition of silver from the silver sulfate so formed, followed by conversion of the weight of silver to sulfur by the appropriate factor, completes the analysis. Compounds containing halogen cannot be analyzed for sulfur by this method and inherent errors necessitate the application of a correction factor in calculating the amount of silver deposited.

Belcher and Spooner (*2*) adapted their procedure for the ultimate analysis of coal to the microanalysis of organic compounds. The simultaneous determination of carbon, hydrogen, and sulfur is effected by combustion at 800° C. with an oxygen flow of 50 ml. per minute in a tube containing no catalyst or oxidant other than oxygen itself. A flowmeter is required to measure the fast rate of oxygen flow and a transparent silica combustion tube is employed to withstand the minimum temperature designated. These authors indicate that sulfur is quantitatively absorbed and retained as silver sulfate by a roll of silver gauze inserted near the exit end of the combustion tube. The silver sulfate is extracted with boiling water and the loss in weight of the silver multiplied by the appropriate factor gives the percentage of sulfur. Considerable experimentation is necessary to position the gauze properly in the combustion tube. Moreover, with samples that are too large or high in sulfur content, an empirical factor is necessary in

converting the weight of silver sulfate into a corresponding weight of sulfur.

The authors have attempted to duplicate the experiments of Belcher and Spooner, but with only moderate success. With compounds of relatively simple structure, precision is difficult to attain, and for samples containing large amounts of sulfur, the same low results of these authors were noted. Furthermore, with liquids and solids of low melting points, difficulty was encountered in ensuring complete combustion at the fast rates of flow used. The lack of consistent accuracy and precision possibly may be attributed to the high speed of the oxygen, to the high temperature which is well above that which favors the maximum formation of sulfur trioxide, and to the absence of a platinum catalyst which would ensure complete conversion of sulfur dioxide to sulfur trioxide.

It was felt, however, that the method as developed by Belcher and Spooner held promise, and with some modification could be made to yield satisfactory results for all types of organic compounds and for a sample of any sulfur content. Moreover, it was believed that greater applicability would result from the exclusive use of conventional microequipment.

APPARATUS

The essential features of the simplified apparatus are shown in Figure 1.

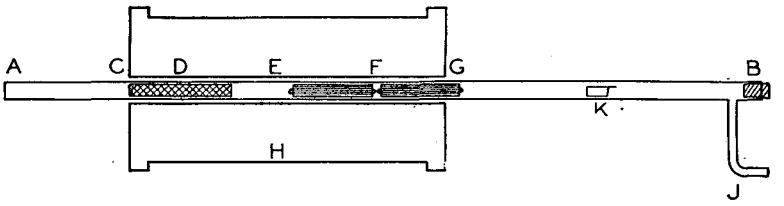

Figure 1. Combustion Apparatus

Commercial tank oxygen is passed directly into a standard A.C.S. pressure regulator (*14*), filled with saturated sodium carbonate, thence through a drying tube filled with anhydrous magnesium perchlorate, and finally into a bubble counter containing 5% sodium hydroxide (these items of equipment are not shown), before entering the side arm, *J*. The standard Pyrex microcombustion tube, *AB*, of A.C.S. specifications is modified by cutting off the conventional reduced end at *A*, so that the entrance and exit ends have the same internal diameter. After this operation the over-all tube length is about 48 cm. Entrance end *B* is closed with a stopper except during introduction of platinum boat *K* containing the sample. Exit end *A* remains open to the atmosphere. The rate of oxygen flow is established by attaching a Mariotte bottle at *A* and adjusting the pressure regulator until a velocity of 5 to 10 ml. per minute is attained. After the desired rate is established, the Mariotte bottle is permanently disconnected and the rate of flow is checked periodically by observing the bubble counter.

Microfurnace *H* may be of any standard type and should be electrically heated, as there is scarcely any justification for using gas long burners in the modern laboratory. In this investigation a Fisher microcombustion furnace of 20-cm. over-all length was employed. Distance *GB* is also 20 cm., so that 8 cm. of tube protrude from the exit end of the furnace. This last distance, *AC*, is not critical except that its shortness will minimize possible loss from abrasion when the silver gauze at *D* is introduced and removed. This absorbent is so prepared from 20-mesh silver gauze (American Platinum Works, Newark, N. J.) (whose frayed or cut edges have been folded in) that a roll from 6 to 7 cm. long is produced. For the standard microcombustion tube, from three to four turns of gauze will be required to produce a compact roll whose weight will be approximately 5 to 6 grams. The roll should fit the tube with moderate snugness but not so tightly that it cannot be removed easily with a platinum wire hook. One end of this gauze should be flush with the exit end of the furnace as shown. The two six-finned platinum contacts at *EFG* are the usual A.C.S. micro "stars" and are so placed end to end that one end of contact *FG* protrudes about 1 cm. from the entrance end of the furnace.

Before use, a new silver gauze roll should be dipped very briefly in dilute nitric acid to remove any possible sulfide or other coating, washed thoroughly with distilled water, and then successively with alcohol and ether. The roll should then be placed in the furnace as noted above, and actual operating conditions of temperature and oxygen flow noted under Procedure should be established. After 10 minutes under these conditions, the silver roll should be withdrawn, cooled, and weighed. This procedure of heating and cooling is continued until constant weight (±10 micrograms) of the roll is established.

A probing thermocouple was used initially to learn the various temperatures existing within the furnace for a given input. As a result of the study, a normal combustion temperature of 650° C. is maintained at *E*, the center and hottest zone of the furnace. Many authors quote and practice the findings of Knietsch (*9*), who observed that at 400° C. there is approximately quantitative conversion of sulfur dioxide to trioxide in the presence of oxygen and a platinum catalyst. However, Yost and Russell (*18*) indicate that the optimum temperature with respect both to rate of reaction and yield is about 665° C. Thus, a close approach to this temperature is attained when the maximum temperature of the furnace is fixed at 650° C. Furthermore, the large temperature differential that exists between *E* and *G* ensures that at some point along the platinum contacts a correct temperature will be found for the catalytic "cracking" of each sample. Because of this differential in the Fisher furnace, the temperature at the center of silver gauze *D* is approximately 450° C. Huffman (*7*) found that quantitative formation of silver sulfate takes place at temperatures as low as 350° C., but that the silver becomes more active as the temperature increases and a good result still can be obtained at 550° C. It appears that wide variations in temperature are permissible, provided only that the maximum operating temperature is adequate to ensure complete combustion of all types of samples, and that the melting point of the silver gauze is not exceeded.

PROCEDURE

Preparative and manipulative procedures for an analysis are conventional.

The furnace is brought to a temperature of 650° C. and the clean, dry, silver gauze roll is weighed and positioned inside the combustion tube as indicated above. A sample of from 3 to 5 mg. is introduced in a platinum boat, the stopper at *B* is replaced, and the flow rate of oxygen is adjusted to, say, 6 to 8 ml. per minute.

Combustion is carried out with a gas short burner, exercising the usual precautions. The rate at which the sample is vaporized and burned depends largely upon the structure of the compound analyzed and upon the flow rate of oxygen, but 15 minutes represent an average required time at the indicated oxygen velocity. The familiar reburning operation in many instances may be unnecessary, but is strongly recommended as part of a standard procedure. In any case, a brief flushing-out period should follow combustion to permit all pyrolysis products to pass the silver gauze.

When the combustion is complete, the silver gauze is transferred to a cooling block for 10 minutes, and then weighed. The gain in weight noted here (in the absence of halogens) is due to sulfate formation; multiplying this weight increase by the factor 0.3337 gives the weight of sulfur in the sample analyzed.

When chlorine, bromine, and iodine are present, the original weighing of the clean silver gauze may be omitted. In this case, following the combustion, the gauze roll is removed from the tube, and is cooled and weighed as before. It is then placed in a beaker and covered by boiling distilled water for approximately 5 minutes (longer boiling does no harm) to dissolve and remove the silver sulfate formed during the combustion. The solubilities of the silver halides (except silver fluoride) are so small that these compounds will not be extracted. The gauze is removed, washed thoroughly with distilled water and successively with alcohol and ether, then carefully dried directly in a standard microregenerating or drying block, and weighed after cooling. The loss in weight of the silver roll after these operations represents the weight of silver sulfate formed during the analysis; multiplication by the factor 0.1028 gives the weight of sulfur in the material under analysis.

Because of the low melting points of the silver halides and the possibility of their volatilization from the silver roll during subsequent combustions, it is well to rid the roll of these compounds if samples containing halogens, as well as sulfur, have been analyzed. This is particularly true when the next sample to be burned con-

tains no halogens, and the direct weighing procedure without water extraction is to be used. Because in this latter procedure the gauze roll is weighed before and after combustion, any halide volatilization during combustion would introduce an obvious error.

The usual solvents for silver halides are effective.

To remove silver chloride and relatively small amounts of silver bromide, the gauze roll is immersed in hot 10% ammonia water for approximately 5 minutes; for larger quantities of silver bromide and for silver iodide a hot 10% solution of sodium thiosulfate is used. In all cases, these solvents and the reaction products are then removed from the silver by thorough washing with hot distilled water, alcohol, and ether as described previously. Where a large number of sulfur-containing compounds, with and without halogens, are to be analyzed, it may be well to follow the water extraction procedure exclusively. Because here all weighings follow combustion, volatilization losses during combustion are of no concern, and only occasionally may it be necessary to rid the silver gauze of accumulated halides that might interfere with silver sulfate formation.

DISCUSSION

Table I presents the results of the analyses of various known compounds, together with determinations on research materials. The data indicate that the accuracy and precision of the method are satisfactory for the determination of sulfur in a variety of substances without interference from the other elements shown. Although no compound containing both fluorine and sulfur has been analyzed as yet by the authors, interference from fluorine is to be anticipated because of the solubility of silver fluoride which would be formed during a combustion. This compound would be extracted along with silver sulfate when the silver gauze was placed in boiling water.

Table I. Analysis of Organic Sulfur Compounds

Sample	Elements Present (Other Than Sulfur)	Per Cent Sulfur Theory	Found	Average deviation from theory
3-B	C H O	13.92	13.80	0.12
6-B	C H O	14.29	14.34	0.05
R-353	C H O	15.11	14.92, 14.98	0.16
5-B	C H O	16.34	16.38	0.04
n-Butylsulfone	C H O	17.98	18.12, 18.08	0.12
Sulfonal	C H O	28.08	27.93, 28.07	0.08
B-IV-7B-12	C H N	11.93	12.00, 12.07	0.11
B-V-2-6	C H N	18.20	18.20, 18.27	0.04
Allyl thiourea	C H N	27.60	27.58, 27.73	0.06
Thiourea	C H N	42.12	42.06	0.06
2-Bromothiophene	C H Br	19.66	19.57, 19.58	0.08
2-Iodothiophene	C H I	15.26	15.31	0.05
H-77	C H O N	10.46	10.32	0.14
R-356	C H O N	12.46	12.52, 12.40	0.00
H-46	C H O N	12.91	12.92, 12.89	0.00
R-354	C H O N	13.19	13.13, 13.20	0.02
M-53	C H O N	13.87	13.88	0.01
R-357	C H O N	13.99	14.06, 13.92	0.00
S-II	C H O N	14.64	14.67, 14.59	0.01
Sulfanilic acid	C H O N	18.51	18.54, 18.51	0.02
l-Cystine	C H O N	26.68	26.63, 26.77	0.02
R-355	C H N Cl	12.16	12.02	0.14
B-IV-48-3	C H N Cl	13.20	13.14, 13.22	0.02
M-51	C H O Cl	15.52	15.38	0.14

Table II. Comparison of Direct Weighing and Extraction Procedures

Sample	Per Cent Sulfur Theory	Found (as SO_4^{--})[a]	Found (as Ag_2SO_4)[b]
l-Cystine	26.68	26.62	26.63
Sulfonal	28.08	27.97	27.93
		28.14	28.07
Allyl thiourea	27.60	27.51	27.58
		27.68	27.73
n-Butylsulfone	17.98	17.99	18.12
		17.88	18.08
H-77	10.46	10.32	10.32

[a] Gain in weight of silver gauze through SO_4^{--} (Ag_2SO_4) formation.
[b] Loss in weight of silver gauze through Ag_2SO_4 water extraction

The gain in weight of a clean silver gauze roll during a combustion may be used to compute sulfur content directly when the halogens are absent. Such a procedure obviates the need for the hot water extraction, washing, and drying of the gauze before weighing. As a check on the validity of this method, a number of halogen-free compounds were analyzed and their sulfur contents calculated both from the gain in weight of the silver through sulfate formation, and from the loss in weight of the silver through subsequent silver sulfate extraction. The satisfactory agreement between values obtained by the two procedures is shown in Table II.

To date, frequent blank determinations have not been found necessary. Apparently the tank oxygen used (Air Reduction Company) does not contain impurities in an amount sufficient to cause a noticeable error in the sulfur determination. It would be well to make a blank run each time a new tank of oxygen is used for the first time. Further, preliminary blank determinations, later abandoned, indicated no appreciable loss of silver metal in the washing procedure in which silver sulfate is extracted by boiling water from the silver gauze roll.

Clark and Stillson (*4*) recently presented a critical analysis of important factors to be considered in the microdetermination of carbon and hydrogen. As a result of their observations, they stress the importance of proper combustion time and combustion tube filling in ensuring the satisfactory pyrolysis of a wide variety of types and structures of organic substances. They recommend the use of platinum gauze as an aid to complete combustion, and indicate that from 7 to 15 minutes may be required for the vaporization of a sample, depending upon the type of material analyzed. Results in this laboratory for the pyrolysis of sulfur compounds agree completely with the report of these authors. It was found that any attempt to save time and effort through the use of an unpacked combustion tube, rapid flow rate of oxygen, and shortened combustion time resulted in a material sacrifice of accuracy. No data are available to indicate how many determinations may be made before a given silver gauze roll must be replaced. Of the rolls employed by the authors, one used for over 50 determinations still gives satisfactory results.

SILVER-OXYGEN-SULFUR TRIOXIDE REACTION

It is logical that during the course of this investigation some consideration was given to the reaction mechanism by which silver sulfate is formed quantitatively. Although this phase of the work is not complete, it is believed that the results obtained thus far may be of interest.

Dennstedt (*5*) postulated that, in the presence of oxygen, water (formed during combustion), and a platinum catalyst, the greater part of the sulfur present in an organic compound is converted to sulfuric acid; this acid then reacts with silver to form silver sulfate. To verify or disprove the reaction hypothesis of Dennstedt, the authors burned samples of C.P. sulfur under the procedure conditions outlined above. For these experiments, however, anhydrous oxygen was used to guarantee as completely as possible the absence of water. In a typical determination the recovery of sulfur, calculated from silver sulfate formation, was 100.1%. This result would point to the improbability of sulfuric acid formation and subsequent reaction with silver to form silver sulfate.

Kirner (*8*), in his study of the mechanism of this reaction, considered it more likely that sulfur trioxide reacts directly with silver, forming silver sulfite, which then immediately oxidizes to sulfate.

To test the validity of this suggestion, pure silver sulfite was prepared in this laboratory from silver nitrate and sulfur dioxide. With the microfurnace at its normal operation temperature, a weighed sample of silver sulfite in a platinum boat was placed in the combustion tube at the position normally occupied by the absorbing silver gauze. An immediate darkening in color of the sample was noted upon its introduction to this heated zone of the tube, and no further change in weight was found after 5 minutes

of heating. During this period, however, the silver sulfite lost approximately 33% of its available sulfur dioxide. This observation had been noted previously by Lewis and co-workers (*10*), who reported that silver sulfite evolved only about one third of the theoretical amount of sulfur dioxide, and that the residue could be heated to fusion without further loss of sulfur dioxide. Although this evidence may not be conclusive, the fact that the silver sulfite in the authors' experiment lost weight at the normal temperature and under the operating conditions assumed by the absorbing silver gauze in the outlined method, suggests that it is unlikely that sulfur trioxide can react with silver to yield silver sulfite which is then oxidized to silver sulfate. The latter reaction would require a gain in weight on the part of silver sulfite.

Further experiments relating to the thermal stability of silver sulfite and its reaction products at various temperatures, and to the mode of formation of silver sulfate are now being carried out. It is too early to suggest a possible reaction mechanism until sufficient supporting evidence has been obtained.

CONCLUSION

A micromethod for the determination of sulfur in organic compounds is reported. A dry combustion, catalyzed by platinum, is carried out, during which the sulfur trioxide formed reacts with silver to form silver sulfate quantitatively. Results on samples varying widely in sulfur content can be reproduced with an average absolute precision of 0.04%; average accuracy as indicated by absolute deviation from theory is 0.06%.

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Colorimetric Determination of Copper in Water

PHILIP W. WEST AND MARIA COMPERE, *Louisiana State University, Baton Rouge, La.*

Dithio-oxamide, in conjunction with malonic acid, is recommended for the determination of small amounts of copper in water. The malonic acid functions as a conditioning agent, serving both to buffer the system and to sequester interfering ions. The method is rapid and accurate.

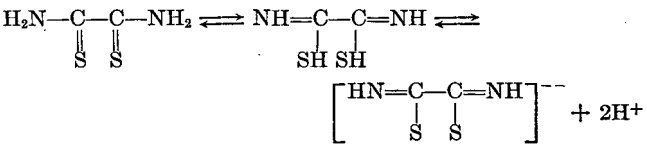
PRESENT methods for the determination of copper in water require tedious separations, either by precipitation or extraction, for the elimination of interfering effects of diverse ions, and often entail concentrating the samples to be analyzed. A rapid procedure, inherently free from interferences and based on a reaction of such sensitivity that concentration of samples becomes unnecessary, uses dithio-oxamide as the primary reagent with malonic acid as a conditioning agent.

Dithio-oxamide was introduced as an analytical reagent by Rây and Rây (*3*) in 1926 but its use has been limited because of interfering reactions which occur in the presence of such common metals as iron, manganese, cobalt, and nickel. Feigl and Kapulitzas (*2*) successfully employed capillary separations for eliminating interferences in spot test analyses and West (*4*) showed that malonic acid can be used as a sequestering agent for the elimination of interfering ions, permitting direct spot test detection of copper. The present investigation was undertaken to extend the latter studies to quantitative applications, particularly in the field of water analysis.

EXPERIMENTAL

Color System. Dithio-oxamide is capable of yielding a discernible color with as little as 0.006 microgram of copper at limiting concentrations of 1 part in 2,500,000. For extremely small concentrations of copper the test color is an olive green; with more concentrated solutions a dark green precipitate is formed which may be so intensely colored that it appears black. Because of the extreme insolubility of the reaction product, even low concentrations of copper yield precipitates. In the present studies use of gum arabic as a stabilizing agent permitted colorimetric estimations by preventing the flocculation of the reaction product.

Because the reagent exists in tautomeric forms,



it was to be expected that pH changes would affect its reactivity. Quantitative studies confirmed this expectation and established conclusively the necessity of employing fixed hydrogen ion concentrations for all quantitative applications of this reagent.

The investigations showed that use of malonic acid can be extended advantageously to quantitative analyses. The malonic acid not only serves to eliminate interferences, but also acts as a buffer. Figure 1 shows the transmittancy characteristics of the color system.

Reagents. A saturated solution of dithio-oxamide was prepared by adding about 1.0 gram of the reagent (Eastman) to 100 ml. of 95% ethanol and warming on a steam bath for 15 minutes. Malonic acid conditioner was prepared by dissolving 100 grams of the C.P. chemical in about 250 ml. of distilled water; 14 grams of C.P. sodium hydroxide were then added, the mixture was diluted to 500 ml., and its pH was checked; the pH of the malonic acid buffer should be 2.5 ± 0.1. A 1.0% aqueous solution of gum arabic, prepared fresh each day, was used. Standard copper solutions were prepared (*1*).

Apparatus. Spectrophotometric studies were made using a

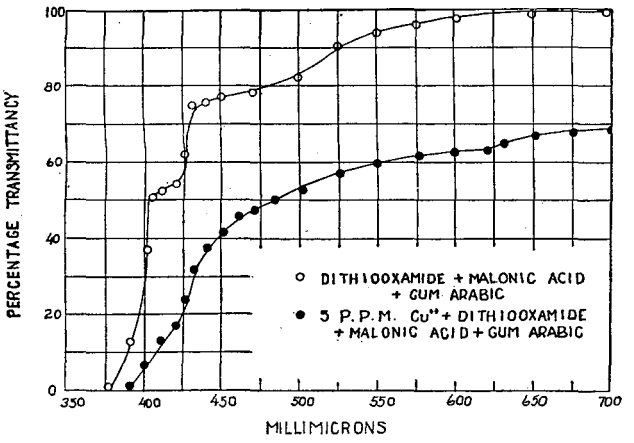


Figure 1. Transmittancy Characteristics of Color System

Beckman Model DU spectrophotometer with 0.998-cm. corex cells. Colorimetric investigations were performed using both visual observations with Nessler tubes and photometric measurements employing an Evelyn filter photometer. All pH determinations were made using a Beckman Model G pH meter.

Procedure. To 50.0 ml. of the sample to be analyzed add 2 ml. of malonic acid, 5 ml. of gum arabic, and 5 ml. of dithiooxamide; mix thoroughly and compare against standards or measure the color intensity photometrically, using a wave length of 620 mμ. Visual estimations of copper concentrations can be made over a range of 0 to 5 p.p.m. with an accuracy of better than 0.5 p.p.m. For very low concentrations it is possible to estimate to 0.1 p.p.m. As the color system has been found to be stable for 1 to 2 months, permanent standards can be used. Photometric estimation of concentration is considerably more accurate than the visual method, and can be extended to much higher concentration ranges. Using a Beckman spectrophotometer, copper can be estimated to 0.01 p.p.m. over a range of 0 to 15 p.p.m.

Table I. Composition of Water Samples Used in Copper Recovery Studies

	Sample I	Sample II	Sample III	Sample IV
Hydrogen-ion concentration, pH	9	8.4	7.0	9.0
Color	5	5	5	5
	P.p.m.	*P.p.m.*	*P.p.m.*	*P.p.m.*
Total solids (dried at 180° C.)	225.0	224.0	181.0	244.0
Total hardness (as $CaCO_3$)	14.1	127.5	52.0	10.2
Silica (SiO_2)	20.5	5.5	48.5	21.8
Iron and aluminum oxides (R_2O_3)	4.5	4.5	4.7	4.0
Alkalies (as Na)	83.0	18.0	30.0	90.0
Calcium (Ca)	4.1	40.2	12.5	0.0
Magnesium (Mg)	0.8	6.4	4.8	2.4
Iron (Fe)	0.3	0.4	0.7	0.2
Manganese (Mn)	0.0	0.0	0.0	0.0
Zinc (Zn)	0.0	0.0	0.0	0.0
Nitrate (NO_3)	6.0	6.0	5.0	0.2
Chloride (Cl)	6.8	18.7	12.2	7.5
Sulfate (SO_4)	12.3	44.8	4.7	9.3
Alkalinity				
Total, as CO_3	100.2	55.8	53.4	111.3
Bicarbonate, as $CaCO_3$	125.0	82.6	89.0	155.5
Carbonate, as $CaCO_3$	42.0	5.2	0.0	30.0
Hydroxide, as $CaCO_3$	0.0	0.0	0.0	0.0

Sample I. Deep well (2400 feet), Standard Oil Co., Baton Rouge
Sample II. Clarified Mississippi River water
Sample III. Shallow well (400 feet), Standard Oil Co., Baton Rouge
Sample IV. Baton Rouge City supply (deep wells)

Table II. Recovery of Copper Added to Waters[a]

Sample No.	Copper Added	Copper Found	Deviation
	P. p. m.	*P. p. m.*	*P. p. m.*
I	0.00	0.00	0.00
	1.00	0.97	−0.03
	3.00	2.99	−0.01
	6.00	6.00	0.00
II	0.00	0.00	0.00
	1.00	0.96	−0.04
	3.00	2.95	−0.05
	6.00	6.06	0.06
III	0.00	0.00	0.00
	1.00	0.97	−0.03
	3.00	2.94	−0.06
	6.00	6.10	0.10
IV	0.00	0.00	0.00
	1.00	1.03	0.03
	3.00	2.90	−0.10
	6.00	6.00	0.00
		Av.	0.03

[a] General composition of waters used is shown in Table I. No copper present in original samples.

Table III. Precision of Measurements

Run No.	Percentage Transmittancy (3.0 P.p.m. Cu) Reading 1	Reading 2	Reading 3	Average
1	80.2	81.0	80.2	80.47
2	80.1	80.0	80.8	80.30
3	79.8	79.6	79.3	79.57
4	80.0	80.2	80.0	80.07
5	80.3	80.0	80.3	80.20
6	80.0	79.4	79.2	79.53
7	79.5	79.6	79.8	79.63
8	79.8	79.8	79.6	79.73
9	79.7	79.5	79.6	79.60
10	79.5	79.2	79.8	79.50
			Av.	79.50
			σ_i =	0.39
			σ_{mean} =	0.13
			Probable error, i =	0.26
			Probable error of average =	0.09
	Percentage Transmittancy (0.5 P.p.m. Cu)			
1	93.5	93.4	93.6	93.50
2	93.3	93.2	93.5	93.33
3	93.6	93.8	93.8	93.71
4	93.0	93.4	93.3	93.23
5	93.7	93.8	93.6	93.70
6	94.0	93.8	93.8	93.86
7	92.8	93.0	93.0	93.93
8	92.8	92.8	92.8	92.80
9	93.0	93.3	93.5	93.26
10	93.8	93.7	93.7	93.73
			Av.	93.40
			σ_i =	0.35
			σ_{mean} =	0.12
			Probable error, i =	0.23
			Probable error of mean =	0.08

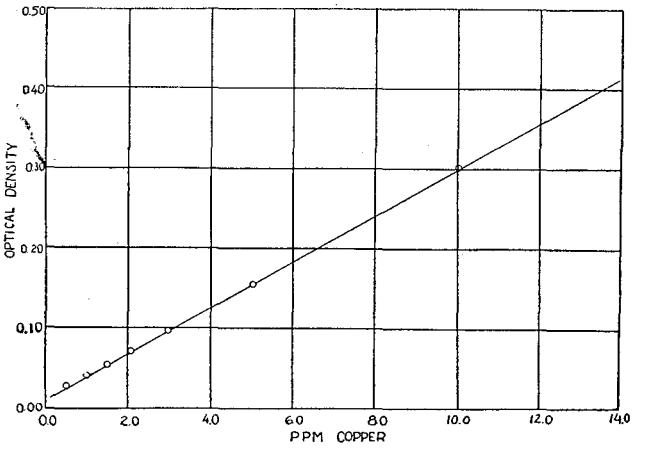


Figure 2. Optical Density *vs.* Concentration of Copper-Dithio-oxamide Color System

INTERFERENCE STUDIES

Possible interfering effects of ions commonly found in waters were investigated spectrophotometrically. The following ions were studied over the concentrations indicated and found to be without deleterious effect: ammonium (0 to 5 p.p.m.), bicarbonate (0 to 400 p.p.m.), calcium (0 to 100 p.p.m.), chloride (0 to 400 p.p.m.), magnesium (0 to 100 p.p.m.), manganese (0 to 5 p.p.m.), potassium (0 to 100 p.p.m.), sodium (0 to 150 p.p.m.), sulfate (0 to 400 p.p.m.), and zinc (0 to 5 p.p.m.). Ordinary amounts of free chlorine (up to 10 p.p.m.) were without effect. Because of the general tendency of iron to interfere with tests for copper, special attention was paid to its behavior. With dithio-

oxamide alone, iron reacts to form a yellowish-brown precipitate. Although this compound shows very little absorption in the wavelength region of interest in copper analysis, it acts to compete with the copper for reagent, and thus causes low results. By use of malonic acid, however, the iron is sequestered to permit accurate determinations of copper in the presence of as much as 2.5 p.p.m. of iron; as much as 10 p.p.m. of iron can be tolerated by doubling the prescribed amount of malonic acid used, if standardizations are made in like manner.

PRECISION AND ACCURACY

The applicability of the dithio-oxamide procedure was studied with local waters (Table I). The accuracy of the method in determining added known amounts of copper is shown in Table II. The data presented were obtained using an Evelyn filter photometer operated on the macro scale. All measurements were made using a single selected test tube as the cell rather than a series of matched tubes, to eliminate variations in cell constants.

The general precision of the method was studied, using a Beckman Model DU spectrophotometer which was considered the most suitable instrument available for such work. The observations used were made at two concentrations of copper (0.5 and 3.0 p.p.m.) as a check on possible instrumental variation. The two copper samples were prepared by adding the calculated amounts of standard copper solution to Baton Rouge tap water (Table I). Transmittancy values were obtained by averaging three readings on each test solution, reporting the averages to two decimal places. As shown in Table III, the standard deviation of the mean of ten observations, in terms of percentage transmittancy, was less than 0.13 and the probable error of the mean was 0.09. For a single measurement the probable error was 0.26 which, when expressed in terms of copper concentrations, indicates that a single determination should yield results correct to a ± 0.03 p.p.m. over the concentration range studied.

The method described can be considered applicable to the direct determination of copper in potable waters. Where colored waters are to be examined the spectrophotometric procedure should be employed, using a blank of the water being analyzed for the transmittancy measurements.

Although the procedure is intended for rapid determinations of copper, it is capable of unusually good precision over the concentration ranges for which it is intended to apply.

ACKNOWLEDGMENT

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NOTES ON ANALYTICAL PROCEDURES . . .

Infrared Absorption Spectrum of Gamma-Benzene Hexachloride

H. L. CUPPLES

Bureau of Entomology and Plant Quarantine, Beltsville, Md.

THE infrared absorption spectra of the isomers of benzene hexachloride (hexachlorocyclohexane) in the rock-salt range, 2 to 15μ, provide a method for quantitatively determining the isomers in technical and purified mixtures. Daasch (*1*) has described a method for this analysis, including spectrograms of

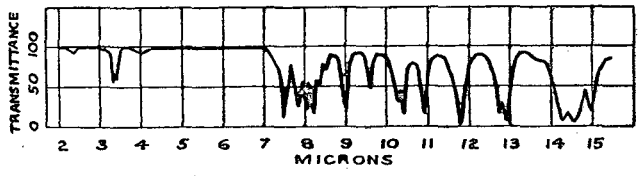

Figure 1. Spectrum of Gamma-Benzene Hexachloride
100 grams per liter in carbon bisulfide and carbon tetrachloride. Cell thickness, 0.5 mm.

five isomers in the range 2 to 24μ. Kauer, DuVall, and Alquist (*2*) have published spectrograms of the isomers in the range 2 to 14μ. In applying this method for determining the isomers of benzene hexachloride, the writer has measured the absorption of the gamma isomer in the range 2 to 15μ, using an infrared spectrometer equipped with sodium chloride prism, windows, and absorption cells, and using a solid, glass, or lithium fluoride shutter to minimize stray light.

The spectrogram of γ-benzene hexachloride (Figure 1) differs from that given by Daasch in two major respects: Negligible absorption is found in the 6μ region, where Daasch observed a weak, broad absorption band; and a moderately strong absorption band is found at 14.96μ, which Daasch did not observe. The writer's observations also show a weak band at 2.4μ. The absence of substantial absorption at 6μ is in agreement with the spectrogram of Kauer, DuVall, and Alquist, which does not include the range 14 to 15μ.

The existence of the band at 14.96μ has been confirmed by measurements on three samples of highly purified gamma isomer, with cell thicknesses of 0.1 and 0.5 mm., and in both carbon bisulfide and carbon tetrachloride solvent.

ACKNOWLEDGMENT

The author thanks the Naval Research Laboratory and the Hooker Electrochemical Company for two samples (both products of the latter) melting at 112.5–113.5° C., and the Dow Chemical Company for the third, for which a melting point was not obtained.

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Conductance Method for Checking Accuracy of Water Analyses

J. R. ROSSUM

California Water Service Company, San Jose, Calif.

RAPID and accurate methods are available for determining all the major constituents forming ions in natural waters (*1*, *3*, *4*) except sodium. If sodium is determined, the accuracy of the analyses may be established by showing that the sum of concentrations of the cations is equal to that of the anions. Considerable time can be saved by computing sodium by difference, but if this is done, there is need for a rapid, precise, method for verifying the total ion concentration.

The electrical conductivity method of Gustafson and Behrman (*2*) appeared promising, but lacked the desired precision. This method tacitly assumes that Kohlrausch's law holds for finite concentrations, that the specific conductance is a linear function of concentration over small ranges, and that calcium, magnesium, and sodium have equal equivalent conductances.

As the principal salts in natural waters are strong electrolytes and concentrations in the neighborhood of only 0.001 *N* are involved, the first assumption may be expected to hold with reasonable accuracy.

It can be shown that less than 1% error is introduced by the second assumption over the concentration range 0.8 to 1.2 milliequivalent per liter by substituting empirical constants in the equation:

$$\lambda = \frac{K}{c} = \lambda_0 - b\sqrt{c}$$

where λ is the equivalent conductance, λ_0 is the equivalent conductance at infinite dilution, K is the specific conductance, c is the concentration, and b is a constant.

A perusal of a table of equivalent conductances at infinite dilution indicates that considerable error may be introduced by the third assumption.

Table I. Factors

Constituent	Micromhos per Milliequivalent per Liter at 25° C.	Micromhos per P.P.M. at 25° C.
Chloride	75.9	2.14
Sulfate	73.9	1.54
Carbonate	84.6	2.82
Bicarbonate	43.6	0.715
Nitrate	71.0	1.15
Calcium	52.0	2.60
Magnesium	46.6	3.82
Sodium	49.6	2.16

Accordingly, a table of factors was devised, which, when multiplied by the concentration of the corresponding ion, gives the specific conductance contributed by that ion, provided that the total concentration is such as to have a specific conductance of approximately 100 micromhos at 25° C.

As these factors are essentially the equivalent conductance at 0.001 *N*, they were computed in a manner analogous to that used for computing the equivalent conductance of the individual ions at infinite dilution. Gustafson and Berhman's data were used freely in these computations, along with other data found in textbooks on physical chemistry. Some of the factors have been slightly modified as experience on actual analyses has indicated. As finally accepted, these factors are shown in Table I.

Apparatus. A Leeds & Northrup alternating current resistance bridge is used in conjunction with a dip type conductance cell having a constant of 0.1. Any instrument capable of measuring specific conductance over the range of from 50 to 50,000 micromhos with an error not exceeding 1% may be used.

Procedure. The conductance of the water sample is measured in the usual manner, and from this value, a dilution is chosen such that the specific conductance of the diluted sample will be between 90 and 120 micromhos. The proper volume of sample is then pipetted, into a volumetric flask, made up to the mark with cool, boiled, distilled water having a known specific conductance of not over 2 micromhos at 25° C., and thoroughly mixed. The resistance is measured after carefully adjusting the temperature to exactly 25° C. The diluted specific conductance is obtained from the following formula:

$$K_d = \frac{AD \times 10^6}{R_d} - (D - 1)\,K_w$$

where K_d is the diluted specific conductance in micromhos, A is the cell constant, D is the dilution factor, R_d is the measured resistance in ohms, and K_w is the specific conductivity of the distilled water in micromhos.

DISCUSSION

The procedure requires less than 15 minutes, including calculations. The author prefers to adjust the temperature to exactly 25° C. rather than to assume that the conductance increases linearly with temperature and make the indicated correction. The cool, boiled, distilled water used for dilution is conveniently kept in a 10-liter Pyrex bottle equipped with a plug of Absorbite to protect it from carbon dioxide in the air. Standard work sheets for water analyses in this laboratory are arranged to facilitate the necessary calculations and comparisons.

It has been the author's practice to redetermine constituents when the specific conductance as computed from chemical analysis is more than 1.5% greater or 2% less than the diluted specific conductance. Of a typical group of 100 consecutive analyses 92% fell within this range. The average deviation of the computed from the measured specific conductance was 0.78%. Less importance is attached to negative deviations, because the presence of minor constituents would increase the measured conductance. Inasmuch as sodium is determined by difference, small amounts of potassium or ammonium, reported as sodium, would increase the measured conductance because these ions have a much higher equivalent conductance than sodium.

The method is not valid for waters having a specific conductance of less than 90 micromhos, but the author has used it successfully on brines with a specific conductance as high as 25,000 micromhos. It is not applicable to waters having unusually high or low pH values, since the equivalent conductance of both hydrogen and hydroxyl ions is comparatively high. Essentially all the author's analyses are of water having a pH of between 7 and 9, and he has made no investigation of the results that can be obtained outside this range.

The method provides an accurate check on the negative ions, but when sodium is estimated by difference, comparatively large errors in the positive ions will cause only small deviations in a computed specific conductance.

This procedure has been used for 2 years on over 800 water samples that represent a variety of both ground and surface water supplies throughout the state of California.

ACKNOWLEDGMENT

The assistance of Primo A. Villarruz in making many of the analyses is gratefully acknowledged.

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Vacuum Distillation Apparatus for Microquantities

M. J. BABCOCK[1]

Northwestern University, Evanston, Ill.

SCHNEIDER (*3*) has recently reviewed apparatus for distillation of microquantities. Other forms have been described by Gould *et al.* (*1*). Though there is frequent need for purification of small quantities of liquids in identification work, such apparatus is not widely used because of difficulty in construction. The apparatus described below may be readily constructed from a test tube, a piece of glass tubing, and two rubber stoppers by a person unskilled in glass blowing.

APPARATUS

The sequence of operations in construction of the distillation tube from glass tubing of 5-mm. inside diameter is as follows:

Bulb *A* is blown and pressed in slightly at the lower end. A rubber stopper cut to 8-mm. length is placed between *A* and *B*, which is a lopsided blister, blown on one side of the tube. Bulb *C* is blown. A hole just larger than *C* is blown in the bottom of a 25 × 200 mm. test tube. A 5-mm. hole is made at position *H* by pressing a wire through the softened test tube. The apparatus is then assembled as indicated in Figure 1. It is helpful in judging the size of fractions to mark the bulbs with paint at the 0.1- and 0.2-ml. levels (with the tube held at a 45° angle) before assembling.

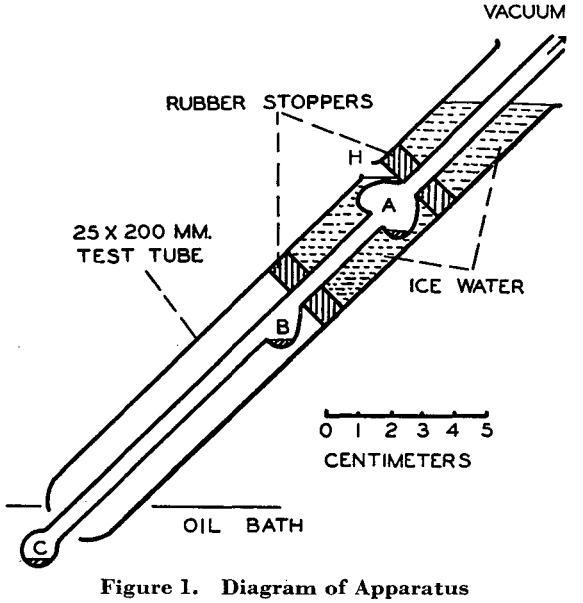

Figure 1. Diagram of Apparatus

Distillations are made with the tube at a 45° angle and *C* heated by a mechanically stirred oil bath. The sample is introduced into *C* with a pipet made from 3-mm. diameter tubing. Ice or other suitable coolant is placed in the chamber surrounding the tube above *A*. The tube is inclined to a 45° angle with *B* on the top side, the distillation tube is then connected to the vacuum system, and the more volatile material is distilled into *A* by slowly heating the oil bath.

When sufficient distillate has collected in *A*, the lower end of the tube is raised out of the oil bath to an angle of about 30° with the horizontal and heating of the oil bath is discontinued. Ice water from a wash bottle is promptly introduced through *H* to condense vapors between *B* and *A*. After about a minute the tube is carefully rotated on its longitudinal axis until *B* is on the bottom side. *C* is then carefully lowered into the bath and distillation continued until sufficient distillate has collected in *B*. The distillation is stopped by raising *C* out of the bath until the tube is nearly horizontal and then releasing the vacuum. If a distillation is prolonged until the condensing water warms appreciably, the water may be replaced or circulated by using an aspirator to draw off the excess as cold water is introduced.

After the rubber tubing has been disconnected, the fractions from *A*, *B*, and *C* are removed by capillary pipets or capillary siphons, or by drawing up directly into capillaries to be used in various tests. A convenient device is a tube 3 mm. in diameter, drawn out to a curved capillary at one end and with a 15-mm. bulb at the other end. The bulb is warmed and gradually draws up the liquid as it cools.

The small surface area and absence of ground joints minimize holdup due to the formation of a film over the glass surfaces.

As the second fraction does not pass over a condenser or fraction cutter used for the first fraction, it is not contaminated by traces from the first fraction.

Because the fractions are not formed by dropwise transfer from a condenser (*1*), there is no theoretical lower limit to the quantity that can be distilled.

Heat rising between the tubes from the oil bath prevents excessive heat loss from the column.

The all-glass construction without joints avoids the possibility of leakage or contamination with stopcock lubricant. The apparatus is quickly set up and may be readily cleaned by filling with solvent.

The apparatus would appear to be useful for sealed tube reactions at moderate pressures followed by distillation (without losses due to transfer of the sample).

The apparatus effects a good separation of substances having fairly close boiling points.

EXPERIMENTAL

The efficiency of the distillation apparatus was tested by distillation of high-boiling, nonazeotropic binary mixtures at pressures of approximately 1 mm.

Three distillations were made with each of the following mixtures. 49% *p*-cymene (boiling point 177° C.)—51% *n*-caproic acid (boiling point 204° C.) and 50% diphenylmethane (boiling point 266° C.)—50% dimethylphthalate (boiling point 284° C.) Samples weighing approximately 0.15 gram were separated into a volatile fraction, a middle fraction, and the residue. These fractions were removed with capillary pipets and weighed.

The total material thus recovered from the apparatus amounted to 88 to 94% (average, 91%) of the original samples. The size of the volatile fractions ranged from 22 to 43% and the residues ranged from 20 to 49% of the total recovered material in the different distillations. The composition of each sample was determined from its refractive index on the assumption of a linear relationship. With the first pair (27° difference in boiling points at atmospheric pressure) both the volatile and residual fractions had purities greater than 99%. With the second binary mixture (18° difference in boiling points) the volatile fractions were 98% pure diphenylmethane and the residual fractions were 96% pure dimethylphthalate in each test.

The efficiency of the apparatus is probably due in large part to the slow rate of distillation. Rose (*2*) has shown that with an unpacked column 6 mm. in diameter and 30 cm. long the efficiency rises from 2 to 17 theoretical plates as the throughput rate is decreased from 1 to 0.17 ml. per minute. In the above experiments approximately 0.1 ml. was distilled during 10 to 30 minutes, an average of 0.005 ml. per minute. As distillation of 10 ml. at this rate would require 33 hours, a microdistillation may be preferred even when larger samples are available, if it is desired to purify only enough material to permit identification. No bumping occurs in the microdistillation because at the low distillation rate the liquid evaporates rather than boils.

[1] Present address, Rutgers University, New Brunswick, N. J

Table I. Distillation of Limonene-Aniline-Benzyl Alcohol Mixture

	First Distillation		Redistillation of Middle Fraction	
	Weight, gram	Reffactive index	Weight, gram	Refractive index
Volatile fraction	0.215	...	0.008	1.5770
Middle fraction	0.053	1.5782	0.012	1.5814
Residual fraction	0.148	...	0.013	1.5761

The usual function of distillation is to separate a reaction product from other substances, some of which may have higher, others lower, boiling points.

This use is illustrated by distillation of a ternary mixture containing by volume 25% *d*-limonene (boiling point 177.8° C.; n^{20} 1.4743), 50% aniline (boiling point 184.35° C.; n^{20} 1.5863), and 25% benzyl alcohol (boiling point 205.5° C.; n^{20} 1.5396). A 0.435-gram sample was distilled at 10-mm. pressure and a rate of 0.01 gram per minute, and 0.045 gram of the middle fraction was then redistilled under the same conditions.

The data are given in Table I. The presence of either limonene or benzyl alcohol as impurity in the aniline would lower the refractive index. Preliminary tests showed that aniline solutions containing less than 10% by volume of limonene, benzyl alcohol, or both gave refractive indexes within 1% of values calculated on the assumption of linear relationships between refractive index and composition by volume. The distillation data indicate that the middle fraction from the first distillation contained 83 to 93% aniline, and that from the redistillation contained 90 to 96% aniline by volume, depending on whether the impurity is assumed to be benzyl alcohol or limonene.

A second distillation not only serves to purify the material further, but gives an indication of the homogeneity and the trend in the physical constants as the substance is purified. Thus, in the above example, the refractive index data show that the middle fraction from the first distillation was not homogeneous and that the impurities were substances of lower refractive index.

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RECEIVED May 28, 1948.

Buret for Precise Measurement of Small Volumes of Gases

S. S. BURKE, JR., *University of Wisconsin, Madison, Wis.*

DURING studies of analytical micromethods for determining nitrous oxide and other respired gases in anesthetic mixtures, a buret was devised which includes the following features:

A constant, controlled pressure is exerted upon the sample of gas as its volume is being measured.

No calibration corrections are necessary.
The confining fluid is mercury.
The long axis is horizontal.
The buret is a separate unit, exclusively an instrument for measurement, independent of other components of the analysis.
The volume readings are relative values.

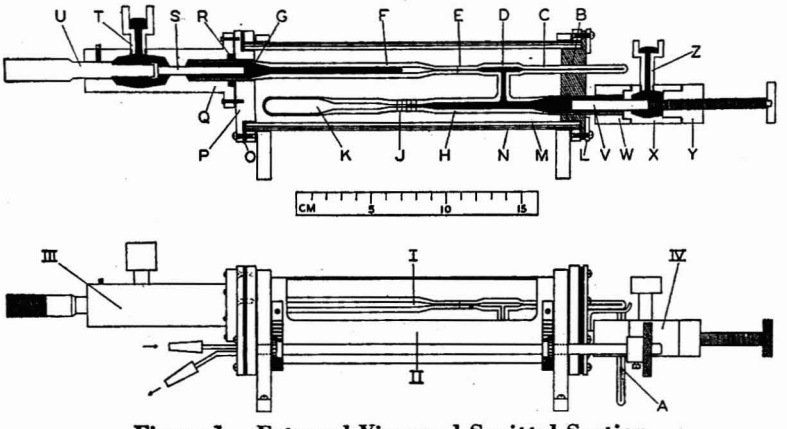

Figure 1. External View and Sagittal Section

I. Glass capillary assembly (values represent inside diameters)
- *A.* Buret tip, 0.7 mm.
- *B.* Rubber stopper
- *C.* Intake and delivery capillary, 0.7 mm.
- *D.* T-segment, 2 mm.
- *E.* Volume-adjusting capillary, 0.7 mm.
- *F.* Buret tube, 3–4 mm.
- *G.* Buret chamber, 8 mm.
- *H.* Barometer tube, 4 mm.
- *J.* Pressure-adjusting scale, 1 mm.
- *K.* Barometer bulb, 8 mm.; volume, 2.25 cu. cm.

II. Water jacket assembly
- *L.* Right end plate
- *M.* Glass water jacket
- *N.* Metal jacket
- *O.* Rubber gasket
- *P.* Left end plate

III. Micrometer assembly
- *Q.* Plastic housing
- *R.* Rubber gasket
- *S.* Machined steel piston
- *T.* Chimney reservoir
- *U.* Micrometer head

IV. Pressure control assembly
- *V.* Pressure control piston
- *W.* Section 1, fixation
- *X.* Section 2, mercury seal
- *Y.* Section 3, activating thread
- *Z.* Chimney reservoir

The design of the buret is derived from a combination of certain characteristics of previously reported types (*1–3*, *5–7*) with the principle of the thermobarometer of the Haldane apparatus and the principle of measured mercury displacement by a cylinder of uniform diameter as adapted from the work of Scholander (*4*). In the buret here reported, a barometer bulb encloses a fixed quantity of air which is readjusted to the same arbitrary volume for each reading. The pressure within this bulb is in equilibrium with the pressure of the sample of gas through the shortest possible path with the least possible resistance. If the temperature of the water surrounding the barometer bulb and the buret tube is uniform and constant, such a device materially reduces the error in measurement caused by variations in pressure of the sample. The volume of gas being determined is represented by the distance through which a cylinder of uniform cross-sectional area is moved into a mercury chamber within the buret, as indicated by the difference in two readings of a micrometer scale.

Figure 1 shows constructional details; for the sake of brevity, extensive discussion of these details has been omitted. (Specific procedure for construction and operation of the buret may be obtained by correspondence with the author.) The dimensions indicated have been found to be critical values.

The diagrams of Figure 2 show the successive steps in the movement of a sample of gas within the buret during the process of its measurement.

PRECISION OF MEASUREMENT

In the experience of the author with other instruments for microanalysis of gases, certain disadvantages appeared to be in-

Table I. Variability of Micrometer Readings

Trial	Micrometer Readings[a] R_1	R_2	Volume[a]	Error[b]
1	0.7747	0.2608	0.5139	+0.00015
2	0.7747	0.2608	0.5139	+0.00015
3	0.7748	0.2608	0.5140	+0.00025
4	0.7744	0.2608	0.5136	−0.00015
5	0.7747	0.2608	0.5139	+0.00015
6	0.7283	0.2148	0.5135	−0.00025
7	0.7284	0.2148	0.5136	−0.00015
8	0.7285	0.2148	0.5137	−0.00005
		Av.	0.51375	±0.00016

[a] Micrometer scale units, 0.1000 = 45.5 cu. mm.
[b] Calculated as deviation from average volume.

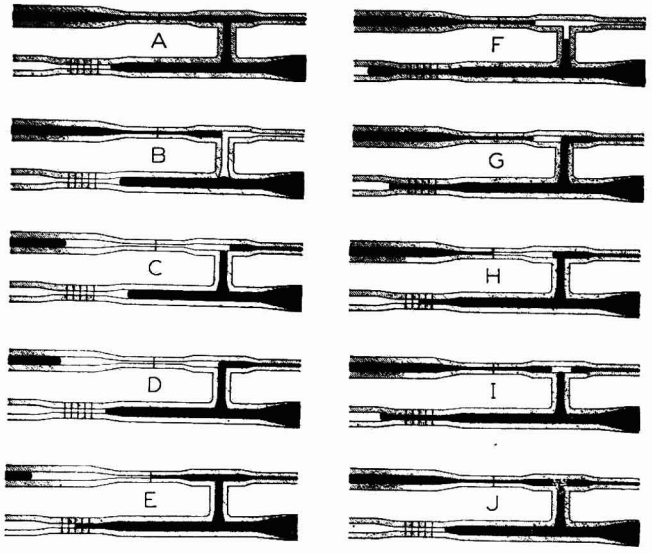

Figure 2. Sequence Diagram Showing Course of Gas Sample Through Process of Measurement

A. Normal condition, filled with mercury except for air enclosed within barometer bulb
B. Internal pressure reduced
C, D. Micrometer piston withdrawn
E. First reading, R_1, barometer set arbitrarily at mid-scale, P_0
F, G. Partial ejection of sample
H. Second reading, R_2, vertical connecting tube filled with mercury
I. Final ejection of sample
J. Normal condition

herent in the principle of measuring the length of a segment of gas enclosed by mercury in a capillary tube between two meniscus boundaries. Aside from the difficulty in procuring a capillary tube of sufficient length with a uniform bore or the alternate difficulties associated with calibration of one which is not of uniform bore, a troublesome problem which can be encountered is regulation of the pressure of the sample itself at the time a reading of its volume is taken. It is not justifiable to assume, under the actual conditions of analysis, that a dependable equilibrium always exists between the pressure of the sample and the pressure of the atmosphere when a segment of mercury is interposed in the intervening capillary, although errors from this source can be reduced by scrupulous attention to cleanliness of both mercury and glass surfaces. Furthermore, the deposition of foreign materials within a capillary during repeated readings can alter the bore appreciably in irregular fashion and render calibration corrections at any given time more or less unreliable.

With the buret described, the volume of sample is translated into the accurately measured length of a known uniform cylinder. This cylinder never comes in contact with the gas sample and consequently is relatively unaffected by the presence of the impurities. Because the regulated pressure is transmitted to the sample through not more than 2 cm. of small-bore capillary, the unpredictable effects of surface forces are minimized. Since only one of the two meniscus boundaries between gas sample and confining mercury is subject to effects of these surface forces, the errors from this source are still further reduced.

The barometer indicating the pressure exerted by the sample will function efficiently and dependably only if the interior of the buret is isolated from the atmosphere as a fixed and separate system. For this reason, during actual analysis, continuity of the mercury thread in the tip of the buret is interrupted by a minute gas bubble which effectively blocks any flow of mercury at the existing small gradient of pressure. It can be shown from the equation for the general gas law that the ratio of pressure of the sample to pressure of the air in the barometer bulb changes insignificantly with ordinary variations in temperature. For a 10° rise from 25° to 35° C., the error in reading a given volume would amount to 0.1%. The error involved in the thermal expansion of the mercury in the buret tube between the micrometer and the sample was directly determined by actual measurement. It was found for the normal 0.1° C. maximum variation in the temperature of the circulating water in the jacket of the buret that an error of only 0.02 cu. mm. would be introduced even if the change took place within the brief period of 1 minute usually required to obtain R_1 and R_2. The observed constancy of R_2 during actual use of the buret confirms this finding.

Representative tabular data have been included to show the accuracy that can be expected from this apparatus under satisfactory conditions. Readings are expressed in English scale units because this happened to be the type of micrometer available; each decimal fraction, 0.1000 inch, is equivalent to 45.5-cu. mm. volume of the micrometer piston. In actual analysis, only the relative values and not the absolute values of the micrometer readings are ordinarily required in the calculation of results. The uniform diameter of the micrometer piston was checked prior to assembly by direct measurement with a micrometer caliper. In addition, functional tests with a given small quantity of gas were made by measuring its volume in different ranges of the micrometer scale without allowing the gas to leave the interior of the buret. The close agreement of the results within 0.0001 scale unit, or 0.05 cu. mm., provided additional evidence of the linear uniformity of volume of the micrometer piston. Similar measurements of a larger volume of approximately 225 cu. mm. show the variability indicated by the eight consecutive readings listed in Table I. The observed deviations may be attributed largely to the fact that compressible gas lies between the displacing piston and the meniscus which is adjusted to the reference mark of the buret capillary.

Although the foregoing discussion deals solely with the intrinsic accuracy of the buret, this device has been used in the analysis of various gas mixtures according to the techniques of Blacet and Leighton (*1*), as modified by Seevers and Stormont (*5*), with a reliable accuracy of 0.1 to 0.2% of the volume of the sample. In the experience of the author, determinations have been made with greater convenience and facility than with other similar instruments.

Finally, the principal variable component of measurement with this apparatus is the value obtained for the first reading, R_1, where the gas sample is interposed between the reference mark and the micrometer. Errors due to this variability are smaller than the deviations to be expected with measurements in a capillary tube; they are reduced to a minimum by interruption of the pressure continuity of the interior system with the atmosphere, by proper setting of the micrometer, and by careful maintenance of a clean mercury bath.

ACKNOWLEDGMENT

The author performed this work as a fellow in anesthesiology of the National Research Council. Grateful acknowledgment for construction of the machined parts of the apparatus is made to J. S. Hipple, former mechanician of the Wisconsin General Hospital.

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RECEIVED January 30, 1948.

Simplified Blacet-Leighton Apparatus for Gas Microanalysis

VICTOR M. LEWIS, *University of Massachusetts, Amherst Mass.*

THE capillary buret type of gas microanalysis apparatus has found extensive use in many branches of chemistry. In its initial form, it was described by Blacet and Leighton (*1*) and the technique of its use in the analysis of volumes as low as 20 cu. mm. of various gaseous mixtures has been fully described (*2–5*). This piece of equipment, however, is relatively complicated, expensive to purchase, and difficult to make in the laboratory. It is also relatively tedious to operate, and the microburet is hard to clean. Difficulty is also frequently experienced in getting the last small bubble of gas into the microburet from the analysis chamber. Swearingen *et al.* (*6*) described a horizontal modification of this apparatus which eliminated the trouble resulting from the necessity for equalizing the mercury level in the reservoir with that at the zero mark in the microburet. It also exerted less pressure on the mercury-actuating mechanism, with consequent more positive control of the mercury thread and less trouble with mercury leaks. The rubber mercury actuator described in the paper, however, has been found unsatisfactory in operation.

The apparatus described here, and used with excellent results combines features described in various publications and can be readily constructed from standard equipment.

The mercury-actuating mechanism (Figure 1) is a mercury valve of the type sold by Arthur H. Thomas Co., Philadelphia, Pa., for use with the Rehberg microburet. This is fitted with a standard taper metal joint No. 14/35. The gas microburet consists of a piece of uniform bore capillary tubing joined at one end to a short length (1 cm.) of wider bore capillary tube which acts as a trap to prevent drawing the gas sample into the valve. The wider capillary tube is fused to a No. 14/35 ground-glass joint for attachment to the mercury valve, and the opposite end of the microburet is fused to the gas analysis chamber (Figure 2), which is a piece of glass tubing approximately 6 mm. in internal bore. The capillary tube has a right-angle bend in it, so that the analysis chamber dips into the mercury reservoir. It is jacketed by part of a 50-ml. buret, the graduations on which serve for making readings in the microburet. The guide for the absorbent holder consists of a piece of brass rod through which is drilled a hole large enough to take the glass rod. The guide is attached to an upright support by means of a clamp holder. Additional gas reservoirs of the type described by Blacet and Leighton (*1*) may be attached to the side of the mercury reservoir by means of spring clips. The complete apparatus is shown in Figure 3.

In operation, the gas sample is introduced into the analysis chamber and its volume is measured by drawing it up into the horizontal part of the microburet. Absorption takes place when the absorbent is introduced into the chamber, and after absorption the volume is again measured. Thus all operations are performed without transferring the sample; this results in both a saving of time and an increase in accuracy.

If the microburet is attached to the valve by means of a ground-glass joint, it may be readily removed for cleaning, or interchangeable burets of different capillary bores may be used.

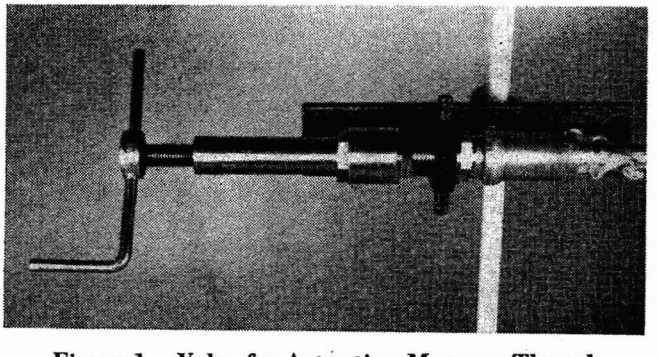

Figure 1. Valve for Actuating Mercury Thread

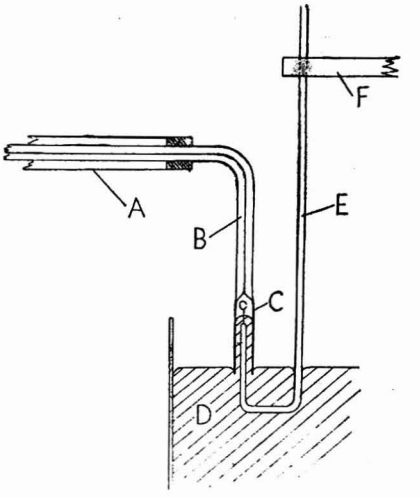

Figure 2. Details of Gas Analysis Chamber

A. 50-ml. buret
B. Capillary microburet
C. Gas analysis chamber
D. Mercury reservoir
E. Absorbent holder
F. Guide for absorbent holder

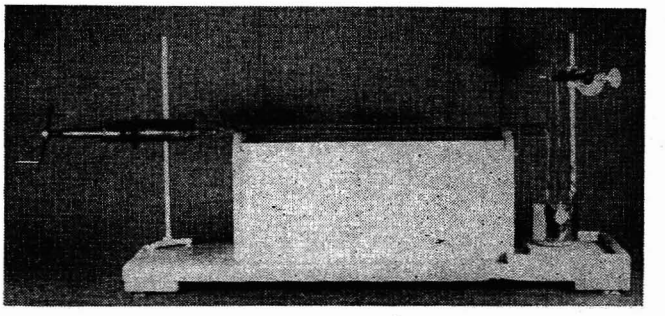

Figure 3. Assembly of Gas Microanalysis Apparatus

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RECEIVED November 10, 1947. Contribution 642, Massachussetts Agricultural Experiment Station.

Still for Flash or Molecular Distillation

MARVIN H. GOLD[1]

The Visking Corporation, Chicago 38, Ill.

A GREAT deal of work has been done on the development of molecular stills. In this quest for distillation equipment to operate under high vacuum, the obvious has been somewhat overlooked and relegated to an obscure position. The fact remains that a great many organic substances have a reasonably low boiling point at pressures produced by the ordinary vacuum pump or water aspirator. However, they may be heat-sensitive to long exposures to the temperatures needed for their distillation in the usual distillation apparatus. An ideal approach

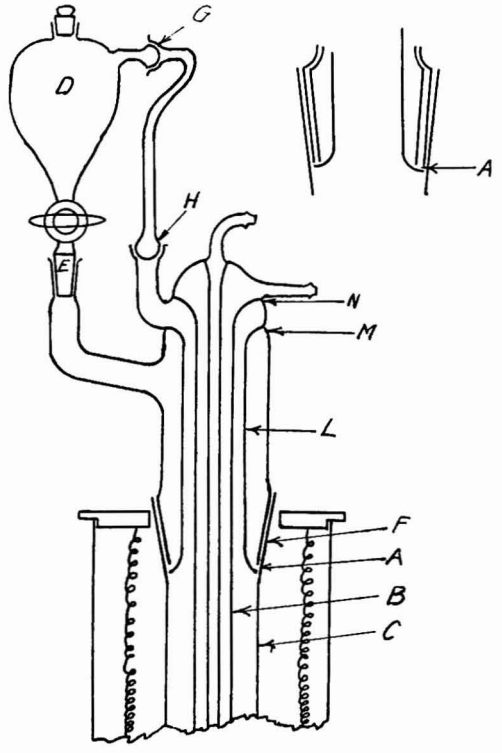

Figure 1

then is to carry out such distillations with a minimum exposure of the distilland in the heated portion of the apparatus. The "falling film" type of apparatus fulfills the above requirements adequately and frequently without going to the extreme of using a high vacuum.

The apparatus described here is designed for general purpose use in the organic chemical laboratory. The author makes no claim as to the efficiency or effectiveness as compared to the present commercial stills. However, it is an inexpensive, simple, and compact laboratory apparatus which requires no special skill in its operation.

Quackenbush and Steenbock (*1*) have surveyed the subject rather thoroughly. The apparatus used in this laboratory is modeled after some of their suggestions, but the design has been somewhat simplified and all moving parts have been eliminated. The present apparatus uses a capillary ring to spread the distilland over the evaporating surface. In the case of viscous materials the flow is aided by having the heating jacket project above the capillary ring. The distilland then flows down over the heated evaporating surface and flash or molecularly distills (depending upon the pressures used) over to the inner condenser. The distillate is collected in a receiver directly below the condenser and the residue flows off to the side into another receiver. No provision has been made for continuous recycling. However, as little or no material remains in contact with the hot evaporator, there is little danger in admitting air immediately and pouring the residual distilland back into the dropping funnel for recycling.

[1] Present address, Aerojet Engineering Corp., Azusa, Calif.

CONSTRUCTION OF APPARATUS

The critical part of the apparatus is the capillary ring shown at *A* in Figure 1. The taper selected for this joint is a ₹ 50/50. About 5 mm. are cut or ground off the end of the inner member. When section *L* is sealed into position, the bottom flare makes a capillary opening or ring with the bottom of the inner joint, *F*, and with the face of the outer member of the joint. This step is a critical operation and both capillaries should be of the order of 0.5 mm. An exaggerated illustration of the capillary ring is shown in the upper right-hand corner of Figure 1. The dropping funnel, *D*, has a volume of 300 ml. It is connected by means of the ground joint, *E* (₹ 14/35) and supported by the pressure equalizer tube, connected at *G* and *H* (18/9 spherical joints). *L*, which forms the capillary ring, is a section of Pyrex 30 × 100 mm. sealed in at *M* with thickness of glass at the flare about the same as the remainder of the tube. The condenser, *B*, is 16 × 540 mm. sealed into the head at *N* and is equipped for an inlet and outlet for the cooling medium.

The evaporator, *C*, is a Pyrex tube 45 × 450 mm. which has a ₹ 50/50 outer joint sealed to the top. At the bottom it is connected through an annulus to inner joints *I* and *J* (₹ 24/40) for distilland and distillate, respectively. The outer joint, *K* (₹ 24/40), leads directly to the vacuum source. The evaporator is heated by a jacket containing sixteen 30-cm. (12-inch) vertical strands of No. 24 Chromel wire. A 360° thermometer is mounted in contact with the evaporator wall and the temperature is controlled by means of a variable transformer.

The joints are all lubricated with a suitable grease. Dow-Corning high vacuum silicone lubricant has been found adequate, but some slight contamination may always be expected at the heated joint, *A*.

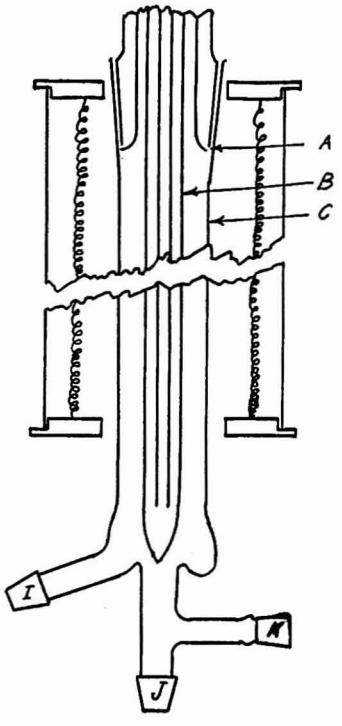

Figure 2

OPERATION OF THE STILL

The material to be distilled is placed in *D* and the system is evacuated through *K*. When the desired vacuum is reached the distilland is allowed to flow down into the evaporator. As it reaches the capillary ring it flows around it, making a bed of liquid several millimeters deep. When sufficient hydrostatic head has been developed, the liquid flows down the side of the evaporator in a thin film or a number of fine streams, depending upon the ability of the liquid to wet the glass. Sufficient degassing occurs in one or two passes. Then the evaporator is heated to the desired temperature and the material distilled.

Long-chain aliphatic acid chlorides are notably difficult to distill. They eliminate large volumes of hydrogen chloride and give low yields upon distillation in the ordinary Claisen-type

apparatus. Using the falling film method described here, compounds such as stearoyl chloride and sebacyl chloride have been rapidly distilled to give clear water-white products at 1 to 5 mm.

ACKNOWLEDGMENT

The author gratefully acknowledges the aid of H. S. Martin of the H. S. Martin Glass Company, Evanston, Ill., for assistance in the design and construction of this apparatus, and Leonard J. Druker of the Visking Corporation for his numerous tests of the design under laboratory conditions.

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RECEIVED June 5, 1948.

Vacuum-Jacketed Vapor Dividing Reflux Head

W. R. DOTY

California Research Corporation, Richmond, Calif.

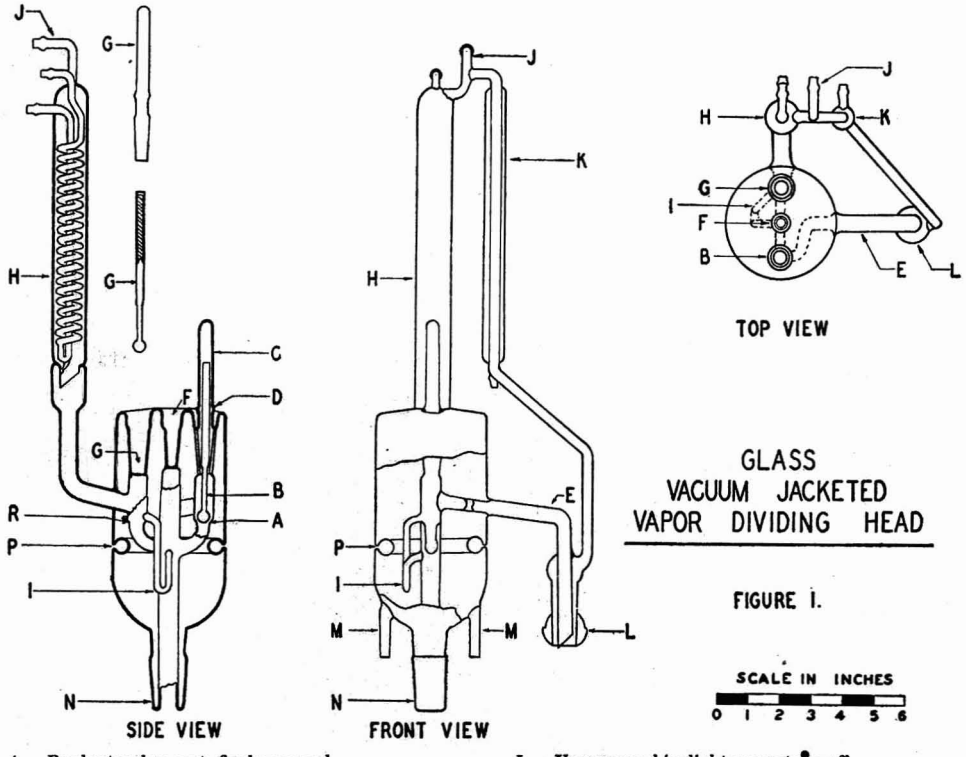
THE advantages of the vapor dividing head over the more common liquid dividing head have been summarized by Collins and Lantz (*1*) as follows:

1. There is less product leakage at total reflux.
2. The moving parts are more accessible.
3. The reflux ratios are closer to the "off-on" ratio of the timer.
4. There is no leakage of reflux to take off during flooding.

In the commercially available head (Glass Engineering Laboratories, Belmont, Calif.) described by Collins and Lantz these advantages are compromised by the fact that the single solenoid operated valve in its "product-on" position closes the throat of the reflux condenser. As a result of this construction the valve traps some liquid in the condenser and when the valve changes to the "product-off" position some of this liquid is transferred to the product line. In operation at high reflux ratios this characteristic causes a reduction in the reflux ratio.

The head described below overcomes the above difficulties by employing two separate single-acting valves, one of which closes the reflux condenser while the other opens the product line and vice versa. The liquid reflux, therefore, never comes in contact with the product take-off valve and only saturated vapor passes the latter.

The condenser is integral with the head, and access to the valves is provided through two 14/35 standard-taper ground joints. As these are not exposed to appreciable quantities of liquid, they cause no trouble due to sticking or leaking.



A. Product valve seat, finely ground
B. Product valve
C. Standard taper valve sleeve, removable for regrinding, replacing, or cleaning valve
D. Bulge to support solenoid
E. Product take-off line
F. Thermometer or pyrometer point well
G. Reflux valve detail
H. Reflux condenser
I. Liquid seal to allow reflux run-back while valve is closed
J. Vacuum and/or light vapor take-off
K. Pressure equalizing line with reflux condenser for condensation of light product vapors
L. To standard design product cooler and cut taker and/or receiver
M. Tubulations for silvering and evacuating
N. Standard taper to fit distillation column
P. Expansion bellows
R. Reflux valve seat, finely ground

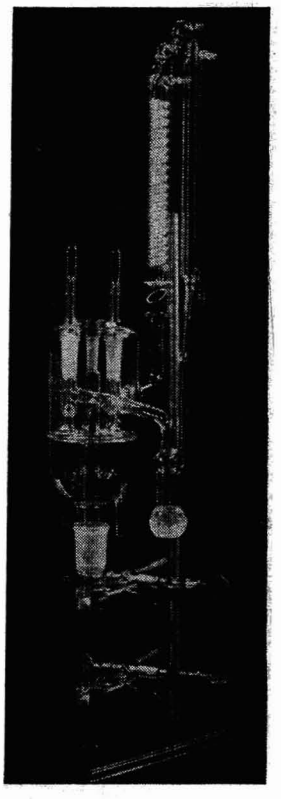


Figure 2

In this design a liquid-sealed reflux return line (*I*, Figure 1) by-passes the reflux valve. This prevents the valve from trapping liquid in the reflux condenser and so smooths out the operation of the column and tends to minimize flooding.

Figure 1 gives elevations, top view, and details of the head.

Operation. The head has been operated with a variety of types of columns and under pressures varying from atmospheric to a few millimeters. It is equally satisfactory for either pressure condition, although its mechanical advantages are particularly noticeable under vacuum. Under atmospheric pressure its maximum capacity without flooding is about 3600 ml. per hour. When it does flood, it is at the base of the reflux valve. The throughput can be increased at the expense of a slightly larger holdup by increasing the diameter of the liquid seal (*I*, Figure 1) in the reflux line.

The valves are operated by either alternating or direct current solenoids, which, in turn, are actuated by a timer. The timer must be arranged so that it simultaneously cuts one solenoid into the circuit as the other is cut out. Both mechanical and electronic timers have been used and units have been fabricated which permit the adjustment of the reflux ratio with a single dial. Ratios varying from 1:1 to 100:1 are easily obtainable and the actual reflux ratios are very close to the "off-on" ratios of the timer.

The head and its accessories are readily adapted to multiple setups and as many as six stills have been operated in a battery by one man.

Figure 2 shows the finished vapor dividing head unsilvered.

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RECEIVED June 24, 1948

Small Laboratory Centrifugal Molecular Still

R. M. BIEHLER, K. C. D. HICKMAN, AND E. S. PERRY

Distillation Products, Inc., Rochester, N. Y.

A REQUIREMENT for efficient, quantitative molecular distillation is that the distilland shall be exposed in a thin film with uniformity of area, thickness, and rate of feed. This has been done in various ways, the most promising of which at present is the use of a heated centrifugal cone for spreading a distilland supplied at constant rate.

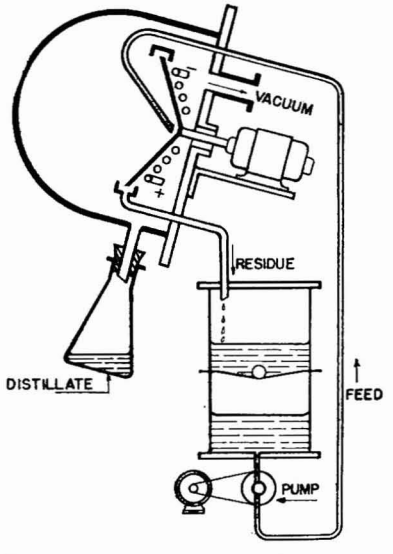

Figure 1. Centrifugal Molecular Still of Cyclic Batch Type

The simplest, complete distillation unit embodying this arrangement is a cyclic batch still with double reservoir (*2*). Figure 1 shows this to comprise a still head, two reservoirs, a circulating pump, and a manifold for attaching a vacuum system. There are necessarily many component parts and constructional pieces in making a versatile unit of this kind. The problem in designing a small centrifugal still suitable for laboratory bench use is to diminish the number of parts without sacrificing the functions. The progress that has been made to date in meeting these requirements is described in this paper. In Figure 2 is shown a model of the complete still unit.

CYCLIC BATCH CENTRIFUGAL MOLECULAR STILL

Simplification has been secured by placing all the working parts of the still, including reservoirs, circulating pump, and evaporator, inside a single vessel which takes the form of an inverted bell jar with modified contour. From the diagrammatic elevation in Figure 3, it is seen that the mechanism is hung internally from a top plate which is supported by an external cabinet containing the controls and the various meters. The heart of the still is the cast-aluminum rotary evaporator, which contains an embedded

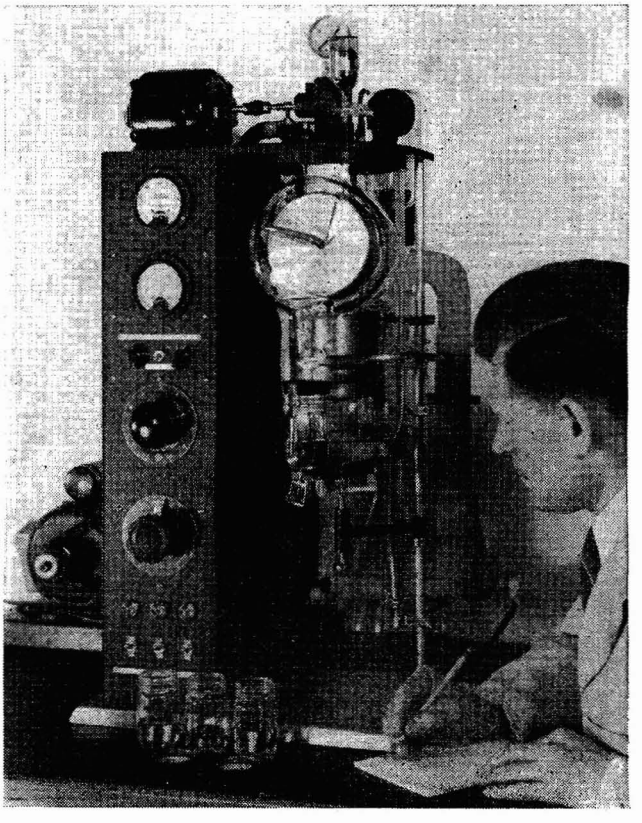

Figure 2. Five-Inch Centrifugal Molecular Still

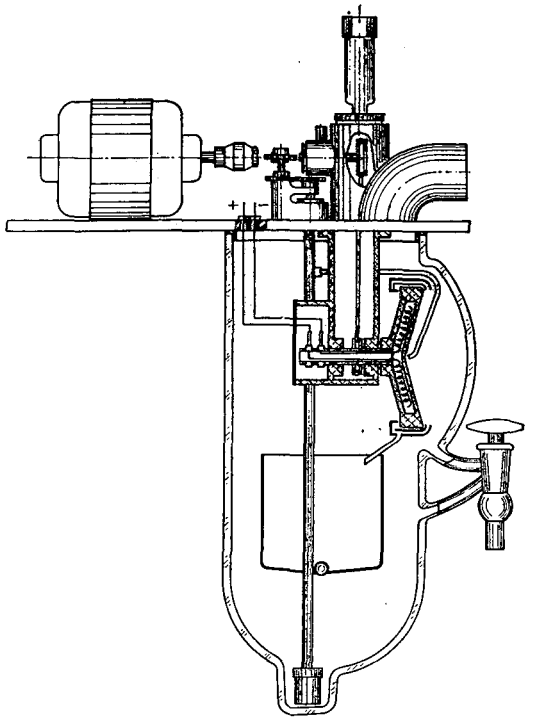

Figure 3. Elevation of Centrifugal Molecular Still

electrical resistance heating element. The cast-in element supplies heat rapidly and uniformly to the distilland. No hot glowing elements are exposed to the vapors in the still and the hottest part of the still is the rotor surface itself. Leads from the heater pass through the shaft to slip rings which are contained, but separately housed, in the bell jar. This design feature obviates the necessity of placing the vacuum seal on the hot rotor shaft. Electrical contact to the slip rings is made through two spring-loaded carbon brushes.

The bearing housing is an aluminum casting, suspended from the top plate. Drive is by a coiled spring wire belt which connects with a countershaft held in a projection of the housing on the upper side of the top plate. Small commercial seals serve to maintain a vacuum. The shaft is carried by shielded ball bearings which can be lubricated by heavy grease or oil, but they are inevitably lubricated by small quantities of distillate. The mechanism for feeding the distilland consists of a long tube and internal shaft extending from the top plate to the bottom of the glass bell. At the far end there is a tiny gear pump which is designed with a wide entrance port for receiving viscous fluids under low head and for minimizing vapor lock. The speed of the gear pump can be varied from 25 to 180 cc. per minute by a simple transmission, even while the still is in operation under vacuum. The distilland is led onto the rotor by a slanting tube and spreads out in a film which is 0.01 to 0.1 mm. thick at the periphery, according to the viscosity. From the edge, the distilland passes into a rotating gutter fastened to the rotor. At the back of the gutter there is a depression where the spent distilland collects momentarily and in this depression there rides a thin metal knife to which is attached a thermocouple (Figure 4). Liquid spills over the rotating edge of the gutter into a stationary gutter, whence it falls by gravity onto a small loop of tubing which is cooled by air or water. This same tube embraces the bearing housing to keep the latter at a lower temperature than the rotor, so that the bearings will remain lubricated by traces of condensate.

The arrangement for ascertaining the temperature of the distilland is one of a number that have been tried, including movable thermocouples riding on the liquid film in front of the still, radiation thermocouples, and embedded thermocouples with slip ring connections. The dragging couple described has proved to be the most reliable and trouble-proof under ordinary conditions. The shielding which the two gutters provide and their proximity to the hot rotor keep the temperature readings reliable. Comparison of readings obtained with this arrangement and others devised in the laboratory indicates that they reflect the true temperature of the evaporating surface within ±5° C. In special cases where the residues at the end of the distillation are extremely viscous, the knife with thermocouple may be damaged if it is allowed to freeze in the residue. This can be prevented by flushing the viscous residue out while the evaporator is still hot or by lifting the couple out of the groove while the rotor is still hot.

The distilland, considerably chilled by contact with the water, cooled loop with consequent reduction of thermal hazard (*3*)- passes to the upper reservoir. When the bell jar which forms the lower reservoir is empty, the contents of the upper reservoir can be dumped by means of an externally operated ball valve.

The condenser is formed by a bulge blown into the side of the glass bell jar. It is intended that this portion shall be cooled by a small electric fan or blast of compressed air. Cooling may be interrupted when it is necessary to melt down solid distillates. With adequate air cooling, condensation is virtually complete. Nevertheless, small quantities of "light ends" condense on the main body of the bell jar and gradually fall down into the residue. There is thus an inherent tendency to contaminate later fractions with traces of earlier ones, particularly if the material distills over a wide temperature range. This could be remedied in various ways, such as splitting the bell jar and placing an intermediate collar to collect the drainings, or providing a second internal metal reservoir, thus leaving the bottom of the bell jar to collect the drainings. These could then be drained off separately. The advantages to be gained by including this feature appeared small in comparison to the inconvenience in operation which would result from their inclusion. The present design was, therefore, adopted in favor of the more complex arrangement.

The pumping system which produces vacuum consists of a booster-type, double jet, glass, oil diffusion pump (designed by G. Kuipers of this laboratory), conveniently employing butyl phthalate. The maximum micron per liter per second throughput capacity of the vapor pump has been arranged to give its preferred service in the range 1 to 10μ in which the still is intended to operate. One or more freezing traps may be placed in series with the still and the booster and the mechanical fore-pump.

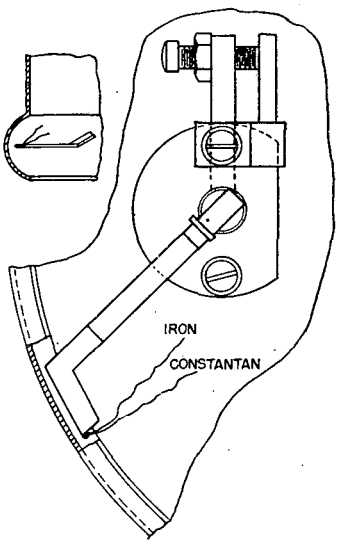

Figure 4. Thermocouple Assembly

OPERATION

It is usually preferable to charge a cyclic still with distilland while the still is under rough vacuum. The material then undergoes a preliminary degassing, the extent of which is governed by the rate of charging.

In the present still, the distilland is admitted from the external glass funnel through the second small tube onto the rotor while the latter is running. Bubbles are broken up by the shear forces on the rotor and the liquid is substantially degassed by the act of admission. A second cycle over the hot rotor with dry ice and acetone placed in the trap near the fore-pump generally renders the distilland sufficiently degassed for distillation to be commenced. If desired, distilland may be charged into the lower reservoir through the tubulation provided for withdrawing the residue.

When the vacuum has fallen to less than 1 mm., the booster pump is energized and as soon as this is seen to be in operation, refrigerant is placed in the trap next to the still. The pressure

should now fall to below 10μ and the cycle of distillation can be commenced.

In the molecular still time and temperature take the place of temperature and pressure for the management of distillation; hence it is convenient to adjust the still to the exact conditions required and allow the preliminary distillates to pass back into the distilland in the lower reservoir. This is accomplished by the three-way stopcock which connects the condenser to the lower portion of the reservoir. Distillation is usually performed in cycles at regular temperature intervals, taking off a fraction at each temperature. At the end of each cycle, the contents of the upper reservoir are dumped into the lower reservoir, to become the feed material for the next cycle.

At the end of the distillation, the oil pump and motor are switched off. The pump fluid and residue are allowed to cool before air is admitted into the still. The rotor is best cooled by constant recirculation of the residue. After the vacuum is released, the residue is drained from the lower reservoir.

Cleaning of the still after distillation is a relatively simple operation and is, indeed, one of the points that received special attention during design. No dismantling is usually required, although for occasional thorough cleaning the bell jar can be removed. After most distillations it is sufficient merely to circulate a nonflammable solvent through the system by means of the feed pump. Aspiration of air through the apparatus after draining the solvents leaves it clean and dry. Some heavy organic mixtures will reach the consistency of a stiff asphalt before the end of distillation. If the still is shut down and the viscous residues are allowed to cool in place, it becomes difficult to clean. It is imperative, therefore, to rinse out the still with a suitable solvent while the rotor is still hot, which can be done under vacuum or atmospheric pressure according to choice of solvent. The rapid evaporation of the solvent floods the whole interior with distillate and washes the viscous residues into the lower reservoir, from which they may be drained and replaced by successive charges of clean solvent. The still is not intended to be used at any substantial pressure or with flammable materials, and a vacuum-operated safety switch prevents current reaching the rotor at pressures corresponding with flammable materials, such as acetone.

PERFORMANCE

The authors have as yet no absolutely accurate data on the conditions required to give optimum separation in a molecular still; it is not known when one full molecular plate has been achieved. The most certain appraisal is, therefore, a quantitative comparison of performance at different rates of feed and with the performance of other stills.

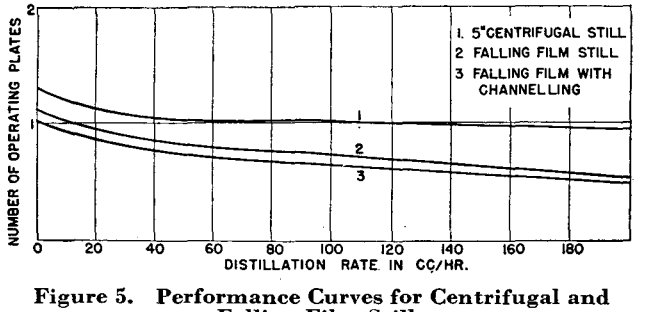

Figure 5. Performance Curves for Centrifugal and Falling Film Stills

Using the binary plate mixture described elsewhere (*4*), the authors have compared the performance of the 12.5-cm. (5-inch) centrifugal with the falling film, cyclic batch still for different throughputs of Octoil and Octoil-S. The degrees of separation, compared with a unit plate measured at 100μ, are shown in Figure 5. It is seen that the separatory power of the centrifugal rotor remains unimpaired for relatively high rates of feed.

Another means of assessment is the elimination curve (*1*) technique. Results of comparing the separation of celanthene red and dimethylanthraquinone on both falling film and centrifugal stills are presented in Figure 6. The centrifugal still gives sharper and narrower peaks, representing a better separation of constituents.

The usual rate of molecular distillation is in a range of satura-

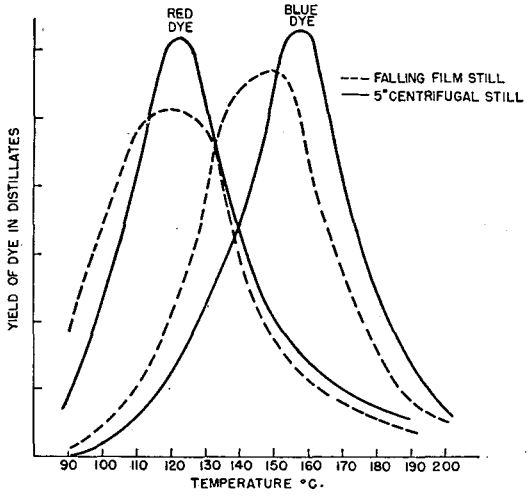

Figure 6. Elimination Curves

tion pressures from a fraction of a micron to 10μ, at which upper limit between 5 and 7 grams of distillate will collect each second from each square meter of evaporating surface. The little 5-inch rotor has performed distillations at 30 or more microns saturation pressure and has evaporated soybean oil, for instance, in a continuous stream of distillate with a rotor temperature ranging between 350° and 400° C.; both rotor and residual oil have remained bright. The still has also been used on Fischer-Tropsch residues and asphalts which failed to yield distillates in other apparatus.

SCOPE AND USE OF STILL

The still described shows features of interest and marks certain advantages. There is, however, no finality in the design of surface evaporators and there are many additions to be made in the present still before it can meet all needs. Constructed as it is from aluminum and steel, it offers in the rotor excellent heat transfer and low catalytic activity to the distilland even at the high temperatures employed. Plain steel is used only where the parts could not be obtained in noncorrosive metals, and these parts at no time contact the hot distillands. While definitely not intended for use with corrosive materials such as acid chlorides or free fatty acids, if such substances must be handled, corrosion is reduced to a minimum. Again, the reservoirs and feed lines are not serviced by heating coils or cooling means for manipulating materials of abnormal viscosity and thermal lability. Such modifications as are needed under these circumstances can, however, be applied without much difficulty. The material in the upper reservoir can be kept molten by an infrared heat lamp and the contents of the bottom reservoir by a Glass-Col jacket.

Operating Features

R.p.m. of rotor	1750
Diameter of rotor, cm.	12.7
Effective distilling area, sq. cm.	100
Heat input of rotor, watts	0–500
Thickness of distilland film, mm.	0.01–0.1
Time of exposure per cycle, sec.	0.03–1.0
Thermal hazard (*3*) at 1μ	D = 0.03–1.0
Recommended throughput, g./min.	35–100
Size of charge, liters	0.1–1.5

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Micromethod for Determination of Tryptophan in Bacteria and Proteins

EDWARD STEERS AND M. G. SEVAG

School of Medicine, University of Pennsylvania, Philadelphia 4, Pa.

IN THE course of a study on the tryptophan metabolism of staphylococci in relation to resistance to sulfonamides (*6*) the authors have used the method of Sullivan and Hess (*8*) with certain modifications for the determination of tryptophan. These studies led to the development of the following micromethod, which permits the analysis of samples of protein (casein, bacteria, etc.) containing as little as 6 micrograms of tryptophan in a 10-ml. reaction system.

DIGESTION OF PROTEINS

Five samples of protein, casein, staphylococci (washed bacterial sediment dried with alcohol and ether), dialyzed samples of crystalline egg albumin, lysozyme (*1*), and ribonuclease (*5*), were digested in sodium hydroxide solution in a 56° C. water bath for 1 hour. Two milliliters of 5 *N* sodium hydroxide were used to digest all samples except casein and tryptophan. The alkali concentration for casein and *l*-tryptophan (in 1% casein hydrolyzate solution) was 1 *N* sodium hydroxide.

It is generally recommended that tissue proteins be hydrolyzed in strong alkaline solution by autoclaving for 5 hours (*3*). Gunness *et al.* (*4*) recommended 10 ml. of 5 *N* sodium hydroxide in sealed ampoules for autoclaving 0.5 to 1.0 gram of dry bacterial cells at 6.8 kg. (15 pounds) steam pressure (121° C.) for 10 hours.

The authors have checked these procedures in the macromethod and found loss of tryptophan. The method recommended represents optimal conditions for the analysis of bacterial cells for tryptophan. The tryptophan content of the proteins studied did not suffer destruction under these conditions.

Table I. Effect of Temperature on Development of Color in Determination of Tryptophan

Substance	Amount, Mg.	Temperature, ° C.	Klett-Summerson Reading	Tryptophan, %
l-Tryptophan	0.124	45	95	...
Casein	10	45	94	1.23
		20[a]	47	0.61
Staphylococcal cells	50	56[a]	204	0.53
		37[a]	75	0.21
		6[a]	48	0.13

[a] During addition of acid heat of reaction in various systems was maintained at ice-bath temperature. Each system was then warmed to indicated temperatures for 15 minutes.

ANALYSIS

To 1 ml. of the alkaline digest of the protein, containing 6 to 60 micrograms of tryptophan, in a 10-ml. standard Klett-Summerson colorimetric tube are added 0.1 ml. of Ehrlich's reagent (5% *p*-dimethylaminobenzaldehyde in 10% sulfuric acid solution), 0.04 ml. of 2% sodium nitrate, and 5 ml. of concentrated hydrochloric acid. [This concentration of sodium nitrate represents a twofold increase over the amount recommended by Bates (*2*). This amount of sodium nitrate is required for maximal color development because of volume relations and the increased amount of alkali used for digestion.] After the mixture is heated for 1 minute in a 56° C. water bath, it is allowed to stand at room temperature for 15 minutes. The system is then diluted to the 10-ml. mark with 17.5% hydrochloric acid solution and permitted to stand for an additional 15 minutes. The sample is then read in a photoelectric colorimeter using a 560 mμ filter (Klett-Summerson No. 56). If the salt formed upon the addition of the excess acid to the alkaline solution fails to dissolve upon final dilution, the reaction system may be filtered through a dry paper before reading.

The determination of the effect of endogenous heat on the maximal color development showed that in the macromethod there is sufficient heat (45° C.) liberated by the neutralization of alkali with the acid. The heat thus generated is sufficient for the maximal color development. If this heat is reduced to 20° C. by cooling, immediately after or during the addition of the acid, the color development is impaired (Table I).

In the micromethod, because of the small volume of alkali used, sufficient heat is not generated and the heat liberated in the Klett tubes is rapidly dissipated because of the larger surface per unit volume. Therefore heating this reaction mixture for 1 minute at 56° C. enables maximum color development. Further treatment is carried out at room temperature.

Table II. Protective Action of Amino Acids on Development of Color in Determination of Tryptophan

	System	Klett-Summerson Reading
1.	124 γ tryptophan in 5 ml. H_2O	96
2.	124 γ tryptophan in 5 ml. H_2O + 25 me. NaOH	51
3.	124 γ tryptophan in 5 ml. 1% casein hydrolyzate soln. + 25 me. NaOH	95
4.	10 mg. casein + 5 ml. H_2O + 25 me. NaOH	94
5.	10 mg. casein, 125 γ tryptophan, in 5 ml. H_2O + 25 me. NaOH	184

The amount of tryptophan in the sample is determined by comparison of the reading with a standard curve obtained from known amounts of tryptophan analyzed in the same manner. The tryptophan standard curve is obtained by analysis of aliquots (range 6 to 60 micrograms per ml.) of a solution of *l*-tryptophan in 1% casein hydrolyzate (pH 7.35), each milliliter of which contains 60 micrograms of added tryptophan and 1 milliequivalent of sodium hydroxide.

The 1% casein hydrolyzate solution used as solvent for the *l*-tryptophan was prepared according to the method of Straus *et al.* (*7*), using vitamin-free 10% casein hydrolyzate manufactured by General Biochemicals, Inc. Analysis of the 1% casein hydrolyzate solution by the macro- and micromethods showed no tryptophan. When 500 ml. of the 1% casein hydrolyzate solution were concentrated in vacuo in an atmosphere of nitrogen, at a water bath temperature of 45° C. to a final volume at 35 ml., samples were analyzed by the macro- and micromethods for tryptophan with negative results. Furthermore, the 1% casein hydrolyzate medium did not support the growth of a strain of *Staphylococcus aureus* which requires tryptophan for growth.

The function of the 1% casein hydrolyzate solution as solvent for the *l*-tryptophan is to prevent any oxidation that would occur during alkaline digestion (Table II).

Table III. Determination of Tryptophan

Protein Samples	Macromethod Wt. of sample, Mg.	Macromethod Tryptophan, %	Micromethod Wt. of sample, Mg.	Micromethod Tryptophan, %
Casein	10	1.24[a]	0.5	1.22
Egg albumin	10	1.19[a]	1.0	1.30
Ribonuclease[b]	15	1.33	1.0	1.36
Lysozyme[b]	4	6.30	0.5	6.30
Staphylococcus aureus (strain 4A)	40	0.63	4.0	0.62

[a] Sullivan and Hess (*8*) reported 1.24% for casein and 1.20% tryptophan for egg elbumin.

[b] The authors are indebted to M. Kunitz, Rockefeller Institute for Medical Research, Princeton, N. J., for crystalline ribonuclease and to H. D. Lightbody, Western Regional Research Laboratory, Albany, Calif., for lysozyme sample.

These data show that a minimal temperature of 45° C. is necessary for the development of maximum color, and that the analysis of pure tryptophan requires an amino acid environment such as casein hydrolyzate, to prevent its destruction during alkaline treatment. Making use of these precautions, the results obtained with various materials are given in Table III.

Results would indicate that the modification of the method of Sullivan and Hess for the determination of tryptophan is adaptable to use with microquantities of protein.

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Spectrophotometric Determination of Iron in Ores with Kojic Acid

J. P. MEHLIG AND M. J. SHEPHERD, JR.
Oregon State College, Corvallis, Ore.

MELLON (*8*) has pointed out that, in view of the very general belief that colorimetric determinations are limited to maximum concentrations of a few parts per million of the desired constituent, there is need for further study regarding the upper limit for reliable work with modern instruments. This point of view deserves more attention than it usually receives. Some spectrophotometric work of this nature has been reported by the senior author and his co-workers (*3–7*).

The purpose of the work described in this paper was to apply kojic acid, 5-hydroxy-2-(hydroxymethyl)-1,4-pyrone, to the spectrophotometric determination of iron in ores in an effort to furnish further proof that such determinations are not limited to a micro scale, but are practical for macroquantities as well.

The reaction between kojic acid and ferric iron to produce a yellowish-orange complex found its first analytical application in the colorimetric determination of the acid with ferric chloride (*1, 10*). Moss and Mellon (*9*) reversed this process, using kojic acid as the reagent for the colorimetric determination of iron, and made a critical spectrophotometric study of the effect of diverse ions and other factors upon the color system. Kojic acid is the first pyrone derivative to be used as a reagent for iron.

APPARATUS AND SOLUTIONS

All spectrophotometric measurements were made with a Cenco-Sheard spectrophotelometer. All pH measurements were made with a Beckman pH meter. An aqueous solution containing 1 gram of kojic acid per 1000 ml., a commercial 3% solution of hydrogen peroxide, and an aqueous solution containing 250 grams of ammonium acetate per 1000 ml. were used.

Standard iron solutions, containing 1, 2, 3, 4, and 5 mg. of iron per 1000 ml., were prepared by dissolving the calculated weights of 99.95% ferrous ammonium sulfate hexahydrate in water, and adding 25 ml. of 12 *M* hydrochloric acid and enough hydrogen peroxide to ensure complete oxidation of the iron to the ferric condition. The excess of peroxide was decomposed by boiling and each solution after cooling was accurately diluted to 1000 ml.

REFERENCE CURVE

To produce the color system 1 ml. of the appropriate standard solution of iron was carefully measured with a microburet into a 100-ml. volumetric flask and 10 ml. of kojic acid solution were added, followed by 10 ml. of ammonium acetate solution to provide a pH value of 6.3 to 6.5. The reagents must be added in the order given; if the ammonium acetate solution is added before the kojic acid the reddish-brown color of ferric acetate interferes. The volume was then made up to 100 ml. A yellowish-orange color developed immediately. The transmittancy at 440 mμ (*9*) was determined for each solution in a 1-cm. cell. The entrance slit was set at a width of 2.5 mm. and the exit slit at 20 mμ. The transmittancy was calculated by dividing the transmittancy of the standard solution by the transmittancy of the blank solvent.

A reference curve was plotted correlating the logarithm of the extinction with the concentration of iron in milligrams per liter. No portion of this curve was a straight line. The deviation from a straight line was undoubtedly caused by the limitations of the instrument, as Moss and Mellon (*9*) have shown by using a General Electric spectrophotometer that the system does obey Beer's law for concentrations up to at least 20 mg. of iron per liter.

Table I. Results Obtained with Kojic Acid

Sample No.	Iron by Dichromate Method %	Iron by Kojic Acid Method %	Difference %
1	41.73	41.75	+0.02
2	44.44	44.20	−0.24
3	28.22	28.25	+0.03
4	33.95	33.75	−0.20
5	38.25	38.25	0.00
6	42.52	42.50	−0.02
7	52.83	52.70	−0.13
8	57.90	57.75	−0.15
9	52.20	52.25	+0.05
10	54.04	53.88	−0.16
11	35.11	35.12	+0.01
12	34.45	34.35	−0.10
13	34.30	34.25	−0.05

DETERMINATION OF IRON IN ORES

Approximately 0.4 gram of iron ore was accurately weighed and transferred to a 250-ml. beaker, 25 ml. of 12 *M* hydrochloric acid were added, the beaker was covered with a watch glass, and the mixture was warmed on a hot plate until solution was complete or only a white, siliceous residue remained. Any ferrous iron was oxidized by adding 2 ml. of hydrogen peroxide. After dilution and boiling to decompose the excess of peroxide, the solution was transferred to a 1000-ml. volumetric flask, filtered if necessary and the residue thoroughly washed, made up to volume, and thoroughly shaken. A 1-ml. aliquot was carefully measured with a microburet into a 100-ml. volumetric flask and the procedure from this point for the determination of the transmittancy at 440 mμ was the same as that described under Reference Curve.

The concentration of iron in milligrams per liter corresponding to the logarithm of the extinction was read off from the reference curve and the percentage of iron in the ore was calculated.

The results obtained for 13 ores are shown in Table I along with the values given by the dichromate titrimetric method (*2*). The greatest difference between the two methods was 0.24% and the average difference was 0.09%. The percentage error varied

from 0.00 to 0.59 with an average of 0.21%. Results may be duplicated on the same sample with a precision of about ±0.05%.

DISCUSSION

Because the intensity of the color system is affected by excess of kojic acid, it is necessary to measure carefully the quantity used. Ten milliliters were found sufficient for 10 to 20 mg. of iron per liter (*9*).

The acid concentration may exert considerable influence on the intensity and hue of the color system and must be controlled within fairly narrow limits. The optimum pH range has been found to be 5.5 to 7.0 (*9*). At the lower value precipitation of iron compounds is avoided. Excessive acidity or basicity tends to destroy the color.

Spectrophotometric study (*9*) has shown that the color system is stable for at least 5 weeks at the pH range indicated above.

According to Moss and Mellon (*9*) the most important interfering ions are cyanide, fluoride, iodide, nitrite, oxalate, phosphate, pyrophosphate, sulfite, aluminum, and zinc.

The method is as rapid as a number of similar methods for iron (*4–7*) and is easily carried out. The color system reaches its maximum intensity immediately and is stable for several weeks. The principal diverse ions which interfere are not normally present in iron ores.

As there is no sharp break in the spectral transmittancy curve of the color system, the chance for error in the measurement of the transmittancy is increased by even a slight error in the wave length setting.

Any error arising in the measurement of 1 ml. of solution for the determination of the higher percentages of iron is lessened by using the same calibrated buret each time. A length of 20 cm. for 1 ml. is recommended.

ACKNOWLEDGMENTS

The writers wish to thank the General Research Council of Oregon State College, whose grant-in-aid made the work possible, and H. N. Barham of Kansas State College, who supplied the kojic acid.

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RECEIVED September 10, 1947

Volumetric Determination of Iron

Liquid Zinc Amalgam and Chromous Chloride as Reductors

WILLIAM D. COOKE, FRED HAZEL, AND WALLACE M. McNABB
University of Pennsylvania, Philadelphia, Pa.

DURING an investigation of a reaction involving pure iron salts, it became necessary to carry out approximately 400 iron determinations. Of the methods available, reduction by liquid zinc amalgam was rapid but inconvenient because an inert atmosphere had to be maintained for complete reduction (*3, 4*). In the present work, the inert atmosphere has been eliminated and a small amount of chromous chloride used to complete the reduction.

Solutions of ferric salts, acidified with either sulfuric or hydrochloric acid, were reduced by treating with liquid zinc amalgam. After separation of the amalgam, the residual ferric ion was reduced by the addition of a few drops of chromous chloride solution. The reactions involving the chromous ion were followed by a low potential redox indicator, phenosafranine (oxidation-reduction potential −0.28 volt). Complete reduction of the ferric ion was indicated by the color change of the indicator from pink (oxidized form) to colorless. The reverse color change indicated complete oxidation of the excess chromous ion by atmospheric oxygen. No evidence of oxidation of ferrous iron by air was observed under the conditions of the experiment (*1*, p. 390). The method was found to be more rapid and less cumbersome than reduction with liquid zinc amalgam in an inert atmosphere. Good precision and accuracy were obtained.

REAGENTS

Potassium Dichromate. Standard solutions of National Bureau of Standards potassium dichromate were made up by weight.

Diphenylamine Sulfonate. A 0.32% water solution of diphenylamine sulfonate was prepared from the barium salt (*7*).

Zinc Amalgam. Six grams of C.P. zinc (powdered, or 20- or 30-mesh) were mixed with 25 ml. of clean mercury and a few milliliters of dilute sulfuric acid were added. The mixture was placed on a steam bath for 1 hour, then washed with water. This amount of amalgam was found to be sufficient to reduce about 100 samples containing 0.1 gram of iron.

Table I. Determination of Iron

Fe Taken *Gram*	Fe Found *Gram*	Error %
0.1508	0.1508	0
	0.1509	0.1
	0.1508	0
	0.1507	0.1
	Mean 0.1508	
0.0905	0.0905	0
	0.0905	0
	0.0904	0.1
	0.0905	0
	0.0905	0
	Mean 0.0905	
0.04523	0.04527	0.1
	0.04523	0
	0.04519	0.1
	Mean 0.04523	
0.00905	0.00905	0.0
	0.00904	0.1
	0.00901	0.4
	0.00902	0.3
	Mean 0.00903	

Chromous Chloride Solution. Approximately 0.5 *N* solution of chromic chloride in 0.5 to 1 *N* hydrochloric acid was placed in a dropping bottle with 15 ml. of liquid zinc amalgam and shaken vigorously for a few minutes until the color changed to a deep blue. Occasional shaking was necessary to regenerate the chromous ion.

Phenosafranine. A 0.02% water solution.

Iron Solution. The concentration of the iron solution was determined by reduction in a Jones reductor, and titration with standard dichromate.

PROCEDURE

Ten milliliters of liquid zinc amalgam were placed in a 125-ml. separatory funnel, and aliquot portions of the ferric salt solution were pipetted into the funnel. The solutions were acidified and diluted to a volume of 50 ml., giving a final acid concentration of 1 to 7 *N* sulfuric or 1 to 3 *N* hydrochloric. The mixture was shaken vigorously for 30 to 60 seconds. One to 3 ml. of reagent grade carbon tetrachloride were added and the amalgam was withdrawn. One to 2 drops of phenosafranine indicator were added, followed by chromous chloride solution (usually 4 to 5 drops) until the pink color of the indicator disappeared and a clear green tint was visible. The solution was swirled 15 to 20 seconds or until the pink color reappeared. One milliliter of phosphoric acid and 0.2 ml. of 0.32% diphenylamine sulfonate were added and the solution was titrated with a standard solution of potassium dichromate to a deep purple color. An indicator correction of 0.03 ml. of 0.1 *N* potassium dichromate was subtracted for each 0.2 ml. of indicator used.

DISCUSSION

The favorable application of chromous chloride to the procedure is enhanced by the use of the indicator, phenosafranine. The color change of this indicator occurs at an oxidation-reduction potential, −0.28 volt, which is between that of the chromous-chromic ion potential and the potential corresponding to oxidation by atmospheric oxygen. These relationships are shown in Table II, in which phenosafranine is designed as In.

The potentials reveal that reduction of the indicator does not occur until reduction of the iron has been accomplished and the indicator is oxidized by atmospheric oxygen only after oxidation of the chromous ion is complete.

Results given in Table I shows that the procedure is capable of good accuracy and precision. The use of a separatory funnel and a small amount of carbon tetrachloride for separating the amalgam makes it possible to carry out complete determinations more rapidly and with as good or better accuracy than by conventional methods (*1*, *5*).

Table II. Standard Oxidation-Reduction Potentials

		Volts	
1.	$Zn = Zn^{++} + 2e^-$	0.762	(*2*)
2.	$Cr^{++} = Cr^{+++} + e^-$ (blue → green)	0.41	(*2*)
3.	$H_3In^{++} = In^+ + 3H^+ + 2e^-$ (colorless → pink)	−0.28	(*6*)
4.	$Fe^{++} = Fe^{+++} + e^-$	−0.771	(*2*)
5.	$2H_2O = O_2 + 4H^+ + 4e^-$	−1.229	

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Nomographs for Paraffin-Naphthene Split in the Type Analysis of Gasoline

GEORGE W. THOMSON
Ethyl Corporation, Detroit, Mich.

IN the type analysis of gasoline by the method developed by Kurtz and his associates (*2*) the relative proportions of paraffins and naphthenes in cuts which are free of aromatics and olefins are obtained from the index of refraction, n_D^{20}, and density, d_4^{20} of the cuts. The volume per cent of naphthenes in the mixture is obtained from a plot of the refractivity intercept, $n_D^{20} - d_4^{20}/2$,

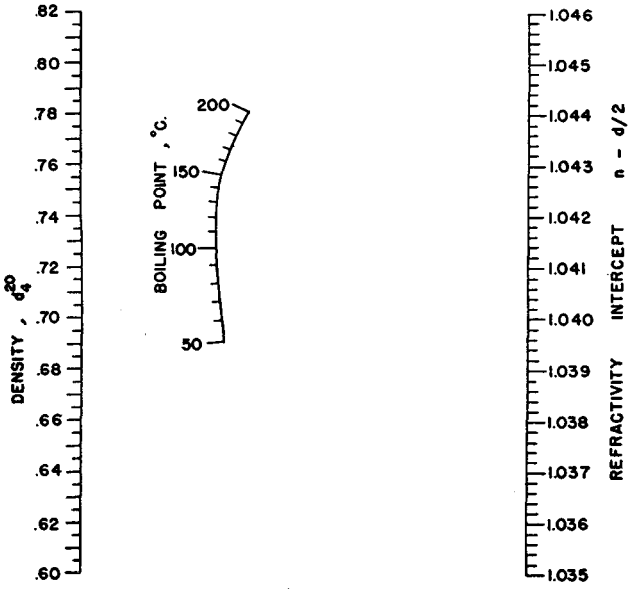

Figure 1. Nomograph 1

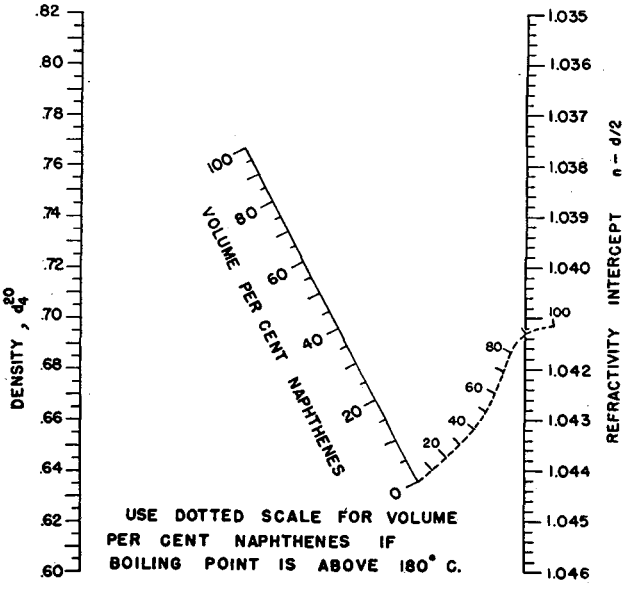

Figure 2. Nomograph 2

Table I. Example of Use of Nomographs

	Cut 4	Bottoms
d_4^{20}	0.7072	0.7992
n_D^{20}	1.3946	1.4413
$n_D^{20} - d_4^{20}/2$	1.0410	1.0417
Estimated boiling point from Figure 1	76	189
Volume per cent naphthenes in cut, from Figure 2	45	83

against density (*2*, Figure 1). The present paper presents two nomographs which may be used in place of their plot. The new charts are easier to read and obviate the necessity of interpolating between the 10% lines of the original figure. Similar charts have been in use for this purpose in this laboratory and elsewhere since the method first appeared as a restricted emergency test method of the American Society for Testing Materials (*1*) in 1943.

The procedure for using these nomographs is as follows. The approximate boiling point of the cut is obtained from Figure 1. If it is above 180° C., the small dotted scale of Figure 2 must be used. The volume per cent naphthenes is then obtained from Figure 2, using the appropriate composition scale.

As examples of the use of the charts, consider the data (*2*, Table VI) in Table I on two cuts of a gasoline; the cuts had been freed of olefins and aromatics.

The nomographs are as accurate as the original charts and are subject to the same limitations, which have been discussed at length (*2*).

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RECEIVED August 25, 1948.

CRYSTALLOGRAPHIC DATA

Contributed by Armour Research Foundation of Illinois Institute of Technology

18. Zinc Acetate Dihydrate ($ZnC_2H_3O_2.2H_2O$)

Zinc acetate dihydrate crystallizes readily from water either macroscopically or on a microscope slide. The crystals obtained are satisfactory for x-ray, microscopic, or goniometric work.

CRYSTAL MORPHOLOGY (determined by W. C. McCrone and J. Krc).

Crystal System. Monoclinic.

Form and Habit. Tablets and rods elongated parallel to *b;* basal pinacoid, {001}; orthopinacoid, {100}; clinodome, {011}; bipyramid, {111}; and occasionally negative hemiorthodome, {101}.

Axial Ratio. $a:b:c = 2.73:1.0:2.05$.

Interfacial Angles (Polar). $100 \wedge 101 = 47°$; $011 \wedge 01\bar{1} = 52° 40'$.

Beta Angle. 99.6°.

Twinning Plane. 100.

X-RAY DIFFRACTION DATA (determined by J. Whitney and I. Corvin).

Cell Dimensions. $a = 14.53$ Å.; $b = 5.33$ Å.; $c = 10.91$ Å.

Formula Weights per Cell. 4.

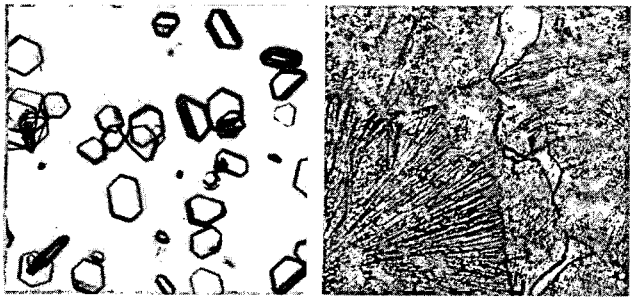


Figure 1. Zinc Acetate Dihydrate

Left. **Crystals from water on microscope slide** *Right.* **Fusion preparation on microscope slide**

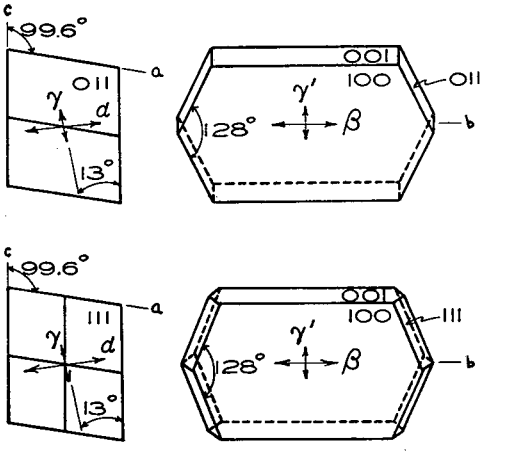


Figure 2. Orthographic Projections for Two Common Habits of Zinc Acetate Dihydrate

Formula Weight. 219.50.

Density. 1.747 (buoyancy); 1.740 (x-ray).

Principal Lines

d	I/I_1	d	I/I_1
14.48	0.06		
7.11	1.00	2.218	...
5.39	0.38	2.140	0.08
4.94	0.04	2.104	...
4.63	0.20	2.049	0.07
4.40	0.38	2.023	0.04
3.97	0.25	1.991	0.07
3.77	0.11	1.956	0.06
3.65	Very weak	1.918	0.05
3.54	0.24	1.811	Very weak
3.23	0.27	1.799	Very weak
3.14	0.10	1.781	Very weak
3.003	Very weak	1.753	Very weak
2.843	0.05	1.709	Very weak
2.678	0.08	1.682	Very weak
2.502	0.04	1.617	Very weak
2.404	0.06	1.589	Very weak
2.360	0.09	1.566	Very weak
2.289	Very weak	1.532	Very weak

OPTICAL PROPERTIES (determined by W. C. McCrone).
Refractive Indexes (5893 Å.; 25° C.). $\alpha = 1.432 \pm 0.002$. $\beta = 1.492 \pm 0.002$. $\gamma = 1.553 \pm 0.002$.
Optic Axial Angles (5893 Å.; 25° C.). $2V = 87°$. $2H = 89°$
Dispersion. $r > b$.
Optic Axial Plane. 010.
Sign of Double Refraction. Positive.
Acute Bisectrix. $\gamma \wedge c = 13°$ in acute β.
Extinction. $\alpha \wedge a = 24°$ in obtuse β.

Molecular Refraction (R) (5893 Å.; 25° C.). $\sqrt[3]{\alpha\beta\gamma} = 1.492$. R(calcd.) = 36.0 (if $R_{Zn} = 4.8$). R(obsd.) = 36.0.
FUSION DATA (determined by W. C. McCrone).
Zinc acetate dihydrate when heated melts just below 100° C. and dissolves partially in its own water of hydration. This water is soon lost on continued heating and the mass resolidifies as anhydrous zinc acetate. The anhydrous salt melts at about 240° C. and on cooling solidifies spontaneously to give spherulites. Most of the crystals show low birefringence with an optic axis interference figure, $2V$ about 80°, negative, little or no dispersion.

BOOK REVIEWS

Manual of Clinical Laboratory Methods. *Opal E. Hepler.* 4th ed. xv + 387 pages. Charles C Thomas, 327 East Lawrence St., Springfield, Ill., 1949. Price, $8.50.

This volume represents an expansion and enlargement of several earlier editions issued in planograph form. Its general availability will be more than welcome to many hospitals and clinical laboratories in which a rigid and accurate routine is of greater importance than background and fundamental understanding of the basis of the procedures used or of their interpretation. It covers the entire field of clinical laboratory methods including chemical, bacteriological, mycological, immunological, and other techniques, in the typical style of an industrial control manual. All instructions are outlined in A, B, C and 1, 2, 3 order, in a clear, terse, and completely dogmatic style. Unnecessary words have been ruthlessly eliminated, except for certain duplications of procedures applicable to more than one type of sample—a common practice in industrial manuals to avoid loss of time in referring back.

The subjects covered, in order, are urinalysis, hematology, gastric and duodenal contents, liver function tests, feces, sputum, cerebrospinal fluid, body fluids, pregnancy tests, bacteriology, mycology, serology, blood groups, clinical chemistry, allergy extracts, tissue sectioning, basal metabolism, electrocardiography, and solutions. Each working procedure is given in order of operations, and the interpretation is given just as concisely and usually without detail or reasons. Methods are ordinarily identified by the names of their authors, and no references are included. For most constituents or operations one method only is given for any single examination or analysis.

The routine clinical laboratory technician will find this volume as essential as his right hand, provided he or she does not disagree with the choice of procedures. The necessity of making choices or decisions is eliminated, and will result in great economy of time in routine operations. The academic scientist, research worker, or even the physician will find it useful chiefly as a broad source of operational detail for unfamiliar procedures. Certainly a large number of the analysis and examination procedures will be considered inadequate or unsatisfactory by the competent scientist. The best existing techniques are not always chosen and often far too little attention is given to interferences and analytical uncertainties. This is in complete accord with the expected use of the volume by strictly routine workers, not by research or investigative personnel.

The typography, printing, and binding appear to be excellent. Many simplified drawings are given as well as a considerable number of good black and white and color plates of cytological and histological specimens. For a book of this kind a further saving of time by some form of marginal indexing would appear desirable.

PAUL L. KIRK

Radioactive Measurements with Nuclear Emulsions. *Herman Yagoda.* ix + 356 pages. John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y., 1949. Price, $5.

This book is unique in that it brings together in one comprehensive treatment a thorough description of the theory and use of the photographic emulsion as an analytical tool in the study of problems involving radioactive emanations, together with the description of detailed techniques for the use of this tool in problems of chemistry, biology, crystallography, mineralogy, and metallurgy. Yagoda brings out clearly the importance and possibilities of the autoradiographic method wherein the photographic emulsion has given the possibility of detection and location of submicroscopic groupings of radioactive atoms with a sensitivity several orders of magnitude beyond that of microchemical techniques. The historical development of the subject of autoradiography with complete bibliographical references is especially good. It is made clear that with the newly available artificial radioactive isotopes, the improved emulsions now available, and the new techniques of sample preparation, the methods of autoradiography will become increasingly important.

To the scientific worker contemplating experiments in the field of radiotracer work with the photographic emulsion, this book is to be especially recommended. It describes the photographic emulsion, its advantages and limitations, gives numerous illustrations of sample preparation and handling for a variety of fields of work, describes methods of exposing and processing the emulsion, and gives detailed information on techniques of microscopy to be used and on the interpretation of the resulting autoradiograms.

The last third of the book contains a good description of the uses and applications of the photographic emulsion in nuclear physics wherein problems in the fields of nuclear reactions, fission processes, cosmic radiation, and meson theory are treated.

JULIAN H. WEBB

Spectroscopy and Combustion Theory. *A. G. Gaydon.* 2nd ed. revised. xii + 242 pages. Chapman and Hall, Ltd., 37 Essex St., London, England, 1948. Price, 25s.

It may be safely assumed that the experienced investigator in the combustion field is fully acquainted with the first edition of Gaydon's excellent book, "Spectroscopy and Combustion Theory." To the chemist just entering the field of flames and explosions, the broad background offered by this book makes it an essential to his education. The author's proved ability to present a clear picture of the quantitative as well as qualitative aspects of the problem further recommends the work to any scien-

tist interested in the mechanisms of light emission from reaction systems.

Much of the new material presented in the second edition reflects Gaydon's recent acceptance of the importance of atomic oxygen in combustion. His application of nitric oxide as a reagent for oxygen atoms in flames forms the core of the one new chapter. The theory of dissociation continua is dealt with briefly and the less familiar subject of unquantized emission due to association reactions in much more detail.

Gaydon includes in the new edition several sections of practical value to the experimentalist. The methods of study of emission spectra are discussed in more detail but nothing has been added to the equally important part on absorption spectra. The measurement of flame temperatures is given more complete treatment than in the original edition, including a useful compilation of calculated compositions and temperatures of some flame gases.

The student of thermodynamics will find the chapter on dissociation energies of value, particularly the section on the heat of sublimation of carbon. Of practical interest is the amplified section on the mechanism of carbon formation in flames.

Though the emission spectra of hydrocarbon flames are discussed in some detail, the combustion engineer will be disappointed by the extreme brevity of the sections dealing with gaseous explosions. None of the important advances in this field since 1940 are included.

Because approximately 95% of the text of the original is repeated verbatim in the second edition, and the major portion of the new additions has been adequately covered by Gaydon's recent publications, this reviewer is inclined to question the necessity of a new edition at this time. However, he has no intention to discount the unusual skill of the author in presenting a complex subject in a concise and lucid manner.

A. Wesley Horton

Practical Analysis. Graphical and Numerical Methods. *Fr. A. Willers.* Translated by *R. T. Beyer.* x + 422 pages. Dover Publications, Inc., 1790 Broadway, New York, N. Y., 1948. Price, $6.

Perhaps a more specific title for this book would be "Practical Mathematical Analysis and Computation." The first of the six chapters discusses numerical calculation and its aids, such as the slide rule, calculating machines, charts, and nomograms. All chemists who are concerned with rapid or routine calculation and presentation of experimental data would probably benefit by reading this chapter. Chapters 2, 3, 4, and 6 deal with interpolation, approximate integration and differentiation of functions, theory of equations, and approximate integration of ordinary differential equations. Most of these are not of interest to the chemist, except for a few specific applications. The fifth chapter, on curve-fitting and empirical functions, is of some general interest.

The book is mainly a translation of Willers' German work, published originally in 1928. Two parts, dealing with the slide rule and calculating machine, are written to accommodate instruments of American design. It would have been appropriate to revise and expand the reference lists to include more available and recent works in English. Use of generalized procedures or theorems is illustrated by many well-worked, specific examples. These examples are really outstanding, and they help the lay mathematician greatly in application and understanding.

The subject material is rigorously treated. For an understanding of the whole book, a good mathematical grounding through differential equations is necessary, though there are parts that require less preparation. While the text and style are clear and not undesirably concise, the book is designed for study and reference rather than for easy reading. The publishers state that this work is universally recognized as the most complete in the field, and that there is no other single book in which the various methods are so carefully evaluated and compared. The reviewer is inclined to agree with this statement.

Walter J. Blaedel

Qualitative and Volumetric Analysis. *J. C. Giblin.* 1st ed. xiv + 175 pages. Longmans, Green and Co., 55 Fifth Ave., New York, N. Y., 1948. Price, $1.60.

The author is a member of the Society of Public Analysts and Other Analytical Chemists and senior chemistry master at the Royal Grammar School in Worcester. The object of the book is "to provide a complete course in qualitative and volumetric analysis up to university scholarship standard." The small volume, which might be carried in a large pocket, is a laboratory guide for beginners in qualitative analysis and in titrimetry. The two subjects are separately treated.

The first 63 pages give what might be appropriately called "tables for the identification of cations and anions." Then follows a section of 20 pages on "Organic Reagents for Metals and Acid Radicals." The presentation of the classical scheme of analysis is in the European tradition. There is no statement on the size of sample to be taken, and the decision on quantity of reagents and their concentration is left to the judgment of the students. This provides the students with an excellent opportunity for learning, by trial and error, the elementary facts of inorganic chemistry, and much may be said in favor of this approach.

The second half of the booklet, pages 85 to 170, gives brief laboratory directions for a course in titrimetry with the use of color indicators. The selection of the sixty experiments is ingenious in the sense that it should stimulate the imagination of the students concerning the great variety of problems that can be solved by simple titrations. The directions are rather sketchy, however, and in some experiments the results must lack precision and accuracy. Still, a good teacher could base on this laboratory text an excellent survey course for students of medicine or chemical engineering.

A. A. Benedetti-Pichler

Scientific and Industrial Glass Blowing and Laboratory Techniques. *W. E. Barr* and *Victor J. Anhorn.* viii + 388 pages. Instruments Publishing Co., Pittsburgh, Pa., 1949. Price, $6.

For many years there has been a great demand for a comp ete manual on the art of constructing experimental glass apparatus, including the many new developments in this field, so highly necessary in modern laboratories. This book explains for the scientist-glassblower, as well as for the more skilled glass technician, a wide variety of techniques heretofore known only to experienced and highly skilled glassblowers.

Besides the very interesting descriptions of apparatus building, and the liberal use of helpful diagrams and illustrations, there is a vast amount of technical data which have not previously been collected in one convenient manual. The reader will find this book completely up to date, as many highly modern commercial laboratories have been consulted in its preparation.

The authors have well fulfilled their objectives as stated in the preface: knowledge of basic glass characteristics and fundamental techniques; advanced techniques, of which the section dealing with high vacuum techniques is especially commended; and description of advanced equipment for special applications in modern laboratories. This book will fill a need long felt by those researchers who are interested in building their own experimental glass apparatus.

C. C. van Hespen

Organic Reagents to Be Discussed at Second Analytical Symposium

FRITZ FEIGL, world-famous analytical chemist now living in Brazil, will visit the United States this summer to be the featured speaker at the Second Annual Analytical Symposium cosponsored by the Division of Analytical and Micro Chemistry and ANALYTICAL CHEMISTRY.

The symposium will be held June 24 and 25 at Wesleyan University, Middletown, Conn. The subject will be "Organic Reagents." S. E. Q. Ashley, General Electric Company and general chairman of the symposium, has announced the following list of papers and authors:

The Role of Organic Reagents in the Chemistry of Specific, Selective, and Sensitive Reactions. FRITZ FEIGL

Polysubstituted 1,10-Phenanthroline and Bipyridine Derivatives as Multiple Range Redox Indicators. Further Applications in Their Use as Specific Reagents for Anion Analysis. WARREN W. BRANDT AND G. FREDERICK SMITH

Spot Test Chromatography as Analytical Tools in Organic Chemistry. THOMAS REISSMANN, EDWARD PRICE, AND MARY L. WILLARD

Water-Soluble 1,2-Dioximes as Analytical Reagents. CHARLES V. BANKS

Precipitation of Thorium from Homogeneous Solution. LOUIS A. GORDON, C. VANSELOW, AND H. H. WILLARD

Fluorometric Reagents for Aluminum, Beryllium, Boron, Thorium, and Zinc. CHARLES E. WHITE

Organic Reagents in Amperometric Titrations. I. M. KOLTHOFF

The Extraction of Cupferrates. N. H. FURMAN, W. B. MASON, AND J. S. PEKOLA

Determination of End Unsaturation in Organic Compounds. CLARK E. BRICKER AND K. H. ROBERTS

Preparation and Colorimetric Properties of Aluminon. W. H. SMITH AND E. E. SAGER

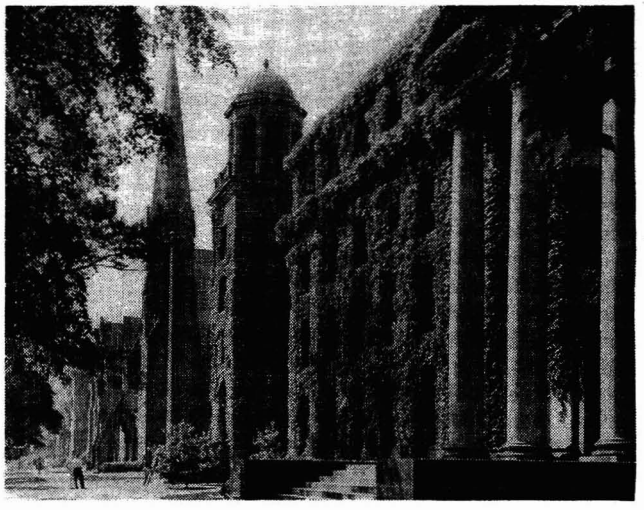
The Spectrophotometric Evaluation of Spot Tests. EARL H. WINSLOW AND H. A. LIEBHAFSKY

Interferences with Reactions between Organic Reagents and Metal Ions. PHILIP W. WEST

Colorimetric Method for the Determination of Microgram Quantities of Boron. GORDON H. ELLIS, E. M. ZOOK, AND OSKAR BAUDISCH

Determination of Beryllium with Alkannin and Naphthazarin. A. L. UNDERWOOD AND W. F. NEUMAN

Preparation of Alkannin and Naphthazarin. T. Y. TORIBARA AND A. L. UNDERWOOD



Wesleyan University

DINNER MEETING

On Friday evening at 7:00 P.M. there will be a dinner meeting. Arthur B. Lamb, editor of the *Journal of the American Chemical Society*, will act as toastmaster and William E. Kappauf, Jr., associate professor of psychology, Princeton University, will give the principal address. His topic is "Applied Aspects of the Psychology of Vision." After the dinner meeting there will be a general mixer at which refreshments will be provided.

ARRANGEMENTS FOR MEETING

M. Gilbert Burford of Wesleyan University and chairman of the committee on local arrangements has released the following information regarding attendance at the symposium.

Registration. Registration will be in the Hall Laboratory of Chemistry on Thursday, June 23, from 7:00 to 10:00 P.M.; on Friday from 9:00 A.M. to 6:00 P.M.; and on Saturday from 8:00 A.M. to 12:00 noon. The first session will start at 1:30 P.M. on Friday.

Registration fees will be $3 for individual members of the Society, designated representatives of corporation members (only one for each corporation membership), and visitors other than chemists or chemical engineers residing in the United States; $6 for nonmember chemists or chemical engineers residing in the United States, regardless of nationality. Associates of divisions or of local sections are not members of the A.C.S. and, if they are chemists or chemical engineers, are subject to the $6 fee. Full-time students of chemistry, both graduate and undergraduate, are given the courtesy of registration on the same basis as members of the Society—in this case $3.

Reservations. It is necessary that reservations be sent in before the meeting. All requests must reach Middletown by June 9. Those wishing to share a room with a specified individual should include a separate application for each person, preferably in the same letter.

Clip coupon and send promptly.

Reservation for Second Annual Summer Symposium

Sponsored by the Division of Analytical and Micro Chemistry and ANALYTICAL CHEMISTRY

Wesleyan University, June 24 and 25, 1949

Name (print):.....

Address (print):.....

.....

Date of Arrival:.....Via railroad or car?.....

Application for: All meals.....Banquet alone.....

Single room.....Double room.....

Roommate desired.....

Will you share a double room if single rooms are exhausted?.....

Applications must be sent to Dr. George Matsuyama, Department of Chemistry, Wesleyan University, Middletown, Conn., before June 9, 1949. Please do not send remittances.

Housing. Rooms will be available in the university dormitories for Thursday, Friday, and Saturday nights, June 23 to 25. Accommodations for married couples and single women can be provided, although these may be somewhat limited. There are only a few single rooms available and double occupancy is urged. Rates for individuals are $3.50 (including 50-cent deposit for the key) for the whole period of stay—one, two, or three nights. Married couples will be charged $5.50 (including 50-cent deposit for key). Bedding will be provided but the university cannot supply towels. Arrangements can be made for some rooms in private homes adjacent to the campus at prices ranging from $3 to $5 per night. Special mention should be made on the application form if such accommodations are desired.

Meals. Meals will be served through special catering. It is therefore especially necessary that reservations be sent in before the meeting. The price for lunch on Friday, the banquet Friday evening, and breakfast and lunch on Saturday will be $8.50. Arrangements can be made separately for the banquet alone at a price of $3.50.

Transportation. Middletown may be reached by the New York, New Haven, and Hartford Railroad (Springfield line) to Meriden, Conn. These trains run on daylight saving time from Grand Central Station. Bus service to Middletown connects with all trains at the Meriden station. Those coming from the west via New York Central may prefer to come down from Springfield, Mass., to Meriden. If there is sufficient indication ahead of time as to the numbers arriving by various trains, special arrangements will be made for transportation from Meriden. Ask the bus driver to let you off at Downey House, which is on the Wesleyan campus in Middletown.

CORRESPONDENCE

SIR: In a recent paper in this journal Adams [ANAL. CHEM., 20, 891 (1948)] claimed that the polarographic half-wave potential for the reduction of Ti (IV) to Ti (III) in a supporting electrolyte composed of 1 *N* sulfuric acid, 8% urea, and saturated with sodium oxalate is greatly dependent on the concentration of titanium. He reported a negative shift of over 0.4 volt when the concentration of titanium was increased from 0.06 to 9.3 millimolar. Adams also claimed that the half-wave potential of titanium in the foregoing supporting electrolyte undergoes a large negative shift (about 0.5 volt) when ferric iron is added in concentrations up to 19 millimolar. According to our experience these conclusions are erroneous.

We have repeated Adams' measurements with identically the same supporting electrolyte (1 *N* sulfuric acid, 8% urea, saturated with sodium oxalate). The measurements were made at 25° C. with a low-resistance H-cell [Lingane and Laitinen, IND. ENG. CHEM., ANAL. ED., 11, 504 (1939)] containing a saturated calomel anode. The cell resistance was less than 500 ohms, and hence correction for *iR* drop was negligible. Polarograms were recorded with a calibrated Sargent-Heyrovský Model XI photographic polarograph, whose reliability has been conclusively established. Air was removed from the solution with pure nitrogen. With concentrations of titanium between 0.46 and 14 millimolar we found that the half-wave potential was constant at -0.285 ± 0.005 volt versus the saturated calomel electrode. Furthermore, we found that ferric iron in concentrations up to 15 millimolar does not have any appreciable influence on the half-wave potential of titanium.

We believe that Adams' erroneous conclusions are due primarily to his use of a cell with a very large resistance, and his failure to correct for the correspondingly large *iR* drop. This correction is a linear function of the current at the half-wave point, and hence of the concentration of reducible ion. Adams does not describe his cell in detail but does mention the use of a Beckman No. 9740 saturated calomel reference electrode, which is known to have a large resistance. This type of electrode is intended only for potentiometric (null point) measurements, and is entirely unsuitable as a working reference anode for polarographic measurements. It is also known that the type of recording polarograph used by Adams yields erroneously large values of half-wave potentials as a result of recorder lag, and this error increases with increasing wave height.

We have not been able to confirm Adams' conclusion that urea has a beneficial influence on the wave form of titanium, and have found that it does not function satisfactorily as a maximum suppressor when the titanium concentration is larger than about 5 millimolar.

Harvard University
Cambridge 38, Mass.
JAMES J. LINGANE
VICTOR VANDENBOSCH

SIR: The procedure outlined in this journal [ANAL. CHEM., 20, 891 (1948)] for the polarographic determination of titanium has been used with success for control work during the pilot plant operation of the extraction of alumina from clay. Additional determinations of titanium in alumina which had been treated with hydrogen fluoride and aluminum fluoride have been completed by this procedure, as the usual colorimetric procedure for titanium using hydrogen peroxide was not applicable in the presence of fluoride owing to the bleaching effect.

The conditions for the analysis were outlined in the paper—i.e., a high resistance calomel electrode and a Leeds & Northrup Electrochemograph. No correction was made for the *iR* drop. I am not familiar with the characteristics of the Sargent-Heyrovský type polarographs, and am thus unable to compare the conflicting conclusions.

The effect of urea, as well as a large number of commonly employed maximum suppressors, was thoroughly studied, and it was found that the specified concentration of urea was both adequate and necessary under the conditions stated in the procedure.

State College of Washington
Pullman, Wash.
DONALD F. ADAMS

The Analyst's Calendar

Symposium on Fine Particles and Resolution. Armour Research Foundation, Stevens Hotel, Chicago, Ill., June 9 to 11

American Council of Commercial Laboratories. Curtis Hotel, Minneapolis, Minn., June 23 and 24

American Society for X-Ray and Electron Diffraction. Cornell University, Ithaca, N. Y., June 23 to 25

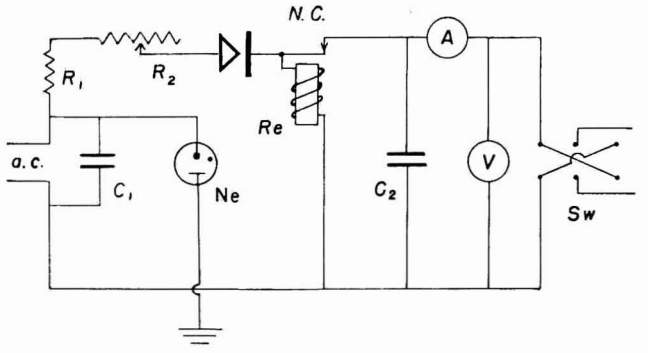
Second Annual Summer Symposium on Analytical Chemistry. Wesleyan University, Middletown, Conn., June 24 and 25

Fourth Instrument Conference and Exhibit. Municipal Auditorium, St. Louis, Mo., September 12 to 16

AIDS FOR THE ANALYST . . . . .

Electrolysis Microapparatus. Alexander P. Marion, Queens College, Flushing, N. Y.

An alternating–direct current transformerless electrolytic apparatus is useful in separations on a micro scale requiring currents of less than 0.2 ampere. Rectification of the alternating current is accomplished by a miniature selenium rectifier stack available at reasonable cost at local radio supply distributors. On direct current the series combination of R_1 and R_2 can be used to limit the current to the required amount.



A. 0-300 milliammeter, d.c.
C_1. 0.01-mfd., 600-volt, paper
C_2. 2000-mfd., 6-volt, electrolytic
Ne. Neon lamp, 0.25-watt, with resistor
R_1. 300-ohm, 25-watt
R_2. 15,000-ohm, 0.2-amp.
Re. Relay, normally closed
Sw. Double-pole double-throw switch
V. 0-6 voltmeter, d.c.

As the output from the rectifier is half-wave, some filtering action is necessary to smooth out the fluctuations. The 2000-mfd. condenser, C_2, serves satisfactorily and when checked on an oscilloscope showed a very slight ripple under full load and no ripple whatsoever under a light load. The regulation of the unit is improved by bleeding some of the available current through the coil of the relay, which must be normally closed. Because it serves as a protective device in case the potential across it exceeds 6 volts, it must have a coil resistance of approximately 1200 ohms and be activated by a direct current of 5 milliamperes. Other low-current 6-volt relays would be expected to function satisfactorily, but the lower the coil resistance the less current is available for the electrolysis. The relay may be replaced by a suitable resistor, but the full resistance of R_2 must then be placed in the circuit before the electrodes are removed from the solution; otherwise the output voltage will soar and both the voltmeter and the filter condenser will be ruined. With the relay in the circuit, however, these components are protected; the relay also sounds as a warning buzzer in such a case.

The rectifier element is a miniature, five-plate, selenium stack similar to No. 404D2795 of the Federal Telephone and Radio Corporation. The polarity of the electrodes can be reversed by the double-pole double-throw switch, *Sw*. R_1 is a current-limiting resistor used as a safeguard against burning out the apparatus, should a low resistance be placed across the electrodes with R_2 near zero setting.

The variable resistance, R_2, is a tubular resistor capable of passing 0.2 ampere and is used in this laboratory model in order to obtain any specified voltage at any current from a few milliamperes to the maximum rating. For routine analyses where the resistances of the solutions being electrolyzed fall within a restricted range, a rheostat of smaller ohmage could be used and the series resistance, R_1, increased accordingly.

Caution. One side of the alternating current line is brought directly to an electrode terminal. Should this happen to be the ungrounded side, a shock hazard is present. The neon lamp, which should be of the 0.25-watt type with a current-limiting resistor incorporated in the base, will eliminate this hazard if the plug connection to the power line is such that this lamp glows when the other side is connected to a good electrical ground. As a further precaution the electrodes should be inserted with the apparatus disconnected completely from the power lines or a double-pole single-throw on-off switch should be used to break both legs of the input.

Automatic Washing Apparatus for Precipitates. Alois Langer, Research Laboratories, Westinghouse Electric Corporation, East Pittsburgh, Pa.

In the preparation of precipitates for quantitative analysis of their elements in order to establish the composition, it is sometimes necessary to wash them very thoroughly to remove traces of foreign material. Especially with some of the voluminous precipitates of metals with organic reagents, the washing procedure is rather slow. To perform such an operation without any attention, even though several liters of washing liquid might be used, an apparatus was designed as shown schematically in Figure 1. The filtering follows the cycle prescribed for washing analytical precipitates—draining the liquid as far as possible before the next liquid is added and then filling the filter entirely each time.

The precipitate rests on a filter paper, the size of which is chosen according to the amount of the precipitate. The filter paper has to be laid firmly to the walls of funnel *F*, so that no air is sucked in between the glass and the filter paper during the washing. The washing liquid is stored in bottle *B*, and the disposed solution drops into flask *C*. As *B* and *C* form a closed system, by connecting them through tubing *A* as indicated, the amount of air displaced in *C* by the washing fluid will displace the same amount of liquid in *B*, which will flow through tubing *D* onto the precipitate, thus making the washing continuous. In order to make the procedure intermittent, a siphoning device is introduced between *B* and *F*. Siphon arm *S* is movable in funnel *E* by sliding in rubber tube *T*, thus making the amount of liquid to be dispensed at one time variable according to the filter size. The liquid flows through holes onto cone *H*, whereby the liquid is dispersed evenly over the whole precipitate. In order to eliminate dust and excessive evaporation of the liquid, the unit is shielded by a transparent cover, *P*. When once adjusted, the washing proceeds as long as there is liquid present in *B*. Only large fluctuations in room temperature disturb somewhat the smooth operation of the device.

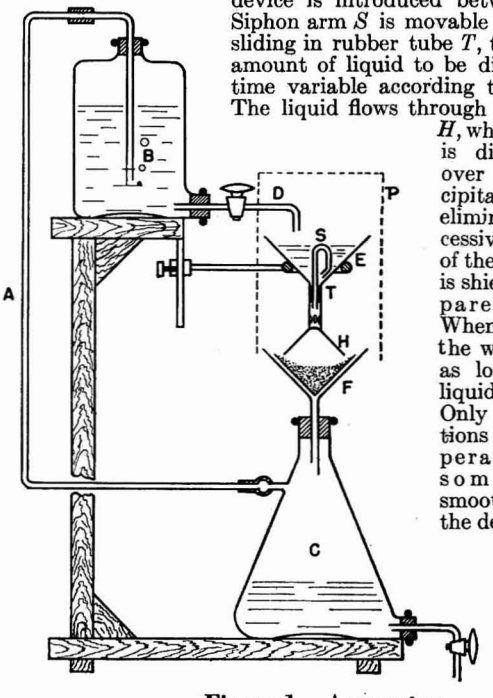


Figure 1. Apparatus