# INDUSTRIAL AND ENGINEERING CHEMISTRY

## ANALYTICAL EDITION

WALTER J. MURPHY, EDITOR • ISSUED NOVEMBER 21, 1944 • VOL. 16, NO. 11 • CONSECUTIVE NO. 22








29,600 copies of this issue printed.


Published by the American Chemical Society at Easton, Pa. Editorial Office: 1155 16th Street, N. W., Washington 6, D. C.; telephone, Republic 5301; cable, Jiechem (Washington). Business Office: American Chemical Society, 1155 16th Street, N. W., Washington 6, D. C. Advertising Office: 332 West 42nd Street, New York 18, N. Y.; telephone, Bryant 9-4430.

Entered as second-class matter at the Post Office at Easton, Pa., under the Act of March 3, 1879, as 24 times a year—Industrial Edition monthly on the 1st, Analytical Edition monthly on the 15th. Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918.

Remittances and orders for subscriptions and for single copies, notices of changes of address and new professional connections, and claims for missing numbers should be sent to the American Chemical Society, 1155 16th Street, N. W., Washington 6, D. C. Changes of address for the Industrial Edition must be received on or before the 18th of the preceding month and for the Analytical Edition not later than the 30th of the preceding month. Claims for missing numbers will not be allowed (1) if received more than 60 days from date of issue (owing to the hazards of wartime delivery, no claims can be honored from subscribers outside of North America), (2) if loss was due to failure of notice of change of address to be received before the dates specified in the preceding sentence, or (3) if the reason for claim is "missing from files".

Annual subscription—Industrial Edition and Analytical Edition sold only as a unit, members $3.00, nonmembers $4.00. Postage to countries not in the Pan-American Union $2.25; Canadian postage $0.75. Single copies—current issues, Industrial Edition $0.75, Analytical Edition $0.50; back numbers, Industrial Edition $0.80, Analytical Edition prices on request; special rates to members.

The American Chemical Society also publishes *Chemical and Engineering News*, *Chemical Abstracts*, and *Journal of the American Chemical Society*. Rates on request.

INDUSTRIAL AND ENGINEERING CHEMISTRY
Analytical Edition
PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY
WALTER J. MURPHY, EDITOR

# Techniques of Quantitative Spectrographic Analysis

J. RAYNOR CHURCHILL, Aluminum Company of America, New Kensington, Pa.

SPECTROGRAPHIC methods are in many respects unique, since in no other method of determining composition are so many different fields of science and technology embraced. The preparation of the sample often entails problems in chemistry, metallurgy, and machining practices. The excitation of the spectrum may involve chemical reactions, thermodynamics, electronics, and atomic physics. The spectrograph itself introduces a wide variety of problems in optics and mechanical design. The photography and measurement of the spectrum involve a host of problems in photographic technique, organic and inorganic chemistry, temperature control, mechanical design, electricity, electronics, and optics. All of the widely varied problems encountered are closely related, and the variable factors in sampling, excitation, photography, and measurement are interdependent. Any problem in one phase of the spectrographic procedure necessarily involves all or most of the other phases of the spectrographic procedure as a whole. We cannot consider the excitation source without also considering the type of samples to be analyzed, the spectrograph, the photographic process, and the photometry of the spectra. We cannot discuss the photometry of spectrograms without reference to the materials analyzed, the excitation source, the spectrograph used, and the photographic procedure.

Because of the almost unlimited number of combinations and permutations of electrical, optical, chemical, and physical variables possible in spectrographic analysis and because of the interdependence of these variables on each other, there is no optimum value for any one of the variables except in relation to all of the others. Similarly, in comparing apparatus, it cannot be said that any one spectrograph, microphotometer, or source unit is superior. We must always think in terms of combinations of conditions, combinations of circumstances, and combinations of equipment. It is possible, in fact very frequent, that two widely different spectrographic procedures using dissimilar apparatus are found to be equally effective in the analysis of a particular material. Neither the specific procedural steps involved nor the instruments used are necessarily interchangeable individually between two such methods.

In the laboratories of Aluminum Company of America, specific techniques have been developed for use with particular combinations of equipment. It is fully recognized not only that widely different techniques might prove equally satisfactory with the same combinations of equipment, but that other combinations of equipment might be just as satisfactory. In the following discussion of spectrographic techniques, most of the material was

*The Analytical Edition of Industrial and Engineering Chemistry is concerned largely with the publication of papers submitted to it by authors, and emphasis is placed on original material. Authors naturally lay greater stress on the advantages rather than the disadvantages of their techniques and methods, and this sometimes results, especially in the field of instrumental analysis, in misconceptions on the part of those who are not specialists.*

*To help analytical chemists keep abreast of developments, with knowledge of limitations as well as advantages of various methods, invited papers will be printed from time to time, written by specialists in various fields. L. T. Hallett, associate editor, is devoting a considerable portion of his time to the development of such papers. These will not be reviews, but will be presented for the purpose of evaluating methods and apparatus as analytical tools and will emphasize the rigorous standardization and care that are often required in their use.*

*Three papers on spectrographic analysis, published in this issue, serve to introduce this new editorial policy: "Techniques of Quantitative Spectrographic Analysis" by J. Raynor Churchill, "Proposed Minimum Requirements for Emission Spectrographic Equipment Used in Quantitative Analysis" by Charles D. Guettel, and "Qualitative Spectrographic Analysis" by G. W. Standen.*

Walter J. Murphy, EDITOR

derived from the collective experience of the many spectrographic laboratories of Aluminum Company of America.

## EXCITATION

In devising a spectrographic procedure to meet a particular need, the first decision to be made is to select a suitable excitation source. The choice of a source unit depends upon the spectral response required—i.e., sensitivity of detection—the quantitative accuracy desired, the specific nature of the elements sought, and the characteristics, both physical and chemical, of the samples to be analyzed. The excitation sources ordinarily used in emission spectrography fall into three broad classes: direct current arcs, alternating current arcs, and alternating current sparks. Each has its advantages in particular applications and, since the important differences between the three classes are in degree and not in kind, there is a wide overlapping of the fields of use.

Direct Current Arc. Until recently, the direct current arc has been the most widely used excitation source. Because of its high ultimate sensitivity and versatility of application, the direct current arc has been the general all-purpose source, without which the spectrographic laboratory was considered incomplete. Recent improvements in other sources and their use have altered this situation to such an extent that many modern spectrographic laboratories rarely use the direct current arc in quantitative metallurgical analysis, and in some specialized routine laboratories no arc facilities are provided.

The conventional direct current arc consists of a power source having an open circuit voltage of at least 220 volts and a variable resistance to regulate the current passing through the arc gap. The actual voltage drop across the gap is, of course, much lower than across the supply line and depends upon the current used, the resistance of the electrodes, and the resistance of the gap. Currents ranging from 3 to 10 amperes are generally used with metal electrodes, and currents ranging from 10 to 20 amperes are used with such nonvolatile materials as alumina, zirconia, or columbia. Metal samples are often used as self-electrodes in the arc when the melting point of the samples is sufficiently high. In most other cases the sample is placed in a cavity in a graphite rod which is used as the lower electrode. A second graphite rod is used as the upper electrode.

There are almost as many shapes of electrodes as there are laboratories using the arc. Lower electrodes vary from 0.125 to 0.3125 inch in diameter and vary in design from a simple rod containing a small cavity in the tip to the much more elaborate types providing capsules or platforms for holding the sample and constrictions to reduce heat loss. Simple electrodes are prepared on a motor-driven cutter, while the more complicated shapes are generally made on a lathe. The remarkable lack of unanimity among different laboratories in the choice of electrode dimensions and shapes seems to be caused partly by actual differences in analytical problems and partly by personal preferences and prejudices of spectrographers.

The direct current arc yields higher sensitivities of detection than most other sources for most of the elements detected by emission, and can be applied readily to almost any type of material. Most general qualitative analyses and many quantitative determinations of minute constituents, therefore, are best handled by the direct current arc. However, the general erraticness and poor reproducibility generally associated with the arc have prevented a wide application to the quantitative determination of any but minor constituents or trace elements. The disadvantages of this source in quantitative work arise largely from the fact that arc excitation is almost purely a thermal phenomenon. Any variable, such as gap spacing, electrode form, or matrix composition, which affects the amount of heat produced in the arc or the transfer of heat from the arc will affect the spectral intensities produced. When certain metals are present in the arc, oxides form rapidly and accumulate as a crust or beads, causing the arc to wander and sputter and to behave in a rather erratic manner. Also, the selective volatilization of the various constituents in the sample presents serious problems in controlling the discharge and in quantitative interpretation.

While the disadvantages discussed have largely excluded the direct current arc from most high constituent work other than qualitative or semiquantitative tests, it should not be inferred that these defects are insurmountable. Recent experiments in a number of laboratories have indicated that the objectionable effects usually associated with the direct current arc can be greatly reduced by the use of special types of electrodes and by the addition of fluxes or "buffers". Promising results on refractories, ore materials, and stainless steel samples have been obtained in several laboratories.

In the aluminum industry the direct current arc has been invaluable as a qualitative tool and has been applied to the determination of many minor constituents and trace elements. In most routine analysis on aluminum alloys, however, adequate response can be obtained with excitation sources of greater inherent stability than the direct current arc.

Alternating Current Arc. A more reproducible source than the direct current arc is available in the alternating current arc. This source, first described by Duffendack and Thompson (*3*), consists essentially of a 2000- to 4000-volt transformer equipped with a variable reactance or variable resistance, or both, to control its output. Currents of 2 to 4 amperes are generally used with this apparatus.

The alternating current arc produces a somewhat more stable arc than the direct current arc at a small sacrifice of sensitivity of detection. As in the case of any other excitation source, the alternating current arc has a field in which its characteristic deficiencies are at a minimum. As a quantitative tool the alternating current arc has been applied most effectively in the analysis of caustic liquors and certain salts and in these applications its sensitivity rivals that of the direct current arc, and the reproducibility is much better. On metal samples the alternating current arc is in most cases superior to the direct current arc in reproducibility but inferior in sensitivity of detection. Most of the shortcomings of the direct current arc appear to a somewhat lower degree in the alternating current arc.

In the aluminum industry, the alternating current arc has been a valuable tool in laboratories primarily interested in secondary aluminum. In this application, it provides a rapid and economical means of obtaining a qualitative analysis combined with a sufficiently accurate quantitative analysis for scrap sorting purposes. Among primary producers of aluminum, the alternating current arc has received little application because of a need for higher quantitative accuracy.

Alternating Current Spark. At present most quantitative spectrographic analysis of metals is accomplished by means of excitation sources classified as spark units. Formerly a conventional spark unit consisted essentially of a 10,000- to 40,000-volt transformer, a capacitance of 0.002 to 0.02 mfd., an inductance of a few hundredths or a few tenths of a millihenry, and sometimes a resistance of a few ohms. The analysis gap, the self-inductance, and the resistance were used in series across the secondary of the transformer, with the capacitance connected in parallel with the gap. Spark units of this type were used in most metallurgical applications of the spectrograph until more refined excitation units became available.

The above-described type of spark unit is often referred to as an uncontrolled spark or as a free-running spark to distinguish it from spark units of more recent manufacture equipped with synchronous gaps, auxiliary gaps, tuned circuits, or inductively coupled quenching circuits. Figure 1 shows a schematic wiring diagram of the controlled spark in its most popular form, which differs from the uncontrolled spark only in the insertion of the synchronous gap developed by Feussner (*4*). The synchronous gap serves two purposes: (1) It serves as a timing switch, permitting the unit to produce only one discharge (one train of oscillations) per cycle or half cycle. (2) The additional spark gap or gaps in series with the analytical gap have a stabilizing effect. Much the same effect is produced by the use of a station-

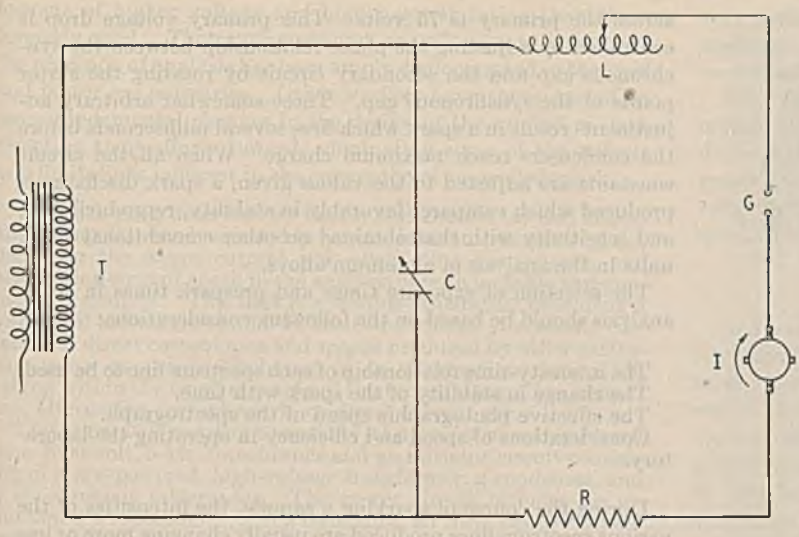



Figure 1. Typical Circuit for Controlled Spark Discharge

ary auxiliary spark gap subjected to a controlled air stream in place of the synchronous gap, although commercial models all employ the synchronous gap. Controlled spark units sometimes have a semifixed impedance in the primary which is more or less tuned with respect to the secondary to produce a condition approaching resonance. Other refinements, claimed to increase the stability of the discharge but not generally provided on commercial models, may include ultraviolet irradiation of either the analytical gap or the synchronous gap, or both, controlled air streams impinging on either or both gaps, or tuned quenching circuits inductively coupled with the spark circuit.

Controlled spark discharges, similar to those produced by the Feussner spark, have been produced by the use of electronic interrupters. Such a spark unit, developed for general spectrographic work, has been described by Malpica and Berry (*8*). Electronically controlled spark units have not been developed to the extent of those using mechanical interrupters and have received little application in industry. Because of possibilities of greater flexibility, more precise control, and elimination of moving parts, electronically controlled spark units may be expected to become increasingly important.

With the possible exception of new excitation units developed very recently, no other excitation unit has equaled the controlled spark unit in reproducibility and dependability in the quantitative analysis of metal samples. Accordingly, the spark unit has largely replaced both the direct current arc and the alternating current arc in most applications where its sensitivity of detection is sufficient and where there is a need for high precision. The chief limitations in the application of the spark lie in its low response as compared to the direct current arc or the alternating current arc, and the difficulties and inconveniences encountered in handling samples in certain physical forms, such as powders or solutions.

In connection with the high reproducibility of the controlled spark discharge, the literature contains frequent mention of standard deviations of 1% or less in repetitive analyses. While such claims are based on factual data and can be closely reproduced in most laboratories properly equipped for quantitative spark work, the standard deviations given should not be literally interpreted as measuring the expected accuracy of an analysis. These data are obtained on repetitive tests on the same sample, and the sample is generally specially selected for uniformity in order to remove all sampling effects in studying the discharge. Such tests yield valuable information as to precision or reproducibility on a particular sample but do not measure the actual effective precision of the analysis, nor even that portion of the analytical error which should be properly ascribed to excitation. It has been found that spectral response in a spark source is affected by the following factors not taken into account by simple reproducibility tests reported in the literature:

Composition of the matrix.
Physical form of the electrodes.
Differences in oxidation effects on samples and standards.
Particle size of dispersed constituents in the sample.
States of combination of the elements in the sample.
Metallurgical history of metal samples.

The above factors enter into most routine analysis by spark methods and cause changes in excitation which in turn produce measurable errors in analysis. In routine practice, every attempt is made to keep such variables at a minimum, but with conventional equipment and under conventional procedures, these effects result in a greater variability of excitation and hence greater analytical errors than would be predicted by simple reproducibility tests. Obviously, reproducibility is of little value if it is found that the result reproducibly obtained on a particular sample is in error because of some unknown difference between the sample analyzed and the standard sample.

Aluminum and magnesium alloys are particularly prone to show changes in the relative excitation of different wave lengths with changes in microstructure or metallurgical history. In routine analysis it is highly desirable, therefore, that the dimensions and form of the electrodes and the metallurgical history be carefully reproduced. When differences of this sort necessarily exist between analysis samples and standard samples, the quantitative effect of the differences must be evaluated and a correction applied in calculating the composition of the sample.

In routine analysis of aluminum alloys, it has been found that with spark excitation, the average deviation between spectrographic and chemical results usually lies between 2 and 3% of the amount present. Well over 90% of the results will show deviations of less than 5% and few, if any, will show deviations in excess of 10%. These figures are, of course, only approximations, since there are slight differences in the accuracy obtained on different elements and in different concentration ranges. The figures given are based on actual experience with relatively untrained spectrographic operators in routine laboratories and are less favorable but more pertinent than data taken in special tests undertaken to determine the best possible accuracy obtainable.

There are two main systems of applying the alternating current spark to the direct analysis of metal samples. Many laboratories, particularly in the steel industry, use two rod-shaped specimens as self-electrodes. Probably a greater number of laboratories use the system developed by Aluminum Research Laboratories involving the use of a machined flat surface of the sample as one electrode and a graphite rod as a counterelectrode. The choice between these two methods is often only a matter of convenience and usually depends on the forms in which samples are received, and on the standard samples available. Figure 2 shows the Petrey spark stand developed especially to handle disk-type samples.

The top plate of the spark stand serves both as support and electrical connection to the analytical sample. The lower electrode is high-purity graphite rod, 0.25 inch in diameter with a tapered end culminating in a hemisphere of about 0.06-inch radius. A freshly cut electrode is used for every test, and the gap is adjusted with the aid of the pivoting gap gage attached to the top plate on the left-hand side. The sample shown on the spark stand is a routine sample of the type regularly used by Aluminum Company of America, and consists of a circular disk originally 0.25 inch thick and 2.5 inches in diameter, cast in a cold steel mold. The sample as cast is usually recessed to a depth of about 0.10 inch in the central portion of one side to facilitate machining. The sample is so positioned on the spark stand that the center of the

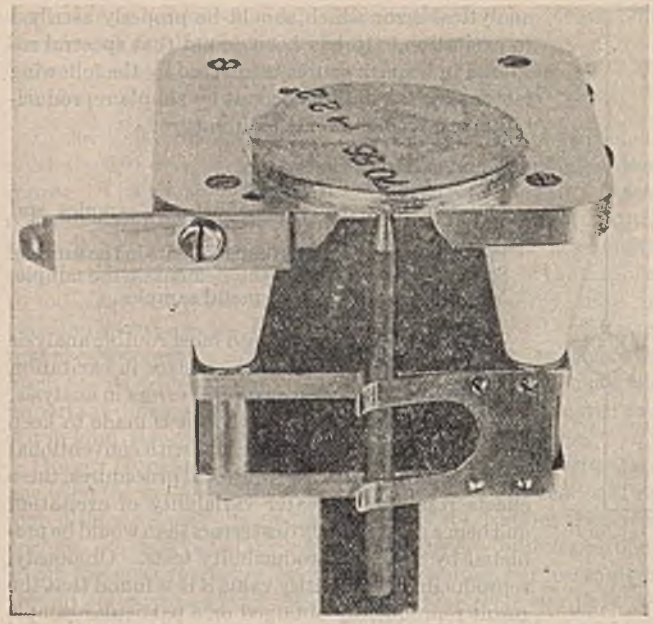


Figure 2. Petrey Spark Stand

spark falls approximately 0.375 inch from the edge of the sample and removed from the pouring sprue by an arc of 90° to 150°. The surface to be sparked is machined to a depth of 0.05 to 0.06 inch.

Following are the conditions of excitation employed on A.R.L.–Dietert controlled spark units in the routine laboratories of Aluminum Company of America:

| | |
|---|---|
| Nominal power setting | 2 kw. |
| Capacitance | 0.021 mfd. |
| Self-inductance | 1.44 mh. |
| Secondary resistance | None |
| Rated peak voltage of transformer | 35,000 |
| Primary current | 6.6 amperes |
| Primary voltage | 75 volts |
| Exposure | 10 seconds |
| Prespark | 10 seconds |

The nominal power setting of 2 kw. on this unit actually represents a power input of about 1.3 kw. This represents a relatively high-powered spark, permitting the use of the rather short exposure time of 10 seconds. The self-inductance of 1.44 mh. is provided by employing the full self-inductance provided in the spark unit itself (0.36 mh.) plus three additional coils of 0.36 mh. each. The figure of 1.44 mh. is the nominal figure supplied by the manufacturer. The actual value has not been accurately measured in these laboratories and is not considered very important, for the reason that a large excess of self-inductance is used and the character of the discharge is not affected by small changes in self-inductance under the particular electrical conditions employed. There are three main reasons for using this unusually large amount of self-inductance: (1) It favors the excitation of certain arc lines required in the analysis of aluminum alloys. (2) It produces spectra of low spectral background and low in air lines. (3) When self-inductance is sufficiently high, accidental changes in self-inductance resulting from changes in relative positions of source unit, spectrograph, electrical leads, and miscellaneous metal objects in the vicinity of the spark unit have a negligible effect on the discharge.

This spark unit contains an inductive reactance in the primary which is "tuned" with respect to the capacitance and other circuit constants. In actual practice, this "tuning" is accomplished empirically by adjusting the air gap or number of turns in the reactance to produce a certain primary current for each of the three power settings of the instrument. On the 2-kw. power setting, the primary reactance is adjusted so that there will be a current of 6.6 amperes in the transformer primary when the voltage drop across the primary is 75 volts. This primary voltage drop is controlled by adjusting the phase relationship between the synchronous gap and the secondary circuit by rotating the stator points of the synchronous gap. These somewhat arbitrary adjustments result in a spark which fires several milliseconds before the condensers reach maximum charge. When all the circuit constants are adjusted to the values given, a spark discharge is produced which compares favorably in stability, reproducibility, and sensitivity with that obtained on other conventional spark units in the analysis of aluminum alloys.

The selection of exposure times and prespark times in spark analysis should be based on the following considerations:

The intensity-time relationship of each spectrum line to be used.
The change in stability of the spark with time.
The effective photographic speed of the spectrograph.
Considerations of speed and efficiency in operating the laboratory.

During the course of sparking a sample, the intensities of the various spectrum lines produced are usually changing more or less continuously. The rise in temperature of the electrodes, the accumulation of vapors in the spark, the oxidation of the electrodes, the depletion of the more volatile constituents in the area sparked, and the change in spark gap as the electrode tips are volatilized, all tend to cause changes in intensity during the spark exposure. Because of differences in physical and chemical properties, no two elements behave in precisely the same way and at any particular time, lines of two different elements may be changing in opposite directions. Difference in behavior between the elements is usually greatest and the reproducibility of intensity ratios poorest during the first few seconds of sparking. As the discharge proceeds, the rate of change of both individual line intensities and intensity ratios between different lines gradually diminishes as the various factors controlling intensities approach a quasi-equilibrium. If the sparking duration is prolonged sufficiently the reproducibility of intensitie and intensity ratios again begins to deteriorate as the electrodes become pitted and encrusted with oxide. In most cases this condition obtains before the intensity ratios reach an equilibrium value. This is particularly true of aluminum and magnesium alloys. The 10-second prespark and 10-second exposure used in Aluminum Company of America laboratories are based on careful time *vs.* intensity studies, on statistical studies of reproducibility, and on considerations of time consumption and efficiency. As in the case of most other decisions in selecting optimum operating conditions, this decision was necessarily a compromise.

While the Petrey stand was originally designed to accommodate relatively massive samples on which a sufficiently large flat surface could be machined, many laboratories using this stand are called upon to handle other types of samples, such as wire, rods, rivets, drillings, powdered materials, and miscellaneous small fragments of materials. The Petrey stand can be conveniently adapted to the handling of metal samples of various sizes and shapes by the use of suitable clamps and holders. Powdered samples are usually formed into pellets by means of a briquetting press, with an addition of de-ashed natural graphite if the sample is a nonconductor of electricity or has poor briquetting properties. Such pellets are supported on the Petrey stand by special adapters and are sparked by essentially the technique used on metal electrodes.

Recent Developments in Excitation Units. Recognizing the need for excitation units of higher reproducibility, greater sensitivity of detection, and greater freedom from metallurgical effects, a number of laboratories have attempted to improve on the conventional controlled spark. These efforts have proceeded along two main channels. One group of workers has concentrated its efforts along the lines of improving the controlled spark by close attention to the mechanical construction of the interrupter, the use of voltage regulators of various types, and the use of trans-

formers of higher voltage and higher power rating than those formerly used. That such measures are effective in improving the precision of analysis has been amply demonstrated in the steel and motor car industries. Other workers have concentrated on more fundamental changes in the design of the excitation unit, directing their efforts towards eliminating some of the defects and limitations inherent in the conventional controlled spark.

One such unit, described by Hasler and Dietert (*5*) and Hasler and Kemp (*7*), has been used in several laboratories as a replacement for the direct current arc, alternating current arc, and alternating current spark in the analysis of both metallic and nonmetallic samples. This unit is a flexible apparatus, producing a variety of discharges similar to the conventional alternating current and direct current arcs and sparks produced by other excitation units, as well as discharges of an intermediate nature not falling within the usual meaning of the terms, alternating current arc, alternating current spark, or direct current arc.

The apparatus consists essentially of a power circuit powered by a 1000-volt, 5-kw. transformer and an initiator circuit consisting of a low-powered, high-voltage transformer, a condenser, and a synchronous interrupter. The power circuit includes an inductance, a capacitance, and a resistance, all three being variable over a rather wide range. Power circuit and initiator circuit are connected across the analytical gap in parallel and are rectified in the same sense. Because of the low voltage of the power circuit, the use of much larger capacitances than those employed in ordinary spark units is feasible, and resistance becomes an important and useful variable in controlling the nature of the discharge. The relatively low-powered initiator contributes only slightly to the spectra produced and, therefore, may be regarded as only a timer. The removal of the synchronous interrupter from the discharge circuit is an important improvement over the controlled spark unit in which a part of the intensity variations are traceable to the interrupter. Other features include a built-in voltage regulator actuated by the discharge circuit, a built-in oscillograph connected to show either the charge or discharge cycles, or both, a peak voltmeter in the discharge circuit, ultraviolet irradiation of the synchronous gap, "wiper contacts" on the shaft of the interrupter motor arranged so as to short the discharge condensers after each discharge train, and convenient controls for varying any of the circuit constants independently.

This instrument is too new to be judged on a basis of practical routine performance, but sufficient evidence has already accumulated to indicate that this unit, or units of similar fundamental design, may produce substantial improvements in certain routine analyses. No really comprehensive investigation of this source unit has yet been made, and because of the large number of combinations and permutations of electrical conditions provided, it will probably be many months before optimum conditions are definitely established for even the most common analyses. At Aluminum Research Laboratories, two types of discharge produced by this type of unit have been found extremely useful, one which will give spectra of excellent reproducibility when applied to most elements generally determined by spark technique, and one which will give remarkably good sensitivity of detection. Following are the circuit constants and general characteristics of these two discharges:

| | Type A | Type B |
|---|---|---|
| Voltage | 940 volts | 940 volts |
| Capacitance | 5 mfd. | 60 mfd. |
| Inductance | 480 microns | 480 microns |
| Resistance | 100 ohms | 50 ohms |
| Sensitivity | Comparable to A.C. spark | Equal to or better than D.C. arc |
| Reproducibility | Comparable to A.C. spark | Better than A.C. arc |
| Accuracy | Better than A.C. spark | Better than A.C. arc |

Type A produces results having approximately the same reproducibility as the controlled spark but yielding somewhat better accuracy in some cases because of a marked reduction in effects caused by the presence of other elements and by the metallurgical history of the sample. The Type B discharge appears to be superior in almost every respect to any discharge of comparable sensitivity of detection which can be produced on conventional arc or spark equipment.

While the results obtained under the conditions described indicate that such an excitation source is more generally useful than any other unit commercially available at the present time, it is very unlikely that these conditions are the optimum for the analysis of metals other than aluminum, since no comprehensive investigation has yet been made along these lines.

While virtually all the routine metallurgical analysis of Aluminum Company of America laboratories is now carried out on controlled spark units, it is probable that the spark units will be greatly modified or replaced by excitation units now under development. In the remainder of this paper, only the controlled spark units of the type currently used are considered.

## THE SPECTROGRAPH

In the selection of spectrographic equipment, the spectrograph itself usually represents the least difficult problem of any of the main pieces of equipment. Except for certain specialized work, any of the popular spectrographs are adequate for most routine applications. Very often the selection of a spectrograph is guided more by availability, policy, and personal preference than by any important difference in optics or mechanical design. The following considerations, however, should not be overlooked in the selection of the spectrograph:

Resolving power.
Linear dispersion (Ångströms per mm. at the plate or film, not angular dispersion as expressed by the physicist).
Wave-length range covered by a single spectrogram.
Relative amount of scattered light ("Littrow fog", for example).
Photographic speed.
Quality of the slit.
Flexibility.

With respect to resolving power and linear dispersion, any of the larger standard prism spectrographs or the available grating instruments using original gratings are adequate. While there has been some prejudice against 1.5-meter grating instruments in the ferrous field, recent applications in industry seem to indicate the adequacy of these instruments for steel analysis. Actually, the dispersion of a spectrograph is less important than resolving power in any comparison among popular makes. Present-day spectroscopic plates and films have sufficiently fine-grained emulsions to shift the emphasis from dispersion to resolving power. In a number of instances where closely adjacent lines must be used in the analysis of various materials at Aluminum Research Laboratories, it has been found that a 1.5-meter grating instrument yields slightly better results than the standard prism instruments at wave lengths above about 2800 Ångströms. Part of this effect appears to be caused by the inherent difference in resolving power and part by the fact that the particular grating instrument used shows less deviation from theoretical performance under conditions of changing temperature, mechanical shock, and hard usage. For very complicated spectra, such as those obtained from rare earth elements or elements of very high atomic number, any of the prism instruments or small fixed-setting grating instruments may be inadequate. For such work, larger more flexible grating instruments are usually required.

The wave-length range which can be photographed in a single spectrogram is very important in some applications. The advantages of being able to include in a single spectrogram suitable lines of all the elements to be determined in a sample are obvious. It is even more important in qualitative analysis, where occasionally the spectrographer is called upon for a complete qualitative analysis on a sample too small for more than one test. Greater dispersion, therefore, may be a disadvantage in some cases and it is usually necessary to compromise between dispersion and wave-length range. Among prism instruments of relatively high dispersion, an available Wadsworth-type spectrograph has the advantage of the additional spectrum range afforded by use of a 14-inch plate in lieu of the 10-inch plate used on comparable prism instruments. This is carried further on one of the newer grating spectrographs which uses either two 10-inch plates placed end to end or a single 20-inch film or plate.

**Table I. Characteristics of Several Makes of Spectrographs**

| | A.R.L.–Dietert | Baird (Large) | B. & L. (Littrow) | Gaertner (2 Lens) | Hilger (Littrow) | Jarrell-Ash (Grating) |
|---|---|---|---|---|---|---|
| Resolving power[a] | 2 | 1 | 3 | 3 | 3 | 1 |
| Dispersion[a] | 3 | 1 | 2 | 2 | 2 | 1 |
| Wave-length range (single spectrogram) | 2 | 4 | 3 | 1 | 3 | 2 |
| Scattered light | 2 | 1 | 2 | 1 | 2 | 1 |
| Resistance to vibration and shock | 1 | 1 | 2 | 2 | 1 | 2 |
| Auxiliary equipment available | 1 | 2 | 3 | 3 | 2 | 2 |
| Photographic speed | 2 | 3 | 1 | 1 | 1 | ..[b] |
| Slit | Adjustable | Fixed | Adjustable | Adjustable | Adjustable | ..[b] |
| Wave-length setting | Semi-fixed | Continuously variable | Stepwise variable | Continuously variable | Continuously variable | Continuously variable |

[a] Comparison limited to wave lengths most widely used in metallurgical analysis (2000–4000 Å.).
[b] No data available as yet.

NOTE. The numbers, 1, 2, and 3 denote the rank of the various instruments when arranged in descending order with respect to the particular attribute or quality compared, based on the manufacturers' literature and the author's experience.

In the determination of minor impurities with spectral sources of very high total intensities and when long exposures are required, a troublesome effect is encountered on all Littrow spectrographs. This effect, often referred to as Littrow fog, is a general fogging of the plate or film by the light reflected from the front face of the collimator lens. This inherent defect in the Littrow design is ameliorated to some degree in most Littrow spectrographs by masking the center of the lens or by tilting the lens slightly. The effect is eliminated in the Wadsworth-type prism spectrograph and scattered light of this sort is not encountered to any large degree on most grating spectrographs.

Most of the popular commercial spectrographs have similar photographic speeds. Grating spectrographs are more variable in this respect because of the poor reproducibility of the reflectivity of gratings. Grating instruments also differ appreciably as to relative response at different wave lengths, even among spectrographs of the same make. The relative speed of the grating at different wave lengths can be roughly controlled by the method of ruling. A grating ruled in such a way as to distribute the light intensity as evenly as possible among orders or wave lengths is usually a relatively slow grating at any specific wave length. When two or more grating instruments are to be used interchangeably in the same laboratory, it is desirable that the gratings be approximately matched by selection.

Most of the commercial spectrographs have slits of adjustable width. In the opinion of the author, most of the adjustable slits supplied on the popular makes of spectrographs are unsatisfactory. The laboratories of Aluminum Company of America have encountered a considerable amount of trouble and annoyance from inaccurate graduations, poor reproducibility of slit width, nonparallelism of jaws, damage by untrained operators, and sticking of the adjustment mechanism. Most of these defective slits have been replaced by commercially available fixed slits.

An important characteristic of a spectrograph is its flexibility—that is, the ease with which its wave-length range may be changed and the convenience and speed of adapting the apparatus successively to widely different problems. The latter depends to a larger extent on the optical bench and accessories than on the spectrograph itself. Most of the larger prism and grating spectrographs are of the so-called automatic type, an automatic spectrograph being one whose wave-length range may be adjusted by means of a single control, either a simple crank or a switch governing a motor. Among prism spectrographs, those which have a single control which simultaneously alters prism rotation, distance from collimator to plate or slit, and plate tilt in nonstepwise fashion are more satisfactory than those on which a number of fixed wave-length settings are provided. Several of the large grating spectrographs have satisfactory motor-driven mechanisms for changing wave-length range. The 1.5-meter grating instruments used widely in nonferrous analysis may be termed semiadjustable instruments. Camera and grating are permanently located on a diameter of the Rowland circle, and the wave-length range is determined by the position of the optical bench. The instrument is usually so arranged that the bench can be placed at two or three different positions to produce two or three wave-length ranges. When more than one wave-length region is required at frequent intervals, it is impractical to move the bench and it is customary to provide a permanent bench for each wave-length range required.

Whether or not it is important or even desirable to have a spectrograph whose wave-length range can be changed conveniently depends, of course, on the nature of the analytical work to be handled.

Research-type laboratories or any laboratories handling a wide variety of materials require flexible instruments. In some routine applications where a single wave-length range suffices for all analyses, as in the case of some routine aluminum laboratories, a fixed setting instrument may be preferable.

Table I summarizes a comparison among spectrographs used in metallurgical analysis in the United States. The so-called "medium" quartz spectrographs have been omitted because of the fact that these instruments are not used in modern industrial applications to as large an extent as the larger instruments. It should not be inferred, however, that the medium quartz instrument is necessarily inferior in all applications. These smaller instruments are adequate for many analyses of materials yielding relatively simple spectra, and in some work, the much greater wave-length range covered by a single spectrogram may be an important advantage. Nonferrous metal laboratories in Canada, Great Britain, and Germany have made rather wide use of medium quartz instruments. Excellent medium quartz spectrographs have been produced by a number of manufacturers. Today, in the United States, most spectrographic laboratories occasionally encounter analytical problems which require instruments of higher dispersion. Accordingly, since the cost of the spectrograph is small compared to the saving in analytical costs in replacing wet chemical methods with spectrographic methods, most industrial laboratories prefer to use one of the larger prism or grating instruments.

In general, the mode of use and the optical accessories are essentially the same for the various types of spectrographs. On any spectrograph, the external optical system is as important as the optical system in the spectrograph itself in making quantitative analyses. There are three main considerations in selecting the external system to be used on any spectrograph: (1) A representative or reproducible sample of the emitted light must be presented to the spectrograph. (2) The exposed portion of the spectrographic slit (or secondary aperture, in the case of astigmatic instruments) must be uniformly illuminated. (3) The light entering the collimator or grating must equally represent all points on the slit or secondary aperture. Also to be considered in the selection of the optical system is the effective photographic speed of the instrument.

The most generally satisfactory optical system consists of a lens placed near the slit or secondary aperture of the spectrograph, with the analysis gap so positioned with respect to the lens that an image of the gap is focused on the grating or collimator. The focal length of the lens employed depends upon what portion of the spark is to be sampled and on the photographic speed required. The maximum photographic speed which can be obtained without impairing the spectral line uniformity is produced by using a focal length such that the source

image precisely fills the collimator or grating. In spark work, the entire spark column, or a carefully limited central section of the spark, is usually sampled. In most laboratories spherical lenses are used for this purpose. However, some laboratories prefer to use a cylindrical lens placed with its axis horizontal, so that focus is obtained only in the vertical direction. Either a cylindrical or spherical lens used in the above manner will produce spectrum lines uniform along their lengths and will satisfy the requirements of light sampling. The spherical lens yields higher photographic speeds on astigmatic spectrographs, while the cylindrical lens is somewhat less critical in its positioning from side to side and makes the wandering of the spark or arc around the electrodes less effective in changing the intensity reaching the grating or prism. For many purposes, no condensing lens is required. In this case, there is a certain minimum distance from source to spectrograph, below which the previously mentioned requirements of the optical system are not met.

Spectrographic laboratories of Aluminum Company of America employ all the general types of spectrographs discussed. In routine work these instruments are used interchangeably by essentially the same techniques and with only those modifications in accessories necessary to suit the physical dimensions of the instruments and to compensate for differences in focal length and photographic speed.

## PHOTOGRAPHY OF THE SPECTRUM

The next problem in the development of a spectrographic method is the photography of the spectrum. While it is probable that direct quantitative interpretation of the spectrum by photoelectric means will eventually supersede photography to a great extent, it is even more probable that photography will remain one of the main problems of the spectrographic analyst for some time to come. Direct-reading instruments, such as the Quantameter (*6*), have been described in the literature, but such apparatus is not as yet commercially available. Accordingly, this discussion will be limited to photographic techniques of recording and measuring spectrum lines.

Among spectrographers there exists a diversity of opinion as to the relative merits of glass plates and films in quantitative work. The consensus of opinion seems to be that film is more consistent in contrast and response than plates. On the other hand, film is more difficult to handle during processing and densitometry, and only one available densitometer is equipped with a film holder. In Aluminum Company of America laboratories, considerable annoyance has arisen because of defective films and plates, the occurrence of defects being more frequent in plates than in film. Usually the choice between film and plates has been made by the manufacturer of the spectrograph, and most commercial instruments are equipped to handle one or the other, but not both. Similar emulsion types are available on both films and plates and the following comments apply to both:

In selecting a photographic emulsion for a particular analytical job, the most important considerations are response of the film to the wave lengths required, contrast and change in contrast with wave length, grain size of the emulsion, and ease and speed of processing. The following emulsions have been selected on the basis of the foregoing considerations for use in Aluminum Company of America laboratories:

| Emulsion | Application |
|---|---|
| Spectrum Analysis No. 1 | Routine analysis of aluminum and magnesium |
| 103-F, W. & W. process panchromatic | General qualitative and quantitative tests for all elements except potassium |
| I-L | Qualitative and quantitative analysis, including potassium |
| I-N | Specific tests for potassium |

Spectrum Analysis No. 1 (probably the most widely used spectroscopic emulsion in the United States) is fine grained, has high contrast (gamma—1.9 to 2.0 as used in Aluminum Company of America laboratories), satisfactory speed, and excellent processing characteristics. Its principal defect is its relatively rapid change of gamma with wave length. Ideally, of course, the emulsion should have the same gamma at any two wave lengths to be used in combination with each other. Although emulsions superior to Spectrum Analysis No. 1 in this respect have been developed, they have been objectionably slow in processing, somewhat coarse grained, and, in the case of film, inconvenient to handle on a routine basis because of excessive curling. It is the hope of most spectrographers that a film of uniform gamma, having the other desirable characteristics of Spectrum Analysis No. 1, will become available. Within rather broad limits the actual value of gamma is less important than the variation of gamma with wave length. A high gamma, if reproducible, makes densitometric measurements less critical, while a low gamma permits the use of a particular set of wave lengths over a larger range of concentrations.

In quantitative spectrographic analysis the development and processing of the photographic emulsion are highly important. Composition, agitation, and temperature of the developer must be reproduced very closely. The effective strength of a freshly prepared batch of developer changes rather rapidly on exposure to air and by depletion during the first few films or plates developed in it, but the change becomes more gradual thereafter. The use of fresh developer for every film or plate is not satisfactory because of variation in the amount of oxidation occurring during preparation and storage, and because of differences produced by minor variations in technique and purity of chemicals used. A satisfactory means of maintaining developer at sufficiently constant activity is the periodic replacement of a part of the developer in the tray with new developer. In Aluminum Company of America routine laboratories, half of the developer in the tray is replaced with new developer at regular intervals ranging from 2 to 4 hours, depending on the quantities of film or plates developed.

The temperature of the developer and the rate and method of agitation are also highly important. The agitation should be accomplished in such a way that the same amount of movement of the developer is produced at all points on the emulsion. No commercially available spectrographic developing machines are altogether adequate in this respect. Developing machines using longitudinally rocking trays produce slightly greater development near the ends of the trays and must be carefully regulated to prevent standing waves in the developing solution. Brushing the emulsion during development is a recognized technique for high-quality photographic work, but the brushing action must be accomplished mechanically rather than manually to obtain the desired reproducibility of development. Agitation by paddles moving close to, but not touching, the film has been suggested, and a wide variety of developing machines providing various types of oscillatory movement of the plate or developing solution, or both, have been used successfully.

One developing machine easily adaptable to routine spectrographic work is available commercially. While this machine provides only a simple longitudinal rocking motion, thereby falling short of the ideal machine for the most uniform development, it does have an acceptable thermostatic temperature-control system and has given reasonably satisfactory service in many routine laboratories. Machines of this type used in laboratories of Aluminum Company of America have given satisfactory results when properly adjusted. In using such a machine it is necessary to maintain the volume of developer within rather close limits and to adjust the agitation rate accordingly. The films or plates will still show some nonuniformity in development along their lengths, but as long as the films or plates are always placed in the same position relative to the tray, the effects are so slight and so reproducible as largely to cancel out in the spectrographic calculations. It is hoped that improved developing machines will become available in the near future.

In most spectrographic laboratories, developer, shortstop, and fixing solutions are all contained in the developing machine. Combination shortstop and hardening solutions, and combination fixing and hardening solutions are sometimes used. One satisfactory combination, probably the most widely used in American routine laboratories, consists of a dilute acetic acid solution used as a shortstop, and a fixing solution supplied commercially in liquid form for x-ray work.

Following are the essential details of the development and processing of the technique used in the routine laboratories of Aluminum Company of America:

Development for 3 minutes in Eastman Formula D-19 at 65° F.

Immersion for 2 to 3 seconds in 5% solution of acetic acid.

Fixation in x-ray fixing solution. The film or plate is allowed to remain in the fixer a few seconds after clearing, the total immersion time being on the order of 10 to 15 seconds.

The emulsion is lightly swabbed with a dripping wet cellulose sponge and the excess water removed by wiping with an almost dry sponge.

Films are dried in an infrared film dryer. Plates are dried in a warm current of air, either in a commercially available machine or in an apparatus prepared locally. SA-No. 1 films or plates are dried in about 1.5 minutes. Most other emulsions require longer periods.

The above technique was not designed for maximum speed. The development time can be greatly reduced by using a stronger developer or higher intensities, but there is some possibility of impairing reproducibility of development. Much more rapid developing and processing techniques are used successfully in laboratories in which high-speed analysis is a prime requisite, such as those of the Ford Motor Company and General Motors Corp.

Spectrographic emulsions are affected rather strongly by changes in relative humidity. For the most accurate work, it is highly desirable that the spectrographic laboratory be maintained at constant temperature and humidity.

## PHOTOMETRY

With the exception of the emission source, the microphotometer is the most critical piece of equipment in the spectrographic laboratory. (Certain manufacturers apply the term "densitometer" to instruments of this type. In this paper the more accurately descriptive term "microphotometer" is applied to all makes.) Among the commercially available microphotometers, no one instrument will necessarily satisfy all the requirements of a particular laboratory. All available instruments have desirable and undesirable features and many laboratories have found it necessary either to build their own microphotometers or to modify purchased instruments. All the present standard makes of microphotometers have been improved and the most active manufacturers in the field plan substantial improvements when conditions permit. At present the choice among standard makes is largely governed by the photographic material to be used—i.e., whether film or plates—by the availability of the various makes, and by the preference for recording or nonrecording instruments. If more than one make is available for a particular application, the following qualities should be compared:

Stability.

Legibility of scale or chart paper and the precision with which it can be read.

Area of the emulsion whose transmission or density is being measured at any one instant.

Area and magnification of the field of view on the spectrogram.

Whether or not the instrument is equipped or can easily be equipped with a wave-length scale or comparison spectrogram.

Operator comfort and operator fatigue.

Stability is highly important, for if the instrument will not yield dependable, reproducible readings, the other considerations are meaningless. The galvanometer scale, meter scale, or whatever means are provided for registering the measured function of density, should be sufficiently large for easy reading, should have a sufficient number of graduations to yield readings of the desired precision with a minimum of interpolation, and should occupy such a position that the operator is not required to turn or incline his head in looking back and forth from spectrogram to meter or galvanometer scale.

The area of the emulsion included by the beam of light reaching the photocell should be large enough to include a large number of emulsion grains, thus providing insurance against errors caused by nonuniformity within the grains themselves and random differences between individual grains. Optimum slit dimensions are governed by the grain size of the emulsion, the width and transverse contour of the line images to be measured, and the available length of line on the film or plate. With modern fine-grained emulsions, it is generally conceded that 10,000 square microns is a satisfactory cross-sectional area for the light beam. The width of the beam should be substantially less than the width of the spectrum line to ensure that the microphotometer is permitted to yield a deflection representing the maximum blackness of the image, and the beam should be shorter than the spectrum line by an amount sufficient to provide a practical margin of safety in adjusting the position of the spectrogram with respect to the beam. The beam should be provided with a rotary adjustment, so that it can be made parallel to the spectrum line mage. If the light beam is rectangular, its maximum length is limited by the curvature of the spectrum line image in the case of prism instruments, and if it is desired that relatively long spectrum lines be measured on prism spectrographs, a curved photometer beam is desirable. In analytical procedures designed for maximum speed on individual samples, the area covered by the light beam can be made relatively large by using long slits on the spectrograph. In procedures designed primarily for the most economical handling of large numbers of samples, as in the procedures used by Aluminum Company of America, relatively short slits are used in order to record a larger number of spectra per plate or film.

The area and magnification of the portion of the spectrogram visible to the operator during or immediately before measurement are important. The operator should be able to see a sufficient spectral range to enable him to orient himself quickly through the recognition of familiar groups of lines. The spectrogram should be magnified sufficiently to prevent the measurement of the wrong line when the desired line lies close to other lines and to permit the detection of dust particles or flaws in the emulsion or emulsion base which would introduce errors in measurement. In most applications, a magnification at least tenfold is desirable. For most purposes a field of view including 50 Ångströms is adequate if a satisfactory wave-length scale is used. If no wave-length scale is available a field of view of 100 or 200 Ångströms is usually desirable.

A wave-length scale or comparison spectrum, preferably both, semipermanently mounted in the microphotometer, is a desirable accessory for operational speed and convenience. This is particularly true in the training of inexperienced operators in routine applications, where the operator must develop speed in measurement before becoming thoroughly familiar with the spectra involved in the analysis. As operators become more experienced, the wave-length scale and standard spectrum are used less and less until finally they are used only for occasional reference.

Considerations of operator comfort and fatigue should be given a great deal of weight in the selection of an instrument for routine use. Several otherwise excellent microphotometers have been faulty in this respect and an instrument which is quite satisfactory for occasional use in research type work may be altogether inadequate for continuous use in a routine application because of the failure of the designer to consider the comfort of the operator. The following points are important in this connection:

Adequate illumination of all meters, scales, and dials regularly read during measurement.

Magnification, illumination, and clarity of the spectrogram image viewed during measurement.

Positions of spectrogram image and scale registering the measurement. Both should be approximately at eye level and close together.

Arrangement and ease of manipulation of controls.

Posture of operator during measurement. Instruments which require the operator to work with head or back inclined are particularly undesirable in continuous operation. The most generally satisfactory instruments with respect to operator fatigue are those in which the operator sits with back and head erect and can view both the spectrogram and the galvanometer or meter dial at approximately eye level.

When two or more microphotometers are to be used interchangeably in the same laboratory, a further requirement must be met. The relationship between deflection and photographic density should be the same for all the instruments to be used interchangeably. Otherwise, a separate emulsion calibration would be required for each instrument, causing complication and possible confusion in the analytical operations. For this reason, in Aluminum Company of America laboratories, microphotometers which are very nearly linear or can be adjusted to linearity are preferred. By a linear microphotometer is meant one whose deflections are directly proportional to the transmission of the photographic emulsion.

The amount of scattered light reaching the photocell is a very important consideration in the design of a microphotometer. However, in the author's experience, scattered light has been of secondary importance in choosing between standard makes of microphotometers, simply because the available instruments have been reasonably satisfactory in this respect. The most important effects of scattered light are the loss of sensitivity in the measurement of weak lines and the change in the response curve (the curve relating deflection and transmission). Since the latter is automatically taken care of in calibration, an increase in the proportion of scattered light merely necessitates higher reproducibility of deflections and greater precision in reading deflections. All other considerations being equal, an instrument producing a minimum of scattered light obviously is desirable.

The arrangement and mechanism of the various controls on the microphotometer are important in any particular application, but the requirements vary considerably among different applications. In mass production work, where greater emphasis is placed on economy than on the speed of an individual analysis, large numbers of spectra of relatively small height are used. In such applications an accurate rack and pinion mechanism or its equivalent is required for rapidly adjusting the position of the spectrogram prior to measurement. In high-speed analysis using spectra of larger height, the vertical positioning of the spectra is less critical and a manual sliding adjustment may be preferred for mechanical simplicity. In all cases, the controls should be arranged for maximum accessibility and ease of manipulation. Elaborate and complicated controls, either electrical or mechanical, should be avoided.

In the accurate measurement of a spectrum line, the speed of scanning the line is limited by the period of the galvanometer, meter, or other registering mechanism. If the line is scanned too rapidly, the proper deflection obviously will not be attained. Equally obvious is the desirability of scanning as rapidly as possible for economy of time. Hence, there is an optimum scanning speed which depends on the characteristics of the particular microphotometer and the width of the spectrum lines. In order to ensure a close approximation of this optimum scanning speed, a motor-driven scanning mechanism is to be preferred, providing that the mechanism is not overcomplicated. However, at least one very satisfactory standard make employs manual scanning. Regardless of the means provided for scanning, at least two types of movement parallel to the spectrum should be provided—a coarse movement for positioning the spectrogram prior to measurement, and a fine motion for actual scanning. One excellent microphotometer actually provides four such movements, the carriage being movable by manually pushing on it, by turning a crank, or by the use of a vernier knob, while the fourth motion is provided by the motor-driven movement of a receiver slit during scanning. At least one of these movements is superfluous.

**Table II. Characteristics of Three Makes of Microphotometers**

| | Leeds & Northrup | University of Michigan | A.R.L.-Dietert |
|---|---|---|---|
| Stability | 1 | 2 | 3 |
| Legibility of scale | 1 | 1 | 1 |
| Densitometered area | 3 | 1 | 2 |
| Field of view | 3 | 2 | 1 |
| Linearity | 2 | 2 | 1 |
| Provision for wave-length scale | No | No | Yes |
| Provision for reference spectrogram | No | Yes | Yes |
| Scanning | Synchronous motor | Manual | Synchronous motor |
| Racking | Rack and pinion | Manual | Rack and pinion |
| Plate or film holder | Plate | Plate | Plate and film |
| Position of film or plate | Vertical | Horizontal | Horizontal |
| Necessity for optical alignment | Each plate | Occasional | Occasional |
| Amplifier | Yes | No | Yes |

NOTE. Numbers 1, 2, and 3 denote rank of instruments when arranged in descending order with respect to the particular attribute or quality compared, based on manufacturers' literature and the author's experience.

Aside from the many successful instruments built by the users themselves or custom-built by instrument manufacturers, there are at least three satisfactory microphotometers available to American industry. Table II gives a comparison of these three instruments based on the experience of laboratories using them.

In laboratories employing spectrographs using 35-mm. film, the choice of the microphotometer is virtually limited to one designed specifically for the measurement of film. Most available instruments not only lack any provision for mounting film, but are very sensitive to the focus of the light beam on the emulsion or the focus of the spectrogram image on a slit. The difficulty of mounting a film in such a way that it will lie exactly in a plane perpendicular to the optic axis makes the application of several available microphotometers to the measurement of 35-mm. film rather impractical.

While a number of other makes of microphotometers are used in analytical work, only those which are currently available and are applicable to the methods described are included in this comparison.

Since most of the manipulative steps in photometric measurement are dictated by the design of the instrument used, there are only a few points in connection with the technique which require discussion. In most spectrographic procedures, the microphotometer is adjusted to yield certain standard deflections for unexposed emulsion and for complete opacity. On most conventional instruments, the adjustment is so made that a scale reading of 100 is obtained on unexposed emulsion and a reading of zero on an image of infinite density. If such an instrument is linear, the deflection registered represents per cent light transmission of the emulsion area measured. Unexposed emulsion is to be preferred to spectral background for adjusting the maximum deflection, even when significant amounts of spectral background are superimposed on the lines to be measured. In some laboratories, the deflection is set to the desired maximum in the spectrum itself at some selected point near the line to be measured. This is done as a means of correcting for spectral background and serves as such a correction in the proper direction, but not usually of the proper magnitude. This practice often results in greater errors in final analytical results than setting on unexposed emulsion and ignoring spectral background. The best procedure in most analyses is to do everything possible to keep spectral background to a minimum and then to correct for it either rigorously or not at all. Corrections for spectral background will be discussed further under "Calibrations and Calculations".

Two routine systems of photometric measurement are used in Aluminum Company of America laboratories. These are generally referred to as the vertical system and the horizontal system. In the vertical system, the operator measures a spectrum line of a given wave length in all spectra on the film or plate before proceeding to the next line. In the horizontal system, the operator measures the internal standard line and all the analysis lines in one spectrum before proceeding to the next spectrum. The vertical system requires somewhat less time for a group of samples but an instrument of greater stability.

The vertical system of measurement is used in those routine laboratories of Aluminum Company of America which are equipped with recording microphotometers. The high stability of the recording instruments used removes the principal disadvantage of vertical reading. Moreover, the arrangement of controls and the lack of any adequate comparator feature make horizontal reading impractical on the particular instruments used.

In Aluminum Company of America laboratories using nonrecording instruments, the horizontal system is usually employed for three main reasons: (1) Calculations are made concurrently with densitometric measurements and calculation is faster and more convenient when all data on a particular sample are presented in sequence before proceeding to the next sample. (2) The excellent field of view and convenient controls of the particular instruments employed largely eliminate the disadvantages of horizontal reading on a less conveniently arranged instrument. (3) Horizontal reading is slightly more accurate, since the effects of any drift of the microphotometer are minimized.

In the laboratories using this system, the adjustment of zero and clear film deflection is made before starting to measure the first spectrum and is checked between spectra at intervals whose frequency depends upon the stability of the microphotometer. In no case, however, is the zero or clear film deflection deliberately changed or adjusted during or between measurements on the same spectrum. If the validity of the adjustment is in doubt during the course of measuring a spectrogram, the settings are checked and the entire set of lines remeasured for the spectrum. Differences in unexposed film transmission at different locations on the film are ignored and the clear film deflection is always adjusted at the same location on the film. Corrective adjustments, intended to reduce errors caused by differences in unexposed emulsion readings at different locations on the film, have been found actually to increase the errors in routine analysis because the uncertainty of setting is directly effective in introducing an error in the measurement of intensity ratios. When the lines are measured with the same setting of the instrument, even though that setting be subjected to appreciable error (as much as 1 or 2% in routine work), the effect of the uncertainty of adjustment on the analysis line is virtually cancelled by the effect on the internal standard.

In most laboratories, pairs of operators are used as microphotometer-calculator teams. One member of the team operates the microphotometer and reads the deflections aloud, and the other makes the calculations and copies the data, often making out the final report as fast as measurements are made. Teams operating in this way have attained speeds of well over 400 reported determinations per elapsed hour in laboratories organized for large mass production of analyses.

While the actual manipulations of measurement are simple and any reasonably dexterous person can attain the speed and dependability of measurement required, the microphotometer team in a routine laboratory must carry the largest part of the responsibility for the entire analytical procedure. Of all the crew members, they are best situated to observe both the end results, the symptoms of maladjusted apparatus, or faulty technique. They must detect faults or symptoms of faults in the procedure and apparatus, such as the following:

Out of focus spectra.
Misaligned spectrograph slit.
Obstructions in the slit or elsewhere in the light path of the spectrograph.
Poor line uniformity because of misaligned optics on the spectrograph.
Poor reproducibility of absolute densities or of duplicate analyses.
Excessive changes in emulsion or concentration calibrations.
Excessively weak or strong spectrograms.
Evidences of defective development or processing technique on the films or plates.
Fogging of films by friction in camera exit.
Fogging of films or plates by light leaks in spectrograph or darkroom.
Scratched, dirty, or originally defective films or plates.
Erraticness of microphotometer when spark unit is turned on. This may be either the result of poor electrical shield or symptomatic of a fault in the spark unit.

In addition, the microphotometer team must select the analyses to be rechecked, must recognize unusual or unreasonable results, and must detect and report unexpected elements not included in the regular routine analysis. They must also detect any defects in the operation of the microphotometer, and should be able to make the necessary adjustments, replacements, and minor repairs necessary for efficient, uninterrupted operation.

## CALIBRATIONS AND CALCULATIONS

General Considerations. Methods for the quantitative interpretation of emission spectra fall into two general classes, comparison standard methods and internal standard methods. The term "comparison standard" is applied to all methods in which concentration is deduced from the blackness of the analysis line in the spectrum of the sample as compared to its blackness in spectra of standards. Internal standard methods embrace all methods in which concentration is determined through its relationship to the intensity ratio of a line of the element to be determined and a line of another element present in constant amount.

Comparison standard methods are used, at least to a limited extent, in most general analytical laboratories. While, in general, they are less accurate than internal standard methods, they are often more practical or convenient, particularly in cases where an internal standard line of suitable characteristics is not available. In the determination of minor impurities, comparison standard methods are often adequate and in a few special cases the absolute reproducibility of intensities is such that the comparison standard method approaches the internal standard method in accuracy.

The internal standard method owes its general superiority to the fact that variations in the internal standard line provide automatic correction for variations in excitation, optical alignment, exposure, and, to a limited extent, for variations in the response of the photographic emulsion. In the internal standard method it is assumed that all variables other than concentration affect the measured intensities of the analysis line and internal standard line to the same degree. Unfortunately, this assumption is not rigorously correct. Except in cases where the ionization and excitation potentials of the two elements are similar, changes in electrical conditions may affect the two lines differently. Moreover, differences in boiling point, stability of compounds, or self-reversal effects may also affect intensity ratios. In addition to these factors affecting the actual intensity ratios, a number of factors may affect the measurement of the relative intensities of the two lines in such a way as to affect the apparent intensity ratios. Misalignment of the source with respect to the optics, or of the optics in relation to each other, may produce a substantial change in apparent intensity ratio in cases where the intensity distribution of the two wave lengths is different in the source. (In other words, the sampling of the two wave lengths may not be proportional.)

The internal standard system corrects for variations in exposure time only to the extent that the reciprocity law of the photographic plate holds. Variations in the response of the photographic emulsion introduce errors in intensity ratios unless taken care of by calibration corrections. In view of the effects of these variables which influence intensity ratios, it is obvious that while the internal standard method tends to correct for the variables other than concentration, the correction it actually applies may not be precisely accurate. Since the magnitude of these effects decreases as the reproducibility of absolute intensity increases, every effort should be made towards the elimination of all variables which will affect intensities or intensity measurements. Whenever possible, measurements are restricted to line pairs of very similar excitation characteristics. Of course, in many analyses the analyst has little choice in the selection of lines. In the analysis of aluminum alloys, for example, the choice of lines available is so limited that little attention can be paid to atomic origins. In all applications, the validity of the fundamental assumptions of the internal standard method and the reliability of the results obtained depend upon the reproducibility of excitation optics and photography. For maximum accuracy, the method resolves itself into one in which an attempt is made to remove all variables in absolute intensities and then an approximate correction is applied to take care of the residual variability in the overall procedure.

Bearing in mind the foregoing limitations, the basic assumption of the internal standard method can be expressed by the simple relationship

$$C = f(I_a/I_s)$$

where $C$ is concentration, $I_a$ and $I_s$ are the relative intensities of the analysis line and internal standard line, respectively, and $f$ is simply used as a symbol to denote a mathematical function of the single variable $I_a/I_s$. While no assumptions concerning the nature of this function need be made, the form of the analytical curves derived from experimental data indicates that the following equation holds within the range of concentration over which an internal standard line is used:

$$\log C = K_1 \log I_a/I_s + K_2$$

For most practical purposes $K_1$ may be considered a constant, since the curves relating log $C$ and log $I_a/I_s$ generally have a negligible curvature in the relatively short range over which the particular line pair is used. Actually, of course, $K_1$ is a variable which is a function of self-reversal and other excitation effects. $K_2$ is virtually constant within any particular series of tests within a limited period of time, but has been found to vary over longer periods. Changes in $K_2$ are simply manifestations of the familiar "curve-drift" which will be discussed later.

Somewhat more rigorous equations relating concentration and intensity ratio have been suggested, but they are of only academic interest to the spectrographer involved in practical, quantitative analysis. The only assumption of the internal standard method as to the relationship between concentrations and intensities is that concentration is a function of the single variable, $I_a/I_s$.

Emulsion Calibration. Since the internal standard method involves the determination of intensity ratios, the first step in the procedure is the conversion of the data obtained from the microphotometer to relative intensities. Until a few years ago, this was accomplished by simply restricting all photometric measurements to the approximately straight-line portion of the H. and D. curve of the plate and assuming that $\log I = K \log T$, $T$ being the photometric deflection. With this assumption, deflection ratios were used directly in place of intensity ratios. This method is still used by a few laboratories in this country and by a considerable number of British laboratories. However, the general consensus today favors the methods of somewhat wider scope and greater accuracy, involving the actual calibration of the photographic emulsion in terms of relative intensities. Following are the five principal methods of emulsion calibration used in quantitative spectrography:

1. *Inverse Square Method.* This method consists of simply preparing a number of exposures using the source at various measured distances from the spectrograph slit with no lenses or other optical parts intervening between source and slit. It is complicated to some degree by diffraction effects at the slit and by changes in the sampling of the light as the distance from source to slit is varied. On prism spectrographs the method has seen practical use in a number of applications. The accuracy obtained depends, of course, on the absolute reproducibility of intensity and exposure time. This fact, together with considerations of speed and convenience, makes the inverse square method impractical in most routine work and restricts its application largely to special research problems and to verification work supplementing other methods of calibration.

2. *Step Wedge or Step Filter Method.* A step wedge or step filter placed at the vertical focus of the spectrograph (at the slit of a stigmatic instrument, at the secondary focus of an astigmatic instrument) may be used for the simultaneous production of a number of exposures of known relative intensities. The relative transmission of the various steps with respect to the wave lengths at which the calibration is to be made must be known in advance or determined by some other means of calibration. The chief disadvantages of this method lie in its dependence on uniformity of illumination and in the unavailability of satisfactory filters or wedges with respect to quality and uniformity of relative transmission at different wave lengths.

3. *Step Sector Method.* This is the most widely used system of emulsion calibration in quantitative spectrography. The design and mechanism of the step sector and the method of preparing step spectrograms have been described repeatedly in the literature and in the instructions supplied by the manufacturers of the equipment.

In the step sector method a series of calibration spectrograms is produced simultaneously through the use of a rotating disk having a series of stepped apertures so arranged that the ratio of the exposures of any two successive steps will be a constant, usually in the neighborhood of 1.5 or 2.0. The sector disk is placed immediately in front of the slit on a stigmatic spectrograph and at the secondary focus of an astigmatic spectrograph. Most step sectors have from 4 to 9 steps, although only 2 steps are actually required. It is assumed that the rotation of the sector is sufficiently rapid that the relative exposures produced by the various apertures can be treated as relative intensities, and the calibration curve may be prepared by simply plotting microphotometer deflections as ordinates against relative exposures as abscissas for several spectrum lines and fitting the curves together by moving them laterally until they are partially superimposed.

A more accurate and convenient means for combining the data from a number of wave lengths or from different step spectrograms is provided by the Preliminary Curve Method. This method consists of first plotting each deflection against the deflection for the same wave length in the succeeding step of the step spectrogram. In other words, the deflection for any given intensity, $I$, is plotted against the deflection for an intensity of $rI$, $r$ being the ratio between the successive exposures. After all the data are plotted in this way on either linear or logarithmic coordinates, the best smooth curve is drawn and a series of data, which will represent the average of all the individual series, can be read from the curve and used to prepare the final emulsion calibration curve. The use of a preliminary curve is dealt with in greater detail in the Two-Line Method described below.

While its practical usefulness is evidenced by its wide use in industry, the step sector method has the following disadvantages:

*a.* Large errors possible from stroboscopic effects with intermittent sources, such as the alternating current spark.

*b.* Small errors introduced by effects of the intermittency introduced both by the sector and the source itself on the response of the photographic emulsion.

*c.* Nonuniform illumination of the sector and nonuniform sampling of the light as a result of any defects in lenses or spectrograph slit, or as a result of target effects originating in nonuniform grating or prism.

*d.* Highly critical adjustment of sector, light source, and lenses necessary for accurate work.

*e.* Time consumption and inconvenience in having to make a special test under conditions usually differing from regular analytical exposure.

4. *Methods Involving Groups of Previously Calibrated Lines.* A calibration method involving the use of groups of iron lines whose relative intensities have been previously determined has been rather widely used for a number of years. In it, an attempt is made to select lines which not only cover the necessary range

of intensities in a single exposure but are invariant in relative intensity with respect to each other. The relative intensity values must be determined originally by one of the other calibration methods on the particular apparatus to be used in analysis. This method is particularly applicable to the analysis of iron and steel, since the iron spectrum affords a relatively wide selection of lines. The method, of course, can be applied to any other material by simply recording iron spectra on the plates or films for calibration purposes.

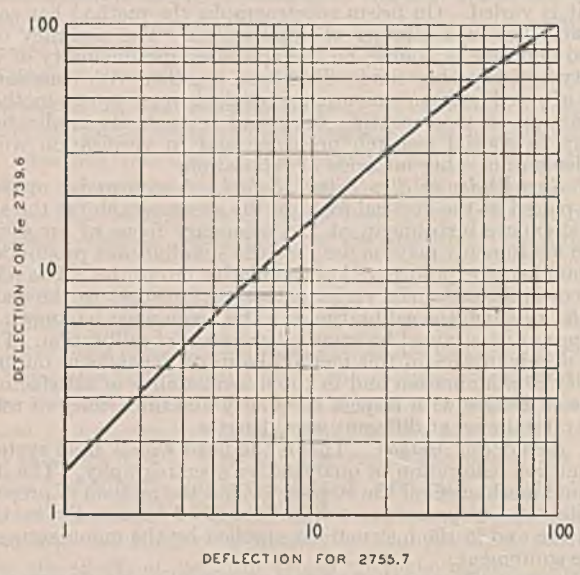



**Figure 3. Preliminary Curve Used in Two-Line Calibration Method**

In general, the method is superior to the step sector method and easier to use, once the large amount of preliminary experimental work has been done. As a matter of fact, the only serious objections are the relatively large amount of preliminary work which must be done in each laboratory and on each spectrograph and the direct dependence of analytical accuracy on the quality of this preliminary work. Attempts to transfer the relative intensity data on the calibration group from one type of apparatus to another have indicated that it is unsafe to base the work of one laboratory on a calibration group evaluated in another laboratory, unless the apparatus in the two laboratories is very similar and the excitation techniques are identical. The method could be based on calibration groups comprising lines of an element other than iron, but the author is unaware of any published works giving data on other elements. Most of the common nonferrous alloys have spectra too poor in lines to be used directly for calibration purposes by this method. In such cases, the use of iron groups is feasible and simply requires the preparation of iron spectra whenever a calibration is to be made.

5. *Two-Line Method.* This method combines most of the advantages of the foregoing methods and avoids most of their disadvantages. Because it has not been published before, a more detailed treatment is given in the following section.

Two-Line Method of Emulsion Calibration. In the two-line method, as in foregoing calibration methods, the starting point in calibration is the accumulation of data consisting of a number of microphotometer readings on the photographed images of spectrum lines bearing some fixed ratio of intensity to each other. In all cases, one significant datum is provided by two readings, one representing an intensity weaker or stronger by some fixed ratio than the other. In the step sector method, this ratio is determined by the ratio between successive step sector apertures, while in the two-line system the ratio is fixed by the inherent intensity relationship between two spectrum lines of different wave lengths. The actual intensity ratio of these two lines need not be known except very roughly.

The line pair used in the two-line method must have the following qualities:

It must occur at accurately measurable densities in the routine spectrograms of at least a portion of the samples analyzed daily in the laboratory.

The intensity ratio between the two lines should lie somewhere between 1.2 and 2.0.

The intensity ratio between the two lines must remain constant under ordinary operating conditions and be independent of composition over the range of routine analysis in which the lines are to be used. This is accomplished by using two lines of the same element which have similar excitation characteristics.

The wave lengths of the two lines should differ by no more than 100 Å. (the less the better) and should lie more or less centrally with respect to the wave-length range over which the calibration is to be used.

The lines must be sharply defined and free from interfering effects by other elements occurring in the alloy used for calibration.

In aluminum alloys, the iron spectrum affords the best opportunity for the selection of the calibration pair. Following are three line pairs which have been found satisfactory for use in routine laboratories engaged in the analysis of aluminum:

| Line Pair | Intensity Ratio | Suitable Alloys |
|---|---|---|
| Fe (I) 3047.6/Fe (I) 3037.4 | 1.26 | 85, 122 |
| Fe (I) 2966.9/Fe (I) 3037.4 | 1.56 | 85, 122 |
| Fe (II) 2755.7/Fe (II) 2739.6 | 1.23 | 2S, 14S, 17S, 24S, 53S, 195 |

The intensity ratios given are based on determinations made under the following conditions:

| | |
|---|---|
| Power setting | 2 kw.[a] |
| Spark gap | 3 mm. |
| Lower electrode | Graphite, 0.06-inch radius hemispherical tip |
| Upper electrodes | Machined aluminum disks |
| Spectrographs | Large two-lens prism, 1.5-meter grating |

[a] Nominal value indicated by the switch markings on spark unit.

It has been found that these intensity ratios are accurately reproduced on grating and prism instruments in different laboratories under the above conditions, and are virtually unaffected by the variables present in the routine procedures used in Aluminum Company of America laboratories. The actual values of the intensity ratios given, of course, are subject to the systematic errors of the step spectrum method but, as was mentioned earlier, the precise value of the intensity ratio of the calibration pair need not be known in the two-line method.

To carry out an emulsion calibration by the two-line method, a series of spectrograms is prepared using a sample selected from routine production and containing iron in such quantity that the range of deflections over which emulsion calibration is desired can be produced with optics as the only variable. Exposure time, slit width, power, self-inductance, electrode arrangement, and all other conditions of exposure and excitation, with the exception of the optical arrangement, should be the same as in routine analysis. The illumination should be varied from exposure to exposure in small steps. This may be done most conveniently on prism instruments by varying the distance from source to slit (using no condensing lens). On grating instruments the variation may be accomplished by changing the grating aperture or by using mesh screens or neutral filters. (The use of grating aperture as a variable with source image at grating requires that the line pair used shall have the same intensity ratio throughout the spark. For practical purposes, the lines given meet this requirement.) The series of exposures should include deflections over the entire range of deflections to be encountered in analysis. The films or plates must be processed under the same conditions as routine analytical spectrograms.

Both members of the line pair are measured in all the spectrograms, setting the full-scale deflection on an unexposed area of the film and measuring each member of the pair in each spectrum before proceeding to the next spectrum. For purposes of convenience, it will be assumed that the microphotometer is so designed and so adjusted that a reading of 100.0 is obtained on unexposed emulsion and a reading of zero on an image of infinite density.

From the deflection data a graph is prepared, preferably on logarithmic coordinates, plotting each deflection recorded for one of the members of the calibration pair against the deflection for the other member in the same spectrum. The curve so obtained is called the preliminary curve. A typical preliminary curve for the line pair, Fe 2739.5/Fe 2755.7, shown in Figure 3, was pre-

pared from data on Eastman SA No. 1 film. The sole purpose of such a curve is to provide a means of determining for any particular deflection produced by an intensity $I$, the deflection produce by an intensity equal to $rI$, where $r$ is the intensity ratio of the calibration lines. This curve has the same function and significance as the preliminary curve in the step sector method, where $r$ becomes the ratio between successive step sector apertures.

The final emulsion calibration curve is prepared from a series of points determined from the preliminary curve as follows:

As the initial point on the emulsion curve, select a deflection higher than any to be used in routine analysis, 98.0, for example. Refer this value to the preliminary curve and determine the deflection for $r$ times the intensity represented by a deflection of 98.0. Referring to the example curve shown in Figure 3, where deflections for $rI$ are plotted as abscissas, an ordinate of 98.0 corresponds to an abscissa of 96.7; 96.7 is now applied as ordinate and a third deflection is read on the abscissa scale. Proceed in this manner, recording each deflection value read from the ordinate scale and applying it as an abscissa to determine the next value, until deflections smaller than any used in routine analysis are obtained.

Table III shows the data so obtained from the preliminary curve in Figure 3. If the value of $r$, the intensity ratio of the calibration pair, is known, the data from Table I may be used to plot the familiar H. and D. curve. If the value of $r$ is not precisely known, and for the most precise work it cannot be assumed to be known exactly, the photometric deflection, $T$ or log $T$, is plotted against log $a^n$, where $a$ is an arbitrarily selected number to be used in place of $r$ and $n$ is the exponent applied to $r$ to obtain relative intensities (see column 1, Table III). The emulsion calibration curves obtained when a value of 1.5 is assigned to $a$ are shown by the solid lines in Figure 4. The numerical values for $a^n$ are shown in the third column of Table III.

The calibration pair used to assemble these data was known to have an intensity ratio of 1.23. Had actual relative intensities been used as abscissas, the curve shown by the broken lines in Figure 4 would have been obtained. Either of these two curves could be used as the emulsion calibration curve, the only difference being that in the case represented by the broken curve, microphotometer deflections would be translated into relative intensities, while in the more general case represented by the solid line, all relative intensities would be raised to a constant power, log $a$/log $r$. Since, according to the basic assumptions of the internal standard method, concentration is a function of the single variable intensity ratio, it makes no difference whether or not numerical values of the relative intensities observed are raised to a power, as long as that power is a constant. It is, therefore, obvious that it is unnecessary to know the precise intensity of the calibration pair. (Similarly, in the step spectrum method it is unnecessary to know the ratio between the apertures, as long as the ratio between each two successive apertures is the same).

**Table III. Typical Data Used in Plotting Emulsion Calibration Curves**

| $n$ | Deflection (Read from Preliminary Curve) | $a^n$ ($a = r = 1.23$) | $a^n$ ($a = 1.50$) |
|---|---|---|---|
| 0 | 98.0 | 1.00 | 1.00 |
| 1 | 96.7 | 1.23 | 1.50 |
| 2 | 94.5 | 1.51 | 2.25 |
| 3 | 90.9 | 1.86 | 3.38 |
| 4 | 85.7 | 2.29 | 5.06 |
| 5 | 78.2 | 2.82 | 7.59 |
| 6 | 68.0 | 3.46 | 11.4 |
| 7 | 55.3 | 4.26 | 17.1 |
| 8 | 42.2 | 5.24 | 25.6 |
| 9 | 30.5 | 6.44 | 38.4 |
| 10 | 20.8 | 7.93 | 57.7 |
| 11 | 13.6 | 9.75 | 86.5 |
| 12 | 8.8 | 12.0 | 129.8 |
| 13 | 5.6 | 14.8 | 194.6 |
| 14 | 3.6 | 18.1 | 291.9 |
| 15 | 2.3 | 22.3 | 437.9 |
| 16 | 1.5 | 27.4 | 656.9 |

NOTE. These data were prepared from preliminary curve shown in Figure 3 and used to prepare emulsion calibration curves shown in Figure 4.

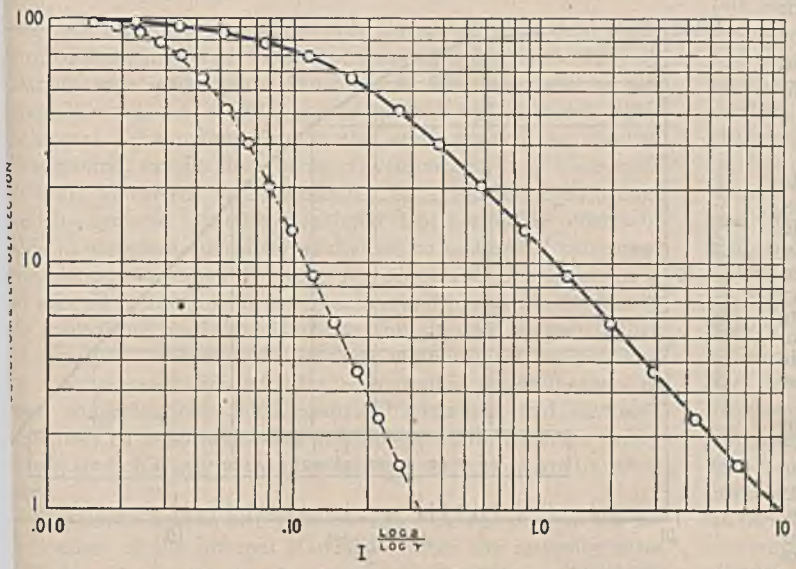



Figure 4. Emulsion Calibration Curves

The emulsion calibration curve prepared in the two-line method is used in exactly the same way as the calibration curves prepared by the other methods described. The use of the arbitrary constant $a$ in place of the intensity ratio of the calibration pair does not alter the mode of application of the calibration curve and does not affect any of the succeeding steps in the calculation procedure. For purposes of simplicity and clarity, the constant exponent introduced when $a \neq r$ will be disregarded and it is understood that whenever relative intensity or intensity ratios are mentioned, the actual numerical values used may be raised to the power log $a$/log $r$. This will have no effect on the procedure or results.

CALCULATION OF INTENSITY RATIOS. The intensity ratio represented by the deflections produced by two spectrum lines may be determined by simply referring the deflections to the emulsion calibration curve and dividing the numerical values of relative intensity obtained. An easier and faster procedure is available when the emulsion calibration curve is mounted on a conventional calculating board with a sliding logarithmic abscissa scale.

For purposes of illustration, assume that the analysis line gives a deflection of 28.0 and the internal standard line a deflection of 11.6. Referring these deflections to the typical calibration curve (solid line) in Figure 5, $I_a$, the relative intensity for the analysis line, is found to be 0.152, and $I_s$, the relative intensity of the internal standard line, is 0.351. The intensity ratio then is 0.152/0.351 or 0.433. Since the numerical values assigned to the abscissa scale are only relative and since this scale is logarith mic, it is obvious that the value obtained for the intensity raito is independent of the position of the scale relative to the curve. Accordingly, a more direct determination of $I_a/I_s$ can be made by moving either the curve or the abscissa scale horizontally until $I_s$ becomes unity, whereupon $I_a/I_s$ becomes equal to $I_a$. In the specific example considered above, the curve would be moved to the position shown by the broken line, so that a deflection of 11.6 corresponded to a relative intensity of unity. The value of $I_a/I_s$ is then the abscissa corresponding to a deflection of 28.0.

While the illustration used in the above example was for a log-log calibration curve as used on a nonrecording microphotometer, the same considerations apply and the same procedure is used on the semilogarithmic plot often used for recording microphotometers.

PREPARATION OF EMULSION CALIBRATION SCALES. When a nonrecording microphotometer is used in Aluminum Company of America laboratories the emulsion calibration curve is projected on a scale to be used slide rule fashion

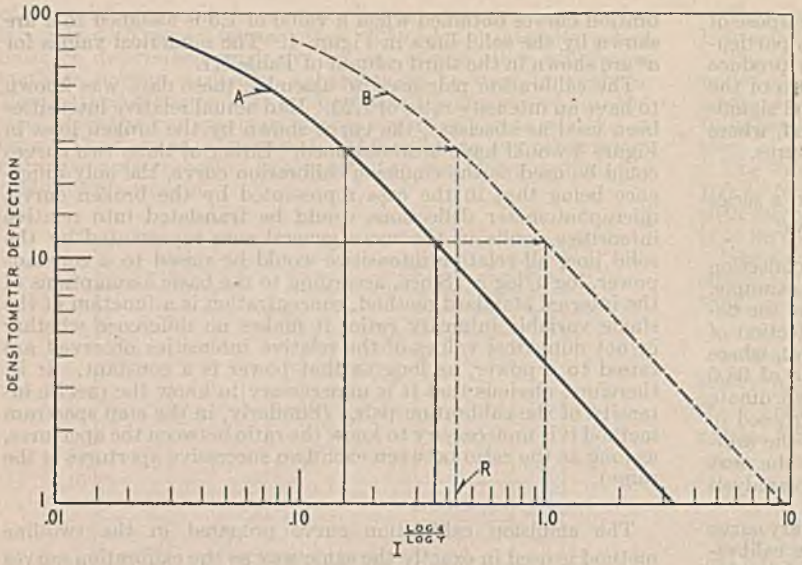



Figure 5. Calculation of Intensity Ratio from Emulsion Calibration Curve

with a logarithmic scale to calculate $I_a/I_s$ values. The method of preparing this scale is shown in Figure 6.

The entire ordinate scale from deflections of about 3 to 95 is projected as shown in the figure for the six values, 5, 10, 20, 40, 60, and 90. The scale prepared as described above will be referred to as the "emulsion calibration scale", or simply as "the calibration scale", in further discussions. The calibration scale is used slide rule fashion with the fundamental log scale to determine $I_a/I_s$ values from deflection data. To do this, the two scales are adjusted with respect to one another, so that unity on the log scale coincides with the deflection for the internal standard line as read on the calibration scale. The value of $I_a/I_s$ appears on the log scale at the point in juxtaposition with the deflection for the analysis line on the calibration scale.

The foregoing slide rule technique is practical only when the characteristics of the film used and the method of development and processing are sufficiently reproducible that the emulsion calibration curve does not have to be changed very frequently. This method was developed for use in the aluminum industry, where it has been found highly satisfactory from a standpoint of efficiency, accuracy, and convenience, particularly when the Dunn-Lowry calculator is used.

Periodic Checking of Emulsion Calibration Curves and Calibration Scales in Two-Line Method. After the emulsion calibration curve or scale has been prepared and put into service, it should be checked at regular intervals. Two types of verification tests are suggested as a regular part of the analytical routine.

A series of measurements of the calibration pair should be made every day in regular production spectrograms. The data so obtained are referred to the emulsion calibration curve or scale and the fundamental log scale, and the apparent value of the intensity ratio is determined. If the result is greater or less than the intensity ratio (real or arbitrary) used in the original calibration, the response of the emulsion has changed, and if immediate corrective steps in photographic processing do not restore the original value of intensity ratio, a new calibration curve or scale is prepared.

A second type of verification test of greater rigor should be applied whenever the foregoing test indicates a change in contrast, when starting to use a new emulsion batch, or when a faulty calibration is indicated by inconsistencies among percentage scales. This test consists of preparing a series of spectrograms of the alloy used for the original calibration at three different intensity levels. The effective photographic speed of the spectrograph should be adjusted to yield low, medium, and high microphotometer deflections for the three series of tests. The calibration pair is measured in all the spectra and the intensity ratios are determined. If the emulsion calibration curve or scale is still valid, the average ratio obtained in each of the three groups of reading will be equal to the original value.

In ordinary spectrographic work, the curved portion of the calibration curve is a function of the straight-line portion, as long as the same emulsion formula is used. Accordingly, the calibration scales obtained in the laboratory over a period of time may be classified according to the slopes of the straight-line portions of the curves and can be preserved for future use at such a time as tests indicate a slope represented among former curves.

Background Corrections. In the foregoing procedure the effect of spectral background (continuum) was ignored. In most industrial procedures, the excitation conditions, the optical arrangement, and the exposure time are selected with a view towards keeping spectral background to a minimum, and in the most widely used spark techniques the background is kept sufficiently low to have no significant effect on analytical results. When determining small amounts of certain constituents by either arc or spark techniques, excessive spectral backgrounds are sometimes unavoidable. In such cases the analyst has no recourse but to make a correction for background. Unfortunately, no rigorous method of background correction has been developed and whenever the background is sufficient to require correction the errors in analysis will be greater than when no background is present, regardless of the method of correction. The amount of background which may be tolerated without correction depends upon the absolute reproducibility of densities, the source of the background, the degree to which the photographic emulsion shows the Eberhart effect, and the accuracy required of the analysis.

Obviously, if the reproducibility of the densities of both lines and background is high, much larger amounts of background may be tolerated. If the background is caused by the major components of the samples and if its intensity is proportional to the intensity of the internal standard line, the only systematic errors introduced by spectral background are those due to the Eberhart effect. Spark analyses are generally in this

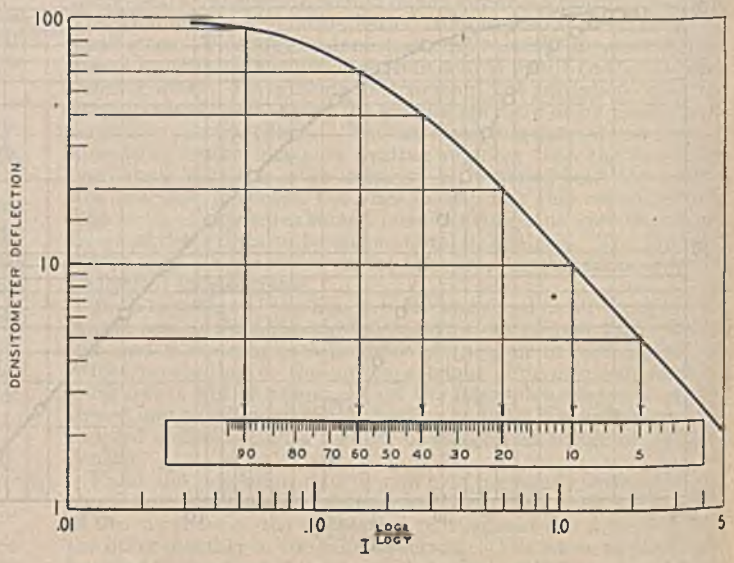



Figure 6. Preparation of Emulsion Calibration Scale

category and, if an emulsion and a processing technique which would eliminate the Eberhart effect were available, background corrections would be of no value in most spark work. Excessive background would still be undesirable, since the reduction in the sensitivity of the test by inclusion of background in the measurements would increase the random error of analysis. Background caused by the matrix or by the internal standard element can sometimes be expressed graphically as a function of the intensity of the internal standard and a correction applied which takes into account the Eberhart effect. This is accomplished by correlating the emulsion calibration curves of the continuum and the spectrum lines. The method can be applied to slide rule type calculations by the addition of a third scale providing the correction.

When the background is affected by variables which cannot be assumed to be a function of the intensity of the internal standard line, as often is the case in direct current arc techniques, a more rigorous correction method may be required. Many practical expedients have been employed, the most common being the following:

*a.* Calculation of "net densities" of the spectrum lines by using the deflection of the background adjacent to the line in place of $I_0$, the deflection for complete transparency in the conventional density formula

$$D = \log_{10} I_0/I$$

*b.* Adjusting the deflection to 100 for the background near the line (equivalent to *a*).

*c.* Numerically adding the difference in deflection between background and unexposed emulsion to the observed line deflection.

*d.* Converting the deflection of the background near the line to intensity by the use of an emulsion calibration curve prepared for a continuum and subtracting this intensity from the total intensity of the line plus background as determined from the conventional emulsion calibration curve.

None of the foregoing methods is rigorously correct and their use is justified only when the end results are found by experiment to be sufficiently accurate. Of the four methods given, *d* is generally more accurate, but it is cumbersome and time-consuming. A modification of this procedure is described by Strock (*11*). Strock also gives an excellent discussion of the problem of background correction as encountered in direct current arc work and while his method is too cumbersome for most high-speed, high-volume, industrial applications, it is probably the closest approach to a rigorous method of background correction.

In the foregoing discussion, only the so-called spectral background was considered. On some spectrographs, particularly on Littrow-type instruments, the plate or film may bear an appreciable amount of background caused by scattered light. Scattered light presents much the same problem as spectral background, except that, being polychromatic, it is even more difficult to correct for accurately. Both spectral background and background caused by scattered light are highly objectionable in excessive quantities, and since no method of correction completely eliminates the errors introduced, the best practice is to take all precautions to keep background to a minimum and to do everything possible to improve the absolute reproducibility of densities. Fortunately, in most metallurgical analysis and in a large proportion of all spectrographic determinations of high concentrations, both spectral background and scattered light can be kept sufficiently low and absolute densities reproduced to such a degree that background corrections are unnecessary.

Working Curves and Percentage Scales. Under the assumptions of the internal standard system the intensity ratio $I_a/I_s$ for a particular alloy or material is a function of the single variable, concentration. Therefore, when the value of $I_a/I_s$ has been determined as described above, concentration can be determined if sufficient data on samples of known composition are available. The correlation of such data is generally accomplished graphically and, because of the nature of the mathematical relationship between concentration and the intensity function, it is convenient to use a log-log plot. Such a graph is called a "working curve". For purposes of this discussion the working curve is defined as a graph on which concentration expressed in per cent is plotted logarithmically on the ordinate scale against $R$ plotted logarithmically on the abscissa scale.

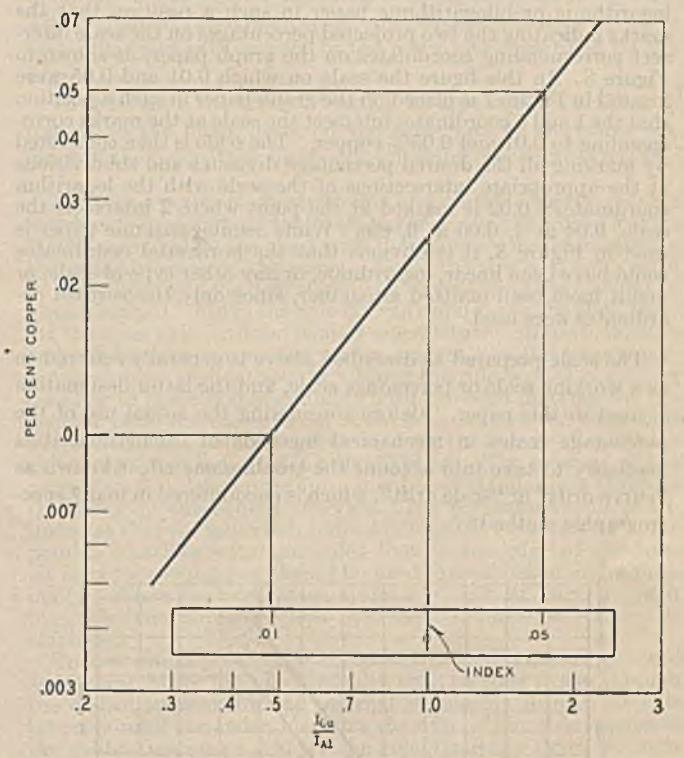



**Figure 7. Projection of Initial Values on Percentage Scale from Typical Working Curve**

Working curves are based on relatively large amounts of data obtained from standard samples containing known amounts of the element to be determined. All details of excitation and photography should conform to the practice to be used in analyzing unknowns. The arithmetic mean $I_a/I_s$ value is used as abscissa, and the known percentage as ordinate in determining each point on the working curve. In many cases the working curve is a straight line within the ranges of concentration covered by a particular line pair. In most routine work the assumption of linearity is sufficiently valid. Self-reversal, failure to correct for excessive background at the analysis line, and the effects of increasing concentration on the behavior of the internal standard line each may contribute to curvature of the working curve. In the routine analysis of aluminum it has been found that the deviation from linearity is insignificant except when measuring very weak lines without making a background correction.

Once the working curve is plotted it can be used directly, for the determination of per cent constituent if $I_a/I_s$ is known. However, a simpler and more rapid procedure is possible. In the determination of $I_a/I_s$ by the use of either the emulsion calibration curve or the emulsion calibration scale, $I_a/I_s$ is read directly from the fundamental log scale. Since concentration is assumed to be a function of the single variable $I_a/I_s$, it is obvious that a concentration scale bearing an index mark to denote the location of unity on the fundamental log scale can be used in place of the log scale. Since the concentration corresponding to each value

of $I_a/I_s$ can be read from the working curve, the preparation of this scale is easily accomplished. The procedure is as follows:

Consider the typical working curve shown in Figure 7. To prepare a percentage scale from this curve, all percentage readings can be projected from the ordinate scale onto the percentage scale, as shown for 0.01 and 0.05%. This procedure can be carried out precisely as described for the preparation of the emulsion calibration scale. However, when the working curve is a straight line, the following simpler and more rapid procedure is used:

Project only two percentages on the scale, selecting percentages near the two extremes of the working curve. Also mark the scale with the index line (the point corresponding to $I_a/I_s = 1$). Remove the scale from the calculating board and place it on semilogarithmic or bilogarithmic paper in such a position that the marks indicating the two projected percentages on the scale intersect corresponding coordinates on the graph paper, as shown in Figure 8. In this figure the scale on which 0.01 and 0.05 were located in Figure 7 is placed on the graph paper in such a position that the 1 and 5 coordinates intersect the scale at the marks corresponding to 0.01 and 0.05% copper. The scale is then completed by marking all the desired percentage divisions and subdivisions at the appropriate intersections of the scale with the logarithm coordinates: 0.02 is marked at the point where 2 intersects the scale, 0.04 at 4, 0.06 at 6, etc. While semilogarithmic paper is used in Figure 8, it is obvious that the horizontal coordinates could have been linear, logarithmic, or any other type of scale, or might have been omitted altogether, since only the vertical coordinates were used.

The scale prepared as described above is generally referred to as a working scale or percentage scale, and the latter designation is used in this paper. Before considering the actual use of the percentage scales in mechanical methods of calculation, it is necessary to take into account the troublesome effect known as "curve drift" or "scale drift", which is encountered in many spectrographic methods.

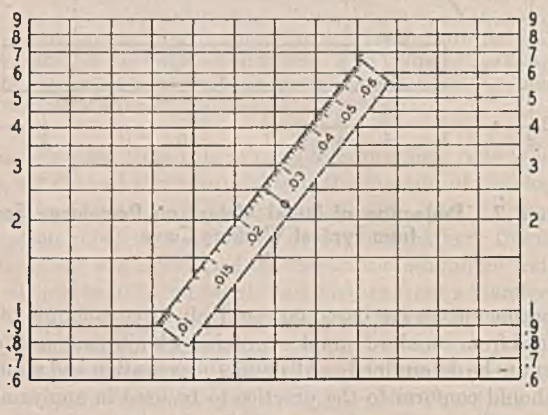



**Figure 8. Preparation of Final Percentage Scale**

Curve Drift or Scale Drift. In the internal standard system it is assumed that the intensity ratio is a function of the single variable intensity ratio. If this were rigorously true, a permanent standardization could be made and no further standard spectra would be required in a routine application. Unfortunately, however, there are many variables in present-day procedures other than concentration which affect the measured intensity ratios. As a result, working curves and percentage scales show a slight irregular drift and it is necessary to run frequent standard samples to correct for this drift. While all the causes of drift are not understood, it is known that a part of the drift is caused by an actual change in intensity ratio and a part is caused by errors in measurement of intensity ratio. The principal factors affecting the actual intensity ratio produced by the spark are atmospheric conditions and gradual deterioration in apparatus. The apparent drift caused by errors in measurement are largely introduced by variables in the photographic process. The photographic errors are caused by inherent, systematic nonuniformities introduced by methods of manufacture, by the rather large effects of humidity on the emulsion, by changes in the relative response of the emulsion to different wave lengths, and by systematic errors resulting from the use of commercially available developing machines which develop rather reproducibly but not uniformly. A small but significant portion of the apparent curve drift is caused by defects in emulsion calibration in large-scale routine work.

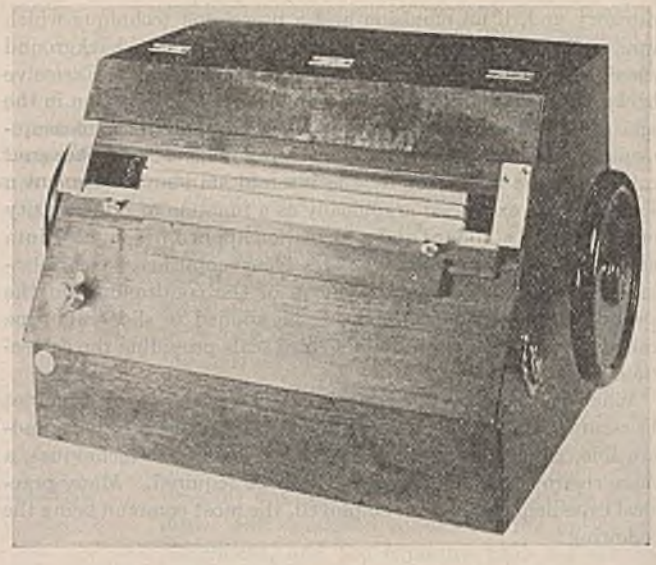


**Figure 9. Dunn-Lowry Calculator for Spectrographic Analysis**

Curve drift is a serious problem in the analysis of aluminum alloys but almost negligible in the analysis of iron and steel. This difference is due largely to the differences between the spectra of iron and aluminum. The aluminum spectrum contain so few lines suitable for use as internal standards that it is necessary to use line pairs of widely different characteristics and widely different wave lengths in routine analysis. Add to this the troublesome surface effects caused by the formation of aluminum oxide on the electrode surface and it is apparent that the analysis of aluminum presents problems not to be expected in steel or in many other materials. The use of dissimilar line pairs and line pairs differing substantially in wave length magnifies most of the inherent defects of the internal standard method and invalidates several of the fundamental assumptions of the internal standard method. Moreover, the experimental errors introduced by variations in excitation, photography, development, and densitometry are magnified. The apparently greater curve drift encountered in the analysis of aluminum is only a manifestation of the failure of the internal standard method resulting from the necessary violation of some of its cardinal principles.

It has been found experimentally that the net effect of curve drift can be treated as a proportional change in all intensity ratios for a particular line pair. Accordingly, the necessary correction can be made by applying a factor to all intensity ratios. This fact was established empirically by experimental methods and applies only to the normal shifting of working curves under carefully controlled conditions with adequate emulsion calibration, and only within the relatively small range (two- to threefold on a concentration basis) over which a particular line pair is used in the routine analysis of aluminum alloys. Correcting for curve drift is then essentially merely the determination of the index—that is, finding of the concentration at which intensity ratio equals unity. The routine procedure for determining the index is given in the following sections on mechanical calculators.

The Dunn-Lowry Calculator. The Dunn-Lowry calculator (Figure 9) is an adaptation of the "squirrel cage" slide rule developed by Aluminum Company of America for routine spectrographic calculations.

It consists essentially of a cylindrical drum bearing the percentage scales for the various elements and alloys, and a rule bearing the emulsion calibration scale. The percentage scales are mounted on wood or metal rules whose faces form the periphery of the cylinder. Each rule can be moved laterally to compensate for index shift. The calibration scale is so arranged that it may be made to slide laterally with respect to the drum and is so positioned that any percentage scale on the drum can be brought into juxtaposition with it by rotating the drum. An index line is inscribed on a small glass or plastic tab permanently fastened to the window frame of the calculator. This index corresponds to an intensity ratio of unity and all percentage scales are adjusted with reference to this point before use. This line will be referred to simply as the index line.

After the calibration scale and the percentage scales have been prepared as previously described, the first step in the use of the calculator is the index adjustment of the percentage scales. To determine the index of a particular percentage scale, the following procedure is followed:

Measure the analysis and internal line photometrically in a series of spectrograms of a standard containing the same order of magnitude of the element to be determined as expected in the samples to be analyzed. (Two or more standards of different composition may be used without altering the subsequent procedure.) Set the percentage scale so that the expected index is near the index of the calculator, but do not move the percentage scale again until the final index is determined. For each spectrum, adjust the calibration scale so that the deflection for the analysis line falls in juxtaposition with the known concentration on the percentage scale, and record the concentration reading coinciding with the deflection of the internal standard line. This percentage is the percentage at which the intensity ratio is unity and the average of the percentages so determined for all of the spectrograms is the "index". Slide the percentage scale until the index so determined coincides with the index line on the calculator. For the continual index adjustment of a percentage scale in regular use, the half-correction method is used. This method consists of taking as the final setting of the index the arithmetic mean of the index as determined immediately before the analysis, and the index as used during the immediately previous analyses. This method is used in all Aluminum Company of America laboratories in continuous routine operation.

The per cent constituent on an analysis sample is calculated on the Dunn-Lowry calculator by simply adjusting the calibration scale so that the deflection for the internal standard falls at the index mark, and reading per cent constituent on the percentage scale at the point which falls in juxtaposition with the deflection for the analysis line. When more than one determination on a particular sample is referred to the same internal standard line, the calibration scale is adjusted only once and the various elements are calculated by bringing the appropriate percentage scales successively into view on the calculator.

Multiple Determination Calculating Rule. The multiple determination calculating rule is a type of slide rule calculator developed by Aluminum Company of America for use with recording microphotometers in routine analysis.

The rule is designed for use on a special calculating board consisting essentially of a drawing board equipped with a movable horizontal bar which will move up and down on the board but will not move sideways. This bar is equipped with bearings, guides, or a pulley arrangement, so that it will remain parallel to the front edge of the board at all times. A rectangular opening, approximating the dimensions of the largest microphotometer chart likely to be encountered, is cut in the central portion of the board. A glass plate is inserted in this opening, flush with the top surface of the board. The plate is illuminated with fluorescent type incandescent tubes from below. The calibration curve is fastened semipermanently on this glass plate and charts representing analyses are superimposed on this chart. The horizontal rulings on the chart and the abscissa coordinates of the calibrating curve are made parallel to the bar on the calculator by aligning the chart and curve with suitable reference marks. It is desirable that the calculator be equipped with a clamping mechanism to hold the chart paper in place. Otherwise, scotch tape or thumb tacks are used.

A photograph of a multiple calculating rule mounted on a calculating board is shown in Figure 10. This calculating rule is equipped with a replaceable nest of scales. A separate nest of scales is used for each different alloy analyzed. The front edge of the rule is metal and is close to the surface of the board. A vertical hairline is ruled on the glass slide at a position corresponding to the pointer which rides along the edge of the rule. The individual percentage scales are adjustable with respect to each other and with respect to the index mark inscribed on the edge of the rule.

To determine the correct location of a percentage scale with respect to the index mark on the rule—i.e., to determine the index of the percentage scale—the following procedure is used:

Measure a series of spectrograms of a suitable spectrographic standard. Superimpose the chart paper on the calibration curve, taking care to align the chart with the reference marks indicating the ordinate scale on the curve. Move the rule vertically until its edge intersects the deflection peak representing the element to be determined. Move the rule laterally and move the slide bearing the cross hair until the pointer intersects the calibration curve and the hairline crosses the percentage scale at the known percentage of the element sought. Move the rule vertically (taking care not to move it horizontally) until the edge matches the deflection peak for the internal standard. Adjust the cross hair slide so that the pointer again intersects the curve. Record the percentage now indicated by the hairline. The average of the percentages so determined for a number of standards is taken as the index for subsequent analyses. The percentage scale is adjusted so that the index determined falls at the cross hair when the pointer coincides with the index line on the edge of the rule. At least four exposures should be used to establish an index originally. When the percentage scales are used at very frequent intervals, the half-correction system (described previously) is employed.

To determine percentage composition on unknowns, proceed as follows: Move the rule vertically until its edge passes through the deflection peak for the internal standard. Adjust the rule laterally until the index mark on the edge of the rule intersects the calibration curve. Move the rule vertically (with no horizontal movement) until the edge of the rule coincides with the deflection peak of the analysis line. Move the cross hair slide until the pointer intersects the curve, and read the analytical result on the appropriate percentage scale. Of course, if more than one constituent is to be determined with reference to the same internal standard, the rule is adjusted laterally with respect to the internal standard deflection only once, and the various

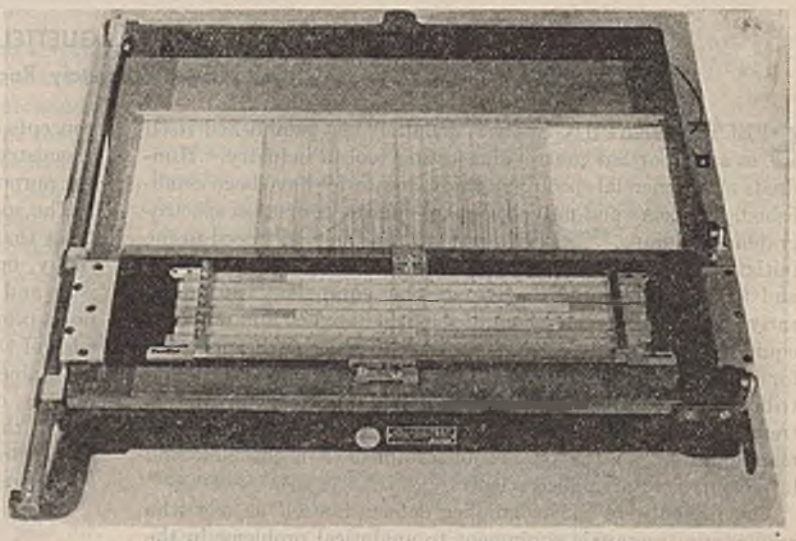


Figure 10. Multiple Determination Calculating Rule Used with Recording Microphotometers

elements are determined successively by simply moving vertically to the deflection peaks and reading percentages on the appropriate scales.

### SUMMARY

The techniques discussed have been those developed specifically to meet problems encountered in the routine analysis of aluminum. While an attempt has been made to treat the subject from a broader viewpoint than that of a spectrographer specializing in aluminum alloys, the emphasis has naturally been greater on those problems which are most serious in aluminum analysis. The specific methods of analysis best suited for one type of material usually cannot be transferred to another type without some modification, but the underlying principles involved in all spectrographic analyses are much the same, and the problems encountered differ in degree but not in kind.

It may seem that an overly critical attitude was taken towards commercially available apparatus. It was the deliberate intention of the author to emphasize the defects of existing equipment for the double purpose of helping prospective users in the selection of apparatus and in offering constructive criticism which may aid the manufacturers of apparatus in meeting the practical requirements of routine spectrography. Emphasis on the limitations and sources of error in the spectrographic procedure was also intentional. The overly euphemistic treatment of spectrographic procedures characteristic of much of the literature in recent years no longer serves any useful purpose. No longer is it necessary for spectrographers to act as salesmen for their art or the apparatus they use. Frank recognition of the imperfections and limitations of existing techniques will not only aid in relegating it to its proper position in the analytical scheme but will foster developmental work aimed at improving these techniques. It is the opinion of the author that the most important advances in routine spectrographic analysis will come through the improvement in or elimination of the photographic films and plates and in the development of improved excitation sources. Free exchange of information along these lines and a critical appraisal of techniques and apparatus in the literature will bring the fundamental improvements now under development to earlier fruition.

### ACKNOWLEDGMENTS

The foresight and constructive guidance of H. V. Churchill, chief chemist of the Aluminum Company of America, have been large factors in bringing spectrographic analysis to its present status in the aluminum industry. The author also gratefully acknowledges the contributions of the laboratory staff of Aluminum Research Laboratories and of the men and women of the plant laboratories of the Aluminum Company of America, on whose collective experience this paper is based. Finally, a special acknowledgment is offered to the manufacturers of spectrographic equipment for their splendid cooperation and assistance in making possible the great expansion of spectrographic analysis during the present emergency.

### BIBLIOGRAPHY

(1) Baly, E. C. C., "Spectroscopy", London, Longmans Green & Co., 1924.
(2) Brode, W. R., "Chemical Spectroscopy", 2nd ed., New York, John Wiley & Sons, 1943.
(3) Duffendack, O. S., and Thompson, K. B., *Proc. Am. Soc. Testing Materials*, 36, II, 310 (1936).
(4) Feussner, O., *Arch. Eisenhüttenw.*, 6, 551 (1932).
(5) Hasler, M. F., and Dietert, H. W., *J. Optical Soc. Am.*, 33, 218 (1943).
(6) *Ibid.*, p. 687 (abstract).
(7) Hasler, M. F., and Kemp, J. W., *Ibid.*, 34, 21 (1944).
(8) Malpica, J. T. M., and Berry, T. H., *Gen. Elec. Rev.*, 44, 563 (1941).
(9) Mees, C. E. K., "Theory of the Photographic Process", New York, Macmillan Co., 1942.
(10) Sawyer, R. A., "Experimental Spectroscopy", New York, Prentice-Hall, 1944.
(11) Strock, L. W., *J. Optical Soc. Am.*, 32, 103 (1942).
(12) Twyman, F., "Spectrochemical Analysis of Metals and Alloys", London, Charles Griffin and Co., 1941.

# Emission Spectrographic Equipment Used in Quantitative Analysis

## Proposed Minimum Requirements

CHARLES L. GUETTEL
Rock Island Arsenal Laboratory, Rock Island, Ill.

SPECTROGRAPHIC analysis definitely has established itself as an important control and testing tool in industry. Hundreds of commercial spectrographic laboratories have been established. Colleges and universities are offering courses in spectrographic technique. This excellent progress may be traced to the initiative of many academicians in the field of applied physics and to manufacturers of spectrographic equipment who at an early stage in the development of the field designed and provided equipment for others not in a position to build such apparatus for themselves. The spectrographer, although he has also contributed his share to the advancement of spectrography, is extremely grateful to these early pioneering spectroscopists and manufacturers for the foundation established in this new and interesting field of applied science.

The present-day spectrographer defines himself as one who applies spectrographic equipment to analytical problems in the laboratory and thus differs from the spectroscopist who may design such equipment or may be concerned with the theoretical concepts of spectra. A spectrographer who has been trained in chemistry may prefer to call himself a spectrochemist, but for the purpose of this paper he is included in the former category.

The spectrographer does not claim to be an expert in all the fields that are involved in spectrographic analysis—i.e., photography, optics, electronics and electrical circuits, general chemistry and physics, etc. He may have specialized in one of these fields prior to entering spectrography, but any necessary knowledge of the other fields is usually acquired as further experience is obtained. However, on comparing notes with other spectrographers, on studying numerous publications, and on experimenting in the laboratory, he finds one question which he cannot answer to his satisfaction—what is to be expected of commercial spectrographic equipment?

### REASONS FOR MINIMUM REQUIREMENTS

Although no adopted minimum standards exist for emission spectrographic equipment in general, the spectrographer finds

himself in a field where enough literature has accumulated to justify an index of subject matter (*2*) and a compendium of operating conditions (*1*). Enormous publicity has popularized the field of spectrography through layman periodicals, commercial advertising, conferences on spectrographic analysis, and technical journals covering fields as far apart as biology is from metallurgy. The employer of the spectrographer reads of these events and his enthusiastic expectation for results of high precision and accuracy may overwhelm him, especially after appropriating thousands of dollars for his spectrographic installation. Such a condition may place the spectrographer in a "do or die" situation if his results are adverse. However, no matter how excellent the technique of the spectrographer may be, his results cannot be any better than the merits of his equipment permit.

The spectrographer, whose vocation in most cases has been created by the joint efforts of the field of physics and the manufacturers of spectrographic equipment, has now reached a stage in his own development where he is getting bold enough to turn to his "creators" and demand specific minimum standards for this much-publicized equipment to protect his own interests. The offspring definitely is growing up!

The American Chemical Society has high standards for chemicals of reagent grade. The American Society for Testing Materials has a multitude of requirements in effect for apparatus used for testing purposes. Many other technical groups have such requirements. It is logical that the equipment of the spectrographer be covered by similar standards.

The spectrographer does not request complete standardization of equipment at this time, although further standardization would permit a more common spectrographic language. Standardization may be the result of future development work. However, the field is still fertile for competition between manufacturers of spectrographic equipment and for difference of opinion between spectrographers concerning who has, or what is, the best spectrograph, densitometer, or excitation unit, for a given application. Nevertheless, this variety of opinion concerning major issues in the spectrographic field still does not eliminate the necessity of establishing minimum standards for any piece of emission spectrographic equipment.

The spectrographic equipment manufacturer should not be required to work out the details of a given analysis. Most of the development work has to be left to the ingenuity of the individual spectrographer. However, the presence of a representative of the equipment manufacturer during the early period of a new installation has proved extremely helpful to the spectrographer. This period could be used advantageously in aiding to check the equipment thoroughly for its ability to meet adopted minimum standards.

It is realized that of the many mass production parts of which modern spectrographic equipment is composed, all may not meet absolute perfection. Such a condition may cause occasional difference in performance of units of the same type and model. However, the assembled equipment should at least be capable of meeting certain minimum requirements, so that the spectrographer more easily may isolate errors due to technique from those arising from possible defects in the apparatus. If the equipment continued to meet the minimum standards with the accepted techniques, the spectrographer could check his own variations of the techniques thoroughly before complaining to the equipment manufacturer about adverse results. Thus, the latter also would be protected by the requirements.

Since the field of spectrography has grown more rapidly than the ability to train personnel for handling its possibilities, many lengthy requisitions and procurement specifications have been written by individuals whose knowledge of the field was not established until after the apparatus was bought and paid for. This has been especially true during the present emergency when a rapid means of analysis had to be installed in a short period of time. If only for the benefit of these newcomers, guiding minimum requirements are justified.

**A proposal is made to establish minimum requirements for equipment used in precise and accurate emission spectrographic analysis with the view of stimulating discussion toward the development of final minimum requirements. A discussion of reasons for the requirements is given, followed by a discussion of the nature of such requirements. Proposed minimum requirements for the spectrograph, densitometer or microphotometer, and excitation equipment are presented. The accepted minimum precision of the final results is given in terms of an empirical relationship between the average deviation and the level of concentration. The conditions under which the minimum precision is determined are given. The requirements emphasize the performance of the equipment rather than detailed construction of apparatus.**

Specifications for spectrographic equipment should include not only description of parts with physical dimensions and diagrams of electrical circuits, but also the nature of results to be obtained, expressed in terms of universally adopted factors of precision and accuracy. When a chemist orders an analytical balance, the size of the pans and length of the beam are by far subordinate to the sensitivity and reproducibility obtained with the instrument. A spectrographer should have a similar attitude toward his equipment.

It should not be interpreted that the writer has had difficulties with equipment on all points covered by the proposed requirements. On the contrary, personal experience with commercial equipment plus the knowledge gained by visits to numerous other spectrographic laboratories, many of which used equipment made by different firms, proves that in general the commercial instruments have eliminated many previous difficulties and have paved the way for higher standards. Only for the reasons given are the requirements being considered.

It is one thing to advocate minimum requirements and quite another thing actually to present them. However, it is expected that the reader will accept this effort in the spirit of keeping the standard of spectrographic analysis on a high plane.

## NATURE OF MINIMUM REQUIREMENTS

The minimum requirements should be practical, brief, and as simple as possible. They should apply to emission spectrographic equipment in general and should not emphasize any one type, mounting, or optical system. Thus, the requirements should avoid any reference to spectrographic topics which are problems of applied technique and personal choice—i.e., the prism versus the grating, the electrical characteristics of the excitation, the film versus the plate, the type of photographic emulsion, and the type of counter or supporting electrodes. Unless lengthy and cumbersome procedures are needed to overcome defects of a given instrument, a condition which is rare if not extinct, the emphasis should be on the nature of the readings or recordings expressed in terms of precision rather than on the details of the mechanism which produced the readings or recordings.

Sawyer and Vincent have presented a paper on "Specifications and Testing of Spectrochemical Apparatus" (*3*). Any adopted requirements or purchase specifications should be supplemented by a study of their paper. However, an inexperienced spectrographer may hesitate to apply portions of its contents to test his new equipment, because of his own temporary lack of knowledge of the optics involved. The method suggested by Sawyer and Vincent to determine errors which arise in spectrochemical analysis, in this writer's opinion, would be a means to check the accuracy of results reported by a so-called established spectrographic

laboratory, operated by an experienced spectrographer who has mastered the equipment in question. Its value in establishing requirements for new equipment would depend on how rapidly a spectrographer could learn to appreciate the significant difference between his systematic, and accidental or random errors. Although it may not have been the intention of Sawyer and Vincent in their specifications and tests, one of the purposes of the present proposal is to give to the technician who is inexperienced in spectrography minimum requirements which can be incorporated practically verbatim into a purchase order requisition for emission spectrographic equipment. The proposed requirements are given toward the end of this paper. Following is a discussion concerning their nature:

*Nature of Requirements. a.* It is admitted that the requirements for the spectrograph may be considered as vague. Differences in dispersion, linear and nonlinear, with corresponding degrees of resolution, are available, since there is a variety of mountings and optical systems provided in commercial spectrographs. The choice of instrument thus depends on its application to a given type of analysis. This portion of the requirements is also influenced by the opinion of the writer, in that the spectrograph itself is considered third in importance after the excitation equipment and densitometer in relation to precise and accurate quantitative analysis. Any defects in the spectrograph are usually of a constant nature and even these, although covered by the requirements in a general manner, have been eliminated or diminished to an insignificant minimum by good design—i.e., lengthy exposure times, scattered and stray light, ghost lines, and light leakage.

*b.* No reference is made in the spectrograph requirements to obvious incorporations such as a variable slit width, or a racking camera.

*c.* A means of spectrum line identification has been included in the densitometer or microphotometer requirements, since any line must be identified before being evaluated. Whether this means of identification is physically part of the densitometer or microphotometer or contained in some auxiliary apparatus is of no concern of the requirements. The use of exposed wave-length scales on photographic emulsions, or the projection of iron spectra, wave-length scales, commercial master plates, and known spectra master plates made by the spectrographer, depends on the complexity of the unknown spectra, the number of lines to be identified, and the magnification required to detect the necessary details that can be resolved by the dispersing medium of the spectrograph.

*d.* The reproducibility of all readings or recordings and corresponding indicator settings has been emphasized in the densitometer or microphotometer requirements. The maximum deviation is used instead of standard deviation for purposes of simplicity and in place of average deviation to assure that the reading or recording, any one of which may represent a single quantitative analysis to be reported on the basis of the given reading or recording, does not fall out of the desired range.

*e.* It is realized that some densitometers or microphotometers use a log density scale rather than a linear transmission scale. In these cases it would be necessary to convert to the linear form for the purpose of checking the proposed requirements.

*f.* The two terms "reading" and "recording" have been used throughout to include both the nonrecording and recording types of instrument. The terms "densitometer" and "microphotometer" have been used together in the requirements without exception for the benefit of those firms which prefer to describe their instrument as one or the other.

*g.* The minimum requirements for the excitation equipment are considered after specifying the nature of the other units, since the performance of the excitation equipment is "registered" by the spectrograph and "examined" by the densitometer or microphotometer. Thus, the final precision test, although listed under the excitation equipment requirements, should be interpreted as including any lack of precision inherent in the other units. It is assumed, however, that if the spectrograph and densitometer or microphotometer meet their respective requirements by the results of tests which are to a great degree independent of the merits or defects of the excitation equipment, and if the technique is of satisfactory quality, most of any remaining lack of precision in the final result can be traced to errors in the light source. Therefore, it is believed that the inclusion of final precision and accuracy tests under "Excitation Equipment" is justified—especially when the requirements describe the excitation equipment as being used in conjunction with other units which already are specified.

*h.* The specifications for the intensity of the light source, as suggested by Sawyer and Vincent (*3*), have been included in the requirements for the excitation equipment.

*i.* The precision also has been emphasized in the excitation equipment requirements. Reproducibility tests for excitation units many times are questionable, owing to lack of knowledge concerning the homogeneity of the samples. This situation is further complicated by the fact that in most cases there are no accepted independent means for checking homogeneity. However, any establishment that confidently cannot produce a reasonably homogeneous sample for quantitative tests should not consider spectrographic equipment. Such a condition should be decided prior to any installation, by the establishment submitting samples to the equipment manufacturer or to other spectrographic laboratories having available techniques for reproducibility tests using the type of equipment and material in question. It is realized that reproducibility is a function of technique as well as the precision of the equipment. Thus, the homogeneity tests should be made with established techniques having acceptable reproducibility. If such techniques are not available for the analysis in question, an agreement should exist between the establishment contemplating the use of spectrographic equipment and the manufacturer of such equipment, whereby either the latter agrees to develop a reproducible technique for checking sample homogeneity or the former purchases the equipment at his own risk, leaving problems of sampling and reproducibility to his own research and development. Regardless of the nature of such an agreement, a sample is either a representative specimen for spectrographic analysis or it is not. There is no compromise.

*j.* Any one given magnitude of a numerical value to express acceptable precision covering all concentration ranges encountered in spectrographic analysis would be questionable if not impossible to attain. A spectrographer checking his precision in very low concentration ranges may take pride in his low average deviation from the mean in percentage concentration of the element in the sample, but his per cent average deviation may be extremely high. (The per cent average deviation is the $\frac{\text{average deviation}}{\text{mean result}} \times 100$.) Likewise, a spectrographer checking precision in a comparatively high concentration range may enjoy his low per cent average deviation, but his high average deviation from the mean in percentage concentration of the element in the sample may justify the substitution of the wet-analysis technique for the spectrographic method.

It is realized that by choosing proper analytical lines, the accidental errors occurring in spectrographic analysis tend to have a constant percentage relationship to the quantity to be determined, regardless of its amount. However, a 10% average deviation may be acceptable precision at a concentration level of 0.1% but would not be acceptable at a concentration of 5.0% when competing with other independent means of analysis. In order to justify the use of spectrographic analysis at higher concentration levels, lower per cent average deviations are required to obtain acceptable precision. Therefore, in the proposed requirements an empirical relationship has been established between the minimum accepted precision and the concentration level where higher average deviations are permitted and lower per cent

average deviations are required for higher concentration ranges. This relationship also is in accord with the fact that in spectrographic analysis, as in other methods of analysis, lower relative precision is required in determining small constituents than large ones, at least in part because of the relation of sampling technique and constituent homogeneity limitations at extremely low concentrations.

At attempt has been made to adjust the empirical relationship to actual experience and to reports in general spectrographic literature suggesting what minimum requirements should be expected for equipment to give the usual claimed precision for concentrations between 0.0001 and 5.0%. The evaluations in the empirical relationship also were influenced by the usual precision attained by the independent wet analysis—a method which may be substituted if the spectrographic analysis fails to equal or improve the precision obtained with the chemical technique.

Since there appears to be an appreciable difference in techniques used for concentrations below approximately 0.05% as compared to conditions used above this figure, the empirical relationship is divided into a low and medium range. Techniques calibrated for the medium range cannot claim the degree of precision in their lower concentrations as would lower range techniques specializing in concentration ranges which the medium range overlaps. The extreme lower concentrations of the medium range are usually considered merely as residuals, while the lower range technique claims a higher degree of precision for the same range of concentrations. No effort is made to cover the high range concentrations—i.e., above 5%—in this paper.

Many spectrographers will claim more precise results than required by the empirical relationship, especially in the low range. However, it should be realized that the precision specified here is a minimum requirement. It is expected that improvements in technique may lead to more precise work.

Some spectrographers may desire a more statistical approach to precision by adopting the standard deviation rather than the average deviation. Such a modification may be an improvement. However, it is believed that the suggested empirical relationship would be comprehended more easily in terms of the average deviation.

*k.* Through personal experience and by contact with other spectrographers, it has been found that many in the field experience shifting of analytical working curves without any known change in technique. It becomes necessary to run a series of standards to determine the nature of the shift and make corrections accordingly. The reason for this shifting is not usually known. The use of small correction factors may not be inconvenient if the precision would remain satisfactory, but any extreme shifting of curves requiring abnormally high correction factors would indicate a poor day-to-day accuracy. If there has been no change in technique, the shifting must be due to some instrumental variation, although the source of variation may be unknown. The requirements given attempt to cover adequately any such shifting of analytical working curves.

*l.* No reference is made to requirements for photographic processing apparatus or calculating mechanisms, as both are assumed to be classified in the category of technique.

*m.* The minimum requirements have been written primarily for those control and testing laboratories requiring precise and accurate routine quantitative analysis. There may be some laboratories whose work involves only qualitative analysis and where a densitometer or microphotometer would not be used. Other establishments may require results of only a semiquantitative nature where the requirements for the densitometer or microphotometer and excitation equipment could be less rigid. Such cases should be covered by mutual agreement and understanding.

With references of this discussion in mind, the following proposed requirements have been written. The small letters following the subtitles refer to parts of the above discussion.

## PROPOSED MINIMUM REQUIREMENTS

### I. The Spectrograph (*a*, *b*)

1. The spectrograph shall give ample dispersion, resolution, definition, and wave-length range of spectrum lines to accomplish the given analysis. Where possible, the actual values for the required dispersion, resolution, and wave-length range shall be obtained from spectrographers specializing in the field of the given analysis.
2. The absorption of light in the process of dispersion shall be sufficiently low to permit exposure periods of 2 minutes or less, as further specified in III, 2.
3. The optical system shall consist of high-grade materials designed to keep phenomena such as scattered and stray light, production of ghost lines, and deterioration of optical parts at a minimum.
4. Light leakage, as noted by the fogging of highly sensitive photographic emulsions, shall be eliminated.
5. The construction and mounting shall be substantially rigid to permit permanent alignment of all optical parts.

### II. The Densitometer or Microphotometer (*c*, *d*, *e*, *f*)

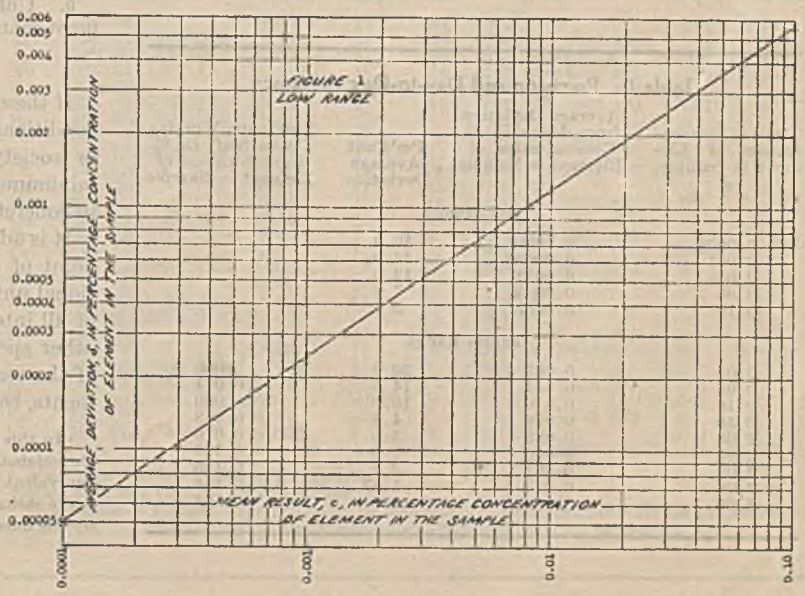
1. A positive means of spectrum line identification shall be provided to accomplish the given analysis.
2. The densitometer or microphotometer shall provide a linear relationship between light transmission and indicator response, so as to permit uniform sensitivity between 0 and 100% transmission. A means for checking the linearity of the instrument shall be provided.
3. The densitometer or microphotometer reproducibility while reading or recording within one spectrogram on a given photographic emulsion shall include the following conditions:

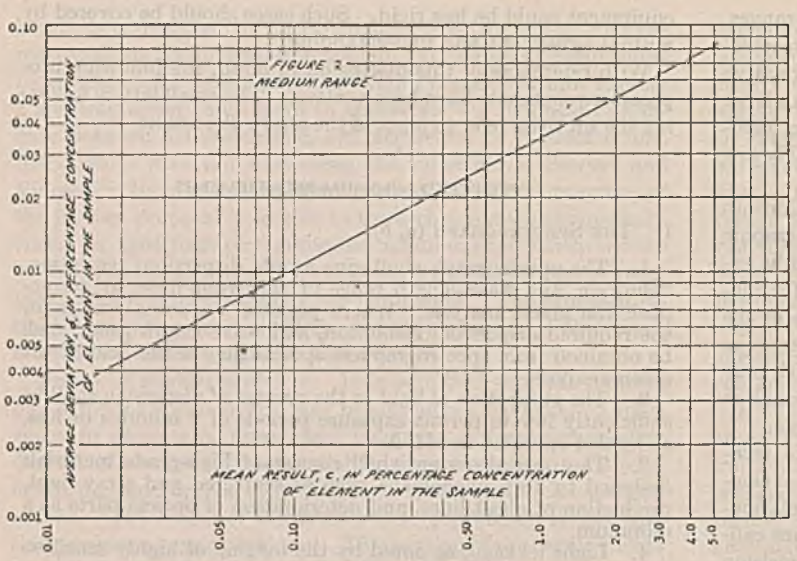
*a.* Five check readings or recordings on any one of the uniform, adopted spectrum lines shall fall within a maximum deviation of 0.2% of full linear scale deflection without intermediate adjustment of the full-opaque setting or the clear emulsion setting.

*b.* The full-opaque setting and the clear emulsion setting shall be repeated with the degree of precision required to permit the maximum deviation in line readings or recordings as specified in part *a* of this section.

### III. The Excitation Equipment (*g*, *h*, *i*, *j*, *k*)

1. The sensitivity of the excitation equipment as determined in conjunction with a spectrograph as specified in I shall be such that the desired minimum concentration of the element or elements in question shall be detected; or the minimum possible concentration of the given element or elements to be detected shall be known to the spectrographer.






2. The excitation equipment used in conjunction with a spectrograph as specified in I shall produce a light source of sufficient intensity to provide an adequate exposure on standard photographic emulsions, without a condensing lens (a lens may be used with astigmatic instruments in those wave-length regions only where long focal distances would be inconvenient), in not over 2 minutes, with the source 10 inches or more from the slit of the spectrograph (see I, 2). (This requirement is to be used for testing the intensity of the light source, and with part I, 2, the speed of the spectrograph, and does not imply that established routine techniques have to be bound by the conditions given.)

3. The resulting accepted precision using the excitation equipment in conjunction with a spectrograph as specified in I and a densitometer or microphotometer as specified in II shall be determined as follows:

*a.* The accepted precision in the determination of any one element shall be expressed as the average deviation, $\delta$, in percentage concentration of the element in the sample, from the mean result, $c$, of eight or more individual trials. The highest accepted value of $\delta$ shall depend on the magnitude of $c$ in percentage concentration of the element in the sample, as given in the empirical relationship between columns 1 and 2 of Table I. The medium range should not be used for techniques specializing in concentrations of less than 0.1%. The precision may be described further as per cent average deviation as given in column 3 of Table I, and defined as $\frac{\delta}{c} \times 100$. For intermediate values of $c$ and $\delta$, see Figures 1 and 2, where the empirical values of $\delta$ in Table I follow within close approximation a straight line when plotted against $c$ on the given logarithmic axes. (For those who desire a mathematical expression for the empirical relationship as given by the curves in Figures 1 and 2, the equation

$$\log \delta = \log b + n \log c \text{ or } \delta = bc^n$$

may be used, where $\delta$ is the average deviation from the mean in percentage concentration of the element in the sample, $b$ is the log axis intercept when $c$ is unity, $n$ is the slope, and $c$ is the mean percentage concentration of the element in the sample.)

*b.* The individual results used to determine the value $\delta$ shall be obtained from an analytical working curve based on a technique as specified in III, 2, *c*, and on standard or routine samples of accepted, known concentration meeting the homogeneity requirements in III, 2, *d*.

*c.* The analytical working curve and the value of $\delta$ shall be determined by using a technique (including choice of spectrum line pair, optical adjustments, emulsion calibration method, photographic processing, and type of photographic emulsion, electrodes, and discharge) which is acceptable to the spectrographer and the manufacturer of the equipment.

*d.* The standard or routine samples of known concentration used to calibrate the analytical working curve and to determine the value, $\delta$, shall be acceptable only if the equipment manufacturer and spectrographer agree that the sample material used is representative of a satisfactorily homogeneous specimen. The degree of homogeneity of routine samples should be known prior to the installation of the equipment.

4. The day-to-day accuracy of the excitation equipment used in conjunction with a spectrograph as specified in I and a densitometer or microphotometer as specified in II shall be such that any correction factors, as determined by checking the accepted standard samples with the established technique, shall not shift the original analytical working curve beyond the values in per cent concentration of the element in the samples as given in column 4 of Table I[1], over a test period of 90 days, provided:

*a.* The spectrographer has not varied his technique in obtaining the results in question.

*b.* The spectrographer has maintained all parts of the equipment as specified by the manufacturer of the equipment.

## IV. Auxiliary Equipment

1. The maximum variation in input voltage permitted for any unit of the installation, while achieving the ultimate precision and accuracy attainable from the unit, shall so be specified by the manufacturer of the equipment in order that a proper decision may be made concerning auxiliary input voltage control.

2. Any other auxiliary equipment or information required to obtain the performance as described in these requirements shall so be specified by the manufacturer of the equipment.

## V. General Remarks

These requirements are subject to change for reasons as follows by a majority vote of any group adopting them:

*a.* Advancements in the field of emission spectrography.

*b.* Unfair disadvantages to either spectrographer or equipment manufacturer.

### FINAL DISCUSSION

If these requirements are found to be too rigid or too lax, the conditions may be changed by the majority opinion of any group or society considering such requirements. Nevertheless, the minimum capabilities of the equipment at least will be expressed in concrete terminology.

It is admitted that the requirements may emphasize the viewpoint of a spectrographer. If any incompleteness or unintentional unfairness has been noted, the suggestions and criticisms of all interested spectroscopists, equipment manufacturers, and other spectrographers will be most welcome and appreciated. If the reader has been convinced of the need for such requirements, the paper has served its purpose.

[1] In this case column 1 of Table I represents the concentration values of the original working analytical curve. The values given in column 4 are equivalent to twice the values as given in column 2. The maximum working curve shifts for the low range have been left open for discussion as indicated by the question marks.

**Table I. Precision and Day-to-Day Accuracy**

| Mean % Concentration of Element in Sample, $c$ | Average Deviation from Mean in % Concentration of Element in Sample, $\delta$ | Per Cent Average Deviation | Maximum Working Curve Shift in % Concentration of Element in Sample |
|---|---|---|---|
| | Low Range | | |
| 0.0001 | 0.00005 | 50.0 | ? |
| 0.001 | 0.00025 | 25.0 | ? |
| 0.01 | 0.0012 | 12.0 | ? |
| 0.05 | 0.0035 | 7.0 | ? |
| 0.10 | 0.0057 | 5.7 | ? |
| | Medium Range | | |
| 0.01 | 0.003 | 30.0 | ±0.006 |
| 0.05 | 0.007 | 14.0 | 0.014 |
| 0.10 | 0.010 | 10.0 | 0.020 |
| 0.50 | 0.024 | 4.8 | 0.048 |
| 1.00 | 0.035 | 3.5 | 0.070 |
| 2.00 | 0.050 | 2.5 | 0.100 |
| 3.00 | 0.063 | 2.1 | 0.126 |
| 4.00 | 0.073 | 1.83 | 0.146 |
| 5.00 | 0.082 | 1.64 | 0.164 |

ACKNOWLEDGMENT

The writer is indebted to members of the staff of the Rock Island Arsenal Laboratory for their constructive criticisms.

LITERATURE CITED

(1) Hodge, E. S., *J. Optical Soc. Am.*, 33, 656 (1943).
(2) Meggers, W. F., and Scribner, B. F., "Index to the Literature on Spectrochemical Analysis, 1920–1939", American Society for Testing Materials, 1941.
(3) Sawyer, R. A., and Vincent, H. B., *J. Optical Soc. Am.*, 31, 47 (1941).

THE opinions expressed in this article are those of the author and not of the Ordnance Department.

# Qualitative Spectrographic Analysis

G. W. STANDEN
Research Division, Technical Department, The New Jersey Zinc Company (of Pa.), Palmerton, Pa.

**A system of qualitative analysis for the metallic elements using the spectrograph as a tool, is described and its advantages and limitations are indicated. Allowance is made for differences in sensitivity by comparing the unknown spectrum with standard spectra which permit a semiquantitative estimation of each element found.**

THE usefulness of the spectrograph as a tool for qualitative chemical analysis has long been recognized. During the last 15 years, however, the emphasis has been on quantitative analysis, in which field much research has been carried out, resulting in widespread use of the spectrograph in the analytical laboratory. Meanwhile, qualitative analysis continues as a useful but less publicized function of the spectrograph. This paper describes a system of qualitative analysis for the metallic elements and indicates its advantages and its limitations.

Identification of elements in spectrographic analysis is very positive even when dealing with very low concentrations. The sensitivity is generally excellent and superior to other methods. The very sensitivity of spectrographic analysis, however, is often its most disconcerting feature. When the analyst reports the presence of fifteen to twenty elements in a sample that was suspected of containing about five, the report is confusing unless the identification is accompanied by a statement of the approximate relative concentrations of the elements found. The more semiquantitative a qualitative analysis can be made, the more useful it is.

The requirements of a qualitative analysis may best be indicated by listing three of the principal applications:

1. As a preliminary to quantitative analysis, to indicate what elements should be determined and what separations may be required to avoid interferences.
2. As an aid to qualitative x-ray diffraction analysis to limit the search for an x-ray pattern match to compounds containing the principal elements found.
3. To detect the presence of beneficial or deleterious trace elements in raw materials and finished products.

In the first two of these and in other applications, a semiquantitative analysis is much more valuable than simple identification of the presence or absence of constituents.

In the early stages of the practice of qualitative analysis in this laboratory, the analytical report of the elements found was accompanied by a visual estimate of the intensities of the spectral lines, using the following arbitrary designations: vs, very strong; s, strong; m, moderate; w, weak; f, faint; vf, very faint; and xf, extremely faint.

In interpreting such an analysis, allowance must be made for the relative sensitivities of detection of the various elements—for example, phosphorus reported as weak would be present to a much higher concentration than magnesium also reported as weak. Thus, the person unacquainted with the relative sensi-

**Table I. Range of Spectrum in Which Elements May Be Detected with Greater Sensitivity**

| Range 1 (7000–3200 Å.) | Range 2 (3400–2370 Å.) | Equal Sensitivity in Range 1 or 2 |
|---|---|---|
| Ba, Ca, Cr, Cs, Li, Na, Rb, Sr | Ag, Al, As, Au, B, Be, Bi, Cb, Cd[a], Ce, Co, Cu, Er, Fe, Ga, Ge, Hg, In, Ir, La, Mg, Mn, Mo, Nd, Ni, P, Pb, Pd, Pt, Sb, Si, Sn, Ta, Te, Th, Ti, U, V, W, Y, Zn, Zr | K[b], Rh, Tl |

[a] For greatest sensitivity in detection of Cd, a line at 2288.018 Å. beyond Range 2 must be used.
[b] For greatest sensitivity in detection of K, a red-sensitive plate such as Eastman Spectroscopic Plate 1-L must be used to record the 7664.9 and 7698.9 Å. lines.

**Table II. Master Standards for Identification**

| Standard No. | Element and Percentage in Zinc Matrix 10.0% | 1.0% | 0.01% | 0.001% | 0.0001% |
|---|---|---|---|---|---|
| 1 | ... | ... | Ca | Al, Cd, Cu, Pb, Sn | Ag, Bi, Mg, Mn |
| 2 | ... | ... | As | Co, Cr, Ga, Sb, Ti | Be, Ge, Ni, V |
| 3 | ... | ... | P, Tl | In, Ir, Pd, Pt, Rh, W | Au, Mo |
| 4 | ... | ... | Ce, La, Ta, Te | Er, Hg, Th, Y, Zr | B |
| 5 | Na, K, | SrBa, Li | ... | ... | ... |
| 6 | Cs, Rb | U, Nd | Cb | Si, Fe | ... |

**Table III. Most Sensitive Lines and Percentage Limits of Detection**

| Element | Lines, Å. | Limit of Detection, % | Use Range | Element | Lines, Å. | Limit of Detection, % | Use Range |
|---|---|---|---|---|---|---|---|
| Ag | 3280.683 | 0.0001 | II | Mg | 2852.129 | 0.0001 | II |
| Al | 3092.713–3082.155 | 0.001 | II | Mn | 2794.817–2576.104 | 0.0001 | II |
| As | 2780.197–2860.452 | 0.01 | II | Mo | 3132.594 | 0.0001 | II |
| Au | 2675.95 –2427.95 | 0.001 | II | Na | 5895.923–5889.953 | 0.0001 | I |
| B | 2497.733 | 0.0001 | II | Nd | 3328.270–3133.603 | 1.0 | II |
| Ba | 4934.086–6141.716 | 0.01 | I | Ni | 3050.819–3002.491 | 0.0001 | II |
| Be | 3131.072–3130.416 | 0.0001 | II[a] | P | 2535.65 | 0.01 | II |
| Bi | 3067.716 | 0.0001 | II | Pb | 2833.069–2614.178 | 0.0001 | II |
| Ca | 4226.728–3933.666 | 0.001 | I | Pd | 3242.703 | 0.01 | II |
| Cb | 3194.977 | 0.001 | II | Pt | 3064.712–2997.967 | 0.001 | II |
| Cd | 3261.057 | 0.001 | II[b] | Rb | 6298.327 | 1.0 | I |
| Ce | 3201.714 | 0.01 | II | Rh | 3434.893–3396.85 | 0.001 | I or II |
| Co | 2424.930–2521.363 | 0.001 | II | Sb | 2598.062 | 0.001 | II |
| Cr | 4254.346–4274.803 | 0.0001 | I | Si | 2881.578–2516.123 | 0.0001 | II |
| Cs | 4593.177 | 1.0 | I | Sn | 2839.989 | 0.0001 | II |
| Cu | 3247.540–3273.962 | 0.0001 | II | Sr | 4607.331–4077.714 | 0.01 | I |
| Er | 3289.36 | 0.01 | II | Ta | 2714.674 | 0.01 | II |
| Fe | 3020.640–2979.352 | 0.0001 | II | Te | 2385.76 | 0.001 | II |
| Ga | 2943.637–2874.244 | 0.001 | II | Th | 2837.299 | 0.01 | II |
| Ge | 2651.178 | 0.0001 | II | Ti | 3372.800–3234.516 | 0.001 | II |
| Hg | 2536.519 | 0.001 | II | Tl | 5350.46 –2767.87 | 0.01 | I or II |
| In | 3256.090–3039.356 | 0.001 | II | U | 2889.627 | 1.0 | II |
| Ir | 3220.780–2924.792 | 0.01 | II | V | 3183.982–2908.817 | 0.001 | II |
| K | 4044.140–3217.017 | 10.0 | I or II[c] | W | 2946.981 | 0.001 | II |
| La | 3337.488 | 0.1 | II | Y | 3242.280–3216.682 | 0.01 | II |
| Li | 6707.844 | 0.001 | I | Zr | 3391.975 | 0.001 | II |
| | | | | Zn | 3345.020–3302.588 | 0.01 | II[d] |

[a] Most sensitive Be, 2348.6 in Range III.
[b] Most sensitive Cd, 2288.018 in Range III.
[c] Most sensitive K, 7664.9 and 7698.9 Å. A red-sensitive photographic plate such as Eastman spectroscopic 1-L must be used, which yields a sensitivity of 0.01% for potassium.
[d] Graphite base.

## Table IV. Concentration of Elements Which May Interfere with Identification of Traces of Element Sought

Concentration Expressed in Per Cent in Zinc Matrix

| Element Sought | Wave Length | Ag | Al | As | Au | B | Ba | Be | Bi | Ca | Cb | Cd | Ce | Co | Cr | Cs | Cu | Er | Fe | Ga | Ge | Hg | In | Ir | K | La | Li |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ag | 3280.683 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3382.891 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| Al | 3092.713 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3082.155 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| As | 2780.196 | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | 0.1 | .. | 10.0 | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 1.0 | .. |
| | 2860.452 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. |
| Au | 2675.95 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 0.1 | .. | .. | 1.0 | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2427.95 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| B | 2497.733 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2496.778 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| Ba | 2634.783 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. |
| Be | 3130.416 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 0.01 | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3131.072 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 0.01 | .. | 1.0 | .. | 1.0 | .. | .. | 1.0 | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. |
| Bi | 3067.716 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| Ca | 3179.332 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. |
| | 3158.869 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | 0.1 | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. |
| Cb | 3194.977 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 0.1 | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | 10.0 | .. | .. | .. |
| | 3094.183 | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | 10.0 | .. | .. | .. | .. | 10.0 | .. | 10.0 | .. |
| Cd | 3261.057 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | 0.1 | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| Ce | 3201.714 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3194.825 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 0.01 | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| Co | 3405.120 | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2521.363 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. |
| | 2424.930 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 |
| Cr | 3021.558 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 10.0 | .. | .. | 1.0 | .. | .. | .. | .. | .. |
| | 2835.633 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | 1.0 | .. | .. | .. |
| Cu | 3247.540 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. |
| | 3273.962 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| Er | 3289.36 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2891.387 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| Fe | 3020.640 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | 10.0 | 0.1 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3021.073 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2973.237 } | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2973.134 } | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Ga | 2943.637 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | 10.0 | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | 10.0 | .. | 10.0 | .. |
| | 2874.244 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 1.0 | .. | .. | .. | .. | .. | 0.01 | .. | .. | .. | .. | .. | .. | .. | .. |
| Ge | 2651.178 | .. | .. | .. | .. | .. | .. | 0.1 | .. | .. | 1.0 | .. | 10.0 | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3039.064 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | 0.1 | 1.0 | .. | .. | .. |
| Hg | 2536.519 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 0.1 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| In | 3256.090 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | 10.0 | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3039.356 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 10.0 | 1.0 | 10.0 | .. | .. | .. | 10.0 | .. | 0.001 | .. | .. | 1.0 | .. | .. | .. |
| Ir | 3220.780 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | 1.0 | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2924.792 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| K | 3217.017 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | 10.0 | 10.0 | 0.1 | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | 10.0 | .. |
| La | 3337.488 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | 10.0 | 1.0 | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3245.120 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| Li | 3232.61 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2741.31 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | 0.1 | .. | .. | .. | 1.0 | .. | 10.0 | .. | .. | .. | .. | .. | .. |
| Mg | 2852.129 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| Mn | 2794.817 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2798.271 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. |
| | 2605.688 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2593.729 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2576.104 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| Mo | 3132.594 | .. | .. | .. | .. | .. | .. | 0.01 | .. | .. | 10.0 | 10.0 | 1.0 | .. | 0.01 | .. | .. | 10.0 | 1.0 | .. | .. | 10.0 | .. | 10.0 | .. | .. | .. |
| | 3170.347 | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| Na | 2852.828 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2853.031 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. |
| Nd | 3328.270 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 10.0 | 1.0 | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3133.603 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | 1.0 | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | 0.1 | .. | .. | .. |
| Ni | 3050.819 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | 1.0 | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3002.491 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 10.0 | 1.0 | .. | .. | .. | 1.0 | 10.0 | .. | .. | .. | .. | 1.0 | .. | .. | .. |
| P | 2535.65 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | 0.01 | .. | .. | .. | .. | .. | .. | .. | .. |
| Pb | 2833.069 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. |
| Pd | 3242.703 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3404.580 | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | 10.0 | 10.0 | 0.01 | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | 10.0 | .. |
| Pt | 3064.712 | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | 0.1 | .. | .. | 10.0 | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2997.967 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | 10.0 | .. | .. | 10.0 | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. |
| Rh | 3396.85 | .. | .. | .. | .. | .. | .. | .. | 0.1 | .. | .. | .. | 10.0 | .. | .. | .. | .. | 1.0 | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3323.092 | .. | .. | .. | .. | .. | 10.0 | 10.0 | .. | .. | 1.0 | .. | 10.0 | .. | .. | .. | .. | 1.0 | 10.0 | .. | .. | .. | .. | 1.0 | .. | .. | .. |
| Sb | 2598.062 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| Sn | 2839.989 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. |
| | 2863.327 | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| Sr | 3380.711 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | 0.1 | .. |
| Ta | 2714.674 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2647.472 | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | 0.1 | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | 10.0 | .. |
| Te | 2385.76 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2383.25 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | 0.1 | .. | .. | .. | .. | 10.0 | .. | .. | .. |
| Th | 2837.299 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | 10.0 | 1.0 | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. |
| | 2832.319 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 1.0 | .. | .. | .. | 0.01 | .. | .. | .. | .. | 10.0 | .. | .. | .. |
| Ti | 3234.516 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3383.761 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3372.800 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 0.1 | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3199.915 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. |
| Tl | 2767.87 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| U | 2889.627 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2865.679 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 0.1 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| V | 3183.982 | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | 1.0 | .. | 1.0 | .. | .. | .. | .. | 10.0 | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3093.108 | .. | 0.1 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | 10.0 | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| W | 2946.981 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 0.1 | .. | .. | .. | 10.0 | .. | .. | .. | 10.0 | .. | .. | .. | .. | 1.0 | .. | .. | .. |
| | 2944.395 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | 10.0 | 1.0 | 0.1 | .. | .. | .. | .. | .. | .. | .. |
| Y | 3242.280 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. |
| | 3216.682 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 10.0 | 10.0 | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. |
| Zr | 3391.975 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | 10.0 | .. | 1.0 | .. | .. | 1.0 | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. |

| Element Sought | Wave Length | Mg | Mn | Mo | Na | Nd | Ni | P | Pb | Pd | Pt | Rb | Rh | Sb | Si | Sn | Sr | Ta | Te | Th | Ti | Tl | U | V | W | Y | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ag | 3280.683 | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 0.1 | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3382.891 | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | 10.0 | .. | .. | .. |
| Al | 3092.713 | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3082.155 | .. | 1.0 | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | 10.0 | .. | .. | .. | .. | .. |
| As | 2780.196 | 10.0 | 1.0 | 0.1 | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | 10.0 | .. | 1.0 | .. | .. | .. | .. | 10.0 | .. | 1.0 | .. | .. | .. |
| | 2860.452 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 1.0 | 10.0 | 10.0 | .. | .. | .. |
| Au | 2675.95 | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | 1.0 | .. | .. | 10.0 | .. | 10.0 | 10.0 | 1.0 | .. | .. | .. |
| | 2427.95 | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | 1.0 | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| B | 2497.733 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. |
| | 2496.778 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| Ba | 2634.783 | .. | .. | 10.0 | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| Be | 3130.416 | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | 0.1 | .. | .. | 1.0 | .. | 10.0 | 0.1 | 1.0 | .. | .. | .. |
| | 3131.072 | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | 10.0 | .. | 1.0 | 1.0 | .. | 10.0 | .. | 10.0 | .. | .. | 0.1 |
| Bi | 3067.716 | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | 0.1 | .. | .. | 10.0 | .. | .. | .. | .. | .. |
| Ca | 3179.332 | .. | .. | 10.0 | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 1.0 | 10.0 | .. | .. | .. | .. | 0.1 | .. | .. |
| | 3158.869 | .. | 10.0 | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 10.0 | .. | .. | 10.0 | .. | 10.0 | .. | .. | 10.0 |
| Cb | 3194.977 | .. | .. | 10.0 | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | 10.0 | .. | .. | 10.0 | 10.0 | 10.0 | 1.0 | .. | .. |
| | 3094.183 | .. | .. | 10.0 | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | 10.0 | .. | 10.0 | 0.1 | .. | .. | .. | .. |
| Cd | 3261.057 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | 10.0 | 1.0 | 1.0 | .. | .. | 10.0 |
| Ce | 3201.714 | .. | .. | 1.0 | .. | 1.0 | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | 10.0 | 10.0 | .. | 10.0 | 1.0 | 1.0 | .. | .. | .. |
| | 3194.825 | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | 10.0 | 1.0 | .. | .. |
| Co | 3405.120 | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | 10.0 | .. | .. | .. | 0.1 |
| | 2521.363 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 0.1 | .. | .. | .. |
| | 2424.930 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| Cr | 3021.558 | .. | 10.0 | 10.0 | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | 10.0 | 1.0 | 10.0 | 1.0 | .. | .. |
| | 2835.633 | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 10.0 | 1.0 | 1.0 | .. | .. | .. |
| Cu | 3247.540 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 3273.962 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| Er | 3289.36 | .. | .. | 1.0 | .. | 1.0 | .. | .. | .. | .. | .. | .. | 0.1 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | 1.0 | .. | 0.01 | .. | 10.0 |
| | 2891.387 | .. | 1.0 | 0.1 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 0.1 | .. | .. | 10.0 | 1.0 | .. | .. | .. | .. |
| Fe | 3020.640 | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 0.1 |
| | 3021.073 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. |
| | 2973.237 } | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | 10.0 | .. | .. | .. |
| | 2973.134 } | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Ga | 2943.637 | .. | 10.0 | .. | .. | .. | 0.1 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | 1.0 | 1.0 | 1.0 | .. | .. | .. |
| | 2874.244 | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | 1.0 | 1.0 | .. | .. | .. | .. |
| Ge | 2651.178 | .. | 10.0 | .. | .. | .. | .. | .. | 10.0 | .. | 1.0 | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. |
| | 3039.064 | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | 10.0 | 1.0 | .. | .. | .. |
| Hg | 2536.519 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| In | 3256.090 | .. | 0.01 | 0.1 | .. | 1.0 | .. | .. | .. | .. | 0.1 | .. | .. | .. | .. | .. | .. | .. | .. | 0.1 | .. | .. | 10.0 | 1.0 | 1.0 | 10.0 | .. | .. |
| | 3039.356 | .. | 10.0 | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | 10.0 | 1.0 | .. | .. | .. |
| Ir | 3220.780 | .. | .. | 1.0 | .. | 10.0 | 10.0 | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | 10.0 | .. | .. | .. | 10.0 | .. | .. | .. |
| | 2924.792 | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 10.0 | .. | .. | 10.0 | 0.01 | .. | .. | .. | 1.0 |
| K | 3217.017 | .. | 0.1 | .. | .. | 1.0 | 1.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | 10.0 | 0.1 | .. | 10.0 | 0.1 | .. | 0.1 | .. | .. |
| La | 3337.488 | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 10.0 | .. | .. | 10.0 | .. | 10.0 | 1.0 | .. | .. |
| | 3245.120 | .. | .. | .. | .. | 10.0 | 10.0 | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| Li | 3232.61 | .. | .. | 1.0 | .. | .. | 0.01 | .. | .. | 10.0 | .. | .. | 1.0 | 0.01 | .. | .. | .. | 10.0 | .. | 1.0 | 1.0 | .. | 10.0 | 10.0 | 0.1 | .. | .. | 10.0 |
| | 2741.31 | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. |
| Mg | 2852.129 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 |
| Mn | 2794.817 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2798.271 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 10.0 | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. | 10.0 |
| | 2605.688 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | 2593.729 | .. | .. | 0.1 | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | 1.0 | .. | .. | .. | .. | .. | .. | .. |
| | 2576.104 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| Mo | 3132.594 | .. | 1.0 | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | .. | 10.0 | .. | .. | 0.01 | .. | .. | .. | 10.0 |
| | 3170.347 | .. | .. | .. | .. | .. | 10.0 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 1.0 | .. | 1.0 | .. | .. | 10.0 | .. | 1.0 | .. | .. | .. |

(Continued on page 678)

(Continued from page 677)

| Element Sought | Wave Length | Mg | Mn | Mo | Na | Nd | Ni | P | Pb | Pd | Pt | Rb | Rh | Sb | Si | Sn | Sr | Ta | Te | Th | Ti | Tl | U | V | W | Y | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Na | 3852.828 | 1.0 | | | | | | | | | | | | | | | | | | | | | 10.0 | 0.1 | 10.0 | | | |
| | 2853.031 | 1.0 | | 0.1 | | | | | | | 1.0 | | | | | | | | | | | | 10.0 | 0.1 | 10.0 | | | |
| Nd | 3328.270 | | | | | | | | | | | | | | | | | | | | | | | 10.0 | 1.0 | 0.01 | | |
| | 3133.603 | | | 10.0 | | | | | | | | | | | | | | | | | | | | 0.1 | 1.0 | 10.0 | | |
| Ni | 3050.819 | | | | | 10.0 | 0.1 | | | | | | | | | | 10.0 | | | 1.0 | | | 10.0 | | | | | 0.1 |
| | 3002.491 | | 1.0 | 10.0 | | | | | | | 0.1 | | | | | | 10.0 | | | 1.0 | 10.0 | | 10.0 | 0.1 | | | | |
| P | 2535.65 | | 10.0 | | | | | | | | | | | | | | | | | 0.1 | | | | 1.0 | | | | |
| Pb | 2833.069 | | | | | | | | | | | | | | | | 10.0 | | | | | | | | | | | |
| Pd | 3242.703 | | | | | 10.0 | 0.1 | | | | | | | | | | | 1.0 | | 10.0 | 1.0 | | 10.0 | | | | | |
| | 3404.580 | | | 1.0 | | 10.0 | 0.01 | | | 10.0 | | | | | | | | | | 10.0 | 10.0 | | 10.0 | 10.0 | 10.0 | 0.1 | | 0.1 |
| Pt | 3064.712 | | | 1.0 | | | | | | 0.01 | | | | | | | | | | | | | | | | | | 1.0 |
| | 2997.967 | | 10.0 | 10.0 | | | | | | | | | | | | | | | | | | | | | 0.1 | | | 1.0 |
| Rb | 3396.85 | | | | | 10.0 | 10.0 | | | 10.0 | | | | | | | | | | | | | | | 1.0 | | | 10.0 |
| | 3323.092 | | | | | 10.0 | | | | | | | | 1.0 | | | | | | 10.0 | | | 10.0 | | | 0.01 | | 0.1 |
| Sb | 2598.062 | | 1.0 | | | | | | | | | | | | | | 10.0 | | | | | | | | | | | |
| Sn | 2839.989 | | 1.0 | | | | | | | | | | | | | | 10.0 | | | 10.0 | | | 10.0 | | 10.0 | | | |
| | 2863.327 | | 10.0 | | | | | | | | | | | | | | | | | | | | | | | | | |
| Sr | 3380.711 | | | 1.0 | | 1.0 | 0.01 | | | 10.0 | | | | | | | | | | | | | | | | | | |
| Ta | 2714.674 | | | | | | | | | | | | | | | | | 0.1 | | | | | 10.0 | | | | | |
| | 2647.472 | | | | | | | | | | | | | | | | | | | 10.0 | | | 10.0 | | | | | |
| Te | 2385.76 | | | | | | | | | | | | | | | | | | | | | | 1.0 | | | | | |
| | 2383.25 | | | 10.0 | | | | | | | | | 0.1 | | | | | | | | | | | | | | | |
| Th | 2837.299 | | | 10.0 | | 10.0 | | | | | | | | | | | | | | | | | | | | | | |
| | 2832.319 | | | | | 10.0 | | | 10.0 | | | | | | | | | | | | | | 1.0 | | 1.0 | | | 0.1 |
| Ti | 3234.516 | | | | | 1.0 | 0.1 | | | | | | | | | | | 10.0 | | | 0.1 | | 10.0 | | 10.0 | | | |
| | 3383.761 | | | | | | | | | | | | | | | | | | | | | | | 10.0 | | | | |
| | 3372.800 | | | | | | | | | 0.1 | | | | | | | | | | | | | | | | 0.1 | | |
| | 3199.916 | | | | | | | | | | | | | | | | | | | | | | 10.0 | | 10.0 | | | |
| Tl | 2767.87 | | | | | | | | | | | | | | | | | 10.0 | | | | | 10.0 | | | | | |
| U | 2889.627 | | 0.1 | 10.0 | | 10.0 | 0.1 | | | 10.0 | | | | | | | | | | | | | | 0.01 | | | | 10.0 |
| | 2865.679 | | | 10.0 | | 10.0 | 1.0 | | | | | | | | | | | | | | | | | | | | | 1.0 |
| V | 3183.982 | | | | | | | | | | | | | | | | | 10.0 | | | 1.0 | | 10.0 | | 1.0 | | | 1.0 |
| | 3093.108 | 0.1 | | | | 10.0 | | | | | | | | | | | | 10.0 | | | 1.0 | | 1.0 | | 10.0 | | | 10.0 |
| W | 2946.981 | | | | | | | | | | | | | | | | | 1.0 | | | | | | | | | | |
| | 2944.395 | | 1.0 | 10.0 | | | 10.0 | | | | | | | | | | | | | | | | 10.0 | | | | | 10.0 |
| Y | 3242.280 | | | | | 10.0 | 1.0 | | | 0.1 | | | | | | | | 1.0 | | 1.0 | 0.01 | | | | 10.0 | | | 1.0 |
| | 3216.682 | | 0.1 | 1.0 | | | 0.1 | | | | | | | | | | | 1.0 | | 1.0 | 0.1 | | 1.0 | | | | | 1.0 |
| Zr | 3391.975 | | | 10.0 | | 10.0 | 1.0 | | | | | | 1.0 | | | | | 1.0 | | 0.1 | | | 10.0 | | | 10.0 | | 1.0 |

tivities would be misled by an analytical report based only on line intensity.

As a result of this weakness of the method, a system was devised to allow for differences in sensitivity by comparing the unknown spectrum with standard spectra which permit a semiquantitative estimation of each element found. The details of the spectrography and interpretation are given in this paper.

## SPECTROGRAPHY

Of the various means of exciting the spectra, the direct current arc with graphite electrodes is probably the best for general detection of metallic constituents from the standpoint of sensitivity, general applicability, and convenience. The electrodes are mounted vertically, the sample being placed in a crater drilled in the tip of the lower electrode. This means of excitation is used in nearly all cases of qualitative analysis in this laboratory. A large Littrow-type quartz spectrograph is used to record the spectra.

One procedure is to place approximately 0.1 gram of the unknown in a crater drilled in the tip of a graphite electrode. With this electrode as positive pole and a counterelectrode of graphite, a 10-ampere direct current arc is struck to excite the spectrum. The exposure is continued until all the sample appears to have been volatilized, 5 to 15 minutes, depending upon the nature of the sample. Under such conditions, the more volatile elements are vaporized in the initial stages and the more refractory elements fuse down to a bead at the bottom of the crater and are vaporized more slowly. Complete vaporization of the sample is necessary for a reliable analysis. In this paper this type of arc is referred to as the conventional direct current arc.

For several years this laboratory has been using a more rapid technique, the Hasler high streaming velocity arc (*1*, *2*) which has been adapted to qualitative analysis.

The sample is put into the form of a fine powder and intimately mixed with carbon powder obtained by the charring of sucrose. (Graphite powder is not suitable for this purpose.) This mixture is packed into the crater of a specially formed graphite electrode and then volatilized in the direct current arc. Under these conditions the sample passes very rapidly into the arc flame, the gases developed by the burning sucrose carbon powder literally blowing the powder into the arc flame. Most samples are completely removed from the electrode in 0.5 minute. This type of arc seems to effect a uniform transfer of the sample from the electrode to the arc as compared to the fractional distillation taking place in the conventional arc.

The tip of a 0.78-cm. (0.3125-inch) diameter graphite electrode is drilled with a special cutter so as to form an annular hole 0.6 cm. (0.25 inch) in outside diameter, 0.3 cm. (0.125 inch) in inside diameter, and 0.78 cm. (0.3125 inch) deep. This leaves a center pole of 0.3 cm. (0.125 inch) diameter at the center of the crater. The unknown sample is dissolved in acid, preferably nitric, and the solution evaporated to dryness in a fused quartz dish, and heated gently over a Bunsen burner substantially to decompose the nitrates into oxides. If the sample is already in powder form, this solution step may be omitted. The powder is then ground in an agate mortar to a fineness equivalent to through 200-mesh and thoroughly mixed. The powder should not be screened because of the danger of contamination. Approximately equal volume portions of the powdered sample and sucrose carbon are intimately mixed and ground in an agate mortar and the annular hole electrode crater is filled with this mixture. A special metal funnel is used, fitting over the

electrode in such a manner that none of the powder is lost during transfer. With zinc-base samples, a standard quantity of 50 mg. of sample powder and 50 mg. of sucrose carbon is used. In all cases exposure time is standardized at one minute.

Spectra obtained from this type arc are much more free of background than the arc formerly used and the exposure time is only one tenth as long.

Comparative tests have been made between the conventional direct current arc and the high streaming velocity arc on a variety of samples. The relative concentrations of the elements in an unknown are indicated to be substantially the same by the two methods. The high streaming velocity arc method is somewhat more sensitive, since a few trace elements are usually detected which were not detected by the conventional arc method. The very large decrease in exposure time results in an important increase in speed, and saving in labor.

Most metals have their most sensitive lines in the ultraviolet portion of the spectrum. A few metals (barium, calcium, chromium, cesium, lithium, sodium, rubidium, and strontium show greater sensitivity in the visible spectrum, however, and if the amounts of these elements are small their spectral lines may have to be sought also in the visible spectrum. With the Littrow spectrograph, this requires the taking of two plates. In this laboratory these two spectral regions are designated as Range 1 (or visible) extending from 7000 to 3200 Å., and Range 2 (or ultraviolet) extending from 3400 to 2370 Å. Table I shows the range of the spectrum in which the elements may be detected with greater sensitivity.

The data of Table I are based on experimental tests of sensitivity in a zinc matrix, using the direct current arc between graphite electrodes. With other matrices, other supporting electrodes, self-electrodes, other excitation conditions, or other photographic plates, the grouping would probably be different.

As a matter of routine practice the spectrum is usually photographed in Range 2 only. Evidence for all of the elements listed in Table I is sought. If some elements not detected in Range 2 and having a greater sensitivity in Range 1 are of especial interest in the particular sample being analyzed, the spectrum will be rephotographed in Range 1. In some cases the spectra will be photographed in both ranges at the outset.

## IDENTIFICATION

To facilitate spectral line identification, a comparison plate is used upon which are recorded the spectra of a group of master standards containing enough of the various elements in a zinc matrix to give several of the strongest lines of each. The compositions of each are listed in Table II.

In routine practice, no attempt is made to identify every line in the spectrum. Rather, a search is made only for each of 53 elements by reference to the master standard plates. Of the elements not specifically sought, eleven are gases, five are nonmetals not detectable in the direct current arc, and twenty are rare metals.

The most sensitive lines under the conditions of spectrography specified in this paper and the approximate limits of detection are listed in Table III. No attempt is made to indicate the sensitivity more precisely than in order of magnitude.

Obvious precautions must be observed in identification. The more lines of a particular element which can be observed, the more certain is its identification. If only the most persistent line shows up faintly, the possibility that that line is a faint line in the spectrum of another constituent or from an electrode impurity must be considered.

A survey has been made of possible line interferences. These interferences may be due to the coincidence of a line of the interfering element with the persistent line of the element sought or to the proximity of a strong line of an interfering element. Table IV shows the concentration of interfering elements which may interfere with the identification of traces of elements sought. The data are derived from zinc-base standards and the percentages expressed in terms of the zinc matrix. The use of the table may be illustrated by an example. Suppose the only line of barium detectable in a sample is the 2634.783 line. If the sample contains 1% of columbium, or 10% of copper, molybdenum, or neodymium, the indicated presence of barium would be open to question.

In most cases, identification can be established by the detection of several lines of each element. If, however, only the most persistent line (or lines) of an element are found, then the possibilities of interference given in Table IV must be considered.

## SEMIQUANTITATIVE EVALUATION

Each element found in the unknown is graded by comparison with the spectra of a series of standard samples made up in a zinc base. Since the standards are in a zinc base, their use is strictly valid only when analyzing zinc-base materials, but it has been the experience in this laboratory that these standards give useful results with other than zinc-base materials—results which are more valid than if no compensation was made for differences in spectral sensitivity of the various constituents of an unknown.

The standards are made as follows: Nine grams of zinc and 1 gram of the element are dissolved in nitric acid. (If the element cannot be dissolved in nitric acid, a small quantity of some other solvent is used to effect a solution, following which the solution of zinc in nitric acid is added.) The resulting solution, containing 90% zinc and 10% element, is converted to a well-mixed oxide powder in the manner described above for preparing unknown samples. In some cases it is not possible to achieve a clear solution, but this does not matter since the solution is evaporated to dryness and the powder is well ground and mixed. This constitutes the 10% standard. A one-tenth aliquot of this weight of powder is then dissolved in nitric acid, together with 9 grams of zinc. From this solution the second standard is prepared, equivalent to 1%. This process is continued until standards are available for 10, 1, 0.1, 0.01, 0.001, and 0.0001%. This is carried out for the 53 elements listed in Table III. In the case of the standards for the grading of zinc, a base of graphite powder is used.

The spectra of the six standards for each of the elements are photographed and kept on file as standard grading plates.

**Table V. Reporting Designations Based on Relative Concentrations**

| Standard, % | Reporting Designation |
|---|---|
| >10.0 | vs |
| 10.0 | s |
| 1.0 | m |
| 0.1 | w |
| 0.01 | f |
| 0.001 | vf |
| 0.0001 | xf |

**Table VI. Comparison between Qualitative and Quantitative Analyses**

| Sample A | | | Sample B | | | Sample C | | | Sample D | | | Sample E | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1[a] | 2[b] | 3[c] | 1[a] | 2[b] | 3[c] | 1[a] | 2[b] | 3[c] | 1[a] | 2[b] | 3[c] | 1[a] | 2[b] | 3[c] |
| Zn | vs | .. | Zn | vs | .. | Cu | vs | 87.8 | Cu | vs | 55.1 | Fe | m-s | 40.0 |
| Pb | m | 0.5 | Ni | w | 0.045 | Al | w-m | 8.8 | Zn | m-s | 42.0 | Ti | m-s | 8.6 |
| Cd | w | 0.17 | Mg | f | 0.08 | Fe | w-m | 2.2 | Al | w-m | 0.83 | Si | m-s | 4.4 |
| Sn | f | 0.006 | Pb | f | 0.055 | Ni | w | .. | Fe | w-m | 0.83 | Mg | w-m | 3.4 |
| In | f | 0.005 | Sn | f | 0.027 | Zn | f-w | < 0.1 | Mn | w-m | 0.66 | Ca | w-m | 5.9 |
| Fe | f | 0.04 | Fe | f | 0.04 | Ag | f-w | .. | Pb | w | 0.13 | Al | w | 1.2 |
| Cu | f | 0.023 | Cu | f | 0.025 | Mn | f · | .. | Sn | f-w | 0.18 | Mn | f-w | 0.35 |
| Ag | vf | .. | Cd | vf | 0.002 | Pb | vf-f | 0.037 | Ni | f | .. | V | vf-f | .. |
| Sb | vf | .. | Mn | vf | 0.006 | Sn | vf-f | 0.024 | Ag | vf-f | .. | Ga | vf | .. |
| Ni | vf | 0.0005 | Mo | vf | .. | Cr | vf | .. | Cr | vf-f | .. | Cu | xf-vf | .. |
| | | | Bi | xf | 0.0005 | Be | xf-vf | .. | Sb | xf-vf | .. | | | |

[a] Elements detected.
[b] Qualitative grading of relative concentration.
[c] Quantitative determination where available.

Table VII. Comparison of Moving Plate Method and High Streaming Velocity Arc

| Sample | Found in M.P.M. but Not in H.S.V.A.M. | Found in H.S.V.A.M. but Not in M.P.M. |
|---|---|---|
| A | None | None |
| B | Bi, Be, Ga, Tl, P, Zr, Sr | None |
| C | Ga, As, Ge, Sb, P, Sr, Co | None |
| D | Ti | Zn |
| E | Ni, Cd | None |
| F | None | None |

The spectrum of an unknown is first examined to determine what elements are present by reference to the master standard plates. The plate is then compared visually with the standard grading plates for the elements found, and an estimate is made of the standard to which each element intensity in the unknown most nearly approximates.

Each standard has been assigned an arbitrary grading designation for report purposes, as shown in Table V. An element graded as being nearer the 0.01% standard than to any other standard could be reported as approximately 0.01% or as f. An element judged to be about midway between 0.01 and 0.1% could be reported as approximately 0.05 or as f-w. It is the general practice in this laboratory to report the symbol rather than the approximate percentage. To report an actual figure in per cent, even though modified by the word "approximately", may be misinterpreted by some user of the results as an exact quantitative result.

There are several known sources of error. An effort is made to maintain uniform excitation conditions, plate sensitivity, and plate processing conditions, but these conditions are variable. The photographic errors are particularly serious. Differences in the major constituents of the sample introduce variations in the intensity of the spectra, which cannot be completely controlled or compensated for by any practical methods.

The analytical results on five samples selected at random from samples upon which both qualitative and quantitative analyses have been made are listed in Table VI. Two zinc-base, two copper-base, and one iron-base samples are included. These results indicate the degree of reliability to be expected from the semiquantitative indications given by this system of qualitative analysis.

The average time required for the identification and grading of a qualitative plate is 20 minutes.

### MOVING PLATE METHOD

Occasional use is made of another technique designated as the moving plate method. No claim is made for originality in using this technique but the results obtained thereby in qualitative analysis are worthy of being recorded.

Using simple counter-type graphite electrodes, the sample is volatilized with the direct current arc and the spectrum recorded in successive increments of exposure over the entire 5- to 15-minute period which may be required to volatilize the entire sample. The author's practice is to photograph a spectrum 2 mm. wide for each 30 seconds of exposure, moving the plate 2 mm. vertically every 30 seconds during the total arcing period.

This technique results in a series of spectra showing the elements being volatilized during each increment of the arcing period. This sometimes gives greater sensitivity in detecting some elements, particularly those elements which volatilize over a short period at some portion of the arcing period, probably because the increment of spectrum exposure recorded at the time the particular element is being volatilized is not overexposed with general background.

The results shown in Table VII indicate that the moving plate method is more likely to detect all the elements present than the high streaming velocity arc method.

The additional elements found, however, are trace elements giving very faint spectra. The moving plate method is much more time-consuming and is not used as a matter of routine unless circumstances indicate the need for the very best sensitivity and the most complete analysis.

In grading a plate, the practice is to search each spectrum for each of the 53 elements. The intensity grading, for each element found, is made on the increment of exposure showing this element most strongly, using the same standard grading plates as those used for the high streaming velocity arc. No justification for the validity of relative concentration gradings made in this manner can be made except to say that the gradings are generally in fair agreement with those made by the high streaming velocity arc method.

### ACKNOWLEDGMENT

Appreciation is expressed to M. L. Fuller for his painstaking care in the review of this work and for the preparation of the manuscript.

### LITERATURE CITED

(1) Hasler, M. F., *J. Optical Soc. Am.*, 31, 140 (1941).
(2) Hasler, M. F., and Harvey, C. E., Ind. Eng. Chem., Anal. Ed., 13, 540 (1941).

# Alundum Gas Diffusers

DWIGHT WILLIAMS AND GEORGE S. HAINES
Research Department, Westvaco Chlorine Products Corporation, South Charleston, W. Va.

A VERY convenient and inexpensive gas diffuser for laboratory use can be made by sealing ordinary Pyrex glass tubing to Alundum extraction thimbles. Despite the fact that Alundum has about twice the expansion coefficient of Pyrex, satisfactory seals can be made between the two materials as shown in Figure 1. The large sizes are made by blowing an enlargement in the tubing of desired size and butt-sealing this to the thimble. The smallest size is most conveniently made by lap-sealing the glass tubing to the thimble. The resistance of this type of diffuser is indicated by the data in Table I, showing typical pressure drops across the various size thimbles when passing 1000 ml. of air per minute through water. The Alundum thimbles are available from the Norton Company, Worcester, Mass., for about 50 cents each. The Norton Company recommends Alundum diffusers for use in acid but not in alkaline solutions.

Figure 1

### ACKNOWLEDGMENT

The authors acknowledge the assistance of L. A. Bedwell, who did the necessary glass blowing, and the permission of Westvaco Chlorine Products Corporation to publish this note.

Table I. Pressure Drop across Alundum Diffusers
(Air rate = 1000 ml. per minute)

| Diffuser | | Pressure, |
|---|---|---|
| Dimensions, Mm. | Description | Mm. of Hg |
| 19 × 90 | No. 6839, RA98 | 82 |
| 16 × 70 | No. 11702, RA98 | 92 |
| 15 × 90 | No. 7338, RA98 | 107 |
| 6 × 32 | No. 8133, RA98, sanded | 130 |
| 6 × 32 | No. 8133, RA98 | 152 |

# Determination of Noncondensables in Gas

AARON E. MARKHAM, Research Department, York Corporation, York, Pa.



**An apparatus is described for the quantitative determination of small percentages of noncondensable in an easily condensed gas. The apparatus should be useful for analyses of many gaseous systems, especially in the case of gases for which no chemical absorbents are available. The vapor pressure and liquid density of the condensable gas must be known. The method has been applied to the determination of noncondensable in commercial difluorodichloromethane, Freon-12.**

THE need has arisen in this laboratory in connection with research work on refrigeration for a method of quantitative determination of noncondensable in the presence of large amounts of easily condensed gas. Routine determinations were required for such analyses of dichlorodifluoromethane, boiling point −30° C., when the noncondensable was in the range of 0.001 to 3%. Atmospheric gases constituted the noncondensable.

A method developed by the Kinetic Chemicals Corporation (*1*) was available for the determination of nonabsorbable in kerosene, which in this case is nearly the same as noncondensable. Their method involves the absorption of the condensable gas in kerosene which has been freshly boiled and then saturated with air. However, the method was not satisfactory for the author's purposes, for several reasons. First, a rather large correction (1.6%) must be applied to compensate for air driven out of the kerosene by the dichlorodifluoromethane. Such a correction leads to inaccuracies in the low range of nonabsorbables. Furthermore, a method was desired which measured actual noncondensable without the assumption that it was the same as nonabsorbable. The apparatus described here proved to be rapid in operation and to give reproducible results in the whole range of concentration desired. A complete analysis requires from 10 to 15 minutes, exclusive of calculation.

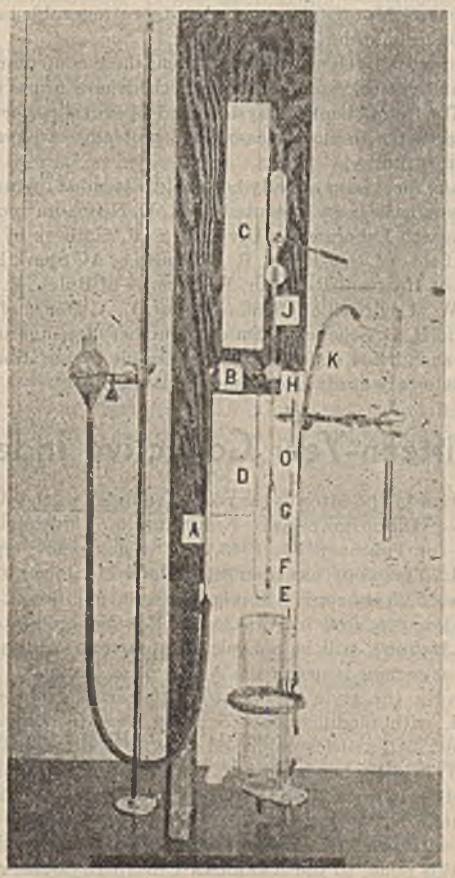



Figure 1

### PRINCIPLE OF THE METHOD

The gas is liquefied by cooling in a graduated tube. The amount of noncondensable is observed and corrected for the presence of condensable gas. The volume of condensate is observed, and converted to gas volume through the known densities of the two phases. From the volumes of condensable and noncondensable, the percentage of noncondensable is calculated to any desired basis.

### APPARATUS

The apparatus, shown in Figures 1 and 2, is of glass, with a rubber tube connection from *A* to a mercury leveling bulb. Tubes *A*, *C*, and *J* are of 7-mm. inside diameter. The capillary tubes have about 2-mm. bore. Bulbs *F* and *E* have volumes of about 0.5 and 1.5 ml., respectively. Tube *G* is graduated from point *O* in convenient increments of volume, depending on tube diameter. The first graduations below *O* are on the capillary, hence correspond to very small increments of volume. The next are on a 6-mm. tube, and the next on a 12-mm. tube, which is the main body of *G*. At the bottom of *G* is a short 4-mm. capillary, graduated at 2-mm. intervals to the mark above *F*. The total volume of *G* is 7.5 ml. The dimensions were calculated to give the maximum accuracy throughout the range of noncondensables expected. This calculation is based on the range of noncondensables to be covered, the relative densities of gas and liquid and the operating temperature. The apparatus was accurately calibrated by the use of mercury. The cold zone is an unsilvered 1-liter vacuum flask, filled with dimethoxytetraethylene glycol, and cooled with dry ice (*2*). A temperature of about −31° C. can be maintained easily for long periods in this way. The flask can be lowered readily to allow the apparatus to warm.

A scale is placed behind *C*, for reading pressure, and the height from a reference point on the scale to the graduations of *G* is known. The graduations are calibrated for height, so that an observation of the mercury levels in *C* and *G* can be reduced to a pressure difference.

### MANIPULATION

By proper manipulation of the stopcocks, with the leveling bulb raised, the apparatus is filled completely with mercury up to the tip of tube *K*, and up tubes *C* and *J* to points about 20 cm. above the cocks. Connection is then made at *K* to the source of gas to be analyzed, and cocks *B* and *H* are turned to shut off the mercury in *C* and *J*, but to allow flow from *K* through to the mercury bulb. The mercury bulb is then lowered slowly, drawing in sample, until the mercury level is in bulb *F*. The vacuum flask, at the low temperature, is then raised to surround the apparatus, and condensation begins. During condensation, the mercury level is adjusted exactly to the mark at the bottom of *F* or *E*, *B* is shut off, and condensation continued till *F* or both bulbs are nearly filled with liquid. (This choice depends on the probable amount of noncondensable present, the larger sample when both bulbs are used permitting more accurate measurement if the percentage of noncondensable is small.) When the condensed liquid nearly reaches the mark at the top of *F*, cock *H* is turned off, and then turned to allow mercury to run down from *J* into the capillary to *O*, thus sealing the tube and driving all gas into the cold zone. (It is evident that the mercury height in *J* must be sufficient to overcome the pressure in the apparatus.)

The apparatus is then allowed to stand for several minutes, to allow the liquid to drain into *F*. With some practice, it is possible to stop the flow, so that this draining will fill the bulb almost exactly to the mark. Any excess can readily be estimated by the graduations on the capillary tube above *F*. The volume of condensable is thus measured as liquid, and its temperature estimated from that in the bath. The mercury bulb is then raised above *B*, and cock *B* turned to connect *A*, *C*, and *D*. The height of mercury in *C*, the top of the liquid meniscus in *G*, the mercury level in *G*, and the temperature of the bath are observed. By manipulation of the pressure, it is possible to adjust the liquid level to a favorable location for reading. From the barometric pressure and the mercury levels, corrected for a small head of liquid above the mercury in *G*, the total pressure on the gas is known. From the temperature and the thermodynamic tables of the liquid, the partial pressure of the liquid is known. Hence the partial pressure of the noncondensable is found, and this

combined with its volume and temperature, leads to the amount of noncondensable, expressible in any desired way, since the amount of condensable is known. The amount of condensable in the vapor phase can be calculated, and added to the volume of condensate, but this correction is negligible.

To empty the apparatus, the mercury from $J$ is slowly drawn through $H$ into $G$, then $H$ is opened, and the vacuum flask is removed. As the liquid boils, it escapes through $J$. A mercury trap at the top of $J$ is desirable.

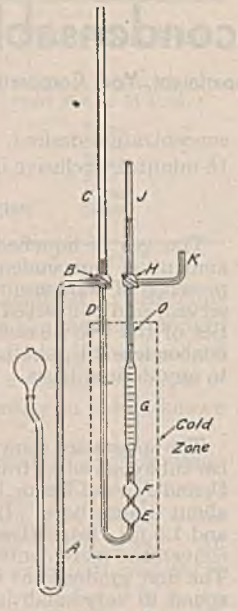



Figure 2

### CHECK RESULTS

Some commercial material of high purity was analyzed by the method just described, giving reproducible results in the range 0.013 to 0.020% noncondensable. To this material was added air in measured proportions, after which the mixture was analyzed as described. The following results illustrate the reproducibility of the analyses as checked by the author in his work:

| % Air Added | % Noncondensable Found |
|---|---|
| 1.25 | 1.23 |
| 1.52 | 1.46 |
| 0.34 | 0.32 |
| 1.16 | 1.13 |
| 1.01 | 1.03 |
| 0.62 | 0.64 |

The discrepancy is probably due as much to the uncertainties in preparing the mixtures as to the analyses.

A source of error lies in the solubility of noncondensable in the condensate. This error, of course, depends on the system under investigation, and in some systems could easily be excessive. By keeping the partial pressure of the noncondensable low, the error can be minimized. In the measurements cited, the temperature of the condensate has been kept about 1° below its normal boiling point, and the pressure during condensation only a few inches greater than atmospheric. Hence the partial pressure of the gas is not more than 7.5 or 10 cm. (3 or 4 in.) of mercury. The temporary increase of partial pressure to about 25 or 30 cm. (10 or 12 inches) when the volume is observed probably results in little increase in the noncondensable dissolved. Condensation near the normal boiling point is probably most satisfactory, since with a small positive pressure in the apparatus the partial pressure of noncondensable is kept small. Furthermore, the vapor pressure of the condensable is frequently better known or more satisfactorily estimated near the normal boiling point. If the noncondensable data are to be used at temperatures other than that of the analyses, it is well to remember that "noncondensable" is a relative term and what is noncondensable at one temperature may be condensable at other temperatures.

If water is present in quantity, it must be removed before the analysis, or the tube will clog with frost. It is advisable to keep a slight positive pressure in the apparatus to avoid the possibility of leaks inward. There is some tendency for dichlorodifluoromethane to leak through ordinary stopcocks. The manipulations described were planned to reduce leakage to a minimum, by the use of moderate pressures, and by separating the gas and liquid from the stopcocks with mercury when possible. Repeated use of the apparatus tends to saturate the stopcock lubricant with gas, which may reduce the leakage. In the range of noncondensable considered here, small losses of condensable are much less important than leakage, either inward or outward, of noncondensable. The use of special stopcocks or of special grease might reduce the leakage, but under the conditions used such refinements appear unnecessary.

Sampling of a gas mixture for analysis is just as important as the analysis, and frequently more difficult to do accurately. In this special case, uniform samples were available of sufficient quantity for an analysis (ca. 100 to 400 ml.). Frequently, however, gas of uniform composition might not be available, or might be available only in very small quantity. The sampling then could easily be a real problem, especially if two phases were present.

### GENERAL APPLICATION

The apparatus should be useful with a wide variety of gases, especially those for which no chemical absorbents are available. Other temperatures of condensation can be used. Tube $C$ can be connected at point $A$ to cover lower pressures, and to provide for the simultaneous measurement of gas and liquid volumes. The addition of more liquid bulbs, or the change of relative volumes of the apparatus, could make the apparatus cover a different range of noncondensable. Provision can be made to withdraw and analyze the noncondensable. This has not been done. It is necessary to know the liquid density and vapor pressure of the condensable gas.

### LITERATURE CITED

(1) Kinetic Chemicals, Inc., Wilmington, Del., *Tech. Paper* 8 (1931).
(2) Wikoff, Cohen, and Grossman, Ind. Eng. Chem., Anal. Ed., 12, 92 (1940).

## General Motors Spectrographic Conferences

A series of spectrographic conferences has been initiated by the General Motors Corp., under the chairmanship of G. M. Rassweiler, Research Laboratories Division, to develop further the applications of these analytical tools. Application of spectrochemical analysis has expanded so rapidly in connection with war production problems that 24 General Motors plants now have spectrographic installations in operation or on order.

Attended only by General Motors men, these conferences provide for frank and critical examination of methods now in use or contemplated. The fundamental physical and chemical aspects are discussed, together with closely associated problems of physics, chemistry, and metallurgy.

Five conferences have already been held, attended by from 40 to 60 men. Papers have been presented by R. E. Nusbaum and D. L. Fry of the Research Laboratories Division, S. F. Simpson of Chevrolet, W. N. Hatfield of Delco-Remy, R. W. Smith of AC Spark Plug, H. H. Grossman of Harrison Radiator, E. Osborne of Buick, F. D. Brookshire and W. R. O'Neill of Cadillac Motor, L. A. Danse of Standards Section, and R. B. Schenck of Buick. Further meetings are planned, as well as such other activities as cooperative preparation of standards and extensive study of methods and equipment.

## Fifteen-Year Collective Index

Publication of the fifteen-year collective index to the Analytical Edition of Industrial and Engineering Chemistry is now scheduled for February 15, 1945, and a domestic prepublication price of $1.75 per copy has been set. Domestic price after publication will be $2.25 per copy. Foreign, 10 cents additional.

This index, prepared by Charles L. Bernier, associate editor of *Chemical Abstracts*, will be a book of more than 100 pages, of the same size as regular issues of the Analytical Edition. In preparing the index the style of *Chemical Abstracts* has been followed, in general, with modifications to make it more adaptable to its special uses. All articles published from 1929 through 1944 are included. This index has been built from scratch, not made by combining yearly indexes. The indexing is uniform and harmonized throughout.

Orders, with check in payment, should be sent with the card inserted in this issue, to the American Chemical Society, 1155 Sixteenth St., N.W., Washington 6, D. C.

# Viscometric Chain Length of Wood Cellulose in Triton F Solution

EDWIN L. LOVELL, Central Chemical Laboratory, Rayonier Incorporated, Shelton, Wash.

**Use of aqueous dimethyldibenzylammonium hydroxide (Triton F) as a cellulose solvent for the determination of average chain length by the viscometric method, in dilute solution, is suggested. A suitable experimental technique is described in detail. Intrinsic viscosity data for a number of cotton and wood celluloses in Triton F are compared with the corresponding degree of polymerization values obtained viscometrically after nitration, and a linear relationship is established. The results are compared with cuprammonium viscosity values, as used in the wood cellulose industry.**

FOR purposes of fundamental research on cellulose in its various forms (linters, wood celluloses, etc.) the need for a good cellulose solvent, giving solutions rather stable to light and air, is readily evident.

At present the only such solvent known appears to be an aqueous solution (about 35%) of the strong base dimethyldibenzylammonium hydroxide, commercially available in experimental quantities as Triton F (Rohm and Haas). The high solvent power of this basic solution has been conclusively shown by Clibbens and co-workers (*3*), who measured the solubility of cottons in the base at different temperatures and concentrations. They found that Triton F "permits complete dissolution of an unmodified cotton at 20° C.". This has been substantiated by other workers. Russell and co-workers (*12*, *13*) have made a detailed study of the methods of dissolving cellulose in this solvent, with attention to time, temperature, concentration of the Triton base, and mode of stirring during solution. They found that at 25° C. there exists a narrow range of concentrations in which the dissolving power is maximum—namely, 1.96 ± 0.01 *N*. This point shifted with temperature, moving to lower concentrations at lower temperatures. For the solution of celluloses of the very highest viscosity, base concentrations of 2.1 to 2.25 *N* gave better results. Brownsett and Clibbens (*3*) give the point of maximum dissolving power as 1.95 *N* at 20° C., with a second maximum at about 2.5 *N*. Once the cellulose solution has been formed, it is no longer necessary to maintain a concentration of base as high as that required to effect solution—for example, dilution of a 1% solution of unmodified cotton cellulose to one-half concentration is possible without precipitation. In general, precipitation does not start until the base concentration is reduced below 0.5 *N*.

Two methods of efficiently dissolving cellulose samples in Triton F have been described. In one (*12*), the cellulose-solvent mixture is mechanically stirred in a large test tube with a heavy glass rod arranged to sweep out a circular path as close as possible to the test-tube wall. By this method, about 2 to 3 hours are required to form a 1% solution. In the second method (*10*), the cellulose and solvent are placed in an all-glass vial containing a glass plunger, and rolled for about 18 hours.

The stability of Triton F cellulose solutions to light and air has been established (*13*) by comparing the viscosities of the solutions when prepared under nitrogen with the viscosities obtained in the presence of air or oxygen. Such demonstrations of the stability of this alkaline solution of cellulose show a most remarkable contrast to the well-known behavior (*1*) of cuprammonium cellulose solutions. However, Triton F cellulose solutions have been shown (*13*) to be subject to a slow viscosity drop with time, the effect being accelerated by a rise in temperature, and furthermore being proportionately greater for higher concentrations of dissolved cellulose. This aging effect has not been satisfactorily explained.

It has been found (*12*, *13*) that the specific viscosities of Triton F solutions of normal and degraded cottons, over a wide range of viscosities, vary in an approximately linear manner with the specific viscosities of cuprammonium solutions at the same cellulose concentration (0.5%). This led to the suggestion that Triton F should be substituted for cuprammonium reagent in commercial practice, in view of the greater stability of its solutions.

Further viscosity data provided in the work of Brownsett and Clibbens (*4*) show especially a unique feature of Triton F viscosity values. Comparison of the viscosities of various oxycelluloses measured in Triton F and cuprammonium reagent, before and after a weak alkaline treatment, reveals that the celluloses having alkali-sensitive linkages (*14*) are not fully hydrolyzed by cuprammonium reagent, whereas Triton F is a strong enough base to split completely all such points of latent degradation. In other words, viscosity measurements in cuprammonium give a value for apparent degradation, whereas in Triton F both apparent and latent degradation are measured.

All these interesting and advantageous properties of Triton F suggest its use as an ideal cellulose solvent for viscometric chain-length determinations, using the very dilute solutions required for such a purpose, rather than the relatively concentrated solutions heretofore reported in the literature. The present paper describes in some detail the experimental method developed through three years of constant use, and provides a mathematical constant for converting the measured viscosity values into terms of average chain length, which may be used for either cotton or wood cellulose.

## EXPERIMENTAL METHODS

MEASUREMENT OF VISCOSITY. All the viscosity measurements were made at 20.00° ± 0.015° C. This degree of accuracy of temperature control is considered necessary for suitable accuracy of the measurements themselves because Triton F has a high viscosity with a rather large temperature coefficient.

The viscometer used (*2*) was constructed according to the detailed specifications contained in British Standard Method No. 188, standard U-tube viscometer No. 2. It was held firmly in a stout rectangular brass frame, which fitted into a frame-holder mounted permanently in the thermostat, and carefully adjusted to the vertical. The meniscus formed by the solution in the viscometer was observed against an illuminated white background.

To permit control of the liquid level in the arms of the viscometer, a U-shaped attachment to the open ends was used. This was arranged so that the solution could be pushed up into one limb by a slight pressure of nitrogen, which pressure could be instantaneously released by turning a stopcock connecting the two limbs. In addition to the convenience of manipulation, this arrangement allowed the solution to be kept under nitrogen during the course of the measurements.

To fill the viscometer, the solution was poured into a 25-ml. Erlenmeyer suction flask, nitrogen being led in through the side arm. The gas pressure was then used to drive the solution through a small-bore glass tube into the right limb of the instrument. The proper volume adjustment was made with a fine pipet after 20 minutes or more in the thermostat.

When a measurement had been completed, the solution (later to be recovered according to a recommended procedure, *12*) was poured from the viscometer and the latter washed out with water, followed by chromic acid cleaning solution. When again to be used, the viscometer was washed with water, alcohol, and ether, and dried for 5 minutes by passing a slow stream of filtered nitrogen through it.

The times of flow were measured to the nearest 0.1 second, for a total time of 260 seconds (solvent alone) to about 300 seconds (cellulose solutions). Each measurement was repeated until 3 or 4 consecutive readings were obtained, which did not deviate from one another by more than ±0.1 second.

PREPARATION OF THE SOLUTIONS. The most convenient method for dissolving cellulose in Triton F, at the very low concentrations required for chain-length measurements, has been found to be that of Mease (*10*), utilizing a glass-stoppered bottle containing a glass plunger which on rotation serves to break up the gels sufficiently so that solution takes place. Thus the solution may be kept under nitrogen at all times. Furthermore, in the absence of any stirring device, accurate weighing of the solution is facilitated.

In these experiments, the dissolving vials used had a capacity of about 11 grams of Triton F cellulose solution, which is a little more than is necessary to fill the viscometer. The ground stoppers were of interchangeable standard taper ₮19/17. For rolling, each vial was fixed into a wide-mouthed container of suitable size. This container and contents were placed on rollers adjusted to make about 1 turn in every 10 seconds. Overnight or about 17 hours' rolling at 25° to 30° C. was necessary safely to complete solution of wood cellulose at the concentrations used.

CONCENTRATION OF THE SOLUTIONS. To obtain an accurate measure of the concentration of cellulose in solution, the following procedure has been convenient: The mixing vial, complete with plunger, was weighed (about 40 grams). About 5 mg. of cellulose were added, and weighed accurately in the vial to the nearest 0.05 mg. After being washed out well with nitrogen, the vial was filled with Triton F, so that only a small bubble of nitrogen remained on top after the stopper was inserted. After rolling, the vial and contents were weighed, and the volume concentration (grams per 100 ml. of solution) was calculated from the previously determined density of the solvent.

The problem of obtaining a representative sample when using such a very small quantity of fiber is of importance. There are in existence methods (*8*) for thoroughly mixing fibrous materials such as wood cellulose. In the experiments recorded here the samples were obtained from regular pulp sheets by thoroughly dispersing portions of several grams in water, filtering on a sintered-glass funnel, and drying from organic solvents at room temperature. The resulting fluffy mats were sampled at random after thorough conditioning (about 5% moisture).

MATERIALS. The wood celluloses used in these experiments comprised both commercial bleached sulfite wood pulps and experimental samples. The standard celluloses were prepared according to the ACS method. The very highest viscosity samples of pure cellulose used were obtained by treating unbleached long-fibered cotton with dilute chlorous acid (pH 4) at 65° C. for 2 hours, washing, extracting with alcohol-benzene, alcohol, and ether, drying in vacuo at room temperature, and finally conditioning in air. Hemlock holocellulose was prepared from thin wood sections (40 $\mu$) by successively chlorinating in an evacuated container and extracting with hot 4% monoethanolamine in 95% ethanol; this sample was also dried from solvents at room temperature, using the sequence alcohol-ether-benzene.

Triton F solution was obtained through the courtesy of Rohm and Haas, and was used as received except for a preliminary filtration (sintered-glass filter) and partial evaporation in vacuo to an apparent strength of 2.10 *N*, and density 1.086 (20° C.). The characteristics of the solution did not appear to change more than slightly over a period of two years.

## VISCOSITY AND CHAIN LENGTH

In order to compare different cellulose samples with one another from the point of view of their average chain lengths, by using viscosity measurements in dilute solution, it is necessary to know the form of the mathematical function relating the chain length to the viscosity. In practice, it is also necessary to know the effect of concentration of the cellulose in solution on the measured viscosity. Both functions will depend upon the nature of the solvent used (*5*).

**Table I. Effect of Cellulose Concentration on Intrinsic Viscosity in Triton F**

| Material | $10^4\ C$, Grams per 100 Ml. | $10^4\left(\frac{\log \eta_r}{C}\right)$ |
|---|---|---|
| Standard cellulose from linters | 414 | 1584 |
| | 538 | 1555 |
| | 664 | 1543 |
| | 939 | 1561 |
| | 1024 | 1549 |
| Acetylation linters | 271 | 2015 |
| | 494 | 2060 |
| | 1010 | 2077 |
| Linters for viscose rayon | 347 | 1463 |
| | 560 | 1466 |

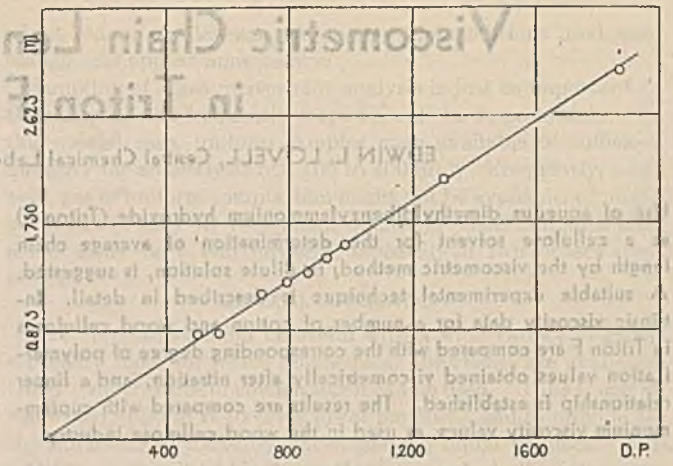



**Figure 1. Effect of Average Degree of Polymerization of Cotton and Wood Celluloses on the Intrinsic Viscosity in Triton F**

If different wood celluloses are to be compared directly, without fractionation into smaller parts of more uniform chain-length, it must be accepted that the chain-length values being used are averages of a special kind, and not necessarily the same average for different solvents. Nevertheless, this fact does not detract from the usefulness of the average values found in a given solvent such as Triton F.

Huggins (*5*) has recently pointed out the general applicability of the following equation relating the viscosity of high-polymer solutions to the chain length.

$$[\eta] = K\,(\overline{M})^{\nu}$$

Here $[\eta]$ is the intrinsic viscosity, defined by the relation

$$[\eta] = \left(\frac{\ln \eta_r}{C}\right)_{C \to 0}$$

the relative viscosity, $\eta_r$, being the ratio of the viscosity of the solution of concentration $C$ (grams per 100 ml. of solution) to that of the pure solvent. For nonhomogeneous samples, $\overline{M}$ is the "viscosity-average" molecular weight, which normally is much higher than the "number-average" molecular weight obtained by osmotic pressure methods. The power $\nu$ has some value between zero and 2, depending on the solute-solvent system.

In the simplest case, $\nu$ is unity, and the equation may be written in the familiar form of Staudinger's rule used by Kraemer and his colleagues (*6*):

$$\text{D.P.} = k[\eta]$$

It will be shown that this equation fits the available data for celluloses from wood and from cotton, within the experimental error.

In making numerous determinations of solution viscosities of different samples it is often customary to choose some small concentration range in which to work, and then use one of the available methods to obtain $[\eta]$ (at zero concentration) from the actually measured values $[\eta]_c$ (measured at a finite concentration, $C$). In the case of most wood celluloses, however, it appears that in the concentration range 0.3 to 0.5 mg. per ml., which it is convenient to use, the value of $[\eta]_c$ remains substantially constant (Table I), and within the experimental error may be used in place of $[\eta]$.

In order to compare the Triton F viscosities with actual mean chain lengths of the celluloses used, the required degrees of polymerization have been obtained by the widely used nitration method (*1*), in which the trinitrate of cellulose is formed under completely anhydrous conditions and the resulting nitrate viscosity measured in an organic solvent; this has been the method used for determining $k$ (*7*) for the system cellulose–Triton F.

Certain limitations of this comparison must be kept in mind. The solution of cellulose in Triton F takes place in an aqueous alkaline medium, whereas the nitration takes place in an anhy-

drous acid. Hence it is obvious from what has already been said regarding the effect of Triton F on points of "latent" degradation in cellulose, that processed celluloses that have been subjected to varying degrees of oxidative purification treatments may be expected to show some differences between acid and alkaline viscometric chain lengths. No doubt this accounts for at least a part of the variability of the experimental points on the [η]-D.P. curve (Figure 1). However, the fact that processed long-fibered cottons and purified linters fit so well into the series of wood celluloses would seem to indicate that the divergency from this cause is not at all serious here. Cellulose nitrate degree of polymerization values are used in the first place because they are possibly the most widely used and fully investigated values at present available.

These results lead to the following relationship:

$$\text{D.P.} = 618 \left(\frac{\log_{10} \eta_r}{C}\right)$$

$C \not> 0.03$ gram per 100 cc. of solution
Triton F 2.10 $N$
Temperature 20.0° C.

## DISCUSSION OF RESULTS

The advantages of Triton F solution as a cellulose solvent, already discussed, are further emphasized by experience with the method in this laboratory. Without the extreme precautions properly required in using cuprammonium solutions (*1*), and without the otherwise inconvenient necessity of carrying out a special nitration, a large number and variety of cellulosic samples—largely wood celluloses of an experimental nature—have been examined and compared as to average chain length, with results that have always been consistent and reproducible.

Quaternary ammonium bases are supposed by Lieser (*9*) to disperse cellulose to single molecules in solution. The present viscosity results now provide further indirect evidence to support this view, as the constant relationship between the trinitrate and quaternary base viscosities over a range of chain lengths (Figure 1) seems inconsistent with the view that micellar particles exist to any great extent in the alkaline solutions. Viewed in the darkfield microscope, the solutions of 0.1% concentration appeared completely free of any larger undissolved particles such as gels.

An important source of difficulty found by previous users of Triton F (*13*) has been the "aging" effect, whereby the solutions of cellulose gradually drop in viscosity with time. The source of this effect has never been definitely ascertained. However, in the case of the very dilute solutions used in the present experiments, the aging effect does not appear to be appreciable. This has been shown by the constancy of results that has been obtained when using different rolling times, no drift being evident even up to 48 hours. Furthermore, the solution kept in the viscometer for a day or more showed no change in viscosity. Thus aging seems to be a characteristic of Triton F cellulose solutions that are moderately or highly concentrated.

The effect of the concentration of quaternary ammonium base on the specific viscosity of the cellulose dissolved in it has not been examined. According to Russell and Hood (*12*) the specific viscosity falls with increasing normality of base. The viscosity of the aqueous base itself changes very rapidly with concentration in solutions strong enough to be used as cellulose solvents.

The technique of viscosity measurement described is not such as readily lends itself to large-scale commercial control practice in a pulp mill, as preparing and weighing the small sample used requires a rather high degree of precision. As a research tool in the field of cellulose chemistry it would appear to have worthwhile advantages. However, the method could possibly be used to advantage as a supplement to routine control practice.

Thus, in technical control work the customary concentrations of wood pulp used run from 1 to 5% in the cuprammonium reagent. However, it is well known that these viscosities have no real meaning in terms of average chain length, particularly in the case of high-viscosity pulps, since what is being measured is a "structural viscosity" (*11*) dependent to a high degree upon many extraneous factors. (The data of Table II offer an illustration of this.) In fact, the cuprammonium viscosity as ordinarily obtained can only be regarded as a cellulose quality factor, reflecting average chain length to some extent but reflecting also to an inordinate degree such factors as the chain-length distribution in the α-cellulose fraction, the nature of any retained hemicelluloses, and even the presence of inorganic contaminants. In dilute solution the effect of any of these factors is relatively small or nonexistent, the controlling variable being the weight or viscometric-average chain length.

It seems apparent therefore that the determination of Triton F viscosities in dilute solution, leading to a value of the average chain length, offers definite advantages for mill control practice as an occasional check on the routine cuprammonium viscosity values, especially when as sometimes happens, these seem to vary in an unexpected manner. The knowledge that the degree of polymerization of a pulp is, or is not, abnormal should prove most helpful in such cases, in view of the many other variables affecting the cuprammonium value.

**Table II. Comparison of Triton F and Nitrate Viscosities of Wood and Cotton Celluloses**

| Cellulose Sample | Cuprammonium Viscosity, Cp. | Triton F $10^3\left(\frac{\log \eta_r}{C}\right)$ | Nitrate D.P.[a] |
|---|---|---|---|
| No. 1 wood cellulose | 1.43 | 850 | 500 |
| No. 2 wood cellulose | 1.93 | 850 | 570 |
| Std. cellulose from linters | 2.10 | 1170 | 710 |
| No. 3 wood cellulose | 4.08 | 1278 | 790 |
| No. 4 wood cellulose | 15.2 | 1340 | 860 |
| Linters A | 3.72 | 1460 | 920 |
| Linters B | 4.59 | 1582 | 980 |
| Linters C | 11.4 | 2119 | 1300 |
| Purified cellulose from cotton | ... | 3000 | 1875 |

[a] Determined in 0.05% ethyl acetate solution (D.P. = 270 [η]).

**Table III. D.P. Values Obtained in Triton F Solution for Typical Cellulose Samples**

| | |
|---|---|
| Rayon-grade bleached sulfite pulps | 500–800 |
| 99% α-cellulose bleached sulfite pulp | 1135 |
| High-viscosity sulfite pulp | 1460 |
| Long-fibered cotton, bleached | 1580 |
| Holocellulose, from western hemlock, after weak alkaline extraction at room temperature | 1640 |

## ACKNOWLEDGMENT

The author wishes to acknowledge his indebtedness to R. L. Mitchell for providing most of the nitrate viscosity values.

## LITERATURE CITED

(1) Berl, E., Ind. Eng. Chem., Anal. Ed., 13, 322–6 (1941).
(2) British Standard Method for Determination of Viscosity of Liquids in Absolute (C.G.S.) Units, pp. 10–11, London. British Standards Institution, Publications Dept., 1937.
(3) Brownsett, T., and Clibbens, D. A., *J. Textile Inst.*, 32, T32–44 (1941).
(4) *Ibid.*, pp. T57–70.
(5) Huggins, M. L., Ind. Eng. Chem., 35, 980–5 (1943).
(6) Kraemer, E. O., in "Chemistry of Large Molecules", p. 90. New York, Interscience Publishers, 1943.
(7) *Ibid.*, p. 91.
(8) Launer, H. F., Natl. Bur. Standards, *Research Paper* 979, 336 (1937).
(9) Lieser, T., *Ann.*, 528, 276 (1937).
(10) Mease, R. T., and Gleysteen, L. F., Natl. Bur. Standards, *Research Paper* 1441, 545 (1941).
(11) Philippoff, W., *Kolloid-Z.*, 83, 163–72 (1938).
(12) Russell, W. W., and Hood, L. N., Jr., Ind. Eng. Chem., Anal. Ed., 14, 202–5 (1942).
(13) Russell, W. W., and Woodberry, N. T., *Ibid.*, 12, 151–4 (1940).
(14) Staudinger, H. and Sohn, A. W., *Ber.*, 72B, 1709–17 (1939).

Contribution No. 1 from the Central Chemical Laboratory of Rayonier Incorporated.

# Water Vapor Permeability of Organic Films

PAUL M. DOTY, CAPTAIN WM. H. AIKEN, AND HERMANN MARK
Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, N. Y.

**An apparatus for a rapid, precise, and reproducible determination of water vapor permeability is described. It seems that two factors, diffusion velocity and solubility, together determine the vapor permeability of a film. Both can be derived from the measurements. Equations based on the validity of Fick's law are tested with commercial films of low permeability. The dependence of permeability on thickness, vapor pressure, and temperature is studied. On the basis of measurements of a number of films a discussion of the process of permeation is presented.**

A MOST important determining factor in the selection of an apparatus with which to measure water vapor permeability is the amount of water that will pass through a film of convenient size and thickness in a relatively short time. For recently developed films that have very low water vapor permeability as compared with previous commercial samples, about $10^{-6}$ to $10^{-7}$ gram of water will pass through a film with an area of about 25 sq. cm. in about an hour under a pressure gradient of about 20 mm. A good MacLeod gage can be adapted to measure quantities of this magnitude with a precision between 5 and 10%. An apparatus based on these considerations is described below. In addition to furnishing a rapid and reproducible absolute measure of the permeability of films, it is also possible to obtain from the same measurement the values of two constants which together determine the amount of water transported through the film under given conditions.

In most cases, as long as mechanical injuries do not cause breaks in the film, the transmission of water vapor can be represented as a process of activated diffusion which has been treated by Daynes (*5*) and Barrer (*1*, *2*).

## THEORY OF PERMEABILITY

UNITS. The amount of water vapor, $Q$, which will pass through a given film at a given temperature depends upon the area, $a$, the thickness, $l$, the vapor pressure difference, $\Delta p$, and the time, $t$, according to the following steady state equation (*1*, *2*):

$$Q = P \frac{a}{l} t \Delta p \tag{1}$$

$P$, the proportionality factor, is termed the permeability constant and characterizes the resistance to water vapor transmission for the material under consideration. The dependence of $Q$ upon the area and the time as expressed in Equation 1 is unquestionable. The validity of the linear dependence of pressure and the inverse linear dependence of thickness are discussed below.

For our purposes, we define the permeability constant as the cubic centimeters of gas at standard temperature and pressure passing per second through a membrane 1 sq. cm. in area and 1 mm. thick when the pressure difference is 1 cm. of mercury. Thus Equation 1 becomes the defining equation, giving $P$ the following units[1]:

$$P = V \frac{l}{\Delta pat} = (\text{cc. of gas}) \frac{\text{mm.}}{(\text{cm. Hg}) \text{ sq. cm. sec.}} \tag{2}$$

Thus the value of $P$ will rate the film material relative to others for water vapor transmission and will also provide data necessary to calculate the amount of water that will pass through the film in a given time if the other constants in Equation 2 are known.

Fick's law (compare *1*) states that the rate of transmission per unit area of a gas through a solid in the direction of the concentration gradient of the gas $\partial c/\partial x$ is given by

$$P' = D \frac{\partial c}{\partial x} \tag{3}$$

where $D$ is the diffusion constant.

Using Henry's law

$$c = Sp \tag{4}$$

to express the concentration in terms of the pressure Equation 3 becomes for a film of thickness, $l$, in a state of steady flow

$$P' = DS \frac{P_2 - P_1}{l} = DS \frac{\Delta p}{l} \tag{5}$$

The diffusion constant, $D$, is the cubic centimeters of gas at S.T.P. passing per second through a centimeter cube of the material when there is a unit concentration gradient across the cube. We define $S$, the solubility coefficient in Henry's law, as the cubic centimeters of gas that will dissolve ideally in 1 cc. of film material when the pressure of the gas is 1 cm. of mercury. Thus $S$ has dimensions of cc. of gas per cc. of film material per cm. of mercury. Since $P'$, the permeation rate constant, has units of cc. of gas per second per sq. cm., the permeability constant, $P$, differs from the permeation rate constant, $P'$, by a factor $l/\Delta p$.

In Equation 2 $l$ was measured in millimeters; in Equation 5 in centimeters; consequently, a factor 10 must be included to correct for this. That is,

$$P = 10P' \frac{l}{\Delta p} \tag{6}$$

Substituting Equation 5 for $P'$ gives

$$P = 10DS \tag{7}$$

which relates the constants defined above.

Consequently, the permeability of a film can be broken down into two contributing factors, the diffusion constant and the solubility coefficient. The first quantity measures the probability that each individual gas molecule will move in the direction of the concentration gradient, the latter is a measure of the number of the gas molecules per unit volume which contribute to this

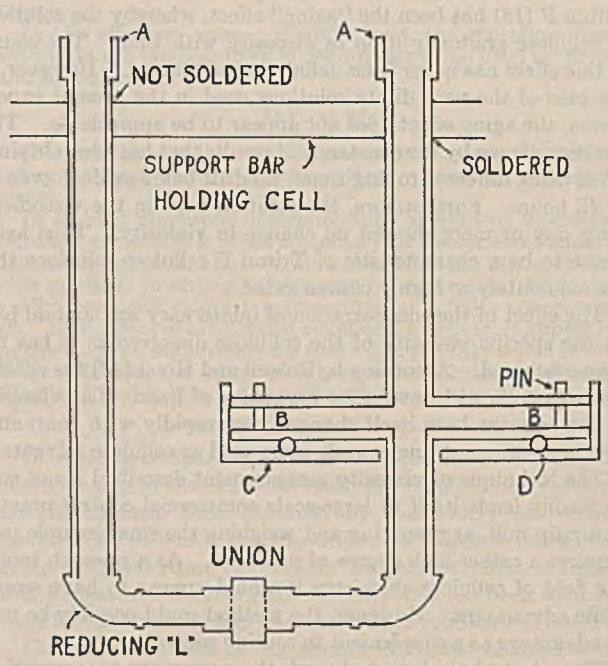



Figure 1. Permeability Cell

[1] It seems to the authors that Barrer has misplaced the mm. unit in this definition (*1*, *2*).

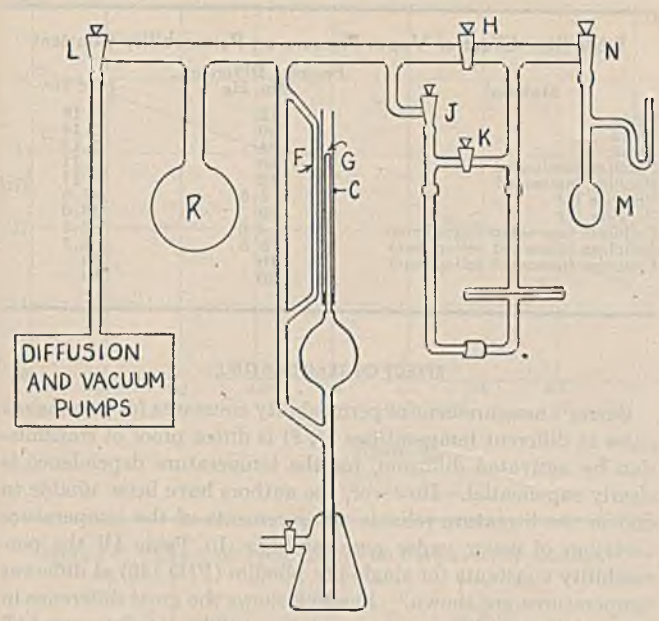



Figure 2. Vacuum System

concentration gradient. The solubility coefficient does not include the water molecules that are sorbed but only those that are ideally dissolved and consequently this may or may not approximate the actual equilibrium solubility.

## APPARATUS AND MEASUREMENTS

Diffusion Cell. A detailed diagram of the diffusion cell (*13*) is shown in Figure 1. The cell is made from brass with all permanent joints silver-soldered. The enlarged ends, *A*, provide for sealing in glass tubing with Picein or deKhotinsky cement. A more permanent metal-glass joint is not used because the seal is occasionally broken while opening or sealing the cell. With a Picein joint a short heating will reseal the joint, whereas a copper-glass joint must usually be entirely replaced. (A similar cell made from Pyrex glass has recently been put into operation successfully.)

In the cell, *B*, rubber jar rings are used for gaskets without lubrication. They may be sealed to the brass plates with rubber cement above and below *B* in Figure 1. Copper gauze is laid under the film for even support.

The cap, *C*, is screwed upward to seal the membrane tightly in the cell. Ball bearings, *D*, are used between the cap and the cell. It is best to have these in a groove with a spacer. The union is fitted with a washer cut from gasket rubber—i.e., rubber with wire screening embedded in it. Both the union and cell need only be tightened with moderate force to secure high-vacuum-tight seals.

Vacuum System. The cell is mounted in a vacuum system as shown in Figure 2. It is essential to have a high-quality MacLeod gage. Water vapor pressure can reliably be measured with the MacLeod gage in the following manner: Surround the capillary with a water jacket as shown in Figure 2. To make a reading allow the mercury to rise above the cutoff point. With a cool flame heat the bulb and the water jacket, then allow the mercury to rise slowly until the mercury in capillary *F* is opposite the top of capillary *G*. The pressure at 0° C. (which is used in the calculations) is given by

$$P = Ch^2 \frac{273}{273 + T}$$

where *C* is the MacLeod gage constant, *h* is the distance in millimeters from the top of capillary *G* to the mercury column, and *T* is the temperature of the water in the water jacket, *C*. *T* must be high enough so that the vapor pressure at temperature *T* is greater than *h*.

All stopcocks are high-vacuum type using Apiezon "L" as lubricant. When stopcocks *H* and *J* are closed, a vacuum of $10^{-6}$ mm. should be obtained. When they are opened to the newly mounted cell the pressure will read about $5 \times 10^{-4}$ mm. if there are no leaks. Pumping for several hours with the thermostat at about 70° is necessary to reduce the outgassing of the metal to such a degree that with pumping a vacuum of $10^{-6}$ mm. is obtained.

The volume of the system into which the water vapor diffuses must be measured. This volume, which should be about 4 liters, is conveniently obtained by means of an auxiliary bulb of known volume connected to the system by means of a stopcock.

The water in flask *M* is frozen and evacuated several times to remove air. The apparatus is now ready for use.

Method of Measurement. Stopcocks *H* and *J* are closed; the cell is opened by unscrewing the cap, *C*, and the union. The film is put in place and the cell and union are screwed shut tightly. Now stopcock *K* is opened to prevent unequal pressure on the film when *H* and *J* are opened. With the pumps going and *L* open, *H* and *J* are opened. Pumping is continued until pressure is 0.01 to 0.03 micron (about half an hour). After this time, a blank is usually run—that is, stopcocks *H*, *K*, and *L* are closed and the pressure is measured at 5-minute intervals for four or five measurements. This pressure-time plot should give a straight line. Then *H* is opened for a short time while the temperature of the water in *M* is adjusted to give the vapor pressure of water that is desired. To begin the measurement *L* and *H* are closed and *N* is opened. The pressure is then measured as described above every few minutes. Measurements are continued until the data give a straight pressure-time plot.

Method of Calculation. The pressure increase during the run must be corrected by subtracting from it the pressure increase measured as the blank. When the corrected pressure is plotted versus the time a graph similar to Figure 3 is obtained. The permeability constant, as defined above, is obtained by using measurements from the graph in the formula:

$$P = \left[p(\text{mm.}) \frac{V}{760}\right] \frac{l}{a\,\Delta p T} \tag{8}$$

where $p$(mm.) is the pressure in millimeters of some arbitrarily chosen point near the end of the plot. *V* is the volume in cubic centimeters into which the gas expands after diffusing. *l* is the thickness in millimeters and *a* is the area in square centimeters. $\Delta p$ is the pressure of water vapor and *T* is the portion of the time axis as shown.

The diffusion constant, *D*, is obtained from

$$D = \frac{l^2}{6L} \tag{9}$$

which is according to Barrer (*1*) the solution of the general Fick's law equation under the existing boundary conditions. *l* is in centimeters and *L* is the time intercept in seconds.

The solubility coefficient is obtained from Equation 7.

Effect of Holes. If there are capillary holes in the film which contribute to its over-all permeability, some water will be transmitted immediately. Thus, the pressure versus time plot will not have an induction period where there is no rise of pressure, but rather the plot will leave the origin in a straight line at an angle

Table I. Water Vapor Permeability of Film Materials[a]

| Film Material | $P \times 10^8$ | $D \times 10^6$ | $S$ | Thickness, Mm. |
|---|---|---|---|---|
| Cellophane (TAPPI standard sample) | 4.7 | 0.39 | 1.2 | 0.035 |
| Cellophane, specially coated | | | | |
| 0.1-mil coating | 5.4 | 0.051 | 10.6 | 0.031 |
| 0.4-mil coating | 0.25 | 0.36 | 0.070 | 0.036 |
| Koroseal (see Table II) | | | | 0.021 |
| Av. value | 5.6 | 0.39 | 1.8 | 0.175 |
| Nylon I | 3.7 | 0.20 | 1.8 | 0.045 |
| II | 260 | 1.1 | 24 | 0.034 |
| III | 6.0 | 0.28 | 2.1 | 0.022 |
| IV | 14.2 | 0.25 | 5.5 | 0.051 |
| Pliofilm (TAPPI standard sample) | 1.3 | 0.15 | 0.88 | 0.082 |
| Polythene | 2.1 | 0.48 | 0.44 | 0.041 |
| Saran (a) | 0.070 | 0.125 | 0.06 | 0.026 |
| Saran (b) (three measurements) | 0.135 | 0.11 | 0.13 | 0.026 |
| Vinylite I, calendered | 470 | 2.3 | 20.5 | 0.102 |
| Vinylite II, cast | 37 | 20 | 0.19 | 0.107 |
| Waxed glassine | 0.45 | 0.54 | 0.083 | 0.045 |
| 3-Ply glassine | 1.2 | 1.2 | 0.10 | 0.083 |
| Ethylcellulose | 510 | 19.3 | 2.6 | 0.505 |

[a] Measurements made at 25° C. and 20-mm. vapor pressure (77° F. and 85% relative humidity).

to the time coordinate. In other words, there will be superimposed upon the ordinary graph (Figure 3) a straight line through the origin. The amount of permeation due to pin holes can be estimated from this.

## RESULTS

A number of results that have been obtained are presented in Table I. These results apply only to the actual films measured. There is such a variation in the permeability of commercial films of the same trade name that it would be incorrect to attach to any class of films the specific value recorded below, which is based on the measurement of only a few film samples. All measurements were made at 25° C. Roman numerals designate film materials of different composition but same commercial name. Letters refer to different measurements on a different portion of the same film sample.

Table II. Effect of Thickness on Permeability Constant

| Thickness, Microns | $P \times 10^9$ |
|---|---|
| Koroseal | |
| 21 | 7.4 |
| 34.5 | 6.9 |
| 47 | 4.6 |
| 99 | 6.4 |
| 134 | 4.5 |
| 150 | 4.1 |
| Polythene (Cast) | |
| 58 | 2.38 |
| 105 | 2.46 |
| 163 | 2.40 |

## DEPENDENCE OF PERMEABILITY ON THICKNESS

Equations 1 and 2 state that the permeability is inversely proportional to thickness and that the permeability constant is independent of thickness. This is not true for films containing hydrophilic material—e.g., natural rubber (*16*)—or for films made from materials that sorb much water—e.g., cellulose.

On the other hand, numerous cases have been recorded where Equations 1 and 2 are valid (*3, 4, 6, 9, 14, 15, 16*).

The authors have extensively studied a series of samples of different thicknesses made in an identical manner from the same material, furnished through the courtesy of the B. F. Goodrich Company. Table II shows the results of repeated determinations of the permeability constants of this film in different thicknesses.

These values of $P$ could be checked within 0.5 unit; consequently, the fluctuations of $P$ were not due to fluctuations in measurements but rather to actual differences in the films. However, over a sevenfold range in thickness the permeability constant showed no significant trend. The necessity of using many samples of different thicknesses in this type of study should be appreciated, for different conclusions could have been drawn if only two of the above samples had been measured. A similar study on films prepared from cast polythene showed no change of permeability constant over the thickness range studied. The results are summarized in Table II.

## EFFECT OF PRESSURE

The quantity of water passing through a film may or may not be directly proportional to the vapor pressure difference. The direct proportionality does not exist in films which contain hydrophilic material or polar groups that sorb water molecules (*16*). However, Equations 1 and 2 may be considered as the ideal law of gas permeability, which, for many films (particularly for those of low permeability) adequately represent the effect of thickness and pressure difference. Deviations from this ideal behavior usually begin to become significant when the film material sorbs water noticeably. This is particularly apparent in the case of cellulose sheeting. In Table III are presented some measurements of permeability constants at different pressure differences. All measurements are at 25° C.

Table III. Effect of Vapor Pressure on Permeability Constant

| Material | Pressure Difference, Mm. Hg | $P \times 10^9$ |
|---|---|---|
| Saran | 15 | 0.16 |
| Saran | 20 | 0.14 |
| Saran | 24 | 0.15 |
| Pliofilm, laminated | 10 | 0.11 |
| Pliofilm, laminated | 18 | 0.11 |
| Vinylite III | 4.6 | 37.8 |
| Vinylite III | 20 | 38.0 |
| Cellulose (uncoated cellophane) | 4.6 | 3.3 |
| Cellulose (uncoated cellophane) | 6.5 | 4.7 |
| Cellulose (uncoated cellophane) | 10 | 68 |
| | 20 | 84 |

## EFFECT OF TEMPERATURE

Barrer's measurement of permeability constants for permanent gases at different temperatures (*1, 2*) is direct proof of transmission by activated diffusion, for the temperature dependence is clearly exponential. However, the authors have been unable to find in the literature reliable measurements of the temperature variation of water vapor permeability. In Table IV the permeability constants for single-ply pliofilm (PID 140) at different temperatures are shown. Figure 3 shows the great difference in permeability at different temperatures. The log $P$ versus $1/T$ plot (compare Figure 4) gives a reasonably straight line, showing that the data can be represented by

$$P = P_0 e^{-E/RT} \tag{10}$$

The energy of activation in this case is about 13,000 calories per mole, diffusing water vapor.

From these measurements and those of Barrer, one may say that in general the permeability of a good film approximately doubles for a 10° C. (18° F.) rise in temperature.

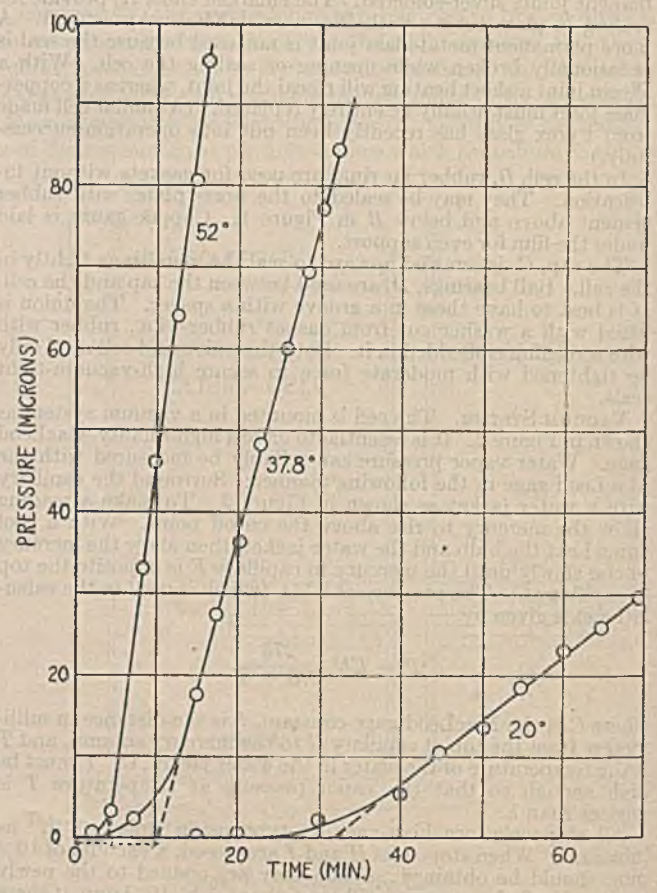



Figure 3

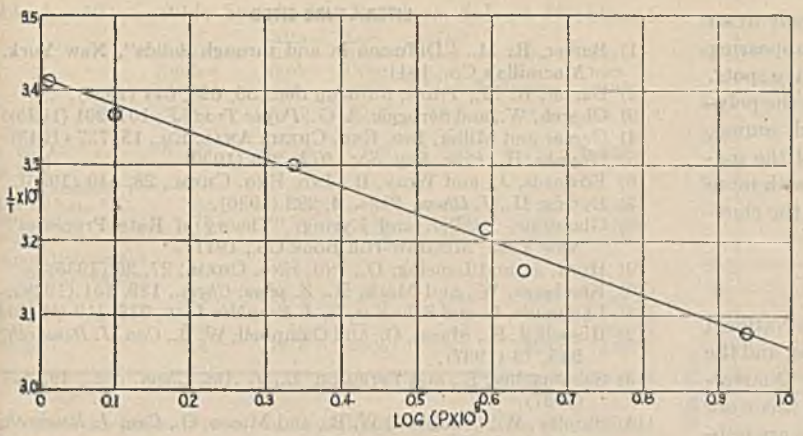



Figure 4

Table IV. Effect of Temperature on Permeability Constant

| $T$, ° C. | | $P \times 10^8$ |
|---|---|---|
| | Pliofilm | |
| 20 | | 1.03 |
| 24 | | 1.26 |
| 30 | | 2.1 |
| 37.8 | | 3.9 |
| 43.5 | | 4.4 |
| 52 | | 8.7 |
| | Vinylite IV | |
| 30 | | 58 |
| 38 | | 74 |
| | Polythene | |
| 25 | | 2.38 |
| 30 | | 3.57 |

## PROCESS OF PERMEATION

On the basis of the foregoing observations and measurements, it seems that the transport of small molecules, such as water, nitrogen, oxygen, hydrogen, etc., through a layer of a polymer can be visualized by two different mechanisms: (1) flow through capillary holes, and (2) activated diffusion through the polymer itself.

The first process involves the presence of a system of preformed crevices or capillaries, the average width of which is larger than the diameter of the diffusing molecules.

Under the influence of its random kinetic motion, an individual molecule eventually will enter into such a capillary. It is then irregularly reflected at the capillary walls and carries out a Brownian movement very similar to the one characteristic for the gaseous state. Whether the net effect of this "free" diffusion will be better described by a Poiseuille flow or by a Knudsen diffusion depends upon the ratio between the mean free path of the molecules and the average diameter of the capillaries. This in turn will be influenced by the vapor pressure of the diffusing gas and the porosity of the polymer. After having been frequently reflected at the walls of the capillaries, the migrating particle finally emerges on the other side of the layer and one elementary step of gas transport through the polymer has taken place. This unactivated diffusion of small molecules through existing crevices (along surfaces of crystallites, between morphological elements, such as fibrillae, etc.) is only moderately temperature-dependent; it is proportional to $T^a$ where $a$ assumes values around 0.5, depending upon the shape of the diffusing molecules and of the character of the capillaries. The net effect, which this mode of transport contributes to the total penetration of the gas through the film, is proportional to the pressure gradient, the time, and the area, and depends in a somewhat complicated manner upon the size and shape of the diffusing molecules and of the channels through which they travel.

The activated diffusion of molecules through the bulk of the polymer itself is of an altogether different character.

Let us assume first for simplicity that the film through which the water is supposed to migrate is homogeneous and in a completely disordered (amorphous) state. It can then be considered to be a liquid of very high viscosity or a glass. Water molecules of the gas space will, under the influence of their random kinetic motions, hit the boundary plane of the film; in many cases they will be reflected elastically, in others they will penetrate into the first few atomic layers of the polymer and then start to diffuse irregularly through the material. Their motion will not (as in the first case) be comparable with the conditions in an ideal gas, but rather to the Brownian movement of a particle which is dissolved in a very viscous liquid. Using the concepts of the viscosity of liquids and particularly of long-chain substances as developed recently by Eyring and his collaborators (*7*, *8*), one arrives at the conclusion that the migrating molecule carries out quasi-elastic vibrations around a certain position, until through the segment movement of the surrounding chains a "hole" is formed in its immediate neighborhood and it moves into this hole, where it vibrates again for a period, long as compared with the time of transition from one hole to the next. Thus the dissolved particle moves through a series of holes, though they are not preexistent but are gradually produced (and disappear again) by thermal vibrations of the segment inside of the polymeric material. The probability for the formation of such a hole is comparatively small and the molecule has therefore to wait comparatively long in one hole until another one is formed in its immediate neighborhood into which it eventually can move. Thermodynamically, the holes are characterized by a certain energy and entropy of formation and these two quantities can be derived from observation of the rate of this "activated" diffusion and from its temperature dependence. The order of magnitude of these two quantities (expressed for one mole of holes) is for water and pliofilm about 12,000 calories per mole for the energy and 10 calories per degree for the entropy of activation.

Finally, there exists a third process for the transportation of a molecule through a polymer, which, in a certain sense, involves a mechanism intermediate between the two mentioned above.

It has been known for some time (*10*) and has been confirmed and considerably elaborated recently (*12*, *14*) that many high polymers, such as cellulose and its derivatives, possess a so-called internal surface, which is accessible for gas molecules and can be measured by adsorption studies. This suggests the existence of very narrow slits and crevices, the walls of which contain a large number of centers of high adsorption power (active spots or points of high intermolecular attraction). In the case of the diffusion of water through cellulose, the hydroxyl groups on the surface of the cellulose crystals presumably are such points of high water-binding capacity. If a water molecule enters such a slit between two crystals, it will be immediately adsorbed at one of these hydroxyl groups and after the heat of adsorption has been dissipated, carry out vibrations in the immediate neighborhood of this group, until by thermal fluctuations it acquires the energy necessary for desorption. It will then re-evaporate into the slit and after a few elastic (inefficient from an adsorption standpoint) collisions with the wall, be adsorbed by another active spot, where it stays for another period, and so on. This process can also be considered to be an activated diffusion, but a diffusion through a preformed slit or system of holes. It is characterized by an energy and entropy of activation, but these two quantities have now another significance than before. The energy of activation (between 8000 and 14,000 calories per mole of water) is the energy necessary to evaporate an adsorbed water molecule from the active spots, while the entropy of activation involves the difference in the modes of vibration and rotation which an individual molecule carries out in the free and adsorbed states, respectively. In this case, both quantities have nothing to do with the irregular segment motion (micro-Brownian movement) of the polymer, but with the specific attraction between the diffusing molecules and certain active groups, which are distributed on the walls of the slit in the polymers.

The real effect of crystallinity on the permeability of high polymers has not yet been investigated and there exist widely different opinions about the relative importance of the crystalline and amorphous areas in a polymer. In this consideration the work of Langmuir and Schaefer (*11*) seems to be of great importance. They found that a single monomolecular crystallized layer was sufficient to cut down the rate of evaporation of water by a factor of about one million.

On the basis of permeability measurements alone it does not seem easy to decide whether the actual experimental qualities

(and their formal interpretation as described above) point to an activated diffusion through gradually forming and disappearing holes or along the surfaces which are covered with active spots. However, it appears that additional information about the polymer, such as the presence of active groups (hydroxyl, amino, carboxyl, carbonyl, etc.) or the crystalline character of the material and the existence of an internal surface, together with more numerous and more precise measurements, may help in the elucidation of the true permeation process.


### ACKNOWLEDGMENT

The authors wish to express their appreciation to the National Research Council Committee on Quartermaster Problems, and the Research and Development Branch of the Office of the Quartermaster General, under whose sponsorship and direction this work was carried out and with whose permission these results are published.

The authors also wish to thank Miss Helen Luben for her very valuable assistance in carrying out the measurements.


### LITERATURE CITED


(1) Barrer, R. M., "Diffusion in and through Solids", New York, Macmillan Co., 1941.
(2) Barrer, R. M., *Trans. Faraday Soc.*, 35, 628, 644 (1939).
(3) Charch, W., and Scroggie, A. G., *Paper Trade J.*, 101, 201 (1935).
(4) Comar and Miller, Ind. Eng. Chem., Anal. Ed., 15, 737 (1943).
(5) Daynes, H., *Proc. Roy. Soc.*, 97A, 286 (1920).
(6) Edwards, J., and Wray, R., Ind. Eng. Chem., 28, 549 (1936).
(7) Eyring, H., *J. Chem. Phys.*, 4, 283 (1936).
(8) Glasstone, Laidler, and Eyring, "Theory of Rate Processes", New York, McGraw-Hill Book Co., 1941.
(9) Hunt, J., and Lansing, D., Ind. Eng. Chem., 27, 26 (1935).
(10) Kaelberer, W., and Mark, H., *Z. phys. Chem.*, 139, 151 (1928).
(11) Langmuir, I., and Schaefer, I., *J. Franklin Inst.*, 235, 119 (1943).
(12) Russell, J. K., Maass, O., and Campbell, W. B., *Can. J. Research*, B15, 13 (1937).
(13) Schumacher, E., and Ferguson, L., *J. Am. Chem. Soc.*, 49, 427 (1927).
(14) Shipley, W., Campbell, W. B., and Maass, O., *Can. J. Research*, B17, 40 (1939).
(15) Staedel, W., *Papier Fabr.*, 31, 535 (1933).
(16) Taylor, R. L., Herrmann, D. B., and Kemp, A. R., Ind. Eng. Chem., 28, 1255 (1936).


# Evaporation Indices of Hydrocarbon Thinners


E. H. McARDLE AND A. E. ROBERTSON

Esso Laboratories, Standard Oil Development Co., Elizabeth, N. J.


ONE of the most distinctive and characteristic properties of a solvent naphtha is its rate of evaporation. Upon this evaporation rate of the solvent itself depends its choice for application to the great variety of organic materials which must be thinned prior to use. The factor of "solvent retention" does modify the evaporation rate of the solvent itself, but contributions of the solute are generally constant in so far as they affect the rates of solvent release of interchangeable solvent naphthas.

It is rather astonishing, therefore, to reflect that until very recently no concerted effort has been made to standardize an acceptable procedure to measure evaporation rate. A number of evaporometers have been described in recent years, but in nearly every case their use has been confined to their parent laboratories (*2, 3, 9–14*). This state of affairs is aptly epitomized in a report of the (British) Institute of Petroleum (*8*):

> An attempt has been made to standardize a suitable relative evaporation test for the examination of solvents to be used in the paint and lacquer industry. From contact with paint research stations and industrial firms, it appears that no suitable well-recognized test is in existence. Those that are actually used are either simple rule-of-thumb tests or require complicated apparatus and are not suitable for routine work. As it is generally agreed that such a test is of value in assessing the behaviour of solvents, advice on the methods used in the U.S.A. was sought from the A.S.T.M., but so far the appropriate committee of that body is taking no steps to standardize a test, as they have not been asked to do so by their members. In the meantime a search is being made of the literature available on the subject, so that the significance of any method can be fully appreciated.

The subject of evaporation rate is now under consideration by the A.S.T.M. The problem of devising a generally satisfactory method, however, requiring inexpensive but accurate and reliable equipment, would appear extremely difficult. Neither volumetric nor gravimetric methods lend themselves readily to operation in a water thermostat; and only a handful of supplier and consumer laboratories are air-conditioned at the present time. Few, if any, gravimetric methods provide for unchanging air flow in the vicinity of the evaporating liquid. Nor is it a simple matter to charge a gravimetric surface with a highly volatile liquid sample without substantial evaporation during the time required for charging. Volumetric apparatus, such as that of Wetlaufer and Gregor (*14*) or the modification employed in the present work, must be up-ended frequently for periodic readings, thus introducing errors due to variation in surface tension, completeness of drainage, and ratio of vapor to liquid volume. Evaporation of solvent naphthas from their solutions of a "standard" vehicle—e.g., varnish-grade linseed oil—would introduce this limiting factor.

In view of these difficulties, an attempt has been made to estimate the evaporation rates of commercial solvent naphthas, from control tests which are normally run on regular shipments—viz., their specific gravities and their volatilities as measured by the A.S.T.M. distillation (*1*).

### EVAPORATION INDICES

As generally plotted, evaporation rate curves represent absolute values for one set of conditions. Presumably, however, slight

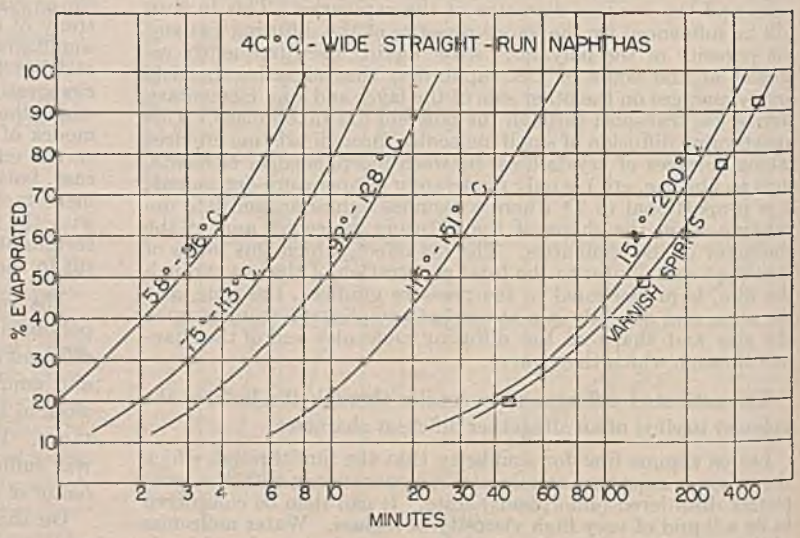



Figure 1

Table I. 40° C.-Wide Straight-Run Petroleum Solvent Naphthas

| | Narrow-Cut Rubber Solvent | Extraction Naphtha | Lacquer Diluent | Narrow Cut V.M. & P. | Mineral Spirits | Varnish Spirits |
|---|---|---|---|---|---|---|
| Gravity, ° A.P.I. | 71.0 | 64.0 | 60.0 | 55.8 | 49.0 | 43.9 |
| Sp. gr. at 60°/60° F. | 0.702 | 0.724 | 0.739 | 0.756 | 0.784 | 0.807 |
| A.S.T.M. distillation | | | | | | |
| Initial b.p., ° C. | 58 | 75 | 92 | 115 | 154 | 154 |
| 50% off | 73 | 90 | 105 | 129 | 170 | 172 |
| End point | 96 | 113 | 128 | 151 | 200 | 198 |
| Evaporation time at 25° C., minutes | | | | | | |
| 20% | 1.0 | 2.0 | 3.4 | 9.5 | 39 | 43 |
| 50% | 2.8 | 5.5 | 9.6 | 24 | 120 | 143 |
| 80% | 5.8 | 10 | 17.7 | 47 | 232 | 300 |
| 95% | 7.6 | 13.6 | 23.5 | 65 | 310 | 400 |

variations in procedure or surroundings will produce the same relative, or comparative, values within a series of naphthas, if each member is run identically. It thus appears likely that if a complete series can be run once under optimum conditions, and then if an actual or hypothetical member be taken for reference, and further if a satisfactory graphical or mathematical relation be established between the reference naphtha and the other members of the series, no further "control" evaporation runs need be made. After the curve for the reference naphtha is arbitrarily plotted, the other members may be described by, say, four points—e.g., their 20, 50, 80, and 95% evaporation times. Knowing these particular points, adequate curves may be plotted, and also information gained concerning their contribution to the behavior of freshly deposited coating films. For example, at the point of 50% evaporated, the coating film viscosity may be increased to, or beyond, that necessary for "setup"; at 80%, nonoxidizing films may have become dust-free; while at 95% evaporated such films are frequently touch-dry (*4*).

Using the data here presented, it is proposed to refer all evaporation times to those of a hypothetical straight-run petroleum naphtha of roughly 40° C. boiling range, and with a 50% A.S.T.M. distillation temperature of 80° C. Then the 20% evaporation time of any actual naphtha, divided by the 20% time of the reference naphtha, will be termed the 20% evaporation index, and written $I_{20}$.

### NARROW-CUT NAPHTHAS

Except for wide-cut rubber solvents, where a 100° C. boiling range is needed for quick setup and long tack time, the great majority of volatile straight-run petroleum thinners boil within 90° F. (50° C.), and of these nearly all except the "mineral spirits" cuts boil within 40° C. Table I lists a representative series of widely used straight-run naphthas, with 50% distillation temperatures from 73° to 172° C.—i.e., with volatilities covering most ordinary requirements. Except for the two mineral spirits which have a 45° C. boiling range, the members of the series boil within 40° C.

With the exception of the "varnish spirits", all items in Table I are distilled from paraffinic crudes, and as a result have specific gravities corresponding to a large paraffinic content. Paraffinic crudes contain minor proportions of aromatics and naphthenes, and are free from olefins; and it can be generally stated that the average domestic paraffinic crude will produce straight-run naphthas whose paraffinic content gradually decreases with increasing boiling range. For a given volatility, the specific gravities shown in Table I are close to those of the majority of 40° C.-wide paraffinic naphthas generally available. Specific gravity will therefore not be taken into account when we are dealing with straight-run naphthas of the paraffinic type.

### EVAPORATION RATE CURVES

The evaporation data shown in Table I are plotted in Figure 1, on semilog paper. For the time being, the nonparaffinic varnish spirits will be neglected.

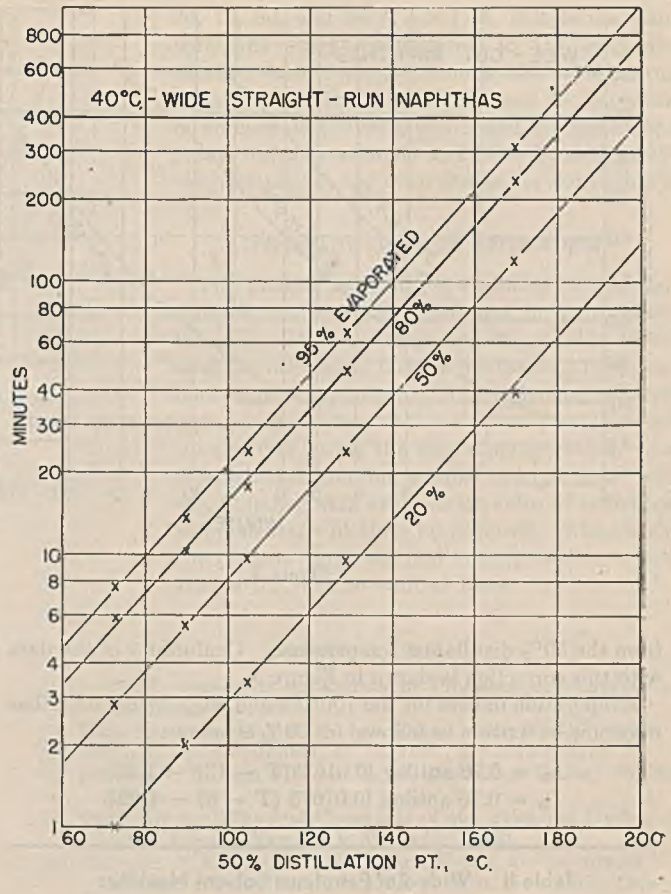



Figure 2

If we now plot, again on semilog paper, the 20, 50, 80, and 95% evaporation points of each of the five narrow-cut straight-run paraffinic type naphthas against their 50% A.S.T.M. distillation temperatures, we have the family of parallel curves shown in Figure 2. Here evaporation time, $t$, in terms of 50% distillation temperature, $T$, in 0° C., is given as follows:

$$\log t_{20} = 0.01675T - 1.22 \qquad \log t_{80} = 0.01675T - 0.48$$
$$\log t_{50} = 0.01675T - 0.77 \qquad \log t_{95} = 0.01675T - 0.36$$

In the case of the hypothetical 40° C.-wide reference naphtha, with 50% distilled at 80° C., we have the following evaporation times: 20% in 1.32 minutes; 50% in 3.7; 80% in 7.2; and 95% in 9.5.

Evaporation indices of actual 40° C.-wide paraffinic type naphthas, $I_{20}$, etc., now become $\frac{t_{20}}{1.32}$, etc., or, from the above equations:

$$I_{20} = 0.76 \text{ antilog } (0.01675T - 1.22)$$
$$I_{50} = 0.27 \text{ antilog } (0.01675T - 0.77)$$
$$I_{80} = 0.138 \text{ antilog } (0.01675T - 0.48)$$
$$I_{95} = 0.105 \text{ antilog } (0.01675T - 0.36)$$

### WIDE-CUT NAPHTHAS

Data on wide-cut naphthas are shown in Table II. These include a rubber solvent, an extraction naphtha, and a varnish makers' and painters' naphtha. The first two naphthas, with boiling ranges of 100° C., evaporate much faster than 40° C.-wide naphthas of the same paraffinic 50% A.S.T.M. distillation temperatures. They nevertheless exhibit closely similar curvatures in their evaporation rate curves, and, as a result, a simple correction can be made by substracting 13° C. (23° F.) from the 50% distillation temperature of the 100° C.-wide naphtha. Figure 3 shows the excellent concordance of the test data with this assumption.

Another exception to the 40° C.-wide line of naphthas is wide-cut V.M. & P., usually boiling from 210° to 320° F.—i.e., 60° C. wide. Here, evaporation rate is estimated by subtracting 8° C.

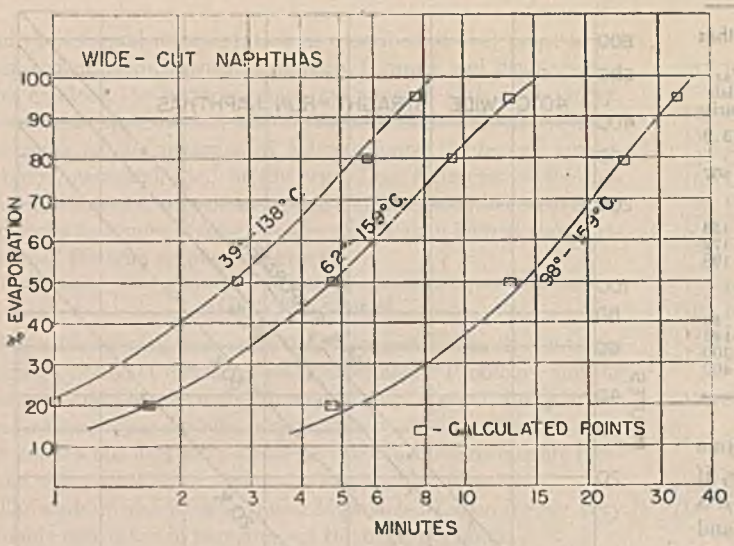



Figure 3

from the 50% distillation temperature. Conformity of the data with this correction is shown in Figure 3.

Evaporation indices for the 100° C. and 60° C.-wide naphthas may now be written as follows, for 20% evaporated:

$$I_{20} = 0.76 \text{ antilog } [0.01675(T - 13) - 1.22]$$
$$I_{20} = 0.76 \text{ antilog } [0.01675\ (T - 8) - 1.22]$$

**Table II. Wide-Cut Petroleum Solvent Naphthas**

| | Wide-Cut Rubber Solvent | Wide-Cut Extraction Naphtha | Wide-Cut V.M. & P. |
|---|---|---|---|
| Gravity, ° A.P.I. | 67.8 | 60.9 | 56.0 |
| Sp. gr. at 60°/60° F. | 0.710 | 0.735 | 0.755 |
| A.S.T.M. distillation | | | |
| Initial B.P., ° C. | 39 | 62 | 98 |
| 50% off | 86 | 100 | 120 |
| End point | 138 | 159 | 159 |
| Evaporation time at 25° C., minutes | | | |
| 20% | 0.9 | 1.7 | 5.5 |
| 50% | 2.7 | 4.7 | 14 |
| 80% | 5.4 | 9.2 | 24.6 |
| 95% | 7.5 | 13.2 | 33 |

**Table III. Latent Heats of Vaporization, Volume Basis**

| Boiling Point ° C. | Latent Heats Aromatic | Latent Heats Straight-run | Latent Heats Difference | Specific Gravity at 60°/60° F. Aromatic | Specific Gravity at 60°/60° F. Straight-run | Specific Gravity at 60°/60° F. Difference | Ratio of Differences |
|---|---|---|---|---|---|---|---|
| | *Calories/cc.* | | | | | | |
| 80 | 83 | 55.5 | 27.5 | 0.879 | 0.712 | 0.167 | 165 |
| 110 | 75.3 | 55 | 20.3 | 0.868 | 0.743 | 0.125 | 162 |
| 140 | 70 | 53.5 | 16.5 | 0.862 | 0.765 | 0.097 | 170 |
| 170 | 66.8 | 52.3 | 14.5 | 0.870 | 0.784 | 0.086 | 169 |

## AROMATIC SOLVENTS

Because of their higher latent heat of vaporization, aromatic hydrocarbons evaporate more slowly at room temperature than paraffins of the same boiling range. The greatest difference is between benzene and an 80° C.-boiling paraffin—i.e., with increasing boiling point, or molecular weight, there is less difference between latent heats of aromatics and paraffins. These differences conform to differences in specific gravity, and the latter can be utilized to estimate evaporation rates of aromatic solvent naphthas from the data on paraffinic naphthas. Table III shows the ratios of these differences to be substantially constant for practical purposes.

In Table III, latent heats have been converted to a volume basis—since A.S.T.M. distillates are read by volume—by multiplying calories per gram at the boiling point by density. Density was not corrected to the same temperature as the boiling point; but, for the purpose of these estimates, no great error is hereby introduced, since (1) the divergence in cubical expansion between aromatics and straight-run petroleum naphthas is fairly small (*6*), and (2) the latent heats of vaporization of similarly boiling aromatics and paraffins roughly parallel each other between room temperature and their boiling points. Data for the aromatics were taken from the Doss compilation (*5*); and the latent heats for the straight-run petroleum fractions from Fallon and Watson (*7*). Specific gravities of 40° C.-wide paraffinic naphthas were taken from Figure 4, which was plotted from data in Table I.

To utilize specific gravities, $G$ and $G_P$, of aromatic solvents and paraffinic naphthas, respectively, as measures of latent heat, we take the following relation:

$$T_P = T + 50\ (G - G_P)$$

where $T_P$ is the 50% temperature of the equivalent paraffinic naphtha, and $T$ is the actual 50% temperature of the aromatic. Thus 10° xylene evaporates at approximately the rate of a 40° C.-wide straight-run naphtha with a 50% distillation temperature of

$$137 + 50(0.862 - 0.765) = 142° \text{ C.}$$

The general expressions for evaporation indices of solvent naphthas other than straight-run paraffinic types become:

$$I_{20} = 0.76 \text{ antilog } [0.01675\{T + 50\ (G - G_P)\} - 1.22]$$
$$I_{50} = 0.27 \text{ antilog } [0.01675\{T + 50\ (G - G_P)\} - 0.77]$$
$$I_{80} = 0.138 \text{ antilog } [0.01675\{T + 50\ (G - G_P)\} - 0.48]$$
$$I_{95} = 0.105 \text{ antilog } [0.01675\{T + 50\ (G - G_P)\} - 0.36]$$

Data in Table IV, which includes a number of commercial aromatic solvents, are plotted in Figure 5. Evaporation points estimated by the above method are also shown in Figure 5, and are listed in Table V. It is important to note that these points are based on weight per cent evaporated. (The volumetric evaporometer used in this work evaporates 2.0 ml. of liquid, and the families of evaporation curves here plotted are all on a volume basis. Most evaporometers operate on a weight basis.)

Concordance, on a weight basis, appears satisfactory in the boiling ranges above toluene. It is noteworthy that 2° toluene and Solvesso No. 1 (a two-thirds aromatic naphtha with similar

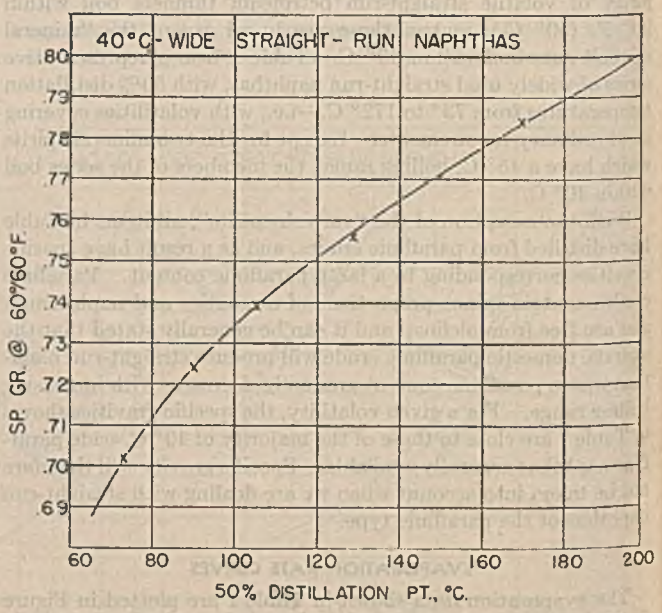



Figure 4

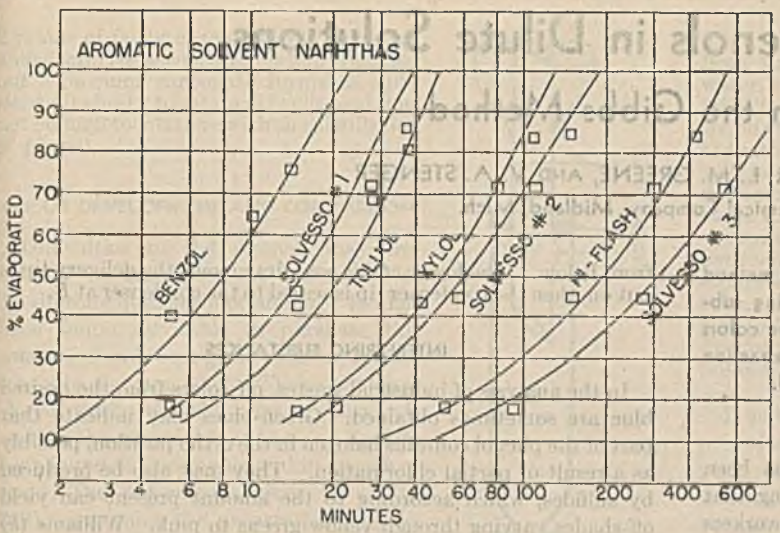



Figure 5

Table IV. Aromatic Solvent Naphthas

| | 2° Benzene | Solvesso 1 | 2° Toluene | 10° Xylene | Solvesso 2 | Coal-Tar Hi-Flash | Solvesso 3 |
|---|---|---|---|---|---|---|---|
| Gravity, ° A.P.I. | 29.5 | 39.3 | 31.6 | 32.6 | 33.6 | 31.1 | 29.5 |
| Sp. gr. at 60°/60° F. | 0.879 | 0.829 | 0.868 | 0.862 | 0.857 | 0.870 | 0.879 |
| A.S.T.M. distillation | | | | | | | |
| Initial b.p., ° C. | 78 | 99 | 108 | 134 | 137 | 152 | 174 |
| 50% off | 80 | 111 | 110 | 137 | 147 | 171 | 187 |
| End point | 83 | 138 | 111 | 142 | 177 | 196 | 209 |
| Evaporation time at 25° C., minutes | | | | | | | |
| 20% | 3 | 5.8 | 8 | 18 | 22 | 60 | 91 |
| 50% | 8 | 15.5 | 21.5 | 51 | 60 | 193 | 310 |
| 80% | 15.2 | 27.3 | 37 | 92 | 122 | 390 | 670 |
| 95% | 21 | 36.0 | 46 | 120 | 170 | 504 | ... |

Table V. Aromatic Solvent Naphthas

| | Specific Gravity Difference | ° C. Added to B.P. | Estimated Evaporation Points, by Weight | | | |
|---|---|---|---|---|---|---|
| Benzene | 0.167 | 8.5 | 1.9 at 16.1% | 5.2 at 40.4% | 10.2 at 64.5% | 14 at 76.5% |
| Solvesso 1 | 0.086 | 4.5 | 5.2 at 18% | 15 at 45% | 28 at 72% | 39 at 85% |
| Toluene | 0.125 | 6 | 5.5 at 17.1% | 15 at 43% | 28 at 69% | 39 at 81% |
| Xylene | 0.097 | 5 | 15 at 17.7% | 42 at 44% | 80 at 71% | 110 at 84% |
| Solvesso 2 | 0.087 | 4.5 | 21 at 18% | 58 at 45% | 111 at 72% | 150 at 85% |
| Hi-Flash | 0.086 | 4.5 | 52 at 18% | 155 at 45% | 300 at 72% | 410 at 85% |
| Solvesso 3 | 0.086 | 4.5 | 94 at 18% | 275 at 45% | 530 at 72% | ... |

50% distillation temperature) parallel each other in evaporation rate in both actual and estimated values; although agreement between these values for the individual solvent leaves something to be desired. Concordance in the case of benzene is poor, although the 76% point is close to actual. Benzene, however, is unique in a number of ways, and it evaporates much faster than other commercial aromatic solvents.

### VARNISH SPIRITS

In the section above on "Evaporation Rate Curves", discussion of varnish spirits was postponed. The difference in specific gravity between the varnish spirits in Table I and the lower solvency mineral spirits—viz., 0.023—necessitates the use of the gravity correction, 50 $(G - G_P)$, and therefore there must be added 1° C. to its already 2° C. higher 50% distillation temperature.

In this connection it may appear, particularly in the case of the large number of mineral spirits commercially available, that an error in reading the 50% distillation temperature will bulk large in estimating evaporation rate. In such an event, the popular "average boiling point"—the arithmetic average of the 10, 20, 30, 70, 80, and 90% A.S.T.M. distillation temperatures—might be preferred to the 50% distillation temperature. Among the straight-run naphthas described in Tables I and II, however, in no case do the 50% points and average boiling points differ by as much as 2° C. Thus the 50% temperature, $T$, has been chosen for convenience

### POSSIBILITY OF WIDER APPLICATION

The present estimates are limited to commercially available solvent naphthas, or hydrocarbon thinners. It nevertheless appears possible to extend the method to include mixtures of hydrocarbons and oxygen-containing solvents, wherein latent heat of vaporization may vary rapidly with composition during the time of evaporation. Additional data covering volume changes upon mixing, together with evaporation rates of individual components, will then be required. Meanwhile, the present rough method is suggested as a substitute for routine control tests.

### LITERATURE CITED

(1) A.S.T.M. Standards on Petroleum Products and Lubricants Committee D-2, D86–40.
(2) Bent, F. A., and Wik, S. N., Ind. Eng. Chem., 28, 312 (1936).
(3) Bogin, C., and Wampner, H. L., *Ibid.*, 29, 1012 (1937).
(4) Dorsch, J. B., and Stewart, J. K., Ind. Eng. Chem., 30, 325 (1938).
(5) Doss, M. P., "Physical Constants of the Principal Hydrocarbons", 4th ed., New York, Texas Co., 1943.
(6) Dunstan, A. E., Nash, A. W., Tizard, Henry, and Brooks, B. T., "Science of Petroleum", Vol. II, p. 1136, New York, Oxford University Press, 1938.
(7) Fallon, J. F., and Watson, K. M., p. 136. Petroleum Division Preprints, A.C.S. Meeting, Pittsburgh, Sept., 1943.
(8) Institute of Petroleum, Subcommittee 9, *J. Inst. Petroleum*, 30, No. 242, 49 (Feb., 1944).
(9) McArdle, E. H., Ind. Eng. Chem., Anal. Ed., 11, 450 (1939).
(10) Metzinger, E. F., *Paint, Oil Chem. Rev.*, 99, No. 10, 9 (May, 1937).
(11) Rubek, D. D., and Dahl, D. W., Ind. Eng. Chem., Anal. Ed., 6, 421 (1934).
(12) Stewart, J. K., Dorsch, J. B., and Hopper, C. B., Ind. Eng. Chem., 29, 899 (1937).
(13) Sweeney, W. J., and McArdle, E. H., *Ibid.*, 33, 787 (1941).
(14) Wetlaufer, L. A., and Gregor, J. B., Ind. Eng. Chem., Anal. Ed., 7, 290 (1935)

Presented before the Division of Paint, Varnish, and Plastics Chemistry at the 108th Meeting of the American Chemical Society, New York, N. Y.

## Corrections

In the article on "Determination of Formaldehyde" [Ind. Eng. Chem., Anal. Ed., 16, 496 (1944)], reference 5 on page 496 should read: Boyd, M. J., and Bambach, Karl, Ind. Eng. Chem., Anal. Ed., 15, 314–15 (1943).

G. C. Whitnack

In the note on "An Observation of Possible Value for Sugar Determinations" [Ind. Eng. Chem., Anal. Ed., 16, 537 (1944)], an error occurs in lines 15 and 33, where "grams" should read "milligrams".

The possibility of iodometric determination of the cuprous iodide has been discussed in detail by Shaffer and Hartman [*J. Biol. Chem.*, 45, 365 (1920–21)].

Daniel Luzon Morris

# Determining Phenols in Dilute Solutions

## Notes on the Gibbs Method

A. W. BESHGETOOR, L. M. GREENE, AND V. A. STENGER
The Dow Chemical Company, Midland, Mich.

**Some suggestions concerning the performance of the Gibbs method are given, dealing especially with the removal of interfering substances and the best conditions for color development. The colors produced by certain phenol derivatives are listed, and an extraction method for the analysis of very dilute solutions is presented.**

THE Gibbs method for determining phenols (*1*) has been used successfully in a number of laboratories, including that of The Dow Chemical Company. Nevertheless some workers have encountered difficulties; Buswell and Dunlop (*4*), for example, prefer to estimate phenol by means of its ultraviolet absorption. However, since the Gibbs procedure is capable of greater sensitivity and requires less expensive equipment, it will probably remain in common use. The present paper is intended to be supplementary to the procedure given in (*1*). The subjects discussed include notes on the distillation apparatus, interfering substances, best conditions for color development, and a procedure for determining phenol in more dilute solutions.

Although many substituted phenols produce colors in the Gibbs method, relatively few give the normal blue color of ordinary phenol and in those cases the sensitivity is usually less. Baylis (*2*) notes that *p*-cresol shows no color while *o*-cresol, like phenol, gives a blue. It is generally true that substitution in the para position reduces the sensitivity considerably, while ortho substitution with hydrocarbon groups has less effect and with halogen atoms shifts the color toward green. The colors produced by several phenols are shown in Table I, with concentration ranges which yield colors of about the proper intensity for comparison in 100-ml. Nessler tubes. All these compounds are volatile with steam and those which give colors with the Gibbs reagent will interfere in the phenol determination.

### DISTILLATION APPARATUS

In Figure 1 is shown a battery of six stills as they are set up in the Dow Analytical Laboratory, where numerous industrial waste and river water samples are run every day.

A Maharg all-glass distillation apparatus (mercury-sealed) is specified in (*1*). It is essential that the apparatus be thoroughly clean. Washing of the flasks and condensers, followed by steaming out with steam from pure water, is to be recommended between determinations, particularly when samples of varying concentration are being analyzed. Flasks with broken or chipped connecting tubes, which allow condensates to collect on the mercury seal, should be avoided.

Changing of receivers beneath the condenser is simplified by the use of an adapter shown in Figure 2. The adapter slides vertically on the condenser tube, cushioned by a rubber washer, *A*, which rests on bulge *B* in the tube. Glass ears at *C* support its weight when the volumetric flask, *D*, is in position. In building the apparatus, the portion of the condenser tip below *E* is first shaped and fitted with the washer. A piece of 1.9-cm. (0.75-inch) inside diameter tubing is drawn down to form the upper end of the adapter, and the condenser tip is inserted from below. The lower end is next drawn out, the delivery tip is put on, then the condenser tip is sealed to the condenser at *E*.

### INTERFERING SUBSTANCES

In the analysis of industrial wastes, off-colors from the desired blue are sometimes obtained. Green-blues may indicate that part of the phenol contains halogen in the ortho position, possibly as a result of partial chlorination. They may also be produced by sulfides, which according to the amount present can yield off-shades varying through yellow-greens to pink. Williams (*9*) suggested removing sulfides with lead oxide or carbonate, while Renzoni (*6*) recommended the use of freshly precipitated cadmium carbonate. The authors have used copper sulfate, adding a small volume of strong copper sulfate solution to the measured sample and filtering into the distilling flask.

To prevent interference from volatile acids such as salicylic in industrial wastes, double distillation may be necessary. The first distillation is made as usual (see 1.6, p. 246, *1*), though sulfuric acid may be substituted for phosphoric if aniline or other weak bases are present. The entire 500 ml. of distillate are then returned to the distillation flask after the latter has been washed,

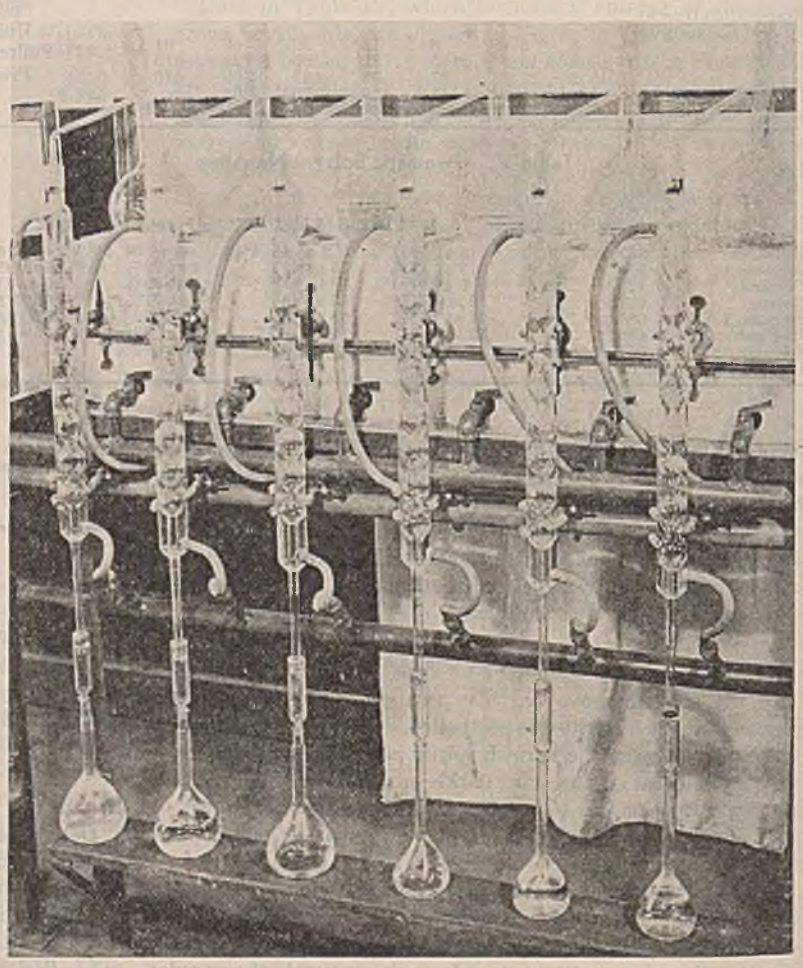


Figure 1. Battery of Six Stills

2 grams of fairly coarse marble chips are added, and the second distillation is carried out. Calcium carbonate furnishes sufficient alkalinity to retain salicylic acid, but not enough to interfere with the distillation of phenol.

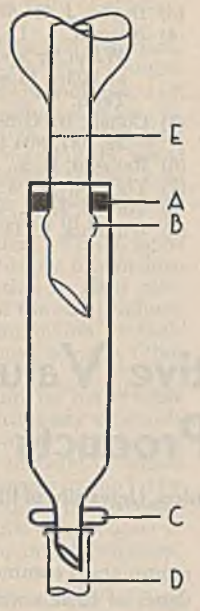



Figure 2. Adapter

### COLOR DEVELOPMENT AND COMPARISON

Difficulties in the method may frequently be traced to the instability of 2,6-dibromoquinonechloroimide. It has been found advisable to purchase this compound in brown glass bottles containing only 1 gram each. These are kept closed until needed; after a bottle is opened the material in it has occasionally been found to decompose within a week or two. The precautions given in (*1*, p. 248), concerning the preparation and use of solutions of this reagent, should be carefully observed. The authors employ the alcoholic solution (1.61) exclusively.

Since the dye produced by reaction of the reagent with phenol is an oxidation-reduction indicator as well as an acid-base indicator (*5*), it is essential that the pH and the oxidation potential be maintained within the specified limits. It is a good practice to add copper sulfate solution to all samples and standards (*1*).

Solutions in the Nessler tubes will turn pink if exposed to sunlight after the addition of reagent. For the best results it is necessary to keep the tubes in the dark during color development. This is conveniently done by keeping them in a box similar to the one illustrated in Figure 3. After 4 hours or longer, the comparison is made in a Fisher Nessler tube support or similar rack, by fluorescent light.

The reaction between phenols and 2,6-dibromoquinonechloroimide proceeds slowly and the color continues to develop for a long period. On this account the samples and standard should be prepared at the same time. In any attempt to determine phenols with a photoelectric colorimeter (*8*), the standard curve should be prepared with allowance of a definite period for color development at a specified temperature. The same conditions should be adhered to carefully in the analysis of a sample.

### ANALYSIS OF MORE DILUTE SOLUTIONS

Various methods for concentrating dilute phenol solutions have been proposed, involving evaporation of an alkaline solution (*7*), distillation (*3*), or extraction of the free phenol with ether (*6*). A procedure based on developing the color in a larger volume of sample and subsequently extracting the colored compound can also be used. This procedure multiplies the sensitivity of the Gibbs method by about 10 and increases the stability of the color.

The reagents are the same as for the usual Gibbs method, with the further inclusion of 1 to 4 hydrochloric acid, chloroform, methanol, or Formula 30 alcohol, and approximately 0.1 *N* alcoholic sodium or potassium hydroxide. More than ordinary care must be taken to obtain phenol-free water for the standards. Add about 200 ml. of finely powdered activated carbon to 37.85 liters (10 gallons) of a good grade of distilled water and agitate with an air stream for 30 minutes. To the suspension add 0.4 gram of aluminum sulfate and 2 grams of sodium bicarbonate, agitate for 15 minutes longer, allow to settle, and filter off as needed.

In the absence of substances which interfere in the ordinary Gibbs method, 1 liter of the neutral sample may be run directly; otherwise a single or double distillation is necessary. A liter of the water is distilled and the entire amount of phenol is considered to be recovered when 900 ml. have been collected in the first distillation, or 850 ml. in the second. Standards containing 0, 0.5, 1.0, 2.0, 3.0, 5.0, 7.0, and 10 parts per billion are prepared from standard phenol solution 1.8 (*1*, p. 247), and phenol-free water. • These should have the same volume as the sample. One milliliter of the standard phenol solution diluted to 1 liter corresponds to 1 part of phenol per billion. To each sample and standard add 20 ml. of alkaline borate buffer solution, 10 ml. of copper sulfate solution, and 3 ml. of the freshly diluted alcoholic 2,6-dibromoquinonechloroimide reagent. Mix well and allow to stand in a dark place overnight.

Transfer to a large separatory funnel, add 5 ml. of 1 to 4 hydrochloric acid and 18 ml. of chloroform, mix well, allow to separate, and draw off the chloroform layer into a 50-ml. Nessler tube. Extract the solution again with 10 ml. of chloroform and add to the same tube. To each tube add 20 ml. of methanol or Formula 30 alcohol and 0.10 ml. of 0.1 *N* alcoholic sodium or potassium hydroxide, invert a few times, and compare the colors.

It is barely possible to detect 0.25 part of phenol per billion, provided that interferences are absent and the standard water is pure. The detection of 0.5 part is rather easy with phenol, which gives a blue-green color. The blank may be slightly yellow because of the presence of excess reagent, the intensity of the yellow color being greater with older reagent. With *o*-chloro-

Table I. Colors of Several Phenols in the Gibbs Test

| Phenol | Color | Concentration Range, Parts per Billion |
|---|---|---|
| Ordinary | Blue | 5–100 |
| *p*-Chloro | Blue | 20–400 |
| *p*-Bromo | Blue | 25–500 |
| *o*-Chloro | Green-blue | 10–150 |
| *o*-Bromo | Green-blue | 10–200 |
| 2,4-Dichloro | Green-blue | 40–800 |
| 2,5-Dichloro | Green-blue | 30–600 |
| 2,6-Dichloro | Green | 30–600 |
| Trichloro | Insensitive | .. |
| Tribromo | Insensitive | .. |
| *o*-Phenyl | Blue | 10–200 |
| 2-Chloro-6-phenyl | Blue | 10–200 |
| 4-Chloro-6-phenyl | Green-blue | 10–200 |
| *p*-Phenyl | Insensitive | .. |
| *p*-*tert*-Butyl | Insensitive | .. |

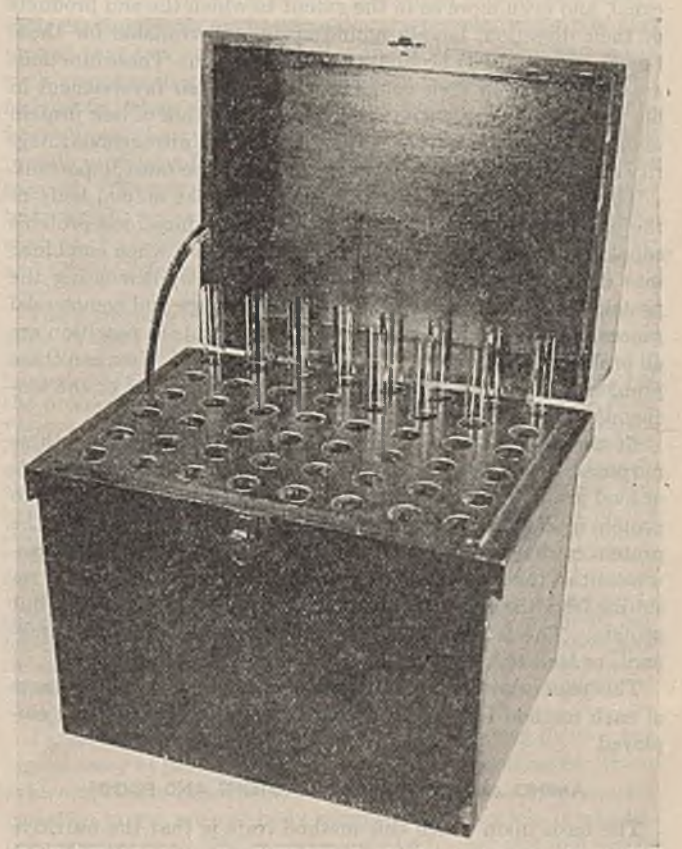


Figure 3. Tube Holder

phenol the color is much the same as with phenol, but the test is only about one half as sensitive. The color from *p*-chlorophenol is more toward the blue, and the sensitivity is only about one fourth that of phenol.

### LITERATURE CITED

(1) Am. Public Health Assoc. and Am. Water Works Assoc., New York, "Standard Methods of Water Analysis", 8th ed., 1936.
(2) Baylis, J. R., *J. Am. Water Works Assoc.*, 19, 604 (1929).
(3) Baylis, J. R., *Water Works and Sewage*, 79, 343 (1932).
(4) Buswell, A. D., and Dunlop, E. C., "Estimation of Phenols in Water by Means of Ultraviolet Absorption Spectra", presented at 103rd Meeting of American Chemical Society, Memphis, Tenn.
(5) Cohen, B., Gibbs, H. D., and Clark, W. M., *Pub. Health Repts.*, 39, 381, 804 (1924).
(6) Renzoni, L. S., *J. Am. Water Works Assoc.*, 32, 1038 (1940).
(7) Theriault, E. J., Ind. Eng. Chem., 21, 343 (1929).
(8) Tucker, I. W., *J. Assoc. Official Agr. Chem.*, 25, 779 (1942).
(9) Williams, R. D., Ind. Eng. Chem., 19, 530 (1927).

# Determination of the Nutritive Value of the Proteins of Food Products

H. H. MITCHELL, Animal Nutrition Division, University of Illinois, Urbana, Ill.

**The nutritive value of food protein cannot be accurately assessed from a determination of the amino acid content, nor from animal feeding experiments that fail to credit the protein with all its functions in the body. A study of the nitrogen economy of the animal when fed the protein to be tested under certain essential conditions is capable of giving a complete and reasonably satisfactory picture of protein utilization in the body, in digestion as well as in metabolism. The net protein value combines all this information in one figure. Illustrations of application of the method to problems of the storage and processing of foods are given.**

THE protein content of food products has an uncertain significance for their evaluation in nutrition, because proteins vary widely in the extent of their digestion in the alimentary canal, and even more so in the extent to which the end products of their digestion, largely amino acids, are available for those functions in the body peculiar to dietary protein. These functions are bewildering in their complexity and in their involvement in life processes, but quantitatively the construction of new protein material in growth and the maintenance of the nitrogenous integrity of the tissues already formed are by far the most important.

The differences that exist in the value to the animal body of the proteins in food products, the extent to which food proteins supplement each other's amino acid deficiencies when combined into diets, particularly the best method of supplementing the proteins of white flour, and the effect of storage and commercial processing on the protein value of food products in nutrition are all problems of importance to food technologists. How can these problems be most effectively tackled in the chemical or the biochemical laboratory?

At the present time, three methods are being used for these purposes: (*a*) determination of the amino acid contents of foods or food proteins, (*b*) measurement of the ratio of gain in weight to protein intake of growing rats subsisting on rations in which the protein content is the only factor limiting growth, and (*c*) measurement of the gain in nitrogen to the bodies of growing rats resulting from the consumption of diets complete in all respects but protein. The latter method can be extended to mature, pregnant, or lactating animals, and to the human subject.

This paper considers briefly the advantages and disadvantages of each method for the purposes for which they are being employed.

### AMINO ACID ANALYSIS OF PROTEINS AND FOODS

The basis upon which this method rests is that the nutritive quality of food proteins is determined entirely, or largely, by their content of amino acids, particularly of those nine or ten amino acids commonly classed as dietary essentials on the evidence of Rose's well-known experiments on growing rats. Undoubtedly the content of a food in those amino acids that the body cannot synthesize from ordinary dietary components sets an upper limit to its usefulness in serving the biological functions of dietary protein; and to this extent the basis is sound.

The amino acid analysis of the proteins in a food product by chemical methods is laborious and the various analyses for individual amino acids are not of equal precision; those for leucine and valine in particular leave much to be desired (*4*). The microbiological methods suggested for determining the amino acid contents of food products are still in the experimental stage. However, it is not too much to hope that in the near future satisfactory methods, chemical or microbiological in nature, will be available for all the amino acids commonly believed to be dietary essentials. It should be emphasized, however, that satisfactory analyses for all these essential amino acids must be at hand before any one food product can be evaluated; otherwise, the possibility exists that the amino acid, or acids, for which no analysis is available may be, or include, the amino acid limiting the nutritive value of the contained proteins.

When the ultimate goal of amino acid analysis of food proteins is attained, it will be possible from the data secured on many foods to predict which are the best in supplying the needs of the body for the essential amino acids, in so far as these needs are known, and in particular to predict which protein mixtures in individual foods will correct best each other's deficiencies in essential amino acids. But these predictions cannot be expressed quantitatively nor can they be made with any great assurance, because the chemical picture of food proteins is inevitably altered and distorted by biological factors before a true picture of nutritional quality is secured.

The disturbing biological factors that impair the usefulness in practical nutrition of a knowledge of the amino acid contents of foods are as follows:

The digestibility of food proteins in the alimentary tract is largely independent of amino acid composition, and may be determined, as Mendel and Fine showed many years ago (*15–19*) by the constituents of foods other than protein. The digestive apparatus of the animal, though remarkably efficient under the most favorable conditions in reducing dietary protein to its ultimate building stones, may be impeded and frustrated in its operation by those nonprotein constituents of food that successfully resist its attack (the cellulosic and hemicellulosic components in particular), while preventing complete access of the proteolytic enzymes to their proper substrates.

The indigestible residue of food protein may not be representative in its amino acid constitution of the food from which it was derived. This may be inferred from the known differences in the ease with which different peptide linkages are split by the digestive enzymes. An instance in point was reported by Jones and

Waterman (*13*) in their study of the digestion in vitro of arachin, the chief protein of the peanut.

The amino acids are liberated from food protein in digestion, not evenly, but at different rates characteristic of the amino acid, or of the manner of its linkage in the protein molecule (*12*, *29*). They are also absorbed into the blood at different rates (*5*).

The fate of the end products of protein digestion in metabolism is not determined solely by their suitability in meeting the needs of the tissues for anabolic purposes. The tissues are also continually in need of energy in the performance of physiological work. The organic nutrients serve interchangeably in the metabolic mixture from which this energy is extracted. Amino acids resulting from protein digestion are thus inevitably drawn into the oxidative reactions of the body in proportion to their relative concentrations in the influx to the tissues of the end products of digestion (*21*, *24*), and probably also in proportion to their relative susceptibility to oxidation with reference to each other and to that of sugars and lipids.

In view of the factors listed above, it would be remarkable indeed if the mixture of amino acids that is ultimately available to the tissues for synthesis of proteins and other nitrogenous tissue constituents were closely similar to the mixture of amino acids present in the food as consumed. Deficiencies in the latter would of course persist through all these vicissitudes, but excesses of certain amino acids may be wiped out, while proportions of others that were originally adequate may develop into deficiencies.

It seems fair to conclude that the amino acid analysis of food proteins may yield information of great significance concerning their nutritive values and their interrelationships in the diet, but that such an analysis cannot take the place of a biological assay. It is doubtful that an amino acid analysis of foods can measure, or explain, the changes in nutritive value that occur during storage and heat processing, especially an improvement in nutritive value such as many legume proteins undergo on heat treatment.

## GROWTH-PROMOTING VALUE OF FOOD PROTEINS

Of the biological assays of food proteins in current use, the most popular undoubtedly is the determination with young albino rats of the ratio of gain in body weight to protein consumed during a 4- to 6-week period on diets containing variable concentrations of protein such that, ordinarily, the concentration used is inadequate to promote maximal growth, being otherwise complete. The method is a simplification of one proposed 25 years ago by Osborne, Mendel, and Ferry (*33*). The original method proposed that food proteins be compared by determining the maximum ratio of gain in weight to protein consumed among ratios secured by varying the concentration of protein in the experimental diet. This maximum ratio for casein was 2.25 at a protein level of 12%, and for lactalbumin, 3.01 at a protein level of 7.9%.

The simplified method in common use has served a useful purpose in comparisons of protein "quality" in the biological sense among many food products studied. For many purposes, it is probably satisfactory, though its most appealing characteristic is its simplicity. Requiring no control of the food intake of the experimental animals and no other measurements than the periodical taking of body weights, it seems to be an ideal technique when comparisons of large numbers of food products are to be made.

The method was subjected to critical scrutiny in a paper published by the author 20 years ago (*23*). In the present connection it may be well to restate the implications of the method, but to discuss them mainly in the light of information revealed since the publication of this review.

In crediting dietary protein only with the growth induced in experimental animals and in permitting an unlimited consumption of food, the method implies that there is no requirement of protein for the mere maintenance of life, since only on such an assumption would it be expected that a constant ratio of gain in weight to protein eaten would be obtained regardless of the intake of protein. The reality of this implication would be difficult to defend at the present time, especially in view of Osborne and Mendel's determinations (*32*) of maintenance requirements for various wheat proteins and the more extensive work of Smuts (*35*). If the implication is wrong, one would expect the ratio of gain in weight to protein consumed to increase on the same diet as the intake of protein (food) increases, since with the greater intake of protein, a greater proportion of it would be available for growth. Hoagland and Snider (*9*) found this to be true in that male rats, consuming larger amounts of food than female rats and consequently growing faster, exhibited almost always the larger ratio of gain to protein eaten. Stewart and associates (*36*) found that a restriction of the food intake of rats lowered considerably the ratio of gain to protein eaten for the same protein source. Thus, for rolled oats the ratio averaged 1.52 under conditions of *ad libitum* feeding, but only 1.14 when the protein (food) consumption was restricted by about 40%. Of the same significance is the fact that the ratio was almost twice as variable with unrestricted feeding as with equalized feeding, the standard deviations being, respectively, 0.167 and 0.094.

The method of measuring protein quality by an efficiency ratio of growth to protein eaten implies that the protein content of the gains in body weight of growing animals is constant regardless of the age or size of animal, the quality of the protein, or the rate of growth. To the extent that the gains differ in their content of protein, fat, and water they do not represent equal nutritive effects, and hence are not comparable. For example, it would be expected that a gram of dietary protein would induce a greater gain in body weight of an animal if this gain contained 15% of protein than if it contained 20%, assuming that other growth essentials are present in adequate amounts. In scientific investigations with farm animals it is generally recognized that live weight increase is not a reliable measure of nutritive effect, a point discussed by Armsby (*2*, pp. 196–9) as early as 1917. Since then evidence of the variable composition of live weight gains has been presented by Mitchell and Carman (*26*) for rats, and by Fraps and Carlyle (*7*) for chickens. Hamilton (*8*) has shown that the live weight gains of growing rats, when put on at the same rate, may vary in their content of protein and energy with varying levels of the same dietary protein, while Kik (*14*) proved that two proteins differing in nutritive value and fed in such amounts to growing rats receiving equal amounts of total food as to induce equal gains in body weight, may produce different proportions of protein in the body weight gains, the better protein producing the higher content of this nutrient in the gains secured. There is a distinct tendency for the more rapid gains in body weight to have the greater content of fat and the smaller content of protein, as Mitchell (*22*) has demonstrated for cattle and Ellis and Zeller (*6*) for pigs.

The disturbing effect of a variable composition of body weight gains in the interpretation of a protein nutrition experiment is well illustrated by an experiment reported from the author's laboratory (*3*) concerned with the comparative nutritive value of the protein of milk curd and of the cheeses produced from it by various types of ripening. When fed in equal amounts in paired-feeding tests, the protein of Limburger cheese was found to be equal to that of fresh milk curd in growth-promoting value, although it was definitely less digestible and possessed a lower biological value. The explanation lay in the composition of the body weight gains: the gains put on by the Limburger cheese ration were definitely lower in protein content and higher in their fat content, than the gains produced on the milk-curd ration. In the same sort of tests, Swiss cheese protein proved superior to milk curd in growth-promoting value, though no better in biological value and definitely inferior in digestibility. An analogous difference in the composition of body weight gains between the cheese ration and the milk-curd ration must have occurred.

Thus, the two clear implications of this method for the biological assay of protein quality in nutrition are untenable. Some evidence of the seriousness of these basic errors in producing variation in the ratio of body weight gain to protein intake has been given above. The situation may be further pictured by the hypothetical illustrations given in Table I, showing to what ex-

**Table I. Effect of Increasing Intake of Same Diet on Ratio of Body Weight Gain to Protein Intake**

| | Case 1 | Case 2 | Case 3 | Case 4 | Case 5 |
|---|---|---|---|---|---|
| Weight of rat, grams | 50 | 50 | 50 | 50 | 50 |
| Daily food, grams | 4 | 5 | 6 | 7 | 8 |
| Daily protein, mg. | 400 | 500 | 600 | 700 | 800 |
| Protein for maintenance, mg. | 200 | 200 | 200 | 200 | 200 |
| Protein for growth, mg. | 200 | 300 | 400 | 500 | 600 |
| Net protein for growth, mg. | 110 | 165 | 220 | 275 | 330 |
| Protein content of gain, % | 23 | 22 | 21 | 20 | 19 |
| Daily gain, grams | 0.48 | 0.75 | 1.05 | 1.37 | 1.74 |
| Gain per gram of protein eaten, grams | 1.20 | 1.50 | 1.75 | 1.96 | 2.17 |

tent the ratio may be changed by changing food intake, although the utilization of the dietary protein remains unaltered.

In each of the five illustrations, the weight of rat is the same, but the daily consumption of food increases from 4 to 8 grams. The diet in all cases is the same and contains 10% of whole wheat protein. The protein requirement for maintenance for this protein was found by Osborne and Mendel (*32*) to approximate 3 mg. per gram of rat per day. This requirement has been raised to 4 mg. because at a 10% level in the diet, utilization in metabolism is less (*21*, *24*). The wheat protein in all cases is assumed to be 85% digestible and to have a biological value of 65% (*27*), the "net protein" thus amounting to 55% (0,85 × 0.65 = 0.55) of the total protein. The protein content of the body weight gains is assumed to decrease from 23 to 19% as the food intake and the rate of growth increase, in conformance with evidence cited above.

These assumptions seem reasonable and to a large extent are based upon experimental evidence. They lead to the expectation that the ratio of body weight gain to protein eaten may be changed, for a whole wheat diet containing 10% of protein, from 1.20 to 2.17 by merely increasing the intake of food. This demonstration accounts for the large experimental error to which the ratio is subjected under conditions of *ad libitum* feeding. It also indicates clearly that this method of assaying protein quality will definitely tend to exaggerate differences in this respect among different protein foods, because the rations containing the better protein foods will generally be consumed in the larger amounts and will thus be given an undue advantage over the poorer protein foods. Equating the food intakes of rats on comparable diets will overcome this effect, but the uncertainty concerning the protein content of body weight gains is inherent in the method.

In brief, this method of assaying food protein biologically may be expected to exaggerate quality differences among proteins when these are considerable, and to obscure them when they are inconsiderable, on account of the large experimental error to which the method is subject as it is ordinarily employed.

## BIOLOGICAL ASSAY OF FOOD PROTEINS BY MEANS OF NITROGEN METABOLISM STUDIES

This method was first introduced by Thomas (*37*) in 1909, and was later adapted to the growing rat by Mitchell (*20*). Many modifications in the method have since been made (*25*, *28*). It is based upon the fact that protein is the only considerable source of dietary nitrogen and that the disposition of protein within the body of an animal can be followed with considerable accuracy by determining the intake and fecal and urinary excretion of nitrogen. When this is done under carefully selected and controlled conditions, it is possible to compute from the data secured (*a*) the digestibility of the protein, (*b*) its utilization in metabolism for all purposes, expressed as a percentage called by Thomas the "biological value", and (*c*) the "net protein content" of the food assayed, equal to the total content times the digestion coefficient (expressed as a decimal) times the biological value (also expressed as a decimal).

Unlike the biological assay method previously considered, this method credits the dietary protein with all its characteristic functions in the body, maintenance as well as growth in the growing rat, and it directly determines the storage of protein in growth rather than assumes that this storage is proportional to body weight gains. Furthermore, its accuracy is such (*25*) that it can detect differences in digestibility and biological value of proteins of a magnitude of two or three percentage units using a battery of only 10 animals.

An illustration of its value in detecting changes in the nutritive value of a food protein (soybean proteins) during storage is afforded by the data summarized in Table II.

The soybeans used in this test were of the Illini variety and the 1942 crop. They were stored at a temperature of 78° to 80° F. in air-tight containers, either whole or as a ground defatted meal that had been heated in the autoclave for 1.5 hours at 17 pounds steam pressure. After 8.5 months, and again after 12 months' storage, containers of both whole beans and autoclaved meal were opened and tested for protein quality by the nitrogen balance method. The whole beans before testing were ground, extracted with ether, and heated for 1.5 hours in the autoclave at 17 pounds' pressure—i.e., the same treatment to which the meal had been subjected prior to storage.

The results indicate that after 8.5 months' storage, the proteins in the beans stored whole with no pretreatment had suffered a marked decrease in digestibility, averaging 7 percentage units, and an even more marked decrease in biological value, averaging 11 percentage units, as compared with the beans ground and heated prior to storage. Both differences were statistically significant. At the end of 12 months' storage, the difference in digestibility between the two products was still distinct, but a clear difference in biological value was not demonstrated, possibly because of two erratic biological values secured for the ground meal. The results confirm and extend those reported by Jones and Gersdorff (*11*), who reported a drop in the digestibility in vitro of the proteins of soybeans on storage.

The results of a similar test on corn proteins are summarized in Table III. In this test the corn was stored either whole or ground, but with no preheating. The method of storing evidently had no effect, either on the digestibility or the biological value of the corn proteins, but storage for 8 months depressed equally the biological value of the proteins in corn stored whole or ground, while leaving the digestibility unaffected. From this outcome, one might conclude that, in the soybean test, it was the preheating, rather than the grinding, that exerted the stabilizing effect on the proteins during storage. The results on corn do not harmonize entirely with those reported by Jones, Divine, and Gersdorff (*10*).

## NET PROTEIN VALUE OF FOOD PRODUCTS

While the nitrogen balance method for the biological assay of protein quality distinguishes between losses of nitrogen in the digestive and in the metabolic processes of the animal body, there are distinct advantages in securing in a single figure an appraisal of the value of a food as a source of dietary protein. Such a figure should involve not only the biological value of the protein and its digestibility, but also its original content of "conventional"

**Table II. Changes in Digestibility and Biological Value of Proteins of Soybeans during Storage**

(All determinations made on beans after autoclaving)

| | Soybeans Stored 8.5 Months | | | | | Soybeans Stored 12 Months | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Whole, Unheated | | Ground, Autoclaved | | | Whole, Unheated | | Ground, Autoclaved | |
| Rat No. | True digestibility | Biological value | True digestibility | Biological value | Rat No. | True digestibility | Biological value | True digestibility | Biological value |
| | % | % | % | % | | % | % | % | % |
| 292 | 77 | 65 | 85 | 80 | 337 | 78 | 60 | .. | .. |
| 295 | 78 | 61 | 83 | 71 | 340 | 79 | 67 | 85 | 71 |
| 298 | 76 | 61 | 86 | 73 | 343 | 80 | 67 | 82 | 82 |
| 301 | 77 | 61 | 84 | 70 | 346 | 77 | 70 | 85 | 67 |
| 304 | 84 | 61 | 85 | 71 | 349 | 81 | 66 | 83 | 52 |
| 293 | 82 | 64 | 88 | 72 | 338 | 79 | 78 | 85 | 73 |
| 296 | 79 | 65 | 85 | 74 | 341 | 81 | 68 | 84 | 67 |
| 299 | 75 | 59 | 84 | 71 | 344 | 79 | 62 | 86 | 68 |
| 302 | 76 | 60 | 87 | 76 | 347 | 81 | 60 | 84 | 76 |
| 305 | 79 | 69 | 86 | 79 | 350 | 79 | 63 | 82 | 67 |
| Av. | 78.3 | 62.6 | 85.3 | 73.7 | | 79.4 | 66.1 | 84.0 | 68.2 |

protein—i.e., N × 6.25. Such a value was proposed by the author and Carman (*27*) many years ago, and has been called the "net protein value" of the food which may be computed on the dry basis or on the fresh basis, as in the tabulation below:

| Food | Total Protein | Digestibility of Protein | Digestible Protein | Biological Value | Net Protein |
|---|---|---|---|---|---|
| | % | % | % | % | % |
| Eggs | 13.4 | 100 | 13.4 | 93 | 12.5 |
| Lean ham | 19.8 | 100 | 19.8 | 74 | 14.6 |
| Wheat | 12.5 | 91 | 11.4 | 67 | 7.6 |
| Soybeans | 32.8 | 84 | 27.6 | 72 | 19.9 |
| Soybeans, stored for 8.5 months | 32.8 | 78 | 25.6 | 63 | 16.1 |

The net protein values as thus computed are mainly of comparative significance, because of the variation to which biological values are subject as the level of protein in the diet changes.

## CRITIQUE OF THE NITROGEN BALANCE METHOD OF ASSAY OF FOOD PROTEIN

Measurements of protein digestibility and of the biological value of the absorbed protein must, in the present state of biochemical technique, be expressed in terms of nitrogen. This is not the most satisfactory situation, because all food nitrogen is not in the form of protein, or amino acids, or amino acid derivatives, nor is the nitrogen of the tissues present there only in such compounds as these. However, the ambiguity introduced into measurements of protein digestibility and biological value by employing nitrogen as a conventional equivalent of protein is not generally large. Certainly no substitute procedure can claim to be as satisfactory. Perhaps a more serious objection to this emphasis upon protein nitrogen is that it neglects the function of dietary protein of providing the body with comparatively large amounts of readily available phosphorus, which is not an integral part of the amino acid structure.

The nitrogen balance method of assessing protein quality was proposed by Thomas at a time when Folin's theory of protein metabolism, with its sharp distinction between exogenous and endogenous metabolism, was commonly accepted. In assuming a constant (biologically speaking) erosion of nitrogenous material from the animal body, commensurate with the maintenance requirement of protein, the method tacitly assumes the reality of Folin's endogenous catabolism. However, the work of Schoenheimer and his associates on amino acid metabolism using the nitrogen isotope may seem to cast doubt upon any assumption of this nature. These revolutionary investigations swept away all sharp distinctions between the endogenous and the exogenous metabolism that form the basis of Folin's theory of protein metabolism. They afford a convincing picture of the dynamic equilibrium existing between the tissue proteins and the amino acids of dietary origin in the circulating fluids of the body. However, they do not change the significance of the end results of protein metabolism as revealed by such a nitrogen balance study as would be undertaken in the course of securing digestion coefficients and biological values according to the Thomas method or some modification of it. The nitrogen in the urine on a nitrogen-free diet still represents a minimum or basal level of nitrogen loss from the tissues, bearing a relationship to the basal metabolism of energy (*35*). Considerable circumstantial evidence can be cited to the effect that this basal rate of nitrogen output in the urine continues at a constant level, biologically speaking, during regimes of adequate protein nutrition.

One of the most convincing bits of evidence of this description may be found in a publication by Ackerson and Blish (*1*) on the utilization of the protein of corn by hens. Nonmolting hens excreted an average of 143 mg. of nitrogen per kg. of body weight per day on a nitrogen-free diet, while molting hens on the same diet excreted 217 mg. However, assuming that these greatly different values for the constant catabolism of nitrogen persisted during periods of feeding a corn diet, the same average biological value of 68 was obtained for a group of 19 nonmolting birds and for a group of 8 molting birds.

The urinary nitrogen during periods when test proteins are being fed consists definitely of two fractions, one the constant contribution from the tissues, and the other related to the level of protein feeding and the efficiency with which the absorbed amino acids satisfy the prevailing requirements of amino acids by the tissues. This fraction is partly of tissue origin and partly of dietary origin, because of the dynamic relation existing between tissue proteins and dietary amino acids. But this dynamic relationship is not anarchistic in character. Through the welter of reactions in which the tissue proteins are involved, the cells and organs of the adult body retain their original form and size and the chemical structures of the protein molecules emerge unchanged, as Schoenheimer and Rittenberg admit (*34*). Discussing the many interconversion reactions divulged by the isotope method, Moss and Schoenheimer (*30*) believe that they cannot be regarded "merely as steps in metabolic degradation. They seem rather to represent automatic and noninterruptable biochemical processes, of synthesis as well as degradation, which are balanced by an unknown regulatory mechanism so that the total amount of the body material and its composition do not change."

**Table III. Changes in Digestibility and Biological Value of Protein (Nitrogen) of Corn (U. S. Hybrid 13) during Storage**

| | Before Storage | | | After Storage for 8 Months | | | |
|---|---|---|---|---|---|---|---|
| | | | | Stored Whole | | Stored Ground | |
| Rat No. | True digestibility | Biological value | Rat No. | True digestibility | Biological value | True digestibility | Biological value |
| | % | % | | % | % | % | % |
| 259 | 90 | 72 | 322 | 91 | 53 | 92 | 60 |
| 261 | 91 | 62 | 325 | 92 | 54 | 92 | 60 |
| 263 | 93 | 69 | 328 | 93 | 57 | 94 | 60 |
| 265 | 94 | 68 | 331 | 91 | 56 | 91 | 55 |
| 267 | 93 | 69 | 334 | 89 | 52 | 90 | 62 |
| 260 | 90 | 62 | 323 | 92 | 60 | 91 | 60 |
| 262 | 89 | 61 | 326 | 93 | 67 | 90 | 59 |
| 264 | 95 | 55 | 329 | 93 | 58 | 91 | 54 |
| 266 | 92 | 62 | 332 | 92 | 61 | 91 | 56 |
| 268 | 96 | 69 | 335 | 91 | 59 | 91 | 60 |
| Av. | 92.3 | 64.9 | | 91.7 | 57.7 | 91.3 | 58.6 |

The "exogenous nitrogen" of the urine, to use the obsolete term of Folin, is thus both of tissue and of diet origin, but the rate of its excretion can nevertheless be assumed to depend solely upon the level of protein intake and upon the extent to which the dietary protein is used in the replacement of tissue losses of nitrogen in the adult animal. In the growing animal the "exogenous nitrogen" of the urine will be reduced to the extent that dietary amino acids are used in the elaboration of new tissue in growth. To all intents and purposes, therefore, this fraction of the urine nitrogen measures the wastage of dietary nitrogen in metabolism under the conditions of diet control imposed in a well-considered determination of the biological value of protein.

The essential accuracy of the assumptions upon which this determination is based has been tested in the author's laboratory by comparison with a method of measuring protein quality that does not involve these assumptions. The results obtained in tests upon two protein sources were found to agree satisfactorily (*25*). The reproducibility of results secured at different times upon the same protein source is also satisfactory as the method is used in this laboratory, although very occasionally unaccountable erratic values, such as three of those listed in Table II, are obtained. Any method of biological assay of food products may thus go "haywire" on occasion.

## NITROGEN REPLACEMENT VALUES

Murlin and his associates (*31*) have introduced a new method of interpreting nitrogen balance data relating to the utilization

Table IV. Replacement Values of Protein of Exploded Wheat[a] on Proteins of Unprocessed Wheat[b]

| Period | Pair No. | Rat No. | Daily Nitrogen Intake: Exploded wheat | Daily Nitrogen Intake: Unprocessed wheat | Daily Nitrogen Intake: Average | Daily Nitrogen Balance: Exploded wheat | Daily Nitrogen Balance: Unprocessed wheat | Daily Nitrogen Balance: Differences | Replacement Values |
|---|---|---|---|---|---|---|---|---|---|
| | | | Mg. | Mg. | Mg. | Mg. | Mg. | Mg. | % |
| I, 5% protein in diets | 1 | 1 | 150 | ... | ... | −3.5 | ... | ... | ... |
| | | 2 | ... | 159 | 155 | ... | 17.3 | 20.8 | 86 |
| | 2 | 3 | 134 | ... | ... | −8.9 | ... | ... | ... |
| | | 4 | ... | 142 | 138 | ... | 9.3 | 18.2 | 87 |
| | 3 | 5 | 134 | ... | ... | 15.4 | ... | ... | ... |
| | | 6 | ... | 142 | 138 | ... | 5.4 | −10.0 | 107 |
| | 4 | 7 | 134 | ... | ... | −5.8 | ... | ... | ... |
| | | 8 | ... | 142 | 138 | ... | 12.1 | 17.9 | 87 |
| | 5 | 9 | 134 | ... | ... | −14.4 | ... | ... | ... |
| | | 10 | ... | 142 | 138 | ... | 5.9 | 20.3 | 85 |
| II, 4% protein in diets | 1 | 1 | ... | 87 | ... | ... | −15.8 | ... | ... |
| | | 2 | 88 | ... | 87 | −26.3 | ... | 10.5 | 88 |
| | 2 | 3 | ... | 78 | ... | ... | −17.0 | ... | ... |
| | | 4 | 79 | ... | 78 | −34.8 | ... | 17.8 | 77 |
| | 3 | 5 | ... | 61 | ... | ... | −25.5 | ... | ... |
| | | 6 | 62 | ... | 61 | −34.6 | ... | 9.1 | 86 |
| | 4 | 7 | ... | 89 | ... | ... | −7.9 | ... | ... |
| | | 8 | 90 | ... | 89 | −31.5 | ... | 23.6 | 74 |
| | 5 | 9 | ... | 95 | ... | ... | −18.2 | ... | ... |
| | | 10 | 96 | ... | 95 | −29.1 | ... | 10.9 | 89 |
| Av. | | | | | | | | | 86.8 |

[a] "Puffed Wheat", Quaker Oats Co.
[b] Test carried out with aid of funds from General Mills, Inc.

of protein in nutrition that possesses the advantage of removing the need of a standardizing period for the determination of the body's contribution to the fecal and urinary nitrogen. It was devised especially for use in experiments on human subjects, for whom low-protein diets are extremely unpalatable. The method simply compares the nitrogen balances of adult experimental subjects on the same intake of nitrogen from the food under test and in another period, from a reference protein of high nutritive value, such as the protein of milk or of egg.

The method may be applied to such a problem as that of the injury to food protein brought about by heat processing. In Table IV, the method has been used to assess the extent of heat injury induced in the whole wheat kernel by subjecting it to the "gun explosion" method of preparing a breakfast food. Five pairs of adult rats have been carried through two nitrogen metabolism periods, one rat in each pair receiving its protein from processed wheat and the other rat in equal amounts from unprocessed wheat. In the second metabolism period the sources of protein for the paired rats were reversed. The replacement values given in the last column of the table indicate the extent of heat injury and were computed by the formula

$$R.V. = 100 - \left[\frac{B_1 - B_2}{I} \times 100\right]$$

in which $B_1$ is the nitrogen balance of the rat subsisting on the unprocessed wheat diet, $B_2$ is the nitrogen balance of its pair mate subsisting on the processed wheat diet, and $I$ is the average of the nitrogen intakes of the two rats in the pair, which should be practically the same.

The average replacement value of 86.8 shows that the processing of wheat by the gun explosion method has impaired the protein value in adult rodent nutrition by 13.2%. For growing animals, the impairment may be greater than this. It is interesting to note that, with adult human subjects, Murlin, Nasset, and Marsh (*31*) report egg replacement values of 70 and 57 for two whole wheat cereals (Ralston's Wheat Cereal and Puffed Wheat) subjected, respectively, to mild processing and to the extreme heat of the gun explosion process. The latter value is 81.4% of the former, equivalent to a heat injury to the contained protein of 18.6%.

### LITERATURE CITED


(1) Ackerson, C. W., and Blish, M. J., *Poultry Sci.*, 5, 226–32 (1926).
(2) Armsby, H. P., "Nutrition of Farm Animals", p. 743, New York, Macmillan Co., 1917.
(3) Beadles, J. R., Quisenberry, J. H., Nakamura, F. I., and Mitchell, H. H., *J. Agr. Research*, 47, 947 (1933).
(4) Block, R. J., and Bolling, D., "Amino Acid Composition of Proteins and Natural Foods. Analytical Methods and Results", Springfield, Ill., C. C. Thomas, 1944.
(5) Chase, B. W., and Lewis, H. B., *J. Biol. Chem.*, 106, 315-21 (1934).
(6) Ellis, N. R., and Zeller, J. H., U. S. Dept. Agr., *Tech. Bull.* 413 (1934).
(7) Fraps, G. S., and Carlyle, E. C., *J. Agr. Research*, 59 777–81 (1939).
(8) Hamilton, T. S., *J. Nutrition*, 17, 565–82 (1939).
(9) Hoagland, R., and Snider, G. G., *J. Agr. Research*, 32 1025–40 (1926).
(10) Jones, D. B., Divine, J. P., and Gersdorff, C. E. F., *Cereal Chem.*, 19, 819–30 (1942).
(11) Jones, D. B., and Gersdorff, C. E. F., *J. Am. Chem. Soc.*, 60, 723 (1938).
(12) Jones, D. B., and Gersdorff, C. E. F., *J. Biol. Chem.*, 101, 657–67 (1933).
(13) Jones, D. B., and Waterman, H. C., *Ibid.*, 52, 357 (1922).
(14) Kik, M. C., Arkansas Agr. Expt. Sta., *Bull.* 352 (1938).
(15) Mendel, L. B., and Fine, M. S., *J. Biol. Chem.*, 10 303–25 (1911–12).
(16) *Ibid.*, 10, 339–43 (1911–12).
(17) *Ibid.*, 10, 345–52 (1911–12).
(18) *Ibid.*, 10, 433–58 (1911–12).
(19) *Ibid.*, 11, 1–3, 5–26 (1912).
(20) Mitchell, H. H., *J. Biol. Chem.*, 58, 873 (1924).
(21) *Ibid.*, 58, 905–22 (1924).
(22) Mitchell, H. H., Natl. Res. Council, *Bull.* 67 (1928).
(23) Mitchell, H. H., *Physiol. Revs.*, 4, 424–78 (1924).
(24) Mitchell, H. H., and Beadles, J. R., *J. Biol. Chem.*, 71, 429 (1927).
(25) Mitchell, H. H., Burroughs, E. W., and Beadles, J. R., *J. Nutrition*, 11, 257–274 (1936).
(26) Mitchell, H. H., and Carman, G. G., *Am. J. Physiol.*, 76, 398-410 (1926).
(27) Mitchell, H. H., and Carman, G. G., *J. Biol. Chem.*, 60, 613 (1924).
(28) *Ibid.*, 68, 183–215 (1926).
(29) Mitchell, H. H., and Hamilton, T. S., "Biochemistry of the Amino Acids", A.C.S. Monograph No. 48, New York, Reinhold Publishing Corp., 1929.
(30) Moss, A. R., and Schoenheimer, R., *J. Biol. Chem.*, 135, 415 (1940).
(31) Murlin, J. R., Nasset, E. B., and Marsh, M. E., *J. Nutrition*, 16, 249–69 (1938).
(32) Osborne, T. B., and Mendel, L. B., *J. Biol. Chem.*, 37, 557–601 (1919).
(33) Osborne, T. B., Mendel, L. B., and Ferry, E. L., *Ibid.*, 37, 223-9 (1919).
(34) Schoenheimer, R., and Rittenberg, D., *Physiol. Revs.*, 20, 218 (1940).
(35) Smuts, D. B., *J. Nutrition*, 9, 403–33 (1935).
(36) Stewart, R. A., Hensley, G. W., and Peters, F. N., Jr., *Ibid.*, 26, 519–26 (1943).
(37) Thomas, Karl, *Arch. Anat. Physiol., Physiol. Abt.*, 219–302 (1909).


This article represents a complete revision for publication purposes of a paper presented before the Division of Agricultural and Food Chemistry at the 107th Meeting of the American Chemical Society, Cleveland, Ohio.

## WPB Restrictions on Laboratory Equipment

WPB reduced the number of types of laboratory equipment that may be sold or delivered only upon authorization by amendment to Order L-144, issued October 22.

Types of laboratory equipment which are in short supply are still subject to control: analytical balances (sensitivity 0.05 mg. or more sensitive); centrifuges valued at more than $80 each; hydrogen-ion meters, electrometric type; metalloscopes and metallographs; microscopes, stereoscopic wide field; Abbe refractometers; spectrographs (quartz), spectrophotometers (quartz), and spectrometers (infrared); and vacuum pumps (one micron or higher vacuum).

# Determination of Crude Lipid in Vegetable Matter

JOHN P. NIELSEN AND G. S. BOHART, Western Regional Research Laboratory, Albany, Calif.

**A method is proposed for extracting crude lipid from vegetable products. The complete procedure including preparation of the sample can be carried out in a relatively short time. The method yields considerably larger quantities of crude lipid from certain types of vegetable material such as immature seeds than do the commonly accepted procedures for crude fat. It is equally well adapted to wet or dry ground products.**

MEASUREMENT of maturity in vegetables is of importance to the grower, processor, and consumer. Maturity at harvest may affect yield of raw product, processing behavior, and quality and yield of final product. Many vegetables store starch, which can be measured as an index of maturity. Soybeans, however, do not store starch, and sweet corn presents analytical difficulties due to its glycogen content (*2*). These and other vegetables increase in lipid content as they mature and a simple method for the determination of crude lipid might serve as an index of maturity.

In common methods for determining crude fat or ether extract, the sample is dried, ground, and extracted with petroleum ether for a number of hours. In some cases the extracted matter is then reground and the extraction repeated. The petroleum ether is then evaporated and the extract weighed. These procedures are time-consuming, especially in the case of material of high water content and products which have to be reground in a mortar with sand. The drying of the samples, particularly those which are immature and contain highly active enzyme systems, may introduce errors due to the actions of these enzymes at the elevated temperatures of drying.

A method by which an analysis, including the preparation of the sample, can be carried out in a relatively short time has been developed and is presented here. The method is simple and involves the use of standard laboratory equipment. The chief departures from common methods for crude fat determination are: the use of a Waring Blendor or comparable disintegrator for comminuting the sample, use of acetone as an initial extracting solvent, and elimination of extractors. The extract is taken up with petroleum ether in the latter part of the method; the material finally weighed is only that which is soluble in petroleum ether. The method has proved highly satisfactory on materials analyzed comparatively by both procedures, but its indiscriminate use, especially on hard oil seeds which may not be disintegrated by the proposed procedure, is not recommended.

## ANALYTICAL PROCEDURE

REAGENTS. Redistilled acetone. Redistilled petroleum ether, boiling range 35° to 59° C. (Skellysolve F). Sodium chloride. Filter aid.

APPARATUS. Aside from beakers the only apparatus required is a Waring Blendor or similar device, three 125-ml. suction flasks, two 60-ml. Büchner-type funnels with fritted-glass filter disks of medium porosity, and a source of vacuum.

One of the fritted-glass filters is used for the initial aqueous-acetone extraction and the other for clarifying petroleum ether solutions of lipids. Water and other substances contributing to the turbidity of petroleum ether solutions of lipids are likely to be drawn through a bare fritted-glass filter, especially if a high vacuum is employed. To ensure a clear filtrate, the fritted surface of the filter is coated with about 0.5 gram of Super Cel or other suitable diatomaceous earth, and a low vacuum is maintained in the system by the aid of a bubble bottle. The bubble bottle consists of a suction flask partly filled with water and having its side tube connected with both the vacuum line and the filtering system. A glass tube which passes through a one-hole stopper in the flask is adjusted so that its lower end is immersed to a depth of 5 or 7.5 cm. (2 or 3 inches) in the water. When the vacuum is turned on until bubbles of air are drawn through the water, a constant, reduced pressure exists in the system.

PROCEDURE. Grind 100 grams or more of the vegetable with an equal weight of water in a Waring Blendor for 3 to 5 minutes. If dehydrated products are to be used, soak 6 to 8 hours in 6 parts of water before disintegrating.

Weigh 5 grams of the resulting puree in a 10-ml. beaker and add 25 ml. of acetone from a pipet, stirring constantly. Transfer to a fritted-glass filter which has been connected by a cork stopper with a suction flask and apply suction until the liquid above the solids has been drawn into the flask, but interrupt the vacuum while the solids still appear distinctly wet.

Wash the beaker with about 5 ml. of acetone, scraping most of the solids from the sides into the liquid, and pour the material into the filter. Stir the contents of the filter with a glass rod having a rounded tip and apply suction as before. Wash the cake in the filter with 4 more 5-ml. portions of solvent, stirring after each addition and interrupting the vacuum before each new addition of acetone. Suction should be continued after the last 2 washings, however, until the cake in the filter appears dry.

Transfer the contents of the suction flask to a 250-ml. beaker and add about 1 gram of sodium chloride to prevent the formation of emulsion in the next step. Add a boiling stone, place the covered beaker on a steam bath, and evaporate most of the acetone. This will require about 15 minutes. Cool, and add 5 ml. of petroleum ether from a pipet, washing down the sides of the beaker. Rotate gently so as to expose all the lower surface of the beaker to the solvent, until masses of fat have disappeared. In some instances this may require several minutes. Carefully decant the petroleum ether layer into a fritted-glass filter coated with filter aid and apply mild vacuum. Repeat the petroleum ether extraction with two more 5-ml. portions.

The aqueous salt solution still retains a small amount of lipid in the form of an emulsion. To recover this, dissolve by adding 5 ml. of acetone and then replace the beaker on the steam bath to evaporate the fat solvent. Most of the formerly emulsified lipid will now be found floating on the water surface or adhering to the beaker at the water line. Cool and extract with three more 5-ml. portions of petroleum ether as before. Discard the salt solution and wash the lipid from the outside of the beaker lip into the filter with petroleum ether.

After the filter has drained, wash it with five 1-ml. portions of solvent, rotating the filter after each addition of petroleum ether to bring the diatomaceous earth into suspension. The rotating procedure prevents channeling of the solvent. In most instances, the diatomaceous cake will remain sufficiently porous to permit its use for several filtrations without renewal. Transfer the contents of the receiver to a 50-ml. tared beaker and evaporate the solvent by placing the beaker in an enameled pan on a steam bath until the odor of petroleum ether has disappeared. Cool the beaker and weigh. (If preferred, a tared 50-ml. flask can be used and the solvent removed by connecting with vacuum at room temperature until constant weight is obtained. Results will be substantially the same by both methods.)

**Table I. Typical Crude Lipid Determinations on Undried, Immature Soybeans and Sweet Corn**

| Sample No. | Soybeans, Blanched | Soybeans, Unblanched | Sweet Corn, Blanched | Sweet Corn, Unblanched |
|---|---|---|---|---|
| | *Per Cent of Crude Lipid* | | | |
| 1 | 5.42 | 4.79 | 1.75 | 0.98 |
| 2 | 5.43 | 4.73 | 1.74 | 0.99 |
| 3 | 5.33 | 4.70 | 1.78 | 0.96 |
| 4 | 5.38 | 4.66 | 1.72 | 0.99 |

## RESULTS

As illustrated in Table I, results of crude lipid analyses in quadruplicate by the aqueous-acetone method are in good agreement. In the course of a considerable number of determinations on soybeans, sweet corn, and lima beans, results in duplicate seldom differed by more than 3% of the total crude lipid present. It has been found, however, that the percentage of lipid obtained by this method is consistently higher than that resulting from extraction with petroleum ether in the Soxhlet apparatus. The lipid ratio for the two methods is approximately constant for any one product, but may vary greatly between different products or

**Table II. Extraction of Crude Lipids from Various Products and Modifications of the Same Product**

| Product | A Petroleum Ether Extraction by Soxhlet | B Extraction of Thimble Residue by Proposed Method | C Extraction by Proposed Method | $\frac{B}{A} \times 100$ | $\frac{C - (A+B)}{C} \times 100$ |
|---|---|---|---|---|---|
| | *Per cent lipid*[a] | | | | |
| Soybeans, mature, blanched | 18.56 | 2.14 | 21.23 | 10.1 | +2.5 |
| Soybeans, immature, blanched | 14.96 | 3.03 | 18.15 | 16.8 | +0.9 |
| Soybeans, immature, unblanched | 9.93 | 5.22 | 15.06 | 34.5 | −0.6 |
| Sweet corn, immature, blanched | 4.94 | 1.08 | 6.00 | 18.0 | −0.3 |
| Sweet corn, immature, unblanched | 3.23 | 1.25 | 4.60 | 27.9 | +2.0 |
| Copra meal | 6.69 | 0.29 | 7.21 | 4.2 | +2.0 |
| Ripe olives, flesh, canned | 70.77 | 0.37 | 70.35 | 0.5 | −1.1 |
| Peanuts, shelled, roasted | 49.92 | 1.37 | 50.37 | 2.7 | −1.8 |
| Avocado, flesh, ripe | 58.81 | 1.25 | 59.31 | 2.1 | −1.3 |

[a] Dry basis.

between samples of the same product when one has been modified by a processing treatment, such as blanching. Results shown in Table II illustrate these variations.

Extraction of lipid in the Soxhlet apparatus was carried out as follows:

Approximately 10 grams of 40-mesh material previously dried to constant weight in a vacuum at 70° C. were folded in a large No. 2 Whatman filter. To facilitate drainage of the petroleum ether solvent and to increase the extraction rate, the Soxhlet thimble holding the wrapped sample was supported 1.25 cm. (0.5 inch) above the bottom of the thimble tube by a glass stopper (*4*). Rapid extraction was continued for 4 hours, at which time the sample was removed and thoroughly ground with an equal weight of sand in a large mortar. After it was replaced in the Soxhlet apparatus, the material was again extracted for a period of 4 hours. If turbidity was observed in the Soxhlet receiving flask, the solution was clarified by filtration with the fritted-glass filter as described above. Several samples were extracted for an additional 8 hours. Less than 0.5% of the total lipid extracted was obtained during this period.

In order to isolate the petroleum ether-soluble material obtained by the aqueous-acetone method but not extractable in the Soxhlet apparatus, the thimble residue after extraction was transferred to a fritted-glass filter and repeatedly treated with an equal weight of water, followed by extraction with acetone. After extraction the acetone was evaporated and the lipid taken up with petroleum ether in the manner described previously.

By reference to Table II it will be seen that the lipid value obtained by the Soxhlet extraction plus that obtained by the proposed method on the Soxhlet thimble residue equals approximately the value obtained on the original material by the proposed aqueous-acetone method.

On the basis of the percentage of lipid obtained from soybeans (Table II), it appears that the petroleum ether–soluble material remaining in the sample after Soxhlet extraction is greater in immature beans than in the mature product. In a similar way the proportion of lipid retained by the sample after Soxhlet extraction is greater in unblanched soybeans and unblanched sweet corn than in the comparable blanched vegetable.

In view of the higher results obtained with the aqueous-acetone method as compared with the Soxhlet apparatus, some of the tests commonly employed for the identification of a fat were applied to three types of petroleum ether extract obtained from blanched, immature soybeans and sweet corn. The results are shown in Table III. The methods used were official procedures of the Association of Official Agricultural Chemists (*1*) except that somewhat lower quantities of lipids were employed than those recommended.

It is clear from Table III that the material obtained from the Soxhlet thimble residue of the petroleum ether extraction is actually of a fatty nature and not merely an oil-soluble substance of unknown constitution, although some significant differences in values are observed. For example, their saponification numbers are above 200 for both soybeans and sweet corn, whereas the bulk of the total lipids is somewhat under this figure. Iodine values of the residual lipids, on the other hand, are low. The presence of low-molecular-weight saturated acids, such as butyric lauric, and myristic, is suggested (*3*). Butyric acid is strongly indicated because of the high content of soluble acids in the saponified acids, and this is borne out by the low Hehner value. The somewhat high free fatty acid content of the Soxhlet residues is noteworthy.

To determine whether a combination of carbohydrates and proteins was responsible for any of the increase in yield, tests were applied to the petroleum ether–soluble material extractable by water and acetone after extraction by the usual procedure in the Soxhlet. The nitrogen content of material extracted from corn was 0.36% and from soybeans, 0.86%. The phosphorus content of the material extracted from corn was 1.1% and from soybeans, 2.5%. Sugar tests, including the phenylhydrazine test, Benedict's, and the orcinol test, all gave negative results. The reducing value with alkaline ferricyanide was small and showed only a slight increase after 90 minutes of hydrolysis with 1 *N* sulfuric acid. If it is assumed that the nitrogen found was present as lecithin, the corn extract would contain 20% and the soybeans 48% of this lipid. Since the molecular ratio of nitrogen to phosphorus was less than one, it is probable that protein was not present.

This investigation has not revealed why lipids are not entirely extracted from dried vegetable products by petroleum ether in the Soxhlet apparatus. One observation has been made, however, which may contribute to an explanation of this fact. When acetone is evaporated from water-acetone extracts in the aqueous-acetone method a certain amount of a material having a waxlike appearance separates out in the saline solution along with the lipid. This material appears to be insoluble in petroleum ether. It is also nearly insoluble in water, acetone, and 95% alcohol, but is readily soluble in either 50% aqueous acetone or 50% aqueous alcohol. Should some of the lipid particles in a dried vegetable be entirely enveloped in this substance it appears unlikely that petroleum ether could extract them. In the aqueous-acetone method, on the other hand, any lipid surrounded by this waxy material would be liberated by the solvent action of water-acetone mixtures employed for the initial extraction.

The relationship between the maturity and the percentage of

**Table III. Results of Characterization Tests**

| | Soybeans | | | Sweet Corn | | |
|---|---|---|---|---|---|---|
| | Petroleum ether Soxhlet | Proposed method on thimble residue | Proposed method | Petroleum ether Soxhlet | Proposed method on thimble residue | Proposed method |
| Total lipid, % | 14.96 | 3.03 | 18.15 | 4.94 | 1.08 | 6.00 |
| Saponification No. | 194 | 220 | 196 | 196 | 204 | 197 |
| Iodine No. | 139 | 88 | 132 | 105 | 74 | 98 |
| Hehner No. | 91.2 | 66.6 | 85.8 | 92.4 | 62.2 | 90.1 |
| Mean molecular weight of insoluble nonvolatile acids | 288 | 318 | 289 | 291 | 321 | 301 |
| Soluble acids as % butyric | 3.2 | 12.8 | 5.6 | 2.4 | 15.1 | 6.4 |
| Free fatty acid as % oleic | 1.5 | 6.7 | 2.7 | 1.4 | 8.5 | 2.7 |

**Table IV. Relationship of Maturity of Soybeans and Sweet Corn to Lipid Content on Wet Basis**

| Soybeans | | Sweet Corn | |
|---|---|---|---|
| Harvest date | % lipid | Harvest date | % lipid |
| 9/16/42 | 3.76 | 8/18/42 | 0.98 |
| 9/19/42 | 4.25 | 8/21/42 | 1.28 |
| 9/22/42 | 4.56 | 8/24/42 | 1.39 |
| 9/28/42 | 4.81 | | |
| 9/18/42 | 3.74 | 8/20/42 | 0.87 |
| 9/21/42 | 4.10 | 8/24/42 | 1.06 |
| 9/25/42 | 4.34 | 8/25/42 | 1.06 |
| 9/30/42 | 4.97 | | |
| | | 8/20/42 | 1.03 |
| | | 8/24/42 | 1.28 |
| | | 8/26/42 | 1.37 |

lipid in soybeans and sweet corn has been mentioned previously. Typical data are shown in Table IV. The maturity range studied was such that prime quality, from the standpoint of edibility as a green vegetable, fell at about the middle of the range.

ACKNOWLEDGMENT

The authors wish to thank E. B. Kester and G. R. Van Atta of this laboratory for advice and assistance.

LITERATURE CITED

(1) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, 1940.
(2) Hassid, W. Z., and McCready, R. M., *J. Am. Chem. Soc.*, 63, 1632 (1941).
(3) Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes", 6th ed., Vol. 1, p. 532, London, Macmillan Co., 1921.
(4) Neustadt, M. H., Ind. Eng. Chem., Anal. Ed., 14, 431 (1942).

# Determination of Copper and Zinc in Their Naphthenates

A. S. WEATHERBURN, M. W. WEATHERBURN, AND C. H. BAYLEY, National Research Council, Ottawa, Canada

**Two methods are described for the estimation of copper and zinc in the naphthenates of these metals. The first method is applicable to the analysis of either petroleum solvent solutions or aqueous emulsion of the naphthenates, while the second is limited to the analysis of emulsions. (1) The naphthenate is hydrolyzed by heating with hydrochloric acid, the liberated naphthenic acids are separated, and the metal content of the remaining aqueous portion is determined by the usual volumetric methods. This procedure gives higher and more consistent results than are obtained by igniting the sample and determining the metal content of the ash. (2) The naphthenate emulsion is hydrolyzed by heating with hydrochloric acid, and the volume of the liberated naphthenic acids is measured. This volume is converted into terms of the metal content of the original emulsion by multiplication by a suitable factor. This method is recommended for routine control of processing baths.**

THE copper and zinc salts of naphthenic acids have recently attained some prominence as rotproofing compounds for the treatment of fabrics and cordage. These compounds are usually applied as a solution in petroleum solvents or as an aqueous emulsion of such solutions.

A survey of the literature reveals no method for the determination of copper or zinc in such solutions or emulsions. Methods are available, however, for the determination of copper (*2*) and zinc (*3*) in fabrics proofed by these processes, and these methods have been applied to the analysis of solutions or emulsions of copper or zinc naphthenates: A measured sample is taken, the solvent burned or evaporated off, the residue ignited at a controlled temperature, the ash extracted with acid, and the metal content of the acid solution determined volumetrically.

A method similar to the above has been employed by Gottsch and Grodman (*4*) in the determination of cobalt, manganese, lead, and zinc in paint driers and boiled linseed oil. These authors have reported low and inaccurate results in the case of lead and zinc, and point out that at best the ashing method requires careful manipulation and strict control of the ignition temperature. They attribute their low results in the case of lead to fusion of the metallic oxide with the glaze of the crucible. It has been observed by the present authors that copper behaves in a similar manner if the ignition temperature is too high. In the case of zinc the low results are believed to be due to sublimation.

In addition to these considerations, the ashing method is subject to error due to loss of sample by spattering during the ignition. This is particularly true of the emulsions where the water must be evaporated off before igniting the residue.

Thus, while the ignition method will give accurate results with proper manipulation, the time and skill required to obtain such results render it somewhat unsatisfactory as a control method.

## LABORATORY METHOD

A method has been developed in these laboratories which, in addition to being rapid, gives higher and more consistent results than are generally obtained by the ignition method referred to above. This method consists essentially of heating a measured sample of the solution or emulsion with hydrochloric acid until complete hydrolysis of the naphthenate is brought about. The naphthenic acids and solvent separate as a clear oily layer and the metal in the form of the chloride dissolves in the lower aqueous layer. The two layers are separated and the copper or zinc is determined by the usual volumetric method (*5*, *6*).

Procedure. A sample of the solution or emulsion estimated to contain 50 to 100 mg. of the metal is weighed (or pipetted) into a 250-ml. beaker and 10 ml. of 1 to 1 hydrochloric acid are added. The mixture is boiled for 2 to 3 minutes on a hot plate with rapid stirring. When the hydrolysis is complete the naphthenic acids dissolved in the solvent present separate as a clear, light yellow layer. (The completeness of hydrolysis under this treatment was proved in the following manner: The ether extracts from six determinations were combined, the ether was distilled off, and the residue was ignited. There was no visible ash, and no trace of either copper or zinc was detected.) The contents of the beaker are cooled, transferred to a separatory funnel, and 20 to 25 ml. of petroleum ether are added. The lower aqueous layer is drawn off into the original beaker, the ether layer is washed twice with 15-ml. portions of distilled water, and the washings are added to the beaker.

After the final washing and when the two layers have begun to separate out, a small quantity (3 to 5 ml.) of isopropyl alcohol is added. This helps to give a clear separation of the layers in cases where there is a tendency for emulsions to form at the interface.

The metal content of the aqueous acid solution is then determined by any of the standard volumetric methods.

*Determination of Copper.* The aqueous solution is made alkaline with ammonium hydroxide and a slight excess of glacial acetic acid is added, followed by about 2 grams of potassium iodide. The solution is titrated with sodium thiosulfate, starch indicator being added as the end point is approached. A convenient concentration of the sodium thiosulfate solution for use with the recommended sample weight is 12 grams per liter. This solution will have a copper factor of about 3 mg. of copper per ml., and should be standardized against pure copper.

This method has been found to give accurate results on solutions of pure copper naphthenate in petroleum solvent. After hydrolysis with hydrochloric acid, dilution of the organic layer with petroleum ether, and separation of the two layers, no trace of copper was found in the ether layer. It was therefore assumed that all the copper originally present was now contained in the aqueous layer. This solution was saturated with hydrogen sulfide, the precipitate was filtered off and redissolved in acid, and the copper content was estimated volumetrically. These results were in very close agreement with those obtained on the same solution using the hydrolysis method, excluding the hydrogen sulfide precipitation.

It is possible, however, that in actual practice there may be organic matter present which would tend to cause erroneously high results. Such organic matter may be added to the bath in the form of textile finishing agents, or may be picked up by the bath from fabric already processed. In cases where the presence of such organic matter is known or suspected, the procedure should be modified in the following manner:

After separation from the ether layer the acid solution is diluted to 200 to 300 ml. and saturated with hydrogen sulfide. The precipitated copper sulfide is filtered off on a sintered-glass crucible, washed with water, and redissolved in aqua regia. A few drops of sulfuric acid are added and the solution is evaporated to dryness. The residue is redissolved in 50 to 75 ml. of distilled water containing a few drops of sulfuric acid, the solution is made alkaline with ammonium hydroxide, and the procedure is continued as above.

*Determination of Zinc.* The aqueous solution is made alkaline with ammonium hydroxide, neutralized to phenolphthalein with 6 *N* hydrochloric acid, and 6 ml. more of the acid are added. Two drops of ferrous sulfate solution (2.5 grams per liter) are added, and the solution is diluted to about 200 ml. and heated to boiling. The solution is titrated while hot with potassium ferrocyanide solution, using the "split beaker" technique—i.e., a small portion of the solution is set aside and the remainder titrated rapidly. When the end point has been passed the small portion is returned to the beaker and the titration continued more cautiously until the exact end point is reached. As the titration proceeds the solution becomes a deep blue color which fades sharply to a pale green at the end point. A convenient concentration for the potassium ferrocyanide solution is 13 grams per liter, which yields a solution having a zinc factor of about 3 mg. of zinc per ml. The solution should be standardized against pure zinc.

**Table I. Comparison of Analytical Methods**

| Sample | Metal Content: Ignition method | Metal Content: Hydrolysis method |
|---|---|---|
| | % | % |
| Copper naphthenate solution in petroleum solvent (solution A) | 1.18 | 1.31 |
| | 1.27 | 1.31 |
| | 1.29 | 1.31 |
| | 1.25 | 1.31 |
| | 1.27 | .. |
| Copper naphthenate solution in petroleum solvent (solution B) | 1.53 | 1.64 |
| | 1.51 | 1.64 |
| | 1.45 | 1.63 |
| | 1.46 | .. |
| Copper naphthenate, aqueous emulsion | 3.27 | 4.18 |
| | 3.08 | 4.23 |
| | 3.55 | 4.24 |
| | 3.16 | .. |
| Zinc naphthenate solution in petroleum solvent | 7.44 | 8.17 |
| | 7.26 | 8.17 |
| | 7.27 | 8.21 |
| | 7.38 | 8.23 |
| | 7.78 | .. |
| Zinc naphthenate, aqueous emulsion | 4.53 | 4.70 |
| | 4.49 | 4.67 |

**Table II. Determination of Conversion Factors**

| Sample | Metal Content by Hydrolysis Method: Copper[a] | Metal Content by Hydrolysis Method: Zinc[a] | Volume by Acid Bottle Method | Factor |
|---|---|---|---|---|
| | % | % | *Units* | |
| Copper naphthenate | | | | |
| Emulsion A | 0.446 | ... | 44 | 0.010 |
| Emulsion B | 0.604 | ... | 61 | 0.010 |
| Emulsion C | 0.654 | ... | 65 | 0.010 |
| Zinc naphthenate | | | | |
| Emulsion D | ... | 0.130 | 10 | 0.013 |
| Emulsion E | ... | 0.258 | 20 | 0.013 |
| Emulsion F | ... | 0.234 | 25 | 0.013 |
| Emulsion G | ... | 0.464 | 36 | 0.013 |

[a] Percentages expressed as grams of metal per 100 ml. of emulsion.

A comparison of the results obtained by the ignition method and the hydrolysis method on various solutions and emulsions of copper naphthenate and zinc naphthenate is given in Table I.

Examination of Table I shows that the hydrolysis method gives results which are higher and in general more consistent than those obtained by the ignition method. These discrepancies in the results obtained by the ignition method are believed to be due to mechanical losses during ashing of the sample. The hydrolysis method is rapid, requiring only about 30 minutes for a complete analysis, and involves no specialized equipment.

## PROCESS CONTROL METHOD

A rapid method has been devised for the estimation of copper or zinc in aqueous emulsions of the naphthenates of these metals. The method is recommended for use in process control, since a minimum of equipment is required and a determination can be completed in 20 to 25 minutes. Such a method is of value in the treatment of fabrics by the emulsion process. Since there is a gradual depletion of the metal content of the processing bath, it is necessary to make frequent analyses in order to maintain the metal concentration at the required level.

The determination is based on hydrolysis of the naphthenate, measurement of the naphthenic acids produced, and estimation of the metal content by use of a suitable factor. The method as outlined is applicable to the analysis of emulsions having a concentration range of approximately 0.01 to 1.00% of the metal. It may be applied to the analysis of more concentrated emulsions by suitable dilution of the emulsion before sampling.

A flask similar to that used for measuring the sulfuric acid absorption of petroleum products (*1*) is used for the determination. The flask has a capacity of approximately 50 ml. exclusive of the graduated neck, which has a capacity of 10 ml. and can be read to 0.1 ml.

Fifty milliliters of the emulsion are measured into the flask, 8 to 9 ml. of 1 to 1 hydrochloric acid are added, and the flask is thoroughly shaken. It is then placed in a bath of boiling water for 15 to 20 minutes, or until there is a clear separation of the two layers. The flask is cooled to room temperature and the volume of the upper layer is read. The percentage of metal represented by a unit volume of the upper layer is obtained by comparison with the metal content of the emulsion as determined by the hydrolysis method. This factor will be constant for all emulsions made by aqueous dilution of any one stock, but will vary slightly for concentrated emulsions from different sources. This is explained by the fact that petroleum solvent is used to dissolve the naphthenate before making up the concentrated emulsion; the volume of upper layer obtained in this analysis will thus depend on the amount of solvent used. The appropriate factor should therefore be calculated by determination of metal content of the same stock emulsion by the hydrolysis method.

For example, a sample on analysis by the hydrolysis method showed a zinc content of 0.464%. This same emulsion by the "acid bottle" method gave a reading of 36 units. The factor is therefore $\frac{0.464 \times 1}{36} = 0.013\%$ zinc per unit. Each fresh batch of stock emulsion must be checked in this manner and if any appreciable difference in the factor is obtained, the hydrolysis method rather than the acid bottle method should be applied to the analysis of dilute emulsions made from a mixture of two stock emulsions. To demonstrate the accuracy of the method factors were calculated for various dilutions of concentrated emulsions (Table II).

The data presented in Table II indicate that an analysis by this method is accurate to two significant figures, which is sufficient to serve as a means of process control. In addition the procedure is rapid, requires a minimum of equipment, and may be performed by unskilled personnel.

## ACKNOWLEDGMENTS

The authors wish to express their thanks to B. W. Deane and Co., McIntyre Bldg., Victoria Square, Montreal, and to Nuoded Products of Canada, Ltd., Imperial Bank Bldg., Leasidx (Toronto), Ontario, for supplying experimental materials.

## LITERATURE CITED

(1) Am. Soc. Testing Materials, Standards on Petroleum Products and Lubricants, p. 387, D484–40 (1942).
(2) British Standard Specification (ARP Series) for Rotproofed Jute, Hessian Sandbags, BS/ARP 57, British Standards Institution, 28 Victoria St., London, S.W. 1, England (1941).
(3) British Standard Specification (ARP Series) for Rot- and Waterproofing of Jute Canvas, BS/ARP 58, British Standards Institution, 28 Victoria St., London, S.W. 1, England (1941).
(4) Gottsch, F., and Grodman, B., *Proc. Am. Soc. Testing Materials*, 40, 1206 (1940).
(5) Scott, W. W., "Standard Methods of Chemical Analysis", 4th ed., Vol. 2, p. 193b, New York, D. Van Nostrand Co., 1925.
(6) Treadwell, F. P., and Hall, W. T., "Analytical Chemistry", 9th ed., Vol. 2, p. 667, New York, John Wiley & Sons, 1942.

# Photometric Determination of Silica in Aluminous Materials

## By the Molybdenum Blue Reaction

J. A. BRABSON, I. W. HARVEY, G. E. MAXWELL[1], AND O. A. SCHAEFFER[2]
Tennessee Valley Authority, Wilson Dam, Ala.

**A photometric method, based on the molybdenum blue reaction, is described for the determination of silica in sodium aluminate solutions and calcined alumina, and of silicon in metallic aluminum. Adjustment of pH is made with an indicator, thereby eliminating the necessity for a pH meter. The effect of aluminum salt concentration upon color development is minimized by the use of two calibration curves. The method may be used for the estimation of silica content from 0.01 to 1.0% in calcined alumina by varying the size of the sample. A precision of 4% at the optimum amount of silica determinable by this method may be expected when the method is applied to homogeneous samples.**

THE rapid and accurate determination of silica in sodium aluminate solutions and calcined alumina, and of silicon in aluminum, is an important factor in the evaluation of alkaline processes for the production of aluminum. The usual gravimetric determinations not only are time-consuming but may yield low results because of the solubility of silica in the acid used for dehydration (*2*). Several procedures have been described for the use of the molybdisilicic acid reaction (*1*) in the determination of silicon content of aluminum. Pavelka and Morth (*5*) used the molybdenum blue reaction (*3, 4, 6*) for the microanalysis of aluminum for silicon and phosphorus. Possible interference of color-producing impurities in sodium aluminate solutions upon the determination of silica by the molybdisilicic acid method made it desirable to determine silica by the molybdenum blue method. This paper describes a rapid and accurate method based on this reaction.

### APPARATUS

A filter photometer (Fisher AC Electrophotometer) fitted with a 650-mμ red filter and 2-cm. absorption cells was used for color measurements. A glass electrode apparatus (Leeds & Northrup Universal pH potentiometer) was used for the pH determinations.

### REAGENTS

HYDROCHLORIC ACID (1 + 9). Dilute 50 ml. of the concentrated acid to 500 ml.

ACETIC ACID BUFFER. Mix one volume of glacial acetic acid with two volumes of water.

THYMOL BLUE INDICATOR SOLUTION. Dissolve 0.4 gram of thymol blue in 10 ml. of freshly prepared 5% sodium hydroxide solution contained in a 300-ml. platinum dish. Dilute to 250 ml. and neutralize with dilute hydrochloric acid to an orange color; avoid an excess, which would precipitate the indicator. Transfer the solution to a 500-ml. flask and dilute to the mark.

AMMONIUM MOLYBDATE SOLUTION. Dissolve 25 grams of the salt, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 250 ml. of water. Allow to stand 24 hours and filter. Do not allow solution to stand over a week before using.

SODIUM SULFITE SOLUTION. Dissolve 170 grams of the anhydrous salt in about 900 ml. of water. Filter and dilute to 1000 ml.

ALUMINUM CHLORIDE SOLUTION. Dissolve in water either 52.3 grams of the anhydrous salt or 94.8 grams of the hexahydrate, acidify with a few drops of hydrochloric acid, filter, and dilute to 500 ml. (10 ml. ≈ 0.4 gram of alumina).

STANDARD SILICA SOLUTION. Weigh out an amount of sodium metasilicate, $Na_2SiO_3.5H_2O$, the silica content of which has been carefully determined gravimetrically, which will be equivalent to 0.0500 gram of silica and dissolve in 500.0 ml. of water (1 ml. ≈ 0.1 mg. of silica). Prepare this solution on the same day it is to be used. When making the gravimetric analysis, use a sufficiently large sample so that the error due to solubility of silica in the dehydrating acid will be kept to a minimum.

BORIC OXIDE. Ignite boric acid in a platinum dish.

### PROCEDURE

The method has a working range of from 0.0 to 1.0 mg. of silica per 250 ml. in the presence of from 0.0 to 0.4 gram of alumina. If a sample containing 0.1 gram of alumina be considered the minimum practicable size, silica in quantities up to 1% may be determined.

Alkaline decomposition methods were chosen for attack of solid samples because these methods convert the silica to a soluble form suitable for determination without danger of volatilization or dehydration. Although different methods are used to convert the samples to sodium aluminate solutions, the final step is identical for all materials listed.

PREPARATION OF SAMPLES FOR ANALYSIS. *Sodium Aluminate Solutions.* Transfer a suitable aliquot containing not more than 0.4 gram of alumina to a 250-ml. beaker containing 100 ml. of water and dilute to 170 ml.

*Calcined Alumina.* Transfer a sample of from 0.1 to 0.4 gram of alumina (depending upon the silica content) to a 125-ml. platinum dish, cover with 4 grams of anhydrous sodium carbonate and 0.7 gram of boric oxide, and mix intimately by stirring with a platinum wire. Fuse at 1000° C. with a blast lamp, or preferably in a muffle furnace, until a perfectly clear melt is obtained. A 15-minute fusion time is usually sufficient for complete decomposition of the material. Cool, cover the melt with 50 ml. of water, and digest on a steam bath until the melt dissolves. Cool to room temperature and transfer the solution to a 250-ml. beaker containing 50 ml. of water. Rinse the dish, add the washings to the beaker, and dilute to 170 ml.

*Aluminum Metal.* Transfer a sample of from 0.05 to 0.20 gram (depending upon the silicon content) to a 125-ml. platinum dish, add 50 ml. of water and five pellets (about 0.6 gram) of sodium hydroxide. Let stand until the sample disintegrates, then add a few drops of 3% hydrogen peroxide, and digest for 15 minutes on a steam bath. Cool to room temperature and transfer the solution to a 250-ml. beaker containing 50 ml. of water. Rinse the dish, add the washings to the beaker, and dilute to 170 ml.

DETERMINATION OF SILICA. Immediately following the transfer of the alkaline solution to the beaker, add 8 drops of thymol blue indicator and add concentrated hydrochloric acid, dropwise, until the aluminum hydroxide, which first precipitates, is nearly dissolved and the solution has a yellow color. Do not bring the color of the indicator to red. Add 1 + 9 hydrochloric acid dropwise, stirring constantly, until the aluminum hydroxide completely dissolves and the indicator assumes a permanent pink color. This operation is critical in the adjustment of pH and may require as much as 5 minutes' time with samples of higher aluminum salt concentration. Add 5.0 ml. of 1 + 9 hydrochloric acid, 5.0 ml. of 1 + 2 acetic acid, and 5.0 ml. of ammonium molybdate solution in the succession named. Stir the solution between additions of reagents and stir vigorously for 1 minute after the addition of the molybdate reagent. Wait 5 minutes for the molybdisilicic acid to develop, then transfer to a 250-ml. volumetric flask. Reduce the molybdisilicic acid by adding slowly from a pipet, with vigorous shaking, 20 ml. of 17% sodium sulfite solution. Eight minutes after the addition of sulfite, add 5.0 ml. more of 1 + 2 acetic acid, dilute to the mark, and mix thoroughly. Thirty minutes after the addition of the sulfite, determine the color intensity of the solution with a photometer fitted with a red filter. Use distilled water in the reference cell. (When applying the method to highly colored liquors from the Bayer process, use an equivalent portion of this solution in the reference cell.) Read the amount of silica present from the proper cali-

[1] Present address, U. S. Navy.
[2] Present address, Harvard University, Cambridge, Mass.

**Table I. Effect of Aluminum Salt Concentration upon pH Adjustment and Color Development[a]**

| $Al_2O_3$ Present, Gram | pH before Molybdate Addition | pH after Transmittance Measurement | Transmittance, % |
|---|---|---|---|
| 0.00 | 1.38 ± 0.03 | 4.24 ± 0.00 | 61.5 ± 0.0 |
| 0.08 | 1.41 ± 0.04 | 4.18 ± 0.00 | 61.0 ± 0.1 |
| 0.20 | 1.38 ± 0.03 | 4.00 ± 0.01 | 61.9 ± 0.1 |
| 0.40 | 1.34 ± 0.05 | 3.72 ± 0.02 | 62.9 ± 0.1 |
| 0.60 | 1.26 ± 0.04 | 3.40 ± 0.02 | 61.6 ± 0.1 |
| 0.80 | 1.09 ± 0.01 | 3.12 ± 0.00 | 61.0 ± 0.1 |

[a] All values are averages for three determinations.

bration curve. Determine a blank on the reagents and subtract this value from the total silica to obtain the net silica in the sample.

Preparation of Calibration Curve. To counteract the effect of aluminum salt concentration on color development, prepare two calibration curves based on 0.2 and 0.4 gram of alumina. Use suitable aliquots of the standard silica solution to determine 11 points on each curve (including the blank) in steps of 0.1 mg. of silica.

Dissolve four sodium hydroxide pellets (0.5 gram) in 50 ml. of water contained in a platinum dish and add the desired quantities of standard silica and aluminum chloride solutions. Transfer the alkaline solution to a 250-ml. beaker containing 50 ml. of water. Rinse the dish, add the washings to the beaker, and dilute to 170 ml. Continue the analysis as outlined under the determination of silica.

Construct a calibration curve, plotting the silica concentration against the color intensity. Draw a curve beginning at 100% transmittance, or zero extinction, parallel to the original curve which includes the silica derived from the sodium hydroxide and aluminum chloride, as well as the other reagents. This represents the true calibration curve and, of course, necessitates the determination and subtraction of a blank for each set of reagents used. The curves are slightly concave and their slopes vary with different amounts of alumina.

## EXPERIMENTAL

Adjustment of pH. The determination of silica by the molybdenum blue reaction is dependent upon the amount of molybdisilicic acid formed, which in turn is affected by variations in pH. It was established experimentally that for maximum development of molybdisilicic acid the pH must be adjusted to between 1.0 and 1.4 before the addition of molybdate. Of the several techniques tried for the adjustment of pH the one described above proved most successful. Measurements of the pH of prepared solutions of varying alumina content used in the preparation of calibration curves and of actual samples indicated that the pH could be adjusted by the method described to 1.35 ± 0.1 pH before the addition of molybdate. Typical data on pH obtained by this procedure are given in Table I.

Progression of Color. Kahler (*4*) pointed out that the use of acetic acid at a relatively high pH caused considerable color progression. This effect could not be disregarded if acetic acid were to be used to prevent the hydrolysis of aluminum salts. To check the color progression of molybdenum blue, with and without the presence of aluminum salts, solutions were prepared in the same manner as for the calibration curves. The molybdisilicic acid formed by the addition of ammonium molybdate was reduced with sodium sulfite as described in the procedure, the solutions were immediately diluted to 250 ml., and transmittance measurements were made at several time intervals. Results of typical tests are shown in Figure 1.

It was found that the rate of color development levels off after 10 minutes, although the maximum intensity of color is not reached for several hours. The presence of aluminum salts also appeared to retard maximum color development. Although the results shown in Figure 1 were obtained on clear solutions, interference from hydrolysis of aluminum salts was encountered on some of the samples. This difficulty was met by varying the procedure slightly to incorporate the addition of 5 ml. more of 1 + 2 acetic acid, 8 minutes after the addition of sulfite.

Effect of Aluminum Salts. Using the conditions outlined above, a series of tests was made to see what effect variations in aluminum salt concentration have upon color development. During these tests, 0.5 mg. of silica was added to each sample, and the addition of alumina was varied from 0.0 through 0.8 gram. These tests also included pH determinations before the addition of ammonium molybdate and after the measurement of transmittance. The results are given in Table I.

Apparently, increases in concentrations of aluminum salts, up to 0.4 gram of alumina, cause a corresponding retardation of color development. These variations, obviously too significant to be ignored, were minimized by the preparation of two calibration curves covering the range 0.1 to 0.4 gram of alumina. At least three factors may exert an influence upon the lower transmittance values found with the 0.6- and 0.8-gram alumina concentrations. These are lower initial pH values before addition of molybdate, lower pH during reduction with sulfite, and traces of silica from the aluminum salts. Difficulty in redissolving these larger amounts of alumina made continued study of these points inadvisable.

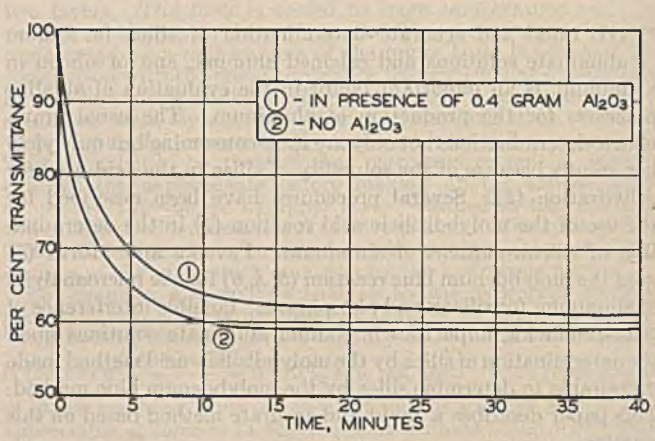



**Figure 1. Progression of Molybdenum Blue**

Effect of Sodium and Boron Salts. Before applying the method to the analysis of calcined alumina, the effects of larger amounts of sodium salts and of boron salts were investigated. Solutions similar to those used for the preparation of calibration curves and containing 2.6 grams of sodium hydroxide and 0.7 gram of boric oxide were analyzed for silica. The results, after subtraction of reagent blanks, indicated no effect from these fluxing reagents.

Effect of Iron Salts. Solutions identical with those used for checking the effects of boron and sodium, to which had been added 0.5 and 1.5 mg. of $Fe_2O_3$ as ferric chloride, were analyzed for silica. No significant difference in results was observed.

Effect of Phosphorus. Solutions similar to those used for preparation of calibration curves and containing 0.2 gram of

**Table II. Effect of Phosphorus on Photometric Determination of Silica**

| $SiO_2$ Added *Mg.* | $P_2O_5$ Added *Mg.* | $SiO_2$ Found *Mg.* |
|---|---|---|
| 0.20 | 0.2 | 0.21 |
| 0.20 | 0.5 | 0.22 |
| 0.20 | 1.0 | 0.24 |
| 0.60 | 0.2 | 0.61 |
| 0.60 | 0.5 | 0.65 |
| 0.60 | 1.0 | 0.70 |
| 1.00 | 0.2 | 1.02 |
| 1.00 | 0.5 | 1.07 |
| 1.00 | 1.0 | 1.11 |

alumina in each instance and varying quantities of silica and phosphorus pentoxide as phosphoric acid were analyzed in the usual manner. Results are shown in Table II.

The interference from phosphorus was considerable. However, the lowest amount tested was larger than the amount ordinarily encountered in 0.4 gram of alumina. Approximate corrections for phosphorus are probably feasible in the few instances where the phosphorus pentoxide content of the sample exceeds 0.2 mg.

### APPLICATION TO SODIUM ALUMINATE SOLUTIONS

Two samples of highly colored sodium aluminate liquors from the Bayer process were analyzed gravimetrically by double dehydration with sulfuric acid and by the photometric method. Results are shown in Table III.

**Table III. Comparative Analyses for Silica in Sodium Aluminate Solutions**

| Sample No. | $SiO_2$, Grams per Liter Gravimetric | Photometric |
|---|---|---|
| 1[a] | 0.287 ± 0.005 | 0.287 ± 0.002 |
| 2[a] | 0.319 ± 0.014 | 0.326 ± 0.001 |

[a] Average of three values.

### APPLICATION TO CALCINED ALUMINA

Three samples of calcined alumina previously analyzed by the standard gravimetric method, which involves decomposition of the sample with potassium pyrosulfate and double dehydration of the silica with sulfuric acid, were analyzed by the photometric method (Table IV).

### APPLICATION TO ALUMINUM METAL

Three samples of aluminum metal were analyzed gravimetrically by double dehydration with sulfuric acid after decomposition with sodium hydroxide and hydrogen peroxide and by the photometric method. The results are shown in Table V.

For comparative purposes, the data in Tables III, IV, and V were reported to one significant figure more than is justified by the accuracy of the methods used.

### PRECISION AND ACCURACY

The precision of the method is illustrated best by the analysis of the sodium aluminate solutions. On the basis of the results in Table III and similar results from the analysis of less highly colored liquors, the method is believed to have a precision within 0.02 mg. of silica. On the basis of the optimum amount of silica determinable, 0.5 mg., this represents a precision of 4%.

**Table IV. Comparative Analyses for Silica in Calcined Alumina**

| Sample No. | $SiO_2$, Per Cent Gravimetric[a] | Photometric[b] |
|---|---|---|
| 1 | 0.041 ± 0.001 | 0.041 ± 0.011 |
| 2 | 0.076 ± 0.010 | 0.077 ± 0.006 |
| 3[c] | 0.256 ± 0.008 | 0.294 ± 0.009 |

[a] Average of three values.
[b] Average of six values.
[c] Sample 3 contained 0.57% of $P_2O_5$. Difference in results is attributed to positive error caused by presence of $P_2O_5$.

This degree of precision was not attained in the analysis of alumina and aluminum. A comparison of the results in Tables IV and V, obtained by both gravimetric and photometric methods, indicates that the precision of the two methods is essentially the same. Possible heterogeneity of the samples may have affected results obtained when using both the gravimetric and photometric procedures.

The data in Tables IV and V indicate that, although there is good agreement between the two methods when applied to alumina, consistently high results are obtained when the photometric method is applied to aluminum. This discrepancy cannot be explained by incomplete oxidation of silicon, since clear solutions resulted when the sodium hydroxide-hydrogen peroxide solutions of the samples were acidified with sulfuric acid.

An explanation of the discrepancy between the results obtained in the analysis of alumina and those obtained in the analysis of aluminum may be derived from consideration of (*a*) the loss of silica during a double dehydration with sulfuric acid, and (*b*) the silica content of the analytical reagents used. Hillebrand and Lundell (*2*) reported consistently low results in the gravimetric determination of silica, and attribute the losses to the solubility of silica in the dehydrating acid (hydrochloric or sulfuric). The error inherent in the gravimetric method was verified experimentally by analyzing solutions of aluminum sulfate to which known amounts of silica had been added. Low results were obtained in every analysis. The principal reagents entering into the analyses were those used to effect dissolution of the samples—namely, potassium pyrosulfate for the alumina and sodium hydroxide for the aluminum. Both reagents contained traces of silica detectable by spectrographic means. Since the quantity of reagent used with the alumina was about 12 times that used with the aluminum, the silica loss during dehydration of the alumina solution may have been compensated by reagent impurity, whereas no such compensation occurred in dehydration of the solution of aluminum. In view of this probability, together with the fact that the discrepancies between the gravimetric and photometric analyses of aluminum represent differences of the order of only 1 mg. of silica per 5 grams of alumina, it was concluded that the results obtained photometrically probably represent more nearly the absolute silica content of aluminous materials.

**Table V. Comparative Analyses for Silicon in Aluminum**

| Sample No. | Si, Per Cent Gravimetric | Photometric |
|---|---|---|
| 1[a] | 0.094 ± 0.008 | 0.117 ± 0.001 |
| 2[a] | 0.259 ± 0.005 | 0.293 ± 0.013 |
| 3[b] | 0.278 ± 0.008 | 0.297 ± 0.004 |

[a] Average of six values.
[b] Average of three values.

### DISCUSSION

The method described makes use of the molybdenum blue reaction for determining silica under carefully controlled conditions. Variables are compensated for by means of calibration curves for combinations of reagents that simulate actual samples. Some of the conditions were chosen arbitrarily; others were determined experimentally.

A number of calibration curves for solutions of varying concentrations of aluminum salts were prepared. Although the curves for 0.1 and 0.2 gram of alumina were sufficiently concordant to be considered identical, an appreciable difference was noted in the curves based on 0.08 and 0.40 gram of alumina. This made advisable the use of more than one calibration curve. When curves are constructed for 0.2 and 0.4 gram of alumina per 250 ml., samples containing from 0.0 to 0.4 gram of alumina may be analyzed with reasonable accuracy. For more precise work it is necessary to prepare calibration curves covering the range 0.0 to 0.1 gram of alumina per 250 ml.

No attempt has been made to apply this method to aluminum alloys.

### LITERATURE CITED

(1) Dienert, F., and Wandenbulcke, F., *Compt. rend.*, 176, 1478 (1923).
(2) Hillebrand, W. F., and Lundell, G. E. F., "Applied Inorganic Analysis", p. 540, New York, John Wiley & Sons, 1929.
(3) Isaacs, L., *Bull. soc. chim. biol.*, 6, 157 (1924).
(4) Kahler, H. L., Ind. Eng. Chem., Anal. Ed., 13, 536 (1941).
(5) Pavelka, F., and Morth, H., *Mikrochemie*, 16, 239 (1934).
(6) Woods, J. T., and Mellon, M. G., Ind. Eng. Chem., Anal. Ed., 13, 760 (1941).

# VISCOSITY MEASUREMENT

## Master Viscometers

M. R. CANNON, School of Chemistry and Physics, The Pennsylvania State College, State College, Pa.

**This paper describes the construction and operation of two types of master viscometers designed for accurately calibrating the various types of routine viscometers now in extensive use. The first instrument is calibrated directly with water at 20° C. The remaining instruments of larger bore are then calibrated against the first by means of hydrocarbons of suitable viscosity. These calibrated master viscometers are used to establish accurately the viscosity of a whole series of calibrating fluids to be used in calibrating routine viscometers. Since some fluids change in viscosity with age, the master instruments are employed to check the standard fluids two or three times per year. The opaque-type master is useful in handling very dark or opaque liquids and in studying the drainage effect in viscosity measurements.**

IN TWO previous papers (*3*, *4*) simple and accurate routine viscometers were described for the measurement of the viscosities of liquids ranging from one third to more than two thousand times the viscosity of water. A special design (*4*) is necessary for the case where the test liquid is so dark or opaque that the operator cannot see through glass that is wet with a thin film of it.

Before these routine viscometers are usable it is necessary to calibrate them accurately. This paper describes suitable master viscometers which were designed and are now used by many laboratories for this special purpose. Obviously, it is not necessary for each laboratory to secure master viscometers, since calibrated routine viscometers are available through scientific supply companies. However, many large laboratories desire to maintain complete calibration facilities and for them master viscometers are recommended. It is unnecessary to use master viscometers in the calibration of the special-type routine viscometer for nonviscous liquids (viscosity range of 0.3 to 2 centipoises) shown as Figure 2 in reference (*3*), since these can be calibrated directly with water (*1*).

### OPERATION OF MASTER VISCOMETERS

These instruments are used in exactly the same manner as the routine viscometers (*3*, *4*); in fact, the only major difference is in capillary length and the height of driving liquid head. Most of the errors encountered in viscometry are caused by a loss of driving head and can be reduced in magnitude by having a large driving head. In this respect the master viscometers have four times the head available in the routine type. When made with the dimensions shown they will fit readily into a constant-temperature bath 60 cm. (24 inches) deep.

In order to charge, the instrument is held in an inverted vertical position with the capillary side submerged in the liquid under test. Suction is then applied to the other arm of the instrument and the meniscus is brought to mark *F*. The instrument is then revolved to its normal vertical position and placed in the constant-temperature bath. It may be quickly aligned to a vertical position with the aid of a small plumb bob made from a piece of silk thread and a small piece of lead wire attached to a small cork to fit into the 1.2-cm. viscometer leg.

When the bath temperature is attained suction is applied to raise the meniscus into bulb *A*, Figure 1. The efflux time is then measured for the liquid to discharge from between the etched marks above and below bulb *B*. Check runs are made by repeating this procedure. When using the master instrument (Figure 2) it is necessary to close the upper capillary with a short piece of rubber tubing and pinchclamp after allowing the fluid to drain from the upper capillary into *A*; times are measured for filling bulbs *C* and *D* after bath temperature is attained. Viscosities calculated by the constants for *C* and *D* should agree.

Unlike the master viscometer of Figure 1, check runs can be made with the opaque type only by cleaning and reloading. The opaque type has the advantage of no drainage errors and opaque liquids can be tested. It has the disadvantages of longer time to attain bath temperature (as much as five times as long as the other type), since the oil is stagnant during heating, and a lengthy time for check runs. In general, the normal type shown as Figure 1 is preferable, but if one wishes to study drainage, handle opaque liquids, or increase rates of shear by applied external pressure the opaque type is best. Where external pressures are applied to increase shearing rate, drainage errors would be serious in the normal-type viscometer.

### CALIBRATION PROCEDURE

The viscosity of water is probably known to a higher degree of accuracy than any other liquid. Its complete stability and general availability make it an excellent reference liquid for all relative viscosity measurements. Therefore, a master viscometer of small capillary bore is calibrated by means of distilled water at 20° C. where the kinematic viscosity of water is 1.007 centi-

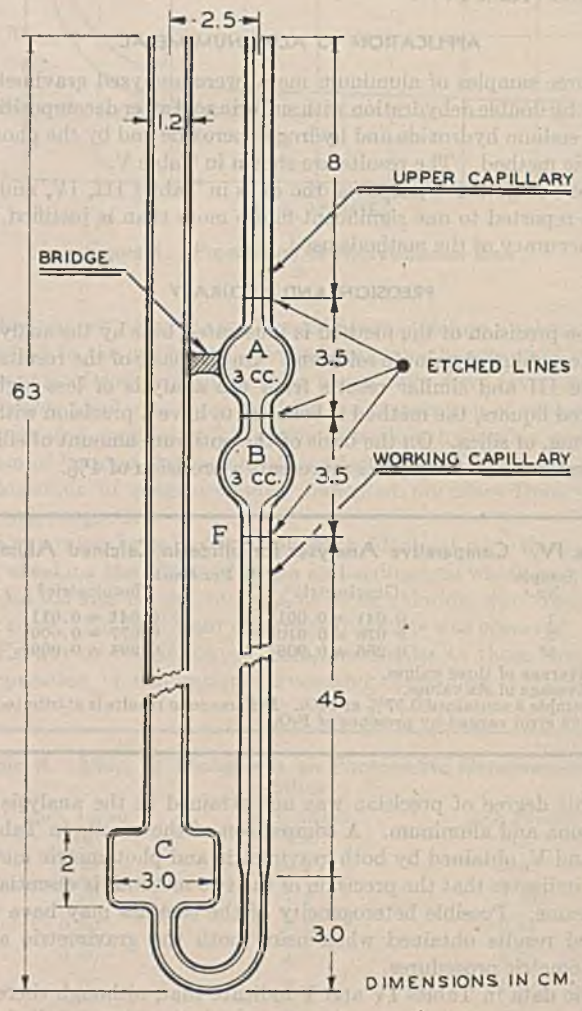



Figure 1. Master Viscometer, Normal Type

stokes. This figure may be inaccurate to the extent of ±0.5%. However, if all laboratories use this figure relative viscosities can be measured with a higher degree of accuracy, since the measurement of relative viscosities is much simpler than the measurement of absolute viscosities. Fortunately, practically all viscometers in use in this country and abroad have been calibrated using this primary reference viscosity of 1.007 cs. at 20° C., thanks largely to the efforts of the viscosity subcommittee of the American Society of Testing Materials. In addition, values of 0.689 centistoke for water at 100° F. (37.78° C.) and 0.518 centistoke at 130° F. (54.44° C.) are recommended by A.S.T.M.

When the small-bore master viscometer has been calibrated with water, a more viscous hydrocarbon may be tested in it and this in turn used to calibrate a second master viscometer of larger capillary bore, which could not be calibrated directly with water because of high capillary velocity with resulting low efflux time and a high and inaccurately known kinetic energy correction. A third and fourth master viscometer of successive larger capillary bores may then be calibrated in a similar manner. In order to avoid cumulative error in this step-up procedure, each may be further checked against the first master viscometer by means of suitable oils. When the fourth is checked against the first it means that the efflux time may be 4 minutes in the fourth and 24 hours in the first. While this procedure is lengthy, it need be done but once each year when master viscometers are checked.

When the master viscometers are calibrated, a series of oils or pure hydrocarbons is then tested and their viscosities are accurately established. These standardized fluids are then employed for the daily, weekly, or monthly calibrations of routine viscometers such as the Cannon-Fenske type (*3*, *4*), the Ubbelohde type (*8*), the Zeitfuchs type (*9*), or any of the other accurate routine viscometers now in extensive use.

The calibrating fluids should be carefully selected or prepared. Many lubricating oils increase in viscosity from 0.5 to 1.0% per year by aging at room temperature. In general, these can be stabilized by desludging with aluminum chloride or by solvent refining followed by the addition of a suitable oxidation inhibitor. Since the oils are stored at room temperature stabilizing is not difficult. A series of high viscosity index stabilized oils in use since 1933 has not changed in viscosity by 0.2% to date. It is preferable to store in glass rather than metal cans and it should be a laboratory rule that when a sample of oil is removed from storage it should be discarded after use.

The number of oils to be standardized for use as calibrating fluids will vary with the needs of laboratories. The writer finds a series of 14 such oils ranging in viscosity from 1 to 3000 centistokes by a rough factor of 2 between each adjacent pair (1 cs., 2 cs., 4 cs., etc.) to be very convenient. One can operate with fewer oils but calibrations will require a longer time.

It is necessary to calibrate a viscometer at only one temperature, since the change of viscometer constant with temperature is very small and can be calculated (*3*). This variation of constant with temperature amounts to only 0.5% for a change of 43.33° C. (110° F.) in the routine type (*3*, *4*) as proved by experiment. It is much smaller in the master type described here. This change in constant with temperature is due to a change in volume of liquid in the instrument with temperature change since the viscometers are charged at room temperature.

## MAGNITUDE AND SOURCE OF ERRORS

Viscosity is usually calculated from efflux times by means of Poiseuille's equation corrected for kinetic energy loss as follows:

$$KV = \frac{\omega}{\rho} = \frac{\pi g H r^4 t}{8LV} - \frac{mV}{8\pi L t}$$

This is usually given as:

$$KV = Ct - \frac{B}{t}$$

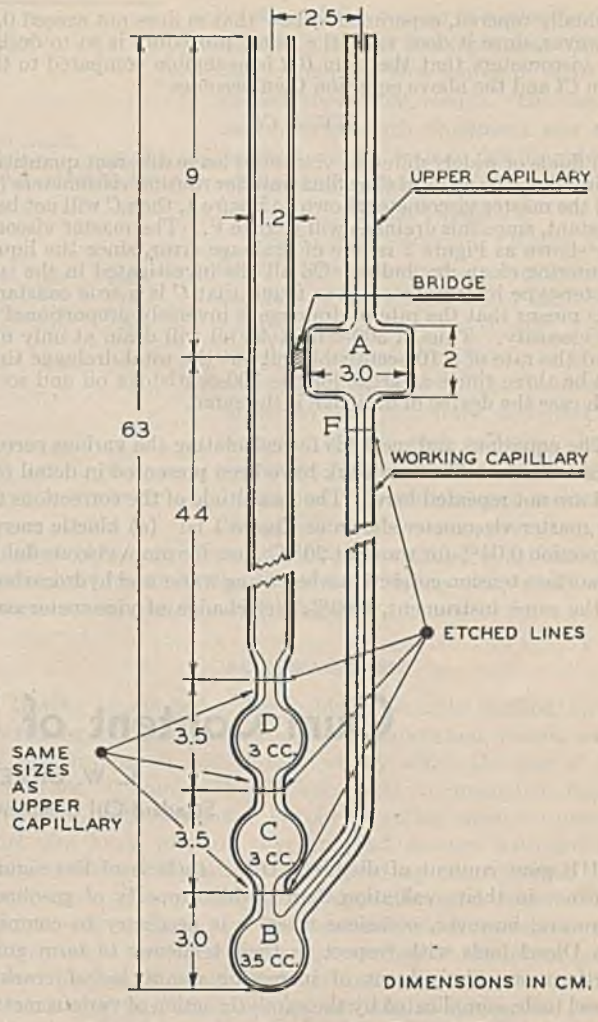



**Figure 2. Master Viscometer, Opaque Type**

where $KV$ = kinematic viscosity in stokes
$\omega$ = viscosity in poises
$\rho$ = density in grams per cc.
$g$ = gravitational constant in cm. per second per second
$H$ = driving fluid head in cm.
$r$ = capillary radius in cm.
$t$ = efflux time in seconds
$L$ = capillary length in cm.
$V$ = efflux volume in cc.
$m$ = kinetic energy correction coefficient

$$C = \frac{\pi g H r^4}{8LV}$$

$$B = \frac{mV}{8\pi L}$$

Hundreds of experiments have shown that $C$ is a constant for long capillary viscometers. However, $B$ will be a constant only if $m$, the kinetic energy correction coefficient, is a constant. From a theoretical standpoint one would not expect $m$ to be a constant and recent extensive measurements indicate that $m$ varies with Reynolds number as well as with the shape of the capillary entrance and exit. If one employs a symmetrical viscometer the value of $m$ will be different for flow to left than for flow to right. Bingham and Geddes (*2*) and Spooner and Serex (*7*) have made such measurements and found wide variations in $m$—for example, (*2*) an $m$ of 1.46 for flow to left and an $m$ of 0.74 for flow to right, and (*7*) an $m$ of 3.05 for flow to left and an $m$ of 1.52 for flow to right. This indicates the extreme sensitiveness of this loss of driving force at the capillary ends. It is, of course, not surprising to find a different value of $m$ for different flow directions, since the exit end of the capillary contributes more to $m$ than does the entrance end. Consequently, if there are slight differences in the shape of the two ends $m$ will vary with direction of flow.

For the master viscometers described here and the routine viscometers previously described, where all capillary ends are

gradually tapered, experiments show that $m$ does not exceed 0.5. However, since it does vary, the safest procedure is so to design the viscometers that the term $B/t$ is negligible compared to the term $Ct$ and the above equation then becomes

$$KV = Ct$$

If fluids of widely different viscosities leave different quantities of liquid on the walls of the efflux bulb for routine viscometers (*3*) and the master viscometer shown as Figure 1, then $C$ will not be a constant, since this drainage will change $V$. The master viscometer shown as Figure 2 is free of drainage error, since the liquid is entering clean dry bulbs. On all oils investigated in the two master-type instruments it was found that $C$ is a true constant. This means that the rate of drainage is inversely proportional to the viscosity. Thus, a 300-centistoke oil will drain at only one third the rate of a 100-centistoke oil but the total drainage time will be three times as great for the 300-centistoke oil and so in each case the degree of drainage is the same.

The equations and methods for calculating the various corrections in basic calibration work have been presented in detail (*3*), and are not repeated here. The magnitude of the corrections for the master viscometer shown as Figure 1 is: (*a*) kinetic energy correction 0.04% for water at 20° C., less for more viscous fluids; (*b*) surface tension correction when using water and hydrocarbons in the same instrument, 0.09%; (*c*) change of viscometer constant with temperature, 0.03% per 30° C. change in temperature. For the master viscometer shown as Figure 2 the same figures apply, except (*c*) is 0.1% per 30° C. since the charge is greater.

Results are reproducible in these instruments to within 0.1% and consequently relative viscosities can be measured to that degree of precision. Absolute viscosities depend upon the error inherent in the value of 1.007 centistokes taken for water at 20° C. This is probably in the order of ±0.5%. These master viscometers are an improvement over those described earlier (*5*, *6*). The capillary diameter required for a given constant $C$ can be calculated from the equations above.

### LITERATURE CITED


(1) Am. Soc. Testing Materials, "Standards on Petroleum Products and Lubricants", Designation D445–39T.
(2) Bingham, E. C., and Geddes, J. A., *Physics*, 4, 203 (1933).
(3) Cannon, M. R., and Fenske, M. R., Ind. Eng. Chem., Anal. Ed., 10, 297 (1938).
(4) *Ibid.*, 13, 299 (1941).
(5) Cannon, M. R., and Fenske, M. R., *Oil and Gas J.*, 33, 52 (1935).
(6) *Ibid.*, 34, 45 (1936).
(7) Spooner, L. W., and Serex, P., *Physics*, 6, 162 (1935).
(8) Ubbelohde, L., Ind. Eng. Chem., Anal. Ed., 9, 85 (1937).
(9) Zeitfuchs, E. H., *Natl. Petroleum News*, 29, 68 (1937).


# Gum Content of Distillate Diesel Fuels


L. W. DICKEY AND ROY HENRY

Standard Oil Company of California, Richmond, Calif.


THE gum content of distillate Diesel fuels is of less significance in their evaluation than is this property of gasolines; there are, however, occasions when it is necessary to compare two Diesel fuels with respect to their tendency to form gum. Furthermore, the advent of increasing quantities of cracked Diesel fuels, complicated by the catalytic action of various metals with which such fuels may come in contact, makes it pertinent to establish a method by which the gum content, preformed and potential, may be determined.

The following conditions for the evaporation of the fuel were established as satisfactory, after testing out numerous variations.

### APPARATUS

Erlenmeyer flask, capacity 50 ml. Condenser, Liebig type, water-cooled, with adapter, preferably sealed on. Filtering flask, capacity 1 liter. Oil bath. Source of inert gas (natural, artificial, nitrogen, carbon dioxide). Vacuum pump.

### PROCEDURE

Transfer 25 ml. of the Diesel fuel to a tared 50-ml. Erlenmeyer flask. Connect the flask to the condenser and to the source of inert gas by means of a cork stopper fitted with two glass tubes, the ends of which are flush with the bottom of the cork. Attach the filtering flask to the condenser adapter by means of a rubber stopper, and connect the side arm of the flask to a source of vacuum. Apply a vacuum of 50 to 55 cm. (20 to 22 inches) of mercury to the assembly, and pass gas into the system at a rate of approximately 250 ml. per minute.

Immerse the flask in an oil bath heated to that temperature at which the sample will be evaporated practically to dryness in 45 ± 5 minutes. (This temperature will generally be approximately 150° F. below the 90% point of the A.S.T.M. D158 distillation.) At the end of the specified time increase the bath temperature 50° F., and increase the rate of gas flow to approximately 500 ml. per minute. Maintain these conditions for 10 to 15 minutes; then remove the oil bath, shut off the vacuum, and increase the flow of gas until the pressure in the system is approximately atmospheric.

Disconnect the tared Erlenmeyer flask, add 25 ml. of a mixture of equal parts of carbon tetrachloride and acetone to the flask, and evaporate to dryness on the steam bath. Connect the flask to the condenser as before, again apply the vacuum, and with the gas flow and temperature as previously established for the end phase of the evaporation heat the flask for approximately 15 minutes. Disconnect the flask as previously described, clean the outside thoroughly, and weigh.

$$\text{Mg of gum per 100 ml.} = \text{mg. gain in weight} \times 4$$

Following the procedure outlined samples of Diesel fuels and various distillate fractions of similar boiling range were tested, primarily to establish the repeatability of the method over as wide a range as was possible with the stocks available. The data are presented in Table I.

### VARIABLES INVESTIGATED

The procedure described constitutes a purely empirical test, as are all similar methods for measuring gum in petroleum products. It is therefore necessary that all details of the test be standardized and followed if results of useful precision are to be obtained.

The following variables were investigated in arriving at the selected test conditions.

Degree of Vacuum. A vacuum of 50 to 55 cm. (20 to 22 inches) of mercury was found adequate to volatilize 25 ml. of fuel within an hour, varying the temperature to suit the stock and keeping this to a reasonable maximum. With this degree of vacuum there is little danger of collapsing the flask, and it is easier to avoid trouble from leaks.

Evaporation Time. Polymerization under the conditions existing in the test is a function of both time and temperature. The total period during which the sample is heated is set at about one hour. This period was arbitrarily selected, and further experience with the test, using a wider range of fuels, may show that the heating period can be reduced or that a longer period would be more satisfactory.

Amount of Sample. The amount of sample selected, 25 ml., is sufficient to give a weighable residue with the Diesel fuels available to the authors, and it behaved satisfactorily in the apparatus selected. The residue from smaller samples must be multiplied by a larger factor, and small errors, obviously, would be proportionally magnified.

**Table I. Gum in Petroleum Products**

| | Cracked Naphtha Rerun Still Bottoms | | Gas Oil | | | Commercial Diesel Base. Untreated | Gas Oil | | Commercial Diesel, Treated | | | Gas Oil (Cracked) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Untreated | Treated | A | B | C | | D | E | A | B | C | |
| Gravity, ° A.P.I. | 29.2 | 28.9 | 33.1 | 31.4 | 31.8 | 38.3 | 34.3 | 29.1 | 38.8 | 39.1 | 41.2 | 28.4 |
| Distillation, A.S.T.M. D158 | | | | | | | | | | | | |
| 10% | 442 | 442 | 560 | 430 | 436 | 378 | 483 | 614 | 390 | 398 | 390 | 456 |
| 50% | 480 | 480 | 596 | 522 | 530 | 436 | 538 | 650 | 432 | 438 | 427 | 503 |
| 90% | 573 | 573 | 653 | 640 | 648 | 510 | 579 | 660 | 504 | 510 | 492 | 611 |
| End point | 617 | 617 | 693 | 715 | 719 | 564 | 616 | 692 | 560 | 565 | 548 | 654 |
| Gum, mg. per 100 | 82 | 27 | 30 | 70 | 60 | 8 | 18 | 40 | 12 | 8 | 8 | 52 |
| ml. | 86 | 26 | 29 | 70 | 58 | 6 | 22 | 41 | 14 | 9 | 9 | 48 |
| Evaporation temperature, ° F. | | | | | | | | | | | | |
| Start | 400 | 400 | 500 | 450 | 450 | 350 | 400 | 500 | 350 | 350 | 350 | 450 |
| Final | 450 | 450 | 550 | 500 | 500 | 400 | 450 | 550 | 400 | 400 | 400 | 500 |

**Table II. Results of Tests**

| Sample | Residue *Mg./100 ml.* | |
|---|---|---|
| Fuel Sample 1 | | |
| Without oxidation | 8 | |
| | 12 | Av. 9 |
| | 8 | |
| 5 hours in bomb, no catalyst | 16 | |
| | 16 | Av. 19 |
| | 20 | |
| 5 hours in bomb, iron and brass catalyst | 88 | |
| | 92 | Av. 90 |
| | 90 | |
| Fuel Sample 2 | | |
| Without oxidation | 124 | |
| | 128 | Av. 125 |
| | 124 | |
| 5 hours in bomb, no catalyst | 212 | |
| | 216 | Av. 215 |
| | 216 | |
| 5 hours in bomb, iron and brass catalyst | 1464 | |
| | 1452 | Av. 1458 |
| | 1460 | |

Rate of Gas Flow. In order to keep oxidation and polymerization at a minimum the oil vapors should be removed speedily from the flask. A current of inert gas does this satisfactorily. Natural gas was used in this work because it was available and cheap, but nitrogen or carbon dioxide would be equally satisfactory. Artificial gas varies considerably in composition and purity; however, there seems no reason why it would not serve the purpose as well as natural gas.

The rate of gas flow does not appear to be critical. At 250 ml. per minute the velocity is just sufficient to sweep out the oil vapors. A higher rate of gas flow accelerates the evaporation, but oil was carried over mechanically and there was some cooling of the flask, both factors causing erratic results. However, it was found that the gas flow could be increased to advantage when the evaporation was practically complete.

Temperature of Evaporation. It is obvious from the distillation range of oils covered by the general term "distillate Diesel fuels" that it is not possible or at least not desirable to specify a single bath temperature for the test, if a limiting evaporation period is also specified. From the standpoint of polymerization a uniform temperature for all fuels is desirable; however, this would force completion of the evaporation of certain samples at an undesirably rapid rate, whereas the evaporation of other fuels would be unduly prolonged. The authors' work indicated that the temperature of the 90% point of the A.S.T.M. D158 distillation minus 150° F. correlated fairly well with the desired evaporation period, at least sufficiently to give a good lead to the operator testing an unknown stock.

Re-evaporation of Residue. The residue obtained by simply evaporating to an apparently oil-free condition contained varying amounts of oil held by a surface layer of nonvolatile gum. Solution of the residue in acetone–carbon tetrachloride, and re-evaporation to dryness, eliminated this source of error and yielded repeatable results. On the oils used a single such treatment was sufficient; however, it may be desirable to repeat this, giving a check on the approach to "constant" weight.

Nonvolatile Residue Other Than Gum. Diesel fuels may contain small amounts of lubricating oil or other nonvolatile oil-soluble substances, either added intentionally or present as the result of contamination. The residue obtained by the procedure described will obviously include such material; hence, the entire "gum" content may not be deleterious. No satisfactory method of distinguishing between gum—i.e., the product of the oxidation and/or polymerization of hydrocarbons normally present in the Diesel fuel boiling range—and other nonvolatile material has been found.

## ACCELERATED TEST

Having established a reasonably repeatable method for determining the "gum" in a sample by evaporation, various means of establishing an accelerated test, by which the rate of gum formation in stored Diesel fuel might be predicted, became available. The dominant factors operating upon an unstable fuel are heat, pressure, oxygen, and contact with catalytically active metals, all of which speed up the reactions which form gum. The possibilities in apparatus and range of conditions are endless, and the method which correlates most closely with service and storage conditions cannot be established until considerably more is known on the subject. For the authors' purpose it seemed suitable to subject the fuel to the same conditions as are set up by the Government for aviation gasoline—i.e., a bomb under 45 kg. (100 pounds) oxygen pressure, at 212° F., using a catalyst. Iron and brass were the catalysts selected, and in the tests reported below approximately 100 sq. cm. (15 square inches) surface, of both metals in each test bottle, were used; a 5-hour test was judged to be suitable; and a 200-ml. sample in a 235-ml. (8-ounce) sample bottle was taken. Obviously, in a standardized test the composition of the metal rods, as well as their surface area, should be specified.

Table II shows the results of tests made under these conditions, employing the previously developed evaporation method for measuring the gum formed.

Continuous pressure charts were made during the heating of these samples. Sample 1 showed practically no pressure drop; sample 2 without catalyst showed an early pressure drop, but the curve did not continue downward appreciably; the same sample, with catalyst, showed a similar early drop, which continued throughout the 5 hours. The indications of the pressure-drop curves are in line with the gum tests of the samples.

## SUMMARY

The evaporation procedure selected is sharply repeatable even with such a high "gum" residue as 1400 mg. per 100 ml.—i.e., using successive portions of the same oxidized sample—and the authors believe that it gives a useful measure of nonvolatile gummy material dissolved in the oil when tested. They have no data as to the amount which can be tolerated in actual service.

The Army induction bomb and test with iron and brass catalyst may be used to obtain an accelerated test. The authors have no data on the correlation of this accelerated test with service.

# Determination of Lithium in Its Minerals

SILVE KALLMANN, Ledoux & Co., 155 Sixth Ave, New York, N. Y.

**Since the methods of J. L. Smith and Berzelius for the decomposition of minerals of the silicate type and the isolation of the alkali chlorides are unsatisfactory for the determination of lithium in its minerals, a combination of the two procedures is proposed. The sample is treated with hydrofluoric acid and most interfering elements are eliminated by precipitation with calcium hydroxide. The residue, which invariably occludes some lithium, is submitted to a fusion similar to that of Smith. Reprecipitation of all precipitates obtained in the course of analysis is essential. For the separation of lithium from the other members of the alkali family, gravimetric methods are unreliable and extraction methods require repeated treatments of the insoluble residue. Of the precipitation methods, the *n*-hexanol and 2-ethylhexanol methods are considered best for moderate amounts of lithium, retreatment of the insoluble precipitate being required for larger quantities of lithium. The *n*-butyl alcohol–hydrogen chloride method of Willard and Smith can be extended to the separation of lithium from both sodium and potassium. The proposed procedure is held superior to any other method used at the present time for the separation of lithium from sodium and potassium.**

LIKE so many other metallic elements, lithium metal was scarcely known to the public at the beginning of this century, only 25 years ago making its entry into the field of industrial application. Large tonnages of the metal, its minerals, and chemical compounds, however, are produced today and are adsorbed notably by the glass, ceramic, air-conditioning, and metallurgical industries, but also in the electrical and pharmaceutical fields (*25*). Lithium has now been listed as essential by both the American and British war agencies (*16*).

The United States is the leading producer and consumer of lithium metal and apparently has the largest known ore reserves.

## COMPOSITION OF LITHIUM MINERALS

The composition of the principal lithium minerals is of importance to the analyst, in determining the proper analytical procedure to be followed.

Main Lithium Minerals:

- Spodumene, $LiAl(SiO_3)_2$, containing 4 to 8% $Li_2O$ and generally a little sodium.
- Amblygonite, $Li(AlF)PO_4$, containing 8 to 9% $Li_2O$; lithium may be partly replaced by sodium and fluorine by hydroxyl.
- Lepidolite, composition variable, ranging from that of polylithionite to that of lithium-bearing muscovite, approximating $KLi[Al(OH,F)_2]Al(SiO_3)_3$ containing from 2 to 4% $Li_2O$.
- Triphylite, $Li(Fe,Mn)PO_4$, containing from 2 to 4% $Li_2O$.
- Petalite, $LiAl(Si_2O_5)_2$, containing from 2 to 4% $Li_2O$.
- Zinnwaldite, LiF, KF, FeO, $Al_2O_3$, $3SiO_2$, containing 2 to 3% $Li_2O$.

Somewhat Less Important Lithium Minerals:

- Taeniolite, $KLiMg_2Si_4O_{10}F_2$.
- Polylithionite, $KLi_2AlSi_4O_{10}F_2$.

More than 100 other minerals contain small amounts of lithium.

## DETECTION OF LITHIUM

Volatile lithium compounds color the flame a bright crimson; the flame test may therefore be used to detect lithium in minerals. The interference of sodium can be overcome by the use of a proper color screen. In the presence of strontium, a little barium chloride added to the solution and examined in the flame will first show the crimson of lithium, then the green of barium, and finally, the red of strontium.

Spectroscopic methods have been proposed since 1912 for the detection and determination of minute quantities of lithium (*13*, *35*), they are worthless, however, for quantitative analysis if weighable amounts of lithium are present.

In the flame spectrum, which is less sensitive to foreign elements than either the arc or spark spectrum, there are two sharply defined lines: a weak line Li$\beta$ of wave length 6104 and a bright red line Li$\alpha$ of wave length 6708. The presence of nearly $10^{-6}$ mg. of lithium can be detected in this way. In the arc spectrum a blue line appears, besides eighteen other feebler lines (*23*).

## COMBINED J. LAWRENCE SMITH–BERZELIUS PROCEDURE FOR ISOLATION OF LITHIUM AND OTHER ALKALI METALS

In separating lithium from other elements with which it is associated in its minerals, too little attention is sometimes paid to the vast differences in the solubility of many lithium compounds compared with other alkali compounds. Lithium fluoride, oxalate, carbonate, and phosphate are so much more insoluble in water and in an excess of the respective reagents than are the corresponding sodium and potassium compounds, that numerous qualitative and quantitative methods based on the formation of lithium fluoride (*2*, *11*), lithium carbonate (*1*, *10*, *24*), and lithium phosphate (*3*, *6*, *22*) have been proposed.

Unless special precautions are employed, considerable quantities of lithium may be lost if the scheme of operation recommended for the isolation of the other alkali metals is indiscriminately employed in the determination of lithium.

Despite this unique chemical behavior, otherwise excellent textbooks on mineral analysis (*15*, *31*, *33*) have failed to present an adequate and specific procedure for the initial decomposition of lithium minerals, but usually refer to two classical methods which are most valuable for the isolation of sodium and potassium—the J. Lawrence Smith method (*37*) or the even more ancient method of Berzelius (*5*).

Lundell and Hoffman (*21*) have noted that some lithium remains in the extracted residue from the J. Lawrence Smith fusion, and numerous tests carried out by this writer would indicate that igniting this extracted residue, transferring it to the platinum or nickel crucible originally used, and reheating it with more ammonium chloride—a cumbersome and very tedious procedure—will not always guarantee complete recovery of all lithium.

The Berzelius method, on the other hand, involving the use of hydrofluoric acid and sulfuric acid, and modifications proposed by Low (*20*), Krishnaya (*19*), and Scholes (*32*), are even less attractive. Appreciable lithium frequently remains in the extracted residue, partly due to occlusion, partly because of incomplete decomposition of the mineral. In addition, magnesium, if present, will accompany the alkalies, and its troublesome removal is always imperative, lest it be found with the final lithium sulfate, provided organic solvents are used for separating lithium from the other alkali metals.

The removal of large amounts of sulfate ion by precipitation as barium sulfate, which is apt to occlude considerable lithium (*12*, *39*) is another drawback of the Berzelius method.

Of the alternative ways of eliminating the hydrofluoric acid, evaporation with perchloric acid or volatilization as hydrofluosilicic acid have been proposed (*40*). While these modifications, particularly the latter, are of considerable importance for the determination of sodium and potassium in feldspars or other silicate minerals known to be low in magnesium, they leave complete decomposition of lithium minerals as uncertain as before. Moreover, magnesium, if present, would accompany the lithium as in the original Berzelius method. As many lithium minerals contain large amounts of phosphate ion (amblygonite, triphylite) the removal of which is imperative, the above modifications of the Berzelius method cannot directly be applied to the determination of lithium.

Removal of fluoride ion by precipitation as calcium fluoride was suggested by Koenig (*18*). The method was severely criticized by Willard and co-authors (*40*), who tried it in the deter-

mination of sodium plus potassium in a high-potassium feldspar, claiming that the calcium hydroxide precipitate retained as much as 50 mg. of the 0.2440 gram of sodium plus potassium expected.

This writer carried out a number of experiments to test Koenig's method. While apparently no procedure involving the use of hydrofluoric acid achieves complete decomposition of certain lithium minerals, and Willard's criticism regarding retention of alkali by the calcium hydroxide precipitate seems justified, parts of Koenig's method are excellent and have found their way into the procedure developed by this writer.

In other methods used in the past Berzelius (*4*) decomposed lithium minerals of the silica type (spodumene, lepidolite, petalite, zinnwaldite) by fusion with twice their weight of calcium and barium carbonate. Troost (*38*) fused lepidolite with an equal weight of barium carbonate, half its weight of barium sulfate, and one third its weight of potassium sulfate. Weinland and Storz treated triphylite with aqua regia and Mueller (*24*) decomposed the same mineral with hydrochloric acid.

New Procedure. The proposed procedure, combining the best features of the Berzelius method as modified by Koenig (*18*) with some parts of the J. Lawrence Smith method (*37*), starts by treating the sample with hydrofluoric acid, followed by the Koenig modification to eliminate the fluoride ion. The bulk of the lithium will be found in the water extract. The extracted residue, which is practically free from silica, contains comparatively small but frequently weighable amounts of lithium, owing to incomplete decomposition of the sample and occlusion by the calcium hydroxide, partly caused by incomplete conversion of the lithium fluoride into the hydroxide. The residue is ignited in a platinum crucible of the usual shape and is then submitted to a fusion similar to that proposed by J. Lawrence Smith. This fusion can be achieved, as silica has been largely removed by the initial hydrofluoric acid treatment, at a comparatively low temperature, say 700° C. The extracted residue from this fusion is always free from weighable amounts of lithium.

The method is applicable to all lithium minerals, of both silicate and phosphate type.

(Throughout all operations Pyrex beakers were used with good success, although some chemists claim that the best of glassware is attacked at slightly elevated temperatures, causing low lithium results when ammonium chloride salts are expelled in beakers.)

The amount of lithium which may be expected to be retained in the first calcium hydroxide precipitate, on account of incomplete decomposition of the sample and occlusion, is illustrated in Table I.

**Table I. Retention of Lithium by Calcium Hydroxide Precipitate**

| Type of Sample | Lithium Oxide Found: In $Ca(OH)_2$ extract | In $Ca(OH)_2$ ppt. by occlusion | In $Ca(OH)_2$ ppt. (undecomposed sample) |
|---|---|---|---|
| | *Mg.* | *Mg.* | *Mg.* |
| Spodumene | 25.3 | 2.7 | 4.3 |
| | 26.4 | 2.0 | 3.9 |
| | 18.9 | 3.2 | 4.4 |
| Amblygonite | 31.0 | 4.9 | 1.8 |
| | 32.3 | 4.6 | 2.4 |
| | 28.4 | 5.6 | 2.9 |

Transfer 0.5 gram of the 200-mesh sample, dried at 110° C., to a 50- to 100-ml. platinum dish, moisten with water, add 25 ml. of hydrofluoric acid, and evaporate to dryness on the water bath. Add 10 ml. more of the hydrofluoric acid and repeat the evaporation, finally drying the salts at about 150° C. on a hot plate or in an electric oven.

Digest the residue with 25 ml. of hot water for about 5 minutes (complete solution is rare when dealing with high-grade lithium minerals), then wash the solution quantitatively into a 250-ml. beaker containing 2 grams of calcium oxide in 75 ml. of water. Police and rinse the platinum dish, adding the washings to the beaker. (The calcium oxide used is prepared by ignition of the special grade of carbonate mostly used for the J. Lawrence Smith fusion.)

Boil contents of beaker for about 2 minutes, allow precipitate to settle for a short time, then decant the supernatant liquid through a 12-cm. No. 40 Whatman filter paper. Finally transfer the precipitate onto the paper and wash it six times with hot water or, if the presence of magnesium is known or suspected, with hot water containing calcium hydroxide. Police the beaker, or remove any precipitate adhering to the beaker with a piece of filter paper moistened with dilute hydrochloric acid. Hold the residue (residue I).

To the filtrate, which has been received in a 400-ml. beaker, add 1 ml. of ammonia and two 1.25-cm. (0.5-inch) cubes of ammonium carbonate. Heat to boiling, filter immediately through an 11-cm. No. 40 Whatman filter paper, and wash the residue (residue II) with 1 to 50 ammonia containing some ammonium carbonate. Wipe the beaker with a small piece of filter paper moistened with dilute hydrochloric acid. Hold the filtrate (filtrate A).

Combine the papers containing residues I and II and ignite in a 30-ml. platinum crucible. Mix the residue intimately with 1 gram of ammonium chloride and cover the crucible with a tightly fitting platinum cover. Insert the crucible for two-thirds of its depth in a hole in an asbestos pad and heat it, at a low heat first, until the charge has melted or sintered.

Transfer the cold platinum crucible to a 250-ml. beaker, cover the crucible with hot water, and allow to stand in a warm place for at least 6 hours. Remove crucible from beaker and loosen and return to the beaker, with the help of a stirring rod or a policeman, any cake or precipitate adhering to the crucible. Heat solution to boiling, filter the supernatant liquid through a 12-cm. No. 40 Whatman filter paper into a 400-ml. beaker, finally transfer the residue onto the filter paper, and wash it, as specified above, with hot water or hot water containing calcium hydroxide. Discard the residue, which is free from lithium compounds.

To the filtrate add 1 ml. of ammonia and two 1.25-cm. (0.5-inch) cubes of ammonium carbonate. Heat to boiling, filter through an 11-cm. No. 40 Whatman filter paper, and wash the precipitate with dilute ammonia containing ammonium carbonate. Wash precipitate back into original beaker and dissolve it in a few drops of hydrochloric acid. Render the solution just ammoniacal and repeat the ammonium carbonate separation, finally filtering through original paper into the main filtrate (filtrate B). Discard the residue.

Combine filtrates A and B and evaporate to dryness on a water bath. When bone dry, volatilize the ammonium salts by placing the uncovered beaker on a hot plate and gradually heating to the full heat of the plate. Allow to cool, add 30 ml. of hot water to effect solution of the salts, then 4 drops of ammonia and 6 to 8 drops of saturated ammonium oxalate solution. Heat to boiling, allow precipitate to settle for one hour, then filter off on a 9-cm. No. 40 Whatman paper and wash six times with a 1% solution of ammonium oxalate.

Wash precipitate back into original beaker and dissolve it in a little hydrochloric acid. Repeat ammonium oxalate separation, finally filtering through original paper into main solution.

Evaporate solution, which has been received in a 250-ml. beaker to dryness on the water bath and volatilize the ammonium chloride as before.

(As lithium invariably must be separated at a later stage from the other members of the alkali family, the sulfate ion should be removed at this point because of the sparing solubility of lithium sulfate in most reagents employed. In case the barium sulfate precipitate appears small, it need not be filtered but should be removed with the excess of the barium in the subsequent ammonium carbonate separation.)

Take dry salts up with about 30 ml. of hot water and 3 drops of hydrochloric acid and, after heating to boiling, add dropwise sufficient 10% barium chloride to guarantee complete precipitation of the sulfate ion. Allow precipitate to settle for 2 hours, filter through a small No. 40 Whatman filter paper, and wash it ten times with hot water.

To the filtrate, in a 250-ml. beaker, add sufficient ammonia to render the solution ammoniacal, then two 1.25-cm. (0.5-inch) cubes of ammonium carbonate. Heat to boiling and filter off the barium carbonate, washing the precipitate with dilute ammonia–ammonium carbonate wash solution. Dissolve the precipitate in a few drops of hydrochloric acid and reprecipitate with ammonia and ammonium carbonate, finally filtering through original paper into main filtrate and discarding the precipitate.

Evaporate the combined filtrates, in a 250-ml. beaker, to dryness and volatilize the ammonium chloride salts on a hot plate. Take salts up with 40 ml. of water and small amounts of ammonia, ammonium carbonate, and ammonium oxalate. After heating the solution to boiling and allowing it to stand for at least 2 hours, filter the small residue on a small filter paper and wash it with dilute ammonia–ammonium carbonate solution. Wash the precipitate back into original beaker, dissolve in hydrochloric acid, and reprecipitate with ammonia, ammonium carbonate, and ammonium oxalate. Discard the final precipitate.

Evaporate the combined filtrates to dryness and volatilize

the ammonium chloride. Moisten the salts with dilute hydrochloric acid, again evaporate to dryness, and heat strongly on hot plate to expel any remaining ammonium chloride.

The dry salts obtained in this way consist of the combined chlorides of the alkali metals, possibly contaminated by a little ammonium chloride. If required, the ammonium chloride can be quantitatively removed by washing the above hydrochloric acid solution into a platinum dish, evaporating to dryness, and heating at a dull red heat over a Bunsen burner, but observing all precautions necessitated by the volatility of the alkali chlorides.

Corroboration and Verification. In numerous lithium determinations of various lithium minerals, all residues or precipitates, marked in the above procedure as "discarded", were tested and found free from weighable amounts of lithium. In some cases, however, the residues, when examined by the flame test, gave a faint crimson color.

As no standard samples of lithium minerals have been available to this writer, artificial mixtures of lithium and the elements with which it is associated in minerals were made up. Lithium, after being isolated by the procedure described above, was finally weighed as the sulfate. In order to avoid the separation of lithium from other alkali metals—a subject discussed below—no potassium or sodium salts were introduced into the artificial mineral. A solution of lithium chloride was used in these experiments which was checked by pipetting out aliquot portions and determining their lithium content by evaporating with sulfuric acid and weighing as the sulfate (Table II).

**Table II. Accuracy of Proposed Procedure**

| LiCl Taken Equivalent to $Li_2SO_4$ | Artificial Mineral, in Addition to LiCl, Contained | $Li_2SO_4$ Found |
|---|---|---|
| *Gram* | *Gram* | *Gram* |
| 0.0735 | $SiO_2$ = 0.1500 | 0.0727 |
| 0.0735 | $Al_2O_3$ = 0.1500 | 0.0731 |
| 0.0735 | $AlPO_4$ = 0.1000 | 0.0740 |
| 0.1470 | MgCl = 0.0100 | 0.1477 |
| 0.1470 | $Fe_2O_3$ = 0.0200 | 0.1481 |
| 0.1470 | $CaF_2$ = 0.0200 | 0.1466 |
| 0.2205 | | 0.2193 |
| 0.2205 | | 0.2200 |
| 0.2205 | | 0.2204 |

## REVISED AND EXTENDED *n*-BUTYL ALCOHOL–HYDROGEN CHLORIDE METHOD FOR SEPARATION OF LITHIUM FROM SODIUM AND POTASSIUM

In the usual course of analysis for the determination of sodium and potassium, lithium, if ignored, will cause high results for either sodium or potassium, depending on the procedure employed. If potassium is determined as the perchlorate or the chloroplatinate and sodium calculated from the combined chlorides of the alkali metals, lithium will count as sodium because of the solubility of its perchlorate or chloroplatinate in the reagents used. On the other hand, if sodium is determined as the triple acetate, part of the lithium will accompany the sodium while the remainder counts as potassium.

Precipitation of Lithium. Before the appearance of Gooch's article in 1887 (*14*) the most favored method was that of Berzelius (*6*) as modified by Mayer (*22*), which is based on precipitation of lithium as the phosphate. Today, the method is considered tedious in operation and incompatible with accuracy.

Carnot (*11*) took advantage of the sparing solubility of lithium fluoride in alcohol and dilute ammonia, compared with that of sodium fluoride. The method has some merits for the preliminary separation of lithium from sodium, prior to the precipitation of the latter as triple acetate (*2*) and for the preparation of pure lithium salts (*29*). Mueller (*24*) and more recently Caley (*10*) precipitated lithium as carbonate. Of the more recent methods in which lithium is precipitated, separation as potassium ferric periodate (*27*), as stearate (*8*), and as complex periodate (*80*) should be mentioned.

Some of the above methods are qualitative or semiquantitative, others are confined to the determination of small amounts of lithium, but none is suited for the quantitative separation and determination of lithium as it is found in most lithium minerals.

Extraction of Lithium and Precipitation of Chlorides of Other Alkali Metals. Most methods in use today take advantage of the ready solubility of lithium chloride and the insolubility of the chlorides of the other members of the alkali family in various solvents or mixtures of organic solvents. The methods are of two types, distinguished by extraction of lithium chloride or precipitation of the other chlorides.

The first group comprises the larger number of methods:

The alcohol-ether extraction method of Rammelsberg (*28*).
The pyridine method of Kahlenberg and Krauskop (*17*).
The isobutyl alcohol method of Winkler (*42*).
The acetone method of Brown and Reedy (*7*).
The dioxane method of Sinka (*34*).

The main objection to methods in this category are their pronounced tendency toward occlusion of lithium chloride inside the crystals of the other alkali chlorides and also the formation of insoluble lithium hydroxide, thus necessitating repeated treatments of the insoluble residue. The methods are tedious in operation and error-inviting because of the number of manipulations involved.

The other general type of procedure consists in dissolving the mixed chlorides in a small amount of water from which the alkali chlorides, other than lithium chloride, are precipitated either by adding an organic agent, as in Palkin's alcohol-ether precipitation method (*26*), or by dehydrating the aqueous solution of the mixed chlorides with organic solvents of a high boiling point, as in the amyl alcohol method of Gooch (*14*) and the *n*-hexanol and 2-ethylhexanol methods of Caley and Axilrod (*9*).

In the hands of this writer, Palkin's method has not yielded satisfactory results, as many as three separations being required to separate 40 mg. of lithium oxide from 15 mg. of sodium oxide. The isoamyl alcohol method of Gooch "has the disadvantage that neither potassium nor sodium chlorides are quantitatively insoluble in isoamyl alcohol, so that relatively large corrections must be applied for the amounts of salts that dissolve along with the lithium chloride" (*9*). Caley and Axilrod's methods are excellent for the separation of small amounts of lithium chloride (LiCl < 60 mg.) from moderate amounts of sodium and potassium chlorides. Because of the comparatively sparing solubility of lithium chloride in *n*-hexanol and 2-ethylhexanol (see Table III) the separation appears unsatisfactory, judging from the data given by the authors, for amounts of lithium chloride as low as 120 mg., unless two separations are carried out.

The *n*-Butyl Alcohol–Hydrogen Chloride Method of Willard and Smith. The method of Willard and Smith (*41*) for the separation and determination of lithium and sodium, involving the use of *n*-butyl alcohol as a solvent for the lithium and a 20% solution of hydrogen chloride in *n*-butyl alcohol as a precipitant for the sodium, is a combination of the two types of methods cited above, in that sodium and lithium are first extracted from the mixed alkali perchlorates, sodium being precipitated in the extract.

The method has, despite its numerous excellent features, not found the recognition it deserves. This is largely due to the authors' insistence on confining their procedure to the separation and determination of lithium and failing to extend their investigation to the separation of lithium from potassium. It is therefore hardly surprising that Willard and Smith's method is not used in routine or control work for the determination of lithium in its minerals, and that its application has been largely confined to the quantitative separation and determination of lithium, sodium, and potassium. A condensed description of the latter process, as given by Smith and Ross (*36*), is here quoted to facilitate discussion of the method.

The combined perchlorates of potassium, sodium, and lithium, free from an excess of perchloric acid, are treated with a mixture of equal parts of *n*-butyl alcohol and ethyl acetate, two extractions with intermediate solution of the potassium perchlorate being required. Potassium is finally weighed as the perchlorate.

**Table III. Solubilities of Chlorides and Perchlorates**

| Solvent | NaCl | KCl | LiCl |
|---|---|---|---|
| | *Grams per 100 grams of solvent* | | |
| Ethyl alcohol | 0.0649 | 0.0294 | 2.54 |
| Amyl alcohol | 0.002 | 0.0007 | 9.03 |
| *n*-Butyl alcohol | 0.005 | 0.0030 | 12.98 |
| *n*-Butyl alcohol containing 6% HCl + 0.5% $HClO_4$ | 0.0007 | 0.0005 | 10.61 |
| Isobutyl alcohol | 0.00047 | 0.0008 | 10.57 |
| *n*-hexyl alcohol | 0.0010 | 0.00005 | 7.2 |
| 2-Ethylhexanol | 0.0001 | 0.0000 | 3.7 |
| Acetone | 0.000 | 0.000 | 3.86 |
| Pyridine | 0.000 | 0.000 | 13.39 |
| Dioxane | 0.000 | 0.000 | ... |
| | $NaClO_4$ | $KClO_4$ | $LiClO_4$ |
| | *Grams per 100 grams of saturated solution* | | |
| Ethyl alcohol | 12.82 | 0.012 | 60.28 |
| *n*-Butyl alcohol | 1.83 | 0.0045 | 44.23 |
| Ethyl acetate | 8.80 | 0.0015 | 48.75 |
| 50% *n*-butyl alcohol + 50% ethyl acetate | 11.99 | 0.0025 | ... |
| Isobutyl alcohol | 0.78 | 0.005 | 36.73 |

**Table IV. Separation and Determination of Sodium and Lithium**

| NaCl Taken | NaCl Found | LiCl Taken Equivalent to $Li_2SO_4$ | $Li_2SO_4$ Found | Volume of Filtrate and Washings |
|---|---|---|---|---|
| *Grams* | *Grams* | *Gram* | *Gram* | *Ml.* |
| 0.0500 | 0.0498 | 0.0735 | 0.0738 | 40 |
| 0.1000 | 0.0997 | 0.0735 | 0.0737 | 40 |
| 0.1000 | 0.1003 | 0.7350 | 0.7354 | 40 |
| 0.2500 | 0.2492 | 0.2205 | 0.2211 | 40 |
| 0.4000 | 0.3994 | 0.2205 | 0.2209 | 50 |
| 0.6000 | 0.5995 | 0.2205 | 0.2216 | 60 |
| 1.0000 | 0.9990 | 0.2205 | 0.2212 | 75 |
| 1.2000 | 1.1991 | 0.2205 | 0.2213 | 85 |
| 1.5000 | 1.4989 | 0.2205 | 0.2215 | 100 |
| 2.0000 | 1.9989 | 0.2205 | 0.2213 | 100 |

Ethyl acetate must be expelled by evaporation before precipitation of sodium as sodium chloride from the *n*-butyl alcohol solution of the perchlorates of sodium and lithium is attempted, using for the latter separation a 20% solution of hydrogen chloride in *n*-butyl alcohol. The sodium chloride is either weighed as such or dissolved in water and its chlorine content determined volumetrically by Mohr's method.

Lithium is determined by evaporation of the *n*-butyl alcohol extract, and conversion of the lithium perchlorate into the sulfate, in which form it is weighed.

This writer has extensively used Willard and Smith's method for the separation of lithium from sodium, obtaining excellent results. It should be noted, however, that the authors, in their endeavor to determine both lithium and sodium quantitatively, specify the use of sufficient *n*-butyl alcohol to guarantee a clear solution (free from insoluble sodium perchlorate) before precipitation of sodium as sodium chloride.

Because of the sparing solubility of sodium perchlorate in *n*-butyl alcohol (see Table III) the authors recommend a minimum of 18.5 ml. of *n*-butyl alcohol for every 100 mg. of sodium chloride present. It is obvious that, when separating small amounts of lithium from 1 gram or more of sodium chloride, it is necessary to use inconveniently large quantities of both the *n*-butyl alcohol and the solution of hydrogen chloride in *n*-butyl alcohol. This, in turn, necessitates considerable corrections for the solubility of sodium chloride in the reagents employed.

Experiments carried out by this writer, recorded in Table IV, conclusively show that lithium can be quantitatively separated from larger amounts of sodium by precipitating the latter from considerably smaller volumes of *n*-butyl alcohol than those recommended by Willard and Smith. Prior to the precipitation, the possible presence of insoluble sodium perchlorate, caused by the sparing solubility of the latter in *n*-butyl alcohol, was disregarded. It was found that this insoluble sodium perchlorate, when boiled for one minute with the solution of hydrogen chloride in *n*-butyl alcohol, was quantitatively converted into sodium chloride which is practically insoluble in the reagents employed, as has been shown by Willard and Smith. In the experiments recorded in Table IV the reagents and manipulations suggested by Willard and Smith were used.

Separation of Lithium from Potassium. Willard and Smith's method asks for the removal of potassium as perchlorate prior to the separation of lithium from sodium. As this involves considerable manipulations, an attempt was made to determine whether lithium could be separated from potassium and sodium in a single operation, using the 20% solution of hydrogen chloride in *n*-butyl alcohol as a precipitant.

Potassium salts, other than sulfates or phosphates, when fumed with perchloric acid, are converted into potassium perchlorate only slightly soluble in *n*-butyl alcohol. The effect of the hydrogen chloride solution in butyl alcohol upon the potassium perchlorate was studied by this writer, who found that potassium perchlorate is partly converted into potassium chloride which, however, is only very slightly soluble in butyl alcohol and even less in butyl alcohol containing hydrogen chloride.

To determine the extent of the conversion of potassium perchlorate into potassium chloride, varying amounts of potassium chloride were fumed to dryness with an excess of perchloric acid and the potassium perchlorate was dissolved in water and again evaporated to dryness in order to remove any perchloric acid which had been retained during the crystallization process. The dry salts were boiled, in one series of experiments for 1 minute and in a second series for 5 minutes, with a 6% solution of hydrogen chloride in *n*-butyl alcohol, then filtered on a Gooch crucible and washed with the same alcoholic solution of hydrogen chloride. The crucible was dried for a few minutes at 110° C. and finally for 15 minutes in a muffle at 350°C.

The crucible was weighed, the residue dissolved in hot water, the crucible dried and weighed again, and the chloride ion determined in the water extract volumetrically by Mohr's method. The calculated results are presented in Table V.

It is significant that the extent of the conversion of potassium perchlorate into potassium chloride seems to be independent of the amount of potassium perchlorate originally present, but depends mainly on the concentration of hydrogen chloride in the *n*-butyl alcohol. This indicates that the conversion is, as could be reasonably expected, caused by the slight solubility of potassium perchlorate in *n*-butyl alcohol: The soluble potassium perchlorate is precipitated as potassium chloride, causing the formation of more soluble perchlorate and further precipitation of the chloride, until, after prolonged boiling with the 6% solution of hydrogen chloride in *n*-butyl alcohol, the conversion presumably is complete. As the present investigation is primarily concerned with the determination of lithium, no attempt was made at this time to establish whether potassium perchlorate could be converted quantitatively into potassium chloride with a minimum amount of reagents and manipulations.

**Table V. Conversion of Potassium Perchlorate into Potassium Chloride**

| KCl Taken | KCl Found | $KClO_4$ Found Equivalent to KCl | Length of Boiling | Volume of Filtrate |
|---|---|---|---|---|
| *Grams* | *Gram* | *Grams* | *Min.* | *Ml.* |
| 0.0500 | 0.0324 | 0.0174 | 1 | 35 |
| 0.0500 | 0.0389 | 0.0114 | 5 | 35 |
| 0.1000 | 0.0344 | 0.0659 | 1 | 40 |
| 0.1000 | 0.0435 | 0.0571 | 5 | 60 |
| 0.3000 | 0.0400 | 0.2608 | 1 | 60 |
| 0.5000 | 0.0422 | 0.4585 | 1 | 80 |
| 0.5000 | 0.0537 | 0.4470 | 5 | 80 |
| 1.0000 | 0.0418 | 0.9582 | 1 | 80 |
| 2.0000 | 0.0423 | 1.9580 | 1 | 85 |

The solubility of potassium chloride in anhydrous *n*-butyl alcohol containing 6% hydrogen chloride was found to be about 0.8 mg. per 100 ml. of solution (see Table VI). Hence, the solubility of potassium chloride is reduced from 2.5 mg. per 100 ml. of butyl alcohol to 0.8 mg. by the addition of 6% hydrogen chloride and to about 0.5 mg. by the further addition of 0.2 ml. of perchloric acid. Because of the limited amount of work done, the solubility data recorded here may be somewhat liberally interpreted.

**Table VI. Solubility of Potassium Chloride in Anhydrous *n*-Butyl Alcohol Containing 6% of Hydrogen Chloride**

(*Note.* Weighed quantities of potassium chloride were treated with a 6% solution of hydrogen chloride in *n*-butyl alcohol at a boiling heat. After cooling to 25° ± 1° C., the solution was filtered through a tared Gooch crucible, the residue transferred onto the Gooch and washed with the 6% solution of hydrogen chloride in *n*-butyl alcohol. The crucible was dried and weighed and any loss of weight noted.)

| Volume of Filtrate and Washings | KCl Taken | KCl Left Undissolved | Loss of Weight | Free $HClO_4$ Present | Solubility of KCl in 100 Ml. |
|---|---|---|---|---|---|
| *Ml.* | *Gram* | *Gram* | *Gram* | *%* | *Gram* |
| 35 | 0.2500 | 0.2497 | 0.0003 | ... | 0.0008 |
| 74 | 0.4000 | 0.3993 | 0.0007 | ... | 0.0009 |
| 98 | 0.5000 | 0.4996 | 0.0004 | ... | 0.0008 |
| 104 | 1.0000 | 0.9993 | 0.0007 | ... | 0.0007 |
| 87 | 0.5000 | 0.4996 | 0.0004 | 0.5 | 0.0005 |
| 126 | 0.5000 | 0.4994 | 0.0006 | 0.5 | 0.0005 |

In order to determine the total solubility of potassium perchlorate and potassium chloride in *n*-butyl alcohol containing 6% hydrogen chloride and to prove the accuracy of the proposed procedure, varying amounts of potassium chloride and lithium chloride were fumed with perchloric acid, the excess of the latter was expelled by evaporation, and the dry perchlorates were heated to boiling with *n*-butyl alcohol. Enough 20% solution of hydrogen chloride in *n*-butyl alcohol was added to bring the concentration of the hydrogen chloride to 6%. The cold solution was filtered through a tared Gooch crucible and washed with the 6% solution of hydrogen chloride in *n*-butyl alcohol. Lithium was determined in the filtrate by evaporating the butyl alcohol solution, finally weighing it as the sulfate.

The residue on the Gooch crucible was dissolved in hot water, the filtrate collected in a 250-ml. beaker was fumed to dryness with an excess of perchloric acid, and potassium was finally determined as the perchlorate, using the original Gooch crucible and applying reagents and manipulations recommended by Smith and Ross but making only one extraction with the mixture of ethyl acetate and *n*-butyl alcohol (see Table VII).

**Table VII. Separation and Determination of Potassium and Lithium**

| KCl Taken | $KClO_4$ Found Equivalent to KCl | LiCl Taken Equivalent to $Li_2SO_4$ | $Li_2SO_4$ Found |
|---|---|---|---|
| *Gram* | *Grams* | *Gram* | *Gram* |
| 0.0500 | 0.0498 | 0.0735 | 0.0737 |
| 0.0500 | 0.0502 | 0.2205 | 0.2200 |
| 0.1000 | 0.0995 | 0.2205 | 0.2211 |
| 0.2500 | 0.2503 | 0.2205 | 0.2202 |
| 0.5000 | 0.4994 | 0.2205 | 0.2214 |
| 1.0000 | 0.9999 | 0.2205 | 0.2205 |
| 1.0000 | 1.0004 | 0.4410 | 0.4403 |

The results in Table VII show that the separation of lithium from potassium by the *n*-butyl alcohol–hydrogen chloride method is very satisfactory, making it possible to extend the procedure to the separation of lithium from both sodium and potassium (see Table VIII). Because of the considerable solubility of lithium perchlorate and lithium chloride in *n*-butyl alcohol compared to the sparing solubility of lithium chloride in various other organic solvents recommended for this separation, and the very small solubility of sodium and potassium chlorides in *n*-butyl alcohol containing 6% hydrogen chloride, Willard and Smith's method, as revised and extended by this writer, should be considered superior to any other method used at the present time for the separation of lithium from sodium and potassium.

SEPARATION OF LITHIUM FROM CESIUM AND RUBIDIUM. Cesium and rubidium are rarely encountered in lithium minerals, with the exception of lepidolite, which sometimes contains the two alkali metals in such small quantities that no special provisions for their presence need be considered.

Preliminary work carried out by this writer would indicate that rubidium and cesium perchlorates are also affected by the solution of hydrogen chloride in *n*-butyl alcohol. Because of the smaller solubility of the perchlorates of rubidium and cesium in *n*-butyl alcohol, the conversion into the respective chlorides is smaller. The separation of lithium from rubidium appears to be good, while the separation from cesium seems less satisfactory.

*Procedure for Separation of Lithium from Sodium and Potassium.* The reagents used were identical with those recommended by Willard and Smith, with the exception of the *n*-butyl alcohol. This is now readily obtainable on the market of sufficient purity to do without the elaborate and time-consuming purification procedure employed by Willard and Smith.

The mixed chlorides of potassium, sodium, and lithium, obtained as described above, are dissolved in a little water, 5 ml. of perchloric acid are added, the cover of the beaker is raised with a glass hook, and the solution is evaporated to dryness on a hot plate at a temperature not higher than 350° C.

Twenty milliliters of anhydrous *n*-butyl alcohol and 0.2 ml. of perchloric acid are added to the mixed perchlorates of potassium, sodium, and lithium, the solution is heated to boiling, and 8 ml. of a 20% solution of hydrogen chloride in *n*-butyl alcohol are added, the first milliliter dropwise, while the mixture is constantly stirred. After the solution has cooled to room temperature the precipitate (consisting of sodium chloride and a mixture of potassium chloride and potassium perchlorate) is collected on a glass filter or Gooch crucible and washed about eight times with a 6% solution of hydrogen chloride in *n*-butyl alcohol. The crucible is held if a determination of sodium and/or potassium is also required.

The filtrate and washings, which have been received in a 250-ml. beaker, are diluted with one third their volume of water, thus forming two layers, the lithium chloride and perchlorate being contained in the water layer. The whole is evaporated on the water bath in such a way as to avoid condensation on the upper part of the beaker. (This can easily be done by immersing the beaker through a hole in an asbestos or metal plate into an open metal cylinder which is heated by the steam of the water bath.)

When completely dry, 10 ml. of water, 5 ml. of nitric, 3 ml. of perchloric, and 1 ml. of sulfuric acids are added and the whole is evaporated on a hot plate to strong fumes of sulfuric acid. (This treatment usually is sufficient to destroy any brown coloration due to organic matter; if not, a few drops of nitric acid should be added and the fuming resumed.) The excess sulfuric acid is finally fumed off, 15 ml. of water are added to the cool beaker, and the solution is heated to boiling, transferred to a previously ignited and weighed platinum dish, and evaporated as far as possible on the water bath. The platinum dish is now heated with a small Bunsen flame until all acid has been expelled, finally for one minute at a dull red heat. When cool, the platinum dish is weighed; the increase in weight is lithium sulfate.

For extreme accuracy, the analyst should determine a correction for the solubility of sodium chloride, potassium chloride, and potassium perchlorate in the 6% solution of hydrogen chloride in *n*-butyl alcohol and a blank for all the reagents used. The correction usually is less than 1 mg.

Should determination of sodium and/or potassium be also required, the residue is dissolved on the glass filter or Gooch crucible in hot water and sodium separated from potassium according to standard methods.

**Table VIII. Separation of Lithium from Sodium and Potassium**

| KCl Taken | NaCl Taken | LiCl Taken Equivalent to $Li_2SO_4$ | $Li_2SO_4$ Found |
|---|---|---|---|
| *Gram* | *Gram* | *Gram* | *Gram* |
| 0.0250 | 0.0250 | 0.0735 | 0.0739 |
| 0.0500 | 0.0500 | 0.0735 | 0.0736 |
| 0.0500 | 0.0500 | 0.1470 | 0.1476 |
| 0.0500 | 0.1000 | 0.1470 | 0.1475 |
| 0.1000 | 0.0500 | 0.1470 | 0.1472 |
| 0.1000 | 0.2500 | 0.1470 | 0.1477 |
| 0.2500 | 0.1000 | 0.1470 | 0.1476 |
| 0.5000 | 0.5000 | 0.1470 | 0.1476 |
| 0.2500 | 0.2500 | 0.2205 | 0.2210 |
| 0.2500 | 0.2500 | 0.4410 | 0.4412 |

## LITERATURE CITED


(1) Adams, Benedetti-Pichler, and Bryant, *Mikrochemie*, 26, 29–35 (1939).
(2) Barber and Kolthoff, *J. Am. Chem. Soc.*, 51, 3233 (1929).
(3) Benedikt, *Ann. Chem. Pharm.*, 178, 92 (1875).
(4) Berzelius, "Lehrbuch der Chemie", Vol. 1, p. 777, Dresden, Arnold, 1825.
(5) Berzelius, *Pogg. Ann.*, 1, 169 (1824).
(6) *Ibid.*, 4, 245 (1825).
(7) Brown and Reedy, IND. ENG. CHEM., ANAL. ED., 2, 304–6 (1930).
(8) Caley, *J. Am. Chem. Soc.*, 52, 2754–8 (1930).
(9) Caley and Axilrod, IND. ENG. CHEM., ANAL. ED., 14, 242–4 (1942).
(10) Caley and Baker, *Ibid.*, 11, 101–2 (1939).

(11) Carnot, *Bull. soc. chim.* (3), 1, 280 (1889).
(12) Classen, "Ausgewaehlte Methoden", Vol. I, p. 864, Braunschweig, Vieweg and Sons, 1902.
(13) Coheur, *Rev. universelle mines*, 15, 151–5 (1939).
(14) Gooch, *Am. Chem. J.*, 9, 33–51 (1887).
(15) Hillebrand and Lundell, "Applied Inorganic Analysis", p. 786–95, New York, John Wiley & Sons, 1929.
(16) Houk, U. S. Bur. Mines, *Information Circ.* 7225, 1–4 (1942).
(17) Kahlenberg and Krauskop, *J. Am. Chem. Soc.*, 30, 1104 (1908).
(18) Koenig, Ind. Eng. Chem., Anal. Ed., 7, 314–15 (1935).
(19) Krishnaya, *Chem. News*, 107, 100 (1913).
(20) Low, *Ibid.*, 67, 185 (1893).
(21) Lundell and Hoffman, "Outlines of Methods of Chemical Analysis", p. 75, New York, John Wiley & Sons, 1938.
(22) Mayer, *Ann. Chem. Pharm.*, 98, 193 (1856).
(23) Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. II, pp. 463–5, London, Longmans, Green and Co., 1922.
(24) Mueller, *Ann. Chem. Pharm.*, 85, 251 (1853).
(25) Osborg, "Lithium, Theoretical Study and Practical Applications", New York, Electrochemical Society, 1935.
(26) Palkin, *J. Am. Chem. Soc.*, 38, 233 (1916).
(27) Procke and Uzel, *Mikrochim. Acta*, 3, 105–7 (1938).
(28) Rammelsberg, *Pogg. Ann.*, 66, 79 (1845).
(29) Richards and Willard, *J. Am. Chem. Soc.*, 32, 4 (1910).
(30) Rogers and Caley, Ind. Eng. Chem., Anal. Ed., 15, 209–11 (1943).
(31) Schoeller and Powell, "Analysis of Minerals and Ores of the Rarer Elements", p. 38, London, J. B. Lippincott Co., 1940.
(32) Scholes, *J. Am. Ceram. Soc.*, 16 (3), 342–3 (1933).
(33) Scott, "Standard Methods of Chemical Analysis", Vol. I, p. 888, New York, D. Van Nostrand Co., 1939.
(34) Sinka, *Z. anal. Chem.*, 80, 430–5 (1930).
(35) Skinner and Collins, U. S. Dept. Agr., Bur. Chem., *Bull.* 153, 21–38 (1912).
(36) Smith, G. F., and Ross, *J. Am. Chem. Soc.*, 47, 1020–6 (1925).
(37) Smith, J. L., *Am. J. Sci.* (3), 1, 269 (1871).
(38) Troost, *Compt. rend.*, 43, 921 (1856).
(39) Waller, *J. Am. Chem. Soc.*, 12, 214 (1890).
(40) Willard, Liggett, and Diehl, Ind. Eng. Chem., Anal. Ed., 14, 234–5 (1942).
(41) Willard and Smith, *J. Am. Chem. Soc.*, 44, 2816 (1922).
(42) Winkler, *Z. anal. Chem.*, 52, 628–40 (1913).

# Adaptation of a Waring Blendor for Continuous Emulsification

C. L. COMAR[1], E. J. MILLER, M. N. RICHARD[2], AND E. J. BENNE
Chemical Section, Agricultural Experiment Station, East Lansing, Mich.

IN 1939, Davis (*2*) pointed out the advantages of the Waring Blendor for extracting plant and animal tissues. Since that time this type of machine has been employed by many laboratories, usually in connection with extractive and analytical procedures. It was recognized that the utility of the Blendor was limited by the characteristics of the original container and that the usefulness of the device would be increased if blending vessels of different capacities and shapes were available for operation on the same motor shaft as the original container. Davis devised such vessels but did not describe the method of their construction. Benne (*1*) extended this idea and reported upon the preparation and use of three different kinds of blending vessels which possessed advantages over the commercial container for certain purposes.

This paper reports an adaptation of the Waring Blendor that has been used successfully for the preparation of emulsions by a continuous process. Since small blending vessels which operate on the base of the Blendor are advantageous for certain analytical extractive procedures and are essential to the continuous emulsification process reported in this paper, a convenient method for their construction is described.

## CONSTRUCTION OF SMALL BLENDING VESSELS

The small blending vessels shown in Figure 1 were constructed by making holes 0.75 inch in diameter in the bottom of the glass bottles shown and mounting therein commercial blending assemblies which are obtainable on the market. Appropriate alterations in the blades of these assemblies were made where necessary, so that they could be accommodated by the vessels of smaller size. The holes through the glass were made by penetration with a small steel drill, followed by enlargement of this hole to the proper size with round files of different diameters. Turpentine used on the files during this operation greatly facilitated cutting.

As can be seen, it was necessary to prepare wooden adapters to hold the improvised vessels in position on the motor shaft. Four long, slender screws were inserted into the wooden base, one at the center of each side of the bottle for Nos. 3 and 4, to prevent rotation with the motor shaft. For No. 2 the long screws were replaced by narrow strips of spring steel which were fastened to the base with small screws. To act as shock absorbers, a piece of small-bore rubber tubing of appropriate length was slipped over each of the long screws or steel strips, and a piece of rubber gasket sheeting, shaped to fit the container seat, was placed beneath the wooden adapter.

Although the method described above for making holes through glass vessels is simple and involves no unusual equipment, it is laborious and time-consuming. The authors were interested therefore in the method used by Huddleson (*3*) for this purpose.

This investigator had prepared in the college machine shop a glass-cutting tool similar to those pictured in Figure 2. This tool consisted of a brass tube 0.75 inch in diameter with walls approximately 0.0625 inch thick, attached to a solid steel rod, the upper end of which was reduced to about 0.375 inch in diameter, so that it could be accommodated by the chuck of an electrically driven drill press. The tool is employed by clamping it in the chuck of the press, adding Carborundum powder and a small amount of turpentine to the glass where the hole is desired, lowering the tool into the mass of abrasive, and using it as a core drill against the glass. Two deep nicks in the lower end of the tube and a hole in the wall above permit the turpentine and

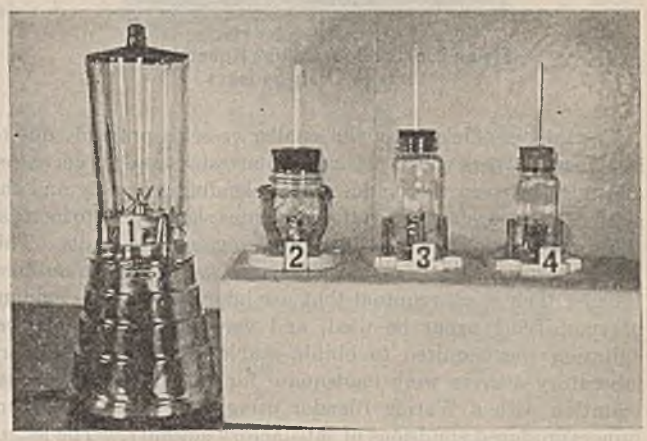



Figure 1. Waring Blendor and Three Containers

[1] Present address, Agricultural Experiment Station, University of Florida, Gainesville, Fla.
[2] Present address, Medical Division, Sharp & Dohme, Inc., Philadelphia, Pa.

abrasive to flow back into the path of the cutting tool. The mixture of turpentine and abrasive is retained in the proper place on a flat or convex surface by molding a reservoir from modeling clay against the glass around the spot to be drilled.

This method of cutting round holes through glass surfaces is satisfactory and reduces to a few minutes the time for a task which formerly required hours. Adapting the blending assemblies to vessels of different size and preparing adapters for holding them in position on the Blendor base must be carried out as before.

### ADAPTATION FOR CONTINUOUS EMULSIFICATION

The Waring Blendor offers a simple and effective mechanical device for preparing paraffin wax-in-water emulsions. A small experimental amount of an emulsion of this type can be prepared by placing hot water and an appropriate emulsifying agent in the blending vessel, starting the motor, and adding the molten wax dropwise. By controlling the temperature of the material and the time of agitation, reproducible conditions can be readily maintained. It was noted that better emulsions could be obtained with an improvised vessel similar to No. 3, Figure 1, than with the container supplied with the machine. When the small vessel was used for this purpose a one-hole rubber stopper was inserted in the top before starting agitation and the molten wax added through the hole.

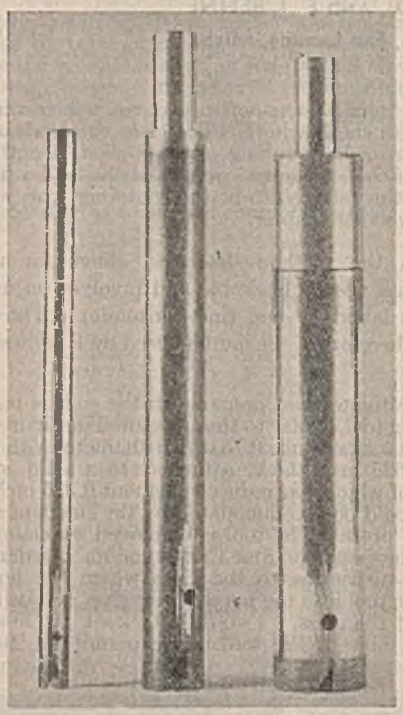


Figure 2. Tools for Cutting Round Holes through Glass Surfaces

The greater efficiency of the smaller vessel is probably due to its square corners which act as swirl arrestors and to decreased clearance between the blades of the blending assembly and the sides of the container, since these features should tend to increase the force of impact of the ingredients against the walls. This was important with the emulsion systems used by the authors, because their work required that a minimum adequate amount of emulsifying agent be used, and very effective mechanical agitation was required to obtain stable emulsions. Ordinary laboratory stirrers were inadequate for this purpose, whereas agitation with a Waring Blendor using one of the small containers produced emulsions of satisfactory stability. The length of the agitation period necessary to achieve the desired state of

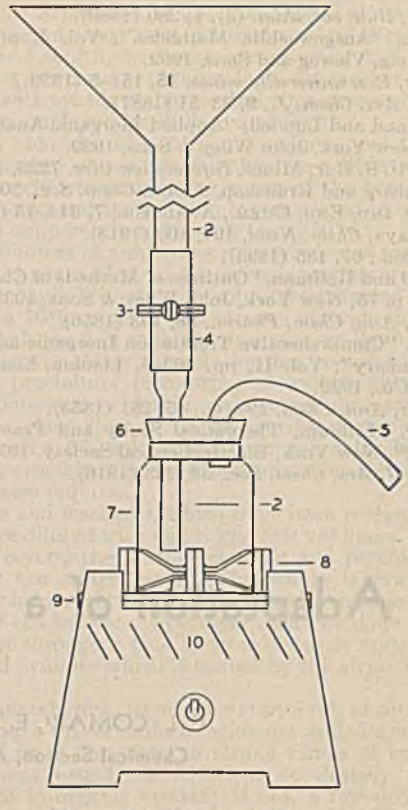



Figure 3. Diagram of Blendor

1. Funnel
2. Glass tubing intake
3. Screw clamp
4. Rubber tubing
5. Outlet
6. Rubber stopper
7. Blending bottle
8. Blade assembly
9. Bottle support
10. Waring Blendor base

emulsification is variable, since in any emulsion system the amount of mechanical agitation required will depend upon the formula used, one of the most important factors being the amount and effectiveness of the emulsifying agent added.

For preparing larger amounts of emulsion a Waring Blendor and one of the smaller blending vessels were arranged for a continuous-flow process as shown by the schematic diagram in Figure 3.

The ingredients of the emulsion flow by gravity from the elevated funnel, which acts as a reservoir, through the glass connecting tube directly onto the blending assembly. The rate of flow is controlled by means of a screw clamp on the rubber tubing connecting the glass tube and the funnel. It was found advisable to heat the ingredients and to mix them with a laboratory stirrer before introducing them into the continuous system. Introduction of the ingredients separately was tried, but afforded no advantages over the other procedure. As will be noted from the figure, the completed emulsion leaves the blending vessel through the top; hence, the cup is entirely full during the emulsifying process. This arrangement effectively prevents the beating of air into the emulsion during its preparation. Using two such Blendor systems simultaneously as much as 16 gallons of concentrated emulsion, equivalent to 160 gallons of diluted spray material, have been prepared in 8 hours in this laboratory.

After the premixing process the diameters of the droplets of the dispersed phase in a standard wax emulsion varied from 1 to 30 microns, with the majority about 5 microns; however, after having been passed through the Blendor system there were very few droplets larger than 2 microns in diameter, and most of them were about 1 micron. Hence, in a laboratory not equipped with a colloid mill the continuous Blendor system offers an inexpensive and effective means of emulsification with a capacity adequate for many experimental purposes.

It is possible that the efficiency of this method of emulsification could be increased by varying the design of the apparatus. For example, greater efficiency might result by reducing the space between the blending assembly and the top of the cup or by introducing the ingredients below the blades, or through the side wall directly onto the blades. A steam- or electrically heated funnel for the reservoir should prove advantageous. Certain of these features are under investigation.

LITERATURE CITED

(1) Benne, E. J., *J. Assoc. Official Agr. Chem.*, 25, 573 (1942).
(2) Davis, W. B., Ind. Eng. Chem., News Ed., 17, 752 (1939).
(3) Huddleson, I. F., Dept. of Bacteriology, Michigan State College, private communication.

Published with permission of the Director of the Experiment Station as Journal Article No. 704 (n.s.). This research was supported in part by the Horace H. Rackham Research Endowment of the Michigan State College of Agriculture and Applied Science for studies on the industrial utilization of agricultural products.

# Determining Hydrogen in Gases

## With a Thermal-Conductivity Apparatus

G. A. WEBB[1] AND G. S. BLACK, Mellon Institute, Pittsburgh, Pa.

**A thermal-conductivity cell was used to determine the hydrogen content of the exhaust gases from a catalytic-dehydrogenation unit. These exhaust gases consisted principally of hydrogen, but contained several other components such as methane, ethylene, carbon dioxide, etc., totaling not more than 30 to 35% by volume. The latter were grouped together and considered as one component to form a simple two-component system. It was determined that, if the cell is calibrated with simple mixtures similar to the gases to be analyzed, an accuracy in the hydrogen analysis of ±1.5% can be obtained. The method is satisfactory for appraisal of dehydrogenation catalysts.**

IN MANY catalytic operations the activity of a catalyst can often be evaluated by analyzing the exit gas. When the exit gas is analyzed by conventional absorption methods, the analytical procedure is time-consuming and large samples are required. Moreover, the analysis of this large sample indicates an average activity over the sampling period which is misleading when dealing with catalysts of short life.

This problem was encountered in a study of the dehydrogenation of ethylbenzene. The actual conversion to styrene was determined by a bromine number analysis of the liquid condensate but it was desirable, especially to give information as to the specificity of the catalysts, to know the hydrogen content of the noncondensable gas.

In this broad catalytic program in which catalysts of widely varied activity were tested, it was found that the average values given by conventional gas absorption analyses were inadequate, and a method capable of giving instantaneous gas compositions was indicated.

The analysis of the exhaust gases by thermal-conductivity means was considered as a solution of this problem. This method is well known for applications involving a binary gaseous mixture, and for more complex mixtures wherein certain components are present in constant amount or can be removed by chemical or physical means (*2*, *3*). The obvious disadvantage to its use in this application is the number of components present in the exit gases. A series of typical analyses of the exhaust gases from a unit evaluating the catalytic dehydrogenation of ethylbenzene to styrene is given in Table I. The results were obtained by the usual volumetric methods for gas analysis.

These exhaust gases consist principally of hydrogen with lesser amounts of other gases. Since the thermal conductivities of the minor components (carbon dioxide, ethylene, nitrogen, etc.) are practically identical when compared to hydrogen, the hydrogen value given by thermal conductivity is not affected by the distribution of the minor components. This is shown by the figures presented in Table II which were calculated on the assumption that the conductivity is proportional to the molecular concentration. From these figures, it is apparent that the exhaust gases can be handled as a two-component system.

[1] Present address, Research Department, Koppers Co., Pittsburgh, Pa.

### APPARATUS

The apparatus consisted of an air thermostat, a milliammeter, a storage battery, and a Minter diffusion-type thermal-conductivity cell (a development of Clarke C. Minter, available through the Gow-Mac Instrument Co., 22 Lawrence St., Newark 5, N. J.).

The Minter cell is made from a machined, 2-inch brass cube which has four hollow cylindrical spaces in it. Each space contains a small, glass-coated, platinum resistance wire. The wires are connected in a conventional Wheatstone-bridge circuit and

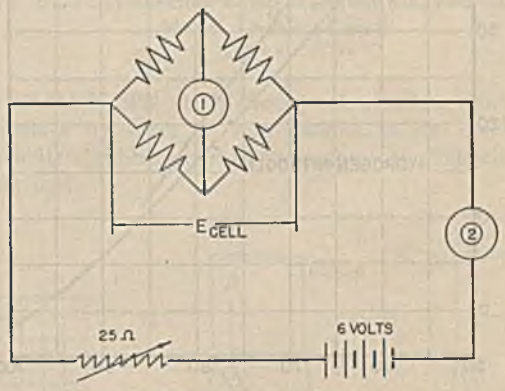



Figure 1. Electrical Circuit for Cell
1. Potentiometer, e
2. Cell current meter, I cell

Table I. Analysis of Miscellaneous Exit Gases from Catalytic Dehydrogenation of Ethylbenzene

| $CO_2$ | $C_3$+ | $C_2H_4$ | $O_2$ | CO | $H_2$ | Paraffins[a] | $N_2$ |
|---|---|---|---|---|---|---|---|
| | | | Per Cent by Volume | | | | |
| 10.6 | 0.2 | 4.2 | 0.8 | 1.4 | 74.0 | 5.8 | 3.0 |
| 0.8 | 0.0 | 7.3 | 0.7 | 1.0 | 78.0 | 9.2 | 3.0 |
| 18.0 | 0.2 | 12.8 | 0.6 | 0.4 | 54.8 | 10.8 | 2.4 |
| 18.8 | 0.0 | 11.2 | 0.4 | 0.2 | 59.6 | 7.6 | 2.2 |
| 11.2 | 1.8 | 5.0 | 0.4 | 0.8 | 70.2 | 1.6 | 9.0 |
| 7.0 | 0.2 | 11.8 | 0.6 | 0.2 | 65.8 | 12.4 | 2.0 |
| 18.1 | 0.1 | 7.9 | 0.6 | 0.4 | 61.6 | 7.8 | 3.5 |
| 13.3 | 0.0 | 2.0 | 0.0 | 1.8 | 75.6 | 7.3 | 0.0 |

[a] Average paraffin index 1.3.

Table II. Calculated Thermal Conductivity of Various Gas Mixtures

| Gas Composition (Per Cent by Volume) | | | | | | Thermal Conductivity, K cal./cm. sec. ° C. × $10^{-5}$ |
|---|---|---|---|---|---|---|
| $CH_4$ | $C_2H_6$ | $C_2H_4$ | $CO_2$ | $N_2$ | $H_2$ | |
| 5 | 5 | 5 | 5 | 5 | 75 | 31.68 |
| 12 | 13 | 0 | 0 | 0 | 75 | 31.86 |
| 0 | 0 | 5 | 20 | 0 | 75 | 31.34 |
| 15 | 0 | 0 | 5 | 5 | 75 | 31.98 |

are heated by passing through the bridge a small direct current of about 0.5 ampere. The internal construction of the cell is such that one pair of opposite resistances in the bridge is exposed to a standard gas, and the other pair is exposed to the unknown gas being compared with the standard. The brass cell is maintained at 30° C., and since this temperature is considerably lower than the temperatures of the resistance wires, heat is lost from the wires to the cell block by the conduction of gases.

Resistance measurements indicate the rate of heat loss from the wires and measure the thermal conductivity of the gases which surround the wires. When the thermal conductivities of the two gases being compared are different, owing to differences in compositions, the resistance wires are cooled at proportionally different rates and their resistance is changed, producing an electrical unbalance in the bridge circuit. This unbalanced condition is read by a potentiometer, and these readings are a function of the gas compositions. The circuit used in this work is shown in Figure 1.

## EXPERIMENT

Various methods have been used in the calibration of this type of conductivity cell (*1*), dynamic methods probably having been preferred because of the advantage of greater accuracy. However, in the present application a direct method was used.

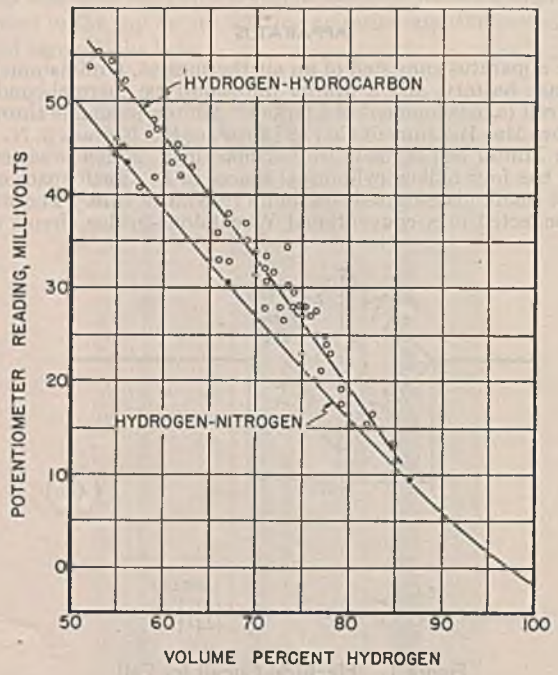



**Figure 2. Correlation of Cell Readings with Hydrogen Content**

Mixtures of hydrogen and nitrogen of various compositions were prepared and passed through the cell for a period of one hour. Cylinder hydrogen was used as the standard gas. The composition of an average sample of these calibration mixtures was determined by the usual method of volumetric gas analysis. The average cell-reading obtained on the potentiometer was plotted against the composition of these mixtures and is shown in Figure 2.

The choice of a nitrogen-hydrogen mixture for the calibration of the cell for establishing a curve of conductivity versus hydrogen content was based upon the magnitude of the thermal conductivity of nitrogen, which lies about halfway between methane and ethylene. Probably a better calibration mixture would have been carbon dioxide–nitrogen and hydrogen.

The data plotted as the upper curve in Figure 2 show the potentiometer readings for a number of exhaust-gas compositions, obtained by separate chemical analyses of the exhaust gases from a number of dehydrogenation runs. The difference between the actual hydrogen content of the exhaust gases and the value obtained from a nitrogen-hydrogen calibration curve is shown in Figure 2.

## DISCUSSION

Examination of Figure 2 shows that the thermal conductivity method can be used to determine the hydrogen content of mixed exit gases from a catalytic dehydrogenation unit, the accuracy being dependent upon the calibration curve used. In the present case the use of a nitrogen-hydrogen calibration curve gave hydrogen figures which were about 4% low. However, using the calibration curve established by the various mixtures themselves, an accuracy of about ±1.5% was obtained.

Obviously, maximum accuracy results when the calibrating mixture is identical with the actual composition to be evaluated, but for the quick appraisal of catalysts it is evident that a calibration with a simple nitrogen-hydrogen mixture will in most cases be satisfactory.

In addition, the method can be used in a comparative manner, without a calibration curve, by evaluating the exhaust gas from a catalyst of known activity, and rating others on the basis of the difference in the thermal conductivity values of the exhaust gases obtained.

## ACKNOWLEDGMENT

The authors are indebted to Miss B. Zehner and to E. E. Fleck, who determined most of the numerical data presented, and to C. C. Minter for his gift of the conductivity cell.

## LITERATURE CITED

(1) Brinker, W. E., Jr., "Characteristics of a Diffusion-Type Thermal Conductivity Cell", doctor's dissertation, University of Pittsburgh, 1940.
(2) Daynes, H. A., "Gas Analysis by Measurement of Thermal Conductivity", London, Cambridge University Press, 1933.
(3) Palmer, P. E., and Weaver, E. R., Bur. Standards, *Tech. Paper* 249 (1924).

# Facilitating Reading of Volumes in Determinations of Moisture by Distillation

C. R. SCHLEY

Lucky Heart Laboratories, Inc., Memphis, Tenn.

IN MOISTURE tests by distillation methods it is occasionally difficult to read accurately the volume of water that has distilled, owing to the collection of small drops on the sides of the tube or to peculiar surface effects at the interface of the liquids (*1*).

It has been found that the addition of a small amount of the solvent containing a wetting agent will eliminate sticking of droplets and aid in the formation of a clear meniscus. Only two agents were tried, Tween 20, made by the Atlas Powder Co., and sodium lauryl sulfate. Both were effective, and it appears probable that other products of the same type would serve equally well in the same capacity.

The amount of wetting agent used must be of the magnitude of one drop or equivalent amount of solid in 20 or 25 ml. of solvent and only 2 or 3 ml. are necessary for one determination. Use of a larger amount tends to cause formation of a dispersion. The solution may be placed in the receiving tube before the determination is begun, or added just before the final reading is taken.

## LITERATURE CITED

(1) Trusler, R. B., *Oil and Soap*, 16, 239–41 (1939).

# NOTES ON ANALYTICAL PROCEDURE

## Preparation of Standard Cerate Solutions from Cerium Titration Residues

FREDERICK R. DUKE AND K. G. STONE
Princeton University, Princeton, N. J.

COMPARED with permanganate and bichromate salts, cerium compounds are rare. Therefore, the procedure for recovery of volumetric cerium described below was developed and has been used in this laboratory for several months:

PROCEDURE. Titration residues containing cerium are collected in a suitable vessel. After a sufficient amount of residue has accumulated, an excess of saturated oxalic acid solution is added, followed by sufficient concentrated sodium hydroxide to complete the precipitation of $Ce_2(C_2O_4)_3.9H_2O$ (*3*). The solution should remain distinctly acidic (0.5 to 1.0 *M* in $H^+$) to prevent the precipitation of alkaline earths, iron, and other alkali-insoluble ions (*4*). After the precipitate settles, the major portion of the supernatant liquid is poured off, and the precipitate is transferred to a Büchner filter. If manganese or uranyl ions are known to be present in the solution, the precipitate is redissolved in the smallest possible volume of concentrated hydrochloric acid. Cerous oxalate is then reprecipitated by dilution to twenty times the volume of hydrochloric acid used. If neither manganese nor uranyl ions are present, the precipitate is washed on the Büchner with 0.1 *M* hydrochloric acid, followed by several water washes, and the material is dried with acetone or alcohol. It is then transferred to a shallow evaporating dish and heated with the yellow-tipped flame of a Méker burner to ignite the oxalate to ceric oxide (*1*). The mass presently turns dark gray in color, and heating is continued with stirring until the gray color is supplanted by the buff of ceric oxide. This operation requires 10 to 15 minutes. The ceric oxide is now ready for use, and may be dissolved in sulfuric or nitric acid and made up to standard. The oxide should be allowed to digest with the concentrated acid for one hour below the boiling point before dilution.

Perchlorato cerate may be prepared by suspending the oxalate in 4 to 6 *M* perchloric acid and electrolytically oxidizing the material, following the method of Smith, Frank, and Kott (*5*).

If phosphoric acid is present in the titration residues, the recovery is impractical, because excessive amounts of sodium hydroxide are required to neutralize the high acid concentration necessary when tetravalent cerium is used with phosphate, and because ceric phosphate is insoluble in acid solutions.

DISCUSSION. The procedure has been tested on solutions containing $Fe^{+++}$, $Mn^{++}$, $(UO_2)^{++}$, $V^{+++++}$, $Mo^{++++++}$, $Cr^{+++}$, $Cu^{++}$, $Co^{++}$, $As^{+++++}$, and $Sb^{+++++}$. Small amounts of $Mn^{++}$ (*2*) and $(UO_2)^{++}$ (*2*) are precipitated along with the cerous oxalate, and must be removed by the hydrochloric acid treatment if they would be likely to interfere in the use of the standard solution. In no other case was the precipitate found to be contaminated.

The percentage recovery of cerium following the procedure described is dependent upon several factors: the concentration of the cerium in the residues; the final acidity of the mother liquor; the nature of the contaminants, manganese and uranyl ion lowering the recovery since a reprecipitation is necessary; the completeness of conversion of the oxalate to the dioxide; and the temperature to which the oxide is heated during the ignition, high temperatures resulting in the formation of some refractory, insoluble ceric oxide. Careful control of the conditions, however, is unwarranted, since the percentage recovery under ordinary conditions seldom falls below 95%.

SUMMARY. Sulfato, nitrato, and perchlorato cerate solutions may be prepared from titration residues containing cerium. The procedure is simple and inexpensive, allowing a recovery of 95%. The only common interferences with the recovery are scandium, yttrium, and the other rare earths and phosphate ion.

### LITERATURE CITED

(1) Chase, W. S., *J. Am. Chem. Soc.*, 39, 1576 (1917).
(2) Hauser, O., *Z. anal. Chem.*, 47, 677 (1908).
(3) Hauser, O., and Wirth, F., *Ibid.*, 47, 389 (1908).
(4) Lundell and Hoffman, "Outlines of Methods of Chemical Analysis", p. 66, New York, John Wiley & Sons, 1938.
(5) Smith, G. F., Frank, G., and Kott, A. E., IND. ENG. CHEM., ANAL. ED., 12, 268 (1940).

## Crucible Holder for Use with Rubber Extraction Apparatus

WM. E. BOYD, Inspection Board of United Kingdom and Canada, Nobel, Ontario, Canada

TO ELIMINATE the difficulty of attaching sintered-glass crucibles by wires or wire baskets to the condensers of Underwriters' rubber extraction apparatus, the following method was devised:

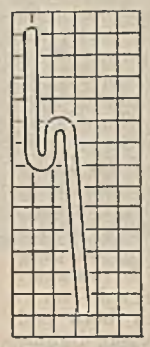


Figure 1


Figure 2

Figure 3

A 5-mm. glass rod is bent as shown in Figure 1, where spaces between parallel lines represent 1-cm. distances. The bent glass rod, dropped into a 400-ml. flask, assumes the position shown in Figure 2. When a sintered-glass crucible is then inserted, the bottom edge exerts a slight pressure on the rod at *A*, Figure 2, causing it to swing around and thus support the crucible as shown in Figure 3.

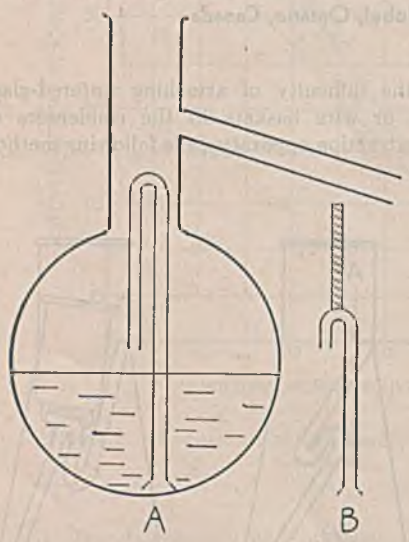
After extraction the crucible is easily lifted out with metal forceps and the rod washed with a small amount of the extracting solvent.

# A Device to Relieve Bumpy Distillations

R. T. HILL AND W. L. JACOBS
Departments of Anatomy and Physiology, Indiana University, School of Medicine, Bloomington, Ind.

TO PREVENT bumping during distillation some mechanism is necessary to disperse the heat applied and to agitate the fluid to be distilled. The device herein described has proved extremely effective. Its principle is basically the same as that involved in a Cottrell (*1*) pump for use in the determination of boiling points of solution. However, the apparatus was devised in the absence of any knowledge of the Cottrell pump.

A glass tube is bent in a U-form, with one arm somewhat shorter than the other, inverted, and introduced into the distilling flask (*A*). The U-tube should be long enough to extend from the bottom of the flask for a short distance into the neck. Its length thus serves to hold it in the upright position. If for any reason a shorter U-tube is desired, a glass rod may be welded to it to hold it upright (*B*). The short arm of the U should be just above the level of the fluid in the flask, while the long arm should rest on the bottom of the flask directly above the source of heat. No attempt should be made to have the end of the long arm fit uniformly around its rim on the bottom of the flask, although no ill effects from a close fit are anticipated. Obviously it should not fit the bottom of the flask so tightly as to prevent the distilling fluid from passing under it. If a large flask is used for distilling a large quantity of fluid, two or three U-tubes should be added, the short arm of one of which is just above fluid level at the start of distillation. The short arms of the other U-tubes should be of different lengths, and below fluid level.




As the fluid reaches the boiling point, the heat will cause fluid and vapor to rise to the top of the tube. Then fluid drops descend in the short arm of the tube by a combination of gravity and the force of the applied heat. In this way agitation is produced and the superheated fluid at the bottom of the flask is partly carried away. When a series of tubes is used, one or more have their short arms above the level of the fluid at all times and as the fluid level drops in the flask, others come in to play. Some advantage is secured, even though both ends are submersed in the fluid, from the circulation of vapor bubbles and fluid through the inverted U-tube. At times it is an advantage to have the long end of the tube flared slightly in the fashion of a funnel (see diagram). The diameter of the glass tube can vary somewhat; an inside diameter of 2 to 3 mm. has been found effective. Modifications can be adapted to meet many needs—particles in the distilling fluid, viscosity, etc.

If the presence of metal in the distilling flask is not objectionable a polished brass or aluminum rod, 3 to 4 mm. in diameter, may take the place of glass.

Many of the authors' friends have used the inverted U-tube method to control bumping, and recently its use has spread to other universities and laboratories.

LITERATURE CITED

(1) Cottrell, F. G., *J. Am. Chem. Soc.*, 41, 721 (1919).

# Take-Off for Recovering Solvent from Rubber Extraction Apparatus

WM. E. BOYD, Inspection Board of United Kingdom and Canada, Nobel, Ontario, Canada

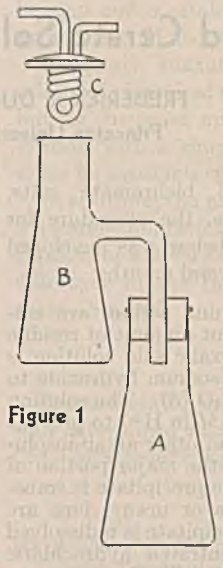



Figure 1

INSTEAD of allowing solvent (carbon tetrachloride) to boil away after extracting material in the Underwriters' rubber extraction apparatus, the following simple take-off was devised.

To a flask of sufficiently wide mouth to accommodate the condenser is attached a piece of glass tubing having an outside diameter of at least 10 cm. and bent in the form illustrated in Figure 1. After extraction has been effected in the extraction flask, *A*, the condenser, *C*, is raised, the extraction thimble is removed, the bent-arm flask, *B*, is connected with the extraction flask, using a cork stopper, and the condenser is placed in the mouth of the bent-arm flask. The solvent is then boiled out of the extraction flask and the condensate caught in the bent-arm flask, care being taken to avoid excessive heating or drying of the solute in the extraction flask.

Solvent recovery is excellent and residual material in *A* is in no way contaminated for further chemical treatment.

# NEW EQUIPMENT and BOOK REVIEW

## Fluoride Tester

The Harrold fluoride tester, a test instrument devised for rapid analysis of a contaminated atmosphere when hydrofluoric acid, sodium fluorides, or calcium fluorides are present, is announced by the Production Equipment Co., 6432 Cass Ave., Detroit 2, Mich. Developed as an aid to safety engineers for the analysis of welding atmospheres and for use in light metal foundries, the complete test kit weighs less than 5 pounds. The air is drawn past a calibrated test paper, which instantly changes color if fluorides are present. Test papers are guaranteed to be stable for 3 months.

## Geiger-Counter Spectrometer

A new x-ray instrument, the Geiger-counter spectrometer, was unveiled publicly at the National Metal Congress and Exposition, held October 16 to 20 in Cleveland, Ohio. A product of the North American Philips Co., Inc., New York, it utilizes a Geiger-Müller tube to measure the intensity and position of interference lines encountered in x-ray diffraction analysis work.

**Laboratory Guide in Chemistry.** *Joseph H. Roe.* 192 pages. C. V. Mosby Co., St. Louis, Mo., 1944. Price, $1.00.

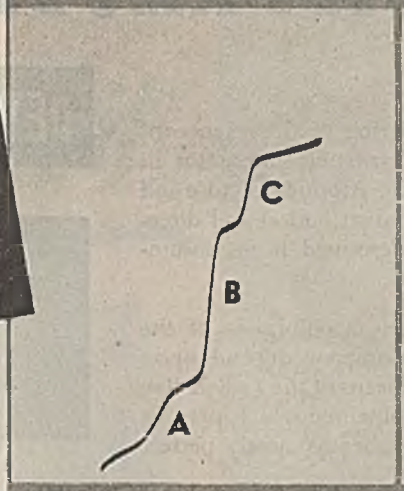
Experiments in this laboratory guide, which is bound in a plastic loose-leaf binding, are designed to accompany the author's textbook "Principles of Chemistry", and were incorporated in former editions of the text. Forty exercises are presented, five of them prepared for this edition.

THE NEW MODEL XII

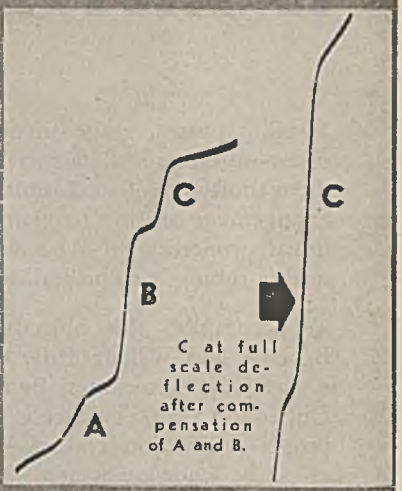
# Heyrovsky Polarograph

incorporates counter current compensation and improved camera.

## USE OF COUNTER CURRENT COMPENSATION




**Before Compensating for Constituents A and B**
Constituent C is the element to be determined, but under the conditions illustrated, the concentrations of constituents A and B are so large that C cannot be measured at maximum sensitivity and accuracy.

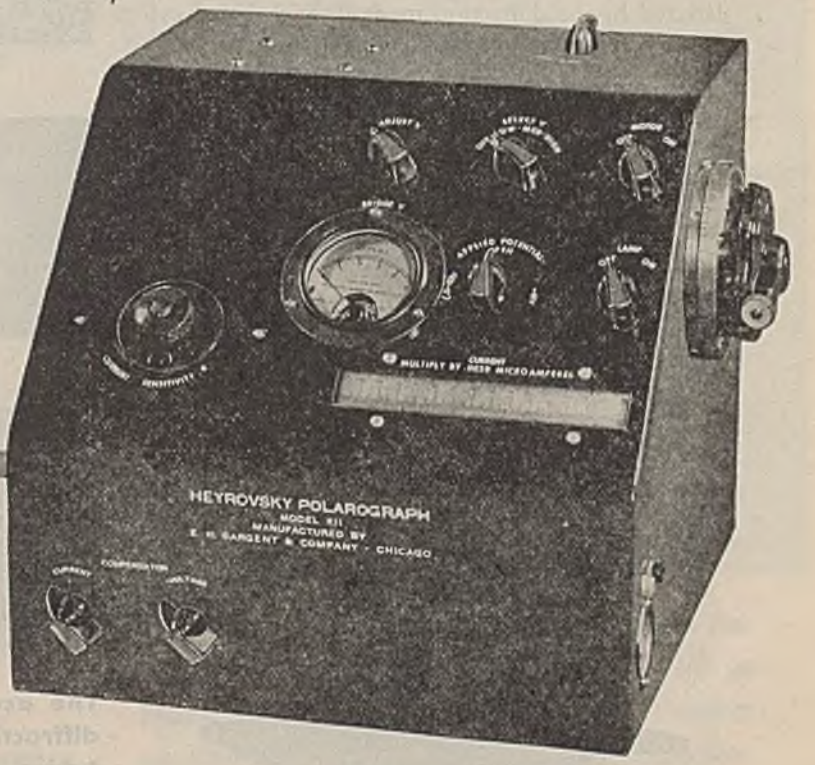



**After Compensating for Constituents A and B**
This clearly illustrates the important advantages of current compensation . . . constituent C can now be measured with maximum accuracy and without the necessity for time-consuming chemical removal of constituents A and B.

• Accuracy; rapidity; the possibility of detecting and identifying minute quantities and of making simultaneous determinations of several components; small sample requirement; preservation of sample and permanent photographic recording of every analysis, are some of the reasons why the Heyrovsky Polarograph is so widely used.

The procedures established thus far by no means define the field of polarography —the perfected instrumental system of the Heyrovsky Polarograph creates unlimited possibilities for analytical and research applications.

A bibliography of more than 700 papers dealing with the polarographic method of analysis and a booklet discussing the Polarograph and polarographic analysis are available without charge on request.




The application of polarographic methods of analysis expands steadily. Some of the applications of the Heyrovsky Polarographs now in use are — Analysis of waters for trace constituents • Observation of deterioration of transformer oils • Detection of incipient lead poisoning • Organic research. Analysis of: Brass • Ferrous alloys • Lead alloys • Magnesium alloys • Nickel alloys • Zinc alloys • Metallic impurities in aluminum • Lead and zinc in paints • Major constituents in plating solutions • Ceramics and glasses • Raw materials for production of rubber • Vulcanized rubber for identification of specific ingredients • Foods • Paper ash and pulping liquors.

**S-29301 POLAROGRAPH—Heyrovsky, American Model XII, Indicating-Recording, With Current Compensator.** Complete with accessories. For operation from 115 volts, A.C. 60 cycle circuits.....**$550.00**

E. H. SARGENT & COMPANY
155-156 EAST SUPERIOR STREET, CHICAGO 11, ILLINOIS
*Michigan Division: 1959 East Jefferson, Detroit 7, Michigan*

# SARGENT

SCIENTIFIC LABORATORY SUPPLIES