be made on the same oil at different temperatures, as no time need be lost in cooling and heating up again. Unfortunately, however, a sufficiently constant supply of electrical energy to hold the calorimeter and oil at a uniform temperature long enough to make the correction reliable is seldom available in a works laboratory.

CONCLUSIONS

The method described is believed to be a simple and satisfactory means of determining the specific heat of liquids, especially at high temperature. It is especially adaptable to plant control work and to laboratory investigations where rapid work and a fair degree of accuracy are required. At high temperatures, and over short temperature ranges the method as described is more accurate than any other of which the writers have knowledge. Accuracy of any desired degree can undoubtedly be obtained by refinements in temperature and electrical energy measurements, and obviously the more perfect the insulation of the calorimeter the larger the proportion of the total energy input consumed in actually raising the temperature of the oil.

THE APPLICATION OF THE THERMAL CONDUCTIVITY METHOD TO THE AUTOMATIC ANALYSIS OF COMPLEX MIXTURES OF GASES¹

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In a previous paper² there was described an automatic electrical method for gas analysis depending upon thermal conductivity, and its application to the determination of certain constituents in various mixtures of gases was illustrated by a number of representative analyses. It is the purpose of the present paper to show how the method may be applied to a much greater variety of analytical purposes than was even suggested in the former paper. The examples are intended to illustrate numerous possible ways of employing the method for complex mixtures, rather than to point out specific applications which would be likely to have industrial importance. As in the previous paper, the numerical results were obtained under laboratory conditions with all accessory apparatus of excellent quality and in accurate adjustment. It does not follow that as good results would be obtained under plant conditions, particularly with a recorder. However, the three recorders actually installed in manufacturing plants have thus far given satisfactory results.

Before further applications are described in detail, it may be well to point out some of the characteristics of the method which favor or limit its usefulness.

Probably the principal limitation upon the usefulness of the method is the fact that we cannot calculate the significance of the indications obtained, but must, in every case, depend upon empirical calibration under conditions closely approximating those of actual service. This limitation makes the method of little or no use for the occasional examination of isolated samples

of gas, especially samples of which the qualitative composition is not known.

The qualitative compositions of most gas mixtures of industrial importance are known, however; their variations in composition are more or less regular; and the probable limits of variation are also known approximately. For the purpose of observing or recording changes in the composition of such mixtures, the thermal conductivity method possesses a combination of advantageous features not possessed by other methods of analysis. Inasmuch as the thermal conductivity of a gas is independent of its pressure over very wide ranges of variation, it is not necessary to provide for the maintenance of the gas at a constant pressure. It has been found that the indications of the apparatus developed at the Bureau of Standards are practically unaffected by small variations in the rate of flow of the gas. These two facts make it possible to obtain a continuous, rather than an intermittent, record of gas composition, and enable us to employ several expedients, to be described later, which are of the utmost importance in dealing with complex mixtures. High sensitivity is secured with apparatus of small dimensions; consequently the time lag between changes in composition and the corresponding indications of the apparatus is quite small, even when the flow of gas is very slow. By the use of refined apparatus far greater sensitivity to variations in the composition of a mixture may be secured, and at less expense, than by any other well-known method.

COMPARISON OF METHODS OF GAS ANALYSIS

For the sake of conveying a more definite idea of the relative advantages of this method and several of the more familiar methods of analysis, under the conditions outlined above to which the thermal conductivity method is suited, a tabular comparison is made in Table I. This table represents the judgment of

TABLE I—RELATIVE ADVANTAGES OF VARIOUS METHODS OF OBSERVING GAS COMPOSITION¹

Desirable Characteristics	Method				
	Thermal Conductivity	Interferometer	Density Balance	Direct Weighing	Chemical Separation and Volumetric Determination
Sensitivity.....	1	2	5	4	3
General applicability.....	3	2	5	4	1
Independence of physical conditions difficult to control.....	2	4	3	5	1
Independence of calibration.....	5	4	3	2	1
Time lag.....	1	2	3	5	4
Time required of observer.....	1	2	3	5	4
Fatigue of observer.....	1	5	2	3	4
Skill required of observer.....	1	4	3	5	2
Computation required.....	1	4	3	5	2
Probable error of observation due to personal equation.....	1	4	3	5	2
Amount of gas required.....	1	4	2	5	3
Probable cost of apparatus.....	3	4	2	5	1
Probable cost of continuous operation.....	1	4	2	5	3

¹ The method possessing the greater advantage is given the smaller number.

the authors, who have had some experience with all the types of apparatus listed, and relates to methods of observing, rather than of recording, analyses. Since the thermal conductivity method loses little of its accuracy or dependability when used with a recorder and is in other respects ideally suited to continuous operation, while the contrary is true of recording apparatus depending upon density or volumetric measure-

¹ Published by permission of the Director of the Bureau of Standards.

² THIS JOURNAL, 12 (1920), 359.

ment, it is at once apparent that this method makes possible a considerable advance over the older methods of recording gas analysis.

APPLICATIONS OF THERMAL CONDUCTIVITY METHOD

The thermal conductivity method is always essentially a comparison of the thermal conductivities of two gases. The method of making this comparison was set forth in sufficient detail in the earlier paper. The present paper deals primarily with the question of what gases to compare in order to obtain useful data in a given case.

METHOD 1. COMPARISON WITH A STANDARD GAS—

Probably the simplest method of application of the thermal conductivity apparatus is the comparison of the mixture to be analyzed with a gas of known composition, called a "standard gas." This method is applicable to the following classes of gas mixtures:

- (a) Mixtures containing only two components.
- (b) Mixtures of two gas mixtures in each of which the proportion of various constituents is known to be constant. This class includes mixtures of a pure gas with mixtures of constant composition.
- (c) Mixtures in which it is known that the constituent of interest has a conductivity widely different from the conductivities of the other constituents, all of which latter conductivities are known to be of nearly the same magnitude.

The determination of helium in mixtures of helium and nitrogen occurring in the later stages of the separation of helium from natural gas, and the determination of the relative proportions of hydrogen and nitrogen in the purified gases used in the synthetic ammonia process are examples of Class (a), which were cited in the earlier paper. Other easy and important applications to this class of mixtures are the determination of hydrogen in electrolytic oxygen and of oxygen in electrolytic hydrogen.

A good example of Class (b) is the determination of the proportions of natural gas, from each of two fields, which enters the helium plant at Petrolia, Texas. Both gases consist of mixtures of methane, nitrogen, ethane, and some higher hydrocarbons, with a small percentage of helium. The composition of each gas is quite constant, but the difference between the two is so great as to render changes in plant operation desirable when their relative proportions are changed. The relative proportions of the gases from the two fields have been successfully recorded for several months, in spite of the fact that the difference between their heat conductivities is approximately only one per cent of the difference between the conductivities of helium and nitrogen. The determination of hydrogen in air, which was reported in the previous paper, is an example of this class of determinations which is extremely easy and accurate.

Class (c) includes the determination of hydrogen in water-gas and in the mixture of nitrogen, hydrogen, and carbon monoxide existing at one stage of the synthetic ammonia process. The conductivities of nitrogen (0.524) and of carbon monoxide (0.499) lie very close together, while that of hydrogen (3.27) is relatively very great. The relative proportions of

nitrogen and carbon monoxide therefore make little difference in the determination of hydrogen. The same relation is practically true in the case of the mixtures of helium, nitrogen, and methane existing at one stage of the helium extraction process, so that the helium content can be determined with considerable accuracy in spite of variations in the relative proportions of methane and nitrogen. The determination of the lifting power of balloon gas is another good example of this class of determination. The impurities likely to occur in hydrogen produced for balloon purposes, and also the gases of the atmosphere, including water vapor and carbon dioxide, all have relative effects upon the lifting power of the balloon gas which approximate their relative effects upon its thermal conductivity. This relation holds whether helium or hydrogen is used in the balloon.

Air and hydrogen have been found to be the gases most generally useful as the standard comparison gas; air is used when the mixture for analysis has a low conductivity, and hydrogen is compared with mixtures which have a high conductivity.

METHOD 2. COMPARISON OF THE GAS BEFORE AND AFTER A CHEMICAL REACTION—The determination of a constituent of a mixture of gases by the comparison of the mixture before and after the removal of the constituent by absorption in a suitable reagent is probably even more important than the comparison with a standard gas. In the previous paper the determination of ammonia and of carbon dioxide in the mixtures of hydrogen and nitrogen existing in a synthetic ammonia plant and the determination of carbon dioxide in air were described. Chlorine, hydrochloric acid, sulfur dioxide, acetylene, water vapor, and many other gases in mixtures of certain kinds appear to be equally subject to determination by this method.

Instead of removing a constituent of the mixture by absorption, we may subject it to any other process which will cause its removal or change its form of combination. The most important process of this kind is that of exposing the gas, preferably in the presence of a catalyst, to a sufficiently high temperature to cause reaction between different constituents of the mixture. For example, the total amount of atmospheric gases in a hydrogen-filled balloon may be determined by comparing the gas with pure hydrogen as a standard, as described above. The oxygen may be determined very accurately, independently of other impurities, by comparing the conductivities of the gas before and after passing through a combustion furnace in which the oxygen is removed by its reaction with hydrogen.

An interesting application of this method is the determination of methane in air by the simple process of comparing the conductivities of the mixture before and after passing over hot copper oxide. The methane is burned to carbon dioxide and water vapor. The gas is either dried or saturated with water vapor at the same temperature both before and after combustion. The net result of the combustion is therefore the replacement of one molecule of methane and two of oxygen by one molecule of carbon dioxide. Since carbon dioxide has only about half of the conductivity of methane, while

oxygen and air are intermediate, this results in a very considerable lowering of the conductivity of the mixture. Some results actually obtained by this method of analysis are shown in Table II.

TABLE II—AUTOMATIC DETERMINATION OF METHANE IN AIR

Volumetric Analysis Per cent CH ₄	Analysis by Thermal Conductivity Method Uncorrected Reading of Instrument	Analysis from Calibration Curve
0.0	-0.03	-0.03
2.5	2.20	2.5
5.0	4.67	5.0
7.65	7.69	7.7

METHOD 3. ADDITION OF A GAS TO THE MIXTURE TO BE ANALYZED, FOLLOWED BY METHOD 2—While the methods already described are probably applicable to a majority of the gas analyses of industrial importance, there are certain important cases where they do not apply, and still others where a modification is desirable. Let us consider, for example, the determination of oxygen in flue gas. After the removal of carbon dioxide, an approximate determination of oxygen could, perhaps, be made by absorbing the oxygen in an appropriate reagent and comparing the conductivity of the gas before and after the absorption, as in the case of the determination of carbon dioxide. The result would be affected, however, by the presence of hydrogen, methane, water vapor, ammonia, oxides of nitrogen, any trace of unabsorbed carbon dioxide, and even carbon monoxide. The effect of these gases is serious only because the difference between the conductivities of oxygen and of nitrogen, which is the principal remaining constituent, is small. If, however, hydrogen were first mixed with the gas, say in equal volumes, the conductivity of the residual mixture of nitrogen and hydrogen would be several times that of the oxygen removed, and the determination of oxygen would be accurate in spite of small variations in the composition of the residue.

FIG. 1—CAPILLARY MIXING DEVICE

The essential feature of this method is the addition of gas in constant proportions to the mixture to be analyzed and the subsequent removal of the desired constituent. The device shown diagrammatically in Fig. 1 readily accomplishes the addition of a constant proportion of a gas. An excess of the mixture to be analyzed is passed through Tube A and an excess of the gas to be added, usually hydrogen, through Tube B. Part of each gas stream flows to waste through F and part flows through the connecting capillary Tube C or D to Tube E and thence to the gas-analysis apparatus. Since both ends of the capillaries are connected, the pressure drop through one is always the same as that through the other, and since the viscosity of a gas is practically independent of pressure and all gases have, within narrow limits, the same thermal coefficient of viscosity, it is only necessary to maintain the two capillaries at the same temperature in order

to insure uniform mixing of the gases by this method. The relative proportions of the two gases may be readily varied by changing the relative lengths and diameters of the capillaries. Of course the relative proportions of the two gases will vary slightly with the composition of the mixture to be analyzed. The total measured effect of a change of composition is, therefore, to a certain small extent a function of viscosity as well as of thermal conductivity; but since viscosity and thermal conductivity are closely related functions of molecular motion, and since the relations depended upon in making a determination are entirely empirical, this fact makes no difference in the convenience or accuracy of the method.

The adjustment of the electrical instruments to give a direct reading on a linear scale is exactly the same as in the other cases. End resistances are determined by trials which make the slide-wire reading correspond to the percentage of the constituent sought in the mixture before the addition of a gas.

It is of interest to determine the amount of enriching gas which will produce a maximum reading by this method when the gas to be determined is removed and no other change takes place. For this purpose we may assume that the simple law of mixtures, as expressed by the following relation, holds:

If A, B, C, . . . N represent the relative volumes of each constituent of a mixture, and $a, b, c, \dots n$, the thermal conductivities of the respective gases when pure, the thermal conductivity of the mixture will be represented by the expression

$$\frac{aA + bB + cC + \dots nN}{A + B + C + \dots N}$$

It is known that this simple law does not hold exactly, but it is, in most cases, a sufficiently close approximation to permit one to determine in advance the feasibility of using thermal conductivity methods for a definite purpose, and to choose between the several procedures usually possible.

Let A represent the number of parts by volume of the gas to be removed by absorption, B the number of parts of the residual gas in the original mixture, and C the number of parts of enriching gas to be added. Let a, b , and c represent the thermal conductivities of the three gases, respectively. It can be shown¹ by the usual method of differential calculus that the ratio of

¹ If we represent by R the ratio of the conductivity of the mixture before to the conductivity of the mixture after the removal of the constituent of which the volume is represented by A, it is evident that the greatest sensitivity will be secured when dR/dA is a maximum. This condition is secured when

$$\frac{d^2R}{dA \cdot dC} = 0 \quad (1)$$

$$\text{Assuming that } R = \frac{bB + cC}{aA + bB + cC} \quad (2)$$

the solution of Equation 1 involves the solution of an equation of the fifth power of C. It is evident, however, that for small values of A, the conditions which make dR/dA a maximum also make R a maximum. It has been found by experiment that R is not far from a linear function of A. Hence, for practical purposes we may always assume that the most favorable condition is found when R is a maximum.

Differentiating Equation 2 with respect to C, equating to zero, and solving for C leads to the equation given in the text.

the conductivity of the mixture after the removal of the desired constituent to the conductivity before the removal is a maximum when the amount of gas used for enrichment is in accordance with the following formula:

$$C = \frac{c(a-b)B \pm \sqrt{c^2(a-b)^2B^2 + (c^2-ac)(acAB + acB^2 - abAB - b^2B^2)}}{c^2-ac}$$

The sign before the radical is positive when c is greater than a , and negative when c is less than a .

By substituting the appropriate values in this equation we find, for example, that the maximum reading for small variations of carbon dioxide in air is obtained when hydrogen is added in the ratio of 0.16 to 1. The maximum reading for small amounts of oxygen in nitrogen prepared from the air is obtained when hydrogen is mixed with the gas in the ratio of 0.44 to 1; the most favorable condition for determining variations in the percentage of oxygen in nearly normal air is obtained by adding hydrogen in the ratio of 0.39 to 1. Hydrogen could be determined in helium by adding carbon dioxide and passing over hot copper oxide. The most favorable condition would be obtained by adding 3 parts of carbon dioxide to one of the original mixture.

FIG. 2.—DETERMINATION OF OXYGEN IN MIXTURES OF OXYGEN AND NITROGEN

In the determination of methane in mixtures of nitrogen, methane, and helium, oxygen is added in constant proportions by means of capillaries, not for the purpose of altering the thermal conductivity of the mixture, but to permit the combustion of the methane. After the addition of oxygen, the determination of methane is made in the same manner as described above for the determination of methane in air. This method has been successfully used with a recorder. The end resistances were adjusted to make the slide-wire reading agree with the volumetric analyses of mixtures containing 0.0 and 9.8 per cent of methane. The recorder then indicated 4.75 per cent of methane in a mixture in which a volumetric analysis indicated 4.73 per cent of methane.

Fig. 2 shows graphically the results obtained by a

procedure in which hydrogen is mixed with the gas for the double purpose of effecting a reaction and serving as an indicator of the extent of the reaction by modifying the conductivity of the residual gas. Here oxygen in mixtures of oxygen and atmospheric nitrogen was determined by mixing the gas with an excess of hydrogen by means of the capillary device, passing the mixture through a combustion tube, and comparing the conductivities of the mixtures existing before and after the combustion. The readings depend upon the amount of hydrogen left in the nitrogen after the combustion, and since there is a change of two volumes of hydrogen for every one of oxygen, the method is extremely sensitive. It will be observed that all the points fall very close to a regular curve, which happens to have several times as great a curvature, over a range of 20 per cent, as does the calibration curve for any other determination thus far made.

METHOD 4. SUCCESSIVE COMBUSTION WITH OXYGEN AND HYDROGEN—A difficult class of mixtures to deal with by comparisons of thermal conductivity is that of mixtures of various combustible gases containing hydrogen and, in some cases, oxygen. For the purpose of analyzing such mixtures, the following method has been applied successfully in the laboratory to the determination of carbon monoxide in the presence of large amounts of hydrogen.

Into a slow stream of the gas to be analyzed is run a stream of oxygen from an electrolytic generator having platinum electrodes and containing a potassium hydroxide solution as the electrolyte. The mixture is passed into a small electrically heated combustion tube, containing, preferably, copper oxide, and through a carbon dioxide absorber. It is then mixed with the hydrogen from the electrolytic generator supplying the oxygen and passed through a second combustion tube similar to the first. The electrolysis of an alkali (freed from carbonates by precipitation with barium hydroxide) between platinum electrodes produces hydrogen and oxygen in exactly equivalent proportions. Let us suppose that nitrogen or other inert gas were alone in the original sample. Then the hydrogen and oxygen introduced will combine in the second furnace to form water which may be eliminated, leaving the original gas unchanged. If, however, the original mixture contains carbon monoxide, methane, or other combustible constituent, an amount of oxygen sufficient to burn the combustible gas completely will be removed in the first combustion tube, and a corresponding amount of hydrogen will be in excess in the second. The gas leaving the second combustion tube will, therefore, contain hydrogen in place of all the combustible gases originally present. If, as is usually the case, the inert gas is of constant composition (atmospheric nitrogen), the oxygen equivalent of the total amount of combustible may be found directly and accurately by a comparison of the gas resulting from this so-called "double combustion" with a standard gas (hydrogen or air). Since the hydrogen in the original gas was replaced by hydrogen, a comparison of the gas before and after the double combustion process gives directly the sum of the combustible gases, other than hydrogen, present.

If it is the above data that are desired, oxygen, if originally present, must first be removed by bubbling through a solution of potassium pyrogallate or other reagent. However, if it were desired to learn the excess of reducing gases over the oxygen present, these data could be recorded directly by performing the double combustion as indicated and comparing the resulting mixture with a standard gas. The excess of combustible gas other than hydrogen over the oxygen present could equally well be recorded directly, in case anyone were interested in such data. A comparison of the mixtures resulting from the double combustion of two samples of the gas to be analyzed, from one of which the oxygen was first removed, would obviously give the oxygen content of the gas directly.

Table III gives results obtained by this method in the determination of carbon monoxide in a mixture of nitrogen and hydrogen. Unit A consisted of a thermal conductivity unit, having active wires of 1 mil (0.025 mm.) platinum 15 cm. long, and a Köhler-Rausch slide wire of approximately 30 ohms resistance. Unit B consisted of a thermal conductivity unit having active wires of 2 mil (0.05 mm.) platinum 10 cm. long, and a 7-ohm slide wire from a Leeds and Northrup recording Wheatstone bridge. The extension resistances of the slide wires had, of course, been adjusted previously to making the readings here given.

TABLE III—DETERMINATION OF CARBON MONOXIDE IN A MIXTURE OF NITROGEN, HYDROGEN, AND CARBON MONOXIDE

Volumetric Analysis			Analysis by Thermal Conductivity Method	
Per cent	Per cent	Per cent	Unit A	Unit B
H ₂	N ₂	CO	Per cent	Per cent
66.1	33.7	0.21	0.21	..
69.4	29.5	1.10	1.12	..
70.5	27.4	2.13	2.13	..
70.3	27.4	2.25	2.25	..
70.0	27.2	2.77	2.77	..
68.8	26.6	4.62	4.63	..
68.7	26.6	4.70	4.70	..
51.8	5.8	42.43	42.43	42.4
51.0	5.6	43.43	43.53	43.5
50.2	5.6	44.15	44.24	44.5
48.5	5.4	46.25	46.20	46.1
47.4	5.2	47.40	47.40	47.4

COMBINATIONS OF THE BASIC METHODS—So many combinations of the basic methods already described are possible that it is not worth while trying to enumerate all of them. Probably the most important is the combination of methods in which a combustible gas containing carbon is burned and the resulting carbon dioxide is determined by absorption. This should prove a useful method, for example, in processes for the recovery of organic solvents. Oxygen may be added by means of the capillary device, if necessary, in order to secure complete combustion.

An equally interesting possibility is that of determining impurities in soluble gases, such as ammonia or carbon dioxide. The amount of gas in commercial ammonia, for example, would be so small as to affect the conductivity of the ammonia very slightly. If, however, we add a small amount of hydrogen to the ammonia by the capillary method and then absorb the ammonia, the amount of gas of low conductivity will be given with considerable accuracy by comparison with a standard gas according to Method 1. The residue so obtained would be in excellent condition for a determination of each of the individual absorbable con-

stituents, such as carbon monoxide and oxygen, according to Method 2. If a second sample of ammonia were absorbed without the previous addition of hydrogen, and the residue compared with a standard gas, a comparison with the first sample would indicate the hydrogen with considerable accuracy.

This suggests again the possibility of obtaining useful data by comparing the thermal conductivities of the mixtures resulting from two different methods of treatment of the same gas. One example of this was mentioned in the case of the determination of oxygen in combustible gases of unknown composition.

Only one other example will be given, that of the complete analysis of the rather complex mixture existing in the gases which have passed through the reaction chamber in the synthetic ammonia processes. We are dealing here with a mixture containing approximately one part of nitrogen to three of hydrogen, some ammonia, argon, and considerable amounts of hydrocarbons, principally methane. It is important to know the amounts of both the hydrocarbons and the argon, since they become an increasingly large portion of the mixture as the gas is passed again and again through the ammonia converter, until they slow down the reaction to such an extent that it is no longer profitable to employ the mixture.

The mixture as a whole has a high conductivity, somewhat more than three-quarters that of hydrogen. The moderate amount of ammonia present can, therefore, be determined easily and accurately by Method 2, sulfuric acid being used as the absorbent. As compared with hydrogen, the conductivities of all the remaining gases lie close together, that of methane and of argon being on opposite sides of nitrogen. Hydrogen can, therefore, be quite accurately determined by a comparison with pure hydrogen, according to Method 1. Methane could now be most accurately determined by Method 4, but the apparatus would be quite complicated, and for the purpose in view, a simpler method will give sufficiently accurate results. Oxygen is mixed with the gas in slight excess (Method 3), the mixture is passed through a combustion tube (Method 2b) and the resulting carbon dioxide determined by absorption (Method 2a). The excess oxygen is absorbed, and the residual gas, containing only nitrogen and argon, is compared with air as a standard (Method 1). We thus have a direct determination of ammonia, hydrogen, and total carbon, and a determination of the ratio of argon to nitrogen in the residue after the removal of the other constituents.

GENERAL APPLICABILITY OF THE METHODS DESCRIBED

It is quite evident that the thermal conductivity method gives no information regarding the qualitative composition of an unknown mixture of gases; and that it can be applied quantitatively only when much is known about the probable identity and amounts of the constituents likely to occur in the gas mixture for analysis. The greatest usefulness of the method is certain to be in the continuous or frequent analysis of gas mixtures in industrial control work; and, fortunately, most mixtures of which it is industrially important to know the composition vary in a some-

what regular manner. Each class of gas mixtures must be studied individually with regard to the probable limits of variation of every constituent; but unless the mixtures are extremely complex a method can generally be found for indicating the composition of the mixture, although the data may not be expressed in the familiar units of percentage of the original mixture. Thus when several constituents are determined in a single mixture, the amount of some of them must generally be expressed in percentage of the residue remaining after the removal of other constituents. The data obtainable should not be less useful to a plant operator on that account after he has learned to interpret them.

SUMMARY

The limitations and advantages of the method of gas analysis depending upon thermal conductivity, which was described in an earlier paper, are discussed.

Several novel expedients are described by the use of which the method may be employed for the analysis of a great variety of gas mixtures of industrial importance, and their specific application is shown by many examples.

LABORATORY CONTROL OF WHEAT FLOUR MILLING¹

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This article does not aim to present much information which might be called original in the strictly scientific sense. Its purpose is rather to point out an analytical procedure for the cereal chemist, particularly the flour-mill chemist, that differs considerably from those he ordinarily follows. This procedure is modeled after those used in control laboratories of industrial plants like smelters, sugar-beet factories, and others, where the process is one of refining or extracting the desired product from crude sources. In the laboratories of such plants samples of raw materials and of the different finished products are analyzed, thus keeping a check on the efficiency of factory operations. The flour-mill chemist ordinarily confines his activities to tests on the finished flour, but would increase the value of his services appreciably by including determinations of the flour content of wheat as it is received at the mill, and of the offal as it comes from the bins. From the results of such analyses the efficiency of milling operations may always be known. These results may also have other applications, as will be pointed out later.

THE WHEAT KERNEL

For milling purposes the wheat kernel may be regarded as composed of three distinct parts: the bran or outer seed coats, including the aleurone layer, the embryo or germ, and the inner endosperm or flour-producing portion. These different parts can be seen by cutting the kernel transversely or longitudinally. It is more difficult to determine what percentage of

the whole kernel each constitutes. This can be done only by a slow and tedious process of mechanical separation which Aimé Girard¹ performed as follows:

The kernels were soaked in water until they became plastic but not too soft, a treatment which required several days. Experiment showed that only an inconsiderable amount of material dissolved in the water in this process. The several layers of the seed coat were next removed by means of a scalpel, dried at 105° to 110° C., and weighed. The dry seed was split along the groove, and the germ was removed with pincers. Girard found the composition of the kernel to be

	Per cent
Bran (outer seed coats).....	14.36
Germ.....	1.43
Endosperm.....	84.21
TOTAL.....	100.00

Fleurent² reports the composition of three different wheats as follows:

	Average Wt. of Kernels Gram	Endosperm Per cent	Embryo Per cent	Bran Per cent
Russian.....	0.030	84.95	2.00	13.05
Algerian.....	0.048	84.99	1.50	13.51
Canadian.....	0.037	84.94	2.05	13.01

BRAN—The bran functions as an exo-skeleton or protective structure for the rest of the kernel, and is adapted to this purpose in chemical composition and physical structure.

Histological examination of cross-sections of the wheat kernel shows that the bran coat consists of several layers and membranes. The first three outer layers, called the epicarp, mesocarp, and endocarp, together constitute the pericarp. Beneath the endocarp are found, in the order named, the seminal tissue, the hyaline band, and the protein or aleurone layer. Botanically, the aleurone layer belongs to the endosperm, and is sometimes called the outer endosperm, but in commercial milling processes it is always separated with the bran, to which it adheres very firmly, and it may, therefore, be regarded as one of the seed coats of which the bran is composed.

The table of Girard (Table I) gives quantitatively the location of the different substances that are found in the outer covering, expressed in per cent of the entire bran coat.

TABLE I				
PERICARP				
Water.....	3.58			
Non-nitrogenous fiber.....	24.43			
Nitrogenous material.....	2.41			
Ash.....	0.58			31.00
SEMINAL TISSUE				
Water.....	0.92			
Non-nitrogenous material.....	5.06			
Nitrogenous material.....	1.25			
Ash.....	0.46			7.69
HYALINE BAND AND PROTEIN LAYER				
Water.....	7.23			
Cellulose material.....	29.61			
Nitrogenous material.....	15.21			
Fatty material.....	5.60			
Ash.....	3.66			61.31
TOTAL.....				100.00

By adding the percentages of each substance as given separately for the three different regions in the preceding table, Girard computed the composition of the entire bran as follows:

¹ "Le Froment et Sa Mouture," 1903, pp. 28-44.

² *Compt. rend.*, 124 (1896), 327.

¹ The authors desire to express their thanks to Dr. I. K. Phelps for his helpful suggestions in this work and for his criticisms in the preparation of the manuscript.