

dichromate in a liter of water. The ferrous sulfate solution may be made by dissolving 8 g. of ferrous ammonium sulfate and 50 cc. of sulfuric acid in 1 l. of water which is then diluted until it is of the same strength as the dichromate solution. These solutions need frequent renewal. The dichromate solution, which is the standard, must be kept in well-stoppered bottles and should be freshly prepared at least once a week. One cubic centimeter of this dichromate solution is equivalent to 0.1 per cent of vanadium in a 1-g. sample.

The titration of the nitric acid solution of the oxidized vanadium corresponds to 99 per cent of the vanadium present. Accordingly this may be calculated by dividing by 0.99 or approximated by adding 1 per cent of the amount found by titration. The vanadium retained by the tungsten is not ordinarily determined in most of the published methods. As indicated above, this corresponds in the case of 1-g. samples to 0.001 per cent of vanadium for each per cent of tungsten present. This may be calculated and added, or in the case of most tungsten vanadium steels, it may be closely enough approximated by adding 0.014 per cent since these usually contain 13 to 15 per cent of tungsten.

#### THE DETERMINATION OF CHROMIUM IN CHROME-VANADIUM STEELS

Dissolve 1 g. of samples containing less than 5 per cent of chromium in 70 cc. of sulfuric acid (sp. gr. 1.20). Use smaller samples when the percentage of chromium is higher. In chromium and chromium vanadium steels it is often necessary to evaporate until salts separate to decompose carbides. Dilute the solution cautiously to a volume of 75 cc. This evaporation does not appear to be necessary, nor is it desirable, in the case of tungsten steels. After dissolving the separated salts, or after solution of the tungsten steel, 2 cc. of nitric acid are added cautiously. The solution is then boiled about 5 min. It is next diluted with hot water to a volume of 250 to 300 cc. and heated to boiling. To the boiling solution are added 10 cc. of silver nitrate solution (2.5 g. per l.) and 20 cc. of ammonium persulfate solution (100 g. per l.). For higher percentages of chromium larger amounts of persulfate should be used. The amount to use can be determined by observing the color of the solution which should become permanently colored with permanganic acid after 2 or 3 min. The solution should be allowed to boil at least 8 min. after the last addition of persulfate to permit of the complete decomposition of the latter. While still boiling, add 5 cc. of dilute hydrochloric acid (1 : 3) and continue boiling at least 5 min. After cooling to 20° C. the solution is ready to titrate.

A solution of potassium dichromate is prepared by dissolving 2.829 g. of the salt in enough water to make a liter. The iron solution is prepared by dissolving 23 g. of ferrous ammonium sulfate and 100 cc. of sulfuric acid in enough water to make a liter. The iron solution is then diluted to correspond to the dichromate solution. One cubic centimeter of this solution is equivalent to 0.1 per cent of chromium in a 1-g. sample. The dichromate solution should be renewed at least

once a week and the ferrous sulfate solution should be compared with the former daily.

Both chromium and vanadium are titrated, and the end-point observed is the vanadium end-point which has been described by Conant and one of us.<sup>1</sup> Take the number of cubic centimeters of the dichromate solution used in titrating the vanadium, after correction for the fact that the vanadium is only 99 per cent oxidized, but without including that portion which is in the tungstic oxide, and multiply by 0.339. This factor expresses the relation between the dichromate solution used for titrating vanadium and that used for titrating chromium. The number of cubic centimeters so found are to be subtracted from the total titration of chromium and vanadium. This gives the amount used in titrating chromium alone.

To illustrate the results obtained by the application of the methods described above to the analysis of synthetic steels we give the following:

Two grams of bar iron, dissolved as required in the vanadium determination, were treated at the time of solution with chromate solution corresponding to 1.25 per cent chromium and vanadate solution corresponding to 0.272 per cent vanadium. In three such solutions we found 0.27(3), 0.27(1), and 0.27(9) per cent vanadium. To 1 g. of a tungsten steel which was especially prepared under circumstances which would insure the presence of less than 0.01 per cent of chromium or vanadium, we added, at the time of solution, chromate solution corresponding to 4.23(7) per cent chromium and vanadate corresponding to 2.20(8) per cent vanadium. Of course, both the vanadate and chromate were completely reduced in the process of solution. Vanadium determined in three such solutions was found to be 2.19(9), 2.20(2), and 2.19(9). Chromium was determined as 4.23(7), 4.22(0), and 4.21(7).

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#### A SIMPLIFIED WET COMBUSTION METHOD FOR THE DETERMINATION OF CARBON IN SOILS

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The determination of total carbon through oxidation with a mixture of chromic and sulfuric acids is a method given in nearly all treatises on quantitative analysis. As applied to the determination of total carbon in soils and soil extracts, the method has been modified by different investigators, both from the standpoint of increased accuracy in the determination itself and the simplification of the apparatus. Of the modifications recently proposed, that of Gortner<sup>2</sup> provides for the weighing of the carbon dioxide evolved after absorption in potassium hydroxide, while both Ames and Gaither,<sup>3</sup> and, more recently, Schollenberger,<sup>4</sup> have used barium hydroxide as an absorbent, titrating with a standard acid. The first of these modifications is objectionable in that the time

<sup>1</sup> *J. Am. Chem. Soc.*, **38** (1916), 343.

<sup>2</sup> *Soil Science*, **2** (1916), 401.

<sup>3</sup> *This Journal*, **7** (1915), 561.

<sup>4</sup> *Ibid.*, **8** (1916), 1126.

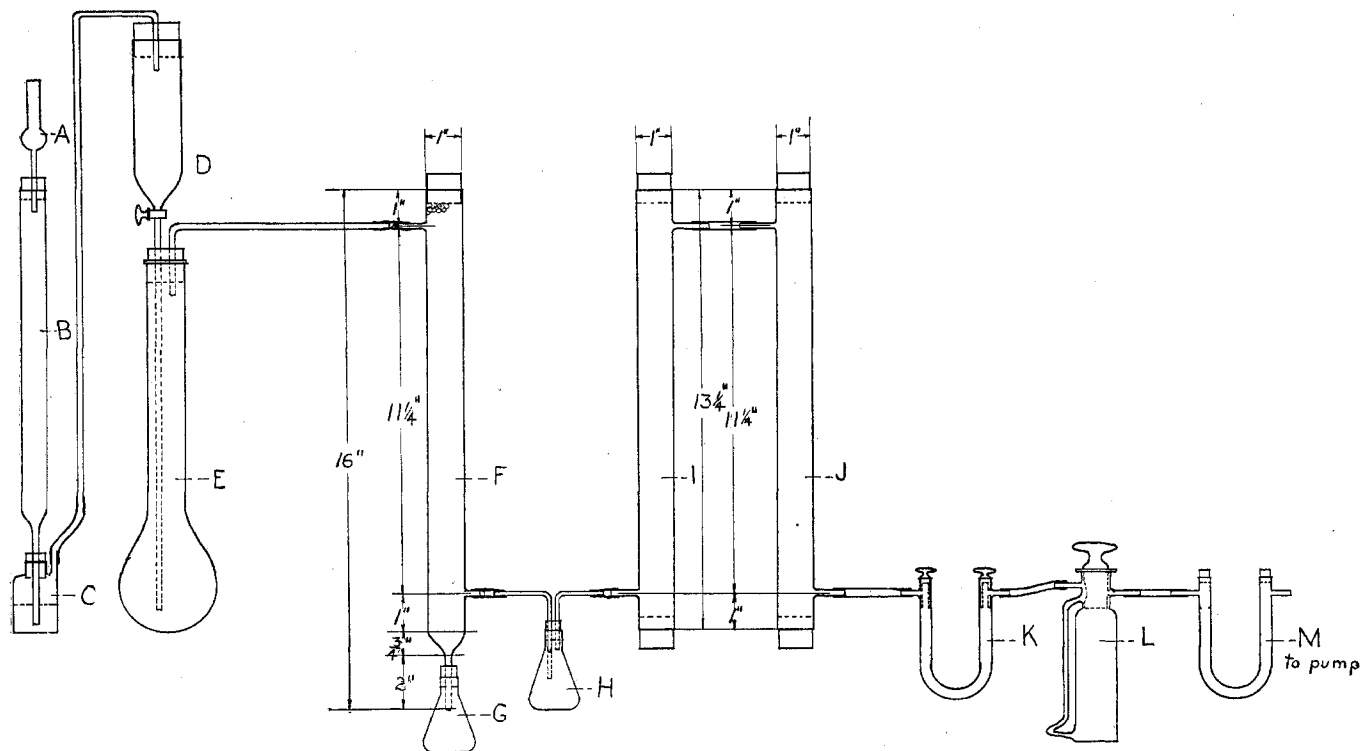


FIG. 1

required is about  $2\frac{1}{2}$  hrs., while the chief objection to the two latter methods lies in the use of barium hydroxide as an absorbent, the inherent difficulties in its protection from the carbon dioxide of the air and in the titration of the excess barium hydroxide. The work in hand requiring the determination of total carbon in a large number of soil samples, the author undertook to modify the apparatus usually used in the wet combustion method to the end that the carbon dioxide evolved might be absorbed in soda lime and thus determined gravimetrically and that the time might be so reduced that the determination could be rapidly as well as accurately made. It is believed that both of these objectives have been attained and that the method outlined below will serve as a practical working scheme for the determination of total carbon in soils or similar substances.

#### REAGENTS

The reagents used are essentially those given by Ames and Gaither,<sup>1</sup> except that the chromic acid solution contained 3.3 g. in 5 cc. of water. This amount of chromic acid, together with 50 cc. of sulfuric acid, were used for each combustion. It was found necessary to boil the chromic acid solution after the addition of a little sulfuric acid to expel any carbon dioxide which might be present.

#### APPARATUS

The form of apparatus finally adopted is essentially different from any proposed heretofore and for that reason will be taken up somewhat at length. The essential details are given in Fig. 1, although the apparatus may be arranged on the table in any manner which circumstances demand. As set up in this lab-

oratory, 4 units occupy less than 6 ft. of table space. The air enters the apparatus through A, which is simply a tube filled with calcium chloride. It next passes through a column of 30-mesh soda lime in B and a small volume of concentrated potassium hydroxide in C. This potassium hydroxide solution is the only liquid in the train and is in place simply as a means of keeping check on the rate of flow of air through the apparatus. The dropping funnel D holds the sulfuric acid before its introduction into the combustion flask E, which is a 300 cc. long-necked Kjeldahl flask. The rate of flow of air through the apparatus is regulated entirely by the stopcock shown as part of the dropping funnel. The first of a series of three scrubbers shown at F is filled with glass beads wet with sulfuric acid. This scrubber takes the place of a condenser usually employed as a part of the purifying train and under operating conditions removes most of the sulfur trioxide fumes which come over from the combustion flask E. The dilute sulfuric acid condensed in F is caught in a 100 cc. Erlenmeyer flask, G, with a second flask, H, of the same size serving to prevent any acid from getting into the scrubber shown at I, which is filled with 30-mesh zinc amalgamated with mercury. The trap H may be partially filled with a concentrated solution of silver sulfate if the scrubber I does not remove all the chlorine as well as sulfur trioxide fumes. It has been found necessary to renew the zinc after about 300 determinations and, if coarser pieces are used, it will be necessary to make the renewal at more frequent intervals. The upper half of J is filled with calcium chloride and the lower half with phosphoric anhydride, the two being separated by a layer of glass wool. The various materials in the three scrubbers are supported by layers

<sup>1</sup> THIS JOURNAL, 7 (1915), 561.

of glass wool extending above the lower inlet or outlet openings. The scrubbers themselves are simple in design and may be easily constructed by any glass blower. After leaving the scrubber, the air current, free from the last traces of sulfur trioxide and water, passes through the U-tube filled with calcium chloride and into the Nesbitt carbon combustion bulb<sup>1</sup> which is filled with 20- to 30-mesh soda lime, except for a small space at the top, which is occupied by a thin layer of phosphoric anhydride. The U-tube K is not a necessary part of the train if a glass stopcock is available, as its only use is to avoid any chance of a current of air passing in reverse direction through the apparatus while the combustion flask E is cooling. The U-tube M completes the train, being filled with calcium chloride and soda lime to avoid any possible contamination of the combustion bulb by stoppage of the pump. The whole system is connected with a suction pump, or any other means of pulling a current of air through the apparatus.

Before making any determinations, it is well to pass a current of carbon dioxide through the entire apparatus<sup>2</sup> to ensure the saturation of the calcium chloride with carbon dioxide. This is done with a piece of glass tubing replacing the combustion bulb L.

#### METHOD OF OPERATION

From 5 to 15 g. of soil are introduced into the combustion flask E, together with 5 cc. of the chromic acid solution. Fifty cc. of sulfuric acid are then run into the flask rapidly and the amount of air passing through the apparatus regulated by observing the rate of passage of the bubbles of air through the potassium hydroxide solution contained in C. A gas flame of a height which will ensure a boiling temperature of the mixture in the combustion flask within a time period of 5 min. is started as soon as all the acid has been run into the flask. Heating is continued for about 20 min., after which the combustion flask E is allowed to cool, aspiration being continued for 5 min. longer, however. The only operation remaining is to close and weigh the absorption bulb L. Aspiration should proceed throughout the entire time period at a rate which will ensure about 5 liters of air being drawn through the apparatus, but not so rapidly that the sulfur trioxide fumes will be carried over in excessive amounts.

In weighing the absorption bulbs, it is well to use a second bulb filled, like the first one, with soda lime, as a counter balance. This procedure renders insignificant errors in weighing, due to differences in the amount of moisture condensed on the surfaces of the bulbs. Under normal working conditions, it has been found possible to weigh with an average error of 0.0010 g. or, in terms of carbon, about 0.02 per cent. It is well to have two complete sets of bulbs so that it will not be necessary to make the weighings while the apparatus is idle. With two sets, it is possible to allow 20 min. after the determination is completed for the bulbs to cool and still have the weigh-

ings made and the bulbs ready for the next series of determinations. In this way the author has made 48 determinations in a day, using four units of the apparatus as shown in Fig. 1.

Whenever it becomes necessary the zinc, calcium chloride, or phosphoric anhydride may be easily removed from the scrubbers by simply removing the rubber stoppers at either end and pushing the material out. A scrubber may be easily renewed in 10 min. with a minimum danger of breakage as compared to the difficulties of renewal and danger of breakage of the U-tubes usually used in drying trains. With a soil containing one per cent of carbon, about 100 determinations may be made with a combustion bulb before the soda lime is exhausted. If desired, phosphoric acid may be used in the combustion chamber as proposed by Schollenberger.<sup>1</sup> If present in an amount greater than the limits of error for the total carbon, carbon in the carbonate form must be determined and subtracted from the figure obtained by above method.

#### ACCURACY

It is recognized that a method which sacrifices accuracy for a gain in time is of very questionable value. As stated above, the error in weighing the combustion bulb amounted to 0.02 per cent in terms of carbon. That the determination itself is subject to practically the same error is shown by the data given in Table I. Ten determinations are recorded, all made upon a sample of soil thoroughly mixed and ground. The maximum variation between any two determinations is 0.023 per cent, while the average variation is less than 0.010 per cent. The absolute accuracy of the determination for carbon on this particular sample was checked by P. L. Hibbard, using a modification of the method proposed by Ames and Gaither, his data agreeing with that in Table I, within the limits of error already given.

TABLE I

No.	Carbon Per cent	No.	Carbon Per cent
1.....	1.358	6.....	1.372
2.....	1.377	7.....	1.354
3.....	1.358	8.....	1.361
4.....	1.351	9.....	1.351
5.....	1.374	10.....	1.372

A series of ten determinations made in duplicate on two soils is given in Table II. These determinations are selected at random from 200 determinations run in duplicate in a study of field variability made upon these soils.

TABLE II

DAVIS SOIL		OAKLEY SOIL	
No.	Per cent Carbon	No.	Per cent Carbon
	I      II		I      II
1.....	1.168    1.167	6.....	0.624    0.641
2.....	0.883    0.910	7.....	0.179    0.178
3.....	1.186    1.210	8.....	0.355    0.382
4.....	1.125    1.120	9.....	0.279    0.311
5.....	1.025    1.044	10.....	0.420    0.442

It will be noted that the greatest difference between the duplicate determinations amounts to 0.027 and 0.032 per cent, respectively. These differences are somewhat greater than the error in weighing the combustion bulbs, but is regarded as an error due to sampling rather than in the method of making the determination.

<sup>1</sup> Made by Scientific Materials Co. Full directions for filling the bulb are furnished with the apparatus.

<sup>2</sup> *J. Am. Chem. Soc.*, **39** (1917), 2057.

<sup>3</sup> *THIS JOURNAL*, **8** (1916), 1126.

A sample of Merck's urea gave 20.28 per cent carbon against a calculated 19.99 per cent, while sucrose gave 41.98 per cent against a calculated 42.08 per cent. It is probable, as has already been noted by Salter,<sup>1</sup> that any oxides of nitrogen which may be formed are reduced in the zinc tube and hence are not a source of error in the determination.

## SUMMARY

A simple, inexpensive apparatus is here reported for the determination of carbon in soils and similar substances by the wet combustion method, using chromic and sulfuric acids. The total time for the determination is about 25 min. Data have been presented showing that the method as outlined is subject to errors of small magnitude.

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## EFFECT OF EXPOSURE ON RAW LINSEED OIL

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The most important property of linseed oil is that, when spread in thin layers and exposed to air, it absorbs oxygen and undergoes little-known changes in composition, yielding an elastic solid skin. This phenomenon is termed "drying" and on it depends the extensive industrial use of linseed oil in the manufacture of paint, varnish, linoleum, etc.

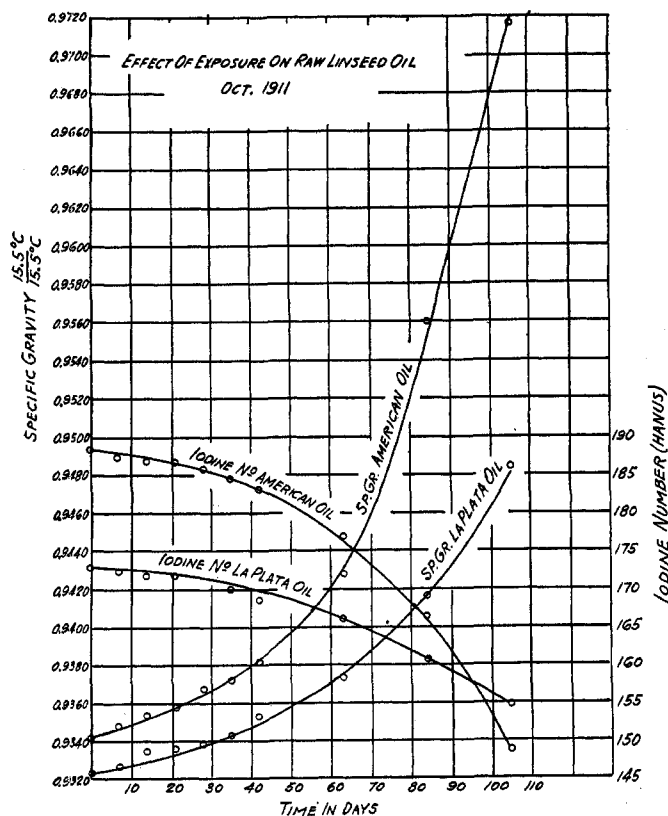


FIG. 1

The changes which take place in linseed oil when exposed to air have been studied by a number of in-

<sup>1</sup> THIS JOURNAL, 8 (1916), 637.

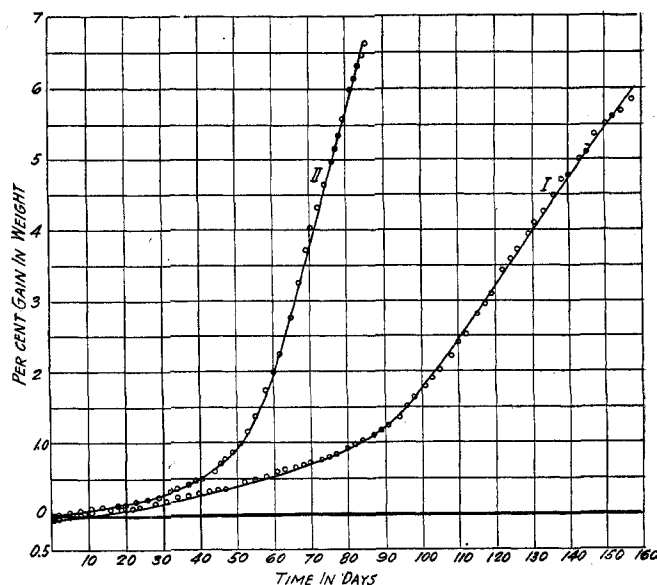


FIG. 2—EFFECT OF EXPOSURE ON RAW LINSEED OIL.

I = 0.95 Sq. Cm. Surface per Gram Oil

II = 2.00 Sq. Cm. Surface per Gram Oil

vestigators. Ballantyne<sup>1</sup> allowed linseed oil to stand in an uncorked bottle exposed to light. The oil was shaken daily and at intervals analyzed. Ballantyne found that under these conditions the iodine number decreased, while the specific gravity and acid number increased without a change in volume.

Sherman and Falk<sup>2</sup> studied the same question similarly and found a lower iodine number and higher specific gravity and a small increase in acidity. These authors found a 3.43 per cent increase in specific gravity calculated on the original weight, while elementary analysis showed that the oil had taken up 3.16 per cent oxygen. They concluded that the greater increase in specific gravity was probably due to a slight contraction in volume.

Sabin<sup>3</sup> exposed raw linseed oil in thin films for 8 mo. and found a specific gravity of 1.098 and a gain in weight of not more than 2 per cent. Assuming a specific gravity of 0.932 for the original oil, Friend<sup>4</sup> calculated a contraction in volume of 13.4 per cent for Sabin's film.

Thompson<sup>5</sup> exposed two varieties of raw linseed oil in thin films for 212 days and found

	Sp. Gr.	Gain in Wt. Per cent	Decrease in Vol. Per cent
North American Oil....	1.16	8.25	13.0
South American Oil....	1.15	7.70	12.4

Friend<sup>6</sup> oxidized raw Calcutta oil by passing air through the oil and by spreading in thin films on glass. He found that as the oil gained in weight the density increased, while the volume increased to a maximum and then slowly decreased.

Except for the determinations of Sabin, of Thompson, and of Friend, there are no data known to the writer

<sup>1</sup> J. Soc. Chem. Ind., 10 (1891), 29.

<sup>2</sup> J. Am. Chem. Soc., 25 (1903), 711; 27 (1905), 605.

<sup>3</sup> THIS JOURNAL, 3 (1911), 84.

<sup>4</sup> J. Chem. Soc., 111 (1917), 162.

<sup>5</sup> Trans. Am. Inst. of Chem. Eng., 8 (1915), 251.

<sup>6</sup> Loc. cit.