varies with the concentration of the solvents employed, the proportions of solvent to material extracted, and possibly other physico-chemical factors, the determination of ammonia nitrogen in hydrolyzed flour, flour extracts, and gluten should form a basis for a more exact knowledge of the proportions in which the various proteins occur in flours. Such methods are obviously unadapted to ordinary analytical use, but afford the best possible method of exact study and careful investigational work. For example, in Table II (3), the per cent of ammonia nitrogen yielded on hydrolysis of the extract with 1 per cent salt solution indicates clearly that protein other than albumin and globulin was extracted, since, as already pointed out, the per cent of ammonia nitrogen yielded by pure albumin and globulin should be lower. It is suggested also that to ascertain how much albumin and globulin are extracted by alcohol of any given percentage it should suffice to hydrolyze the alcoholic extract and determine the percentage of ammonia nitrogen in a similar manner.

Since this article has been in press, the results of a study of the purity of proteins extracted from flour by various solvents, using methods here indicated, have been published by Bailey and Blish.¹

In order to substantiate the evidence that there is a relation between the ammonia nitrogen yielded on hydrolysis of flour, and the total quantity of soluble proteins in the flours in question, the latter were extracted with tap water (since it was thought desirable to use the same solvent as was used in washing out the glutes) and the percentage of "soluble nitrogen" in the total nitrogen of the flour estimated in the extract. Although protein material other than globulin and albumin is extracted in this process, the results should be comparative, and in the order as indicated above, that is to say, the previously indicated relationship between ammonia nitrogen of the hydrolyzed entire flour and the soluble nitrogen should be apparent. That this is true is indicated by the results obtained, as shown in Table IV.

TABLE IV—COMPARISON OF PERCENTAGES OF SOLUBLE NITROGEN IN ENTIRE FLOUR WITH AMMONIA NITROGEN AFTER HYDROLYSIS OF ENTIRE FLOUR

Sample No.	TOTAL NITROGEN	Per cent of total N	
		Soluble N	Ammonia N
B444.....	2.55	15.68	23.00
B440.....	2.17	18.20	21.47
B439.....	1.928	18.67	21.01
B401.....	2.085	18.94	20.81
B452.....	1.917	19.55	19.87
B441.....	2.130	20.42	21.03
B438.....	1.67	26.86	18.85
B445.....	1.26	28.96	18.21

Inspection of Table IV shows that, with the single exception of B441, as the percentage of ammonia nitrogen increases, the percentage of soluble nitrogen decreases, as was expected from the theoretical considerations already discussed.

CONCLUSIONS

I—The individual proteins of strong and weak flours are identical in their chemical constitution, as determined by Van Slyke's method for the analysis of proteins.

[Since this went to press, the attention of the writer

¹ "Concerning the Identity of the Proteins Extracted from Wheat Flour by the Usual Solvents," *J. Biol. Chem.*, **23** (1915), 345-357.

was called to a study of some of the physical constants of gliadin from flours of varying strengths, by Gróh and Friedl,¹ in which they conclude that proteins of different flours have the same constitution.]

II—The ratio of gliadin to glutenin is much more nearly constant in flours of different baking qualities than has heretofore been supposed.

III—There is a far greater variation in the percentages of the so-called "soluble proteins" (albumin and globulin) in flours.

IV—Since the various proteins in the same flour differ widely in their content of ammonia nitrogen, the determination of ammonia nitrogen in flours, in extracts of flours made with various solvents, and in the crude gluten of flours, after their previous complete hydrolysis with strong mineral acid, can be made to serve as an accurate indication of the amounts of the various proteins present, since the proteins of widely different flours have been shown to have the same chemical constitution.

Acknowledgment and sincere thanks are herewith extended to Professor R. W. Thatcher under whose supervision this work was done, also to Dr. R. A. Gortner and Professor C. H. Bailey for many valuable and helpful suggestions.

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THE ANALYSIS OF MAPLE PRODUCTS, V

Miscellaneous Observations on Maple Syrup Incidental to a Search for New Methods of Detecting Adulteration²

By J. F. SNELL

Received August 20, 1915

In the course of a search for new and improved methods of detecting adulteration in maple syrup, the author and his associates have made a number of miscellaneous observations which may be suggestive or otherwise useful to other investigators in this line.

I—EFFECTS OF SOME REAGENTS

It is well known that lead subacetate produces a heavy precipitate in maple syrup and the normal acetate one not so heavy. In the "malic acid value" determination, alcohol and calcium chloride are employed together as precipitants. It appeared to the author not improbable that a systematic search would reveal other precipitating reagents whose behavior might prove equally useful in the examination of maple products. Mr. J. M. Scott made some desultory experiments in this direction and has recorded in his notes "indifferent" results with ether, zinc acetate, uranium acetate, cadmium chloride, bismuth nitrate, copper nitrate and cupric chloride. Mercuric acetate gave a flocculent precipitate which settled on standing and was light yellow in color. Silver nitrate in 50 per cent solution gave a white precipitate which darkened on standing. The author has also observed that barium salts give no precipitate in maple syrup although they do so in solutions of the

¹ *Biochem. Ztschr.*, **66** (1914), 154.

² Presented at the 51st Meeting of the American Chemical Society, Seattle, Aug. 31-Sept. 3, 1915. Previous papers of this series—*THIS JOURNAL*, **5** (1913), 740, 993; **6** (1914), 216, 301.

ash. Alcohol by itself gives a precipitate containing calcium, potassium and organic matter. By far the greater part of the total calcium and of the total potassium of the syrup are precipitated by the addition of a suitable quantity of alcohol. It was Mr. Scott's intention to investigate this alcohol precipitate further, but his removal to another position prevented his returning to the point.

II—EXPERIMENTS WITH SILVER NITRATE

Silver nitrate having been found to give a decided precipitate in maple syrup and none in a syrup made from white sugar, it was thought that a "silver number" might be determined by a method analogous to the Winton method with lead subacetate. Mr. Scott made a number of experiments towards this end. The idea was to add an excess of a standard solution of silver nitrate, filter off the precipitate, determine the residual silver volumetrically, and calculate from the results a "silver number" representing the quantity of silver precipitated by 100 grams of the syrup (or, alternatively, by 100 grams of the dry matter of the syrup). It was found, however, that the longer the solution containing the excess of silver was allowed to stand (and standing appeared to be necessary to allow the precipitate to collect) the lower was the quantity of residual silver. In other words, precipitation of silver continued during a period of several hours. For example, in one series of experiments 50 cc. *N/10* silver nitrate were added to 25 cc. syrup and the mixture made up to 100 cc. Filtered 20 cc. aliquots, taken, respectively, after 1, 2, 4 and 6 hours, required the following quantities of *N/10* sodium chloride to precipitate the residual silver: 8.00 cc., 7.55 cc., 7.40 cc. and 7.20 cc.

It is conceivable that a method using silver nitrate might be worked out, but obviously this circumstance of a slow reaction in the solution resulting in the precipitation of silver would have to be taken into account. The slow reaction would appear to be worthy of study also for its theoretical interest. Has it any connection with the darkening of the precipitate? Is it a reduction? What constituent of maple syrup is it which reacts thus with silver nitrate?

Some experiments with a *N/50* silver nitrate solution, made by Mr. N. C. MacFarlane, are reported in Sections V and VI below.

III—A LEAD SUBACETATE METHOD BASED ON THE WINTON AND CANADIAN METHODS

In Paper II of this series¹ reference was made to some experiments in which an endeavor was made to combine the advantages of the Canadian and the Winton methods of detecting adulteration of maple syrup by the use of lead subacetate.² The outcome of these experiments, made by Mr. Scott, was a method in which 25 grams syrup were treated with 10 cc.³ of lead subacetate solution of sp. gr. 1.25, enough water added to bring the volume to 100 cc. and, after

¹ Snell and Scott, *THIS JOURNAL* 5 (1913), 993.

² *Loc. cit.*, p. 996.

³ Experiments were also made with 15 cc. of the lead subacetate solution. The range of variation of the lead values so obtained was, however, 464 per cent of the minimum as compared with 200 per cent in the method with 10 cc.

standing three hours and filtering, a 10 cc. aliquot taken for determination of unprecipitated lead as in the Winton method. Comparison with a blank, using a syrup made from granulated sugar,¹ enabled one to calculate the amount of lead precipitated by 100 grams of the maple syrup. This quantity of lead was to be the "lead number" of the proposed method.

For comparison with the Canadian and Winton methods this proposed lead number was determined upon twenty of the syrups whose analysis was reported in Paper III²—*viz.*, ten of those which gave high, and ten of those which gave low, Canadian and "modified" Winton lead values.³ The values obtained by the projected method were in all instances lower than those given by the modified Winton method. The ranges of variation of the three lead numbers in these twenty syrups, expressed in percentage of the minimum, were found to be:

	Per cent
Canadian Lead Number	316(a)
Modified Winton Lead Number.....	190
Proposed Lead Number.....	200

(a) The syrup which gave the highest Canadian lead number was not included among the twenty. Hence the range of this value among the twenty syrups is a little smaller than that among the 126 reported in Paper III.

Inasmuch as the lead number determined by the original Winton method (using 25 grams syrup and not reducing to the dry basis) has a narrower general range of variation than the value obtained by reducing the results to the dry matter basis,⁴ it appeared not improbable that if the comparison were made between the *true* Winton and the proposed method, the advantage in favor of the former would be more considerable than that in favor of the modified Winton number. Determination of the true Winton number upon nine of the twenty syrups corroborated this conjecture, the ranges of the values among these nine syrups being as follows:

	Per cent of minimum
Canadian Lead Number	192
Modified Winton Lead Number.....	149
Proposed Lead Number.....	149
True Winton Lead Number.....	119(a)

(a) This is exactly the same range of variation as is shown in McGill's analysis of 47 samples (see Paper III, Table VI, *Loc. cit.*, p. 221). Bryan's results on 481 samples showed a range only slightly higher, *viz.*, 135 per cent (*Loc. cit.*). But if McGill's results and Bryan's are taken in conjunction, the true Winton value shows a range of 286 per cent of the minimum value. One cannot help suspecting, however, that there was some difference in manipulation in the two laboratories which resulted in the Canadian obtaining uniformly lower results than the American.

These results indicate that the proposed lead method, although having a decided advantage over the Canadian lead method in the matter of the range of the value in pure syrups would not be the equal of the Winton method in this respect.⁵

IV—FALLING OFF OF VALUE DUE TO DILUTION WITH SUCROSE

SYRUP—If the proposed new lead subacetate method proved to yield a value which shared with the Canadian

¹ *Loc. cit.*, p. 997.

² Snell and Scott, *THIS JOURNAL*, 6 (1914), 216.

³ Using the quantities of syrup containing 5 grams and 25 grams dry matter, respectively, as prescribed in the Canadian pure food standards.

⁴ See Table VI of Paper III, *Loc. cit.*, p. 221.

⁵ The author desires to reiterate his opinion that the original Winton method, without reduction to the dry basis, is better than any of the modifications of it which have been proposed. Comparison with a blank is, however, essential, and the suggestion is here repeated that a syrup made from (commercial) pure cane sugar be employed in the blank determination. See Paper II, *Loc. cit.*, p. 997.

lead value the advantage of falling off rapidly when the maple syrup is adulterated with a sucrose syrup of the same density, it might be worth recommending in spite of its apparent inferiority to the true Winton lead number in the matter of range of variation. The diminution of the new lead value was compared with that of the Canadian and true Winton values in three syrups, determinations of all three lead numbers being made on the pure syrups and on mixtures of each with sucrose syrup in such proportions as to give syrups containing 90, 80, 70, 50 and 30 per cent of maple syrup. In the first of the three syrups there was little choice among the three methods except in the mixture containing only 30 per cent of maple. For this mixture the Canadian lead value was only 18.7 per cent, the Winton value was 22.1, and the proposed lead number 33.4 per cent of the corresponding values for the pure maple syrup. In other words, the proposed lead method showed itself inferior to either of the old methods. In the other two syrups the proposed method showed a distinct advantage over the Winton method and for some of the mixtures appeared to be even slightly better than the Canadian method.

On the whole this projected lead value had compared sufficiently favorably with the established methods to justify further investigation, had we not hit upon another lead subacetate method which appears much superior to any hitherto proposed and which will form the subject of the next paper of this series.

V—LEAD CONTENT OF THE "CANADIAN LEAD" PRECIPITATE

Mr. J. M. Scott determined the quantity of lead in the Canadian lead precipitates from 8 samples of maple syrup, representing a wide range of Canadian lead number. The precipitate was washed as directed in the Canadian lead method, *i. e.*, four or five times with hot water. It was then dried, weighed and subsequently decomposed with aqua regia, after which the lead was converted into lead sulfate in the usual way and weighed as such. The results obtained are shown in Table I.

TABLE I—"CANADIAN LEAD" PRECIPITATES

No.	SOURCE OF SYRUP	DESCRIPTION	Canadian lead No.	Per cent Pb in ppt.
1	Canada	Composite of 54 syrups	3.44	69.41
2	Canada	Mixture of several syrups	4.40	70.11
3	Dutton, Ont.	Middle run, pan, white of egg	1.74	69.62
4	Brome, Que.	Early run, pan	2.86	68.66
5	Hillsburgh, Ont.	Early run, evaporator	2.01	68.51
6	Wardsville, Ont.	Early run, evaporator	2.33	68.50
7	Orangeville, Ont.	Middle run, evaporator, milk	5.08	68.25
8	Neustadt, Ont.	Early run, kettle, eggs	4.10	66.95
AVERAGE OF NUMBERS 3 TO 8,			3.02	68.415

The results indicate a fairly definite composition in the precipitate, the variation in lead content being just over 3 per cent of the total weight. There appears to be no definite relation between the quantities of precipitate yielded by the syrup (Canadian lead numbers) and the composition of the precipitates. In view of the fact that this precipitate has sometimes been erroneously assumed to consist of normal lead malate, it is worth noting that the latter salt in the anhydrous condition contains only 61.00 per cent of

lead. It is possible that a basic malate¹ may be the essential, or at all events an important, constituent of the precipitate, but evidence to that effect has not yet been adduced. It is our intention to make a study of the organic non-sugar constituents of maple syrup which will embrace a more complete analysis of the lead precipitate as well as of the other precipitates obtainable from maple syrup and not from syrups made from pure sucrose.

VI—ATTEMPTS TO DETERMINE INORGANIC CONSTITUENTS VOLUMETRICALLY

If among the non-sugar constituents of maple syrup one could be found showing a reasonable degree of constancy in all genuine syrups, a convenient method of determining that constituent would obviously constitute a useful method of detecting adulteration.² It appeared a possibility that among the inorganic constituents one might be found answering the requirements.

The recorded analyses of the ash of maple syrup and sugar are comparatively few and the only complete analyses known to the writer are those of Hortvet,³ embracing only two sugars and two syrups. The constituents which have been determined in a larger number of samples—*viz.*, potash, lime, phosphoric acid and sulfuric acid—all show very wide variations in individual syrups. Jones⁴ found the potash in a maple sugar ash as low as 18.26 per cent while Bryan⁵ obtained results in syrups ranging from 24.55 to 54.54. For lime Bryan obtained results running from 13.20 to 36.36; for phosphoric acid, 1.08 to 12.90; for sulfuric acid, 0.00 to 6.18 per cent. The results obtained by the other investigators all fall within the above limits. Mr. J. M. Scott in 1913 made complete analyses of the soluble and insoluble portions of the ash of a syrup compounded of about sixty genuine Canadian syrups. This analysis will probably be published in a future paper of this series dealing with the ash. From its data and the ratio of the soluble to the insoluble ash in the same composite syrup (which ratio happens to be unity) the composition of the total ash can be calculated.

It is as follows:

K ₂ O...	29.07	MgO....	2.34	CO ₂	33.75	SO ₃	1.37
Na ₂ O...	1.97	Fe ₂ O ₃ ...	1.82	SiO ₂	1.22	Cl.....	1.46
CaO...	25.88	Mn ₂ O ₄ ...	0.81	P ₂ O ₅	0.15	Insol. in HF...	0.17
TOTAL, after deducting oxygen-equivalent of the chlorine.....							99.68

It will be noted that the quantity of phosphoric acid found is only one-seventh of the minimum percentage hitherto reported, thus extending the range of variation for this constituent.

It is clear, then, that none of the four ash constituents which have been extensively studied is suitable

¹ Otto's basic lead malate (Liebig's *Ann.*, **127**, 177) contained 73.8 per cent of lead, while the salt he obtained by adding the neutralized or nearly neutralized acid to a boiling excess of lead acetate solution contained 75.83 per cent of lead in its anhydrous condition, which is equivalent to 73.5 per cent in the monohydrate, which Otto found to be stable at 100° C.

² According to Hortvet, the protein (N × 6.25) content is fairly constant and has some value in this direction. So far as the writer is aware, but little attention has been paid to this suggestion of Hortvet's.

³ Hortvet, *J. Am. Chem. Soc.*, **26** (1904), 1541.

⁴ Jones, Vermont Agr. Expt. Station, *18th Annual Report*, **1904-5**, p. 331.

⁵ Bryan, Bureau of Chem., U. S. Dept. Agr., *Bull.* **134**, pp. 82-89.

for our purpose. Magnesia shows less variability (2.34 to 4.65) in the five instances in which it has been determined, but no easy method of determining it in presence of the other constituents of the syrup suggests itself.

The fact that Hortvet found extremely small quantities of chlorine in the ashes he analyzed suggested that a chlorine determination might be useful, particularly in case raw cane sugar or refined molasses were employed in adulterating.¹

Mr. Scott's results, however, showing a very material chlorine content in a composite of so many samples, rather discouraged our hopes as to chlorine. Nevertheless, some experiments in titrating the diluted syrups with *N*/50 silver nitrate were made by Mr. N. C. MacFarlane. Quantities of syrup containing 10 grams of solid matter were treated with 200 cc. water, 10 cc. lead subacetate solution (sp. gr. 1.25) and 10 cc. saturated potassium chromate, the assumption being that the lead would precipitate the organic matter precipitable by silver and at the same time decolorize the liquid, thus enabling the potassium chromate left in solution to act as an indicator in the titration for chlorine. The precipitate was washed with hot water and the filtrate (including washings) titrated with *N*/50 silver nitrate. Nine genuine syrups took from 0.82 to 4.60 cc. of the silver nitrate. The same method, applied to 3 samples of raw cane sugar, gave 4.32, 5.14 and 9.08 as the number of cc. of silver nitrate required for 10 grams dry matter. A sample of beet sugar crystals gave 1.94 and a sample of cane molasses 51.99. The method, accordingly, offers little advantage except in the case of adulteration with molasses.

Experiments were also made in which the syrups were treated with alumina cream instead of lead subacetate. Syrup containing 10 g. solid matter was treated with 200 cc. water and 10 cc. alumina cream. The precipitate was washed with cold water and the filtrate and washings titrated with *N*/50 silver nitrate, using potassium chromate as indicator. The same nine pure syrups as before took 1.01 to 6.40 cc. of the silver nitrate solution. In 12 other genuine maple syrups results were obtained ranging from 2.80 to 8.38. The raw cane sugars took 9.85, 3.64 and 7.52 cc. respectively, the beet sugar 2.23 and the molasses 57.00. The results by the two methods did not run parallel. In general, more silver nitrate was required after the alumina cream than after the lead subacetate treatment, but there were exceptions to this rule.

In view of the probability that the phosphorus in maple syrup is largely in organic combination, it was thought that in spite of the wide variability of the phosphoric acid content of the ash, the amount of phosphorus in the syrup itself precipitable by uranyl acetate might prove to be reasonably constant. Mr. MacFarlane made some titrations which appeared to indicate a fair degree of constancy in this value in the same nine syrups as were used in his experiments with silver nitrate. The results obtained with the

¹ Practical men in Canada appear to be of the opinion that raw sugars or molasses are not commonly used as adulterants, but I have not thought it advisable to ignore the possibility.

raw sugars, however, were very similar to those with the maple syrups. It is doubtful whether the method employed—titration of 20 cc. syrup with a uranyl acetate solution of which 1 cc. is equivalent to 5 mg. of P_2O_5 —was suitable for the measurement of such small quantities of phosphoric acid and it is possible that further investigation along this line might be useful.

VII—ELECTROTITRIMETRIC EXPERIMENTS

The interesting paper of F. H. Hesselink van Suchtelen and Arao Itano,¹ pointing out that measurements of electrical resistance might be employed for the detection of the end-point in precipitation titrations, suggested to us that we might titrate syrups with silver nitrate without previous treatment with lead subacetate or alumina cream, using the electrical resistance as indicator in place of potassium chromate. It was, indeed, found possible to get a definite end-point in this way—indicated by a break in the curve on the plot of electrical resistance with volume of silver nitrate added: 3 cc. syrup were diluted to 30 cc. and *N*/50 silver nitrate added from a burette, the electrical resistance being measured with a dip electrode after the addition of each cc. of the reagent. Fifteen genuine syrups gave end-points at 0.20 to 1.95 cc. silver nitrate. The range of variation is, therefore, too wide to render the method useful.

Similar experiments were made with *N*/10 barium nitrate solution. With this reagent, as might be anticipated from the fact that no precipitate is produced, the resistance-volume curves showed no break.

It then occurred to us that the electrical resistance might be employed to detect the end-point in a titration with lead subacetate solution. Mr. MacFarlane, who had conducted the experiments reported above, made a number of experiments in this line, finally adopting a procedure in which a solution of lead subacetate prepared by diluting a solution of sp. gr. 1.246 (at 15° C.) with ten times its volume of water² was added from a burette to 3 cc. syrup diluted to 30 cc. This method applied to 14 samples of pure syrup gave results varying from 4.5 to 6.8 cc. of the lead subacetate solution—a range of 51 per cent. Later Mr. G. J. Van Zoeren applied this method to 24 syrups of the season of 1915, obtaining results ranging from 4.0 to 5.4. The total range among the 38 syrups is, accordingly, 70 per cent of the minimum.

The dip electrode used in the above experiments was of one of the common forms made for use with poor conductors.³ A new electrode was designed by Mr. Van Zoeren which can be used for both the conductivity test described in Paper I of this series and the volumetric lead subacetate test to be described in Paper VI. A description of this electrode will be published in the *Journal of the American Chemical Society*.

The new electrode being larger than that previously used it became necessary to employ a larger volume of liquid than Mr. MacFarlane had used: 60 cc. were

¹ van Suchtelen and Itano, *J. Am. Chem. Soc.*, **36** (1914), 1793.

² This solution has a density of 1.025.

³ Baird and Tatlock's Catalogue, 1914, No. 5313T.

found to be a suitable quantity of the diluted syrup for the purpose. Experiments were then made in which the concentration of the syrup and subacetate solutions were varied. The results are shown in Table II. The procedure adopted on the basis of these experiments will be described in the next paper. Applied to the same 24 syrups of the season of 1915 as were tested by Mr. MacFarlane's procedure, the Van Zoeren procedure gave results ranging from 4.8 to 6.0. This range amounts to 22 per cent of the mean (5.55) or 25 per cent of the minimum as against 30 per cent of the mean (4.70) or 35 per cent of the minimum for the MacFarlane procedure.

TABLE II—TITRAMETRIC EXPERIMENTS WITH LEAD SUBACETATE

Density of subacetate solution	Cc. syrup diluted to 100 cc.	No. of syrups tested	Range of lead numbers	
			Actual	In per cent of minimum
1.050	10	6	No definite breaks	
	15	23	2.5-4.5	80
	20	8	2.4-4.7	96
1.033	5	16	In 5 instances no breaks	
	8	12	4.0-5.9	41
	10	16	4.7-6.5	38

SUMMARY

1—Silver nitrate added to maple syrup gives a white precipitate which darkens on standing. The precipitation of silver continues during a period of several hours.

2—Mercuric acetate added to maple syrup produces a light yellow precipitate.

3—Alcohol produces a precipitate containing most of the calcium and potassium.

4—A moderately successful attempt was made to combine the advantages of the Winton and Canadian lead subacetate methods.

5—The Canadian lead precipitates from six syrups showed a lead content of 66.95 to 69.62 per cent; average, 68.42. The precipitate from a composite of 54 syrups contained 69.41 per cent of lead, while that from another mixed syrup contained 70.11 per cent.

6—Titration of maple syrup with *N*/50 silver nitrate (1) directly, using electrical resistance measurements to detect the end-point, (2) after treatment with lead subacetate or alumina cream, using potassium chromate as indicator, yielded definite but not useful results.

7—Titration with uranyl acetate gave no useful results.

8—Titration with lead subacetate solutions using electrical resistance as indicator led to a useful method of testing the syrup for purity, which is described in the next paper of the series.

9—A complete analysis of the ash of a composite of about sixty genuine syrups shows more chlorine and less phosphoric acid than the analyses previously recorded.

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A COMPARISON OF METHODS FOR THE DETERMINATION OF SOIL PHOSPHORUS

By W. O. ROBINSON

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Hillebrand¹ outlines the main points of this determination in the following statement: "It is some-

¹ U. S. Geol. Survey, *Bull.* 422 (1910), 144.

times possible to extract all the phosphorus from a rock by simple digestion with nitric acid, but quite as often if not oftener this fails; hence the necessity of resorting to one of the longer methods of extraction * * *. Whatever method is used, great care is required to secure accurate results." This statement applies to soils with the further complication that organic matter is invariably present, sometimes in amounts large enough to require special treatment.

METHODS OF SOLUTION OF THE SOIL

Washington¹ and Fry² have called attention to the presence of apatite inclusions in quartz as affecting the determination of phosphoric acid. Protected in this way the apatite would not, of course, be soluble in acids other than hydrofluoric. Further, there are many phosphate minerals such as variscite, wavellite, and xenotime, which, from the standpoint of determinative mineralogy, are classed as insoluble in acids. These minerals have not been reported as occurring in soils, but there is a possibility of it. Fry³ cites a number of analyses showing that in most cases the total phosphoric acid is not dissolved by acid digestion: from 4 to 100 per cent is extracted. Obviously a method of simple acid digestion will not be generally reliable when applied to soils.

FISCHER'S METHOD—Fischer,⁴ however, has modified an acid digestion method so that it appears to extract the entire amount of phosphorus. The salient feature of this process is an intervening ignition between two acid treatments. Briefly the procedure is as follows: 5-10 grams of soil are treated with 50 cc. of *aqua regia* in a covered quartz dish of appropriate capacity. After the action has ceased the cover is removed and the mass evaporated to dryness. It is then ignited (ostensibly long enough to destroy organic matter) and again treated with *aqua regia*, evaporated to dryness and taken up with nitric acid. Fischer claims that the process gives slightly higher results than the fusion method,⁵ though he proves there is an almost negligible amount of phosphorus left in the insoluble residue. He points out that a larger sample can be conveniently used with his method than with the fusion method, thereby securing a fairer sample of the soil. The author has tested this method on a variety of soils. The samples were well ground and mixed so that but one gram was employed in each case. After the second *aqua regia* treatment, the mass was evaporated once with nitric acid, heated on the hot plate to browning to dehydrate the silica, then taken up with the requisite amount of nitric acid. The results, and for comparison, those obtained by other methods, are given in Table I.

Fair agreement is shown, considering the determina-

¹ "The Chemical Analysis of Rocks," Wiley & Sons, New York (1910), p. 162.

² THIS JOURNAL, 5 (1913), 664.

³ *Loc. cit.*

⁴ *Intern. Mitt. f. Bodenkunde*, 2 (1913), 541.

⁵ Probably due to the difficulty of precipitating small amounts of ammonium phosphomolybdate in presence of much NaNO_3 in the fusion method since Cain and Hostetter [*J. Soc. Chem. Ind.*, 4 (1912), 250] have shown that aqueous solutions of NaNO_3 have a strong solvent effect on the phosphomolybdate when vanadium is present.