

between the different parts of a single plant. These differences have been pointed out by Balch.¹

Phosphorus.—Phosphorus was determined by the official method proposed for the determination of that element in organic substances. The results obtained are given in the following table:

TABLE II.—ANALYSES BY J. A. CULLEN.

No.	Serial No.	Name of Kelp.	Location.	P ₂ O ₅ . Per cent.
1	R 1	<i>Nereocystis luetkeana</i>	San Juan Co., Wash.	0.70
2	R 16	<i>Egregia menziesii</i>	"	1.79
3	R 27	<i>Postelsia palmaeformis</i>	Neah Bay, Wash.	1.04
4	R 28	<i>Macrocystis pyrifera</i>	"	0.81
5	M 2	<i>Macrocystis pyrifera</i>	Monterey Bay, Cal.	1.84
6	M 9	<i>Nereocystis luetkeana</i>	Point Pinos, Cal.	0.83
7	S 10	<i>Macrocystis pyrifera</i>	St. Naples, Cal.	0.66
8	S 15	<i>Macrocystis pyrifera</i>	San Miguel, Cuyler Cove, Cal.	0.71
9	S 17 B	<i>Pelagophycus porra</i>	St. Nicholas, Cal.	0.51

Sulfur.—Sulfur was determined as barium sulfate in the lixiviate of the charred kelp and ash combined. The char from two-gram samples was lixiviated in the manner described in a foregoing paragraph and then burned to whiteness. The ash was dissolved in hydrochloric acid and the resulting solution evaporated to dryness to dehydrate silicic acid. The residue was taken up with acid, the solution filtered and the filtrate added to the lixiviate from the char. Sulfuric acid was determined in the combined solution in the usual way. The results are recorded in the following table:

TABLE III.

No.	Serial No.	Name of Kelp.	Source.	SO ₃ . Per cent.
1	R 6	<i>Nereocystis luetkeana</i>	San Juan Co., Wash.	1.68
2	R 29	<i>Macrocystis pyrifera</i>	Neah Bay, Wash.	2.24
3	M 4	<i>Macrocystis pyrifera</i>	Off Pt. Aulon, Cal.	2.42
4	M 12	<i>Nereocystis luetkeana</i>	Off Pt. Pinos, Cal.	1.08
5	S 14	<i>Macrocystis pyrifera</i>	Santa Cruz, Gull Is.	3.45
6	S 20 A	<i>Pelagophycus porra</i>	Clemente, Smugglers Cove, Cal.	2.33

Organic Constituents.—Little or nothing is known concerning the organic constituents of the Pacific kelps. From the figures in Table I, it can be seen that the organic matter in them rarely falls below 50 per cent. or exceeds 75 per cent. On the average they contain about 1.5 per cent. of nitrogen which, if calculated to protein by the usual factor, is equivalent to 9.4 per cent. protein. This value is about equal to that of other sea weeds examined for that constituent.

Our knowledge concerning the organic constituents of sea algae in general, from which we may derive some idea of what may occur in the Pacific kelps, may be summed up thus: The simple sugars have been identified in certain algae, but they are of rare and scanty occurrence; starch has been said to occur in some varieties, but its identification has not been substantiated; mannan and levulose are of rare occurrence; galactan is common and abundant, and pentosan is the most abundant of all.

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¹ Loc. cit.

A NOTE ON THE DETERMINATION OF IODIDES BY DIRECT TITRATION.¹

By J. W. TURRENTINE.

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Bray and MacKay² have described a method for the determination of iodides in the presence of bromides and chlorides wherein the iodine is liberated from the iodides by standardized potassium permanganate, added titrimetrically, and is extracted as formed by shaking with successive portions of carbon tetrachloride. When the last of the iodine has been set free, the carbon tetrachloride extract is run off from the supernatant aqueous layer and is shaken with a solution of potassium iodide for the extraction of the iodine. The potassium iodide extract is titrated in the usual way with standard thiosulfate solution.

In the analysis of kelps for iodine a method was sought which would admit of the determination of small amounts of iodide with the minimum expenditure of time. For this purpose the initial liberation of the iodine was effected by standardized potassium permanganate and the amount of iodide thereby determined. The method then became strictly a direct titration of iodide in the presence of bromide and chloride. The results obtained were satisfactorily consistent, and the rapidity with which determinations could be made by means of it was such that this account of the method is deemed warranted.

The permanganate solution was standardized against solutions of potassium iodide of known concentration (1.0 g. KI to 1000 cc. H₂O), the iodide of which had been purified by recrystallization and thorough drying.

Portions of the standard iodide solution were transferred, in graduated pipets, to a 250 cc. dropping funnel; 15 cc. of sulphuric acid solution (10 cc. conc. H₂SO₄ to 90 cc. H₂O) and 15 cc. of carbon tetrachloride were added. For the removal of reducing agents, the carbon tetrachloride had been treated for several hours with iodine which was subsequently removed by shaking with sodium thiosulfate solution.

The solution of the permanganate was run in from a burette, and as the titration proceeded the liberated iodine was removed from the aqueous layer by shaking. With the decrease in the concentration of the iodide in this layer, the solubility of the iodine therein decreased, until, as the end of the titration was approached, the solution became entirely colorless. The persistence for one minute of the pink color of the permanganate was taken as the end point. The procedure was identical with that observed in the actual analysis.

At first the color of the carbon tetrachloride layer caused some trouble in discerning the end point, but with experience the trouble disappeared.

Bray and MacKay have pointed out that in the direct titration of iodides by a permanganate solution there is an error introduced by the incomplete reduction of the last of the permanganate to a form intermediate between the heptavalent and the divalent condition. This would appear to be due to the de-

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² J. Am. Chem. Soc., 32, 1193 (1910).

crease in the active mass of the iodide, since it is not observable in the presence of an excess of that substance. For a definite amount of the permanganate, then, the intermediate form of the manganese should not be present in the solution until after the iodide had been reduced to a definite concentration. When the concentration of the former is very low (as is normally the case as the end of the titration is approached), that of the iodide likewise would be very low before the reaction leading to the formation of the intermediate manganese compound appeared. In the titration, accordingly, the incomplete reduction does not occur until a definite and very low concentration of the iodide is reached. This point, it follows—since the reaction is irreversible—must be independent of the original active mass of the iodide. For that reason the error should be a constant rather than a variable one; and if the latter, certainly a correction could be introduced whereby it would be neutralized.

It was observed that values obtained for small amounts of iodide undergoing titration were relatively greater than those obtained for larger amounts. When the blank solutions were titrated in the absence of the iodide, it was found that a small amount of the permanganate (0.2 cc.) was reduced. As this was not observable in the absence of the carbon tetrachloride, the reduction of the permanganate was attributed to the carbon tetrachloride, or to some constituent thereof. When a correction was made for this error the values obtained from the titration of the various volumes of standard iodide were found to be concordant within the probable error of experimentation. These values are given in the following table:

No.	Cc. KI.	Cc. KMnO_4 corrected.	KI value per cc. KMnO_4 corrected.
1	10	1.6	0.00625
2	10	1.6	0.00625
3	10	1.55	0.00645
4	10	1.5	0.00666
5	10	1.6	0.00625
6	10	1.55	0.00645
7	20	3.2	0.00625
8	20	3.2	0.00625
9	20	3.3	0.00606
10	25	4.05	0.00617
11	40	6.55	0.00611
12	40	6.5	0.00615
13	40	6.5	0.00615
14	100	16.5	0.00602

Mean, 0.00624

The range in values in iodide of the solutions titrated in the standardization was the same as that which was expected to be found in the substances to be analyzed. For that reason they cover only a small range. Whether the method is applicable to the determination of larger amounts of iodide can not be said, but *a priori* considerations indicate that it may be employed. It should only be necessary to remove the iodide with successive portions of carbon tetrachloride in order that that layer might not become too concentrated in iodine. Whether new corrections would have to be introduced or not could be determined experimentally.

The permanganate solution was standardized with

solutions containing no chlorides or bromides, while the solutions analyzed contained large amounts of chlorides and presumably some bromides. Bromides in small amounts are commonly found among the saline constituents of sea algae. Whether they were present in the specimens analyzed has not been determined. In this particular, then, the conditions existing during the standardization were not strictly reproduced in the analysis. However, the authors whose method is here applied have explained the conditions under which chlorides and bromides are liable to introduce an error in the determination of iodide and, it is believed, those conditions were strictly observed in the adaptation of the method to the analysis of kelps.

It is a truism that any titration method is reliable in which the solutions employed are standardized against the compound which is to be determined, provided the standardization and the analyses be made under identical conditions.

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DETERMINATION OF TOTAL POTASSIUM IN MINERALS.

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In very many instances only the percentage of potassium in a sample is required to be determined, while the amount of sodium present is a matter of indifference. In such cases, the method of J. Lawrence Smith is long and tedious; the modification of Smith's method, described by Pettit and Ystgard in *Proceedings of the Association of Official Agricultural Chemists* (1906), while shorter, leaves much to be desired. It has the disadvantage that a large amount of an alkaline solution must be evaporated in glass, with the attendant liability of contamination. The calcium carbonate which separates during this evaporation is non-crystalline, adherent, and difficult to wash. Even after filtration, much silica remains in the solution, causing trouble in later operations. In order to overcome these difficulties, and, if possible, to further shorten the time required for a determination, the following method was worked out in this laboratory:

Proceed as in the regular Smith method for total alkalies, until the filtrate from washing out the alkalies from the fusion is obtained. To this add a moderate excess of hydrochloric acid and evaporate to dryness on a steam bath, remote from ammonia fumes. Take up with about 2 cc. of concentrated hydrochloric acid and 25 cc. of hot water, and filter through a special suction filter into a 150 cc. beaker, washing the large beaker and filter well. Add the proper amount of hydrochloroplatinic acid solution, and evaporate on steam bath until of a semi-solid consistency. The large amount of calcium chloride present crystallizes out on cooling, but is readily soluble in acidulated alcohol. The crystalline precipitate of the potassium chloroplatinate is washed with acidulated alcohol,¹ Gladding wash, and 80 per cent. alcohol, on a filter designed especially for this work. After drying to re-

¹ *Jour. Am. Chem. Soc.*, 20, 341.