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ORIGINAL PAPERS.

ON THE CHEMISTRY OF CERTAIN ALGAE OF THE PACIFIC COAST.

By DAVID M. BALCH, S.B. HARV. Received September 13, 1909.

Like most sea-washed regions throughout the world, our Pacific Coast produces many algae peculiar to itself, and some that are more cosmopolitan in character. Some of these are gigantic in size and pelagic as to locality, covering the ocean at about the ro-r2 fathom line with dense fields of their floating foliage. Others, of far lesser growth, are littoral, forming in favored localities a dense fringe at about the limit of extreme low tide, and even beneath tidal fluctuations.

It is my purpose in the following pages—after a brief description of some of the most prominent species and varieties, together with their habitat, range, character and general features—to present numerous analyses of the inorganic constit-

uents of each at different stages of their development, and in some instances of different members of each, with remarks on some unexpected results of these researches. Then will follow a dissertation on the economic value of certain of the huge Laminariaceae, and on measures proposed for the exploitation of our marine forests and the utilization of their products for the needs of commerce. The case of kelp versus wood as material for distillation will be argued at some length. Also the relative advantages, and disadvantages, that govern the winning of potassium from its ocean sourcesunlimited in abundance and ceaselessly renewedand the exploitation by mining of its terrestrial deposits, which, in certain localities, seem also almost inexhaustible.

A peculiar and most interesting sea-weed, Nereocystis, is found in favorable localities all along the western coast of North America, from warm temperature to subarctic regions. Point Conception, Calif., may be regarded as the boundary roughly separating the southern from the northern species; for, although the species overlap in the Santa Barbara Channel, and the northern species may possibly occur even further south, it does not appear that the southern species has been recognized north of Point Conception.

Whether this plant is an annual or a biennial has been matter for debate, but the question seems merely one of definition; there can be no seasons proper at the bottom of the sea. Commencing life late in the autumn, it perfects itself in the following year, the southern species demanding about 12 months, and the northern about 15 months for its life work. Consequently, it is a plant of very rapid growth, its huge bulk and abundant store of alkaline salts being the product of little more than a single year.

I. Nereocystis gigantea—now better known as Pelagophycus Porra Setchell—is the southern species. Taking San Diego Bay as a center, this plant is fairly abundant for a hundred miles both north and south. Its northern limit has been stated above; its southern is uncertain. It is reported on good authority as growing in company with Macrocystis pyrifera—they usually occur associated—at Magdalena Bay, some 500 miles south of San Diego; it probably grows in localities favoring its increase at many intermediate points.

This plant is popularly known as the "Elk Kelp," from the fact that as it lies stranded on a beach and robbed of its leaves by the action of the surf, the incurved arms garnished with the stout, spiky bases of the petioles, strongly remind one of spreading antlers.

(The accompanying illustration, from a mediumsized specimen in a nearly perfect condition, fairly represents its peculiar form.)

It grows about the 10–12 fathom line from loose rocks, or sunken reefs. When full grown it may consist of a solid cylindrical stem some 60 feet in length by one-half inch in diameter, which, starting from the small, highly-branched holdfast that attaches the plant to its base, abruptly expands near its terminus into a hollow cylindrical slightly



conical tube-named the apophysis-which may exceed 6 feet in length by 3 inches in diameterseparated by a sharp choke, or constriction, from a nearly spherical bladder, which rarely exceeds 8 inches in diameter. No true proportion exists between bladder and apophysis-either may be overdeveloped; they are connected by a short and very narrow internal canal. From a common point at the apex of the bladder issue at nearly right angles two opposite horizontal arms, several feet in length, solid, distinctly flattened, and bearing along their upper edge the petioles of the leaves. The petioles, about six in number for each arm of a mature plant, and separated irregularly by intervals of several inches, are stout at the base but quickly become rounded and very slender; they

average 6 or 8 inches in length; each petiole carries a single leaf, but as the petioles are frequently cleft, or divided, near the base, any base may carry two leaves-possibly more. Very rarely specimens have been observed in which the petioles issue alternately from the upper and lower edge of the arm. The leaves differ in shape, size, and texture; these variations may be governed by the progress of their development. The plant as stranded rarely bears even remnants of its immense fronds; or, if the petioles be strong enough to stand the strain, only a few inches of their thick leathery bases-all else has been removed by the surf. The perfect leaves may reach 15 feet or more in length by 20 inches in diameter; they are cuneate at the base, ruffled at the edges, sometimes roughened on the surface by slight spiny projections; often smooth, glossy, and nearly transparent; their color is a rich vellowish brown; the texture sometimes very brittle and flimsy, sometimes comparatively tough. The fluorescence (or sori) occurs in broad dark patches on the leaves.

So much for the mature plant. The infant specimens consist simply of a spherical bladder about 3/4 inch in diameter, crowned by two opposite, short oval leaves, and having a very slender, thread-like stem a few inches in length, terminated by a very small and delicate holdfast; apophysis and arms do not seem to be present even in a rudimentary form. How this fragile little plant can germinate, anchor itself, and grow in the ocean depths, 70 feet beneath the surface, is an interesting matter for consideration. When the bladder has grown to a diameter of about $1^{1}/_{2}$ inches the development of its arms is in progress and consists at first of one petiole each with a terminal leaf; their development progresses by fissure of the terminal. The bladder may reach 3 inches in diameter before the apophysis-which is merely a modified form of the bladder, and serves the same purpose, i. e., to keep the plant upright-is much in evidence; then it increases rapidly in size as the needs of the plant demand.

Pelagophycus contains very little cellulose as woody fiber; the bulk of the plant is composed of sound fleshy cellular tissue saturated with saline solutions, and protected by a thin, glossy external bark, or varnish. Approximately some 90 per cent. of its weight is water. When exposed to the sun and wind the plant dries rapidly; the beautiful leaves, after a few hours' exposure, resemble greenish gray tissue paper; stem and arms dry more

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slowly but are finally converted into a horny substance, very tough and elastic, and not easily broken across or crushed into pieces. The bladder and apophysis contain no liquid in their cavities; owing to the thickness—from 1/2 to 3/4 of an inch—of their fleshy walls they dry slowly, unless split longitudinally or quartered. When the drying has reached a certain stage these parts become covered with a very heavy saline efflorescence, and to such an extent that when bladders from small plants are dried entire nearly 50 per cent. of the salts they contain are thus exuded. With the stem and arms this efflorescence is much less.

* * * * *

In the following studies of the inorganic constituents of algae, specimens were collected at different stages of growth, and in different seasons of the year. They were dried by exposure to sun and wind until efflorescence commenced, then under glass, and finished at 125° C. A weighed portion was then charred, the char exhausted, and the lixiviate brought to a known bulk in centimeters. From this, measured portions were taken for analysis.

I. Pelagophycus Porra (collected in January, 1905), at a very early stage of growth when the plants lacked apophysis, and in many cases arms.

EXPERIMENT I.

Bladders eutire from $1^{1}/_{2}$ to $2^{1}/_{2}$ inches in diameter were sun-dried under glass; efflorescence was very copious, light and flocculent. They were then broken up, the salts separated by sifting, and drying finished at 125° C. A quantity weighing 1500 grams, was then charred with proper precautions; the char, 939 grams, was packed in a percolator and exhausted with hot water. 2000 cc. extracted 593.5 grams of salts; 1000 cc. additional 114.6 grams; 500 cc. additional 5.7 grams; 250 cc. additional 1.2 grams. The lixiviates, colorless and odorless, were brought to 3750 cc. and were found to contain 715 grams of anhydrous salts. Measured portions were taken for analysis:



K was det. by platinum-Na by difference.

To the above 1500 grams belong the effloresced salts shaken from it. This was lightly charred to separate a little organic matter, dissolved in water, filtered from a little mechanically mixed sand, and solution brought to 2250 cc. This contained 601 grams of anhydrous salts.

			Per cent.
A The second	003	equals	0.030
Analysis 2	SO4	49	0.097
	CI		47.850

These effloresced salts are nearly C. P. potassium chloride. This most interesting and unexpected result will be considered at length further on.

To determine, then, the constituents of the alkaline salts of the young bladders of the Pelagophycus the above solutions were mixed in proper proportion and 7.92 grams of the resulting salts analyzed as follows:

			Per ces	nt.	
	CO3 equal	15	0.57		
Analysis 3	SO4 **	**********	0.67		
	K "		40.91	(by platinum)	
KCl, with a little sulphate, 78 per cent.					
NaCl, with	a little ci	ubonate, 22 per	cent.		

Consequently, our 2100 grams of dried bladders have given us 1316 grams (62.67 per cent.) of alkaline salts, of which 78 per cent. (1026 grams) is anhydrous potassium chloride. This equals 48.85 per cent. of the raw material. A large trace of iodine—about 0.1 of one per cent.—is also present.

EXPERIMENT II.

The material used for Exp. I, as above stated, came from very young plants. We will now examine the salts yielded by the bladder, 8 inches in diameter, and the apophysis of a large and mature plant, collected Oct. 1, 1907. Cut into slices and dried under glass; efflorescence not flocculent, but crusty—like candied fruit—and somewhat discolored. Salts were removed by light pounding; both salts and residue were dried at 125° C.; they weighed respectively 92 and 315 grams (407 grams of dry material). This was charred and lixiviated as usual and gave 243 grams of anhydrous salts, or 60 per cent. of the material.

The effloresced salts agree closely with Exp. I.

			Per cent.
	1003	equals	. a trace
Analysis 4	SO4		. 0.79
	CI		. 47.21
	K		. 51.62
KCI, 98.72	per	cent. by platinum.	

Here again we have nearly pure potassium chloride.

A sample of salts obtained by evaporating the mixed lixiviates gave:

		Per cent
Analysis 5	(CO ₃	1.07
	{ SO4	1.68
	C1	47.06

The ratio of KCl to NaCl was found to be as 80 is to 20. Consequently, the 407 grams of material, which gave 243 grams of crude salts, will yield 47.76 per cent. of potassium chloride. Agrees closely with results obtained in Exp. I.

EXPERIMENT III.

Branches.—From a large plant, solid flattened stems having petioles, and small portions of the tough bases of the leaves still attached. Material dried at 125° C. equals 210 grams. Charred and lixiviated as usual gave 104.7 grams salts.

	Γ	er cent
Analysis 6	(CO3 equals	0.92
	(so, "	3.60

As we approach the leaves the percentage of sulphates augments, and we find iodine also increasing. In the salts from bladder and apophysis iodine rarely exceeds 0.1 of one per cent. In the salts from the arms we find 0.328 per cent. Alkaline chlorides are closely as in the preceding analyses. We have then from the arms of the plant 50 per cent. of their weight in crude salts, the value of which is increased by the iodine present.

EXPERIMENT IV.

Leaves.—We now reach the leaves—the laboratory wherein the mysterious, possibly inexplicable, operations of this most interesting plant are carried on, its other members being merely storehouses for their products. Nov. 16, 1906, collected the leaves, nearly intact, from two mediumsized plants, largest 8 feet long, 18 inches wide; a rich golden brown in color, leathery and rather thin; fine print could be read easily through the fresh leaf, which closely resembles corrugated glass. Leaves from one plant darker in color, thicker and apparently more mature. Contained 85 per cent. of water.

617 grams dried at 125° C. gave 174.68 grams of salts (28.31 per cent.) of the following composition:

	Per cent.
	(CO ₃ 0.83
Analysis 7	SO4 6.77
	Cl 45.72
	K 31.41
	1 0.85
ксі	49.24
K-SO.	12.27 equals 61.51 per cent, potassium salts

Although the product of crude salts from the leaves is only about one-half that of other members of the plant, their value is much greater on account of their large percentage of iodine.

Thin flimsy leaves, of quite different character, from another plant were then examined with closely approximate results. 115 grams gave 32.65 grams of salts, or 28.40 per cent., composed as follows:

		Per cent.
Analysis 8	CO3	0.86
	SO4	7.31
	C1	44.47
	I	0.875
	and the set of the area	

EXPERIMENT V.

Stem.—All parts of the plant have been examined except the long cylindrical stem, which I have taken up last, because in bulk and weight it is the least important member, and, moreover, can rarely be collected entire. Though apparently solid the stem has a central pith, or core, much softer than the surrounding tissues.

Stems from 10 to 12 feet in length from several young plants were coiled, sun-dried and finished at 125° C. They were then about 1/8 inch in diameter, and very tough and elastic. 90 grams gave 33.76 grams of salts (37.20 per cent.), composed as follows:

		Per cent.
	CO3	1.81
Analysis 9	SO4	7.66
	Cl	42.71
	I	. 0.55

To the above observations on Pelagophycus porra will be appended some remarks on the distribution of iodine; and also on the inorganic constituents insoluble in water—the true ash. We now pass to the northern representative of these giant Laminariaceae.

II. Nereocystis Leutkeana.—Commencing a little south of Point Conception, California, and extending into the Arctic and even to the shores of Kamtschatka, we have in this plant one of the most common and interesting algae of our north Pacific coasts. It is present everywhere, whether obstructing with its growth bays and island passes, or torn loose and wave-tossed, or stranded on their shores. Firmly anchored at a depth of from 8 to ro fathoms by its branching holdfasts to submerged reefs, or scattered rocks, it covers with its streaming strap-like fronds patches acres in extent so densely as to impede navigation. That this plant differs greatly in form from the southern species is evident from the illustration.

(Photograph of specimen from San Juan Island, Puget Sound, opposite page.) Its slender whip-like stem, the upper one-third of which becomes hollow and gradually expands in diameter from less than 1/2 to 3 or 4 inches, terminates in a small oval bladder separated from the stem by a slight constriction. In an average plant the solid portion of the stem may be 40 feet, the hollow part—the apophysis—about 20 feet in length, the bladder 4 or 5 inches long and about 3 inches in diameter. The huge branching arms, that



carry leaf petioles, so conspicuous in Pelagophycus, are entirely lacking. Its small oval bladder is crowned by a dense mass of narrow fronds which vary in length from 10 to 30 feet. It forms asexual spores in great numbers on the surface of its fronds from August to December in localties about Puget Sound. Its period of growth comprises about 15 months; germinating in the autumn, it perfects itself about the close of the following year.

EXPERIMENT I.

Effloresced salts, from specimens collected at San Juan Island, Puget Sound, about June 1, 1907, were first examined. These had fallen from air-dried material and were mixed with a little organic matter; they were lightly charred, dissolved in water, the solution filtered, and evaporated to dryness. The specimen thus obtained was purely white, weighed 197.8 grams, and had the following composition:

		I CI CCIII.
	(CO ₂	0.082
nalysis 10	SO4	0.090
	Cl	47.740

Consequently, we have here potassium chloride a crude and unpurified product—that very nearly reaches the requirements of a C. P. article. Not a trace of iodine was present, but sodium and magnesium could be recognized.

EXPERIMENT II.

Bladder and Apophysis.—The specimen examined was collected about October 1, 1906, and sent me, undried, from Seattle, Washington, by express. It was evidently stranded, for the leaves were fragmentary and much decayed; the hollow portion of the stem—which carried a very small oval bladder—measured 15 feet in length; the solid part 25 feet.

The hollow portion effloresced very strongly during the drying, and when finished at 125° C. weighed 262 grams, which yielded 153 grams of salts, or 58.51 per cent. of its weight. Composition as follows:

		Per cent.
San San 1	CO3	0.026
Analysis 11	SO4	1.180
	C1	48.580
K plus	Na	50.220

The ratio of K to Na was found to be nearly as 80 is to 20. Iodine was present slightly exceeding 0.1 of one per cent.

EXPERIMENT III.

Stem.—The solid portion, 25 feet in length, of the stem of the above plant furnished 171 grams of dried material, from which 57.3 grams (33.51 per cent.) of salts were extracted.

		Per cent
	CO3	4.41
Analysis 12	SO4	3.92
	C1	42.15
Iodine, two	determinations, 0.39-0.41 p	er cent.

In the condensation of iodine in the solid portion of its stem, this plant agrees with its congener, Pelagophycus, and, as will be shown further on, this feature is common to most of the hard-stemmed algae.

EXPERIMENT IV.

Leaves.—The leaves from Experiments 2 and 3 being badly decayed and not fit for use, others (fragmentary) collected from young plants about June 1, 1907, at San Juan Island, were utilized. Dried at 125° C., they weighed 607 grams. Charred and lixiviated, they gave 270.3 grams of salts, or 44.53 per cent. composition, as follows:

		Per cent	t.
	(CO ₃	0.52	Contract of the second
Analysis 13	SO4	5.26	
	C1	46.52	
	I	0.117	
	K	36.55	det. by platinum
Total potes	ium colte equal 71 r	or cent	

On comparison with Analysis 7, it will be seen that the amount of crude salts from leaves of N. Leut. is more than 50 per cent. higher than from those of Pelagophycus, or as 44.53 is to 28.31. Also that their percentage of potassium is higher as 71 is to 61.5, while iodine is present only as 0.117 is to 0.85. But the leaves of Pelagophycus came from a fine mature specimen collected in November, while those from N. Leut. were from young undeveloped plants collected late in May. Consequently, comparison is faulty, and this matter will be settled by further investigation as soon as mature leaves can be obtained. The increase in sulphates and the storing of iodine in the solid stem both warrant the expectation of a higher percentage in mature leaves.

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111. Macrocystis pyrifera.—Unlike the preceding, this huge and vigorous plant enjoys a very wide range, and seems indifferent as to temperature. Along our coast it extends from Magdalena Bay, Mexico, to Sitka, Alaska; on the South American coast it abounds throughout Fuegia and around Cape Horn and extends north well up toward the equator. It is abundant on the coasts of New Zealand, the southern coasts of Australia, and of scattered islands throughout the Antarctic Ocean. Different species may be noted, but as yet the northern and southern species are considered to be identical.

This plant differs greatly, both in habit and appearance, from the Nereocystes. In localities favoring its growth it forms a dense belt, or grove, covering the surface of the ocean about the ten-fathom line with broad meadows of its graceful foliage. Anchored by its immense holdfast, which may exceed 3 feet in diameter, it quickly branches into a large number of round solid stems, usually less than one-half inch in diameter, and often far exceeding 50 feet in length. From these stems alternately, and at distances usually approximating six inches, grow pear-shaped bladders measuringaccording to the development of the plant-from $\frac{1}{2}$ to 1 inch in diameter, and from 2 to 4 inches in length; the upper, or bulbous, part of the bladder is crowned with a single lanceolate leaf, from 1 to 2 feet in length, beautifully proportioned, and of a rich yellowish brown. According to general statement, the spores-sori-occur on submerged, bladderless leaves near the holdfast.

This plant is doubtless perennial, though its life may not extend over many years. It attains great bulk and weight. Detached leaves and branches are constantly brought to shore by the surf; during rough weather it is often stranded in vast quantities, and entire plants many hundred pounds in weight strew the beaches; these usually include plants of Pelagophycus in their tangled masses, but they are never entire. Its texture throughout is much tougher than in the Nereocystes, and there is a lower percentage of water in its tissues. Its leaves develop in drying an odor as peculiar, and almost as agreeable, as that of new-mown hay a characteristic odor that is permanent.

Macrocystes, then, consists of three principal parts—the stem, the bladder and the leaf. These were taken from a large, mature, plant—collected October, 1907—dried as usual and examined separately. From the material, about 1600 grams in all, a small deposit of effloresced salts fell during the drying.

EXPERIMENT I.

Effloresced salts, charred, dissolved, filtered and evaporated; weighed 43.25 grams; analysis as follows:

	(CO3	0.087
nalysis 14	SO4	0.590
	C1	47.710
No iodine:	faint trace of Mg.	

Here again we have nearly pure potassium chloride.

EXPERIMENT II.

Leaves.—These were fragmentary, and mostly from the basal portion of the leaf next the bladder. 297 grams, treated as usual, gave 64.7 grams of anhydrous salts, equal 21.80 per cent.

		Per cent
Analysis 15	∫ CO ₃	1.80
	SO4	11.20
	Cl	40.44
	I	0.70
	Manager Party and Tax	

EXPERIMENT III.

Bladders.—These varied in length from 3 to 4 inches, and were nearly 1 inch in diameter. 565 grams gave 232.5 grams salts, or about 41.15 per cent.

	(CO ₃	1.08
Analysis 16	SO4	3.15
	I	46.96
	C	0.54

EXPERIMENT IV.

Stems.—About 1/2 inch in diameter. 688 grams, treated as usual, gave 201.75 grams salts, or 29.32 per cent. Per cent.

		Contraction of the second second
Analysis 17	[CO2	3.96
	SO4	5.08
	CI	42.12
	I	0.64
	and the second	

Iodine is very evenly distributed throughout the tissues of this plant.

The solutions were mixed in proper proportions and analyzed: Per cent.

CO3												. 2.38
SO4								•				. 4.91

Carbonate and sulphate were then changed to

chloride and potassium determined by platinum:

	Per cent.
(Cl	50.81
Analysis 18 K	39.41
he potassium salts present	in the crude sal
n Macrocystis are as follows:	Per cent.
KSO4	8.79
KCl	67.76

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froi

76.55

The leaves were fragmentary; had they been intact the amount of sulphate would have been somewhat larger and the chloride less.

The following analysis is from perfect leaves of a smaller and less mature plant:

	rei cent.
(CO ₃	3.43
SO4	12.50
Cl	38.05
I	0.507
	CO3 SO4 Cl I

Three branches with perfect leaves from a young plant were dried. Stems and bladders equaled 730 grams; leaves 2100 grams. The proportion varies, but the leaves may be regarded as forming from two-thirds to three-fourths of the entire weight of the plant.

A careful study of the results of the foregoing analyses leaves us face to face with certain problems of much interest to science, but not easy of comprehension and difficult to explain. It will be noted that these algae, particularly Pelagophycus and Nereocystis, are very rich in potassium chloride—their tissues are gorged with this salt; and this is true not only of the mature plant—when it has attained great bulk and weight, produced its spores, and accomplished its life work—but of the infant plant, just entering life, consisting of little more than two small leaves and a bladder weighing a few grams, which is even richer in potassium.

The comprehensive analysis of sea-water by Dittmar, from specimens collected by the Challenger expedition, assigns to it the following composition. Sp. Gr. 1.026. In 100 parts of water 3.5 parts of salts, as follows:

NaCl MgCl MgSO ₄ CaSO ₄ K ₂ SO ₄ MgBr CaCO ₃	77.758 10.878 4.737 3.600 2.465 0.217 0.345	Also traces of Br, I, Fl. P, Si, Au, Ag, Pb, Cu, Zn, Co. Ni, Fe, Mn, Al, Ba, Sr, Li, and other elements.
Many of the second state of the second state of the	00.000	

It will be observed that potassium sulphate is present in sea-water in the proportion of about 2.5 per cent. of 3.5 per cent., or 0.087 per cent., which very nearly equals 0.04 or 1/25 of one per cent. of potassium.

Although growing in a medium in which sodium abounds, the algae assimilate the far less abundant potassium, preferably as chloride; and, as seems probable without modification, for the organic acids of the plant are chiefly contained with Ca and Mg.

A phenomenon of much interest is the extrusion of potassium chloride, in a state of almost chemical purity, through the skin, or outer tissue, of the drying plant. The salt does not appear until drying is far advanced and the skin of the bladder has become soft and pliable, when it passes rapidly as a light, flaky efflorescence; which, if the material is protected under glass, may reach half an inch in thickness. The composition of the effloresced salts is given in Analyses 2 and 4, and of the crude salts from which they come in Analyses 3 and 5. But Analyses 3 and 5 do not give correctly the composition of the saline solution from which the salts effloresced; they give its composition after carbonization and lixiviation of the charred tissues that contained it. Before these processes its composition was far more complex, inasmuch as organic compounds of calcium, magnesium, sodium, phosphates, and other matters were present.

In the case of Nereocystis, the stems from several large plants, not sufficiently dry to have become brittle, were headed up in a barrel where they remained for nearly two years. On removing the material a few pounds of effloresced salts remained, shaken off during the operation. Their composition is given in Analysis 10, the composition, after carbonization, of the crude salts whence they came in Analyses 11 and 12.

And, again, from Macrocystis. The extruded salts come from the bladders and stems, the leaves do not effloresce; their composition is shown in Analysis 14; that of the saline mixture, after carbonization, from which they come in Analyses 16 and 17. It will be noticed that these show a far larger proportion of alkaline carbonate and sulphate than the preceding, nevertheless their effloresced salts are equally pure.

These natural processes, and their results, are not easy to comprehend or explain. They remind one of the operations of osmosis or dialysis, but results thus obtained by no means correspond as is shown by the following experiment:

A quantity of dried material was ground to a coarse powder, mixed to a thin paste with water, and dialyzed through parchment paper. The liquor from the outer vessel, evaporated to dryness, yielded a yellowish granular salt; 9.56 grams were taken for analysis. Heated to incipient redness, they blackened and considerable organic matter burned off; they were then dissolved in water and solutions and washings brought to 250 cc. Carbonaceous residue on filter was incinerated and gave 0.092 g. of gray ash consisting chiefly of phosphate of lime and magnesia. The solution had the following composition:

		Per cent
Analysis 20	(CO3	0.13
	so	0.35
	C1	50.51

The organic matter burned off weighed 0.83 gram. The proportion of chlorine denotes the presence of about 25 per cent. of sodium chloride. On the whole, salts obtained by dialysis differ essentially from those extruded by the drying plant.

The percentage of sulphuric acid has a wider range than any other constituent of the soluble salts of the algae; less than one per cent. is often present, but I have recognized as high as 47.50 per cent. in the crude salts of a certain rockweed. Its proportion varies greatly in different members of the same plant, a fact everywhere apparent in the preceding analyses. It usually predominates in the leaves. Many algae rich in sulphates are correspondingly rich in iodine, but there are many exceptions.

I have given in the foregoing pages a concise description of the range, relative abundance, life habits, and chemical composition of our three most prominent giant kelps. It now remains to consider their economic value, and the most practical methods for the utilization of their products. It will have been noted that they all abound in potassium salts; that their brief life seems devoted to the task of extracting these salts from the medium in which they grow and storing them in their tissues; that they provide potassium compounds in a state of purity directly suited to our needs.

If we trace potassium to its source we shall find it in the feldspars present in all primitive, or igneous, rocks. Common granite contains about 40 per cent. of feldspar—about 7.5 per cent. of alkalies: gneiss, mica, slate, syenite, etc., are analogous in their composition. Potassium, in addition to its many uses in the arts, is indispensable as a food producer; any source from whence it can be easily and abundantly obtained is of vast importance to humanity. Its natural sources are obvious feldspathic rocks, deposits of mineral salts, growing plants. Since feldspar is everywhere, and con-

tains some 15 per cent. of potassa, why not seek it directly at its source? Because the extraction of potassium from orthoclase, common feldspar, is too difficult and expensive to be practicable. The second source is deposits, beds of natural salts in some localities of vast extent. Our third source is growing plants; and as, obviously, for many reasons land plants are not available as material, we turn to the ocean forests, to marine plants, for our supply. The ocean is a vast reservoir for potassium salts dissolved by the action of the elements from the rocks and carried by the rivers to the sea. They have accumulated there for ages; and, although potassium oxide constitutes but one-twenty-fifth of one per cent. of the weight of sea water-about eleven ounces in a cubic vard-if we take the trouble to calculate the number of cubic yards in a single cubic mile of ocean water, we regard with amazement the mass of potassium oxide contained therein; it is as limitless and inexhaustible as the nitrogen of the atmosphere. If by any means at our command we attempt to extract the dozen ounces of potassium contained in each ton of sea water, we shall find ourselves engaged in a difficult and unremunerative endeavor which we cannot successfully accomplish.

But our marine forests are quietly and ceaselessly accomplishing this task for our advantage. Each plant of the giant kelps stores up yearly, in addition to other valuable products, potassium chloride most liberal in quantity, and of remarkable purity, as the result of a natural process. We have but to gather the plant and utilize its products. If we are not wise enough to do so, the plant having reached maturity decays, its products return to the ocean, are taken up by its successors in the ensuing year, and the opportunity is ours once again.

In the matter of the utilization of the kelps on a large scale for the demands of commerce, two subjects for discussion come next in order:

I. How the raw material can be gathered and handled most conveniently. II. How its several products can be most advantageously extracted. The first is the more important, for on it largely depends the financial success of the enterprise.

I. Gathering the Kelp.—Certain seaweeds—notably Laminaria saccharina—have for ages found their uses whether as applied directly to the soil for fertilizing material, or in supplying crude raw material on a small scale for certain branches of

manufacture. This industry was confined to countries where labor was cheap, and to seasons of the vear when there was little else to do. The plant was cut by hand from outlying reefs and brought to land by boats, or collected where it lay stranded in masses after heavy gales. In either case the material was spread in a convenient place, dried as thoroughly as the weather permitted, drawn into heaps, and burned, the very impure ash resulting was used as a basis for manufacture. The whole process was unscientific, crude, wasteful, and costly in the highest degree; and nothing but the high prices obtained for the several products could have justified such methods. At the present day steam power must be substituted for hand labor, and the sources of waste closed.

A steam scow, or launch, properly fitted with labor-saving appliances, would seem to be the best vehicle for gathering and transporting kelp. It could move quickly from place to place, select the best fields for its operations, cut the plant, draw it on board, carry to shore and unload its cargo—all by steam power and at minimum cost—for, inasmuch as a dredge can raise a cubic yard of silt or sand from a considerable depth and transport it where needed at very moderate cost, there is no reason why a properly equipped craft cannot handle a ton of seaweed to equal advantage.

Handling the Material .- Let us suppose that a cargo of kelp has been landed at the wharf of a drying shed; the next step is to get it into condition for transportation. Freshly lifted from the sea the plant contains from 85 to 90 per cent. of water, is heavy, bulky, and unmanageable, and must first of all be deprived of its superfluous moisture. Though drying progresses very rapidly under the influence of sunshine and wind, in many points this method is objectionable. Drying by artificial heat is to be preferred, and there are methods in common use, perfectly applicable to seaweed, by which large masses of coarse material are easily and cheaply desiccated. If the material is to be transportedfor instance, from several drying sheds at long intervals to a central manufacturing plant-drying should not be pushed too far, but stopped when an efflorescence of salts begins to appear the material is then soft and pliable, and can be pressed, like hay or cotton, into small space; a ton of wet kelp can thus be reduced to a small bale weighing not more than 250 pounds, in which form it is easily transportable and its contents will keep indefinitely, unchanged and without loss. If drying be

carried too far, efflorescence is profuse, the material becomes too tough and elastic to be easily managed, and there is considerable loss in the handling.

11. Treatment of the Dried Material for the Extraction of the Several Products.—Kelp, dried and handled as mentioned above, still contains some 15 per cent. of water. The alkaline salts—chlorides, sulphates, iodides—which constitute from 40 to 50 per cent. of its weight are contained in much vegetable tissue. When inorganic matters unaffected by moderate heat are to be separated from organic, our most obvious course of procedure is to decompose the latter by burning. This process is best carried on by dry distillation, for in this way we can collect, or utilize, products of value both condensable and non-condensable arising from the decomposition of the organic matter.

The distillation of wood-as now largely practised in many countries-may be cited as an example of the progress and results of this operation. Well seasoned, air-dried wood, of any hard variety, is heated in suitable containers; decomposition begins at about 150° C. and is practically complete at 430° C. The chief products are formed continuously throughout the entire process, which proceeds in three characteristic periods: from 150° to 280° acetic acid, methyl alcohol, and wood creosote are the chief products; from 280° to 350° large volumes of gases are given off; from 350° to 430° solid hydrocarbons are distilled. Additional volatilization can be obtained by increased and protracted heating, but only to the extent of about 1.5 per cent. It will be noted that a very moderate heat-not much above the melting point of lead, 325° C .- is sufficient for the greater part of this operation.

The behavior of kelp under similar treatment is analogous but by no means parallel, nor are its products the same. In the distillation of wood the main products are the condensable volatile substances; the charcoal is of little consequence. With kelp it is just the opposite; the char saturated with mineral salts is by far the most important product of the operation. From wood, the watery parts of the distillate are acid; from kelp they are neutral, or slightly alkaline, proving the presence of ammoniacal compounds. In other respects the condensed products are approximately the same,

In the case of wood, complete volatilization is of little consequence; charring need not be perfect; with kelp it must be absolutely so, for, if the char holds unexpelled any portion of the organic products of decomposition, the lixiviates from such char will not be odorless or colorless, and consequently of little use for the production of pure salts. Fortunately, this perfection of the char can be ensured by certain modifications of the process; lixiviates from such a char will yield colorless salts of any degree of purity desired. All iodine present can be easily recovered from the waste liquors of the several operations.

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Kelp versus Wood.—Let us now consider the case from the practical and commercial point of view, and compare the results to be expected from the similar handling of a weighed quantity of each of the above natural products.

Hardwood—preferably beech—selected where it most abounds, is cut, split, stacked—all by manual labor—seasoned for at least a year, and then transported to the plant for distillation. Kelp is cut, loaded, landed, dried and baled—all by the best mechanical labor-saving appliances; and then in a compact and easily handled form transported to the plant for distillation. Both, save for a necessary, but inexpensive, modification in the case of kelp, are treated alike and at the same cost of manufacture.

One ton of thoroughly, dried beechwood gives an average yield of 120 pounds of dry calcium acetate, 8 gallons of tar, 6 gallons of alcohol and acetone.

These, which may have a commercial value of some six dollars, represent all the products usually marketed from a ton of dry wood; the charcoal some 30 bushels—and gases resulting from the operation are utilized as fuel in the establishment.

The condensed products from the distillation of kelp are analogous to those from wood, and may be regarded as approximating them in value. But here all comparison ceases; the non-volatile portion, the charcoal saturated with alkaline salts, is by far the most important product of the process.

One ton of thoroughly air-dried kelp, in addition to valuable by-products volatile and non-volatile, may be depended on for a minimum yield of 500 pounds of pure potassium salts, 3 pounds of iodine.

These are worth above twenty dollars in the markets, and the presumptive value of the several by-products should warrant the statement that the average yield of a ton of air-dried kelp may be stated at twenty-five dollars (\$25.00)—an average which is far more likely to be exceeded, espe-

cially as regards iodine, than reduced in quantity or value.

How much more promising then in its returns is the distillation of kelp than that of wood. Nevertheless, wood is largely and profitably distilled for its volatile products alone.

One other source of potassium remains to be considered. There exist in certain localities vast beds, or deposits, of mineral salts that carry a large percentage of potassium. These mines are at the present time actively operated and yield a large proportion of the potassium compounds in commerce; their output of low-grade manurial salts for agricultural purposes is immense, and, both as regards quantity and cheapness, beyond competition. But with the purer salts which the numberless claims of manufacture and the arts demand, this is by no means the case. The preparation from their ores of a pure potassium chloride or sulphate is a laborious and expensive operation, and there are no byproducts of consequence to reduce the cost of manufacture. But their preparation from kelp presents no difficulties; it yields no rough, complex material so difficult of refinement, for its crudest salts are well on the way toward purity, and can furnish abundantly and cheaply any perfected product that commerce may demand. And again, the by-products from kelp are of prime importance both as regards quantity and value; there is little doubt that they can be made to pay the entire expense involved from the gathering of the raw material to the marketing of its products. Consequently, potassium salts manufactured from kelp should be able to compete in price with any similar products wherever or however produced.

Another most important product of the algae is iodine. This element, of wide use in therapeutics and the arts, was formerly extracted from marine plants; since its discovery in the mother liquors of the purification of Chili-nitre commerce has been supplied chiefly from that source. But the vast deposits of Chili are being rapidly exhausted; their complete extinction is plainly in sight; a few years hence we must look again to the ocean for the world's supply of iodine.

This element, like gold, is present in sea water in infinitesimal proportion. Certain marine plants extract it eagerly, no one can explain how nor why. Two plants are growing side by side on the same stone; in habit, growth and external appearance they are very much the same, but in one of them we find iodine astonishingly abundant, while the other contains not a trace. The ocean is an inexhaustible treasury of varied wealth, but its riches are stored in so attenuated a form that we are powerless to gather them without the aid of natural processes that go on continually. Marine plants include annually certain portions of this wealth, and offer it for our acceptance like dividends due; should we refuse, it is returned to the treasury, and as time advances offered us again and again.

Nevertheless, the old proverb "vilior alga" still holds good; our marine crop is despised and rarely harvested; in speaking of the vegetable growths of the sea the term "weed" is universal. A weed, according to the best definition ever given, is a plant whose virtues yet remain undiscovered. It is fitting, then, that the more prominent members of the numerous genera and species of these plants be studied, and their hidden virtues brought to light.

Assuming it to be not impossible-though by no means probable-that a marine plant may be found sufficiently complacent to have included and stored up gold in its tissues; that such a plant would be widely sought and cultivated there is little doubt. But products of more substantial value to us than gold, by processes that we cannot imitate, are being prepared and stored for us yearly by plants that we at present despise. They draw these products from a source unquestionably inexhaustible. This term is often loosely applied to sources that by no means deserve it; we observe the vast gold reefs of the Rand, and say here is an inexhaustible field for exploitation; we consider the extensive saline deposits of Germany, and repeat the remark; a generation ago we were saying the same of the nitre beds of Chile; that no terrestrial deposit of value can escape depletion the fate of the latter proves.

But with the saline contents of the ocean it is different. They are not only as now existent inexhaustible, but are being constantly augmented, for as long as rain falls on disintegrated rock and its surplus flows into the sea the mineral contents of the ocean will increase.

Every economist views with disfavor the extravagant—in fact criminal—wastefulness of cities great and small, through whose sewers the fertility of a million acres is poured yearly into the sea. The phosphoric and nitrogenous constituents of this waste seem hopelessly lost; but potassium, one of the most important, we can easily recover, for along our coasts are growing with the rapidity and vigor of the bamboo countless millions of marine plants, each one of which may store up during its short life from one to two pounds of chloride and sulphate of potassium.

We are dependent for our food supply on the fertility of our soils; in order that they may remain productive the constituents that make them so removed with each annual crop to distant localities—must be supplied from other sources. The chief of these are phosphates, combined nitrogen, and potassa. The first is supplied by animal waste, and by mineral deposits fairly abundant; the atmosphere is a vast reservoir of nitrogen and oxygen uncombined, which we are rapidly learning how to economically combine to produce the products we need; that we can economically win from a similarly inexhaustible source the third element we require, I have endeavored to make plain in the preceding pages.

This paper will be followed by a second on the chemistry of the more important littoral algae, many of which are of interest, and on some other results of the study of marine growths.

I take this opportunity to express my obligation to the courtesy of Prof. Setchell, of the University of California, and to Prof. Frye, of Washington, for valuable information on the nomenclature and habits of these plants.

CORONADO BEACH, CALIF.

NITRATES IN BOILER-WATERS.

By GEORGE S. JAMIESON. Received October 28, 1909.

The determination of nitrates in the analysis of waters to be used for boiler purposes does not appear to be customary, and, indeed, such determinations may be considered unnecessary in cases where potable waters containing only traces of nitrates are under consideration. However, it sometimes happens that manufacturers, in order to save the cost of city water, employ for this purpose ground waters from densely inhabited districts, and in such cases, where nitrates may be comparatively abundant, their determination is believed to be important.

For the last five years the writer has made it a practice to determine nitrates in boiler waters by means of the well-known colorimetric method used in sanitary examinations. Several ground waters have been analyzed which caused severe corrosion as well as a heavy scale in the boilers, and the conclusion was reached that the nitrates were largely responsible for the corrosion, on account of their oxidizing action at the high temperature reached by the metal in the presence of heavy scale.

A particular instance of a water from a driven well in the city of New Haven may be mentioned. After this water had been used for a short time the boiler tubes were filled with small holes, and were coated with a very thick and hard irregular scale. The water gave the following analysis:

	Parts per million.
Sodium chloride	85.7
Sodium nitrate	26.8
Potassium nitrate	28.1
Magnesium nitrate	. 99.6
Calcium nitrate	. 83.0
Calcium sulphate	. 117.0
Calcium carbonate	25.0
Iron carbonate	9.5
Silica	. 20.0

The quantity of nitrates (182.9 parts per million of NO_a) in this water is very great and although nitrates are very soluble in water, they would not fail to be deposited in the hot scale wherever the water penetrated into it. In fact, small quantities of nitrates were found in the scale itself of this boiler, although they must have been destroyed by heat in the parts of the scale next to the metal.

Another well water from a different locality in New Haven was found to contain 39.85 parts per million of NO_3 , besides large amounts of carbonates and sulphates. This was not recommended for boiler purposes. Both of these well waters were characterized by being very free from organic matter and were neutral in reaction after the carbon dioxide had been boiled off.

Parts per million

A CARLON AND AND A CARLON AND AND A CARLON	and the second of the second second	and the second second second second
Total solids.	Chlorine.	Nitrate NO3.
331.00	25.00	55.35
346.00	22.00	44.30
85.00	9.00	20.68
266.00	23.00	54.47
185.00	9.00	20.37
243.00	26.00	31.62
301.00	23.50	68.20
434.00	58,00	59.78
106.00	11.00	8.85
345.00	25.20	56.07
172.00	7.25	39.85
261.00	22.00	44.30
81.00	9.00	17.71
119.00	12.75	17.71
220.00	20.00	66.44
95.00	6.00	15.58
257.00	12.00	17.71
164.00	14.00	44.30
170.00	11.00	22.14
275.69	11.42	13.00
	Total solids. 331.00 346.00 85.00 266.00 243.00 301.00 434.00 301.00 434.00 106.00 122.00 261.00 81.00 220.00 95.00 257.00 170.00 275.69	Total solids. Chlorine. 331.00 25.00 346.00 22.00 85.00 9.00 266.00 23.00 185.00 9.00 243.00 26.00 301.00 23.50 301.00 23.50 434.00 58.00 106.00 11.00 261.00 22.00 172.00 7.25 261.00 22.00 19.00 12.75 220.00 20.00 95.00 6.00 257.00 12.00 164.00 14.00 275.69 11.42

Further investigations are needed to reach a decision in regard to the amount of nitrates that may be permissible in a boiler water, and also in respect to the protective effect of other constituents.

The table of analyses given above comprises twenty waters from Connecticut, and serves to show the abundance of nitrates in them.

As a comparison with the large quantities of nitrates shown in this table, it may be observed that the average amount of NO_3 in the water supplies of Connecticut cities is only about 1 to 3 parts of NO_3 per million.

SHEFFIELD LABORATORY, NEW HAVEN, CONN.

CRUDE PETROLEUM AS A REDUCING AGENT FOR ZINC ORES.

By HARRY H. HUGHES AND HARRISON HALE. Received September 17, 1909.

The process generally in use for zinc reduction is exceedingly cumbersome, slow and far from satisfactory. Comparatively small quantities of the roasted ore are mixed with coke and coal and heated in clay retorts which must necessarily be of considerable thickness, the zinc distilling over. The time required is about twenty hours and the expense for heat large. In the best of coals there is quite an amount of matter which does not act as a reducing agent. Some of this is not only not helpful to the process but really injurious, as oxygen is furnished which hinders the reduction. These impurities also occupy space in the retort and consume heat the same as ore.

The high percentage of carbon and of hydrogen in crude oil and its resulting reducing power suggest it as a possible reducing agent. Its extreme cheapness makes it all the more desirable. An objection to its use arises at once in the fact that a temperature of at least 1200° C. is required to practically reduce zinc oxide to metallic zinc and before such a temperature could be reached in the usual furnace all the oil would be volatilized, leaving an insufficient amount of carbon to carry on the reduction. Evidently, then, if crude oil can be used economically for zinc ore reduction it must be in a continuous process by which the furnace can be heated to a sufficiently high temperature and the mixture of oxide and oil fed into it. It would seem that under such conditions reduction should take place before any quantity of the oil can escape. To test this assumption a series of experiments was carried out in this laboratory.

An ordinary gas pipe, ${}^{3}/_{4}$ inch in diameter, was connected at right angles with a cup from which

the mixture of ore and oil could be fed by means of a cock. At first this pipe was placed in a Bunsen combustion furnace but no reduction occurred as the necessary temperature could not be reached. It was then passed through a Brown assay furnace, entering through a hole cut in the back and passing out the door with the end nearer the cup being slightly elevated. The coke fire around this gave ample heat without the use of a blast. The pipe extended some inches from the furnace acting as a condenser.

Fifty grams of zinc oxide mixed with enough oil to make it pass through the cock was the usual charge. The oil required for this was in considerable excess of the amount needed for reduction. So-called "black oil," the crude with kerosene and the lighter oils removed, was used at first and later the regular crude; either will answer.

After the furnace was heated the charge was run in. An effort was made to pass it in slowly, but with this rough apparatus usually without success as almost the entire charge passed in at once. An evolution of gas from the oil on the heated surface followed. The charge remained in the heated pipe for twenty to thirty minutes when the pipe was removed and cooled and the contents examined. Beautiful specimens of zinc were found in the condensing portion of the pipe and there was an almost complete absence of "blue powder."

Some of the zinc was feathery as if both the oxide and the oil were in a volatile state when reduction occurred. This reduction in a gaseous condition greatly shortens the time required as the reducing gas is in immediate contact with the oxide to be reduced.

The gas generated by the excess of oil together with the carbon monoxide formed in the reduction was frequently lighted as it passed out of a burner connected with the end of the pipe. It should be possible to use the gases to heat the pipe or other retort containing the charge, largely reducing the fuel expense.

A number of trials were made with uniformly good results. From our experiments we conclude:

First, that zinc ores can be successfully treated, after roasting, by using crude petroleum as a reducing agent.

Second, that the theoretical advantages from the high reducing power of the oil and from the gaseous state of oxide and reducing agent, hold in a practical test. We believe further that a continuous process based on these principles would be much cheaper, more rapid and more easily controlled than any process now in use. Arrangements have already been made for trying out the process on a large scale using the continuous process furnace devised by one of us.¹

WHITCOMB CHEMICAL LABORATORY, DRURY COLLEGE, Springfield, Missouri.

TINCTURE OF IODINE.

By Azor Thurston. Received July 31, 1909.

Prior to the last edition of the United States Pharmacopoeia, tincture of iodine consisted simply of iodine dissolved in alcohol. Owing to the rapid loss of free iodine by the formation of either ethyl or hydrogen iodide the pharmacopoeial standard has been changed, by the addition of potassium iodide, to prevent the conversion of the free iodine into iodides.

In the assay of the tincture determinations should be made for iodine, potassium iodide, ethyl and hydrogen iodides, and alcohol.

lodine is determined by the well-known U. S. P. method by titrating five cubic centimeters with decinormal thiosulphate solution, whereby sodium iodide and sodium tetrathionate are formed: $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$. The number of cubic centimeters decinormal sodium thiosulphate used multiplied by 0.01259 will give the amount in grams of free iodine in 5 cc. of the tincture, and by multiplying the product by 20 gives the number of grams of iodine per 100 cc.

Potassium iodide is estimated according to La-Wall² by evaporating the tincture on a water bath, adding several small successive portions of water, drop by drop, to aid in volatilizing the last portions of the iodine, and weighing the white crystalline residue in a tared watch-glass, which should be used for the experiment.

The writer prefers to determine the potassium iodide as follows: Place 5 cc. of the tincture in a platinum crucible and add 2 cc. dilute sulphuric acid; evaporate on a water bath until the alcohol and most of the free iodine are volatilized, then heat to dryness over direct flame, ignite to whiteness, cool and weigh. The residue will consist of potassium sulphate, and the weight obtained multiplied by 1.9 will equal the amount of potassium iodide

¹ Hughes, Mining World, July 10, 1909. ² Proc. A. P. A., **1907**, 159.

present in 5 cc. of the tincture; this product multiplied by 20 will give the quantity in grams per 100 cc.

Ethyl and Hydrogen Iodides.—A number of methods have been suggested to determine iodine in mixtures containing free iodine, iodides, bromides and chlorides. In nearly every case some manner of liberating the total amount of combined iodine, existing as iodides, and finally estimating the free iodine with sodium thiosulphate, has been recommended. The free iodine, having been determined in a separate portion, is deducted from the total amount of iodine, the difference being the amount of iodides present.

The majority of the methods are applicable in the assay of tincture of iodine, by first determining the free iodine and potassium iodide, as has been outlined, and then estimating the amount of total, combined and free, iodine in the tincture by one of the methods to follow; the iodine in the free state and that existing as potassium iodide is deducted from the total iodine found, and the difference is the amount existing as either ethyl or hydrogen iodide.

Richard¹ determines the amount of free iodine in 10 cc. of the tincture with sodium thiosulphate in the usual manner and then adds a two per cent. solution of potassium iodate; the coloration produced is decolorized with sodium thiosulphate solution. The difference between the thiosulphate solution necessary to decolorize the original tincture and that required to decolorize it after the addition of potassium iodate indicates the amount of hydrogen iodide present.

Cook² proposes the addition of hydrogen peroxide to a solution of iodides acidified with acetic acid. Thus the iodine is liberated; the iodine extracted with chloroform and titrated in the usual manner.

Villiers and Fayolle³ proposed to liberate the iodine from iodide with a solution of ferric chloride, extracting the free iodine with carbon bisulphide, and treating with sodium thiosulphate.

Barrie⁴ liberates the iodine with a 5 per cent. solution of potassium bichromate and a 10 per cent. solution of sulphuric acid, extracts the free iodine with toluene and titrates as usual with sodium thiosulphate.

¹ Proc. A. P. A., 1898, 745.

² J. Soc. Chem. Ind., **1885**, 611. ³ Ibid., **1894**, 1093. Kippenberger¹ liberates the combined iodine by means of chromic acid and extracts the free iodine with chloroform and titrates with sodium thiosulphate solution.

Ditz and Margosches² proposes to modify Barrie's method by using potassium iodate as the oxidizing agent with either dilute hydrochloric or sulphuric acid, $\text{KIO}_3 + 5\text{KI} + 6\text{HCl} = 6\text{KCl} + 3\text{H}_2\text{O} + 3\text{I}_2$, and extracting the free iodine with toluene.

The method used by the writer is as follows: Five cc. of the tincture are placed in a separatory funnel together with 15 cc. dilute sulphuric acid and 30 cubic centimeters decinormal potassium dichromate. Let stand about ten minutes and then add to the mixture 20 cc. carbon tetrachloride. Shake thoroughly, and when the liquids have separated draw off the carbon tetrachloride solution of iodine. Repeat the shaking out three times with successive portions of 10 cc. each of carbon tetrachloride; titrate the combined solutions of iodine with decinormal thiosulphate. From the amount of total iodine thus determined deduct the free iodine and combined iodine as potassium iodide: the difference will be the amount of iodine existing as either ethyl or hydrogen iodide.

Alcohol.—In determining the alcohol in tincture of iodine it becomes necessary to convert the iodine into a non-volatile iodide before distillation.

Alcock³ recommends the shaking of a convenient quantity of the tincture with mercury, until complete inversion of iodine, and then adding a small quantity of sodium or potassium hydroxide to prevent contamination of the distillate with traces of mercuric iodide.

Cameron⁴ states when the iodine is fixed with potash it often causes "bumping" and recommends the use of iron turnings.

Roscoe and Schorlemmer⁵ states when iodine is brought in contact with water and filings of iron or zinc colorless solutions of the respective iodides are formed.

Practically all the methods mentioned are unsatisfactory; in combining with the metals too much time is necessary and in most cases a small amount of volatile iodide is formed, and in using sodium or potassium hydroxide iodoform is formed.

Of the different methods investigated Alcock's proved the most satisfactory.

³ Proc. A. P. A., 1904, 583.

5 "Treatise on Chemistry," Vol. 1, p. 157.

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⁴ Ibid., 1900, 933.

¹ Analyst, **1903**, 256. ² J. Soc. Chem. Ind., **1905**, 45.

⁴ Analyst, 1902, 87.

ON THE DETERMINATION OF POTASSIUM BY THE COBALTI-NITRITE METHOD.¹

By L. T. Bowser. Received July 6, 1909.

Probably the first to make use of the reaction between sodium cobalti-nitrite and potassium as a test for the latter was DeKoninck, and this reagent is often called by his name. He utilized it only for qualitative purposes, however, and Adie and Wood² seem to have been the next to investigate its use. Various other brief statements concerning the reaction are to be found, and for convenience are noted here.3 Crookes4 says: "L. L. DeKoninck finds that if a 10 per cent. solution of sodium nitrite is mixed with cobalt chloride and acetic acid, the liquid forms are agents for the detection of potassium much more sensitive than platinum chloride. An immediate yellow precipitate is obtained in a solution containing one part KCl in 100 parts of water. It is still perceptible if diluted to 1/1000, but in the proportion of 1/2000 a precipitate is no longer obtained. Ammonia gives a similar but much less delicate reaction-sodium, magnesium, calcium, barium, strontium, iron, aluminium, and zinc salts are not precipitated by this reagent." Fresenius⁵ says in part: "This freshly prepared reagent produces a yellow crystalline precipitate of potassium cobalti-nitrite, K3Co(NO2)e.6 In concentrated solutions this takes place immediately, but in more dilute ones only after some time. Ammonium salts give a similar reaction, but only in concentrated solutions." Substantially the same is given by Prescott and Johnson,7 and they also assign for They remark that it the formula, K₃Co(NO₂)₆. is sparingly soluble in water, insoluble in alcohol and in a solution of potassium salts. Autenreith⁸ determines potassium in silicates by precipitating it as the cobalti-nitrite after decomposing the silicate by HF and H2SO4 and removing the heavy metals. He allows the precipitate to stand 24

¹ AUTHOR'S NOTE.—I had begun the study of this method before noticing the first of Mr. Drushel's papers, and thought it proper to carry on the investigation to a greater length than the latter. Although my general procedure chances to be very similar to his, the work has been influenced very little by his published results, and was made with a view of providing an adequate basis for future work, as well as of giving a review of the scattered literature on the subject. —L. T. B.

² Jour. Chem. Soc., 77, 1076. Sutton, "Volumetric Analysis," 9th Ed., pp. 61-3.

³ Erdmann, J. pr. Ch. [1], 97, 385 (1866); Sadtler, Am. J. Sci. [ii], 49, 189 (1870); Rev. of Am. Chem. Res., 1899, 18.

4 "Select Methods in Chemical Analysis," p. 1.

⁶ This is evidently a mistake, and will be referred to later.

7 "Qualitative Chemical Analysis," 6th Ed., p. 224.

⁸ Freiburg i/B. Chem. Univ. Lab., Centr. Min. Geol., 1908, 513-17. Abstract in Chem. Abs., 2, 3038 (1908). hours, then filters and brings into solution and determines as chloroplatinate or perchlorate.

The Method of Adie and Wood .- The only articles, however, in which there is described the full estimation of potassium by this method are the ones by Adie and Wood, and by Drushel. The procedure of Adie and Wood is to add 10 cc. of reagent and I cc. of strong acetic acid to IO cc. of potash solution, allowing to stand over night, filtering the precipitate on a Gooch and washing with ro per cent. acetic acid. The cobalt is precipitated by boiling with 2 or 3 cc. of a 10 per cent. solution of NaOH, the filtered solution made up to 100 cc., and aliquots of 20 cc. are taken for titration with KMnO4. The solution is slowly acidified and KMnO, added until the pink color holds for a minute. According to this procedure 1 cc. of strictly N/10 KMnO, is equal to 0.0007858 gram K₂O. The authors find that the formula of the precipitate is K2NaCo(NO2)6.H2O. Some confusion seems to have occurred by reason of the similarity of this salt to tri-potassium cobaltinitrite, as before noted, and the formula given by Fresenius and by Prescott and Johnson should be that just given. Sutton lays particular emphasis on the necessity of having a concentration of solution such that from 0.5 to 1.0 per cent. of K.O is present, and finds that in too dilute solutions the precipitate runs through the filter.

Drushel's Method .- The method according to Drushel¹ is as follows: The potassium is precipitated as di-potassium-sodium-cobalti-nitrite by an excess of sodium cobalti-nitrite, the mixture evaporated on the steam bath, the precipitate filtered on asbestos and oxidized by hot standard KMnO,. The excess of permanganate is bleached by an excess of standard oxalic acid, and the solution then titrated back to color with permanganate. One cc. of N/10 KMnO4 is equal to 0.0008573 gram K20 by this method. In making the titration a measured excess of KMnO4 is diluted to ten times its volume and heated nearly to boiling, and the precipitate and asbestos are thrown in and stirred up. After 5 to 8 minutes manganese hydroxide separates out, when 5-25 cc. H_2SO_4 (1 : 7) are added, the solution stirred and allowed to stand a few minutes, after which the titration is completed.

Reactions Involved.—The method used for the preparation of the reagent is as follows: 220 grams sodium nitrite are dissolved in 400 cc. of water, 113

^{5 &}quot;Qualitative Analysis" (Wells), 16th Ed., p. 133.

¹ Am. Jour. Sci., **24**, 433-8 (1907); Ibid., **26**, 329-32 (1908); Ibid., **26**, 555-62 (1908).

grams cobalt acetate dissolved in 300 cc. of water and 100 cc. glacial acetic acid added. The solutions are poured together, mixed and gently warmed, NO2 is evolved and evacuated by means of a filter pump kept running over night. The solution is then filtered and made up to a liter, when the reagent is ready for use. In the course of preparation the following reaction occurs, 21Co(C₂H₂O₂)_{2.4}H₂O + $14NaNO_2 + 4H(C_2H_3O_2) = Na_6Co_2(NO_2)_{12}H_2O +$ $8Na(C_{2}H_{2}O_{2}) + 2NO + 6H_{2}O_{2}$, thus giving for its products sodium cobalti-nitrite, sodium acetate, and nitric oxide, which on contact with the air immediately becomes nitrogen peroxide. Similar results follow when the reagent is prepared from cobalt chloride or nitrate. From this equation it may readily be calculated that the ratio of sodium nitrite to cobalt acetate is 220 to 113, the grams per liter given by Adie and Wood. This gives about the maximum strength to which the solution may be made, since both salts are dissolved to about the saturation point. One cc. of this reagent contains 0.1886 gram of sodium cobalti-nitrite, which is equal to 0.0426 gram of K2O. As will be shown later, however, it is actually necessary to use more than this amount of reagent in order to precipitate all the potash in condition suitable for work.

The reaction with a potassium salt in solution is: $Na_{6}Co_{2}(NO_{2})_{12}H_{2}O + 2K_{2}SO_{4} = 2K_{2}NaCo(NO_{2})_{6}$ H₂O + 2Na₂SO₄. The yellow precipitate, dipotassium-sodium-cobalti-nitrite, is very stable, as has been shown by Hofman and Burger¹ to be the case with a number of other cobalti-nitrites of similar nature, and has been found to be practically insoluble in water. When boiled with NaOH, as in the method of Adie and Wood, Co(OH), is precipitated, while the filtrate contains a mixture of sodium and potassium nitrites. The reaction involved in titration with permanganate then becomes: 10KNO₂ + 20NaNO₂ + 6K₂Mn₂O₈ + $_{33}H_2SO_4 = 11K_2SO_4 + 10Na_2SO_4 + 12MnSO_4 +$ $30HNO_3 + 18H_2O$. Hence $K_2Mn_2O_8 = 5/6K_2O$, from which 1 cc. N/10 KMnO₄ = 0.0007858 gram K.O.

When the precipitate is treated directly with permanganate a different and somewhat more complicated reaction occurs. Trivalent cobalt is reduced to bivalent, and in so doing releases one atom of oxygen, which thereupon oxidizes an equivalent amount of the precipitate, thus reducing the amount of permanganate used. The final reaction is in effect: $10(K_2NaCo(NO_2)_6.H_2O) + 11K_2Mn_2O_8 + 58H_2SO_4 = 21K_2SO_4 + 5Na_2SO_4 + 10CoSO_4 + 22MnSO_4 + 60HNO_3 + 38H_2O$. Hence in this case $11K_2Mn_2O_8 = 10K_2O$ and $K_2Mn_2O_8 = 10/11$ K₂O, from which 1 cc. N/10 KMnO₄ = 0.0008573 gram K₂O.

Advantages of the Method .- There is a decided similarity between several of the insoluble potassium salts, in particular the platinichloride, the phosphomolybdate, and the cobalti-nitrite. Each is of a peculiar yellow color, and each is found to be best obtained for quantitative purposes by evaporation on the steam bath. One of the great advantages in the determination of potassium by the platinum method is the high molecular weight of the resulting precipitate, 485.8, giving a factor of 0.1941 for K₂O, which thus reduces to a very small amount any danger from minor errors of manipulation. The molecular weight of K2NaCo(NO2)6. H₂O is 454.61, and the factor for K₂O is 0.2074, thus giving to the determination the same advantage as that by the platinum method. In the opinion of the writer the gravimetric cobalti-nitrite method when properly conducted will be found nearly as accurate for most purposes as the older platinum method. Moreover, it presents a very decided advantage over the latter from the fact that by its aid potassium may be determined with equal accuracy whether it be present as chloride, sulphate or nitrate, and does not vary greatly from the truth when in the form of bicarbonate, chlorate or dibromate. Another of its advantages over the platinum method is the fact that the cost of reagent is very low, about one per cent. per determination.

Investigation of Adie and Wood's Method .- The method of Adie and Wood having given unexpectedly irregular results, a carefully planned and executed series of determinations was made in the hope of ascertaining the factors contributing to this irregularity. Most of the difficulty was found to be due to the method of precipitation, although the titration gave some trouble also. Three solutions were made up, containing 5 grams respectively of KCl, KNO3, and K2SO4 per 500 cc., thus giving about the concentration recommended by Adie and Wood. One cc. then contained 0.00632 gram of K₂O as KCl, 0.004659 gram as KNO₃, or 0.005408 gram as K2SO4. All of the work noted in this paper was conducted upon C. P. salts, for while a method which works well on pure salts may or may not do so with complex substances,

¹ Roy. Acad. Sci. Munich, Ber., 40, 3298-3301. Abstract in Chem. Abs., 1, 2542 (1907).

yet one which will not give good results under such conditions certainly cannot be depended upon for more difficult combinations.

Part of the following determinations were made by the method of Adie and Wood in full; they will be found under the heading "Alkali Method," from the use of NaOH to decompose the cobaltinitrite precipitate. The remaining ones were run by what is designated as the "Acid method," and were conducted identically like those by the alkali method until the potash precipitate had been filtered. The precipitate was then rinsed into a beaker with 25-50 cc. of water, the asbestos being left with it, a measured excess of KMnO4 added, then 5 cc. of 1:1 H2SO4, and the mixture brought to boiling, accompanied by vigorous stirring. When all the precipitate had been decomposed the excess of KMnO, was bleached with N/10 oxalic acid. The amount of potash was obtained by multiplying the cc. of KMnO4 used by the factor 0.0007858 previously derived. In Table I is given the result of a number of determinations, showing the volume of KMnO4 consumed per 0.05 gram K2O, the per cent. of potash found, and the percentage of deviation from the real results.

TABLE I.									
Salt used.	No of dets.	KMnO4. Alka- li method.	KMnO4. Acid method.	Per cent. K20. Alkalimethod.	Per cent. K ₉ O. Acid method.	Per cent. dev. Alkali method.	Per cent. dev. Acid method.		
KCL	4	Max. 68.38 Min. 67.64 Ave 68.03		108.18 106.30 106.90		+ 8.18 + 6.3 + 6.90			
6	6	Max Min Ave	63.45 61.78 62.20		99.72 97.10 97.76		0.28 2.90 2.24		
KNO-	3	Max., 67.07 Min., 62.52 Ave., 64.57		105.4 98.26 101.46		+ 5.40 0.78 + 1.46			
KNO3	6	Max Min Ave	64.61 61.17 62.56		101.54 96.14 98.36		+1.54 3.86 1.64		
K2SÔ4	6	Max., 70.35 Min., 55.25 Ave., 64.32		110.56 86.84 101.09		+10.56 13.16 + 1.09			
	7	Max Min . Ave	63.52 60.42 62.29		99.82 90.46 97.92	•	0.18 5.04 2.08		

General average... 65.52 62.36 102.98 98.02 2.98 1.98

It will be noted that the percentage found by the acid method is lower than that by the alkali, probably owing to the occurrence of a slightly different reaction, also that the average deviation is one per cent. less. The irregularities are entirely too great to permit the use of either method for quantitative purposes. The conditions were exactly the same for both methods, and all the precipitates were allowed to stand 14 hours before filtering. The acid method having been found superior in point of accuracy was used in the subsequent determinations; hence the results shown in Tables II and III are not as unfavorable to the method as they would have been had the original one been followed strictly.

It having thus been shown that, notwithstanding the exercise of the utmost care, considerable irregularities occur in the use of the original method of Adie and Wood, it remained to ascertain what factors might contribute to this end. In Table II is shown the effect of dilution of the potash solution, in this case KCl, upon the amount of potash found.

ТА	BLE II.	
Cc. H ₂ O		Per cent.
added.	Cc. KMnO ₄ .	K ₂ O found.
. 0	61.94	97.34
. 5	59.81	94.00
. 10	57.85	90.92
. 15	54.98	86.40
. 20	53.08	83.42
. 25	50.00	78.58
. 50	30.53	47.98
	TA Cc. H ₂ O added. . 0 . 5 . 10 . 15 . 20 . 25 . 50	$\begin{array}{c} T_{ABLE} \ II. \\ \hline Cc. \ H_{2}O \\ added. \ Cc. \ KMnO_4. \\ . \ 0 \ 61.94 \\ . \ 5 \ 59.81 \\ . \ 10 \ 57.85 \\ . \ 15 \ 54.98 \\ . \ 20 \ 53.08 \\ . \ 25 \ 50.00 \\ . \ 50 \ 30.53 \end{array}$

Fig. 1, based on the results set forth in this table, shows graphically the consequence of dilution, the volume of KMnO, used in the titration of the potash precipitate from a solution of ordinary concentration being taken as the basis of comparison. The curve shows that with minor variations the volume of KMnO₄ consumed, and consequently the percentage of potash recovered, varies inversely with the dilution. A continuation of the curve to the line of o cc. KMnO4 shows that with about 75 cc. of water added to the original solution there would be no precipitation. This dilution would give one part K₂O in 1600 as the point at which precipitation would not occur, thus agreeing closely with the previously noted statement of De Koninck. It is quite noticeable that the solutions so dilute are very slow in giving up their potash to the reagent, the precipitate is finer in grain, and the supernatant solution is darker in color. Moreover, with increasing dilution there is greater difficulty in detaching the precipitate from the sides of the beaker and in the case of the very dilute ones it was impossible to remove it all. Sutton attributes the irregularities of the results with solutions more dilute than 0.5 per cent. K2O to a tendency of the precipitate run through the filter. In order to test the point the filtrates from this dilution series were concentrated and allowed to stand for some

time, then filtered. In every case the results showed practically a blank, hence it is evident that this explanation does not satisfactorily account for the case. The conclusion is forced upon us that such dilution prevents the formation of the precipitate or perhaps decomposes the reagent as fast as added. This matter is a serious one, for in the case of the most determinations it is impracticable if not impossible to bring the dilution within such limits as necessary.

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Another possible cause of irregularity was the length of time allowed before filtration of the precipitate, and accordingly the series shown in Fig. 2 was undertaken to find if this did contribute in any way to the observed variations.



It will be seen that while variations from this cause are not of the magnitude of those occasioned by dilution, they are yet serious enough to cause a very undesirable amount of irregularity. The curves are all based upon the lowest titration result and show that in general the initial result is the lowest, that it rises quickly the first few hours, and gradually settles to a fairly constant quantity. The reagents and asbestos were tested in blank, but no permanganate was consumed for either. No further investigations were conducted on the Adie and Wood method, except a series which will be noted later to determine the effect of other metals present. The results just presented are sufficient to condemn the practice of precipitation by standing for almost all purposes, since it gives very uncertain results at best; the potash found varies inversely with the concentration, and the time of standing exercises considerable influence on it.

Variations Tried .- Having thus found that the method of Adie and Wood was inapplicable to ordinary work, my attention was next directed to the finding of some suitable modification that would be reliable. It was evident that most of the difficulty encountered in the use of my "acid method" lay in the manner of precipitation of the potash, although some slight error was introduced by the method of titration. After several trials of various methods I found, like Drushel, that the most satisfactory way of conducting the precipitation, and of eliminating the errors attributable to dilution and time of standing, was that of evaporating together the potash solution and reagent to pastiness on the steam bath, taking up with water and filtering through a Gooch asbestos filter. Some of the titrations were made like those of the preceding "acid method," but later it was found expedient to defer adding sulphuric acid until after boiling the mixture. It has been found convenient to filter the precipitate on the form of filter devised by Shimer,1 using asbestos for the pad. In no case has any difficulty been experienced in removing the precipitate from the sides of the glass tube, as was noted by Drushel with crucibles. The filter plate should be taken out and rinsed off to avoid the danger of its becoming coated with manganese hydroxide.

Addition of Acetic Acid in Precipitating.—It was found by a series of tests that the presence or absence in precipitating of τ cc. of strong acetic acid made no apparent difference in the titration results, yet its addition should not be neglected, as without it the precipitate clings tenaciously to the dish. A scheme for titrating the filtrate instead of the precipitate was found unavailing. The time consumed in titrating was found to be approximately one-sixth of that required by Drushel's method.

Procedure Adopted.—My modification of the method of Adie and Wood is as follows: The potash is brought into solution by any desired means, any excess of acid is driven off by evaporation, the residue taken up with water and any interfering metals removed by boiling with sodium carbonate, the solution filtered and the precipitate washed with hot water. Filtrate and washings are concentrated, acidified with acetic acid, and the K_2O precipitated as presently described.

1 Jour. Am. Chem. Soc., 27, 287 (1905).

For all the work of this section solutions of various potassium salts were made up having a strength of 0.75 per cent., or 1 cc. contains 0.0075 gram K₂O. In each determination 5 cc. were taken, making a total of 0.0375 gram K2O. By theory this amount should require 43.74 cc. KMnO4, making the volume of permanganate solution used about as large as possible and thus reducing the effect of titration errors. A quantity of potash solution equivalent to 0.0375 gram K₂O is placed in a porcelain evaporating dish, 10 cc. reagent added, and then 1 cc. strong acetic acid. The mixture is evaporated to pastiness on the steam bath, and after cooling is stirred up with 25-50 cc. water and filtered on asbestos, washing with sufficient water to remove the excess of reagent. The precipitate and felt are now transferred to a 250 cc. beaker, any adhering particles of the precipitate being removed from the sides of the tube by rubbing with a rubber tipped rod and rinsing into the beaker. An excess of permanganate is now added and the contents of the beaker brought to boiling. When they begin to darken, 5 cc. H2SO4 (1:1) is added and well agitated, then titration with N/10 oxalic acid and permanganate carried out to the usual end point. The cc. KMnO4 used, multiplied by the factor 0.0008573, gives the grams K2O.

Excess of Reagent.—It has been shown previously that I cc. of reagent is equal to 0.04 gram K_2O , hence 2 cc. would seem to be sufficient for all ordinary purposes. That such is not the case, however, is shown in Table III. These determinations were made on different days, one on KNO₃ and the other on KCl.

		Contraction of the
AD	ST.I	TII.

No.	Cc. KMnO4.	Per cent. K ₂ O.	Cc. reagent.	No.	Cc. KMnO4.	Per cent. K ₂ O.
1	17.9	40.8	1	6	3.75	8.57
2	29.4	67.2	2	7	6.70	15.32
			3	8	10.05	22.45
3	42.9	98.15	4			
4	43.95	100.55	5	9	22.15	50.65
5	44.07	100.75	10	10	43.55	99.57

The tabulated results show that while on some days practically all the potash will be precipitated by 5 cc. of reagent, yet at other times it will not; hence it is necessary to use 10 cc. reagent for each equivalent of 0.04 gram K₂O. Small volumes of the reagent precipitate the potassium in a state of division so fine as to render it impossible to filter without a great deal of running through. The filtrates from precipitations with 5.0 cc. or less of reagent are usually pink, as contrasted with the wine color of those containing a proper excess. In Table IV is shown the result of six determinations conducted exactly as described by Drushel.

			Т	ABLE IV.		
No.	Salt.	Cc. KMnO4.	Wt. K ₂ O.	Diff. K ₂ O.	Per cent K ₂ O.	•
l•	KNO3	45.90	0.03933	+0.00183	104.9	
2	K2SO4	46.10	0.03954	+0.00204	105 4	
3	KNO3	46.25	0.03965	+0.00215	105.75	
ŧ	KNO3	45.45	0.03897	+0.00147	103 9	
5	KNO3	45.85	0.03931	+0.00181	104.8	
5	KNO	45.25	0.03880	+0.00130	103.45	Ave. 104.7 per cent.

It will be seen that the results are higher than they should be, the average being 4.7 per cent. too much. The greatest of care was exercised with all these tests, and no reason is apparent for the high results.

Gravimetric Determination.—In Table V is given the results of six determinations on C. P. salts made by the gravimetric method, weighing the precipitate in carefully dried Gooches:

			TABLE	v.	
No.	Wt. ppt.	Wt. K ₂ O,	Diff. KgO.	Per cent. K ₂ O.	
1	0.1835	0.03805	+0.00055	101.5	
2	0.1834	0.03804	+0.00054	101.5	
3	0.1825	0.03786	+0.00036	101.0	
4	0.1844	0.03827	+0.00077	102.05	
5	0.1823	0.03782	+0.00032	100.85	
6	0.1802	0.03738	-0.00012	99.68	Ave. 101.09 per cent.

The average, 101.09 per cent., is seen to be a trifle higher than that found by the volumetric method, and this would seem to indicate that perhaps there is some secondary reaction occurring that exercises an influence on the composition of the precipitate, which is assumed to be K_2NaCo $(NO_2)_6.H_2O$, as given by Adie and Wood. Some of the minor variations were probably due to exterior conditions, but as the amount of reagent at hand was getting rather limited the series was not repeated.

Results from My Method.—In order to furnish a reliable basis for comparing the amounts of potash found with those actually taken, the series of determinations tabulated in Table VI was made rather extended.

			TABLE	VI.		
Salt used,	No. c deter	of s.	Cc. KMnO4.	Wt. K20.	Diff. K ₂ O.	Per cent K ₂ O.
ксı	10	Max Min Ave	45.20 43.35 44.05	0.03876 0.03734 0.03777	+0.00126 -0.00016 +0.00027	103.30 99.57 100.70
KNO9	10	Max Min Ave	44.65 43.35 43.95	0.03828 0.03717 0.03768	+0.00078 0.00033 +0.00018	102.10 99.12 100.50
K2SO4	8	Max Min Ave	44.60 43.85 44.20	0.03828 0.03760 0.03789	+0.00078 +0.00010 +0.00039	102.10 100.30 100.90

It will be seen that the amount of deviation between different determinations is much greater in the volumetric method than in the gravimetric, the cause probably being in the titration with KMnO₄. It will be found on working over the last five results of Drushel's Table I, that the amount of K,O found is 109.30, 108.00, 107.10, 105.85, and 107.65 per cent. of that taken, while with the first five of his Table II they run 100.40, 102.10, 100.00, 99.37, and 104.20 per cent. of the amount used. It is interesting to note that the average of these ten determinations is 104.40 per cent., as compared with the 104.7 per cent. I obtained in Table V. This would seem to show quite plainly that there is something in the method of titration that gives the difficulty with his method even more than with mine. The method of precipitation as now practiced seems to need but little further attention save as to the removal of interfering substances.

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Radicle Combined with K_2O .—Practically no difference is to be noticed in the accuracy of the determinations whether the acid radicle be Cl, NO_3 , or SO_4 , and this point is worthy of particular emphasis in view of the very decided saving of time, labor, and accuracy possible when it is not necessary to convert the potassium to the chloride form. The results obtained in the determination of potassium combined with various other acid radicles are shown in Table VII:

P44	1912 4	0.0240	TTT
$\mathbf{I} \mathbf{A}$	BLE	c V	TT

No.	Salt.	Cc. KMnO ₄ .	Wt. K2O.	Diff. K ₂ O.	Per cent. K ₂ O.	Ave. per cent.
1	KClO3	44.85	0.03846	+0.00096	102.50	
2	KClO3	45.50	0.03901	+0.00151	104.00	
3	KCl03	45.15	0.03871	+0.00121	103.25	
4	KClO3	44.25	0.03794	+0.00044	101.15	102.70
5	K ₂ CrO ₄	43.45	0.03725	-0.00025	99.35	
6	K2CrO4	42.30	0.03627	-0.00123	96.72	98.05
7	K2Cr2O7	43.30	0.03713	-0.00037	99.00	
8	K ₂ Cr ₂ O ₇	44.35	0.03803	+0.00053	101.40	100.20
9	K ₂ CO ₃	40.25	0.03451	-0.00299	92.03	
10	K2CO3	39.40	0.03378	-0.00372	90.08	
11	K2CO3	38.80	0.03327	-0.00423	88.71	
12	K ₂ CO ₃	39.50	0.03387	-0.00363	90.31	90.28
13	КНСО3	45.50	0.03862	+0.00112	103.00	
14	КНСО3	44.60	0.03828	+0.00078	102.10	
15	КНСО3	44.90	0.03850	+0.00100	102.70	102.60
16	K4Fe(CN)6	43.75	0.03751	± 0.00001	100.00	
17	K4Fe(CN)6					
18	K3Fe(CN)6					
19	K3Fe(CN)6	44.50	0.03820	+0.00070	101.85	

The chlorate gives results somewhat higher than the true ones, the chromate about as much lower. The dichromate seems to give quite reliable results, as is also the case with the ferro- and ferricyanide. With the last two, however, it is not always possible to get an accurate end point, since it is apt to be obscured by a dark color in the solution, whence the two blanks noted. Potash may also be estimated with fair accuracy in the form of bicarbonate, but strangely enough not as carbonate. The results show that the method is directly applicable to almost any salt of potassium except the carbonate.

Interfering Substances.—It having been found that the method is applicable with a fair degree of accuracy to the estimation of potassium combined with various acid radicles, it remained to investigate the influence on the determination of various

			TAI	BLE VIII	•		
Ne -	Foreign		wt	Cc			Per
No.	salt. I	Radicle.	radicle.	KMnO4.	Wt. K20.	Diff. K ₂ O.	K20.
1	Na2HPO4	P2O5	0.5	14.40	0.01235	-0.02515	32.92
2	Na ₂ HPO ₄	P_2O_5	0.1	40.45	0.03469	-0.00281	92.48
3	Na ₂ HPO ₄	P2O5	0.05	43.90	0.03764	+0.00014	100.40
4	Na ₂ HPO ₄	P2O5	0.01	44.10	0.03781	+0.00031	100.80
5	Na2B4O7	B ₂ O ₃	2.5	0.15	0.00013	-0.03737	0.34
6'	Na2B4O7	B ₂ O ₃	0.125	41.10	0.03524	-0.00226	93.97
7 '	Na2B4O7	B2O3	0.05	28.00	0.02401	-0.01349	64.02
8	SiO ₂	SiO ₂	1.0	44.90	0.03850	+0.00100	102.70
9	Na2SiO3	SiO ₂	1.0	9.30	0.00797	-0.02953	21.16
10	BaCl	BaO	1.0	14.00	0.01200	-0.02550	32.01
11	BaCl ₂	BaO	0.1	45.60	0.03910	+0.00160	104.30
12	BaCl ₂	BaO	0.01	44.90	0.03850	+0.00100	102.70
13	MnSO4	MnO	0.5	27.60	0.02366	-0.01384	63.11
14	MnSO4	MnO	0.05	44.50	0.03815	+0.00065	101.75
15	A1.(SO.).	A1=0=	0 3125	1 05	0 00090	-0.03660	2 40
16	Ala(SO4)3	AlaOa	0.0625	40.50	0.03472	-0.00278	92.60
17	Al2(SO4)3	Al ₂ O ₃	0.03125	44.50	0.03815	+0.00065	101.75
18	CuSO	CHO	0.25	33 50	0 02872	-0.00878	76 50
10	CuSO	CuO	0.05	45 40	0.03893	+0.00143	103 80
20	CuSO4	CuO	0.05	41.40	0.03516	-0.00234	93.74
21	Maso	MaQ	1.00	26 70	0 02280	-0.01461	61 05
22	MgSO	MgO	0.10	44 30	0.03798	+0.00048	101.30
23	MgCh	MgO	0.50	32.45	0.02782	-0.00968	74.19
24	MgCl2	MgO	0.05	24.05	0.01969	-0.01781	52.51
25	CaSO	CaO	0 1629	43 15	0.03700	-0.00050	98 66
26	CaCl	CaO	1.00	39.70	0.03404	-0.00246	90.77
27	CaCl	CaO	0.5	41.00	0.03515	-0.00235	93.74
28	CaCl ₂	CaO	0.01	39.15	0.03357	-0.00393	89.51
29	CaCl ₂	CaO	0.1	18.30	0.01569	-0.01181	41.84
30	CaCl ₂	CaO	0:03	27.95	0.02396	-0.01345	63.90
31	CaCl ₂	CaO	0.01	32.45	0.02782	-0.00968	74.19
32	Ca(NO ₃) ₂	CaO	1.0	25.95	0.02285	-0.01425	59.33
33	$Ca(NO_3)_2$	CaO	0.50	0.45	0.00044	-0.03706	1.48
34	$Ca(NO_3)_2$	CáO	0.10	38.75	0.03322	-0.00428	88.60
35	$Ca(NO_3)_2$	CaO	0.10	28.30	0.02426	-0.01224	64.71
36	Ca(NO ₃) ₂	CaO	0.05	40.85	0.03502	-0.00148	93.40
37	$Ca(NO_3)_2$	CaO	0.01	32.80	0.02812	-0.00938	74.99
38	$Ca(NO_3)_2$	CaO	0.01	39.70	0.03404	-0.00346	90.11
39	Fe(NO ₃) ₃	FeO	1.0	7.05	0.00604	-0.03146	16.12
40	Fe(NO ₃) ₃	FeO	0.5	9.65	0.00827	-0.02923	22.06
41	Fe(NO ₃) ₃	FeO	0.2	30.45	0.02611	-0.01039	69.62
42	Fe(NO ₃) ₃	FeO	0.05	43.80	0.03755	+0.00003	03 17
45	Fe(NO ₃)	FeO	0.03	16.05	0.01376	-0.02374	36 70
45	Fe(NO ₃)	FeO	0.01	38.40	0.03292	-0.00458	87.80
46	Fe(NO3)3	FeO	0.005	40.65	0.03485	-0.00265	92.94
47	FeCla	FeO	1.0	2 00	0.00171	-0.03578	4 57
48	FeCla	FeO	0.5	9.00	0.00772	-0.02978	20.58
49	FeCla	FeO	0.2	35.45	0.03040	-0.00710	81.05
50	FeCla	FeO	0.1	44.55	0.03820	+0.00070	101.90
51	FeCla	FeO	0.5	43.80	0.03755	+0.00005	100.15
52	FeCla	FeO	0.04	17.55	0.01505	-0.02245	40.13
53	FeCla	FeO	0.01	41.85	0.03588	-0.00162	95.68
54	FeCla	FeO	0.005	41.40	0.03549	-0.00201	94.66

other substances, evidently a point of vital importance to the value of the method as applied to actual work. All the substances most likely to occur in ordinary samples have been included in this investigation. It has been previously noted that De Koninck says the ordinary metals do not give a precipitate with this reagent. This was found to be true, but nevertheless they may under many conditions work serious harm to the determination. When subjected to the beaker method of precipitation they seem to influence the results but little, but in the evaporation method radically different conditions occur, in consequence of which there are probably reactions between these metals and the potash precipitate which produces great irregularity. My results on this investigation are given in Table VIII.

But little comment is needed on the results given here. They show that in general a small amount of a foreign metal may give results a little high, but a large amount tends to materially reduce the amount of potash recovered. The greatest danger would seem to exist in the case of MgCl₂, the iron and the soluble calcium salts. Evidently it is unsafe to trust a determination where any of these metals are present. Adie and Wood advised precipitating out all these interfering metals by boiling with Na_2CO_3 , and this would seem to be the best procedure.

Irregularity of Results.—Drushel has given a short series of results where metals are present of which brief mention seems appropriate. He seems to have had CaCl₂ and MgCl₂ present in each test, while BaCl₂ and Sr(NO₃)₂ were added in some cases. From the results it seems almost impossible that these could have been subjected to his adopted mode of precipitation in view of what I have found in the preceding determinations. In Table IX is given a comparison of three of his results and three of mine run by the beaker method of precipitation of Adie and Wood:

TABLE IX.

				Drushel	!'s.		
N	Wt. o. CaCl ₂ .	Wt. MgCl ₂ .	Wt. BaCl ₂ .	Gram K ₂ O taken,	Gram K ₂ O found.	Gram error.	Per cent. K2O.
	2 0.3	0.5		0.0237	0.0234	-0.0003	98.74
	7 0.5	1.0		0.0711	0.0713	+0.0002	100.27
(5 0.5	1.0	0.5	0.0237	0.0251	+0.0014	105.90
				Mine			
No		wt	salt t	Gram K ₂ O	Gram. K2O found.	Error.	Per cent. K.O.
10		0.10	101 D	0315	0.03111	-0.00039	98 76
1	Ca(NO ₃)2.	0.15	086 0	0315	0.03033	-0.00017	96.29
2 3	BaCl ₂	0.2	330 C	0.0315	0.03579	+0.00429	113.60

It is worthy of note that there is a general agreement between the two series, and it would seem from this that perhaps his precipitations may have been made by this latter method. The very fact that MgCl, was present in every case would seem evidence enough that this precipitation was not made by evaporation, since this would have unavoidably liberated enough HCl to seriously affect the results. It should be plainly understood in a consideration of these results that it is very unlikely any two workers will be able to obtain the same results with these substances present, for in almost every case extreme irregularity characterizes the determinations thus made. The same general conclusion would surely result however, that small amounts do not matter greatly, but that larger ones must not be present. The one conspicuous and fortunate exception is sodium. From the fact that this is present in the constitution of the precipitate it might be inferred that it would cause no interference, and numerous tests with even very large amounts show this to be the case.

Precautions Necessary .- To insure success in the use of the method the following precautions must be observed. Ammoniacal fumes should be absent. Should reagents or asbestos be of doubtful quality blanks must be run on them and a correction made on the regular results. The potash solu-" tion should not be too dilute previous to precipitation. Do not neglect the addition of strong acetic acid, and should difficulty be experienced at any time with sticking of the precipitate to the sides of the dishes it will be found well to add a somewhat larger amount. Do not allow evaporation to proceed too far as it may in some cases cause trouble. Care should be exercised in evaporating to see that too vigorous a heat is not applied. since when the solution is getting thick it may spirt out of the dish if too hot. In carrying out the titration it is a matter of common occurrence to have manganese hydroxide stick to the sides of the beaker. This must be taken up by a slight excess of oxalic acid, assisted if need be by loosening by a rubber-tipped rod. When all the coating has disappeared the rod should be taken out and rinsed, since rubber would affect the permanganate titration.

Conclusion.—This method seems to be one of great promise and its development will be a matter of interest to all chemists, although to none in such a degree perhaps as with agricultural workers. In conclusion, I wish to acknowledge my indebtedness to Mr. Drushel for the assistance his papers have been to me in the latter part of my work. He has done a great deal of praiseworthy work in connection with the method. A great deal of assistance has also been afforded by the articles previously mentioned. Since the preparation of this article, and too late to be discussed in it, the paper of Shedd¹ has appeared on the applicaiton of Drushel's method to the estimation of total potassium in soils.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

A METHOD FOR THE DETERMINATION OF CITRAL IN LEMON EXTRACTS AND LEMON OILS.

By R. S. HILTNER. Received July 13, 1909.

The method proposed by Chace² for determining citral in lemon oils and extracts has been adopted almost universally by food and drug chemists. It has afforded a valuable means of detecting spurious and adulterated products. Experience has shown that for accuracy the method leaves little to be desired. It is applicable, with slight modifications, to all grades of commercial extracts giving uniformly reliable results. Other methods have been proposed for the estimation of citral, but, according to Chace³ and Gildemeister and Hoffman,⁴ all have failed because of insufficient accuracy.

By the method to be described in the following paragraphs, the author has sought to eliminate certain difficulties encountered in the various other methods. The reagent used, although active with other aldehydes, is much more selective of citral than other reagents that have hitherto been suggested, and reacts negatively with aldehydes, other than citral, commonly present in commercial lemon extracts and oils. Its action, moreover, is quite independent of temperature and time. The proposed method is colorimetric in principle, making use of a dilute alcoholic solution of metaphenylene diamine hydrochloride as the reagent. This substance reacts quickly with citral at room temperature, yielding a clear, yellow-colored solution, the intensity of color being proportional to the amount of citral present. The color produced

4 "The Volatile Oils." Gildemeister and Hoffman, trans. by Edw. Kremers.

is reasonably permanent. The details of the method, as at present developed, are as follows:

REAGENTS.

Metaphenylene Diamine Hydrochloride Solution.-Prepare a 1 per cent. solution of metaphenylene diamine hydrochloride in 50 per cent. ethyl alcohol. Decolorize by shaking with fuller's earth, or animal charcoal, and filter. The solution should be bright and clear, free from suspended matter and practically colorless. It is well to prepare only enough solution for the day's work, as it darkens on standing. The color may be removed from old solutions by shaking again with fuller's earth or animal charcoal.

Standard Citral Solution .- Dissolve 0.250 gram of C. P. citral in 50 per cent. ethyl alcohol and make up the solution to 250 cc.

Alcohol .- For the analysis of lemon extracts, 90 to 95 per cent. alcohol should be used, but for terpeneless extracts alcohol of 50 to 60 per cent. strength is sufficient. Filter to remove any suspended matter. The alcohol need not be purified from aldehyde. If not colorless, render slightly alkaline with sodium hydroxide and distil.

APPARATUS.

Any convenient form of colorimeter may be used. The writer has obtained concordant and satisfactory results with the use of a form of colorimeter designed by Oswald Schreiner¹ and prefers this form. By lining the inner tubes with unglazed, opaque, black paper, so as to eliminate side lights, and leaving only the discs of light at the bottom of the tubes visible, much closer comparisons may be drawn. Good results were secured also with Eggertz tubes. With this latter apparatus alcohol is added, small quantities at a time, to the stronger colored solution until, after shaking and viewing transversely, the colors in the two tubes are exactly matched. Calculations are then made by establishing a proportion between the volume of samples taken and the final dilutions.

MANIPULATION.

All of the operations may be carried on at room temperature. When it is desired to determine citral by weight in the sample, weigh into a 50 cc. graduated flask, 25 grams of the extract and make up to the mark with alcohol (90 to 95 per cent.); stopper the flask and mix the contents thoroughly. Assuming the use of a Schreiner colorimeter, pipette into the colorimeter tube 2 cc. of the above solu-

¹ Jour. Amer. Chem. Soc., 27, 1192 (1905).

¹ THIS JOURNAL, 1, 302 (1909).

² Jour. Amer. Chem. Soc., 28, 1472 (1906). 3 Ibid., 28, 1473 (1906).

tion, add 10 cc. of metaphenylene diamine hydrochloride reagent and complete the volume to 50 cc. (or other standard volume) with alcohol. Compare, at once, the color with that of the standard, which should be prepared at the same time, using 2 cc. of standard citral solution and 10 cc. of the metaphenylene diamine reagent, and making up to the standard volume with alcohol. From the result of this first determination calculate the amount of standard citral solution that should be used in order to give approximately the same citral strength of the sample under examination, then repeat the determination. Make several readings, which should agree closely, and from the average, or the totals, calculate the amount of citral in the sample. In the case of samples colored with naphthol yellow S, or martius yellow, add a drop of concentrated hydrochlorle acid to both sample and standard before adding the metaphenylene diamine reagent. Unless very strongly dyed, the effect of the coloring matter is inappreciable. When the amount of citral in the sample is small (less than 0.1 per cent.) it is well to take a larger aliquot portion of the sample, rather than to take a correspondingly smaller amount of the standard solution, in order to produce a strong yellow, necessary for accurate comparisons.

Citral in lemon oil may be determined with some degree of accuracy, in a similar manner, by first making an "extract." Five to eight grams in 100 cc. of alcohol is a convenient strength to use. The same difficulty obtains here, of course, as with the fuchsin-sulphurous acid method, namely, as stated by Chace that "the error made in comparing the solution and standard becomes so great when multiplied to correct for the dilution that it somewhat impairs the usefulness of the method for oils." However, it is safe to say that the results obtained are accurate within 0.2 or 0.3 per cent.

A number of experiments have shown that at room temperature the metaphenylene diamine hydrochloride reagent produces no color reaction with small amounts of acetaldehyde. It is therefore unnecessary to use aldehyde-free alcohol. The small quantity of acetaldehyde commonly present in rectified commercial alcohol is not visibly affected by the reagent. The maximum intensity of the color reaction with citral seems to be developed immediately and therefore observations may be made at once. The color normally is quite permanent and hence considerable latitude in time is allowable. Observations made immediately and again after half hour standing at room temperature gave practically the same results.

In the case of commercial terpeneless extracts, the yellow color develops to its full extent at once and holds without change for thirty minutes or more. The same is usually true of ordinary extracts containing lemon oil terpenes. Rarely, the yellow color at first produced gradually changes to a vellowish green tint. In this latter case, therefore, it is necessary to make the comparisons of color immediately after adding the reagents. In the course of the year's work in this laboratory, out of a large number of samples examined, only one sample of lemon oil and three of commercial lemon extracts (all purported to be pure products) gave this abnormal color, that is, a vellowish green tint instead of the characteristic yellow. In these four cases, and with the sample of citronellal mentioned below, the colors produced, which varied from yellowish green to greenish blue, are now believed to be due to the blending of the yellow tint from citral with the blue produced by the impurity common to all, probably partially oxidized limonene. This subject is being investigated. Obviously, the citral in such abnormal products cannot be accurately determined by the foregoing method. Quite recently, it was observed that when oil of lemon or oil of orange was allowed to stand exposed to the air for a few days, a greenish vellow color was produced on the addition of the metaphenylene diamine reagent and alcohol; the longer the exposure the darker and more bluish was the color yielded. From this it is inferred that in the few abnormal cases noted the lemon oil had become in part changed by oxidation. Apparently, the terpenes only undergo change, since no terpeneless extracts examined gave any abnormal color. It is obvious too from the foregoing, that alcohol in the extracts prevents the oxidation. Extracts that are properly made from pure fresh oil, direct from the coppers, conditions that usually obtain, may easily be examined for citral by this method.

Other normal constituents of lemon oil seem to be unaffected by metaphenylene diamine hydrochloride. Dilute solutions of citronellal in alcohol yield no color when treated with the reagent, except after standing at least thirty minutes. It was noted that slowly a slight blue or greenish tint developed. From recent experiments it is believed that this final color was due to impurities, terpenes probably, in the citronellal used. The sample was labeled "pure citronellal." It was not tested further to determine its quality.

The effect of the reagent on limonene has not yet been fully determined. Most of the samples of lemon oil tested gave the normal yellow color that was permanent and identical with that produced with pure terpeneless citral solution and correct in intensity for the amount of citral present. Since limonene is present in lemon oil to the extent of about 90 per cent., it is therefore reasonable to infer that it does not react with metaphenylene diamine hydrochloride, or at least does not produce a distinctive color. However, the only sample of limonene obtainable, when dissolved in alcohol and tested with the reagent, produced a strong, clear, indigo-blue color. Here again partial oxidation may account for this abnormal color. The same result was obtained after redistilling the sample. This sample was procured from a very reliable firm and was labeled "pure limonene." It is interesting to note that under the same conditions, ordinary American turpentine, in dilute solution in alcohol, gives the same blue color.

The degree of accuracy of the method is indicated in Table I. Weighed amounts of pure citral were dissolved in 50 per cent. alcohol and tested by the process described. The tests were made under varying conditions of temperature and time of standing after addition of the reagent, using in some cases aldehyde-free alcohol and in others ordinary commercial "rectified spirit" as the diluent.

	T	ABLE I.					
Gram citral per 100 cc.							
No.	Used.	Found.	Difference.				
1	0.0800	0.0849	+0.0049				
2	0.0666	0.0700	+0.0034				
3	0.0500	0 0500	0.0000				
4	0.1000	0.0990	-0.0010				
5	0.0956	0.0946	-0.0010				
6	0.0500	0.0500	0.0000				
7	0.1200	0.1170	-0.0030				
8	0.0610	0.0610	0.0000				
9	0.2000	0.1970	-0.0030				
10	0.0250	0.0243	-0.0007				
11	0.0250	0.0246	-0.0004				
12	0.2025	0.2044	+0.0019				

Table II shows the results of tests of commercial extracts by Chace's method and by the one here proposed.

It is apparent in the following table that fuchsinsulphurous acid tends to give slightly higher values for citral than metaphenylene diamine. This is believed to be due to the positive reaction of the former reagent with acetaldehyde and citronellal which are probably always present in minute quantity in commercial extracts and which give no color reaction with the latter reagent. Sampes Nos. 5, 8 and 9 show slightly less citral by fuchsin than by the other reagent. The significance of this is not clear. It is at least possible that the discrepancy is due to experimental error.

	TABLE II.	Gram citral per 100 cc.			
No. of sample.	Kind of extract.	By fuchsin sulphurous acid.	By meta- phenylene diamine hydrochloride.		
1	Terpeneless	0.100	0.098		
2	"	0.059	0.056		
3	"	0.117	0.098		
4	"	0.117	0.093		
5	"	0.072	0.079		
6	8.4 per cent. lemon oil	0.270	0.264		
7	Terpeneless	0.074	0.064		
8	Made from lemon oil and lemon grass oil, yellow				
	dye	0.016	0.019		
9	Terpeneless	0.045	0.053		
10	5.25 per cent. lemon oil	0.326	0.252		
11	Terpeneless with citral from				
	lemon grass oil	0.313	0.305		
12	Terpeneless	0.137	0.117		
13	"	0.078	0.061		
14		0.096	0.088		
15		0.088	0.086		

In order to ascertain how nearly uniform the results would be by different operators, the same samples of commercial extracts were submitted to three analysts in this laboratory. The results are given in Table III, expressed as percentage of citral.

	1	ABLE	III.				
	Sample No.						
Analyst.	ī.	2.	3-	4.	5.	6.	7.
A. E. Leach	:	0.060	0.102	0.032	0.388		
. H. Wise	0.097	0.060	0.100	0.030		0.098	0.080
S Hiltner	0.098	0.056	0.098	0.040	0.344	0.093	0.079

In brief, the apparent advantages of the method are, first, that all operations may be carried on at room temperature and the tests may be made immediately after adding the reagent. Second, it is unnecessary to use especially purified alcohol, free from aldehyde. Third, more nearly correct results for citral may be secured in the analysis of commercial extracts, since the reagent used acts negatively with acetaldehyde and citronellal, usually present in small quantity in such products.

The author wishes to acknowledge his indebtedness to Mr. Albert E. Leach for his kind assistance and helpful suggestions in this work.

DENVER, COLO., July, 1909.

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THE INFLUENCE OF SHADE UPON THE COM-POSITION OF PLANTS.

By R. W. THATCHER. Received October 26, 1909.

About two years ago the writer, together with H. R. Watkins, published a brief note on the "Influence of Shade during Ripening upon the Proximate Constituents of the Wheat Kernel."¹

The experiments there described have been amplified and extended to other crops than cereals. Different densities of shade, different lengths of time of shading, and various different crops have been employed. The same general methods of arranging the shade and of harvesting the crops were used as are recorded in the former paper. The methods of analysis employed were those of the Official Agricultural Chemists.

A large number of shaded *versus* unshaded samples have been analyzed. Some typical results are included in the accompanying table. Many others might be added, but would serve only to confirm the facts which are probably sufficiently illustrated by those which are presented. nearly dry in maturing, but is quite apparent in the potato tubers.

The percentage of mineral matter or "ash" is higher in the shaded samples in every pair except one, the oats. Other pairs of oats than that included in the table showed an increased percentage of ash in the shaded sample, however. Hence the single exception in the table may be regarded as the only exception to the general rule which has been found in our work.

The percentage of crude protein is higher in the shaded sample in every case. The average increase is about 10 per cent. of the total found in the unshaded sample but in certain individual cases in the potatoes and the wheat it rises to nearly 50 per cent.

The fat content (ether extract) is generally lower in the shaded samples, but there are occasional exceptions. The differences in either direction are usually small and are probably without very much significance. At least, it will take further experiments, using plants which elaborate larger proportions of ether-soluble matter, to afford conclusive

		Acsults of analysis.							
					in C	ompositio	n of dry m	atter.	
Crop and variety.	Kind of shade.	Moisture.	Dry matter.	Ash.	Protein.	Fats.	Fiber.	Starch.	Undetermined.
Potatoes:								A CARE AND	
Burbank	none	77.65	22.35	4.95	9.49	0.13	2.92	70.50	12.01
Burbank	burlap	78.97	21.03	5.19	11.99	0.13	2.82	65.10	14.77
Vigorata	none	77.02	22.98	4.14	8.99	0.38	2.99	72.70	10.80
Vigorata	burlap	79.14	20.86	4.49	10.10	0.20	2.75	70.39	12.27
White elephant	none	78.73	21.27	4.75	9.63	0.49	3.03	67.88	14.22
White elephant	burlap	80.72	19.28	5.09	14.25	0.56	3.10	64.83	12.26
Field peas:									
Gov't, No. 19788	none	6.87	93.13	3.31	28.52	1.49	5.30	53.83	7.55
Gov't, No. 19788	burlap	6.94	93.06	3.41	34.30	1.12	4.73	51.16	5.28
Emmer:		March 1977							
Spring	none	9.96	90.04	2.63	19.43	3.33	2.72	66.90	4.99
Spring	9-oz. ducking	9.28	90.72	2.86	21.82	1.85	1.56	66.13	5.78
Wheat:									
Winter	none	10.19	89.81	1.94	18.94	2.79	4.39	66.92	5.02
Winter	9-oz. ducking	9.95	90.05	2.40	20.13	2.68	3.64	66.46	2.69
Spring	none	8.77	91.23	2.05	18.17	1.74	2.85	66.78	8.41
Spring	burlap	8.70	91.30	3.22	27.80	2.04	3.24	59.24	4.46
Sonora	none	8.49	91.51	1.83	18.73	2.21	2.23	68.84	6.16
Sonora	burlap	8.71	91.29	2.09	19.92	2.06	2.60	66.85	6.48
Oats:		一,当他们;							
Sixty-day	none	6.96	93.04	5.14	18.00	4.84	9.51	49.72	12.79
Sixty-day	burlap	6.69	93.31	4.91	20.04	4.03	9.03	48.32	13.67
Barley									
Bearded	none	8.22	91.78	3.08	19.64	2.57	4.77	62.86	7.08
Bearded	burlap	8.10	91.90	3.10	23.67	2.10	4.83	59.25	7.05
Hullless	none	8.76	91.24	2.43	18.30	2.90	2.30	67.17	6.90
Hullloss	burlan	9.43	90.57	2.76	20.08	2.62	2.14	65.19	7.21

These results show the following effects of the shading:

The moisture content is increased or, conversely, the percentage of dry matter is decreased, in the shaded plants. This is not noticeable in those plants which, like the peas and cereals, become very

1 J. Am. Chem. Soc., 29, 764-767 (1907).

evidence as to the effect of shade on this constituent.

The acid- and alkali-insoluble matter, conventionally designated as "crude fiber," appears to show no regular effect of the shading, being sometimes slightly higher and sometimes slightly lower in the shaded sample. The percentage of starch, as determined by acidhydrolysis, is invariably lower in the shaded sample. But, contrary to our expectations, the effect upon the starch content is less marked than that upon the mineral and nitrogenous matter. In no case is the proportional decrease in starch equal to the corresponding increase in the other two constituents.

The column headed "undetermined" represents the difference between the total of the five proximate constituents as determined by the official methods and 100 per cent. What this undetermined constituent may be or whether it is simply carbohydrate matter not accurately estimated by the admittedly empirical methods of analysis is a question which many investigators have as yet failed to solve. However, if the last three columns were totaled and reported simply as "carbohydrates," the effect of the shading upon this constituent group would be identical with that shown by the starch determinations in every case.

In brief, then, it may be said that the shading, whatever the texture of the material used or the length of the shading period, caused an increase in the percentage of moisture, mineral matter, and nitrogenous matter, and a decreased percentage of starch or carbohydrates. But the increase in other constituents is not directly proportional to the decrease in starch. Hence, we conclude that the changes produced by the shade are not simply a deterrence of the elaboration of starch or carbohydrates in the absence of direct sunlight, but other physiological changes are induced by the shading. This opens an interesting field for study by the plant physiologist. That the attention of other investigators is being attracted to this problem is shown by the recently published results of Lubimenko1 and the controversy between Rawson and Ingle and Evans² as to whether observed changes in composition are actually due to differences in available sunlight or to changes in temperature induced by the shading medium.

The thanks of the writer are due to Mr. H. R. Watkins and to Mr. Geo. A. Olson for the analytical work reported in this article.

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POTASSIUM-IODIDE-STARCH PAPER.

By C. G. STORM. Received September 20, 1909.

The facts which are noted in the literature of explosives concerning the potassium-iodide-starch paper used in the heat test or Abel test, are found to be misleading in many cases, particularly as to its keeping qualities and the effect of light on the paper. The following work on this subject was carried out by the author while in charge of the chemical laboratory of the Navy Smokeless Powder Works, at Indian Head, Md. Heat test paper prepared in this laboratory with proper precautions and preserved in tight stoppered dark bottles has been found in perfect condition after a period of eight years.

The method of preparation is about the same as that usually employed, except that the paper before treating is washed for only a short time in distilled water (dipping for about 10 seconds), also the potassium iodide and starch solutions are cooled before mixing.

The paper used is Schleicher and Schüll's 597. This quality of paper weighs about 5 grams per 100 sq. in. It is cut in strips about $24'' \ge 6''$, and after washing hung on clean cords over night to dry in a room free from fumes.

The best quality of potassium iodide obtainable is recrystallized three times from hot absolute alcohol, then dried and I gram dissolved in 8 oz. distilled water. Corn-starch is well washed by decantation with distilled water, dried at a low temperature, 3 grams rubbed into a paste with a little cold water and poured into 8 oz. boiling water in a flask. After boiling gently for ten minutes, the starch solution is cooled and mixed with the potassium iodide solution in a glass trough.

The washed and dried paper is then at once dipped in this mixture, immersing each strip for about 10 seconds, and hanging one end over a clean cord to dry. The dipping is done in a very dim light and the paper left over night to dry in a perfectly dark room. Every precaution must be taken to insure freedom from contamination in preparing the materials, and absence of laboratory fumes which might cause decomposition. When dry, the paper is cut into pieces about $1'' \ge 3/8''$ and preserved in tight glass-stoppered bottles, the edges of the large strips being first trimmed off about 1/4 in., to remove portions which are sometimes very slightly discolored. The finished paper should be of good white color. It has been found

¹ Bull. Acad. St. Petersb. 1907, 395-426; and Compt. rend., 144 (May, 1907), 1060.

² Transvaal Agr. Jour., 4 (1906); 75, 558-566; 16, 743-754; and 17, 140-148.

that the test paper will invariably give a coloration with acetic acid, the intensity of the test depending on the strength of the acid used. In the report of His Majesty's Inspector of Explosives, for 1907, it is stated that washing the paper in 10 per cent. acetic acid and then in water, before dipping in the KI-starch solution, removes impurities from the paper, thus preventing the discoloration in the acetic acid test. These results have not been confirmed by experiments made by the author.

The method of testing relied on is that of comparing the new paper with regular stock paper which has been found satisfactory. This is done by making comparative tests at 65.5° C., on the same sample of nitrocellulose, under as near as possible the same conditions, a series of five tubes of the sample containing varying amounts of moisture being used for each test and the minimum test of each series noted. A new lot of paper is usually tested within one week after preparation and should give results agreeing closely with those of older lots.

In the following tables are noted the results of comparisons of different papers of widely varying age.

Date of prepara- tion of paper.	Age of paper at time of test.	Nitrocellulose, Lot No.	Heat test at 65.5 C. Min.
12- 7-06	3 months	2462	44
6- 8-06	9 months	2462	46
5-30-06	10 months	2462	44
4-19-06	11 months	2462	44
3-19-06	1.year	2462	44
6-28-05	1.year, 9 months	2462	47
3-18-05	2 years	2462	43
2-10-02	5 years	2462	43
Jan03	3 months	914	36
Apr00	3 years	914	32
9-25-08	5 months	3505 D	34
9-10-07	1 year, 5 months	3505 D	36
6- 8-06	2 years, 8 months	3505 D	35
6-27-05	3 years, 8 months	3505 D	35
8-12-04	4 years, 6 months	3505 D	35
5-23-031	5 years, 9 months	3505 D	21
10-11-021	6 years, 4 months	3505 D	20
7-19-01	7 years, 7 months	3505 D	34
10-24-00	8 years, 4 months	3505 D	33
4- 2-07	2 months	Sample X	26
6-21-07	6 days -		26
10- 5-07	10 days	2812	43
9-10-07	35 days	2812	45
11-12-07	1 day	2855	51
6-21-07	5 months	2855	50
2- 8-07	1 day	2446	50
12- 7-06	2 months	2446	50
12- 7-06	2 days	2377	56
6- 8-06	6 months	2377	52
12 7 06	1 14 months	2413	43
6- 8-06	7 1/2 months	2413	45
0- 0-00	11/ months	2110	16
12- 7-06	1 ½ months	2401 B	10
6- 8-06	1 2 months	2401 B	18

¹ (NOTE.—The papers of 5–23–03 and 10–11–02 were preserved wrapped in paper and placed in a tin box with loosely fitting cover, within a closed drawer. The low test is undoubtedly due to deterioration.) Except where noted, all samples had been kept in tight glass-stoppered black bottles since manufacture, being opened only occasionally for the purpose of taking out a supply of paper.

From these results it is evident that potassiumiodide-starch paper, when properly prepared, is in condition for use within 24 hours after dipping, and when properly preserved will remain in good condition practically indefinitely.

To determine the effect of light, a batch of test paper was divided up in four bottles of different colored glass—plain colorless, amber, blue and black (opaque), the bottles tightly stoppered and sealed, and placed in a window ledge receiving good light but not direct sunlight. After three weeks' exposure, the same lot of nitrocellulose was tested with paper from each bottle and also from the regular stock paper. Results of test:

Paper. Hea	t test at 65.5° C Sample A. Min.
Regular stock	. 59
Colorless bottle	. 48
Amber bottle	. 60+
Blue bottle	. 60+
Black bottle	. 60+

The bottles were then exposed to direct sunlight for a total of 106 hours and samples of nitrocellulose tested with each paper as before:

	Heat te	test 65.5° C.			
Paper.	Sample B. Min.	Sample C. Min,			
Regular stock	21	45			
Colorless bottle	20	46			
Amber bottle	20	51			
Blue bottle	20	44			
Black bottle	20	50			

During a further exposure to light for two months, a large portion of the time to direct sunlight, the blue and brown bottles were broken. Tests of the other samples were as follows:

Paper.	Heat test 65.5° Sample C, Min.
Regular stock	45
Colorless bottle	48
Black bottle	44

C.

Apparently the action of light on heat test paper for even considerable periods is not in the least deleterious, provided there is no contact with moisture or fumes. There are reasons, however, for the belief that the paper, when freshly prepared, is more sensitive to the action of light than after it has aged for a time.

U. S. GEOLOGICAL SURVEY, TECHNOLOGIC BRANCH, PITTSBURG, PENNA.

POTASH TESTS IN COMMERCIAL FERTIL-IZERS.¹

By J. E. BRECKENRIDGE. Received August 29, 1909.

The fact that potash tests in fertilizers as carried out by the methods of the Association of Official Agricultural Chemists are low seems to have been well established.

To determine where this loss occurs and what conditions effect this loss, in 1906 I made the following experiments:

		Theory.	Results by	and a start shirth
1.56		Per	official	Loss.
Exi	P.	cent.	method.	Per
NO	the second s	R ₂ O.	Per cent.	cent.
1	Fresh acid phosphate and muriate of			
	potash	6.23	6.06	0.17
2	Fresh acid phosphate and high-grade			
	sulfate of potash	6.28	5.98	0.30
3	Fresh acid phosphate and double			
	manure salt	7.09	6.79	0.30
4	Fresh acid phosphate and 30 per cent.			
	salt	8.48	8.31	0.17
5	Fresh acid phosphate and 20 per cent.			
	salt	10.19	10.00	0.19
6	Fresh acid phosphate and muriate of			
	potash and 7 per cent. CaCO ₃	6.23	6.07	0.16
7	Fresh acid phosphate and muriate of			
	potash and 7 per cent. CaCO ₃ and 6.5			
	per cent, sulfate of iron	6.23	5.84	0.39
8	Fresh acid phosphate and muriate of			
	potash and 7 per cent. CaCO3 and 6.5			
	per cent, iron and aluminum phos-			
	phate rock	6.23	5.90	0.33
9	Fresh acid phosphate and muriate of			
	potash and 6.5 per cent, CaCO ₃ and			
	6.5 per cent, sulfate of iron and 6.5 per			
	cent NaCl	6.23	6.11	0.12
10	Fresh acid phosphate and 30 per cent.			
	salt and CaCO2 and 6.5 per cent, sul-			
	fate of iron	8.46	7.87	0.59
		The second se	and the second se	

The materials used in experiments Nos. 1, 2, 3, 4 and 5 were weighed into flasks, water added and the whole boiled for one hour, then proceeded as in official method.

The materials used in experiments Nos. 6, 7, 8, and 9 were weighed into flasks and water added to a paste and heated to 212° F. for 20 hours, then proceeded as in official method.

The materials used in experiment No. 10 were weighed into flask and water added to a paste and allowed to stand longer than experiments Nos. 6, 7, 8 and 9—about three days on top of a steam bath—then analyzed by official method.

Remarks.—Potash salts having no chlorine, as high-grade sulfate of potash and double manure salt, give greater loss than muriate of potash, 20 per cent. and 30 per cent. salts.

Compounds of iron and aluminum and lime have the greatest effect in giving low potash results.

¹ Read at meeting of American Chemical Society, Detroit, 1909.

Excess of chlorides lessens this loss as in experiment No. 9, due, I believe, to hydrochloric acid formed by the action of the phosphoric acid in the acid phosphate on the muriate. Any insoluble compounds which might form by the action of the soluble potash on the insoluble material in the rock, especially the silicates of iron, alumina and lime, would at once be dissolved by the hydrochloric acid formed and having ammonium chloride in the solution, when the ammonia and ammonium oxalate are added, the occlusion of potash would be somewhat prevented.

Further investigation led to the following experiments in 1908 and 1909:

Experiments with known amounts of acid phosphate and muriate of potash, allowing the solution as made by the official method, and having had the ammonia and ammonium oxalate, to stand different times before filtering:

Weighed into a 500 cc. flask 9 grams of acid phosphate, testing water-soluble potash 0.02 per cent., and 1 gram muriate of potash, testing watersoluble potash 51.70 per cent. Proceeded as in official method, allowing solution, having had the ammonia and ammonium oxalate, to stand before filtering:

	Result. Per cent. K ₂ O.	Theory. Per cent.	Loss. Per cent.
2 hours	4.84	5.19	0.35
24 hours	4.94		0.25
72 hours	5.06		0.13

Mr. M. H. Pingree, in a paper before this Society at Baltimore, in 1908, found that in allowing the solution to stand two weeks before filtering, the theoretical amount of potash would be found. His results were:

"Sample of acid phosphate and sulfate of potash, analyzed by official method, allowing solution having had the ammonia and ammonium oxalate to stand.

	Per cent. K ₂ O.	Theory. Per cent.	Loss. Per cent.
Ordinary time gave as a result	5.04	5.45	0.41
1 week	5.39		0.06
2 weeks	5.41		0.04

Sample, sulfate of potash, fish, acid phosphate and blood gave by official method:

	Per cent. K ₂ O.	Theory. Per cent.	Loss. Per cent.
Standing ordinary time	5.31	5.62	0.31
1 week	5.48		0.14
2 weeks	5.62		None

There seems to be a secondary reaction, by which the lost potash goes into solution on long standing in presence of ammonia. The weight of sample was reduced to 5 grams in a 500 cc. flask and the official method was followed, allowing solution to stand two hours before filtering. Result:

4.89 per cent. K_2O on theory of 5.19 per cent. Loss, 0.30 per cent.

The following method was tried, which we shall call B, using 5 grams for weight:

Method B.—Placed sample of fertilizer on a 11 cm. filter paper and washed with small portions of cold water into a 500 cc. flask if 5 grams were amount of sample taken, and into a 200 cc. flask if 2 grams were taken, until the flask is about four-fifths full.

Added to washings in the flask 5 cc. hydrochloric acid (concentrated), heated to boiling, made alkaline with ammonia, added ammonium oxalate, cooled at once and filtered and proceeded as in official method. Result:

5.06 per cent. K₂O on a theory of 5.19 per cent., making loss of 0.13 per cent.

Remarks.—We shall notice that washing the sample on filter reduces our loss to 0.13 per cent. K₂O on a theory of 5.19 per cent., while the official method gave us a loss of 0.35 per cent.

To find whether the materials insoluble in acid, as we find them in phosphate of rock, cause this loss, or whether the precipitation by ammonia and ammonium oxalate in the absence of these insoluble materials causes the loss, or both, the following experiments were made:

Experiments with Water Solution of Acid Phosphate and Water Solution of Muriate of Potash, with and without Carbonate of Lime and Hydrate of Lime.—Solution No. 1: 20 grams acid phosphate in 300 cc. of water, heated and filtered into a 500 cc. flask and residue washed to 500 cc.

Solution No. 2: 4 grams muriate of potash in 200 cc. flask, dissolved in water and made to mark.

Exp.	Theory. Per cent		Loss. Per	Gain. Per
No. 1 Added 50 cc. of solution No. 1 at 10 ap of solution No. 2 in 20	K_2O .	Result.	cent.	cent.
cc. flask and proceeded as	in 5.19	5.11	0.08	
2 Added 50 cc. of solution No. 1 an 10 cc. of solution No. 2 and 0.0 gram CaCO ₃ in 200 cc. flask an proceeded as in official metho	nd 05 nd od	5.16	0.03	
3 Added 50 ec. of solution No. 1 ar 10 ec. of solution No. 2 and 0.0 gram CaCO ₃ and 0.6 gram citr acid in 200 ec. flask and pr	1d 05 1c	5.20		0.01
 4 Added 50 cc, of solution No. 1 an 10 cc, of solution No. 2 and 0.0 gram CaCO₃ and 2 cc, hydr chloric acid in 200 cc, flask ar 	id 05 . 0-	5.20		0.01
proceeded as in official metho	d	5 20		0.01

Epx. No.	Theory. Percent. K ₂ O.	Result.	Loss. Per cent.	Gain Per cent.
5 Added 50 cc. of solution No. 1 a 10 cc. of solution No. 2 in 200 flask, added ammonia in excc then hydrochloric acid to sli acidity to clear the soluti heated, added ammonium o late, cooled and proceeded as	and cc. ess, ght on, xa- s in			
official method. The filtr showed no further precipit with ammonia, showing a go separation of lime	ate ate ood	5.09	0.10	
6 Added 50 cc. of solution No. 1 200 cc. flask, added dry Ca to neutralize, if possible, a acidity. The acidity was destroyed by excess so Ca(O) was added until solution w alkaline, then 10 cc. of soluti No. 2 were added, and proceed	in CO ₃ the not H) ₂ vas ion ied			
as in official method		5.04	0.15	

This was to see if calcium phosphate precipitated would occlude any potash when the insoluble material of the acid phosphate was absent.

Remarks.—There seems to be some loss when the insoluble material of the acid phosphate is absent. Addition of hydrochloric acid or citric acid, as in experiments Nos. 3 and 4, seems to overcome this loss.

Experiments to Show the Effect of Magnesium Salts, Iron and Lime Salts when Present in Solutions of Acid Phosphate and Potash, the Insoluble Material of the Acid Phosphate being Absent.—Solution No. 1: Water solution of acid phosphate 40 grams to 500 cc. of water.

Solution No. 2: Water solution of muriate of potash 8 grams to 200 cc.

Exp. No,	Theory.	Result.	Per cent K ₂ O.
1 Added 50 cc. of solution No. 1 and 0.5 gra Ca(OH) ₂ and 10 cc. of solution No. 2 au 0.25 gram MgSO ₄ in 200 cc. flask and pr ceeded as in official method	um nd '0- 5.19	5.12	0.07
2 Same as No. 1 only used MgCl ₂ instead MgSO ₄	of 	5.07	0.12
3 Same as No. 1 and No. 2 only used sulfa of iron instead of magnesium salts	.te	5.01	0.18

Remarks.—Iron seems to have a little effect on losing potash in these tests, magnesium salts not so much as iron.

Inasmuch as the insoluble in acid in phosphate rock becomes the insoluble in water, to a large extent, in acid phosphate, the following experiments, with different grades of phosphate rock and muriate of potash solution, were made to find the effect on losing potash when the official method is used:

These experiments were made by adding the materials together in a 200 cc. flask and proceeding as by official method for potash.

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Results should show evaporating 25 cc. of solution 6.37 per cent. K₂O.

	Experiment No. 1.	Per cent.
1 gram muriate of potash	1.	
	Insoluble and sand	9.30
5 grams of phosphate	Iron and alumina	2.45
rock, testing	Bone phosphate of lime, dry basis,	68.18

Potash determined at once as soon as solution was cold after adding ammonia and ammonium oxalate.

		Result.	Loss. Per cent. K ₂ O.
About 2 hours' sta	nding	6.23	0.14
After 24 hours' sta	anding before filtering	6.15	0.22
	Experiment No. 2.		
			Per cent
gram muriate of potash			
grams of phosphate	Insoluble and sand	• • • • • • • • •	11.20
rock, testing	Iron and alumina	day he	2.40
	Bone phosphate of hind	e, ary ba	515. 03.94
	and the second		Loss. Per cent.
Potash determined	at once	6.15	0.22 .
After 48 hours' sta	anding	6.10	0.27
	Experiment No 2		
	Laperenene 110. 3.		Per cent
gram of muriate of pota	ash.	and the second	a start had the
grams of Tennessee (Insoluble and sand		5.63
phosphate rock, test-	Iron and alumina		6.20
ing (Bone phosphate of lime	e, dry ba	sis. 74.19
			Loss.
Detect determined	The barren of the state of the	6 10	0.27
After 49 hours' sto	at once	6.03	0.27
Alter 48 hours sta	mung	0.05	0.51
and the second	Experiment No. 4.		
	ah.	1997	Per cent
gram of muriate of pota	Isn.		5
	Insoluble and salu		12
grams of rock, testing	Alumina		21
	Phosphoric acid.		45
			Torr
	I	Percent.	Per cent.

	A CONTRACTOR OF A CONTRACTOR O	
otash determined at once	. 5.91	0.46
fter 48 hours' standing	. 5.92	0.45

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CONCLUSIONS.

That as the insoluble in acid in phosphate rock increases, the loss in potash increases.

Phosphate rock having moderate amount of insoluble material and high iron and alumina as in experiment No. 3 has decided effect in losing potash.

Large amounts of iron and alumina with even moderate amounts of insoluble, as in experiment No. 4, where we have about 12 per cent. iron, 21 per cent. alumina, 5 per cent. insoluble material, have the most effect on losing potash.

Is it not reasonable to believe that what has caused this loss is similar to that which takes place in potash solutions in contact with soils, when the potash becomes fixed by the iron, alumina and silica? Such being the conditions there seems to be great chance for rendering water-soluble potash insoluble when we add water to our samples and boil as in official method.

Washing away as soon as possible the soluble material from the insoluble material of fertilizers seems but a reasonable way of overcoming somewhat this possibility of losing potash in our methods.

Comparing official method with method B as given before, we have:

Sample No. 1.—Acid phosphate having about 5 per cent. iron and aluminum oxides.

Sample No. 2.—Muriate of potash testing 51.70 per cent. K.O.

Exp. No.	Result. Per cent. K ₂ O.	Loss. Per cent.	
 Weighed into 500 cc. flask 9 grams sample No. 1 and 1 gram sample No. 2 and analyzed by official method 	4.70	0.47	
2 Weighed 4.5 grams of sample No. 1 and 0.5 gram sample No. 2 on to filter paper and analyzed by method B	5.03	0.14	

Sample of 7 per cent. potash goods, representing about 600 tons, gave by official method 6.70 and 6.72 per cent. K_2O , by method B, 7.10 per cent. K_2O .

For samples having large amounts of organic matter hot water should be used for washing in method B in place of cold water.

LABORATORY OF AMERICAN AGRICULTURAL CHEMICAL COMPANY, CARTERET, NEW JERSEY.

ADDRESSES.

THE DYNAMIC VIEWPOINT OF SOILS.1

By FRANK K. CAMERON.

Within the past decade or decade and a half there has been a marked revival of interest in soils and soil fertility. This has led to the advancement of a number of theories. most of which have the attractive characteristics of apparent simplicity, i. e., they attribute fertility or lack of fertility to some one or perhaps two causes. Another remarkable feature of most of these theories is the certainty and sureness of tone with which they are announced. For instance, one of the most prominent of American agronomists stated in a recent letter that "The currently accepted theory is that the principal factor in the loss of fertility is the loss of humus and nitrogen, and the data at hand seems to me to leave this theory as yet quite competent to explain the facts." And within the past few months we have been advised that "Phosphorus is already the element that limits crop yields on those great soil areas in the corn belt.

¹ Published by permission of the Secretary of Agriculture. Abstract of an address prepared for the Division of Food and Agricultural Chemistry at the Detroit meeting.

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in the wheat belt, and in the cotton belt, which are producing and must produce the great bulk of the crops required to feed and clothe the American people."1 And we are told further: "The supply of nitrogen in the air is absolutely inexhaustible; and the supply of potassium in all normal soils is also practically inexhaustible (potassium can also be recovered if necessary from the ocean's inexhaustible supply); and our deposits of limestone are surely inexhaustible: whereas our total supplies of phosphorus are extremely limited, not only in our most important soils, but also in our natural phosphate deposits, and phosphorus is not contained in the air or in the sea." One cannot help wondering where the fishes get the material for their bones; and if the phosphorus does not go to the sea, where it does go; and why, with good and valid reasons at hand for urging the conservation of our phosphate deposits, this particular argument should have been advanced.

In spite of the agronomist cited above, probably the most widely accepted theory of soil fertility is that known as Liebig's "law of the minimum," which may be stated as follows: Of the mineral elements needed by a plant, that one which is present in the soil in the smallest ratio to the amount needed by the plant, determines the productivity of the soil with regard to that plant. It is further assumed popularly that this law has practical application only with respect to the soil content of phosphoric acid, potash and nitrogen, although Hall² would apparently apply it to the moisture content and physical characteristics of the soil also.

To justify this law it is postulated (1) that soils are usually so deficient in phosphoric acid, or potash or nitrogen that the growing crop cannot obtain enough to maintain efficiently its metabolic processes, and, (2) to get around the analytical results from soils and plants; it is further postulated that the mineral plant food elements exist in the soil in two types of compounds or minerals, available, *i. e.*, soluble and non-available or insoluble.

All these theories, however, are formulated from a static viewpoint of the soil. Their supporters look upon a given field of soil as a fixed, stationary mass of material which remains in place indefinitely, except in so far as some of the constituents are carried away in drainage waters or removed by garnered crops. Therefore, it is argued, since crop roots feed in a limited volume of soil, say the first seven inches, and any given analysis shows so many pounds of phosphorus in the acre seven inches deep, while the crop takes out so many pounds per year, the soil cannot last (*i. e.*, produce crops) longer than so many years, determined by simple division. In order to maintain crop yields it is only necessary to keep adding the amounts of mineral matter as they are removed.

In the present stage of our knowledge, the problem is not, unfortunately, so simple. In studying the relation of plant growth to soils we must consider three things: *viz.*, the plant, or at least the plant roots; the soil moisture, the great natural nutrient medium from which plants draw their mineral sustenance; and the solid particles of the soil.³ Under field conditions all three of these are constantly moving. If the plant roots cease to move, the plant dies. It is inconceivable that the soil moisture should cease to move; when it rains some of the water runs over the surface and into the regional drainage, some evaporates into the air, and some goes into and through the soil. As McGee aptly puts it, these are the "run-off," the "fly-off" and the "cutoff." The "cut-off" passes through the soil, by way of the larger openings, mainly by gravitation; some of it passes out through seepage, etc., to the regional drainage, but some of it remains to rise again towards the surface through the capillary openings of the soil and in films over the surfaces of the soil grains, to ultimately join the fly-off.

There is also much evidence that the solid particles themselves are in constant motion as a result of the action of forces internal to the soil mass. For instance, it has been shown that the structure of the soil and the mutual arrangement of its component particles is dependent upon the character of the moisture films surrounding and connecting these particles, and therefore upon the amount of water which is present.1 The constant change of water content of the normal soil must therefore produce equally frequent changes in the soil structure, with accompanying movements of the particles among themselves. These movements become obvious through the well-known and considerable changes in the volume of soils on wetting or drving, succeeding changes in opposite directions being marked by a noticeable hysteresis or by never being exactly equivalent. The distances through which the soil particles are moved by a single change of water conditions are probably very small, but it is evident that there is here an efficient agency for the continual mixing of the soil itself, and that in time there must be some interchange of material between adjoining masses of soil and between the soil and the subsoil. It is claimed by some authorities that this process tends to segregate the finer particles of the soil at lower depths, but as to this I am not personally certain. It is certain, however, from controlled experiments and observations that the soil motions due to change in the amount and distribution of liquid water are much more important than is popularly supposed, and the still greater motions due to freezing and thawing are matters of common knowledge. The "cracking" of a soil on drying out is another matter of common observation. These cracks are usually of considerable depth, extending to or into the subsoil. The breaking away of the surface soil at the edges of these cracks is by no means an inconsiderable factor in mixing soil and subsoil, tending to bring gradually the latter material nearer the surface.

In every soil in which a crop can grow at all there is a constant bringing of material from the subsoil to the surface of the upper layers of the soil through the activities of earth worms, burrowing mammals, ants, etc. This continual interchange of material between soil and subsoil is undoubtedly very large in the aggregate. Tillage methods, especially plowing, are for the express purpose of breaking up and loosening the soil, and when properly conducted, greatly facilitate the spread of plant roots through the soil, and add to the movements of the soil particles themselves.²

¹ Bulls. 10 and 50, Bureau of Soils, U. S. Dept. Agr.

The inherent power of a root to push itself through a soil, or "root penetration" as it is often styled, if existent at all must generally be exceedingly small, otherwise destruction of the plant tissue would result inevitably. Root penetration must be due to the continued movement of the soil particles, the expanding root merely taking advantage of these movements due in most cases probably to the continually changing thickness of the water films on the soil grains.

¹ University of Illinois, Agr. Exp. Sta., Circular 127 (1909).

² Science, 28, 617 (1908).

³ The soil atmosphere, bacteria, and lower life processes are all dynamic problems obviously, but are not included here specifically, since their several effects are integrated in the factors cited.

The flow of water across the soil surface always produces some motion of the soil particles from place to placesmall in some instances, very large in others. In our rolling lands, where stone fences are usual, frequently the soil is higher on the uphill side of the fences than on the lower; or, on more level lands, on the side from which the prevailing wind blows; and this is true even in lands which are under sod or other protecting vegetable covering for a large part of the time. No less important probably than any other agency is the wind, which is blowing to some extent all the time and which carries into the air soil material to be deposited elsewhere, even at great distances. The carrying power of the wind is now known to be very great. For instance, soil material from the Sahara desert is frequently observed to deposit in Europe, even to considerable latitudes. Certain of our loessial deposits are striking examples, but it is no less certain that on every field, and especially on cultivated fields, there is an annual removal from the surface of considerable amounts of soil material which is deposited elsewhere, and contrariwise, every field is constantly receiving more or less soil material from other areas, frequently at a great distance. Professor Udden,1 in what appears to be a conservative calculation, finds that the carrying power of the winds of the Mississippi Valley into the Gulf of Mexico is about 1,000 times that of the Mississippi River (about 340,500,000 tons annually),2 and the carrying power of the winds over most of the area of the United States, for instance, is of the same order of magnitude. I would not be understood to assert that the actual translocation of soil material by wind is so great as this, but it is undoubtedly very large indeed, and a most important factor affecting the mineral composition of the soil in determining its markedly heterogeneous character with regard to the distribution of rock-forming minerals. The wind is probably the principal agent in making soils far richer in the variety of minerals present than are the rocks from which they are derived.

Space will not permit me to develop further our knowledge of these motions of the soil, and it is not necessary, for they are well known to scientific men generally, and presumably are the common property of all soil investigators. What I have cited is sufficient to remind one that there are forces continually at work changing the actual mineral composition of the surface soil, and that these changes are not only continuous but of an important magnitude. The claim of support from the geologists, sometimes made by the upholders of the static theories, on the ground that the age of the soil is measured by the rate at which some one or more of the elements increase in percentage with depth of soil, is ill founded, and it is very doubtful if any present-day geologist of repute would make or countenance such an argument, any more than any one who has kept pace with modern development in soil work would claim that the potash and phosphoric acid content of the soil would necessarily measure its producing power. An increase of 50 per cent. of fine quartz sand to the soil, for instance, would not necessarily lower its crop-producing power, but might even increase it considerably, although it would lower the percentage of phosphorus and potassium present in the sample.

Returning to the consideration of the soil moisture, it seems obvious, and has been experimentally verified in the

¹ Jour Geol., 2, 318 (1894).

² "Deandation," by R. B. Dole and H. Stabler, Water Supply Paper, 234, U. S. Geological Survey, Dept. Interior, 1909. laboratory a number of times, that the water passing down through a soil under gravitational force dissolves and removes but a small portion of the mineral content. Since this water does not remain long in contact with the soil grains the diffusion of dissolved material from the solution in the finer spaces and the soil films is slight. Our springs, creeks and rivers generally have a low and widely varying mineral content, lower in fact than the mineral content of the extract made by shaking up the surface soil with a small portion of water. On the other hand, with the advent of fair weather conditions, and the consequent evaporation at the surface, the "cut-off" water in returning to the surface through the capillary spaces and the films on the surfaces of the soil grains, is longer in contact with the minerals, and dissolver much more of them and thus it carries towards the surface a relatively large amount of the mineral constituents of the soils. Under ordinary conditions in humid climates, the concentration of the soil moisture is very largely controlled by absorptive phenomena, which are now pretty well understood, which have been the subject of exhaustive investigations, and which are readily accessible to all soil investigators.1

In opposition to this view there has been cited the removal of lime from certain fields at Rothamstead.² But this data is no more pertinent to a normal case than would be the accumulation of alkali under arid and semi-arid conditions. The Rothamstead soils are unusual in containing a very large percentage of lime carbonate; at least this is true of the Broadbalk soils, which I have personally examined. Under the very humid conditions obtaining in England, and under good drainage, it is natural to expect that the surface accumulations of lime would be lowered just as much as would be the case with the sodium chloride content if large masses of rock salt were harrowed into these soils. What one would expect in due course of time would be an adjustment between the amounts of lime carried out by the drainage waters and the amounts rising from the lower depths by the capillary rise of the soil water. The results obtained at Rothamstead are in no wise out of harmony with, but are in accord with and tend to confirm the views above expressed.

The static viewpoint leads its supporters to consider that the one function of a fertilizer is to add needed plant food to the soil, although usually they admit that some minor physical effects may be produced. The dynamic viewpoint leads to the conclusion that fertilizers have probably many other functions; that, in fact, the cases where they are useful *merely* as sources of plant food are probably exceptional. What all the functions of fertilizers are, I do not pretend to know, although I have given to the problem nearly ten years' earnest study with unusual facilities at my command. Fertilizers certainly do affect the physical properties of soils, although in the majority of cases these effects may be of minor importance in influencing plant growth.³ It is

¹ Bulls. 30, 51 and 52, Bureau of Soils, U. S. Dept. of Agr.

² Science, 28, 866 (1908).

³ That the physical effects produced by fertilizer have not yet received adequate attention from soil investigators can hardly be gainsaid. With such amounts of mineral salts as are commonly employed, it is not easy to see how the strictly chemical processes in the soil can be seriously changed or modified. But with our increasing knowledge of the profound physical changes produced by small amounts of solutes, and especially electrolytes, as for instance in the phenomena of floculaion, sedimentation, surface tension, viscosity, density of solvent. very probable that fertilizers have a very important rôle in affecting the enzymes, and the lower plant life in the soil, fungi, molds, bacteria, etc. Convincing evidence has recently been obtained that growing and especially young plants excrete through their roots organic substances giving rise to conditions harmful or injurious to these same plants and to others of the same or closely allied species; and it has been shown experimentally that certain portions or zones of the roots show a very high oxidizing power towards organic substances, which oxidizing power is modified by the presence of various substances, being generally increased by the salts common to commercial fertilizers.¹ It has also been shown that oxidation of the organic root excreta harmful to plants generally produces substances harmless or even beneficial thereto, and it seems to me probable that a function, perhaps sometimes even the main function of fertilizers is to modify the oxidation of organic matter, root excreta included, in the soil. Other effects of fertilizers than those noted have also been observed, but further mention of them would be premature. To sum up, I believe that fertilizers have physical, chemical, and biological rôles, which the "plant food" theory of fertilizers is entirely inadequate to explain. It is certainly a weak point in this theory that although it prevailed for seven or eight decades, to the practical exclusion almost of all others, it has led to no rational quantitative practice, which should be easily determinable if its premises were correct.

The use of the expression "available plant food" by the advocates of the static viewpoint appears to me to be misleading and unfortunate. This expression has an historical and academic significance in connection with the numerous efforts to develop an empirical method of analyzing the soil by extracting it with some solution or other. But as implying that the mineral nutrients do actually exist in the soil in two distinct classes, the idea is without experimental or other scientific justification. So far as we now know, the one and only method by which the plant can obtain mineral nutrients is by absorption from the aqueous solution in the soil, and is a purely gratuitous assumption that any minerals containing phosphoric acid, potassium, or lime, would not yield these constituents to water, given time enough and barring previous saturation of the solution or mechanical removal of the mineral.

Likewise, the distinction between "fertilizers" and "stimulants," which certain authors have sought to make lately, appears to me to be a begging of the question, and an unscientific attempt to "save the face" of the plant food theory of fertilizers. It must be shown that the increased plant growth obtained by adding to the nutrient medium potassium chloride or sodium chloride, respectively, involve essentially different physiological functions in the plant before this distinction will merit any serious consideration.

Again, it is a characteristic feature of the arguments usually advanced by the adherents of the static viewpoint that they are attractively simple. For instance, there has recently been advanced some mathematical deductions on the formation in the soil of monocalcium phosphate from tricalcium phosphate by the action of nitric acid there formed.²

etc., the conviction gains force that the physical properties of soils will need much more serious study before a rational system of fertilizer practice can be developed.

¹ Bull. 56, Bureau of Soils, U. S. Dept. Agr.

² Science, 28, 861 (1908).

It happens, however, that published experimental investigations, notably those of Bassett, in England, and of my own laboratory,¹ show conclusively that no such reaction could possibly take place. And even granting the argument, we are confronted at once with the need of a more rational explanation of the desirability of adding lime.

One of the more important subjects upon which the advocates of the static and the dynamic viewpoints of soils seem to take issue is crop rotation. There are very few, probably, who doubt the desirability of employing rotations, at least in general farming, and every one admits the efficacy of rotations is probably due to a number of causes, elimination of characteristic parasites, insects or plants, improvement in physical conditions of the soil by change of tillage methods incident to crops of different characters, incorporation of organic matter into the soil, etc. A majority, I think, now admit that injurious plant excreta is a probable reason for rotations. But the adherents of the static viewpoint generally hold that the main reason for crop rotation is the "exhaustion" of some one or more mineral plant food constituent in the soil, which is less necessary to the growth of the succeeding crop. On the other hand, from the dynamic viewpoint, no such hypothesis is necessary, and it is moreover highly improbable, although one may admit its possibility as an extreme and exceptional case. From the dynamic viewpoint, it is of course possible, theoretically, to imagine a rotation, which with tillage methods alone will maintain good (not necessarily the maximum) crop yields indefinitely. But no one, so far as I am aware, is advising or is ever likely to advise any such general practice. Cases might be cited where this has been followed with actually increasing yields, but they extend over too short periods of time, or are attended by other special conditions, which would make it rash to draw any general conclusions from them as yet. But, certainly, a recent extreme statement, from the static viewpoint, viz., * * * * "but the effect of crop rotation is always to reduce and never to augment the total supply of mineral plant food in the soil and subsoil," is going entirely too far; is in fact, a conclusion from à priori premises of more than doubtful validity, and is not susceptible of experimental verification. A comparison of many thousands of analyses of European and American soils shows that on the whole the much longer cropped European soils are somewhat richer-certainly as rich-in the so-called mineral plant foods as are the American soils.2 I am not able to see, whatever the prevailing mode of cropping may be, that there is any general or consistent evidence that soils are becoming exhausted of their mineral plant nutrients. The causes of "exhaustion" lie deeper and their explanation must be sought elsewhere.

Another popular impression sometimes assumed as a further proof of the arguments from the static viewpoint is that crop yields are going down. So far as I know, however, every one who has *investigated* the subject has inclined to the opposite conclusion. As every one knows, the popular impression has been strongly urged recently, and I am advised that the Conservation Commission sent out queries as to the yield of crops and land values to about 30,000 representative farmers, approximately 10 to each county in the

¹ For references and detailed discussion, see Bull. **41**, Bureau of Soils, U. S. Dept. Agr.

² Bull. 57, Bureau of Soils, U. S. Dept. Agr.

United States, and the replies were overwhelmingly to the effect that both crop yields and land values were increasing throughout the country. Our own government statistics for the past forty years show the average crop yields are increasing in areas where fertilizers are not used as well as in areas where their use is common. European statistics, which extend back from one to several centuries, not only establish that crop yields are increasing there, but that the great improvements came before the general introduction of commercial fertilizers. The reasons for these facts I will not take space to discuss here, since the whole question will soon be presented in detail elsewhere.

At present, soil chemistry is not simple. Leaving aside such special cases as wind breaks, glass houses, etc., we have three general methods of soil control: viz., cultural methods, about which we have a fairly satisfactory knowledge; crop rotation, about which our knowledge is extensive and steadily increasing-although it must be confessed, it is largely empirical; and thirdly, the use of soil amendments or fertilizers, about which our knowledge is yet meagre, but increasing slowly. It is, of course, patent to every one that fertilizers sometimes, in fact frequently, produce larger crop yields. Sometimes the contrary is true, but it is absolutely certain that at the present time no one can, nor are there any methods available by which one can, safely predict what fertilizers and how much should be used. In the past, three methods of examination have been in vogue: the analyses of soils, the analyses of plants, and plow and field experiments. All of these have had their uses, all have their limitations. Space forbids my discussing them at length here, but I cite them to show that the method of attacking the problem of soil chemistry has in the past been from the analytical point of view alone. This point of view has utterly failed to give us a rational system of fertilizing. Within the last few years it has seemed desirable to some of us to attack the problem from a different point of view, bringing together the known facts about soils and fertilizers, investigating them with all the resources and pertinent methods of modern physics, chemistry and physiology. In this way alone is there hope of progress. While it is undoubtedly true that some, in fact most, of the fertilizers in common use do contain mineral constituents which are essential to plant growth, and their addition to the soil does therefore add mineral plant food, there is a large and steadily increasing mass of evidence that this can be but one function of fertilizers, and I am quite prepared to reiterate that in my judgment it is normally a very minor one.

To sum up:

 Hitherto, the soil has generally been regarded from a static viewpoint. It now appears more rational to view it dynamically.

2. From the static viewpoint, fertilizers are valuable chiefly as sources of plant food. From the dynamic viewpoint this function is generally a minor one, and fertilizers have certainly other important functions of a physical, chemical and biological character.

3. Some advocates of the static viewpoint would make a distinction between *fertilizers* and *stimulants*. But this requires to be shown, and as now used these terms are merely a begging of the question at issue.

4. Every one believes in crop rotations. Advocates of the static viewpoint hold that it always hastens the depletion of mineral plant nutrients in the soil. This is at least doubtful.

5. The advocates of the static viewpoint hold that under copping, mineral plant nutrients necessarily disappear and soil "exhaustion" is due to this fact. But the evidence now available does not warrant these premises, and the cause or causes of exhaustion must be sought elsewhere, among others, in the character of the organic substances in the soil, and the biological processes there taking place.

6. The advocates of the static viewpoint hold that crop yields are decreasing, owing to depletion of available plant food. But crop yields are increasing and factors other than the plant food supply are the dominating ones.

7. To the advocates of the static viewpoint, soil chemistry is simple, and merely a matter of supplying enough mineral nutrients in "available" form for the crop needs. As a matter of fact, soil chemistry is a very complex subject, into which we are just beginning to get glimpses, and the supply of mineral nutrients is only one of the important details in a very intricate problem. Soil fertility will only become simple, if ever, when we have a much fuller and more comprehensive knowledge of the physical, chemical and biological processes taking place in the soil. To attain this knowledge, the soil must be regarded from the dynamic viewpoint.

BUREAU OF SOILS, U. S. DEPT. OF AGRICULTURE, WASHINGTON.

NOTES AND CORRESPONDENCE.

EXPERIMENTS TO FIND, IF POSSIBLE, THE POTASH IN FERTILIZERS HAVING THE POTASH FROM CARBONATE OF POTASH.¹

In view of the fact that in analyzing by official method fertilizers having as high as 8 per cent, of potash from carbonate of potash, we do not get results equal to amount of potash added to the goods, the following work has been done:

Materials and weights used were about the same proportions as used in brands having 6 per cent. ammonia, 4 per cent. phosphoric acid and 8 per cent. potash.

Weighed the amounts independently into 200 cc. flasks.

0.25 gram	carbonate potash testing	66.56%	potash	soluble in	water
1.30 gram	cottonseed meal testing	1.58%	potash	soluble in	water
0.20 gram	castor pomace testing	1.08%	potash	soluble in	water
0.25 gram	bone				

Experiment No. 1. Method D.

Same weights into 200 cc. flask, added 175 cc. cold water, a few drops of methyl orange and standard acid, hydrochloric acid, as used for nitrogen, until effervescence ceased and solution was faintly acid, then at once about 5 cc. strong ammonia, heated and proceeded as in official method. Filtered as soon as cold, which was not over two hours.

Result...... 9.14 per cent. Loss 0.31 per cent.

Experiment No. 2.

Doubled the above weights making 4 grams in 200 cc. ¹ Read at meeting of American Chemical Society, Detroit, 1909. flask, this being the same proportions as in official method, to grams to 500 cc. and made these tests by official method.

Allowed solution having the ammonia and ammonium oxalate to stand

	Per cent.	Loss, per cent.
2 hours before filtering—result	8.24	1.21
24 hours' standing-result,	8.88	0.57
48 hours' standing—result	9.02	0.41

Experiment No. 3.

Method E, regular official method, except we used the proportion of 5 grams to 500 cc. instead of 10 grams.

Allowed the solution, after having the ammonia and ammonium oxalate to stand 2 hours before filtering, evaporated 50 cc.

Experiment No. 4.

Same as No. 3 only allowed solution to stand 24 hours.

Result..... 9.16 per cent. Loss, 0.29 per cent.

Experiment No. 5.

Same as No. 3 and No. 4 only allowed solution to stand 48 hours.

Result, no gain over experiment No. 4.

Tried washing 2 grams on a filter with hot and cold water and neither were satisfactory, great difficulty being experienced in washing on account of the carbonate present and results were low.

We tried burning and taking up with water and had a loss of 0.91 per cent. on 9.31 per cent. theory.

We tried burning and taking up with hydrochloric acid and still had a loss of 0.35 per cent. on 9.31 per cent. theory.

We moistened with sulphuric acid and burned and took up with hydrochloric acid and had a loss of 0.47 per cent. on 9.31 per cent. theory.

SUMMARY AND CONCLUSIONS.

Official method, 10 grams to 500 cc. solution, gives us when solution is allowed to stand before filtering:

	Per cent.	Theory, per cent.	Loss, per cent.
2 hours	8.24	9.45	1.21
5 hours	. 8.70		0.75
24 hours	8.88		0.57
48 hours	. 9.02		0.43

Method E, official method, only used 5 grams to 500 cc. solution proportion. When allowed to stand before filtering.

	Per cent.	Theory, per cent.	Loss, per cent.
2 hours	8.88	9.45	0.57
24 hours	9.16		0.29
18 hours, no gain over 24 ho	ITS		

Method D, neutralizing 2 grams in 200 cc. flask, having 175 cc. water, with hydrochloric acid, using methyl orange as indicator, adding 5 cc. ammonia and proceeding as in official method.

After 2 hours' standing before filtering, 9.18; loss, 0.27 per cent.

Time is a great factor in factory work and we would seem to be justified in using Method D, although Method E, which is the same as official method using proportion of 5 grams to 500 cc. instead of 10 grams, gives us practically the same results by allowing solution to stand 24 hours.

J. E. BRECKENRIDGE.

LABORATORY OF AMERICAN AGRICULTURAL CHEMICAL COMPANY, CARTERET, NEW JERSEY.

NOTE ON A NEW MODIFICATION OF THE KIPP GAS GENERATOR.

The Kipp gas generator is undoubtedly one of the most widely used, and justly popular pieces of chemical apparatus on the market to-day, but the large number of variations of it which have been devised point to the fact that so far no thoroughly satisfactory type has been produced. My own experience with the Kipp apparatus, in the usual form sold by dealers in chemical glassware, has been that while it is admirably adapted to its specific purpose of generating various gases by the wet method, it presents certain difficulties and inconveniences in the matter of charging and cleaning. The opening allowed for the delivery tube is frequently so constricted as to render the process of charging tedious and difficult. While no very perfect cleaning is usually necessary, except in the event of the caking of the active material, washing out is always attended with some difficulty.

With the view of obviating these difficulties without interfering with the otherwise excellent properties of this apparatus, the design described on the following pages has been devised, and found successful.

In this apparatus, a is the usual long-stemmed acid reservoir as used in the common form of Kipp generator, and fits into the base portion with a ground joint at i. The base is made in two portions, the upper one, b, being dome-

shaped, and provided with the usual tubulature, rubber stopper and delivery tube at e. The lower portion, c, of the base is cylindrical, and provided with a tubulature and glass stopper at f. At about two-thirds of the height of c from the bottom the glass is indented completely around to provide a projecting ring of glass on the inside, forming the support for the container for the active material, d. This container is made of porcelain or lead, and is provided with c a perforated bottom, and vertical side walls. It is annular in form, having a hole in the center through which the stem



of the acid reservoir passes, the wall around this hole being of the same height as that of the side walls. The two portions of the base, b and c, fit together at g with a ground joint, the edges of the two portions being continued outward to a flange to provide a grip for small clamps, if these are found necessary.

The first apparatus of this type actually set up was composed of a discarded Novy jar, the acid reservoir from a broken Kipp, and a Buchner's funnel, and practically the same apparatus may be set up by any one by using a desiccator having a tubulature in the cover and a large separatory funnel. The active material may be placed upon a perforated lead plate supported on broken glass tubing or a stand of lead or glass. With a good supply of vaseline at the ground joint g and light clamping there is practically no danger of leakage. Some additional care may be necessary in disconnecting to avoid breaking the stem of the acid reservoir; however, this is scarcely more than is necessary with the ordinary form.

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The advantages claimed for this type of apparatus are:

r. Accessibility of all parts for cleaning and recharging.

2. Stability, as it is not so tall as the usual forms.

3. An even distribution of the active material over a relatively large area.

Another point in the use of gas generators of this type has come to my attention, and as it may not be known to some, I will give it here for the benefit of those who may have had difficulty along this line. It is frequently necessary to force the gas from the generator against a considerable pressure, and under these conditions it sometimes happens that the "head" of acid in the reservoir is not sufficient to entirely overcome this pressure, and the flow of gas is consequently inconveniently slow. To obviate this, I have found a good method is to connect a T-tube with the vertical arm pointing upward, between the gas chamber of the Kipp and the stopcock, and then connecting this vertical arm of the T-tube by means of a piece of stout rubber tubing, with a glass tube, the other end of which is bent so as to pass through a tightly fitting rubber stopper in the tubulature of the acid reservoir of the Kipp. Another means of attaining the same end, is to use a two-hole stopper in the tubulature on the gas chamber, through one opening of which passes the delivery tube and through the other the tube connecting with the top of the acid reservoir. In either case the gas pressure on both sides of the column of acid is kept the same, and the acid flows by gravity down upon the active material.

This principle may also be applied to the generation of gases by the dropping method, where a liquid from a separatory funnel is allowed to drop upon a solid in the bottom of a flask. It not infrequently happens that the back pressure will force the liquid back into the funnel. If the gas-filled space in the flask be connected with the upper opening of the funnel by a piece of glass or rubber tubing, the pressure on both sides will be equal, and the dropping can be regulated by the stopcock on the stem of the funnel. In using either the Kipp generator or the dropping method with this modification, a stop- or pinchcock should be provided as a relief valve at the top of the acid chamber, to be opened when the flow of gas from the generator is stopped.

A somewhat similar device has been used by Manchot and Herzog¹ and by Loevenhart and Kastle.²

When it is necessary to continue the generation of gas in a Kipp apparatus for some time, as in long-continued reduction, drying in hydrogen or carbon dioxide, etc., the acid is apt to become exhausted before the active material, and the addition of fresh acid to the exhausted acid is not always desirable nor feasible. By replacing the ground glass stopper at the tubulature in the base of the generator by a 1-hole rubber stopper bearing a stop- or pinchcock, and inserting a separatory funnel with a bent stem in the tubulature with the delivery tube, and then making the *a* connection between the gas chamber and the separatory through

the neck of the latter, so as to equalize the pressure on both sides of the acid column, as just described, fresh strong acid may be introduced at the same time that the exhausted acid is drawn off, thus continuing the length of action without recharging. It is necessary, or at least preferable to introduce the acid this way, rather than through the acid reservoir, as the strong acid introduced through the latter channel would come directly into the current of the outgoing exhausted acid, and a large portion of it wasted.

F. ALEX. MCDERMOTT.

WASHINGTON, D. C., September, 1909.

A RAPID METHOD FOR DETERMINATION OF SPECIFIC GRAVITY OF COAL.

During the routine work of this laboratory, it is necessary to determine specific gravity on a large number of samples of anthracite coal. As the methods available gave but little satisfaction commensurate with the time and labor entailed, we had recourse, after considerable experimentation, to the herein described procedure.

The apparatus, first of all, is simple, and may be found in almost any laboratory. The first requirement is a stout flask of about 250 cc. capacity, with a long and rather slender neck, terminating in a flaring mouth, such as the "copper determination" flask supplied by the Denver Fire Clay Co. This flask is to be marked at the base of the neck, either by a file scratch or by etching, and its volume up to this mark determined by means of a 100 cc. automatic pipette and a 100 cc. burette, graduated in 0.2 cc.

The burette should have a three-way stopcock, and be connected with a reservoir either below or above the level of its top. In the former case suction is used to fill the burette, while in the latter case gravity is the means. It is better to use the elevated reservoir and gravity feed for the pipette. Of course it is understood that a plain burette and pipette can be used, the form described merely having the advantage of rapidity.

The flask is calibrated as follows: The flask is rinsed with water, inverted, and allowed to drain for one minute; roo cc. water are then added from the pipette, the flask is then filled to the mark from the burette. In calibrating by this method, inaccuracies in either pipette or burette do not militate against the accuracy of the specific gravity result, as the same method is pursued in the final determination.

The actual determination is carried out as follows: 100 graths of coal, previously crushed to about 4 mesh, and carefully sampled, are weighed to 0.1 gram, and placed in the flask. 100 cc. water are run in, a 1-hole stopper fitted with bent glass tube and rubber connection is inserted in the mouth of the flask; suction is applied, and the flask is shaken, care being taken that no water is splashed into the glass tube. When air bubbles cease to be disengaged, the suction is interrupted and the stopper withdrawn. Water is now run in from the burette till the flask is filled to the mark, care being taken to work down any coal which may have stuck to the neck.

The results may be calculated as follows:

S

pecific Gravity =
$$\frac{100}{V_{o} - V_{1}}$$

¹ Liebig's Annalen, **316**, 321 (1901).

² Amer. Chem. Journal, 29, 427-428 (1903).

wherein $V_o =$ volume of the flask; $V_1 =$ number of cc. water added to coal.

No calculation at all need be made if a table of reciprocals be available, as specific gravity = 100 × reciprocal of $V_0 - V_1$. As an example 100 grams coal were taken; volume of flask, $V_0 = 262$ cc.; volume of water added to coal, . $V_1 = 197$ cc.

Specific Gravity =
$$\frac{100}{262 - 197} = 100 \times \frac{1}{65} = 1.54.$$

After making a determination the flask is emptied and rinsed, then allowed to drain for one minute, when another determination may be made.

This method is very rapid and so simple that an inexperienced operator can without difficulty make over 80 determinations per day accurate to within 0.02 unit of specific gravity. It is, of course, self-evident that this method has a wide range of applicability; the gravities of such materials as rocks, drillings, etc., may be determined with ease.

While the authors claim nothing new or radical in this process, still they submit it as a procedure by which results of moderate accuracy can be obtained with great rapidity, while the outlay for special apparatus is practically nil.

> Abraham G. BLAKELEY. Edwin M. Chance.

LABORATORY OF THE P. & R. COAL & IRON CO., POTTSVILLE PA.

LIQUID MIXTURES FOR MAXIMUM AND MINIMUM THERMOMETERS.

A homogeneous liquid mixture may, by a change of temperature or by certain additions, become separated into two layers. For example, a mixture of 15 cc. amyl alcohol, 20 cc. ethyl alcohol, and 32.9 cc. water is homogeneous above 20° C.; but the least lowering of temperature below this, even by one-tenth of one degree, causes the division of the liquid into two nearly equal layers. This phenomenon can be made use of in the construction of an exceedingly delicate minimum thermometer. Convenient volumes of amyl and ethyl alcohols are mixed together, brought to the required temperature, and water gradually added, drop by drop, until a slight turbidity results. The liquid is then sealed in a tube, being first colored with carmine whenever the temperature falls below that at which it was prepared, the two layers separate, and are of different shades. If methyl and ethyl alcohols be used in the same way a maximum thermometer can be prepared.

ROBT. E. BRADLEY.

THE RAPID DETERMINATION OF MANGANESE IN STEEL.

All methods whether color or volumetric, dependent on the oxidation to permanganic acid by red lead or lead dioxide, suffer from the disadvantage of organic matter in these reagents which reduces the Mn_2O_7 after it is formed. Still it is possible to get red lead that serves the purpose, provided a sharp look-out is kept for splints of wood in the liquid after the boiling, and the test is repeated, or done in duplicate with a fresh portion of the standard. But in addition there is a source of error from the carbon in certain steels. It seems that in certain steels—but these steels are the exception and not the rule—the carbon is in such a

condition that red lead (or lead dioxide) does not completely oxidize it, and therefore what is left of the carbon after the boiling with this reagent reduces the permanganic acid to a certain extent, so that repeated results, although agreeing with each other, are too low. The obvious remedy for this is to get rid of the carbon first. The writer therefore finds it convenient to use the filtrate from the silicon determination for the manganese determination, as follows: 2.3510 grams steel are dissolved in 50 cc. water and 10 cc. strong sulphuric acid and evaporated to dense fumes. Then boiled up with water and filtered into an Erlenmever flask marked at 200 cc., and the silica washed twice with water. The filtrate is then diluted to the mark, mixed, 25 cc. withdrawn with a pipette, and transferred to a tall narrow 100 cc. beaker marked at 50 cc. Then diluted up to this mark roughly with 1.20 nitric acid, boiled 15 minutes. removed from the heat and the red lead at once added and stirred, then diluted carefully to the mark, and stirred again. The lead sulphate formed settles instantly and carries with it the excess lead oxide, so that the comparison of the color with a standard steel which has gone through the same process can be made at once (and the quicker the better) by withdrawing 5 cc. with a pipette and transferring to ordinary color carbon comparison tubes. The following results on basic open-hearth steels illustrate this source of error.

			Per cent.
No.	15072	by Williams' method (at another works)	about 0.39
No.	15072	by ordinary color method	0.315-0.345
No.	15072	by modified color as above	0.39
No.	15072	by Volhard's method	0.39
No.	15082	by Williams' method (at another works)	about 0.57
No.	15082	by ordinary color method 0.435-0.455	-0.415-0.435
No.	15082	by modified color as above	0.555
No.	15082	by Volhard's method	0.57
The	color	tests by Mr. A. Kabline.	

GEORGE AUCHY.

A MODIFIED KJELDAHL CONNECTING BULB.

Editor of the Journal of Industrial and Engineering Chemistry:

DEAR SIR: In your October issue, page 737, there was described a modified Kjeldahl Connecting Bulb; the modification will be useful.

I would, however, call attention to another modified form which I designed and have had in use for some time in my laboratory, and is now being used by many other chemists in England.

It consists of a large bulb A, somewhat pear-shaped about 7 cm. in diameter, inside which, to the outlet from the large bulb, is attached a smaller bulb, B, about 2 cm. in diameter

with a hole about 8 mm. diameter blown in the side and an opening about 2 mm. diameter at the bottom. At the lower part of the large bulb is fixed a thin glass plate C perforated with about six holes; the holes are towards the sides of the plate as far as possible from the centre.

This form of bulb has a wide application and especially in the estimation of volatile fatty acids in butter and butter substitutes, ammonia, arsenic and antimony by the distillation



method, for the distillation of tar and tar oils and gen-

erally where the liquid is liable to bump or froth up during the boiling. The risk of spray being carried over into the distillate is practically nil.

Messrs. J. W. Towers & Co., Ltd., Widnes, England, now make and keep a stock of these bulbs.

Yours faithfully,

G. WATSON GRAY.

LIVERPOOL, October 22, 1909.

BOOK REVIEWS AND NOTICES.

Reinforced Concrete in Europe. By ALBERT LADD COLBY. Cloth, 8vo. 260 pp. Easton, Pa.: Chemical Publishing Co.

Mr. Colby has given us in the present volume the results of his extended travel and research abroad in the investigation of the status of reinforced concrete in the principal European countries, its applications, cost and economy, endurance and resistance to fire and other destructive agents, the various systems in use and details of construction. It is a reference work, solely, and presents in convenient form information and data, much of which would otherwise be inaccessible to American engineers. The work shows great care in preparation and arrangement; it is concise but comprehensive and represents a vast amount of work in investigation and painstaking sifting and arrangement of data. It includes authoritative opinions, government rules, recommendations and specifications of cement for reinforced concrete, the metal used for reinforcement, and the mechanbond and form of bars. It covers the practice in England, France, Germany, Austria, Hungary, Switzerland and Italy. It also contains lists and description of foreign government and private testing stations, congresses, technical institutions, associations and committees who have endorsed reinforced concrete as a material of construction or who have adopted resolutions, specifications or rules relating thereto. There is, also, a complete bibliography of books, journals, proceedings, etc., published at home and abroad, giving the date of publication and price of each. Addresses of prominent engineers in each country and of the official and technical testing stations and the various committees and associations add to the value of the volume. As stated, it is essentially a reference work and should be in every working and reference engineering library.

ERNEST B. MCCREADY.

Laboratory Notes on Iron and Steel Analyses. By WALTER MACFARLANE. Cloth-bound, pages xvi and 462, $5 \times 7\frac{1}{2}$ in. 25 illustrations, published by Longmans, Green & Co. New York and London. Price, \$2.50 net.

This volume is the third book by the author on subjects relative to iron and steel, his previous publications being "Laboratory Notes on Practical Metallurgy" and "The Principles and Practice of Iron and Steel Manufacture."

The present volume is a detailed description of actual analytical methods used in daily practice in an iron and steel laboratory in England, which was under the supervision of the author for a number of years. The aim of the book, as stated by the author, has been to set out the complete course of an assay or an analysis in full detail, specifying precise quantities of reagents and convenient sizes of apparatus to be used. The methods given cover the analysis of all raw materials, products, and by-products, special steels, and many miscellaneous estimations that are necessary to the manufacture of iron and steel.

Fifty-five pages are devoted to "Notes on Sampling," "General Notes on Laboratory Operations and Appliances," "Notes on Preparing and Storing Solutions."

A supplement contains the methods for "Analysis of Iron Ores" as published by the Chemical Committee of the United States Steel Corporation.

The methods given, with a few exceptions, are those in general use in the iron and steel laboratories of the United States. Examples and calculations are numerous and will prove valuable aids to students and to those to whom the work is new.

As stated the author's aim is to give detail, and like a good sportsman his aim has been true. The demand for such a publication is growing.

The print, paper and binding of the book are excellent. WILLIAM BRADY.

Alloys and Their Industrial Application. By EDWARD F. LAW. pp. 7 + 270. Numerous plates. London: Chas. Griffin & Co., Ltd. Philadelphia: J. B. Lippincott. 1909. Price, \$4.00 net.

This is an excellent and comprehensive treatise on alloys, systematically considered. After a general introduction, the properties of alloys are considered and the methods of investigation. In the chapter on constitution the application of the phase rule is taken up and also the graphic representation of the properties of alloys. One chapter is devoted to the influence of temperature on the properties of alloys and another chapter to the corrosion of alloys. Three chapters are devoted to copper alloys, one to nickelcopper and special copper alloys, one to lead, tin and antimony alloys, one to anti-friction alloys, one to aluminum alloys, and one to silver and gold alloys. The iron alloys are treated in a chapter of thirty-one pages, which may seem to some too brief a space for this important subject. However, it may be said that the book in general is well proportioned.

Tanners and Chemists Handbook. By LEWIS E. LEVI and EARL V. MANUEL. pp. 363. 8vo. Milwaukee, Wis. Published by the authors. Price, \$5.00.

The authors are chemists with the Pfister & Vogel Leather Company, and undertake in this work to give various tables and other data and methods of analysis of interest to tanners' chemists. It is a useful book but contains a good many tables of easy access elsewhere, for instance in the *Chemiker Kalender*, in smaller and more convenient form. The book is marred by the insertion of advertisements at various points in the body of the book. There is a dictionary of tanning terms, giving English and German equivalents. The price may seem to some rather higher than it should be.

Chemical Conversion Tables for Use in the Analysis of Commercial Fertilizers, Cottonseed, Iron and Food Products. By H. B. BATTLE and W. J. GASCOYNE. pp. 79. 12mo. Baltimore: Williams & Wilkins Pub. Co. 1909. Price, \$2.50.

This work contains tables for various conversions used in the analytical laboratory, and is without question a useful

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work for the busy routine analyst. It has an indented index for ready reference. It will undoubtedly prove of value in the works, commercial and control laboratory where many calculations have to be made quickly. The tables are based on the International Atomic Weights of 1909, as reported by the International Committee. While somewhat high, the price cannot be considered exorbitant for the man who needs such a work, considering the amount of labor required in its preparation and the limited sale for such a book.

Transactions of the American Institute of Chemical Engineers. Vol. I. 1908. pp. 202. Charts and plans in pocket. Large 8vo. New York: D. Van Nostrand Co. Price, \$6,00 net.

This, the first volume of *Transactions of the American Institute of Chemical Engineers*, contains the preliminary discussion and committee reports leading up to the formation of the Institute and some ten scientific papers with discussions presented to the Institute. There is a list which shows that there were one hundred and one members in June, 1909. The papers, considered as a whole, are good and useful to the chemical engineer.

Practical Points for Practical Brewers. By FRANCIS WYATT and EMIL SCHLICHTING. Small 12mo. pp. 176. New York: National Brewers Academy.

This is a small volume of tables, data and calculations of interest to brewers.

Prevention of Industrial Accidents. No. 1. General Pamphlet. By FRANK E. LAW and WM. NEWELL. 12mo. pp. 195. New York: Fidelity & Casualty Co. Price, 25 cents.

This timely and really valuable pamphlet should be in the hands of all works engineers and superintendents. It contains much valuable data relating to accidents in manufacturing plants and around machinery and the prevention thereof. Incidentally, many valuable points are noted relating to the handling of steam boilers, engines, elevators and the factory in general.

Briquetting Tests, at the United States Fuel-Testing Plant, Norfolk, Va., 1907–1908. By CHAS. L. WRIGHT. Bull. 385, U. S. Geological Survey. 8vo., pp. 41. Washington: Government Printing Office. 1909.

This bulletin is of value to coal dealers and fuel engineers and gives in some detail the machinery, and the methods used in briquetting and the tests of briquetting made in various ways from different kinds of coal. At the end of the descriptive matter there is a good bibliography on fuel testing and briquetting.

The United States Geological Survey has just issued a bulletin on "Commercial Deductions from Comparisons of Gasoline and Alcohol Tests on Internal-Combustion Engines," by Robert M. Strong. The tests, which were under the technical direction of R. H. Fernald, engineer in charge of the producer-gas section of the technologic branch, were conducted at the fuel testing plant in St. Louis, Mo., and at Norfolk, Va. The tests dealt primarily with gasoline, forming part of the investigation of mineral fuels provided for by acts of Congress. To determine the relative economy and efficiency of gasoline it was compared with denatured alcohol. When the series of tests was started, it was found that it took from one and one-half to two times as much alcohol as gasoline to produce a given power. With special alcohol engines, entirely suited to the use of alcohol, the latter fuel has been made to do as much work, gallon for gallon as the gasoline.

The Fuel Supply Committee of the Boston Chamber of Commerce has just issued a report on "The Buying and Handling of Steam Coal." In this report a table is given, which shows the average of over 2,000 analyses of coal, tabulated according to various districts in Pennsylvania, Maryland, West Virginia, and Virginia. These analyses have been compiled from bulletins of the U.S. Geological Survey, as well as various commercial interests who are analyzing their coal or having it analyzed. The latter comprises over 1,700 analyses and referring to this the report states: "In compiling these analyses, care and discretion were used in order that only those analyses made from representative samples by proficient chemists should be included. A special representative was engaged to investigate the methods of sampling and analysis, and compile the data of the many consumers who are analyzing the coal which they receive. Many instances were encountered where the results were obviously inaccurate and unreliable. and they were consequently not included in the results presented herewith." In addition to showing the average of the Government and commercial analyses separately in the different districts, they also show the variation in the different constituents of the coal as shown by analysis and B. t. u. This enables one to not only determine the approximate average quality of coal from any one district. but also indicates the variations which may be expected in the moisture, volatile, fixed carbon, ash, sulphur, and B. t. u. independently. There are in all twenty districts represented. There is also given a diagram, showing graphically the variation in each of these constituents from the nine districts from which New England receives the greater part of its coal supply. This diagram is very interesting in that it shows the greater variation in quality of some districts than in others. This report gives more comprehensive and reliable data concerning the quality of coal as shipped from the Northern Appalachian coal fields than has heretofore been published. In this respect it is not only of interest to the chemists and coal consumers of New England but to all those who receive or analyze coals from this part of the country. A few analyses of Rhode Island and Nova Scotia coal are also included.

Statistics have been compiled which show the annual coal consumption of the New England states to be over 24,-000,000 tons. The report also indicates the quantity of this coal as received by all rail and tide water at the various discharging ports, distinguishing between anthracite and bituminous.

Considerable other data and information are given concerning the transportation and handling of coal. Accompanying this report are three maps, one showing the location of the various districts in the Northern Appalachian coal field. The other two are maps of New England, one giving freight rates from the different mining districts to the various stations throughout New England, while the other gives the rates on coal shipped from tide water discharging ports. These maps are $44'' \times 60''$, and are lithographed, showing each 25 cents change in rate in a different color. The smaller changes are indicated by figures. These maps are very interesting in showing the effect of competition upon ratemaking and enable a person to determine the freight rate on coal from any mining district to any point in New England by either all rail or tide water shipment. A copy of this report, including maps, may be obtained from the secretary of the Fuel Supply Committee of the Boston Chamber of Commerce, Boston, Mass., for \$2.50. E. G. BAILEY.

SCIENTIFIC AND INDUSTRIAL SOCIETIES.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS, PHILADELPHIA MEETING.

WEDNESDAY, DECEMBER 8, 1909.

10.00 A.M.

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Meeting at Hotel Walton.

Address of Welcome. Mayor John E. Reyburn.

Business Session.

Reports of Officers and Council.

Reports of Committees.

11.30 A.M.

Reading of Papers.

- (1) "Natural Draft Gas Producers and Gas Furnaces," by Ernest Schmatolla, Discussion by O. K. Zwingenberger and G. E. Barton.
- (2) "The Commercial Extraction of Grease and Oils," by Wm. M. Booth. Discussion by Frederick Dannerth, Louis Olney and Samuel P. Sadtler.

12.30 P.M.

Luncheon at Hotel Walton (75 cents Table d'Hote). 1.30 P.M.

- Visit to Chemical, Engineering and Physical Laboratories of the University of Pa.
- Visit to Commercial Museum of Philadelphia. Dr. W. P. Wilson.

1.00 P.M.

Luncheon at Works of Harrison Bros. & Co., Gray's Ferry Road.

Excursion through works (admission by card only).

7.30 P.M.

Address by Retiring President.

Address—"The Chemical Industries of America," by Prof. Chas. E. Munroe.

THURSDAY, DECEMBER 9TH.

9.30 A.M.

- Members of the Institute and their guests will assemble at Race St. wharf on the Delaware and be conveyed by the city boat *S. H. Ashbridge* to the Torresdale Filtration Plant—returning stop at Tacony to visit the Wool Degreasing Plant of Erbin, Harding & Co.
- 12.30 P.M.

Luncheon at the works of the Welsbach Light Co. as the guests of the Company.

1.30 P.M.

Excursion through the works of the Welsbach Light Co. 3.00 P.M.

Return by boat to Kaighn's Point and excursion through By-Product Coke Oven Plant of the Camden Coke Co.

5.00 P.M.

Return to Chestnut St. wharf, Philadelphia.

7.00 P.M.

Subscription Dinner at Hotel Walton, \$3.00.

9.30 A.M.

Installation of Officers and Business Meeting.

FRIDAY, DECEMBER 10TH.

10.30 A.M.

- Reading of Papers.
- (3) "Multiple Effect Distillation," by F. J. Wood (Mechanical Engineer of Marx & Ravolle's Glycerine Refinery).
- (4) "The Advantages of the Multiple Effect Distillation of Glycerine and Other Products," by A. C. Langmuir. Discussion by S. S. Sadtler and Chas. L. Reese.
- (5) "Reclaiming of Waste India Rubber," by S. P. Sharples. Discussion by Wm. M. Grosvenor.

12.00 M.

Luncheon at Hotel Walton.

1.00 P.M.

Leave Broad St. Station for Trenton, N. J.

2.00 P.M.

Excursions—Trenton Potteries. The Hamilton Rubber Co.

Linoleum Works.

7.30 P.M. Reading of Papers.

- (6) "Materials for Textile Chemical Machines," by Frederick Dannerth, Discussion by Louis A. Olney and J. M. Matthews.
- (7) "The Manufacture of Carbon Bisulphide," by Edward R. Taylor.
- (8) "Chemical Composition of Illinois Coal," by A. Bement.
- (9) "Heat Efficiency of Smokeless Combustion, and Heat Absorbing Capacity of Boilers," by A. Bement.

9.00 P.M.

Final Business Meeting.

SATURDAY, DECEMBER 11TH.

Visit to Cement Plant at Allentown, Pa. Headquarters at Hotel Walton.

AMERICAN SOCIETY FOR TESTING MATERIALS.

COMMITTEE ON STANDARDIZED SPECIFICATIONS FOR COAL.

On June 28 and 29, 1909, there were several meetings of the Committee on Standard Specifications for Coal of the American Society for Testing Materials at the Hotel Traymore, Atlantic City, New Jersey. As a result of these meetings, and the work accomplished through correspondence since the organization of this committee on January 29th, the following preliminary report was submitted by J. A. Holmes, chairman, and was later approved by a majority of the members of this committee. The complete membership of the various sub-committees of this committee was given in the June number of THIS JOURNAL.

In carrying out the instructions of the Society, its Executive Committee has authorized and approved a committee of sixty-seven members to consider and report on the subject of specifications for the purchase of coal.

The first meeting of this committee was held at the Fort Pitt Hotel, Pittsburg, Pa., January 29, 1909. The committee was there organized by the selection of J. A. Holmes as Chairman, B. F. Bush as Secretary, and with sub-committees to take up the consideration of specifications as applied to the following classes of coals:

- Sub-Committee No. 1, on Coals for Steam Power Plants, W. F. M. Goss, Chairman.
- Sub-Committee No. 2, on Coals for Producer Gas Plants, R. H. Fernald, Chairman.
- Sub-Committee No. 3, on Coals for Domestic and Heating Plants, J. E. Woodwell, Chairman.
- Sub-Committee No. 4, on Metallurgical Coals, C. F. Robinson, Chairman.
- Sub-Committee No. 5, on Coals for Illuminating Gas, Alfred H. White, Chairman.
- Sub-Committee No. 6, on Coals for Cement Drying, Brick Kilns, etc., Edward Orton, Jr., Chairman.
- Sub-Committee No. 7, on Sampling and Testing of Coals, D. T. Randall, Chairman.
- Sub-Committee No. 8, on Forms of Contract in Coal Purchases, E. H. Taylor, Chairman.
- Sub-Committee No. 9, on Educational Work in behalf of more Efficient Mining, Preparation, and Use of Coal, J. A. Holmes, Chairman.

The practicability of adopting specifications for the purchase of the above different classes of coals has been discussed by correspondence among the members of the several sub-committees named above, and the general subject of coal specifications has been discussed individually, by correspondence and occasional personal interviews between members of the committee, during the past several months. No forms of specifications have as yet been agreed upon, however, and your committee at this time can but submit a preliminary statement as a report of progress, and ask to be continued.

The committee recognizes the growing interest in the general subject of the purchase of materials under specifications, and it is believed that in all cases where a rational basis for such specifications can be agreed upon, the results of such practice must be beneficial to both producer and consumer, as it enables the consumer to point out more specifically just what he wants; it enables the producer to offer bids on a more intelligent basis, and it makes easier equitable settlements.

In any industry, however, the sudden introduction of a system of ill-digested specifications is likely to work hardship, especially on the producer, without compensating benefits even to the consumer. This is especially apt to be true in an industry so large, so little organized, and contending with so many unsettled problems, as the soft coal industry of to-day. Some of the recently promulgated specifications for the purchase of coal show the extremes to which this system may be carried before the difficulties involved are adequately understood.

Thus one of these recent specifications prescribes that the coals offered for use at a station within easy reach of one of the coal fields should have 15,000 British thermal units and not exceeding 3.25 per cent. ash, 1.00 per cent. sulphur, and 0.90 per cent. moisture. Other specifications have been recently adopted in a number of cases which are equally impracticable and unnecessarily stringent, which prescribe no satisfactory methods of sampling or testing the coals, render premiums impossible and penalties inevitable on coals, the prices of which are already so low as to leave no possibility of profit to the producer except by involving extensive and per-

manent waste of coal in mining. Still other specifications have been fully as irrational and unfair, because leaving the sampling and testing, and in fact the adjustment of differences, entirely in the hands of one of the interested parties, and based on inadequate tests.

Vour committee desires to emphasize at this time certain reforms which are regarded as fundamental accompaniments or outgrowths of the present movement for specifications, and which are essential to the welfare of the coal industry in the United States, namely:

(I) A classification of coals with respect to fuel efficiency; the adaptation of equipment to coals for obtaining the greatest efficiency from each class of these fuels; the continued use at each plant of that type of fuel best adapted to the equipment; the use of low-grade fuels either at the mines or within short distances, and of the high-grade fuels under conditions demanding highest efficiency and requiring distant transportation.

(2) Special efforts on the part of architects and engineers to provide everywhere adequate space for power and heating plants and proper equipment, with a view to making the most efficient use of the fuels that are most available.

(3) Such readjustment in the prices at the mines of the different classes of coals as will render possible clean and safe mining, and the use at local or distant points of all grades of coal worthy of being placed on the fuel list.

The realization of these essential reforms will naturally be slow of accomplishment, but for the hastening of this accomplishment every engineer, and indeed every citizen of the country, should, as a national duty, contribute to the best of his ability.

The committee deprecates the hasty adoption of extreme specifications such as those mentioned above, for the reason that such action does not help but hinders this movement, without any compensating benefits to either producer or consumer. At the same time the committee recognizes the fact that a proper specification should and will, when understood, encourage the use of all grades of fuels; and it should provide, as do some of those now in force, an equitable basis for the adjustment of the differences between producers and consumers.

If continued, your committee will endeavor to submit for the later consideration of the Society forms of specifications for the several types of coal mentioned above, in so far as the use of such specifications may be considered as helpful to industry, and contributing to the equitable relations between interested parties.

Respectfully submitted on behalf of the committee,

J. A. HOLMES, Chairman, B. F. BUSH, Secretary,

AMERICAN CHEMICAL SOCIETY, BOSTON MEETING.

The Boston meeting of the American Chemical Society, held during convocation week, in conjunction with the American Association for the Advancement of Science, will be reported in the February number of THIS JOURNAL. In particular, the meetings of those Divisions devoted to applied chemistry will be reported in as much detail as possible. These Divisions include the Division of Industrial Chemists and Chemical Engineers; the Division of Agricultural Chemists; the Division of Pharmaceutical Chemists; and the Division of Agricultural and Food Chemists.

OFFICIAL REGULATIONS AND RULINGS.

(T. D. 29957.) Denaturing of Olive Oil under Paragraph 639 of the Tariff Act of August 5, 1909.

TREASURY DEPARTMENT, August 20, 1909.

To Collectors and Other Officers of the Customs:

Paragraph 639 of the Tariff Act of August 5, 1909, provides for the free entry of:

Olive oil rendered unfit for use as food or for any but mechanical or manufacturing purposes, by such means as shall be satisfactory to the Secretary of the Treasury and under regulations to be prescribed by him.

Olive oil to be entitled to entry under the foregoing provision of law either must have been denatured abroad in such a manner as to satisfy the collector that it is permanently unfit for use as food or for any but mechanical or manufacturing purposes, or it must be denatured after arrival, under customs supervision and at the expense of the importer, by one of the following methods, to be elected by the importer:

To 100 gallons of the olive oil to be denatured add any of the following substances:

(a) 3 gallons rosin oil, preferably second or third runs.

(b) 3 gallons refined destructively distilled wood turpentine, boiling not lower than 160° C.

(c) 3 gallons mineral oil such as spindle oil, or a rather crude kerosene.

(d) 1/4 gallon pyridin.

(e) 1/2 gallon creosote.

(f) 3 gallons aniline oil.

(g) 6 gallons dark-colored oleic acid.

Oil denatured according to formulae b, d, e and f must be marked as poisonous.

The officer supervising the denaturing is enjoined to take particular care to have the denaturant thoroughly incorporated with the olive oil.

"Sulphured olive oil" obtained by the extraction of olive oil from press cake by means of carbon bisulphid need not be further denatured.

The Department will from time to time prescribe additional formulae, and will consider any formula for special denaturation that may be submitted by any manufacturer.

To insure the protection of the revenue, 100 per cent. of all olive oils claimed to be inedible, or to have been denatured abroad, will be sampled.

No olive oil will be released free of duty under the said paragraph of law until the owner or consignee shall have filed with the collector of customs an affidavit in the following form:

PORT OF -----

I, _____, do solemnly declare that I am the owner or consignee of the olive oil described in the invoice and entry hereto attached, that the same is permanently unfit for use as food and is specially imported in good faith for mechanical or manufacturing purposes.

(Owner or consignee.)

Subscribed and sworn to before me this —— day of ——, 19——.

(Title of officer.) JAMES B. REYNOLDS, Acting Secretary. (T. D. 1529.) Denatured Alcohol.—Formula 1 authorized for use in the manufacture of acetaldehyde.

TREASURY DEPARTMENT,

OFFICE OF COMMISSIONER OF INTERNAL REVENUE, WASHINGTON, D. C., August 10, 1909.

SIR: The application has been received and considered by this office of —— for permission to manufacture acetaldehyde from denatured alcohol under the provisions of Section 40, Part VI of Regulations 30, and for the authorization of formula 1 as a special denaturant for use in its manufacture.

You are informed that the desired permission is hereby accorded provided the acetaldehyde contains no undecomposed alcohol. * * *

Respectfully,

J. C. WHEELER, Acting Commissioner.

MR. FRANK MCCORD,

Collector Eighteenth District, Cleveland, Ohio.

(T. D. 1539.) Adulterated Butter.

Officers are instructed to secure more than one sample from unbroken original packages, if possible, before recommending assessment, and that samples from partly emptied or retail packages should be forwarded only as corroborative evidence.

TREASURY DEPARTMENT,

OFFICE OF COMMISSIONER OF INTERNAL REVENUE,

WASHINGTON, D. C., September 14, 1909.

To Collectors, Internal Revenue Agents, and Others:

Attention is called to the necessity of securing, if possible, samples from more than one unbroken original package of butter for analysis, where such samples alone are to be made the basis of assessment of special tax as manufacturer of adulterated butter and stamp tax on product found to contain 16 per cent. or more of moisture.

Officers should not forward samples from partly emptied original packages or retail packages which might have a pronounced moisture content owing to the possible precipitation of water from the portion removed into the butter remaining in the tub or other receptacle, except as corroborative evidence of other samples taken from unbroken original packages.

Great care should be exercised in securing and identifying the samples as the product of the specific manufacturer against whom assessment is recommended, as this evidence might be the basis of action in court.

No assessment should be so recommended upon the basis of a single sample taken from a broken package, or even a single original package intact, unless there is other evidence tending to establish liability to tax.

Nothing in this decision is to be construed as in conflict or in any way modifying T. D. 1449 and T. D. 1498 upon this subject.

> ROYAL E. CABELL, Commissioner.

The following Notice of Judgments has been issued by the Board of Food and Drug Inspection on November 11 and 16, 1909.

102. Misbranding of distiller's dried grains (as to protein and fat content).

103. Adulteration of eggs (presence of putrid and decomposed animal matter).

104. Adulteration and misbranding of stock feed (as to presence of rice hulls).

105. Adulteration and misbranding of a cereal (as to presence of wheat)

106. Misbranding of a cane sirup (as to presence of glucose). 107. Misbranding of Vermont or maple sugar (as to presence of cane sugar).

108. Misbranding of preserves (underweight).

109. Adulteration and misbranding of cottonseed meal (as to presence of cottonseed hulls).

110. Misbranding of sirup (as to quantity).

III. Misbranding of catsup (as to amount of benzoate of soda present).