is a question worthy of investigation by our national Geological Survey. It may have some bearing on the recent discovery[1] that nitrates are the predominating constituents in some of the western soils impregnated with alkali. The occurrence of these nitrates has been attributed to their formation by bacterial action at the present time. The existence of deposits of nitrates in the country rock in widely distributed areas in the arid West may have some connection with the occurrence of excessive quantities of nitrates in these agricultural soils.

LOGAN, UTAH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MINNESOTA.]

A CHEMICAL STUDY OF LIGNITE. PART II. THE VOLATIL CONSTITUENTS.[2]

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Received March 8, 1911.

In the proximate analysis of lignite, the determination of the volatil constituents is unquestionably of great importance, and like the determination of moisture is deserving of special attention. A considerable portion of the volatil combustible matter in lignite, as determined in the proximate analysis of coal, seems to consist of small particles of carbon carried off by the liberated gases and by the moisture. This is evident from the fact that in addition to the flame produced by the burning of the gaseous constituents themselves, particles of solid combustible matter are carried upward by the gases and appear for an instant as glowing sparks before being completely oxidized. These solid particles are especially noticeable if the lignite contains a large amount of moisture or if the determination is made without first thoroughly drying the sample. Even though the crucible lid fits perfectly, these particles are thrown off when the heat is applied as indicated in the ordinary analysis of bituminous coal. The volatil constituents may be varied from 5 to 12 per cent. by slowly or rapidly raising the temperature to a red heat. The variation is more noticeable, however, in the undried lignite. It was found that not only the quantity of volatil matter but also the composition of the gas varied, depending upon the heating and whether or not the lignite contained its hygroscopic water.

The first experiments were made with the idea of determining the quantity of volatil matter, both by weight and by volume as compared with good bituminous coal. Accordingly, determinations were made by the ordinary method and by heating in an atmosphere of hydrogen.

The samples examined came from the extreme limits of the Dakota, the Canada and the Alaska coal belts. Samples from these different

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[1] Bulletins Nos. 155 and 178, Colorado Agricultural Experiment Station.

[2] For the first paper see THIS JOURNAL, 29, 1488 (1907).

localities were found to vary considerably in their physical properties, indicating that they must have been formed under different physical conditions. Those from the south are brown, slightly resembling good peat. They contain more moisture than those from farther north. They also seem to slack more readily. One of the characteristic features of the southern lignite is the tendency to break up into more or less laminated forms on losing moisture, while those from farther north, on losing moisture, break up with a slightly conchoidal fracture. The Saskatchewan, Alberta and Alaska lignites are darker than the lignite from the beds of southern North Dakota and slightly resemble ordinary anthracite in both color and fracture.

The regular proximate analyses were made according to the Report of the Committee on Coal Analyses.[1]

As already stated,[2] the lignites vary widely in the amount of moisture they contain. Some of the samples from the southern belt contain more than 40 per cent. of moisture or nearly twice as much as samples from the extreme north. This is due partly to the structure of the coal and partly to the fact that most of the beds in the south are very wet, while most of those in the north are comparatively dry.

In order to make the analyses as nearly comparable as possible, the samples were taken just as they came from the mines and dried in air until they had reached an equilibrium.

Under ordinary circumstances the lignites exposed to the air continued to lose moisture until they reached an equilibrium at from 10 to 12 per cent. At this point the loss of moisture practically stops if the lignite exists in pieces of moderate size. If the samples are pulverized, the moisture drops to 7 or 8 per cent. before an equilibrium is reached.

Samples 2 and 3 contain more than the average equilibrium amount of moisture, partly because they seem to be a little more compact, and partly because they were in larger pieces than the others. All of the samples were air-dried in the form in which they came from the mine.

The samples examined were as follows:

1. North Dakota.
2. Saskatchewan, Canada.
3. Alberta, Canada.
4. Klondike in Alaska.
5. Beaver Hill, Alaska.

For convenience, the above numbers have been used to represent the different samples.

The proximate analyses gave the following:

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[1] THIS JOURNAL, **21**, 1116–1145 (1899).

[2] *Ibid.*, **29**, 1488.

Sample.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Moisture	12.95	15.95	22.50	10.20	11.10
Volatil combustible matter.	36.45	34.40	28.30	36.65	37.20
Fixed carbon	42.77	44.38	45.40	48.40	46.43
Ash	4.83	5.27	3.91	4.75	5.27
Sulfur	0.90	0.82	0.70	..	..

Following the above determinations, ultimate analyses of the first three lignites were made. Calculating to moisture-free samples, the results were as follows:

Sample.	No. 1.	No. 2.	No. 3.
Carbon	62.90	66.42	68.10
Hydrogen	4.30	3.78	4.21
Nitrogen	0.81	1.09	1.12
Sulfur	1.03	0.98	0.90
Oxygen	25.46	21.43	20.67
Ash	5.50	6.30	5.00

Carbon and hydrogen were determined by the regular combustion, nitrogen by the Kjeldahl method and sulfur from the residue of a Parr calorimeter combustion. The ash was calculated from the proximate analysis.

Determinations in an Atmosphere of Hydrogen.—In order to compare the volatil matter obtained in the above proximate analyses, with result, obtained by heating at the same temperature in an atmosphere of hydrogen, a special apparatus was made, whereby the air could be entirely excluded during the process of heating. Various forms of apparatus were tried. The one which gave best results (see Fig. 1) consisted of a graphite muffle so arranged that the open end could be securely closed. Through the bottom of the muffle four holes were drilled of such size that platinum crucibles would fit in perfectly. By carefully fitting the crucibles with asbestos paper, they were made practically gas-tight. With this apparatus four analyses could be made at a time. Two small

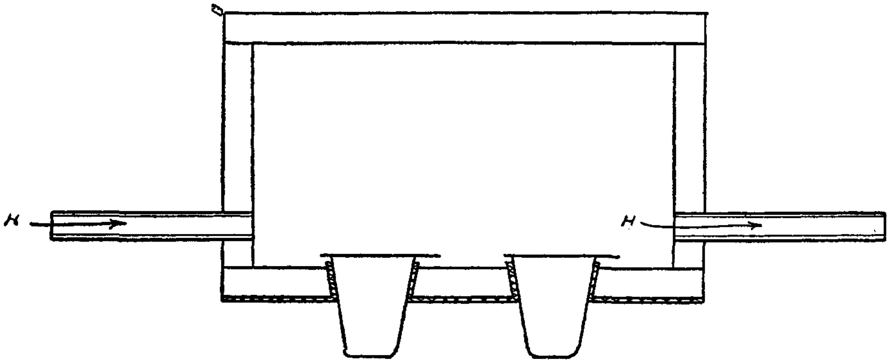

Fig. 1.

holes were bored through the side of the muffle in order that hydrogen could be passed through during the heating. Known weights of lignite were then placed in the crucibles, the air driven out by hydrogen and the determination made by heating in the regular manner at a red heat. In each case duplicate determinations were made.

The following table shows the difference between the amount of volatil matter as determined in an atmosphere of hydrogen and in air under the same conditions.

Sample.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Volatil matter in hydrogen..	28.51	28.60	28.79	28.65	28.57
Volatil matter in air........	35.15	36.20	36.50	36.65	37.20

Destructive Distillation.—That the volumes of gas obtained by destructive distillation of the above samples of lignite might be compared, a series of determinations was made by heating a known quantity of lignite in a platinum distilling flask until all of the volatil material had passed off. The amount of gas was found to vary widely not only in samples of lignite obtained from different localities but also in those obtained from the same locality.

Samples from the far north, including Canada and Alaska, seemed to give more gas than those found further south in the Dakotas.

The following table represents the volumes of gas per gram obtained by heating in a platinum distilling flask at a bright red heat:

Sample.	No. 1.[1]	No. 1*a*.[1]	No. 2.	No. 4.
Volume of gas in cc. from dried lignite.........	400	376	420	450
Volume of gas in cc. from undried lignite.......	500	540	601	620

The total quantity of gas was found to vary widely, especially when the long narrow necked platinum distilling flask was used.

On carefully studying the gases, it was found that the variation was due to moisture in the coal, some of which was probably changed into hydrogen and carbon monoxide by the sudden heating of the sample. This was evident from the analysis of the gas. The platinum distilling flask was therefore discarded and a series of determinations made, using a special shaped iron retort so as to avoid the error resulting in the formation of water gas.

The pulverized lignite was placed in the air-tight iron retort and distilled at a temp. of 800–850° until the gas ceased to pass off. The distillates were led into cooled flasks for the purpose of condensing the water and tarry products. Two flasks were used for condensing the moisture and other readily condensable gases. The first one was kept at 25–30°; it condensed practically all of the water and most of the tar. The second was cooled by ice-water; it condensed in addition to a very small amount

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[1] Samples 1 and 1*a* represent the southern and northern North Dakota lignite. No. 1*a* came from northern North Dakota and in appearance is a mean between the southern Dakota and Saskatchewan lignites.

of water, a white waxy substance which melted at room temperature and which readily oxidized to a dark oily liquid. This white substance was found in all the lignites. It is under investigation at the present time.

The gases were then led into a gasometer but connections were made so that at any time during the distillation, samples of the gas could be drawn off for analysis before they entered the gasometer.

Destructive Distillation of North Dakota Lignite.—North Dakota lignite was subjected to destructive distillation in the apparatus above mentioned. The moisture and the tar were weighed and the gas measured. A number of analyses were made on the same sample.

Three determinations gave the following:

	No. 1.	No. 2.	No. 3.
Fixed carbon and ash	52.60	52.40	52.50
Water	27.20[1]	35.00[1]	36.30
Tar 1st bottle	0.70	0.70	0.70
Tar 2nd bottle	0.70	0.30	0.30
Gas at 0° and 760 mm. liters per 100 grams	17.00	12.50	15.50

An average sample from each distillation was then analyzed. Inasmuch as it was not found convenient to remove the air from the apparatus before beginning the experiments, corrections were necessary in order that the true composition of the gas might be determined. These corrections are found under the columns indicated as air-free gas.

Analysis of Gases.

The gases obtained from distillations 1 and 3 were analyzed with the following results:

	No. 1.		No. 3.	
	Found.	Calculated as air-free.	Found.	Air-free.
CO_2	36.0	41.0	34.5	38.1
Unsaturated hydrocarbons	0.5	0.6	2.0	2.3
O_2	3.1	1.0	3.6	1.6
CO	11.3	12.8	12.2	13.8
CH_4	..	..	24.5	27.5
H_2	..	..	12.5	13.0
N_2	..	..	10.7	3.7

The quantity of oxygen is unusual. After allowing for the oxygen of the air in the apparatus at the beginning of the process, an excess amounting to over 1 per cent. was found in the gas although no signs of leakage in the apparatus could be detected.

The quantity of unsaturated as well as of saturated hydrocarbons is extremely low in all of the lignites. This doubtless accounts for the fact that they are practically smokeless.

Analyses were then made of different samples of gas taken during successive stages of the distillation. The following results were obtained:

[1] Some of the water was lost by being sucked back into the retort after distillation.

Sample taken.	After 500 cc.	After 3 liters.	After 7 liters.	After 8 liters.	After 10 liters.	At end of run.
CO_2	51.20	45.00	38.00	28.00	26.00	26.00
Unsaturated hydrocarbons	0.10	4.40	3.80	1.20	0.20	0.30
O_2	5.40	0.20	0.0	0.80	0.20	1.80
CO	5.60	13.60	12.00	15.00	14.40	12.00
CH_4	0.0	24.40	Not anal.	28.00	26.00	Not anal.
H_2	0.0	11.30	Not anal.	21.00	29.00	Not anal.
N_2	37.70	1.10	Not anal.	7.00	4.20	Not anal.

In the early stages of the distillation, carbon dioxide passed off more rapidly than the other gases, as will be seen from a glance at the above table. After about half of the gas had been driven off, the percentage remained practically constant. This, however, was not the case in the other samples examined. The large amount of nitrogen in the first 500 cc. of gas is due to the fact that the air had not been removed from the apparatus.[1]

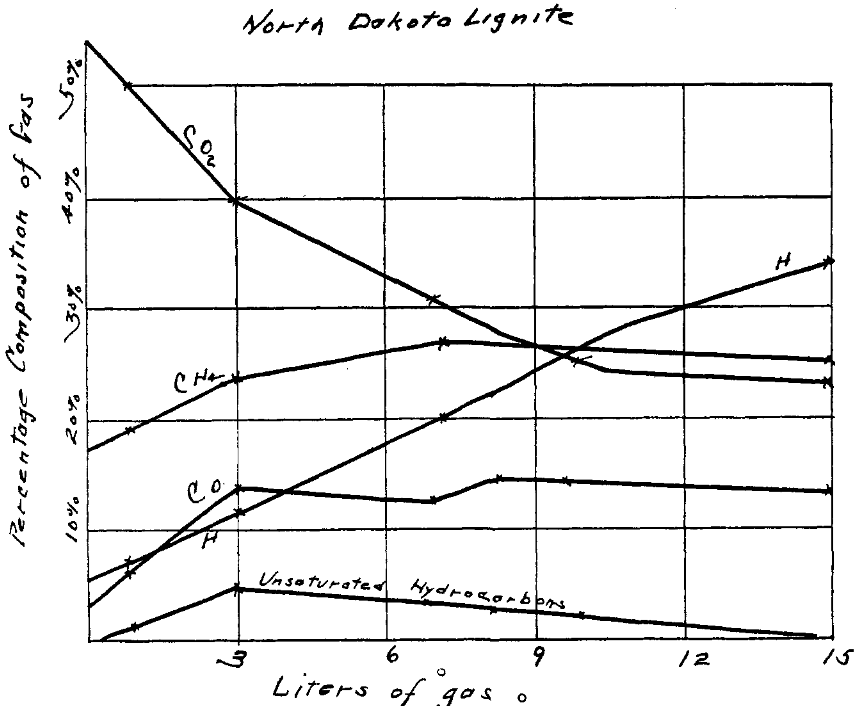

Fig. 2

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[1] In order, however, to avoid the error which would have occurred on account of air in the first 500 cc. of gas as indicated in the above tables, analyses were not used in plotting this and other curves until at least one liter of gas had been drawn off. The marks on the curves indicate the points at which samples were taken for analysis.

The preceding diagram (Fig. 2) will give at a glance the composition of the gas at different stages of the distillation:

Destructive Distillation of Saskatchewan Lignite.

Three samples taken from the mines at Bienfait were subjected to the same process of distillation and at the same temperature as those of North Dakota with following results:

	No. 1.	No. 2.	No. 3.
Fixed carbon and ash	55.50	52.00	52.00
Water	28.00	..	28.00
Tar 1st bottle	0.34	..	0.40
Tar 2nd bottle	0.20	..	0.20
Gas liters per 100 grams	26.00	26.00	26.00

Analyses of average samples of the gas gave the following:

	No. 1.		No. 3.	
	Found.	Air-free.	Found.	Air-free.
CO_2	28.00	29.80	27.40	29.30
Unsaturated hydrocarbons	0.40	0.40	0.40	0.40
O_2	1.10	0.0	2.60	1.40
CO	12.40	13.00	15.10	16.30
CH_4	17.20	18.00	..	..
H_2	30.00	31.80	..	..
N_2	10.90	7.00	..	..

Analyses were then made of different samples of the gas taken during successive stages of the distillation. The following results were obtained:

Sample taken.	After 5 liters.	After 10 liters.	At end.
CO_2	55.60	26.00	16.20
Unsaturated hydrocarbons	1.20	1.00	0.0
O_2	0.80	0.0	0.40
CO	13.00	10.00	17.00
CH_4	17.20	20.60	14.10
H_2	12.20	41.30	41.80
N_2	0.0	1.10	10.50

This gas differed considerably from the North Dakota sample in the total amount of carbon dioxide and in the relative amounts of H and CH_4 evolved, as is graphically shown in the following diagram (Fig. 3).

Destructive Distillation of Alberta Lignite.

Three samples were taken from the mines at Edmonton and distilled exactly as in the previous samples, with the following results:

	No. 1.	No. 2.	No. 3.
Fixed carbon and ash	49.90	49.50	48.80
Water	32.10	33.90	32.10
Tar 1st flask	1.70	1.50	1.50
Tar 2nd flask	0.20	0.20	0.70
Gas liters in 100 grams	13.00	18.00	23.00

Analyses of three average samples of the gas gave the following:

	No. 1.		No. 2.		No. 3.	
	Found.	Air-free.	Found.	Air-free.	Found.	Air-free.
CO_2	14.60	16.80	15.60	16.80	18.00	18.90
Unsaturated hydrocarbons.	0.80	0.90	0.10	0.20	0.80	0.90
O	6.00	4.50	2.30	0.40	0.90	0.0
CO	8.90	10.40	14.20	15.40	14.10	14.80
CH_4	21.50	24.50	20.30	22.00	24.80	26.10
H_2	31.30	36.00	32.40	37.70	33.50	35.20
N_2	16.90	7.90	15.10	7.50	7.90	4.10

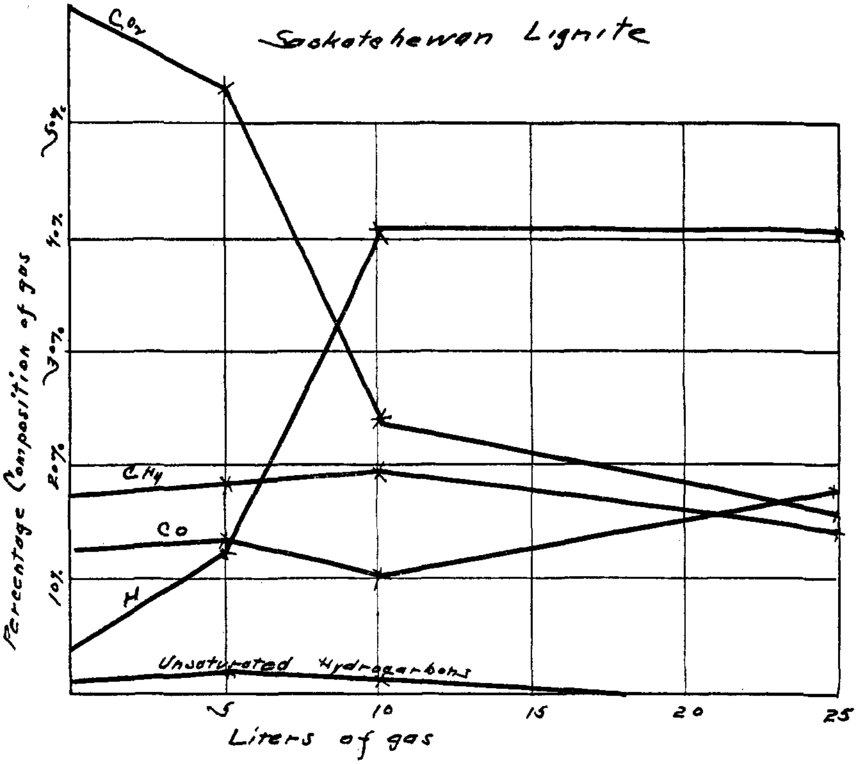

Fig. 3

Analyses were made of different samples of the gas taken during successive stages of the distillation, with the following results:

Sample.	After 3 liters.	After 15 liters.	Finish.
CO_2	21.60	14.80	20.80
Unsaturated hydrocarbons	2.70	0.00	0.00
O_2	1.90	0.00	0.00
CO	9.40	20.60	16.80
CH_4	22.20	15.70	9.40
H_2	24.10	42.60	35.70
N_2	8.10	6.30	17.30

The following diagram (Fig. 4) will show well the way in which the proportion of gases changes during the distillation:

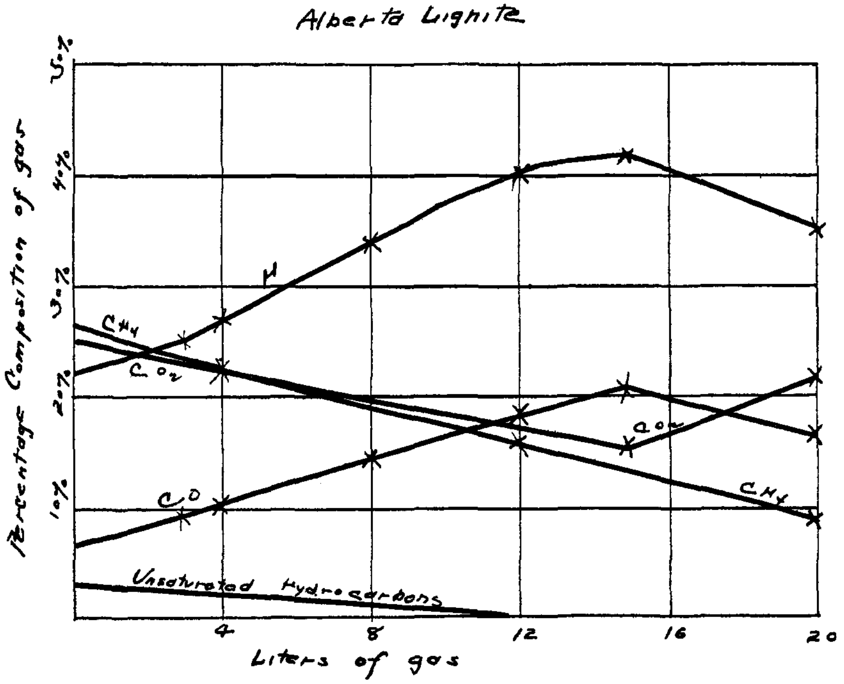

Fig. 4

As the above samples probably represent the extreme range in the composition of the different lignites, the following table will serve as a means of comparing the lignites from the different localities. Averages of three analyses have been taken in most cases.

	N. Dakota.	Saskatchewan.	Alberta.
Coke	52.50	53.20	49.40
Water	36.30	28.00	32.70
Tar	1.00	0.60	1.90
Gas liters in 100 grams	15.00	26.00	18.00

Comparison of Gases (Calculated as Air-free).

	N. Dakota.[2]	Saskatchewan.[1]	Alberta.
CO_2	38.10	29.80	17.50
Unsaturated hydrocarbons	2.30	0.40	0.70
O_2	1.60	0.00	1.60
CO	13.80	13.00	13.50
CH_4	27.50	18.00	24.20
H_2	13.00	31.80	36.30
N_2	3.70	7.00	6.50

[1] Average sample of distillation No. 1 of the Saskatchewan lignite.

[2] Average sample of distillation No. 3 of North Dakota lignite.

Comparing the amounts of coke with fixed carbon and ash of the proximate analysis, it will be seen that there is considerable difference; due, doubtless, to incomplete distillation as the temperature of 830° is evidently not sufficient to drive off all of the volatil matter in some of the samples (see Porter and Ovitz, Bureau of Mines, *Bull.* I). Distillation was apparently complete, however, in the Alberta lignite.

The following table will show the difference between the coke left after the distillation and the fixed carbon obtained by the proximate analysis:

	N. Dakota.	Saskatchewan.	Alberta.
Distillation, coke including ash	52.50	53.20	49.40
Fixed carbon, including ash	47.60	49.65	49.30
	4.90	3.55	0.10

The following table shows the relative amounts of hygroscopic water as compared with the total amount found by destructive distillation:

	N. Dakota.	Saskatchewan.	Alberta.
Per cent. of water obtained by distillation	36.30	28.00	32.70
Per cent. of hygroscopic water	12.95	15.96	22.50
Water produced by distillation	23.35	12.04	10.20
Per cent. of H present (by ultimate anal.)	4.30	3.77	4.21

Calculating the amounts of water found to the dry analysis, the North Dakota lignite would consume 2.98 per cent. of the H to form water, the Saskatchewan 1.59 and the Alberta 1.47, leaving respectively, 1.32, 2.18 and 2.80 per cent. of H to be evolved either as free hydrogen or in the form of hydrocarbons.

From the above data and from the moisture determinations in samples from different localities[1] it is apparent that the composition of the various lignites depends somewhat upon the locality. The southern samples contain more moisture than those from farther north. The total amount of volatil constituents, however, increases slightly as we go northward. The individual gases seem to vary but not regularly. Carbon monoxide is practically constant and marsh gas changes but little. There is, however, an increase in the amount of hydrogen as we pass northward. On the whole, there is but little difference in the volatil constituents from the different samples, although there is a distinct difference in the general physical appearance.

MINNEAPOLIS, MINN.

NOTES.

Preparation of Stannic Iodide and Its Solubility in Certain Organic Solvents.—In the preparation of stannic iodide for use in this laboratory

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[1] Part I, THIS JOURNAL, **29**, 1488.