

THE DETERMINATION OF IODINE IN KANSAS WATERS

by

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INTRODUCTION

Iodine seems to be a factor in the healthful functioning of the thyroid gland in humans, and in wild and domestic animals. Water has long been associated as contributing to the iodine supply. For this reason, it was felt that more should be known about the waters of Kansas relative to their iodine content. With this data it was hoped that further relationships such as geological and those of goiter prevalence could be worked out.

Through the aid of the Extension Department of the Kansas State College of Agriculture and Applied Science, the county agents and a few former students, Dr. Brubaker of the Chemistry Department was able, during the year 1929, to obtain a considerable number of samples of water from those sections of the state having county agents.

Dr. Brubaker (1) and some of his former students started to adapt the method of Hunter (2), used on animal tissues, to the determination of the iodine content of water. The iodides present in the water were oxidized to iodates, in acid solution, by means of sodium hypochlorite. Reactions $HI + 3HClO \rightarrow HIO_3 + 3HCl$. The iodates then set free iodine from potassium iodide which was titrated with standard sodium thiosulfate. Reactions $HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O$, $I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$. The iodine set free was six times

the amount originally present making it possible to use much smaller samples than those reported in the literature some of which use 25 gallon samples. (3)

Preliminary studies were made during the summer of 1930. Iodine recovery was tested by adding known amounts of potassium iodide to distilled water. Tests of Manhattan city water, both that direct from the wells and that passed through the softening plant, were made. These were compared with tests of the same water with a known amount of potassium iodide added. The effect of the addition of known quantities of iron on the recovery of iodine was studied. The effect of varying procedure was determined. Finally experiments to determine the effect of the oxygen of the air were made.

METHOD

The method as worked out from the preceding experiments was applied to the samples collected as previously mentioned. Liter samples, if available, were evaporated in two liter beakers to a volume of about 200 cc using a single Meeker burner as the source of heat. The evaporation required about five hours. These concentrates were poured into an 800 cc Kjeldahl flask the beaker being rinsed with 40 cc of 85% phosphoric acid diluted with an equal volume of distilled water. The beaker was again rinsed with 10 cc of distilled water both rinsings being added to the Kjeldahl flask.

Saturated chlorine water, 25 cc, was added and the contents boiled till the volume was very close to 125 cc. The boiling must be continued at least 15 minutes after potassium iodide starch paper fails to show that chlorine is being given off. If the volume of liquid threatened to go below 125 cc distilled water was added. The contents of the flasks were cooled quickly by placing the flasks in running water and were poured out into casseroles. Titration followed immediately the addition of 10 cc of a 1% solution of potassium iodide. On the disappearance of the yellow color, if immediately if no yellow color appeared, 5 cc of a .05% solution of arrow root starch was added and the titration continued to the disappearance of the blue color. The first end point was taken as the reading no attention being paid to a return color which sometimes developed. The sodium thiosulfate, approximately N/211, was standardized daily with N/211 potassium biniodate. This was then diluted to approximately N/1055 with recently boiled distilled water the results being calculated to N/1055. The number of cc used divided by 50 gives the iodine content in parts per million in the water.

REVIEW OF LITERATURE

History. The world knew long before the discovery of iodine by Courtois in 1811 that certain sea foods were beneficial in preventing or reducing goiter. The Chinese fed foods now known to contain iodine. The Phoenicians are said to have fed burnt sponge. The Greek and Roman and other early civilizations were not entirely ignorant of the relation of marine products to goiter. Why certain foods were beneficial was unknown. (4)*

Davy's discovery in 1815 that burnt sponges contain iodine, followed by the experiments of Coindet in 1820, showing that the administration of tincture of iodine caused certain goiters to disappear, (4) helped to establish what is now taken as a fact that iodine is one of the factors producing beneficial results. (5)

That the water supply might be a factor in the iodine supply was established by Angeline in 1824 and by Cantu in 1825 when they found that spring water reputed to cure goiter contained iodine. (4)

Chatin announced, as a result of extensive investigation in 1850-54, that goiter occurred rarely in regions where

* Primary papers not available for early history.

the soil and water had a high iodine content. Goiter and cretinism were common when the content was low. (4)

Iodine poisoning observed by Coindet in 1820 and the masterly paper by Rillet in 1860, based on studies of overdoses of iodine, slowed up the use of inorganic iodine in the treatment of goiter. (4)

An organic compound of iodine was found in the human thyroid (6) in 1895 by Bauman. Kendall (7) in 1914 isolated a substance containing 65% of iodine from the thyroid gland of a sheep. He called this substance thyroxin. Harrington (8) succeeded in producing thyroxin synthetically in 1926. Failure of the thyroid gland to produce thyroxin in sufficient quantities causes goiter. (9)

Historically these discoveries seem to have established a foundation whereby the goiter of the world should have disappeared long before the present.

Occurrence of Goiter. Goiter still remains in many places in foreign countries and is prevalent in the Great Lakes Region and the Pacific Northwest in the United States. (10) It is prevalent to as high as 71% (11) in Houghton County, Michigan among the school children. Wild and domestic animals also have goiter. Montana (12) loses about 100,000 pigs annually, the so called "hairless" pigs, the disease being associated with enlarged thyroids. Fish in a hatchery near Superior, Wisconsin were found to have goiter. (13)

The first extensive survey of goiter in humans in the United States was that obtained during the World War when 2,510,000 drafted men were examined for goiter and 11,971 cases were found. This data as well as the other data assembled by Olesen (14) from numerous other sources is not conclusive because of the lack of uniformity in making the surveys. Roughly the surveys do show the same areas goitrous. For the state of Kansas the draft figures show 48 cases of goiter representing 1.25 per thousand men examined. The results of the independent surveys are shown in Table I. (15)

Iodine in Relation to Goiter. In recent years iodine poisoning has been less feared and there has been a return to the use of inorganic iodine in water supplies and in iodized salt. Rochester, N.Y. began to add sodium iodide to their water supply in the spring of 1923. The original goiter survey showed that 7% of the school children, chiefly girls in the susceptible age, had visible goiters. In December 1924 a resurvey showed a reduction of 50% in the number of visible goiters. (16) Rochester, June 1, 1932, is continuing the use of sodium iodide to their water supply. (17) The resurveys from Lorain, Ohio, and Arcoostook County, Maine, show no significant changes. (18) These conflicting reports leave a doubt as to the efficiency of inorganic forms of iodine in their effect on thyroid enlargement. Olesen (19)

TABLE I

NUMBER OF EXAMINATIONS AND PERCENTAGE OF THYROID ENLARGEMENTS REPORTED IN KANSAS BY DIFFERENT OBSERVERS, ACCORDING TO AGE AND SEX OF THE INDIVIDUALS EXAMINED, AND LOCATION OF THE PLACE

Place	Ages	Number Examined			Percentage with Goiter			Reported by:	Remarks
		Boys	Girls	Girls	Boys	Girls	Girls		
Cottonwood Falls		96	100	196	3.0	20.0	12.2	State Board	First to eighth grades.
Fort Scott								C.L. Mosley	Goiter has increased 100% in last 10 yrs.
Junction City				1,509			3.0	H.R. Ross	
Strong City		71	80	151	5.6	11.2	8.6	State Board	First to eighth grades.
Topeka	5-18	3,345	3,706		30.9	49.7		E.G. Brown	
Butler County								R.J. Cabeen	Considerable Goiter
Ellis County				1,903			.6	Fred C. Cave	
Do								do	14 cases found in general examination of school children
Jefferson County				3,260			19.2	D.M. Stevens	
Do								do	About 13% of all children 1928
McPherson County	5-18	780	720		38.0	56.0		L.S. Steadman	
Ottawa County				2,000			5.0	C.R. Hepler	Rural District of Central Kansas.
Do							10.0		Survey of 1926.

considers iodized salt as harmless but inefficient. Neither is he willing to advocate the general iodization of water supplies. Kimball (20) shows that the administration of inorganic iodine in syrup form prevented thyroid enlargement in the school girls in Akron, Ohio.

Whether the organic forms of iodine are any better is also in doubt. There is a general belief that it is and some experimental evidence tending to confirm the belief. McClendon (21) found that by feeding inorganic iodine to cows he was able to increase the iodine content of the milk most of the increase being in the skim milk. By feeding foods with high iodine content he was able to increase the iodine content of the fat appreciably.

The surveys show that goiter incidence seems to coincide with the deficiency of iodine in the food and water supplies, though the habits of the people, moving from one area to another, eating canned foods from far divergent sources, having various sources of water supply in the same region, the use of iodized salt and other forms of iodine, all tend to complicate the results of such surveys. McClendon's (22) map of the distribution of iodine based on the analyses of waters from all parts of the United States agrees rather closely with Olesen's (14) map showing the incidence of goiter and based on the draft figures.

Numerous attempts have been made to determine the iodine requirements, that is the minimum amount necessary to prevent thyroid enlargement. Von Fellenberg found that .0143 mg. of iodine a day would maintain an iodine balance. (25) Lunde and Class estimate the amount of iodine necessary to meet the requirements of metabolism as .05 mg. per day but Weston (24) is of the opinion that this is more than ten times the amount necessary to prevent or cure goiter. McClendon (25) reasons from the work of Marine that the total number of goiters represents the total number of thyroids that contain or once contained less than .1% of iodine. Hertzler (26) does not believe the iodine intake to be the whole thing. He (27) points out that there is a familial tendency to goiter. Not only has he had a grandmother, a mother and three daughters consult him at the same time about their goiters, but he has noted where three or more daughters became aware of their goiters long after they left the parental roof. It is well known that iodine is, not only not beneficial in some forms of goiter, but is actually harmful. However if the iodine could be given early enough and would cure the goiter, which Dr. Hertzler is not willing to concede, the later forms would not develop. He (28) has noted individuals who passed through all the stages of goiter, simple colloid, non toxic adenoma, toxic adenoma, and Basedow triad, the individual finally dying of heart

failure. Two other factors must be considered, the amount of iodine intake that is utilized, and the form in which it is given. Von Fellenberg and Lunde reached independent conclusions that 60% (29) of the iodine intake is excreted in the urine. The best form, whether organic or inorganic, has been discussed in a previous paragraph.

Iodine in Water. Since this thesis has to do with the iodine content of water, it will be considered in some detail. Angeline and Cantu, as mentioned previously, found that the water from springs having the reputation of curing goiter contained iodine. The relation between the iodine content of water and goiter has also been pointed out. Weston (30), however, says that the amount of iodine present in drinking waters is, generally speaking, of little consequence as a reliable source of iodine needed by the body. Geiger (31) says, "Apparently, whenever the iodine content of water is less than 23 parts per billion, goiter is common." The survey of McClendon (32) is probably the most extensive that has been made in the United States. His survey shows a maximum amount of 134.7 parts per billion at Mexia, Texas, and a minimum amount of .01 parts per billion at Duluth, Minnesota. Out of the 82 samples reported only 23 showed more than one part per billion. McClendon also reports that the drinking waters of the lower Mississippi

Valley contain from 100 to 1000 times as much iodine as that of the Great Lakes Region. Eldridge (33) made a survey of the water of Michigan and found none in the northern half. In the southern part in general there was 0-2 parts per billion with a narrow strip near the eastern border containing 2-5 parts per billion and a few isolated wells in this strip showed over 5 parts per billion.

The earliest record found of iodine tests in Kansas waters were those by Bailey (34), in which he tested mineral waters for medicinal and other purposes. The record of his tests and those he collected from other sources were collected in Table II. The locality of the wells and springs tested for their iodine content is shown in Plate I. Samples of 5-15 liters (35) were concentrated and treated with potassium dichromate. This set free the iodine which was distilled over into potassium iodide solution and titrated with $N/100$ (36) sodium thiosulfate solution. McClendon (32) made tests on the dry residue of several samples of Kansas waters the results of which are given in Table III. Samples of 10 gallons were evaporated by the city sending the sample. One half teaspoonful of soda was placed in a dishpan and the water evaporated from it till a concentrate of less than a quart remained. The solid portion was discarded and the liquid evaporated to dryness in an evaporating dish. (37) This dry residue was analyzed by McClendon (38) by burning

TABLE II

TESTS OF IODINE CONTENT OF MINERAL WATERS OF KANSAS (BAILEY)

Town	Name of Well or Spring	Depth	Geologic Formation	Iodine Gms per liter
Abilene	Artesian well	1260	Upper and Lower Carboniferous	.0063
Atchison		1353	Mississippi Lime and Above	Trace
Eureka	Mineral well	140	Upper Carboniferous	.0001
Fredonda	Hudson well	1175	Lower Silurian	.0084
Geuda Springs			Tertiary	Trace
Independence	Bromo Magnesium well	300	(Sub-carboniferous (Lower Silurian	.0010
Carbondale	Mineral Springs well	40	Upper Carboniferous	.0005
Geary County	Moss Springs well	80	Permian	Trace
Atchison Co.	Arrington Springs(No. 3)		Upper Carboniferous	Trace

TABLE III
IODINE IN KANSAS WATERS

Town	Iodine P.P.B.	Source
(By McClendon, University of Minnesota, 1923)		
Fort Scott	0.66	Surface
Independence	0.06	"
Salina	3.91	Ground
Lawrence	0.11	Surface
Kansas City	1.89	"
Hutchinson	0.1	Ground
(By Gottlieb, Water and Sewage Laboratory, 1926)		
St. Francis	11.76	Ground
Norton	6.00	"
Phillipsburg	0.45	Surface
Beloit	1.88	"
Great Bend	Trace	Ground
Garden City	"	"
Liberal	0	"
Hutchinson	Trace	"
Wichita	1.42	"
Florence	0.18	"
Herington	3.26	Surface
Emporia	1.23	"
Eureka	0	"
Fredonia	0.51	"
Coffeyville	0	"
Independence	0.06	"
Caney	0	"
Pittsburg	0	Ground
Ottawa	0	Surface
Topoka	1.46	"
Leavenworth	2.27	"
Horton	0	"
Highland	0	Ground
Chanute	0	Surface
Kansas City	0	"

it in a silica tube in a stream of oxygen the burned gases being bubbled through a sodium hydroxide solution. This solution was evaporated to dryness and the residue, along with the ash of the burning, was treated in a ball mill and extracted with alcohol. The residue from the evaporation of the alcohol was dissolved in water and neutralized. Sodium nitrite was added and 1 cc of carbon tetrachloride. The iodine in the carbon tetrachloride was determined colorimetrically.

Selma Gottlieb, Chemist of the State Water Laboratory, used 100 liter samples evaporated in the presence of 6 gms of sodium carbonate by the city sending the sample. Samples arriving in an acid condition were not tested. The results of these tests are given in Table III along with McClendon's. Miss Gottlieb explains the discrepancy of the Kansas City tests on the basis that the river water undoubtedly varies in iodine content. The method used in testing was that of Eldridge. (40) He removed the iodides from the chlorides if the chloride content was more than 70 parts per million. Potassium permanganate solution was added till the color of the solution persisted. Carbon disulfide was added and then sulfuric acid drop by drop. During the addition of the acid the solution was shaken continuously to insure the removal of the iodine by the carbon disulfide. The iodine content of the carbon disulfide was determined colorimetrically.

Iodine in Food. Food as well as water furnishes iodine for bodily use. If the organic form is best the food supply may be of more importance than the water supply. Some work has been done along this line. Forbes (41) and his associates used Kendall's iodate method on a great number of samples of food from all parts of the United States. McClendon (42) has analyzed foods from both goitrous and non-goitrous regions in the United States. He finds a higher iodine content in foods from the non-goitrous regions. The South Carolina Food Research Commission (43), created in 1928, under the direction of Dr. Roe E. Remington (44), has made an extensive study of the foods of South Carolina with respect to iodine content. Comparison of these results with those of McClendon for foods from Washington and Oregon shows a much greater iodine content in the South Carolina foods. Remington (45) used the low temperature ashing method, McClendon's method being similar to the one used for water. Remington (46) also found that the leaves of food plants contain a higher percent of iodine than the roots from the same plants.

Geology of Iodine. Certainly the food and water must get their iodine content from the soil. If the iodine content of the food and water vary then the iodine content of soils must vary. Chatin reached the conclusion that water from sources rich in lime and magnesium and from melting

glaciers are invariably low in iodine content. (47) Von Fellenberg found that the iodine content of rock was much lower than that of the soil from the same rock. (48) He concluded that the increased iodine content of the soil must be due to iodine received from rain water percolating through the soil. McClendon has collected data from a great number of sources showing the iodine content of soils. From the data collected he concludes that rhyolitic soils are deficient in iodine. Von Fellenberg also found that the presence of fossils greatly increased the iodine content of a piece of sedimentary rock. McClendon (48) suggests that, according to the anatomic theory of the disintegration of the elements, the iodine is now largely distributed where it originated. Elements of odd atomic weight are rare making the quantity so small that it is not easily concentrated by geological forces. Remington (49) has established an apparent relationship between the iodine content of South Carolina Foods and the geology of the state, the potato being used as the index food.

RESULTS

Checks on Method. Since the results of tests made on the Manhattan city water in preliminary work were much higher than those reported in the literature in general, attempts were made to determine whether they were due to

greater iodine content in the water or to some defect in the procedure. Iron is present to a large extent in the Manhattan city water and it was thought that it might catalyze the oxidation of the potassium iodide used during titration. Phosphoric acid was used with the idea that it would hold the ferric ions originally present in the water in an unionized form. $Fe^{+++} + PO_4^{---} \rightleftharpoons FePO_4$. Table IV gives the results of tests made with distilled water to which known amounts of potassium iodide were added. The addition of iron up to 5 parts per million did not vary by more than the experimental error.* Test samples were treated by the same method used for water. Up to ten parts per million it may make the readings somewhat high though a test for ferric ion showed a complete suppression. Ten liters of city water were evaporated to 200 cc and the same amount of phosphoric acid added as used in a single liter of the ordinary samples. To this 4 cc of normal potassium sulfocyanate were added. It matched with the comparison tube without the addition of any ferric ions to the comparison tube. This test showed that the phosphoric acid apparently suppressed ten times the amount of iron found in the Manhattan city water.

* N/211 solutions used for this work made experimental errors larger.

TABLE IV
RECOVERY OF IODINE IN THE PRESENCE OF IRON*

Trial	Iron added	I ₂ added	I ₂ recovered	Remarks
1.	.1	.12	Broken	Iron and iodine added expressed as parts per million in a liter of water. Samples reduced to 75 cc volume, diluted to 125 and titrated except as noted. 9-10 reduced to 125 cc titrated. In trials 13, 14, 19, 20, and 29 solution N/1055 was used.
2.	.1	.12	.128	
3.	.2	.12	.128	
4.	.2	.12	.128	
5.	.5	.12	.128	
6.	.5	.12	.128	
7.	1.	.12	.128	
8.	1.	.12	.128	
9.	1.	.12	.146	
10.	1.	.12	.155	
11.	1.	.12	.128	
12.	1.	.12	.128	
13.	1.	.12	.119	
14.	1.	.12	.119	
15.	2.	.12	.137	
16.	2.	.12	.137	
17.	3.	.12	.137	
18.	3.	.12	.128	
19.	3.	.12	.119	
20.	3.	.12	.119	
21.	4.	.12	.128	
22.	4.	.12	.128	
23.	5.	.12	.146	
24.	5.	.12	.174	
25.	5.	.12	.137	
26.	5.	.12	.155	
27.	5.	.12	.137	
28.	5.	.12	.137	
29.	5.	.12	.119	
30.	5.	.12	.137	
31.	5.	.12	.146	
32.	10.	.12	.146	
33.	10.	.12	.146	
34.	10.	.12	.137	
35.	10.	.12	.146	

* All titrations with approximately N/211 solution burette reading in tenths except those noted. KI added as N/211 with same exceptions.

Occasional accidental variations in the volume to be titrated seemed to cause a lack of checks in duplicate determinations. Experiments to find the cause of this variation showed that the titration at low volumes, 75 cc, caused the starch to turn red with poor end points. Reduction to 75 cc with the addition of recently boiled distilled water before titration gave results comparable to those where the concentration was 125 cc without any dilution. The results are shown in Table V, 1-36. However, when the potassium iodide was added at the 75 cc concentration with subsequent dilution to 125 cc the results were high, Table V, 37-50. Other tests made with phosphoric acid, sulfuric acid, and hydrochloric acid confirmed the results of Table V that the acids in too strong a concentration set free iodine from the potassium iodide added before titration. The rigid procedure as explained under "Methods" was found necessary for checks, and this method was followed out in making further tests of iodine recovery first with KI N/1055 then with KI added to Manhattan city water, the results being given in Table VI. These tests seem to indicate that duplicate determinations can be made within the accuracy of .01 parts per million when liter samples are used. Increasing the size of the sample to 10 liters would make it possible to give readings accurate to .001 parts per million. Smaller

TABLE V

21

TESTING IODINE RECOVERY IN RELATION TO CONCENTRATION

Trial	I ₂ added P.P.M.	I ₂ found P.P.M.	Remarks
1.	.12	.121	1-24 Reduced to 75 cc diluted to 125 cc titra- ted.
2.	.12	.121	
3.	.12	.117	
4.	.12	.121	
5.	.12	.116	
6.	.12	.121	
7.	0.	.006	
8.	0.	.006	
9.	.03	.025	
10.	.03	.024	
11.	.03	.024	
12.	.03	.024	
13.	.06	.052	
14.	.06	.052	
15.	.06	.048	
16.	.06	.055	
17.	.06	.060	
18.	.06	.052	
19.	.24	.239	
20.	.24	.237	
21.	.24	.230	
22.	.24	.234	
23.	.24	.230	
24.	.24	.231	
25.	.24	.243	25-30 Reduced to 125 cc and titrated.
26.	.24	.242	
27.	.24	.239	
28.	.24	.235	
29.	.24	.239	
30.	.24	.239	
31.	.12	.122	
32.	.12	.122	
33.	.12	.121	
34.	.12	.117	
35.	0.	0.	
36.	0.	0.	
37.	0.	0.	37-50 Reduced to 75 cc diluted to 125 cc be- fore adding KI
38.	0.	0.	
39.	.03	.031	
40.	.03	.033	

TABLE V (CON'T)

Trial	I ₂ added P.P.M.	I ₂ found P.P.M.	Remarks
41.	.06	.062	
42.	.06	.062	
43.	.12	.121	
44.	.12	.123	
45.	.24	.235	Diluted after adding KI
46.	.24	.235	Diluted before adding KI
47.	.03	.037	Diluted after adding KI
48.	.03	.031	Diluted before adding KI
49.	.06	.064	Diluted after adding KI
50.	.06	.062	Diluted before adding KI

TABLE VI

TESTING IODINE RECOVERY

Trial	I ₂ added P.P.M. in liter H ₂ O	I ₂ found P.P.M. total	I ₂ in water P.P.M.	Remarks
1.	0.00	0.00		Samples 1-36 distilled water
2.	0.00	0.00		
3.	0.00	0.00		
4.	0.00	0.00		
5.	0.00	0.00		
6.	0.00	0.00		
7.	0.03	0.034		
8.	0.03	0.034		
9.	0.03	0.034		
10.	0.03	0.030		
11.	0.03	0.034		
12.	0.03	0.034		
13.	0.06	0.064		
14.	0.06	0.064		
15.	0.06	0.062		

TABLE VI (CON'T)

Trial	I ₂ added P.P.M. in liter H ₂ O	I ₂ found P.P.M. total	I ₂ in water P.P.M.	Remarks
16.	0.06	0.064		
17.	0.06	0.062		
18.	0.06	0.064		
19.	0.12	0.123		
20.	0.12	0.120		
21.	0.12	0.120		
22.	0.12	0.120		
23.	0.12	0.118		
24.	0.12	0.120		
25.	0.24	0.241		
26.	0.24	0.241		
27.	0.24	0.241		
28.	0.24	0.237		
29.	0.24	0.237		
30.	0.24	0.239		
31.	0.012	0.015		
32.	0.012	0.010		
33.	0.012	0.015		
34.	0.012	0.015		
35.	0.012	0.013		
36.	0.012	0.017		
37.	0.00	.082	.082	Samples 37-66 softened city water
38.	0.00	.082	.082	
39.	0.00	.078	.078	
40.	0.00	.065	.065	
41.	0.00	.072	.072	
42.	0.00	.072	.072	
43.	0.00	.086	.086	
44.	0.00	.082	.082	
45.	0.00	.086	.086	
46.	0.00	.082	.082	
47.	0.00	.080	.080	
48.	0.00	.084	.084	
49.	0.00	.053	.053	
50.	0.00	.036	.036	
51.	0.00	.048	.048	
52.	0.00	.036	.036	
53.	0.00	.040	.040	
54.	0.00	.025	.025	
55.	0.12	.202	.082	Samples 49-54 and 61-66 col- lected July 22 and tested Ju. 22 and 23, low for some unex- plained reason.
56.	0.12	.199	.079	
57.	0.12	.199	.079	
58.	0.12	.204	.084	
59.	0.12	.208	.088	
60.	0.12	.208	.088	
61.	0.60	.664	.064	

TABLE VI (CON'T)

Trial	I ₂ added P.P.M. in liter H ₂ O	I ₂ found P.P.M. total	I ₂ in water P.P.M.	Remarks
62.	0.60	.661	.061	
63.	0.60	.647	.047	
64.	0.60	.645	.045	
65.	0.60	.650	.050	
66.	0.60	.641	.041	
67.	0.00	.086	.086	Samples 67-90 untreated city water.
68.	0.00	.090	.090	
69.	0.00	.090	.090	
70.	0.00	.090	.090	
71.	0.00	.092	.092	
72.	0.00	.090	.090	
73.	0.00	.086	.086	
74.	0.00	.086	.086	
75.	0.00	.090	.090	
76.	0.00	.090	.090	
77.	0.00	.090	.090	
78.	0.00	.086	.086	
79.	0.00	.090	.090	
80.	0.00	.086	.086	
81.	0.00	.086	.086	
82.	0.00	.086	.086	
83.	0.00	.086	.086	
84.	0.00	.090	.090	
85.	0.12	.216	.096	
86.	0.12	.214	.094	
87.	0.12	.214	.094	
88.	0.12	.218	.098	
89.	0.12	.218	.098	
90.	0.12	.220	.100	

amounts could be detected by the use of still larger samples. Table VI also shows that treatment which softens the water apparently removes some of its iodine content.

Tests of Kansas Waters. The results of the tests of the water samples from different parts of the state are given in Table VII.

Comparison of Geology of Kansas with Iodine Content of Water Tested. Regarding the geological distribution of iodine in the waters of Kansas there seems to be an apparent relation. Table VIII, Table IX, and Plate I give this relation. The figures of Table VIII are striking in themselves, but when the source of the water is traced it is even more apparent. Table IX shows a comparison of water from the same river at different towns. When we consider that the samples were collected at different times, there is a remarkably close agreement. In the Glacial area, East and North of the heavy black line (Plate I), with the exceptions of Leavenworth and Kansas City which get their water from the Missouri River, all of the wells and springs seem to be in, or from glacial deposits. (52) In the Pennsylvanian some of the water supplies are from rivers originating in the Permian as shown in Plate I. The Chetopa wells are 1135 and 1240 feet deeps and are probably bottomed in the

* Well depths and distance from streams and sources were obtained by answers to letters sent to City Clerks.

TABLE VII

TEST OF SAMPLES OF WATERS FROM VARIOUS LOCALITIES IN KANSAS

Sample	Trial	H ₂ O cc	I ₂ P.P.M.	Locality	Source
1.	1	350	0.	Allen Co., Iola	Neosho river
2.	1	375	.016	Anderson, Garnet	Impounded surface
3.	1	1000	.035	Atchison, Effingham	Ground water
	2	1000	.030		
	3	270	.030		
4.	1	1000	.019	Barber, Medicine Ledge	Elm creek
	2	1000	.021		
	3	1000	.021		
5.	1	1000	.034	Barton, Great Bend	Ground (deep well third strata)
	2	745	.034		
6.	1	1000	.040	Bourbon, Fort Scott	Marmaton river
	2	610	.045		
7.	1	1000	.016	Brown, Hiawatha	Spring and wells 20, 30, 35 ft.
	2	775	.019		
8.	1	1000	.091	Butler, Eldorado	Impounded surface
	2	1000	.089		
	3	675	.097		
9.	1	1000	.037	Chase, Cottonwood Falls	Ground water
	2	930	.040		
10.	1	1000	.094	Cheyenne, St. Francis	Well 20 ft.
	2	1000	.094		
	3	1000	.096		
	4	1000	.096		
	5	1000	.096		
11.	1	1000	.038	Clay, Clay Center	Well 48 ft.
	2	850	.036		
12.	1	1000	.034	Clarke, Ashland	Well 65 ft.
	2	800	.032		
13.	1	1000	.055	Cloud, Concordia	8 wells 132 ft.
	2	850	.059		
14.	1	1000	.024	Coffey, Burlington	Neosho river
	2	840	.024		
15.	1	550	.010	Comanche, Coldwater	Ground
16.	1	1000	.023	Doniphan, Troy	
	2	910	.021		
17.	1	1000	.050	Douglas, Lawrence	Kaw river
	2	800	.055		
18.	1	1000	.056	Edwards, Kinsley	Wells 22, 35 ft.
	2	745	.063		
19.	1	1000	.036	Finney, Garden City	Well 264 ft.
	2	965	.035		

TABLE VII (CON'T)

Sample	Trial	H ₂ O cc	I ₂	Locality	Source
20.	1	1000	.027	Ford, Dodge City	Well 140 ft.
	2	650	.025		
21.	1	1000	.033	Franklin, Ottawa	Marias de Cygnas river
	2	775	.036		
22.	1	1000	.029	Geary, Junction City	Well 60 ft.
	2	875	.028		
23.	1	1000	.020	Gray, Cimarron	Ground
	2	600	.025		
24.	1	1000	.106	Greenwood, Eureka	Fall river
	2	900	.111		
25.	1	1000	.085	Harper, Anthony	Well on Bluff creek
	2	570	.100		
26.	1	1000	.036	Harvey, Farm near Newton, 7 mi. west of Whitewater	Well
	2	765	.035		
27.	1	1000	.051	Harvey, Newton	Ground
28.	1	1000	.053	Hodgeman, Jetmore	Well 42, 40 ft.
	2	825	.056		
29.	1	1000	.038	Jackson, Holton	Well 51 ft.
	2	885	.036		
30.	1	1000	.034	Jefferson, Oskaloosa	Ground springs
	2	610	.038		
31.	1	1000	.056	Johnson, Olathe	Impounded sur- face
	2	775	.056		
32.	1	1000	.027	Kingman, Kingman	Ground
33.	1	1000	.069	Labette, Parsons	Rock heart mineral springs
	2	1000	.071		
	3	1000	.073		
	4	500	.075		
34.	1	1000	.043	Labette, Parsons	Neosho and Little Labette
	2	1000	.049		
	3	1000	.043		
	4	417	.038		
35.	1	1000	.014	Labette, Altamont	Shallow well
	2	900	.014		
36.	1	1000	.036	Labette, Chetopa	Wells 1135, 1240 ft.
	2	1000	.038		
	3	1000	.036		
	4	1000	.036		
37.	1	1000	.036	Leavenworth	Missouri river
	2	950	.032		
38.	1	1000	.048	Lincoln, Lincoln	Well 79 ft.
	2	860	.049		
39.	1	850	.037	Linn, Mound City	Sugar creek
40.	1	1000	.045	Lyons, Emporia	Neosho
	2	730	.041		

TABLE VII (CON'T)

Sample	Trial	H ₂ O cc Amount	I ₂ P.P.M.:	Locality	Source
41.	1	1000	.035	Marion, Marion	Mud creek
	2	950	.026		
42.	1	1000	.059	Marshall, Marys- ville	Blue river
	2	950	.049		
43.	1	1000	.050	Miami, Paola	Bull creek
	2	730	.051		
44.	1	1000	.040	Mitchell, Beloit	Solomon river
	2	1000	.059		
	3	1000	.048		
	4	450	.056		
45.	1	740	.036	Morris, Council Grove	Neosho river
46.	1	1000	.031	Nemaha, Seneca	Ground spring
	2	650	.031		
47.	1	975	.037	Neosho, Erie	Neosho river
48.	1	1000	.063	Ness, Ness City	Well 33 ft.
	2	850	.064		
49.	1	730	.064	Ness, Ness City	Well 55 ft.
50.	1	1000	.036	Ness, Ness City	Well 275 ft.
	2	740	.040		
51.	1	1000	.049	Osage, Lyndon	Salt creek
	2	960	.048		
52.	1	780	.065	Pawnee, Larned	Ground
53.	1	760	.019	Pratt, Pratt	Well 59 ft.
54.	1	800	.097	Rawlins, Atwood	Well 54 ft.
55.	1	1000	.029	Reno, Hutchinson	Ground
	2	1000	.028		
	3	1000	.029		
	4	825	.032		
56.	1	1000	.010	Rice, Lyons	Well 88 ft.
	2	800	.008		
57.	1	1000	.076	Riley, Manhattan	College wells 70 ft.
	2	1000	.080		
	3	1000	.065		
	4	1000	.076		
	5	1000	.087		
	6	1000	.070		
58.	1	1000	Ruined	Riley, Manhattan	Wells 80 ft, raw water
	2	1000	.095		
	3	1000	.091		
	4	1000	.087		
	5	1000	.089		
	6	1000	.091		

TABLE VII (CON'T)

Sample	Trial	H ₂ O cc Amount	I ₂ P.P.M.	Locality	Source
59.	1	1000	.089	Riley, Manhattan	Softened and rapidly filtered.
	2	1000	.083		
	3	1000	.089		
	4	1000	.085		
	5	1000	.085		
	6	1000	.083		
60.	1	1000	.059	Salina, Salina	Six wells 65-85 ft.
	2	830	.064		
61.	1	1000	.020	Sedgwick, Wichita	Wells on Ark. river
	2	1000	.022		
	3	1000	.020		
	4	500	.024		
62.	1	930	.068	Sherman, Goodland	Well 200 ft.
63.	1	1000	.016	Sumner, Wellington	Ground
	2	985	.015		
64.	1	1000	.043	Woodson, Yates Center	Impounded surface
	2	775	.044		
65.	1	1000	.024	Wyandotte, Kansas City	Missouri river

TABLE VIII

RELATION OF IODINE CONTENT TO GEOLOGICAL FORMATION

Geological Formation	: 0-	:.020-	:.040-	:.060-
	:.019	:.039	:.059	: up
	:P.P.M.:	:P.P.M.:	:P.P.M.:	:P.P.M.:
1. Pennsylvanian	:	:	:	:
a. Exclusive of Glacial	: 1	: 7	: 9	: 2
b. Glacial (quaternary)	: 1	: 7	: 0	: 0
2. Permian	: 1	: 8	: 2	: 3
3. Cretaceous	: 0	: 1	: 4	: 4
4. Tertiary	: 2	: 7	: 2	: 2
Total	: 5	: 30	: 17	: 11

TABLE IX

COMPARISON OF SAMPLES FROM SAME RIVER

Town	Source	I ₂ :P.P.M.
Burlington	:Neosho	:.024
Council Grove	: "	:.036
Erie	: "	:.037
Emporia	: "	:.045
Parsons	: " and Little Labette	:.045
Lyons	: Underflow of Arkansas	:.019
Cimarron	: Underflow of Arkansas	:.020
Wichita	: " " "	:.021
Dodge City	: " " "	:.027
Hutchinson	: " " "	:.029
Great Bend	: " " "	:.034
Kinsley	: " " "	:.056
Larned	: " " "	:.065
Kansas City, Kansas	:Missouri	:.024
Leavenworth	: "	:.036
Marysville	:Blue	:.059
Manhattan	:Underflow of Blue	:.086

PLATE I

GEOLOGIC MAP OF KANSAS BY R. C. MOORE
(Additions explained by legend)

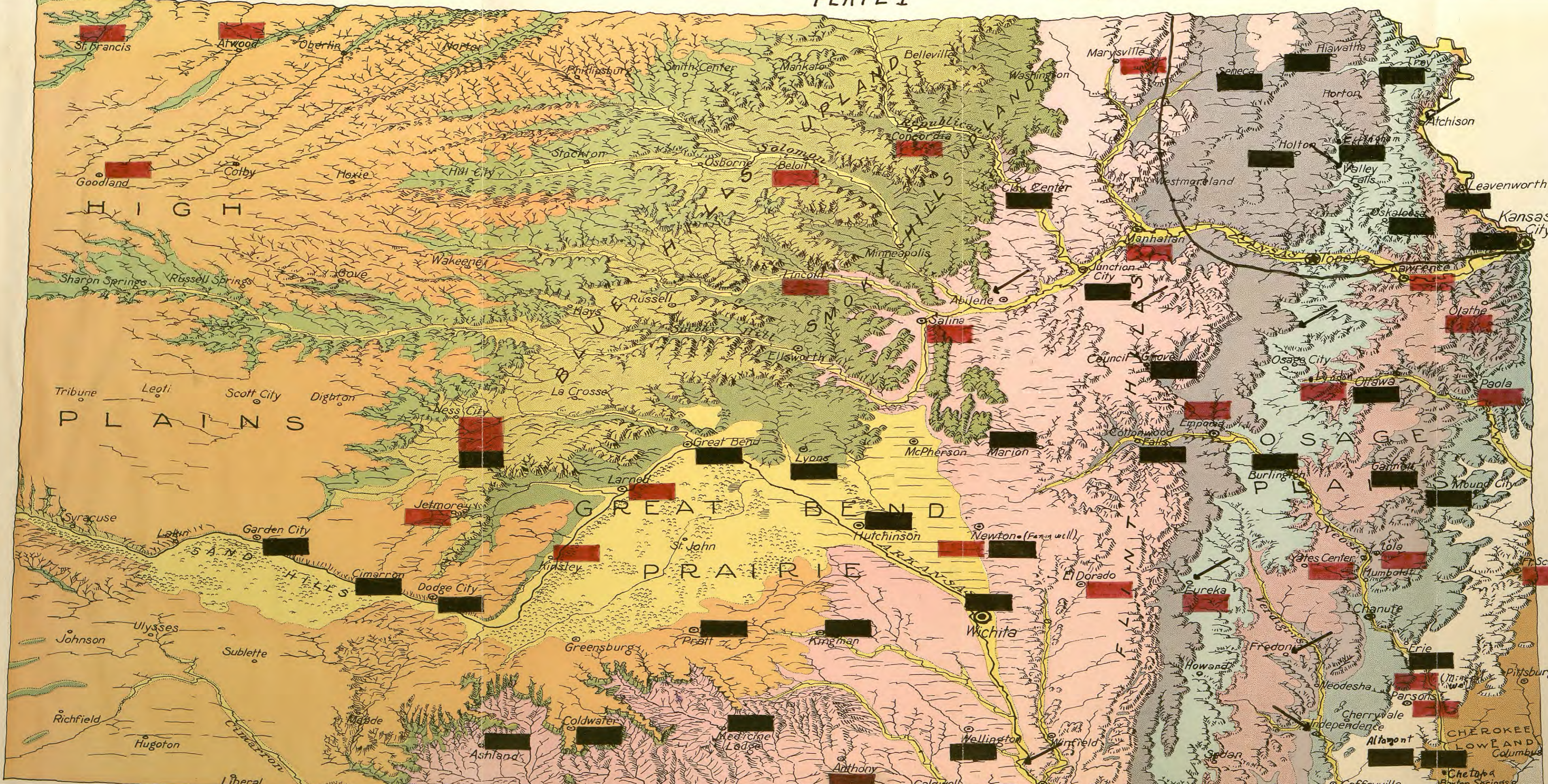
Legend

Glacial area north and east of heavy black line.
Black arrows represent mineral springs or wells, the
iodine content of which was determined by Bailey.

Iodine content in parts per million:

0.000 - 0.039 

0.040 - 0.100 



LEGEND

- Quaternary
 - Alluvium, sand, gravel & loess
- Tertiary
 - Grit, loam & sand
- Cretaceous
 - Pierre
 - Dark clayey shale
 - Niobrara
 - Soft chalk, limestone
 - Benton
 - Dark clayey shale with Greenhorn ls. in the middle.
- Dakota & Comanchean Sandstone & Shale
- Permian
 - Cimarron
 - Red beds
 - Big Blue Group
 - Shale & Limestone
- Pennsylvanian
 - Shale, limestone & sandstone
- Wabausee
- Shawnee
- Douglas
- Lansing
- Kansas City
- Marmaton
- Cherokee
- Mississippian
 - Limestone

Mississippi lime. Chatin found that soils rich in lime and magnesium are low in iodine content. (53) In this area are a number of mineral wells and springs some of which have been tested for iodine content by Bailey and others, Table II. In the Permian, Marysville gets its water supply from the Blue River which drains Cretaceous deposits above Beatrice, Nebraska. (54) Manhattan wells are also in the underflow of the Blue. Salina water is the underflow of the Smoky Hill River also draining Cretaceous territory. Clay Center and Junction City, on the other hand, have a low content and are probably in the underflow of the Republican which drains Cretaceous territory. The source of Eldorado water is impounded surface (51) with no explanation as to why it should be high. The former supply was from a well of high mineral content. Anthony, too, has no definite explanation. Salt deposits there might in some way be accountable. With the exception of the deep well, 275 feet, at Ness City, all the Cretaceous sources are high in iodine content. Lyons was included in the tertiary deposits because the underflow of the Arkansas is the source of their water. The Tertiary and Quaternary deposits have been considered as one, most of the samples tested being from the underflow of the Arkansas. Goodland has a 200 foot well, but no information was obtained to know whether this well is deep enough to obtain

water from the Cretaceous or not. The Kinsley wells are two miles from the river and may obtain water traveling as underflow from the Cretaceous to the Arkansas. Larned is situated similarly, but no information was obtained concerning the source of their water. There is a mineral well at Larned giving a salty brine under a 23.5 pound pressure from a depth of 743 feet in the Dakota sandstone. The same well gave fresh water from 25 feet and a slightly saline water from 400 feet. (56) Neither is there any information concerning the supply at Great Bend which is similarly located with respect to the Dakota sandstone. Great Bend also has a mineral well. (56) Lyons' supply is from the underflow of the Arkansas. Newton, while located in the Permian, takes its water supply from the underflow west of the city. (57) It is thought that the Smoky Hill river at one time drained into the Arkansas. The levels of the Smoky Hill at Marquette and the level of the Arkansas at Halstead are almost identical. (58) Whether this sheet water is moving from the Smoky Hill in an underflow, or in the opposite direction, or neither, is a question. The sands of the equus beds in McPherson County have been examined microscopically and are believed to be decomposed Dakota sandstone. (59) If the water is moving from the Smoky Hill through these sands toward the Arkansas they would be naturally high in iodine content.

Von Pellenberg found that rocks containing fossils in great quantity were higher in iodine content than rocks not containing such fossils. (60) It might be interesting, as well as tending toward conclusions, to study the main geological strata with regard to their fossil content. The Pennsylvanian has many formations in which the fragments of fossils are abundant. (61) Mollusks make up more than 90% (62) of the fauna of the Cretaceous deposits and in some of the formations they are very abundant. The Tertiary and Quaternary deposits including the Glacial are deficient in fauna. The Permian rocks of Kansas contain few fossils. (63) These relationships fit in very well with the findings of Von Pellenberg and with the data of Table VIII.

Haworth (64) gives us three general areas in Kansas in which abundant wellwater can be found, namely the river valleys, the glaciated areas of north west Kansas and the tertiary areas of western Kansas. In the Glacial areas most of the water is found in the glacial pockets the underlying limestone and shale being poor in water supply. (52) In the Pennsylvanian deposits, as you go westward in any particular deposit and strike a water bearing deposit such as sandstone, it becomes more highly mineralized as the wells reach it. This is because the water enters the porous strata at the east and the impervious strata underneath

slopes to the west. During a dry season the farmers began to drill wells in the eastern part of Allen County and found good supplies at moderate depths. Other farmers farther west drilled wells to the same strata till the wells near Iola were 300-400 feet deep. The water in these later wells was highly mineralized. (65) Water does not become salty so quickly as you go westward in the Flint Hills deposits of the Permian. The extent of the fresh water zone is unknown. The salt has been leached out of these deposits for a long time and the water is substantially void of salt. (66) Salt marshes occur in Republic, Cloud, Jewell, Mitchell, and Lincoln counties which drain into the Republican and Solomon rivers and their tributaries. Other salt marshes occur in Stafford and Sumner counties emptying into the Arkansas river. (67) There is also a salt marsh in Greenwood county emptying into the Fall river. (67) There are also many flowing salt wells in the state. (68)

All these would lead to the belief that the waters of Kansas should be high in iodine content. The iodine content of the mineral wells tested was also high, some of the wells being rather shallow. Bailey (69) says that the waters seldom contain as much as 1.5 grains per gallon of the potassium or sodium salt. Using these figures and assuming

that it is the potassium salt, for this would give the lowest iodine content we would have .7 grains per gallon, which divided by the proportionality factor used by Bailey, 58.41 would give .0133 grams per liter or 13300 parts per million. However, the data of McClendon and Gottlieb leave results of Table VII open to grave doubt. Forbes using the Kendall method, where bromine is used instead of chlorine in the iodate method, reports on two tests of water from Wintrop, Washington. Water from Bear Creek .0000077% and well water .0000120% which would be .077 and .120 parts per million respectively. (70) These compare favorably with the amounts determined in Table VII, however, Forbes added sodium salicylate to the slightly acid solution to destroy the last traces of bromine. This was done before the final acidification. Bromine is undoubtedly present in the waters tested. Whether it was completely eliminated by boiling in the acidified solution was not determined. The test where ten liters was treated as a single sample would tend to indicate that if there is an interfering substance the interfering reaction must be a quantitative one. Undoubtedly much more work must be done with the reaction before the results can be considered authoritative.

Geological Relationship of Goiter in Kansas. The geological findings were so apparent that an attempt has been made to associate them with the available goiter surveys. (Table I.) Interpretation of the results is rather difficult because of the lack of definite knowledge concerning the incidence of goiter in Kansas, because of varying opinions as to the amount of iodine necessary to prevent thyroid enlargement and because it is not certain that water is a reliable source of iodine to meet the requirements of the body. Dr. Hertzler (71) mentions the Arkansas Valley as being goitrous though he adds that the extensive literature of the relationship of goiter to geological formation is only of historic interest. If we take the opinion of Geiger as a basis, that 25 parts per billion of iodine in the water is necessary to prevent thyroid enlargement, only 15% to 20% of the samples tested were below that minimum. Choosing arbitrarily the division used in Plate I, more than 50% of the samples were below 40 parts per billion. A comparison on this basis with the goiter surveys of Table I may have some significance. Jefferson county in the Glacial area, Ottawa and Ellis counties in the Cretaceous area, McPherson county in the quaternary, and Butler county in the Permian area, agree with the iodine content of these geological structures in general. The first three are in complete

accord, Jefferson county having a high goiter incidence and Ottawa and Ellis counties having a low incidence. Though no water was tested in McPherson county its sands are probably derived from the Dakota sandstones and as such should be relatively high in iodine content which is not in accord with the prevalence of goiter. Eldorado water in Butler county shows a high iodine content and if any great percent of the examinations were from that town goiter should not be prevalent to such a great extent. The results of the two larger city surveys, Junction City and Topeka, are not so easily interpreted in terms of geological structure. Junction City is again an exception. Taking its water supply from the underflow of the Kansas river it should be high in iodine content. It tested low. Testing low in iodine content it should have a high percent of thyroid enlargement. The survey shows it with a low percent of thyroid enlargement. Topeka is located in the Glacial area and as such agrees with the findings of the survey, however no Topeka water was tested nor was the source of its water supply determined.

CONCLUSIONS

Phosphoric acid seems to be effective in suppressing the ionization of iron present in natural waters and hence the oxygen of the air has little effect on the results of

titrations if the titrations are made quickly and the first end point is accepted as the final reading.

Iodine can be recovered quantitatively within an accuracy of .01 parts per million either in pure samples or added to samples of Manhattan city water, the value for the water tested separately being subtracted from the combined amount found for water and added iodine.

The amount of iodine found in the waters tested is many times higher than that found by other workers on the same or comparable samples with no definite explanation as to the cause of the discrepancy.

There seems to be a definite relationship between the results of the waters tested and the geological structure from which the sample comes. Cretaceous deposits rank highest in iodine content followed by Pennsylvanian, Permian, Tertiary, and Glacial.

The goiter surveys that have been made in the state agree in a general way with the iodine content of the various geological structures. The data is too meager for any detailed conclusions.

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