

ON THE ELECTRICAL CONDUCTIVITY OF URINE IN RELATION TO ITS CHEMICAL COMPOSITION.¹

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Received July 30, 1907.

AMONG the newer applications of the methods of modern physical chemistry some of the most important are certainly those employed in the solution of problems in physiology and physiological chemistry. At first sight one of the least promising of these methods is that of the determination of electrical conductivity as applied to the fluids of the body, but the labors of Roth,² Stewart,³ Bugarszky and Tangl,⁴ and others have shown the possibilities of the method in the examination of blood serum. In respect to inorganic constituents blood serum is much more constant than is urine, and the variations in the conductivity of the latter appear at first sight so irregular as to be beyond simple formulation. This notion, however, is not quite correct. It has been shown by Bugarszky⁵ that certain general relations are easily observed, and among others the connection between the total ash and the conductivity.

It must be remembered that the conductivity of the urine is practically due to the mineral salts present only. The most abundant of all the urinary constituents, the urea, is so near a non-conductor in solution that its effect may be safely neglected. Even the low value given by Trübsbach⁶ is probably high, as shown by some of my own observations with carefully prepared urea. The creatinin, ammonia, xanthin bodies, uric acid and urates have all but a slight conductivity and their effect in lowering the conductivity of the mineral salts is extremely small. For investigations of this kind it is exceedingly difficult to obtain urea pure enough to be used as a standard. Nearly all found in the market contains notable quantities of potassium sulphate, sometimes several per cent., and purification by crystallization from alcohol is attended by great loss. Besides this, in using hot solu-

¹ Read by title at the Pittsburg meeting of the American Chemical Society, July 2, 1902.

² *Centralblatt für Physiologie*, 11, 27 (1897).

³ *Ibid.*, 11, 332 (1897).

⁴ *Ibid.*, 11, 297 and 301 (1897).

⁵ *Pflüger's Archiv für die gesammte Physiologie*, 68, 389 (1897).

⁶ *Ztschr. phys. Chem.*, 16, 708; also in Kohlrausch und Holborn's "Leitvermögen der Elektrolyte," p. 184.

tions in strongest alcohol some of the urea is always converted into ethyl urethane, with further loss on crystallization. Unless, therefore, the urea is very carefully purified its effect on the conductivity may appear sensibly positive instead of negative.

In view of these facts it follows that the conductivity of the urine is a function of the total mineral content and the determination has a value somewhat analogous to that of the specific gravity; but it is much more definite, however, and as the degree of accuracy possible is high the method must certainly prove of value in studies of the metabolism of inorganic substances. To bring out these points I have undertaken recently a number of experiments. In the first of these I have determined the volume, specific gravity, electrical conductivity, chlorine and urea in the urine of two individuals, collected at regular intervals through three days. These results are shown in Tables I and II. The specific gravity was found by the Westphal balance, adjusted for a temperature of 20°. The figures given are referred to water at 4°. The accuracy of the readings was controlled by pycnometer determinations on several samples. The conductivity was found at 20°, always, the temperature being sharply maintained within 0.1°, by the Kohlrausch method, using a U-tube with a resistance capacity, $C = 8.415$. The resistance measurements were made with a large Kohlrausch-Wheatstone bridge, the wire corrections being known, and the values of the 100 and 1000 ohm comparison resistances, also. The urine resistance, R , measured varied between about 250 and 800 ohms, from which the conductivity, K , was found by the formula:

$$K = \frac{C}{R}$$

For an observed resistance of 500 ohms K is therefore 0.016830.

The chlorine was found by the usual Volhard-Arnold process, the liquid being filtered before titration of the excess of silver by the thiocyanate. In the urea titration I used the Liebig process, employing the approximate corrections described by me.¹ The corrections actually used were based on previous experiments with the urine of the same individuals. In the tables the reduced and corrected values only are given, and the chlorine is calculated as sodium chloride. For the purpose in view this is admissible, and

¹ This Journal, 23, 632.

INDIVIDUAL A.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	
	Period.	Volume passed. cc.	Specific gravity at 20° 4.	Conductivity, κ.	Chlorine as sodium chloride. Grams per 100 cc.	Urea. Grams per 100 cc.	Specific gravity— amount due to urea, etc.	Excess of specific gravity over that of water, due to mineral sub- stances.	Fraction of con- ductivity not due to sodium chlo- ride.	Ratio of conductiv- ity to sodium chloride.	
Observations of first day: Excretion = 162 cc. Liquid consumption = 1750 cc.	6-9 A.M.	145	1.024	0.02589	1.516	2.95	1.015	0.017	0.00590	
	9-12	178	1.023	0.03021	1.579	2.55	1.015	0.017	0.00632	
	12-3	135	1.024	0.02834	1.416	2.60	1.016	0.018	0.00692	
	3-6	118	1.027	0.02790	1.292	5.31	1.017	0.019	0.00827	
	6-9 P.M.	128	1.026	0.02694	1.275	2.89	1.017	0.019	0.00757	
	9-6	458	1.025	0.02421	1.170	2.82	1.015	0.017	0.00644	
	MEANS, 3-hour period:			1.024	0.02650	1.298	2.84	1.016	0.018	0.00679	0.0204
	Observations of second day: Excretion = 1265 cc. Liquid consumption = 2100 cc.	6-9 A.M.	192	1.020	0.02645	1.427	2.51	1.012	0.014	0.00486
9-12		245	1.020	0.02926	1.608	1.87	1.014	0.016	0.00491	
12-5		155	1.026	0.02805	1.345	2.65	1.018	0.020	0.00768	
5-6		115	1.026	0.02702	1.211	5.10	1.017	0.019	0.00862	
6-9 P.M.		155	1.025	0.02702	1.298	2.80	1.017	0.019	0.00730	
9-6		405	1.025	0.02122	0.848	3.45	1.015	0.017	0.00772	
MEANS, 5-hour period:			1.024	0.02518	1.179	2.91	1.015	0.017	0.00707	0.0214	
Observations of third day: Excretion = 1324 cc. Liquid consumption = 1670 cc.		6-9 A.M.	230	1.022	0.02683	1.453	2.47	1.015	0.017	0.00515
	9-12	260	1.021	0.02939	1.602	2.18	1.015	0.017	0.00516	
	12-3	160	1.026	0.02792	1.428	2.77	1.018	0.020	0.00635	
	3-6	134	1.026	0.02755	1.345	2.99	1.017	0.019	0.00712	
	6-9 P.M.	146	1.025	0.02580	1.165	2.82	1.017	0.019	0.00810	
	9-6	594	1.023	0.01997	0.731	3.21	1.015	0.015	0.00833	
	MEANS, 3-hour period:			1.024	0.02518	1.179	2.91	1.015	0.017	0.00707	0.0214

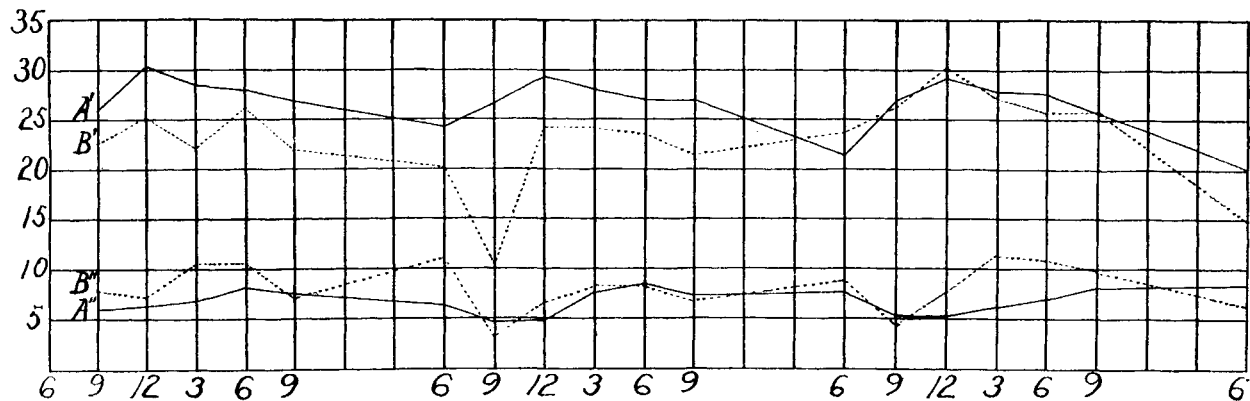
	1.	2.	3.	4.	INDIVIDUAL B.		7.	8.	9.	10.	
	Period.	Volume passed. cc.	Specific gravity at 20° 4'.	Conductivity, K.	Chlorine as sodium chloride. Grams per 100 cc.	Urea. Grams per 100 cc.	Specific gravity— amount due to urea, etc.	Excess of specific gravity over that of water due to mineral sub- stances.	Fraction of con- ductivity not due to sodium chlo- ride.	Ratio of conductiv- ity to sodium chloride.	
Observations of first day: Excretion = 861 cc. Liquid consumption = 1815 cc.	6-9 A. M.	112	1.022	0.02264	0.948	2.35	1.015	0.017	0.00779	...	
	9-12	220	1.019	0.02519	1.182	1.54	1.014	0.016	0.00723	...	
	12-3	77	1.026	0.02226	0.737	3.20	1.016	0.018	0.01052	...	
	3-6	70	1.027	0.02614	0.994	3.52	1.016	0.018	0.01056	...	
	6-9 P. M.	198	1.021	0.02178	0.936	2.49	1.013	0.015	0.00701	...	
	9-12	184	1.026	0.02008	0.562	3.85	1.014	0.016	0.01099	...	
	MEANS, 3-hour period:			1.024	0.02228	0.810	3.08	1.014	0.016	0.00951	0.0275
	Observations of second day: Excretion = 1231 cc. Liquid consumption = 2363 cc.	6-9 A. M.	410	1.007	0.01039	0.456	1.10	1.004	0.006	0.00301	...
		9-12	122	1.017	0.02408	1.119	2.36	1.010	0.012	0.00655	...
		12-3	96	1.023	0.02422	0.998	2.99	1.014	0.016	0.00864	...
3-6		138	1.024	0.02355	0.971	3.11	1.015	0.017	0.00833	...	
6-9 P. M.		180	1.021	0.02144	0.936	2.58	1.013	0.015	0.00678	...	
9-6		285	1.024	0.02369	0.942	3.11	1.015	0.017	0.00893	...	
MEANS, 3-hour period:			1.020	0.02184	0.913	2.70	1.013	0.015	0.00751	0.0239	
Observations of third day: Excretion = 1099 cc. Liquid consumption = 1350 cc.	6-9 A. M.	278	1.015	0.02629	1.439	0.93	1.012	0.014	0.00453	...	
	9-12	158	1.022	0.03037	1.491	1.46	1.018	0.020	0.00782	...	
	12-3	92	1.029	0.02720	1.006	3.19	1.020	0.022	0.01143	...	
	3-6	71	1.030	0.02566	0.948	3.48	1.020	0.022	0.01081	...	
	6-9 P. M.	112	1.027	0.02577	1.023	3.24	1.017	0.019	0.00974	...	
	9-6	388	1.014	0.01492	0.527	1.74	1.009	0.011	0.00639	...	
	MEANS, 3-hour period:			1.021	0.02251	0.936	2.19	1.014	0.016	0.00794	0.0240

besides is perfectly correct as far as the urines of Table I are concerned. For the urines of Table II, individual B, no previous determination of the relation of sodium to potassium had been made.

A consideration of the tables discloses several interesting facts. In both sets the specific gravities appear low for the amounts of urea and salt present, but it must be remembered that they are based on the temperature of 20° referred to water at 4° . The means given for each day are calculated on the assumption that the collections made from 9 P.M. to 6 A.M. represent three 3-hour periods. The mean specific gravities for individual A are constant and the conductivities nearly so. There is no simple relation between the two classes of data. Nor is any relation seen when we subtract from the observed (corrected) specific gravity that fraction due to the urea present. This appears in column 7. To obtain these figures I found the specific gravity of several urea solutions and deduced this mean value; 1 gram of urea in 100 cc. adds 0.0027 to the specific gravity of water or a weak salt solution. For each gram of urea found per 100 cc. I have applied the correction 0.003 to include the effect of the other organic bodies. In column 8 I have given the excess of the specific gravity due to mineral substances over that of water at the standard temperature; *viz.*, 0.9983. The variations here are so slight as to have no practical significance; but in columns 9 and 10 we have numbers which are characteristic and definite enough to afford certain indications. From well-determined values, those found in the tables of Kohlrausch and Holborn, for example, it is possible to calculate the conductivities of weak salt solutions, such as those concerned here. From the total observed conductivity I have taken out the fraction due to the sodium chloride found to be present, and have put down the remaining values in column 9. These numbers represent the conductivities due to salts other than the sodium chloride of the food, and are therefore a measure of the mineral products of metabolism present. We have here mainly the sulphates and phosphates of oxidation and it will be seen that the mean values are pretty constant for individual A, through the three days. For B the results are somewhat less constant but distinctly different from those for A. The fraction of the conductivity due to meta-

bolic products is much greater for B than for A in the mean, and at several periods reaches an amount which is nearly one-half the total. In both cases the chlorine excretion is greatest during the morning hours, while the conductivity due to other salts reaches a maximum later. It will be noticed that these numbers which are given in column 9 bear no close relation to the specific gravity numbers given in columns 3, 7 and 8. The relation of the conductivity to the salt excretion is given in columns 10, and for A is practically constant. For B the ratio is a different one, but not quite a constant. Inasmuch as salt is the chief mineral substance excreted a relation of this kind is a practical necessity. The curves in the adjoining figure show the variations in the total conductivity from period to period, and also the variations in the fraction of the conductivity not due to sodium chloride.

To further show the relation of composition to conductivity a number of complete analyses have been made of mixed normal urines. The conductivities of these urines were found and also the conductivities of artificial mixtures made up from the results of analyses. The analyses are given in the tables. Numbers 1, 2 and 3 are of urines from men consuming a mixed animal and vegetable diet. The results were obtained in April while the weather was cool and the excretion normal. Numbers 4, 5 and 6 are from the urine of vegetarians consuming the mixed nut, vegetable and cereal foods used by the authorities of the Battle Creek Sanitarium. Each urine represented the total day's excretion of three or four individuals, and aside from the special purpose here in view the analyses have considerable scientific value because very few complete examinations are found in the literature. The average excretion for each individual contributing to Nos. 1, 2 and 3 was about 1200 cc., while for the individuals furnishing the urines 4, 5 and 6 the average excretion was about 1000 cc. These results were obtained later, in the warm weather of June.



Explanation of the curves: Curve A' represents the conductivity of the urine from individual A through the three days. A'' shows the variations in the conductivity due to other salts than chlorides for the same period. B' represents the results of the examination for total conductivity for individual B, and B'' finally, the conductivity not due to sodium chloride. The abscissa spaces represent 5-hour periods. The ordinate spaces correspond each to $K \times 0.005$. In the curve A' three distinct maxima are easily seen which correspond closely to minima in A'' . The variations in B' and B'' seem to follow a somewhat different order.

TABLE OF COMPLETE URINE ANALYSES.

Nos. 1, 2 and 3 mixed diet.

Nos. 4, 5 and 6 vegetarian.

Results in grams per 100 cc.

	1.	2	3.	4.	5.	6.
Specific gravity $^{20^{\circ}}_{4^{\circ}}$	1.024	1.020	1.026	1.017	1.028	1.021
Conductivity, K	0.02572	0.02402	0.02793	0.01984	0.02898	0.02251
Potassium, K	0.1980	0.2455	0.2604	0.1416	0.4872	0.3869
Sodium, Na	0.3820	0.3710	0.4647	0.3419	0.3578	0.2705
Calcium, Ca	0.0104	0.0086	0.0132	0.0031	0.0164	0.0130
Magnesium, Mg	0.0092	0.0121	0.0152	0.0144	0.0225	0.0341
Ammonium, NH_4	0.0900	0.0840	0.1080	0.0800	0.0745	0.0576
Chlorine, Cl	0.7366	0.7160	0.7739	0.5254	0.8165	0.5893
Phosphoric acid, PO_4	0.1143	0.1742	0.3135	0.2062	0.3111	0.2230
Sulphuric acid, SO_4	0.1640	0.1964	0.3250	0.1965	0.2790	0.2039
Urea, CON_2H_4	2.85	2.60	2.97	2.11	2.95	2.80
Uric acid, $(C_5H_3N_4O_3)''$	0.0641	0.0691	0.0876	0.0549	0.0769	0.0838
Creatinin, $C_4H_7N_3O$	0.1750	0.1790	0.1414	0.0252	0.0910	0.1050

Some of these results are very interesting but a discussion of peculiarities revealed will be left for another occasion. An attempt was next made to duplicate the urines as nearly as possible by mixing salts, urea and creatinin in certain proportions. It is not possible in any case to obtain a perfectly clear artificial mixture containing all the bases and acids in the proportions found, but mixtures were made by combining the phosphoric acid and the whole of the calcium and magnesium first. The acid phosphate solutions obtained were clear, and strongly acid to litmus. Then the salts were added in amounts shown in the table, the urea and the creatinin also. The uric acid and a part of the ammonium were temporarily left out. In each case 250 cc. of mixture was made, and the conductivity found.

DUPLICATION OF ANALYSES.

Results in grams per 100 cc.

Substances taken.	1.	2.	3.	4.	5	6.
$NaCl$	0.9716	0.9436	1.1819	0.8686	0.9100	0.6880
KCl	0.5089	0.3013	0.1191	0.5554	0.5610
K_2SO_4	0.0804	0.1951	0.4411	0.3154	0.4363	0.3704
$(NH_4)_2SO_4$	0.1646	0.1222	0.1098	0.0312	0.0527
$CaCO_3$	0.0260	0.0215	0.0350	0.0078	0.0410	0.0325
MgO	0.0153	0.0202	0.0250	0.0240	0.0375	0.0568
K_2	0.0312
PO_4	0.1143	0.1742	0.3135	0.2062	0.3111	0.2230
CON_2H_4	2.85	2.60	2.97	2.11	2.95	2.80
$C_4H_7N_3O$	0.175	0.179	0.1414	0.0252	0.0910	0.105
Conductivity found	0.02264	0.02291	0.02628	0.01910	0.02843	0.02059

After finding the conductivity of the clear solutions, the ammonia lacking and the uric acid were added, the ammonia from a strong standard solution. The mixtures were shaken and allowed to

settle some hours, when the conductivities were again found. A slight correction in the results was made on account of the trifling dilution on adding the ammonia. The results were as follows, from the solutions now neutral to litmus paper :

	1.	2.	3.	4.	5.	6.
Remaining NH_4 added.....	0.0451	0.0307	0.0731	0.0715	0.0399	0.0576
Uric acid ($\text{C}_5\text{H}_4\text{N}_4\text{O}_3$) ¹ added	0.0641	0.0691	0.0876	0.0549	0.0769	0.0838
New conductivity at 20°....	0.02352	0.02400	0.02768	0.01944	0.02886	0.02158

It is interesting to note that the new conductivities correspond very nearly with those found for the original urines. The values found before the addition of the uric acid and the ammonia were all sensibly lower, as might be expected, but with the final additions higher conductivity is secured, notwithstanding the fact of the formation of a slight precipitate. The fraction of the conductivity due to the free uric acid or to the urates is small as the investigations of His and Paul¹ would suggest. These results are in a measure a check on the general accuracy of the analyses.

Certain general conclusions may be drawn from these experiments :

1. The electrical conductivity of the urine varies essentially with the amount of inorganic salts present and taken alone is a datum of relatively little importance because of the effect of the large amount of sodium chloride present ; but,

2. After deducting the fraction of the conductivity due to the sodium chloride content a remainder is left which has importance in indicating the extent of certain metabolic changes. The amounts of sodium chloride and other salts and the corresponding conductivities are shown in a manner easy for comparison in the tables of complete analyses and duplications.

3. Inasmuch as the conductivity may be readily and accurately determined the variations in the value of this residual conductivity are of importance in fixing the lag in the rate of inorganic excretion.

4. For the purpose of making other comparisons it may be necessary to determine the conductivity in diluted urine, where the salts act with their maximum capacity. Some work of this kind is in progress.

NORTHWESTERN UNIVERSITY, CHICAGO,
June, 1902.

¹ *Ztschr. physiol. Chem.*, 31, 1.