SIMPLIFIED METHODS FOR QUANTITATIVE ESTIMATION OF CHLORIDS IN THE URINE *

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The process generally followed to determine the amount of chlorids in the urine is precise. It is, nevertheless, complicated and time-consuming, even for the operator in the clinical laboratory. In addition, requiring the use of a buret, volumetric flask, volumetric pipets, filters and porcelain dishes, it demands a quantity of calibrated apparatus, which makes the method almost inaccessible to the general practitioner. The need of a simpler procedure, by which the usefulness of chlorid estimations might be made general, was recognized in Europe some years ago. Achard and Thomas,[1] in France, and H. Strauss,[2] in Germany, have introduced short methods comparable to the technic of albumin determinations by the Esbach tube, which in their opinion greatly facilitate chlorid estimations without sacrificing the degree of accuracy necessary for the diagnostic value of these analyses. Little use, however, seems to have been made of their work, and no references to the repetition or confirmation of their results are available. In order, therefore, to determine whether quantitative chlorid determinations can be made by methods which promise much in convenience, while losing little in precision, I have carried out, under the direction of Dr. Guthrie, the following studies of the methods and instruments of the authors mentioned above.

The two chief processes in use for the quantitative estimation of the chlorids in the urine are the Volhard[3] method and the method of Mohr.[4] On the former, the simplified method of Strauss is based; on the latter, the method of Achard and Thomas. The former of these will be described first, leaving the latter to be considered in the description of the work of Achard and Thomas.

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1. Achard, Ch., and Thomas, L.: Bull. et mém. Soc. méd. d. hôp. de Paris, 1912, xix, 596.
2. Strauss, H.: Praktische Winke fur die chlorarme Ernährung, Berlin, 1910.
3. Volhard: Jour. f. prakt. Chem., 1874, ix, 217.
4. Mohr: Lehrbuch der Titrirmethode., 1862, p. 317.

FILTRATION TO REMOVE SILVER CHLORID UNNECESSARY

The Volhard[3] method, as modified by Drechsel[5] and applied to the urine by Falk[6] and Arnold,[7] consists in the precipitation of the chlorids by an excess of a standardized solution of silver nitrate, the removal of the silver chlorid by filtration and the titration of the excess of silver nitrate with ammonium thiocyanate, using an iron salt as an indicator. This method, modified only as regards the strength of the solutions employed, later was applied to gastric and urinary analysis by Lüttke and Martius.[8] The Lüttke-Martius method is the one used in this laboratory and has been the one employed in these experiments. While this method is accurate, it demands a considerable amount of calibrated apparatus, and requires more than thirty minutes for duplicate determinations. The original Volhard method, however, could be carried out more rapidly than this, as it did not include the removal of the silver chlorid by filtration, the titration with ammonium thiocyanate being done in its presence. In using this method, Drechsel,[5] and more recently Rosanoff and Hill,[9] found difficulty with the end-point, due, they thought, to a reaction between the silver chlorid and the ammonium thiocyanate. To obviate this, Drechsel introduced the step of filtration, which has since been incorporated in this method and its modification by Lüttke and Martius. As the omission of the removal of the silver chlorid is one of the means employed by Strauss in simplifying this technic, it becomes important to determine whether this step has any influence on the results of the titration. Volhard[10] subsequently showed the error in Drechsel's criticism, and Goodall,[11] recently, in a study of sixty urines of widely varying chlorid content, has found that the original Volhard is as accurate as the Volhard modified by the filtration step. Harvey[12] has reached a similar conclusion from numerous experiments on the reaction between these solutions. He has found that in the Volhard method the precipitated silver chlorid does not react with the ammonium thiocyanate while an excess of silver nitrate is present; and further, that after the excess of silver has been removed, the reaction between the silver chlorid and the thiocyanate is markedly retarded by the presence, first, of the ferric salt, and secondly, by the excess of nitric acid in which the silver nitrate is dissolved. To verify this point, I made the determinations shown in Table 1.

5. Drechsel, E.: Jour. f. prakt. Chem., 1877, 191.

6. Falk, A.: Berichte d. deutsch. chem. Gesellsch., 1875, viii, 12.

7. Arnold, C.: Arch. f. d. ges. Physiol., 1885, xxxv, 541.

8. Lüttke and Martius, F.: Die Magensaüre des Menschen, Stuttgart, 1892. (Quoted by Strauss and others.)

9. Rosanoff and Hill: Jour. Am. Chem. Soc., 1907, xxix, 269.

10. Volhard: Liebig's Ann., 1877, cxc, 1.

11. Goodall, H. W.: Boston Med. and Surg. Jour., 1909, clx, 304.

12. Harvey, S. C.: THE ARCHIVES INT. MED., 1910, vi, 12.

TABLE 1.—CHLORID DETERMINATIONS BY LÜTTKE-MARTIUS METHOD

Urine	AgCl Removed by Filtration		AgCl Present		Difference in Grams
	Gm. NaCl in 100 c.c.	Average	Gm. NaCl in 100 c.c.	Average	
I	0.67860	....	0.67860	....	....
	0.67860	0.67860	0.678015	0.678307	0.00293
II	0.3888025	....	0.390195	....	0.0013925
III	0.8541	....	0.857025	....	0.002925

The results summarized in Table 1 show that filtration to remove the silver chlorid is not necessary under the conditions outlined above. As will be seen later, the factors in the analysis by the Strauss method are exactly similar to these.

LÜTTKE-MARTIUS METHOD

As the Volhard, and therefore the Lüttke-Martius, method has been proved accurate, the results obtained by the Lüttke-Martius procedure have been taken as the standard for gauging the accuracy of the other methods tested in these studies. This method, differing from its proto-type only in the strength of the solution employed, is based on the precipitation of chlorids by silver nitrate, and the titration of the excess of silver nitrate by ammonium thiocyanate, using an iron salt as an indicator. Two standardized solutions are required:

1. $N/10$ $AgNO_3$ — an acid solution containing iron ammonium alum. One cubic centimeter of this standardized solution will precipitate 0.00585 gm. NaCl.

2. $N/10$ NH_4SCN — containing 7.6 gms. of ammonium thiocyanate to the liter of solution.

The preparation of these standard solutions will be described in detail in the consideration of the Strauss method.

To make a determination by this method, the procedure is as follows:

By means of a volumetric pipet, 10 c.c. of urine are placed in a 100 c.c. volumetric flask. To this are added 20 c.c. of $N/10$ $AgNO_3$ from a volumetric pipet. This mixture is shaken gently and allowed to stand for five minutes, until the precipitation of chlorids is complete. Distilled water is then poured into the flask, filling it to the 100 mark. The flask is stoppered, shaken well, and allowed to stand for a few minutes. If a reddish color appears in the mixture, as is nearly always the case with highly colored febrile urines, this is cleared by adding three or four drops of a solution of potassium permanganate. The mixture is filtered to remove the silver chlorid. Then, 50 c.c. of the filtrate are put into an evaporating dish by means of a volumetric pipet, and into this $N/10$ NH_4SCN is allowed to run, drop by drop, from a buret. At first, a brown color appears, due to the formation of ferricyanate. But in the presence of an excess of silver nitrate this immediately disappears, giving place to a bluish white precipitate of silver cyanate. The titration is continued until a permanent reddish brown color appears in the fluid. This color, due to the formation of

ferricyanate, occurs permanently when all of the silver has been precipitated. The reading of the buret at this point denotes the excess of silver in 50 c.c., or half of the amount of fluid in the flask. This figure, therefore, must be multiplied by two in order to obtain the amount of the silver in excess in the total volume of the mixture. From this the chlorid content is calculated as follows: For example:

Buret reading shows 6 c.c. N/10 NH$_4$SCN used.

Therefore $6 \times 2 = 12 =$ excess of silver in total mixture. Then 20 c.c. N/10 AgNO$_3$ less $12 = 8 =$ c.c. of silver solution required to precipitate all chlorids in 10 c.c. of urine, and $8 \times 0.00585 = 0.0468 =$ gm. of NaCl in 10 c.c. urine. If the total output of the urine examined were 1 liter, then the total chlorids would be 4.68 gm. per 1,000 c.c.

The amount of silver here employed is capable of indicating at most 11.7 grams of chlorids per liter. Urine, found by a preliminary test to contain more chlorids than this, must be diluted, or a larger quantity of silver nitrate may be added, before the analysis can be made.
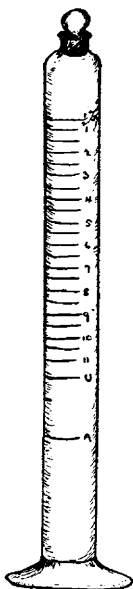

Fig. 1.—Strauss chloridometer.

THE STRAUSS METHOD

The chief simplification of this process has been introduced by Prof. H. Strauss[2] of Berlin. He has condensed into a single tube[13] all of the necessary calibrated apparatus, and claims simplicity together with sufficient clinical accuracy for his method of chlorid determinations. The author has not formally published the results which he has obtained by the use of this instrument, but in a letter has written me that he has been using it for some time with satisfaction. The method is simply the Lüttke-Martius process done in one piece of apparatus. The filtration

13. The Strauss Chloridometer is manufactured by Paul Altmann of Berlin. Price 2.50 marks.

to remove the precipitate of silver chlorid—a step already shown to be unnecessary—is omitted.

The Strauss instrument, shown in Figure 1, is a glass tube 20 cm. long and 2 cm. in diameter. Its lower end is broadened into a base, too small, however, to steady effectually the long cylinder. The upper end is fitted with a ground-glass stopper. Its barrel is calibrated with the marks shown in the figure, to indicate the volumes of silver nitrate solution and of urine to be placed in the tube. Above the mark for the urine, the tube bears a scale reading in 0.5 gm. from 11 gm. to 0.5 gm. These scale marks indicate grams per liter. Urine containing more than 11 gm. of chlorids per liter must be diluted before being analyzed by this method.

For the purpose of the analysis, two standardized solutions[14] are required:
1. N/10 AgNO₃ (Lüttke-Martius' silver solution).
This solution contains 16.966 gm. of silver nitrate to the liter. 1 c.c. of this solution will precipitate 0.00585 gm. NaCl. It is prepared as follows:

    17.5 gm. AgNO₃
    900   c.c. HNO₃ (25 per cent.)
    50   c.c. iron ammonium alum, a cold saturated solution, which is about
            a 10 per cent solution.
Distilled H₂O to 1,000 c.c.

An excess of silver nitrate is used because the salt is somewhat hygroscopic and hence the true amount of silver nitrate is not indicated by the weight of the substance. This solution is standardized in the usual way by titration against known normal hydrochloric acid, the iron salt in the solution acting as an indicator. Thus, 20 c.c. of the silver nitrate solution are added to 20 c.c. of known tenth normal hydrochloric acid. A solution of ammonium thiocyanate is added to this, and the silver solution adjusted until the end-point, or brownish red color, is given on the addition of a very small drop of the thiocyanate. The solution, as made up, will have to be diluted in the process of standardization. This dilution is done by adding a special fluid containing seven parts of distilled water, 2.5 parts of concentrated nitric acid, and 0.5 parts of a 10 per cent. solution of iron ammonium alum. In this way, as has been shown, the factors necessary for a sharp end-point are provided. When kept in a brown bottle, away from the light, this solution remains constant in strength for a long time.

2. N/20 NH₄SCN (3.8 gm. NH₄SCN per liter).
This solution is one-half the strength of the ammonium thiocyanate of the Lüttke-Martius method. Its greater dilution allows a scale of longer intervals to be marked on the tube. It is prepared by dissolving 4 gm. NH₄SCN in 1,000 c.c. of distilled water. Then, by titration with the standardized solution of silver nitrate, in which the iron salt acts as an indicator, it is adjusted by dilution, with water or the addition of more of the thiocyanate, as indicated, so that

    2 c.c. N/20 NH₄SCN = 1 c.c. N/10 AgNO₃.

In order to make a chlorid estimation with the Strauss instrument, N/10 AgNO₃ (Lüttke-Martius' silver solution) is placed in the tube until the bottom of the meniscus corresponds to the mark A. Urine is added until the mark U is reached. These fluids are mixed by gently inverting the tube several

14. Prof. Strauss writes that he has been using such solutions as these prepared by Kahlbaum, and he has found them satisfactory. They are prepared also by pharmaceutical houses in this country.

times. Shaking, which causes the formation of bubbles, must be avoided. The tube is then allowed to stand for five minutes. If a reddish color develop in the mixture, as occurs with all but pale urines, 3 drops of a 10 per cent. solution of potassium permanganate are added. This decolorizes the fluid and the amount of potassium permanganate does not markedly raise the level of the fluid in the tube. In any case, allowance for the increase in the fluid may be made when the scale is read at the end of the titration. After five minutes, N/20 NH₄SCN is run gradually into the tube by means of a buret, pipet, or through a siphon from a bottle of the solution on a shelf. After each addition of the ammonium thiocyanate, the tube is inverted several times gently. As in the case of the Lüttke-Martius' titration, the reddish brown color which appears at first, immediately disappears as long as an excess of silver is present. The addition of ammonium thiocyanate is continued until a definite, permanent reddish-brown color in the fluid is obtained. This end-point, with solutions made up as prescribed, is sharp and lasting. It may be appreciated most readily by holding the tube against a white background. It is well to obtain a good reddish-brown color, for a drop or so of the thiocyanate makes little difference in the scale readings, but a great deal of difference in the intensity of the color. When the titration is complete, the amount of the chlorids in *grams per liter* is read off from the scale.

Experiments to test the accuracy of these instruments, and of the method, were carried out along the following lines:

(a) tests of the calibrations of the tube,
(b) estimations of chlorids in aqueous solutions,
(c) estimations of the chlorids in normal urine,
(d) estimation of the chlorids in urines containing albumin.

In all titrations, results obtained by the Lüttke-Martius method, were taken as the absolute for comparison.

(a) *Calibration of Strauss Tubes.*—The volumes contained between the various marks on Strauss tubes should be as follows: From bottom of tube to the mark A, 10 c.c.; from A to U, 5 c.c.; from U to 11, 1.2 c.c.; and between every mark thereafter on the scale, 0.9 c.c. The calibration of the six tubes imported by this laboratory was tested by comparison with the readings of a standardized buret. By this test, none of the tubes was found to be perfectly accurate. In some the errors were greater than in others, a discrepancy of as much as 0.2 c.c. between the tube-volumes and the absolute scale being noted. As a rule, however, the A and U volumes were found to be in the proper relation. The tubes are put out uncorrected and unaccompanied by any guarantee of accuracy. These errors of workmanship, which, on the whole, are not very large, are therefore to be expected. They do not detract from the value of the tube as a clinical instrument.

(b) *Estimation of Chlorids in Aqueous Solutions.*—Solutions containing sodium chlorid in amounts corresponding to all of the gradations on the apparatus were analyzed. The results of these determinations with the six Strauss tubes are presented in Table 2.

TABLE 2.—ESTIMATION OF CHLORIDS IN AQUEOUS SOLUTION BY STRAUSS'
METHOD COMPARED WITH LÜTTKE-MARTIÜS' METHOD

	Grams NaCl per liter by					
Lüttke-Martius'	Strauss					
Method	Tube 1	Tube 2	Tube 3	Tube 4	Tube 5	Tube 6
0.5	0.5	0.3	0.3	0.5	0.3	0.6
1.228	1.3	1.5	1.5	1.5	1.3	1.4
1.638	1.8	2.05	2.	2.	1.8	2.
2.106	2.1	2.1	2.5	2.1	2.1	1.9
2.574	2.6	2.9	2.7	.....	2.7	3.
3.276	3.5	3.4	3.5	3.5	3.5	3.2
3.627	3.9	3.7	3.7	3.6	3.55	3.6
3.9953	4.	4.05	4.05	4.05	4.	4.4
4.797	4.75	4.75	5.	4.75	5.	4.75
5.0885	4.9	5.1	5.05	5.02	5.1	5.
5.5867	5.6	5.7	5.8	5.8	5.7	5.9
6.101	6.05	6.1	6.	6.1	6.	6.
6.5227	6.75	6.5	6.6	6.6	6.6	6.6
7.254	7.1	7.5	7.5	7.5	7.2	7.1
7.605	7.55	7.6	7.55	7.55	7.8	7.8
8.1607	8.1	8.1	8.15	7.8	8.2	8.
8.5702	8.6	8.7	8.7	8.6	8.5	8.8
9.0967	9.4	9.5	9.3	9.1	9.4	9.5
9.5355	9.55	9.8	9.55	9.5	9.5	10.
10.2667	10.	10.2	10.5	10.6	10.2	10.5
10.764	11.	10.7	11.	10.8	10.7	10.9
11.0565	11.1	11.1	11.2	11.4	11.05	11.3
Max. difference from Lüttke-Martius	0.3033	0.403	0.394	0.3435	0.3033	0.426
Min. difference	0.	0.001	0.0145	0.	0.0047	0.0115
Average difference	0.1516	0.202	0.2042	0.1717	0.154	0.2187

It is shown by this table that the results obtained by the Strauss method are somewhat at variance with the Lüttke-Martius determinations and also exhibit discrepancies between the different tubes. The greatest variation from the absolute (Lüttke-Martius) standard for any amount of chlorids was 0.426 gm. per liter; the smallest was 0. The average of these variations was approximately 0.2 gm. per liter. In nearly all cases the tubes indicated amounts too high. These discrepancies must be attributed to the errors in the calibration of the tubes and to the experimental error in reading the buret. Readings of approximately equal accuracy were obtained from all regions of the scale.

(c) *Estimation of Chlorid in Normal Urine.*—Normal urines of varying chlorid content were analyzed by the Lüttke-Martius and Strauss methods. The results of these tests are summarized in Table 3.

The results of these titrations of the chlorids in urine, even more than those of chlorids in aqueous solution, exhibit the satisfactory accuracy of the Strauss method. In this series (Table 3), the largest discrepancy between the Strauss estimation and the Lüttke-Martius was 0.349 gm. per liter, and this occurred in analyzing a urine containing more than 11 gm. of chlorids per liter. This reading was an approximate one, as the fluid in the tube was below the last scale mark. Even with this, however, the average mean of error was 0.1343 gm. per liter. While this error would be very large in a purely chemical analysis, it is negligible in a clinical estimation. On these results, therefore, it may be concluded that the Strauss method applied to the normal urine is amply accurate to serve as a basis for clinical diagnosis.

TABLE 3.—STRAUSS TUBE ESTIMATION OF CHLORIDS OF NORMAL URINE

Method	Grams NaCl per Liter					
Lüttke-Martius'	2.0475	4.9725	6.903	7.722	9.716	11.349
Strauss—						
Tube 1	2.05	4.8	6.9	7.8	9.5	11.5
Tube 2	2	4.7	7	7.6	9.8	11.5
Tube 3	2	....	6.6	7.7	9.8	11.1
Tube 4	1.9	....	....	7.6	9.6	11
Tube 5	....	5	7.05	7.6	9.7	11.5
Tube 6	....	5	......	7.7	9.8	11.5
Max. difference	0.1475	0.2725	0.303	0.122	0.216	0.349
Min. difference	0.0035	0.0275	0.003	0.022	0.016	0.151
Mean difference	0.0755	0.15	0.153	0.072	0.1165	0.250

Several of the urines in the above series were so highly pigmented that their color interfered with the sharp appearance of the end-point. They were, however, readily decolorized by adding three or four drops of a 10 per cent. solution of potassium permanganate to the mixture in the tube a few minutes before titration. As a rule, the color which develops while the urine stands in contact with the strongly acid silver nitrate solution is made sufficiently pale by dilution from the subsequent addition of the ammonium thiocyanate. But even in normal urine this color may obscure the end-point. It is well, therefore, whenever working with a urine of a deep yellow color to decolorize the mixture in the tube by adding a few drops of the solution of potassium permanganate. Whatever increase in the level of the fluid in the tube is caused by this may be discounted in reading the scale. The advantage of a much more distinct end-point is gained by this step.

(d) *Estimation of Chlorids in Albuminous Urines.* — Although Arnold,[7] in estimating the chlorids in a variety of fluids — milk, blood-serum and urines containing albumin — showed that the presence of

protein in the fluid under analysis did not interfere with the accuracy of the Volhard method, it was considered well to repeat some of his work and to determine whether the Strauss procedure would be disturbed by the presence of protein. It is conceivable that some of the silver of the N/10 silver nitrate solution might become bound to the albumin, forming a silver albuminate, and thus be unavailable in the titration. To test this point solutions of chlorid-free protein of varying concentration were added to normal urine of known chlorid-content and of constant volume, and the resulting mixture was titrated as in the foregoing experiments. The salt-free protein was obtained from blood-serum by dialyzing the serum against changes of distilled water until the water around the dialyzing sac no longer gave a cloudiness with silver nitrate, and the protein in the sac began to precipitate. In this way, solutions of protein were prepared containing from 0.7 to 30 gm. of protein per liter (Tsuchiya). These solutions were shown to be salt-free by Lüttke-Martius determinations. When 10 c.c. of the protein solution were added to 20 c.c. N/10 $AgNO_3$, and the mixture titrated for the excess of silver, the result was found to correspond exactly with what was obtained when those amounts of the standard solutions were titrated. The solutions balanced.

In these tests, however, a heavy yellowish precipitate was formed when the protein was added to the strongly acid silver solution. This precipitate interfered with the analysis only by its bulkiness, when more than 30 gm. of protein per liter were present, but it did not at all disturb the balanced reaction between the standardized silver nitrate and ammonium thiocyanate. The results of a series of titrations with urines containing proteins are given in Table 4.

From Table 4 it is evident that in the time in which the analysis is performed, none of the silver of the standardized solution becomes bound to the protein in such a manner as to render it unavailable for the titration. This table shows that the greatest discrepancy between the Lüttke-Martius and Strauss results was 0.343 gm. of chlorids per liter, and that this occurred only in the analysis of the urine containing 27 gm. of protein per 1,000 c.c. An error as large as this was to be expected from the previous experiments with protein-free urine. But as regards the precipitation of the silver in combination with the protein, the most significant fact is that chloridometry by the Lüttke-Martius method on equal quantities of the same urine, free from or containing protein, gives exactly equal results. Thus by these analyses of urine rendered artificially pathological under controllable conditions, it is shown that the presence of protein in amounts up to 27 gm. per liter does not interfere with the accuracy of the Strauss method.

TABLE 4.—STRAUSS TUBES WITH ALBUMINOUS URINES

URINE A

Tests	25 c.c. Normal Urine. 50 c.c. Water	25 c.c. Same Urine 50 c.c. Protein A	Same Mixture Protein Removed. Vol. Not Restored
Heat and acetic ...	0	+	0
Tsuchiya	*	‡0.7	*
Lüttke-Martius ...	†4.446	4.446	4.5045
Strauss —			
Tube 1	4.2	4.2	4.5
Tube 2	4.5	4.3	4.5

URINE B

Tests	50 c.c. Urine. 50 c.c. H_2O	50 c.c. Same Urine 50 c.c. Protein B	Same Mixture Protein Removed. Vol. Not Restored
Heat and acetic ...	0	+	0
Tsuchiya	*	1.4	....
Lüttke-Martius ...	5.7330	5.7330	5.9670
Strauss—			
Tube 1	5.6	5.7	6
Tube 2	5.7	5.6	6.05

URINE C

Tests	25 c.c. Urine. 50 c.c. H_2O	25 c.c. Urine 50 c.c. Protein C	Same Mixture Protein Removed. Vol. Not Restored
Heat and acetic ...	0	+	0
Tsuchiya	0	10	0
Lüttke-Martius ...	5.2065	5.265	5.3235
Strauss —			
Tube 1	5.1	5.05	....
Tube 2	5.2	5.2	....

URINE D

Tests	10 c.c. Urine 90 c.c. H_2O	10 c.c. Urine 90 c.c. Protein D	Same Mixture Protein Removed. Vol. Restored
Heat and acetic ...	0	+	0
Tsuchiya	....	27	0
Lüttke-Martius ...	2.6910	2.6432	2.2113
Strauss —			
Tube 1	2.8	2.3	2.3
Tube 2	2.6	2.5	2.3

* Not done.
† Chlorids expressed in grams per liter.
‡ Protein expressed in grams per liter.

A source of large error was introduced when the protein was removed from the urine by heat, acetic acid and filtration. The results of titration made after this manipulation are shown in the third column of Table 4. When the estimations are made on the filtrate not restored to the original volume, the amount of chlorids found is too high. But when the analyses are made on the filtrate restored to its original volume by the addition of water, the amounts are too low. The loss of water by evaporation, the carrying down or mechanical "locking up" of chlorids by the heavy precipitate of protein cannot be compensated for by dilution. It is better, therefore, to make the titrations directly in the presence of the protein contained in albuminous urine.

On the basis of the numerous tests described above it may be concluded that the Strauss method is an improvement on the usual methods for determining chlorids. From a clinical standpoint it is a simple, rapid and sufficiently accurate method for determining chlorids in both normal and pathological urine.

CHLORIDOMETRY IN GRADUATED CYLINDERS BY STRAUSS METHOD

Although the Strauss method is a simple and commendable one, it nevertheless retains some points of inaccessibility, as the instrument employed is of foreign manufacture, requiring importation and demanding a rather high price. It seemed well, therefore, to attempt a further simplification of the process. The standardized solutions, obviously, cannot be eliminated. Two of these are required in the Strauss method, but when a laboratory is able to prepare one standardized solution another can be made with only little additional difficulty. The instrument, however, can be simplified. In place of it, a simple graduated 50 c.c. cylinder may be used, and with such a "tube" and a scale for interpreting its results, sufficiently accurate chlorid estimations may be made, as is shown in Table 5.

In making determinations the same solutions and the same amounts of them were put into the cylinders as were used in the Strauss tubes. From the amounts of the various fluids employed, it is evident that when an end-point is reached in the titration, a definite volume of fluid is present in the tube. Thus, for example, it was seen by actual measurement that when the end-point was reached with 5 gm. per liter the Strauss tube contained 26.45 c.c. of total fluids. It follows, moreover, from the volume of silver nitrate solution, the urine and the ammonium thiocyanate, and from their numerical relationships, that the total volume of fluid present for any degree on the scale of chlorids may be calculated. In this way, total volume of fluid may be converted into grams of chlorids per liter, or *vice versa*. For this purpose the following formula has been derived:

Grams chlorids per liter = 20.475 — 0.585 V. Eq. I where V is the total fluid present in the tube.

The formula is derived as follows:

Solutions placed in tube:

5 c.c. or 1/200 of a liter of urine

10 c.c. N/10 $AgNO_3$. Each c.c. of N/10 $AgNO_3$ will precipitate 0.00585 gm. NaCl.

Sum of these solutions = 15 c.c.

N/20 NH_4SCN, of which 2 c.c. N/20 NH_4SCN = 1 c.c. N/10 $AgNO_3$.

V = total fluid at end of titration.

V — 15 = amount of N/20 NH_4SCN used in titration.

V — 15 = Excess of N/10 $AgNo_3$ present after precipitation of chlorids.

$$10 - \frac{V-15}{2} = \text{amount of N/10 } AgNO_3 \text{ used in precipitation of chlorids.}$$

Then

$$[10 - \frac{V-15}{2}] \; 0.00585 = \text{gm. NaCl in 5 c.c. urine.}$$

$$[10 - \frac{V-15}{2}] \; 0.00585 \times 200 = \text{gm. NaCl in 1,000 c.c. urine.}$$

When simplified, this expression is

20.475 — 0.585 V = gm. NaCl per liter of urine. Eq. I.

Example:

Suppose total fluid at end of titration = 21.35 c.c.

Substituting in Equation I:

20.475 — 0.585 x 21.35 = gm. chlorids per liter.

∴ 7.98525 = gm. chlorids per liter.

In this case the Lüttke-Martius determination showed that the chlorids were 7.956 gm. per liter.

By a rearrangement of the terms of this formula, an expression is derived by which the amount of fluid present may be calculated from the number of grams of chlorids per liter in the solution analyzed. This formula would be useful in constructing or checking the calibration of an instrument:

$$V = \frac{20.475 \text{ gm. chlorid per liter}}{0.585} \quad \text{Equation II, where V is the}$$

total fluid in the cylinder at the end of the titration.

From Equation I a scale has been computed for use with the graduated cylinders, from which the numbers of grams of chlorids per liter of the urine, or solution tested, may be read off from the total amount of fluid present at the end of the titration. This scale has been calculated in 0.1 gm. NaCl per liter from 0 to 11.7 gm. per liter. Whereas the scale on the Strauss tube registers from 11 to 0.5 gm. per liter, this scale somewhat extends these limits. By means of it, a range of 1.2 gm. per liter beyond the limits of the Strauss scale is allowed for chlorid estima-

tions in the graduated cylinders. The calculated values of the scale correspond quite accurately to the amounts observed when testing volumetrically the calibrations of the Strauss tubes.

To test this method, a series of determinations were made with ordinary 50 c.c. cylinders chosen at random from the supply in the laboratory and with a certified cylinder of an accurate calibration. The graduations on the ordinary cylinders were for 1 c.c., extending over a tube length of 12.5 cm. The certified cylinder was graduated in 0.2 c.c., extending over a scale length of 25 cm. For these experiments the

SCALE OF CHLORIDOMETRY IN CYLINDERS

Chlorids Gm. per Liter	Volume	Gm.	Volume	Gm.	Volume	Gm.	Volume	Gm.	Volume	Gm.	Volume
0.0	35.000	2.0	31.58	4.0	28.16	6.0	24.74	8.0	21.32	10.0	17.90
0.1	34.829	2.1	31.409	4.1	27.999	6.1	24.569	8.1	21.159	10.1	17.739
0.2	34.671	2.2	31.238	4.2	27.828	6.2	24.398	8.2	20.988	10.2	17.568
0.3	34.487	2.3	31.060	4.3	27.657	6.3	24.227	8.3	20.717	10.3	17.397
0.4	34.316	2.4	30.896	4.4	27.486	6.4	24.056	8.4	20.546	10.4	17.126
0.5	34.128	2.5	30.72	4.5	27.30	6.5	23.88	8.5	20.48	10.5	17.04
0.6	33.971	2.6	30.549	4.6	27.129	6.6	23.709	8.6	20.309	10.6	16.869
0.7	33.803	2.7	30.378	4.7	26.958	6.7	23.538	8.7	20.138	10.7	16.698
0.8	33.632	2.8	30.207	4.8	26.787	6.8	23.367	8.8	19.967	10.8	16.527
0.9	33.461	2.9	30.036	4.9	26.616	6.9	23.196	8.9	19.796	10.9	16.356
1.0	33.29	3.0	29.87	5.0	26.45	7.0	23.03	9.0	19.625	11.0	16.19
1.1	33.119	3.1	29.699	5.1	26.279	7.1	22.869	9.1	19.454	11.1	15.919
1.2	32.948	3.2	29.528	5.2	26.108	7.2	22.698	9.2	19.283	11.2	15.748
1.3	32.771	3.3	29.357	5.3	25.937	7.3	22.527	9.3	19.112	11.3	15.577
1.4	32.606	3.4	29.186	5.4	25.766	7.4	22.356	9.4	18.941	11.4	15.406
1.5	32.435	3.5	29.025	5.5	25.605	7.5	22.175	9.5	18.755	11.5	15.33'
1.6	32.264	3.6	28.854	5.6	25.434	7.6	22.004	9.6	18.584	11.6	15.171
1.7	32.093	3.7	28.683	5.7	25.263	7.7	21.833	9.7	18.413	11.7	15.000
1.8	31.912	3.8	28.512	5.8	25.092	7.8	21.662	9.8	18.242	....	......
1.9	31.741	3.9	28.341	5.9	24.921	7.9	21.491	9.9	18.071	....	......

cylinders were closed with rubber stoppers. Titrations were made in these cylinders according to the Strauss method and the results compared with Lüttke-Martius and Strauss determinations on the same urines. The results of these analyses are shown in Table 5. In this table also are given the results of this method obtained when smaller cylinders (10 c.c.) were used. The significance of this will be described later.

Considering for the present only the results of titration in the 50 c.c. cylinders, it is seen from Table 5 that errors in chloridometry with the ordinary cylinders range from 0.149 to 0.271 gm. of chlorids per liter, while errors with the standardized cylinder are less, being from 0.021 to 0.12 gm. per liter of urine. The larger errors of the ordinary cylinders are explained by the errors found to be existent in their calibrations

when the supposed cubic content between the graduations was measured by means of a buret. The more accurate results with the certified cylinder were to be expected from the accuracy of its calibration and the

TABLE 5.—ESTIMATION OF CHLORIDS IN URINE BY STRAUSS METHOD IN GRADUATED CYLINDERS. RESULTS COMPARED TO STRAUSS TUBE AND LÜTTKE-MARTIUS DETERMINATIONS

Method	Tube and Lüttke-Martius Determinations				In Gm. per liter, Difference from Lüttke-Martius
	Gm. per liter Observed	Gm. per liter by Scale	Volume c.c. Observed	Volume c.c. by Scale	
Lüttke-Martius	0.2340	.....	.....	34.6	....
Strauss tube	Meniscus above scale	.....	.....	.....	....
Ordinary 50 c.c. cyl....	....	0.5	34.1	.....	+0.266
Certified 50 c.c. cyl....	....	0.15	34.75	.....	—0.084
Ordinary 10 c.c. cyl....	....	0.75	6.75	.....	+0.516
Certified 10 c.c. cyl....	....	0.25	6.85	.....	+0.016
Lüttke-Martius	0.7371	.....	.....	33.73	....
Strauss tube 2........	0.7	.....	33.6	.....	—0.0371
50 c.c. cyl. ord.........	....	0.45	34.2	.....	—0.1871
50 c.c. cyl. cert.......	....	0.8	33.6	.....	+0.0629
10 c.c. cyl. ord........	....	1.45	6.5	.....	+0.7189
10 c.c. cyl. cert........	....	0.75	6.75	.....	+0.0189
Lüttke-Martius	4.329	.....	.....	27.6	....
Strauss tube 4........	4.2	.....	27.88	.....	—0.129
50 c.c. cyl. ord.........	....	4.6	27.1	.....	+0.271
50 c.c. cyl. cert.......	....	4.35	27.5	.....	+0.021
10 c.c. cyl. ord........	....	5.1	5.25	.....	+0.771
10 c.c. cyl. cert........	....	4.25	5.55	.....	—0.079
Lüttke-Martius	8.5702	.....	.....	20.35	....
Strauss tube 1........	8.6	.....	20.45	.....	+0.0298
50 c.c. cyl. ord.........	....	8.4	20.5	.....	—0.1702
50 c.c. cyl. cert.......	....	8.6	20.3	.....	+0.0298
50 c.c. cyl. ord.........	....	9.05	3.9	.....	+0.5098
10 c.c. cyl. cert........	....	8.7	4.00	.....	+0.1298
Lüttke-Martius	10.530	.....	.....	17.00	....
Strauss tube 2........	10.6	.....	16.89	.....	+0.07
50 c.c. cyl. ord........	....	10.7	16.6	.....	+0.17
50 c.c. cyl. cert.......	....	10.65	16.7	.....	+0.12
10 c.c. cyl. ord........	....	11.05	3.2	.....	+0.52
10 c.c. cyl. cert.......	....	10.8	3.3	.....	+0.27
Lüttke-Martius	11.349 Meniscus below scale	.....	.....	15.6	....
Strauss tube 2.......		.....	.....	.....	....
50 c.c. cyl. ord........	....	11.1	15.9	.....	—0.149
50 c.c. cyl. cert.......	....	11.25	15.7	.....	—0.099
10 c.c. cyl. ord........	....	11.3	3.1	.....	—0.049
10 c.c. cyl. cert........	....	11.4	3.15	.....	+0.051

length and numerous graduations of its scale. With both kinds of cylinders, chlorid determinations can be made with accuracy equal to that of the Strauss tubes, and the advantages of their longer scales are shown

by the first and last analyses of the series in Table 5, in which the
meniscus was once above and once below the limits of the Strauss scale.
For chlorid estimations by this rapid method, the certified 50 c.c. cylinder
is to be recommended especially.   It has the advantage of being easily
procured, of having accurate calibrations and a long, frequently divided
scale, and in addition gives results that are considerably more accurate
than those obtained by the Strauss tubes.

As the estimation of chlorids in the urine has diagnostic value in the
study of renal function, as well as in the study of many diseases, an
attempt was made to adapt the method of chloridometry in graduated
cylinders to the requirements of urology.   In studying renal function by
means of collecting through a ureteral catheter the urine from one
kidney, often only 1 c.c., or slightly more than this, is obtained.   For the
ordinary Strauss test this amount of urine is insufficient, and it is like-
wise not enough for the test when carried out in 50 c.c. cylinders.   For
this reason small 10 c.c. cylinders were employed in the series of analyses
summarized in Table 5.   One cylinder was an ordinary 10 c.c. graduated
cylinder, the calibrations of which were inaccurate.   The other was a
somewhat longer 10 c.c. cylinder, graduated in 0.1 c.c., with accurate
calibration.   Into these cylinders 1 c.c. of urine and 2 c.c. N/10 AgNO$_3$
(Lüttke-Martius silver solution) were placed.   The titration was then
done by adding N/20 ammonium thiocyanate.   In this way the relations
between the solutions were kept the same as in the ordinary Strauss
method.   As one-fifth of all the solutions used in computing the scale
for chloridometry in graduated cylinders, the results obtained with the
10 c.c. cylinders had only to be multiplied by 5 in order to allow reading
from the amount of fluids in the cylinders the grams of chlorids per liter
of urine tested, by means of the scale computed for the larger cylinders.
Determinations made by these small cylinders, however, exhibited large
discrepancies from the Lüttke-Martius figures.   With the ordinary 10 c.c.
cylinders errors ranged from 0.049 to 0.7189 gm. of chlorids per liter,
while with the certified 10 c.c. cylinders they were from 0.016 to 0.27 gm.
per liter.   With the certified cylinder the readings were within the limits
of desired clinical accuracy.   But, in spite of this, these small cylinders
cannot be recommended for use in making chlorid estimations.   Great
care must be exercised in putting the urine and silver nitrate solution
in the cylinders, for when such small quantities are used, a drop of the
solution left along the sides of the tube will have large effect on the
result of the titration.   It is advisable, therefore, when only small
amounts of urine to be analyzed for chlorids are available, to dilute this
urine carefully a sufficient number of times to give somewhat more than
5 c.c.   More accurate estimations then can be made on the diluted urine
by means of the Strauss method in the tubes or in the graduated cylinders
than are possible with small cylinders, using small quantities of urine.

THE METHOD OF ACHARD AND THOMAS

The other simple method for the determination of chlorids in the urine is that of Achard and Thomas.[1] These authors have devised an instrument comparable to the Esbach tube, and employ the process of Mohr[4] for the titration method. This method is based on the precipitation of chlorids by silver nitrate of known strength added in excess, and the titration for the excess of silver using potassium chromate as an indicator. In Mohr's procedure a certain amount of the urine is placed in a dish, to which is added, drop by drop, a standardized solution of silver nitrate (29.075 gm. $AgNO_3$ dissolved in 1,000 c.c. H_2O; of this solution, 1 c.c. will precipitate 0.01 gm. NaCl). To denote when all the chlorids of the urine have been precipitated a drop or two of a solution

Fig. 2.—Chloridometer of Achard and Thomas.

of potassium chromate are added as an indicator. When the precipitation of chlorids is complete, a reaction takes place between the silver and the chromate, forming silver chromate, which gives a brownish-red color to the mixture. The appearance of the color indicates the end of the reaction, and at this point the amount of chlorids present in the urine is determined from the quantity of the silver used.

The approximate estimation of the chlorids which Achard and Thomas have introduced, rests on the same reaction, but proceeds in the opposite direction. Instead of adding to a fixed amount of urine a variable quantity of silver nitrate, the quantity of urine is varied, while that of the silver nitrate remains constant. This conveniently permits employing only a small amount of the standardized solution of silver

nitrate, and on this basis the method is recommended by the authors as a bedside procedure.   The potassium chromate is added to the silver nitrate in the tube before the addition of any urine.   Silver chromate is formed at once, giving the mixture a deep red color.   To this, the urine is added and the tube inverted several times.   The chromate of silver is decomposed by the successive addition of urine and silver chlorid and a yellowish precipitate is formed.   The end of the reaction occurs when all of the reddish-brown color disappears, and gives place to a light yellow color throughout the fluid and precipitated contents of the tube.   For this test the urine should be slightly acid, rendered so, if necessary, by the addition of a little acetic acid.

The instrument[15] shown in Figure 2, employed by Achard and Thomas, is a tube not unlike the Strauss chloridometer.   This tube is closed by a rubber stopper; its barrel bears a special calibration to indicate the amount of chlorids in the urine thus tested.   At the bottom, a first graduation, marked A, indicates the fixed quantity of the standard solution of silver nitrate to be placed in the tube.   The quantity is 5 c.c. Above this mark, the graduations of the scale indicate in grams per liter various amounts of chlorids.

The scale is constructed according to the following table:

     3.3 c.c. correspond to 15.0 gm. chlorids per 1,000 c.c. of urine.
     5.0 c.c. correspond to 10.0 gm. chlorids per 1,000 c.c. of urine.
     7.1 c.c. correspond to   7.0 gm. chlorids per 1,000 c.c. of urine.
    10.0 c.c. correspond to   5.0 gm. chlorids per 1,000 c.c. of urine.
    12.5 c.c. correspond to   4.0 gm. chlorids per 1,000 c.c. of urine.
    14.0 c.c. correspond to   3.5 gm. chlorids per 1,000 c.c of urine.
    16.0 c.c. correspond to   3.0 gm. chlorids per 1,000 c.c. of urine.
    20.0 c.c. correspond to   2.5 gm. chlorids per 1,000 c.c. of urine.

The total volume in the tube at any of these degrees is the amount given here plus the 5 c.c. of silver nitrate solution.

To make determinations with this tube the following procedures must be carried out:

The tube is filled to the mark A with the standardized solution of silver nitrate (29.075 gm. $AgNO_3$ to 1,000 c.c. H_2O).   To this 3 or 4 drops of a 1:5 solution of potassium chromate are added.   The undiluted urine is then added gradually, mixing the fluids constantly by gentle inversion of the tube.   When the reddish-brown color of the mixture finally changes to a permanent yellow, the end-point is reached.   The chlorids present in grams per liter are read off directly from the scale.

The authors advise using the upper limit of the scale because of the greater accuracy of readings in these regions.   If the amount of chlorids in the urine is above 5 gm. per liter on the first test, a second determination should be made with diluted urine.   Above 5 gm. of chlorid per

15. The Achard and Thomas chloridometer is manufactured by Paul Altmann of Berlin.   Prince 3 marks.

liter make dilutions of 1 to 2, above 10, a dilution of 1 to 4, above 15,
dilute 1 to 6. The results thus obtained are to be multiplied by the
amount of the dilution to estimate the quantity of chlorids in the undi-
luted urine. When the chlorids are less than 2.5 gm. per liter, the silver
nitrate must be diluted; when, to calculate the true chlorid content of
the urine, the observed content should be divided by the degree of the
dilution.

TABLE 6.—ESTIMATION OF CHLORIDS IN AQUEOUS SOLUTIONS BY ACHARD-
THOMAS METHOD COMPARED WITH LÜTTKE-MARTIUS METHOD

Lüttke-Martius Method	Grams NaCl per liter by					
	Achard-Thomas					
	Tube 1	Tube 2	Tube 3	Tube 4	Tube 5	Tube 6
0.5	0.483	0.5	0.583	......	......	......
1.228	1.03	1.0	1.0	1.0	1.0	1.03
1.638	1.33	1.25	1.666	1.5	1.33	1.33
2.106	1.91	1.91	1.8	2.16	2.	1.91
2.574	2.7	2.8	2.75	2.8	2.75	2.8
3.276	3.2	3.25	3.2	3.25	3.2	3.2
3.627	3.6	3.5	3.7	3.55	3.55	3.55
3.9953	4.1	4.05	4.05	4.1	4.1	4.0
4.797	4.5	4.7	4.7	4.7	4.5	4.5
5.085	5.2	5.1	5.2	5.1	5.05	5.0
5.5867	5.35	5.7	5.8	5.9	5.5	5.9
6.101	6.0	6.0	6.1	6.1	6.0	6.0
6.5227	6.5	6.5	6.7	6.5	6.5	6.4
7.254	7.05	7.0	7.1	6.9	7.0	6.9
7.605	7.6	7.5	7.4	7.5	7.2	7.1
8.1607	8.0	7.5	8.0	8.0	7.9	8.0
8.5702	8.0	8.4	8.4	8.3	8.3	8.5
9.0967	9.0	8.5	9.0	8.5	8.5	9.0
9.5355	9.2	9.5	9.5	9.0	9.5	9.5
10.2667	10.1	10.0	10.1	10.1	10.1	10.0
10.764	10.5	10.1	10.5	10.5	10.2	10.2
11.0565	12.0	11.0	11.0	11.0	11.0	11.0
Max. difference from Lüttke-Martius	0.9435	0.664	0.264	0.5967	0.5967	0.564
Min. difference	0.017	0.0	0.028	0.0115	0.0385	0.076
Average difference	0.4802	0.332	0.146	0.304	0.3175	0.320

This instrument and method were tested as follows: (a) Tests of the
calibration; (b) estimation of chlorids in aqueous solution; (c) estima-
tion of chlorids in normal urine, undiluted; (d) estimation of chlorids
in undiluted urine containing albumin. In all titrations results obtained
by the Lüttke-Martius method were taken as the absolute for comparison.

(a) *Tests of the Calibration.*—In comparing by buret readings the
calibration of six of these tubes with the table given by Achard and

Thomas, it was found that the difference between the actual and required cubic content of the tube between the marks of the scale was never more than 0.2 c.c. On the whole, the scale marks were found to be accurately placed.

(b) *Estimation of Chlorids in Aqueous Solution.*—The results of determinations of chlorids in aqueous solution by the Achard-Thomas method as compared with the Lüttke-Martius method are shown in Table 6. The Achard-Thomas determinations are seen to vary from the Lüttke-Martius by as much as 0.9435 gm. of chlorids per liter. Readings were obtained between this degree of error and no error. Nearly all readings were too high. The average error of all readings was about 0.3 gm. per liter. As this series of solutions was the same as that used in testing the Strauss tubes, comparison between these results may be made by reference to Table 2. From this it will be seen that the error in the Strauss determinations (0.2 gm. per liter) were considerably less than this, and in no instance were even one-half as great as some of the errors in the Achard and Thomas estimation.

The explanation of these large errors is provided by the character of the chemical reaction and the construction of the tubes. It has long been admitted that the Mohr method for the estimation of chlorids gives too high results, and this may be taken as one factor in the error under consideration. Furthermore, the end-point of the titration reaction is not a sharp one, especially under the conditions of the analysis in the Achard-Thomas tube. The final color of the titration in the tube does not come suddenly, as in the Strauss method, but develops gradually. A good yellow color is obtained in the fluid of the tube long before all of the brownish-red precipitate disappears. Scale readings of varied degrees. therefore, may be made according as the end-point is judged by the permanent yellow color in the fluid (as the directions specify), or by the complete change in the precipitate (as the chemistry of the reaction demands). This introduces another source of error. All my readings were taken when the precipitate changed completely from brown to yellowish white, as I found that this point gave the most accurate results as compared with the Lüttke-Martius figures. In addition, the scale itself is a source of error. It is constructed with relatively few marks, separated by considerable and varying distances on the tube, with no register between them. The readings, few of which corresponded exactly to the marks on the scale, were taken as the nearest approximations that judgment allowed.

(c) *Estimation of Chlorids in Normal Urines.*—Table 7 presents the results obtained by chloridometry performed on the same series of normal urines used for Table 3, for the Strauss tubes. These results are more like the Lüttke-Martius figures than those in the above table when

aqueous solutions of sodium chlorid were used. The errors in some cases are considerable, however, being as high as 1.299 gm. per liter. This is much a larger error than any in the Strauss determinations, and the use of the tubes in these tests exhibit the same difficulties of inconvenient scale, approximate readings, and uncertain end-point as were described above. Their advantage over the Strauss method is that the color of the urine makes no difference at all in the distinctness of the end-color, when finally this is obtained. Estimations by this method can be made somewhat more rapidly than by the Strauss process.

TABLE 7.—ACHARD AND THOMAS TUBES WITH CHLORIDS OF NORMAL URINE

Method	Gm. NaCl Per Liter					
Lüttke-Martius	2.0475	4.9725	6.903	7.722	9.716	11.349
Achard-Thomas —						
Tube 1	2.0	....	7.0	8.2	8.5	10.05
Tube 2	2.0	4.8	6.8	7.5	9.0	11.0
Tube 3	....	5.0	6.9	8.0	9.0	10.05
Tube 4	....	....	7.0	7.6	8.0	......
Tube 5	....	....	......	......	9.0	......
Tube 6	....	....	......	......	9.0	......
Max. difference	0.0475	0.1725	0.103	0.478	1.216	1.299
Min. difference	0.0475	0.0275	0.003	0.122	0.716	0.349
Mean. difference	0.0475	0.10	0.052	0.300	0.866	0.824

(d) *Estimation of Chlorids in Albuminous Urine.*—A series of urines containing the proteins of blood-serum were analyzed for their chlorid content by the Achard-Thomas method. This series was the same as that for the Strauss tubes, shown in Table 4. Chlorid determinations were made on urines to which salt-free protein had been added in quantities up to 27 gm. per liter. The titrations were all within the limits previously discovered to represent the accuracy of these tubes. In no case was the presence of protein found to interfere with the Achard-Thomas process.

Tests of this method show that because of the inconveniences of its irregular scale, and the uncertainty of its end-point, the Achard-Thomas process is capable of giving only widely approximate results. It has the advantage of being rapid and uninfluenced by the color of the urine tested, while it requires only one standardized solution. But its inaccuracies are so great that its value as a clinical method is considerably less than that of the process of Strauss.

CHLORIDOMETRY BY ACHARD-THOMAS METHOD IN GRADUATED CYLINDERS

This method, like that of Strauss, may be simplified further by eliminating the special apparatus, the chloridometer tube, and employing a graduated 50 c.c. cylinder. The titration may be made in one of these

cylinders and the total volume of fluid noted at the end of the analysis. From the amounts of standard silver nitrate solution, the quantity of urine added and their chlorid equivalent, a formula may be derived by which the total volume of fluid at the end of the titration may be converted into grams of chlorid per liter of urine. Into the cylinder 5 c.c. of standardized Achard and Thomas silver nitrate solution are placed. Of this solution, 1 c.c. will precipitate 0.01 gm. NaCl. To this are added 2 to 3 drops of potassium chromate. Urine is then added until the yellow color appears, determining the end-point as in the ordinary manner. From these quantities the following formula is derived:

V = total volume of fluid in cylinder at end of titration ($V - 5$) = amount of urine added.

$5 \times 0.01 = 0.05$ = amount of NaCl precipitable by 5 c.c. of $AgNO_3$ solution.

As the chlorid content of the amount of urine added ($V - 5$) is 0.05 gm. when the end-point is reached, then

$$\text{Grams NaCl per c.c.} = \frac{0.05}{V - 5}$$

Grams NaCl per c.c. x 1,000 = grams NaCl per liter.

$$\therefore \text{Grams NaCl per liter} = \frac{0.05 \times 1,000}{V - 5} = \frac{50}{V - 5}$$

Example: Suppose $V = 19$

$$\text{Gm. NaCl per liter} = \frac{50}{19 - 5} = \frac{50}{14} = 3.57.$$

This result corresponds to the figures in the table given by Achard and Thomas.

In applying this method, as described above, or by reversing the procedure, adding the silver nitrate solution to the urine, as in the Mohr technic, unsatisfactory results were obtained. The short scale length and the uncertainty of the end-point make the results of titrations in graduated cylinders quite inaccurate. The readings obtained by the cylinders, however, were as accurate as those by the tubes of Achard and Thomas, and the cylinders have the advantage of providing a scale of more calibrations than that on the tubes. But the errors are so great that they prevent recommendation of the method for clinical use.

CONCLUSIONS

Several simplified methods for estimating chlorids in the urine are described and tested. Of these procedures:

1. The Strauss method is found to be simple and rapid and to give results, which, while not exact enough to serve as a basis for metabolic experiments, are sufficiently accurate for clinical purposes.

2. The Strauss method is directly applicable to both normal and albuminous urine.

3. The Strauss method modified by performing the test in a graduated 50 c.c. cylinder, instead of the Strauss tube, gives results more accurate than the original method, and is a simple R process. A scale is computed for use with such cylinders.

4. The Achard and Thomas method is simple and rapid, but because of uncertain end-point and inconvenient scale, is not sufficiently accurate.

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