Summary

1. With normal urines the method of Booth, Schreiber and Zwick permits the quantitative determination of mercury with a loss of about 0.01 to 0.02 mg.
2. Long standing without freezing does not alter the mercury content of the urine specimens.
3. Arsphenamine, bismuth, chloral hydrate, barbital, small amounts of hexamethylenetetramine and small amounts of bromides do not interfere with the standard procedure.
4. Aromatic compounds, such as sodium salicylate, cinchophen and large amounts of hexamethylenetetramine complicate the oxidation to such a degree that it is advisable to avoid the administration of these drugs during a study of mercurial medication.
5. Iodides and large amounts of bromides interfere seriously. A modification of the method involving the addition of sodium nitrite is described which takes care of this interference.
6. The determination of mercury in the feces is best made by destroying the organic matter with potassium permanganate and concentrated nitric acid in place of sulfuric acid, with certain modifications which have been described. This determines 2 to 3 mg. of mercury in the daily stool with a loss of 0.01 to 0.04 mg. of mercury.

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A SPECIFIC REAGENT FOR THE RAPID GRAVIMETRIC DETERMINATION OF SODIUM

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A. Blanchetière[1] made application of Streng's reagent for the detection and precipitation of sodium as the triple salt, uranyl magnesium sodium acetate. According to his statement the precipitate has the formula $(UO_2)_3MgNa(CH_3COO)_9 \cdot 9H_2O$ and is obtained water free after drying for one-half hour at 110°.

A. Kling and A. Lassieur[2] report the results of some experiments and conclude that the method of Blanchetière gives satisfactory results. A critical survey of their data shows, however, that the relative error is -6.0 to $+3.0\%$. Crepaz[3] reports the method too inaccurate for the gravimetric determination of sodium. Recently similar results have been found by Perietzeana,[4] who states that the relative error is -3.0

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[1] Blanchetière, *Bull. soc. chim.*, [4] **33**, 807 (1923).

[2] Kling and Lassieur, *Chimie et industrie*, **12**, 1012 (1924).

[3] Crepaz, *Ann. chim. appl.*, **16**, 219–224 (1926); *C. A.* **20**, 3144 (1926).

[4] Perietzeana, *Bull. soc. chim. România*, **9**, 17–19 (1927); *C. A.*, **22**, 201 (1928).

to +4.1% in solutions containing 0.23–2.3 mg. of sodium. The results which we have obtained with Blanchetière's reagent are still less satisfactory than those reported by the authors mentioned. Probably the results can be improved by using a reagent with a higher concentration of uranyl and magnesium salts than that recommended by Blanchetière. As we have obtained with a uranyl zinc acetate reagent very satisfactory results, we have not made a thorough study of the uranyl magnesium acetate reagent.

We have not been able to confirm the statement of Blanchetière that the crystalline precipitate of uranyl magnesium sodium acetate contains nine molecules of water. The precipitate we obtained lost in weight after drying for twenty hours at 110° about 0.3%. In the abstract[3] of the paper of Crepaz, it is stated that the water content of the salt is one molecule.

The uranyl zinc acetate reagent has approximately the same composition as the one recommended by Kolthoff[5] for the qualitative detection of sodium.

Preparation of Reagent

A.	Uranyl acetate ($2H_2O$)	10 g.	B.	Zinc acetate ($3H_2O$)	30 g.
	Acetic acid, 30%	6 g.		Acetic acid, 30%	3 g.
	Water to make	65 g.		Water to make	65 g.

After the salts in A and B are dissolved by warming, the solutions are mixed and allowed to stand for twenty-four hours. The precipitate of uranyl zinc sodium acetate is filtered off and a solution is obtained that is saturated with the triple salt due to the sodium contained in the chemicals which go to make up the reagent. When kept in Pyrex glass the reagent does not become turbid after long standing.

The reagents required for the determination of sodium are (*a*) uranyl zinc acetate reagent; (*b*) 95% ethyl alcohol saturated with uranyl zinc sodium acetate; (*c*) ether.

Procedure

A known amount of the weighed salt which should not contain more than 8 mg. of sodium is dissolved in 1 cc. of water. Ten cc. of the reagent is added and the whole is well mixed. The solution is allowed to stand for at least thirty minutes and is then filtered through a porous porcelain or glass filter crucible by suction. After the reagent has been removed as completely as possible, the precipitate is washed 5 to 10 times with 2 cc. of the reagent for each washing. The reagent is removed each time completely by suction. The excess is removed by washing the precipitate 5 times with 2 cc. of alcohol each time and finally by washing with ether. The amount of ether used is immaterial as the precipitate is not soluble in it. Air is now drawn through the crucible until the ether is removed. The crucible is wiped clean with a moist cloth, placed in the balance and weighed after ten minutes, or longer. The precipitate has the composition $(UO_2)_3ZnNa(CH_3COO)_9 \cdot 6H_2O$. Weight of precipitate multiplied by 0.01495 = amount of sodium.

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[5] Kolthoff, *Z. anal. Chem.*, **70**, 397 (1927).

Discussion

(*a*) Instead of weighing the small amount of sodium salt given in the procedure, we always proceeded in such a way that a known amount of sodium salt was made up with water to a special weight.

(*b*) The ratio between the volume of the solution of the sodium salt and the reagent must be 1 to 10 or larger than 10. In case 2 cc. of aqueous solution is used, 20 cc. of the reagent should be added.

(*c*) The precipitation of the triple salt is a time reaction. Satisfactory results are obtained by collecting the precipitate after standing for one-half hour. Longer standing has no influence on the results.

(*d*) The solubility of the precipitate increases very much with rise in temperature; consequently, the temperature of the solution at time of filtration should be approximately the same as that at which the reagent was filtered from the triple salt.

(*e*) In most of our experiments we washed with pure 95% alcohol. The results obtained were somewhat too low. The error amounted to about -0.5%. This is due to the slight solubility of the precipitate in 95% alcohol. The solubility is about 0.5 mg. per cc. at room temperature (22°); therefore we recommend that the alcohol be saturated with the precipitate. Especially in the determination of traces of sodium the use of this wash alcohol, saturated with the precipitate, is of importance. In cases where the amount of sodium is about 4 mg., or higher, it is practically immaterial whether the alcohol is saturated with the precipitate, or not. It may be remarked here that the solubility of the precipitate in absolute alcohol is distinctly higher than in 95%, about 2 mg. per cc. in absolute.

Properties of Uranyl Zinc Sodium Acetate.—The salt is nicely crystalline (tetrahedrons) and is readily soluble in water. The solubility is suppressed by an excess of the reagent. In order to get a quantitative precipitation of the sodium, an appreciable excess of the reagent must be used. We did not determine the solubility of the compound in the reagent as the latter was saturated with the triple salt. In order to be sure that the compound was insoluble in the reagent, we washed 300 mg. of the precipitate with 50 cc. of the reagent. No loss in weight was noted. By the addition of an excess of alcohol, it is possible to precipitate the dissolved sodium compound from the reagent. This shows the presence of dissolved sodium triple salt in the reagent.

In the first experiments we tried to weigh the precipitate in the anhydrous form and dried it for this purpose between 100 and 140°. These experiments showed that the water of crystallization is held very tenaciously, and that it was practically impossible to remove this water without decomposing the salt. On drying between 100 and 140° the weight decreased continuously, as may be seen from some of the following experimental figures.

BEHAVIOR OF THE TRIPLE SALT ON DRYING

Calcd. % for $6H_2O$	Loss in weight after drying (average), % 1 hr., 100°	14 hrs., 110°	32 hrs., 110°	1 hr., 125°	6 hrs., 140°
7.03	0.25	5.87	8.05	7.33	9.81

In order to be sure that the precipitate contained six molecules of water we tried to remove the latter at lower temperatures by drying in a vacuum. After drying for two hours between 90 and 100° at 30 mm. pressure, the salt lost 6.94 to 7.03% of water. The theoretical amount for six molecules is 7.03%. Another two hours' drying under the same conditions caused only a slight decrease in weight, a few hundredths of one per cent.

The hydrated salt is very stable at room temperatures. It does not lose its water after remaining over concentrated sulfuric acid or anhydrous calcium chloride for several days. For these reasons it is advantageous to weigh the triple salt in the form obtained at room temperature. This procedure, moreover, shortens the time of analysis.

Experimental

As the precipitate contains only 1.495% of sodium, even small amounts of the latter give relatively large amounts of the salt. One mg. of sodium will give 66.88 mg. of the triple salt; consequently, traces of sodium can be determined by the described method.

The sodium chloride used in the experiments was highly purified and thoroughly dried at 600°. No impurities could be detected in the salt.

One cc. of a standard sodium chloride solution was pipetted and weighed accurately. In this manner the weighing error of the salt was negligibly small.

Results

In Table I the results are reported which were obtained by washing out the reagent with pure 95% alcohol.

TABLE I

DETERMINATION OF SODIUM AS TRIPLE SALT—1CC. SOLUTION + 10CC. REAGENT

Amount of NaCl taken, g.	Time of standing before filtering, hrs.	Weight of ppt., g.	Amount of NaCl found, g.	Error, %
0.01255	50	0.3300	0.01254	−0.1
.01263	50	.3307	.01257	− .5
.01127	50	.2957	.01124	− .3
.01171	50	.3084	.01173	+ .1
.01215	52	.3176	.01207	− .7
.01173	52	.3055	.01161	−1.0
.01185	47	.3110	.01182	−0.3
.01161	47	.3057	.01158	− .3
.01317	47	.3452	.01312	− .4
.01251	47	.3299	.01254	+ .3
.01258	$^1/_2$	.3295	.01252	− .5
.01277	$2^3/_4$	.3353	.01274	− .3
.01296	$^2/_3$	.3400	.01292	− .3

TABLE I (*Concluded*)

Amount of NaCl taken, g.	Time of standing before filtering, hrs.	Weight of ppt., g.	Amount of NaCl found, g.	Error, %
.01320	1/3	.3469	.01318	− .2
.005977	1	.1560	.005928	− .9
.003708	5/6	.0970	.003686	− .6
.02344	24	.6104	.02320	−1.0
.02600	24	.6767	.02571	−1.1

In Table II the experiments are given in which the wash alcohol was saturated with the precipitate.

TABLE II

PRECIPITATE WASHED WITH ALCOHOL SATURATED WITH PRECIPITATE

Amount of NaCl taken, g.	Time of standing before filtering	Weight of ppt., g.	Amount of NaCl found, g.	Error, %
0.01411	2 hours	0.3721	0.01414	+0.2
.01437	2 hours	.3797	.01443	+ .4
.01914	45 minutes	.4940	.01921	+ .3
.01164	50 minutes	.3068	.01165	+ .1
.01426	37 minutes	.3752	.01426	.0
.01589	3 hours	.4172	.01586	− .1
.01456	1 hour	.3860	.01467	+ .7
.01237	30 minutes	.3263	.01240	+ .3
.01419	40 minutes	.3726	.01416	− .2
.002854	2 hours	.0753	.002861	+ .3
.003121	45 minutes	.0822	.003123	+ .1
.006075	30 minutes	.1600	.006080	+ .1

From these analyses it may be concluded that the method gives results accurate to about 0.5%.

Influence of Other Salts

Influence of Potassium.—As the separation of sodium and potassium is of very great practical importance, we made a special study on this point. Kolthoff[5] stated that solutions which contained more than 50 mg. of potassium per cc. gave a precipitate with the reagent; therefore we could expect that large amounts of potassium would interfere with the determination of sodium. Our results are shown in the following table.

TABLE III

INFLUENCE OF POTASSIUM—1CC. SOLUTION + 10CC. REAGENT

NaCl taken, g.	KCl taken, mg.	Time of standing before filtering, hrs.	Weight of ppt., g.	NaCl calcd. from ppt. obtained, g.	Error, %
0.01362	24.3	0.5	0.3576	0.01360	−0.2
.01254	48.7	15	.3286	.01249	− .4
.01177	68.3	16	.3149	.01197	+2
.01311	69.2	20	.3469	.01318	+0.5
.01214	73.3	47	.3416	.01298	+7
.01223	99.0	47	.3502	.01331	+8
.01189	123	47	.3267	.01213	+2

It follows from this table that good results are obtained if less than 50 mg. of potassium chloride per cc. of solution are present. When the potassium chloride content is between 50 and 150 mg. per cc. of solution, too high results are obtained. This is due to the potassium triple salt crystallizing out with the uranyl zinc sodium acetate. On the other hand we have found that when more than 150 mg. of potassium chloride per cc. of solution with 10 cc. of reagent is present, much too low results are obtained. This is due to the fact that the potassium takes much of the reagent for its precipitation as the triple salt and there is not enough of the reagent left for the quantitative precipitation of the sodium; therefore, a part of the latter goes into the filtrate. This is shown by the following experiments.

TABLE IV

INFLUENCE OF POTASSIUM

NaCl taken, g.	KCl taken, mg.	Weight of ppt., g.	NaCl calcd. from ppt. obtained, g.	Reagent used, cc.
0.01219	255	0.2266	0.008611	10
.01242	320	.1795	.006821	10
.01202	400	.3134	.01191	50

For every 50 mg. of potassium chloride per cc. of solution, 10 cc. of the reagent should be added. For cases where the ratio of sodium to potassium is very unfavorable, the potassium may be removed as potassium perchlorate. Details will be given later.

It may be remarked here that if a large amount of potassium is present as sulfate, the method does not give as good results as when the potassium is present as chloride; potassium sulfate is precipitated by the reagent. As barium does not interfere with the sodium determination, the sulfate ions can be easily removed as barium sulfate.

Influence of Ammonium Salts.—Even large amounts of ammonium salts do not interfere, as may be seen from the following results.

TABLE V

INFLUENCE OF AMMONIUM SALTS—1 CC. OF SOLUTION + 10 CC. OF REAGENT

NaCl taken, g.	Ammonium salt taken, g.	Weight of ppt., g.	NaCl found, g.	Error, %
0.01120	1.015 Cl^-	0.2928	0.01113	−0.6
.01174	1.004 SO_4^{--}	.3092	.01175	+ .1
.01358	1.036 NO_3^-	.3589	.01364	+ .4

Influence of Lithium.—Lithium triple salt is still less soluble than the corresponding potassium compound. Experiments are being made to get a good separation between sodium and lithium. Probably the alcohol method may be applied for the extraction of lithium chloride from a mixture of the alkali chlorides.

Influence of Strontium.—Too high results are obtained when strontium is present. If strontium salts are added to the reagent, a fine, white precipitate separates, probably strontium acetate. A continued study on this point is being made.

Influence of Barium, Calcium and Magnesium.—In the concentrations investigated, as given in Table VI, these alkaline earth metals do not have an interfering action, as may be seen from the following results.

TABLE VI

INFLUENCE OF BARIUM, CALCIUM OR MAGNESIUM—1 CC. OF SOLUTION + 10 CC. OF REAGENT

NaCl taken, g.	Alkaline earth salt taken, mg.	Weight of ppt., g.	NaCl found, g.	Error, %
0.01304	178 $MgSO_4$	0.3417	0.01299	−0.4
.01464	825 $CaCl_2 \cdot 6H_2O$	.3874	.01472	+ .5
.01324	200 $Ba(NO_3)_2$	.3464	.01316	− .6

We may mention here that the reagent contains, usually, a little sulfate as an impurity; therefore, if barium is present a little barium salt should be added to the reagent so that the sulfate ions are removed as barium sulfate; otherwise too high results will be obtained.

The sodium determination gives such satisfactory results that the method has already been applied for the quantitative determination of sodium in the commercial salts of the alkaline earth metals.

As concerns the influence of other cations, we may state as a matter of fact that zinc does not influence the results of the sodium determination, and that it may be expected that other cations will not interfere. This point is still under investigation. We believe that the method described will be found to be quite specific for the determination of sodium in the presence of most of the other cations.

From the anions the phosphate ion has an interfering action as it precipitates as uranyl phosphate. Probably the phosphate can be removed in this form with the reagent before the sodium is precipitated.

Large amounts of organic acids, such as oxalic and tartaric, interfere. We plan to make a more systematic investigation on the applicability of the method in many different cases.

The results so far obtained are important enough to expect a general application of this specific and fairly accurate sodium determination.

Summary

1. A procedure is described for precipitating and weighing sodium as $(UO_2)_3ZnNa(CH_3COO)_9 \cdot 6H_2O$.

2. The influence of some cations and anions has been mentioned.

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