Two special pieces of apparatus are described. One is a machine for the rapid measurement of samples of a solution without exposure of the latter to air. The other is a device for shaking a solution while it is being titrated.

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[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF PRINCETON UNIVERSITY]

A NEW QUALITATIVE REAGENT FOR SODIUM

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RECEIVED NOVEMBER 8, 1928 PUBLISHED JULY 5, 1929

It is generally acknowledged that the usual methods for detecting sodium in qualitative analysis are far from satisfactory. The flame test is much too sensitive in that it fails to show whether sodium is present as an essential constituent or whether it is present in traces as an accidental impurity, while the pyroantimonate test is not sufficiently sensitive in the presence of large amounts of potassium and in other respects is an unsatisfactory reagent.

The possibilities suggested by Streng's[1] discovery of a specific microscopical reagent for sodium have not been generally appreciated. This worker found that a solution containing properly adjusted quantities of uranyl acetate, magnesium acetate and acetic acid formed characteristic crystals of a sodium–magnesium uranyl triple acetate when added to solutions containing sodium ions. Streng also noted that certain other bivalent metals might be substituted for magnesium in this reaction and this observation suggested, in part, the present experimental work.

In 1923 Blanchetière[2] devised a magnesium–uranyl acetate reagent that could be used as a precipitant for sodium in ordinary analysis. Kolthoff[3] improved this reagent and tested its value for qualitative purposes. These results were confirmed by Crepaz.[4] Noyes and Bray[5] also showed the value of Blanchetière's magnesium–uranyl acetate reagent as a confirmatory test for sodium in systematic qualitative analysis. In 1927 Kolthoff[6] described a reagent of the same type in which zinc was substituted for magnesium and found that this was an even more sensitive reagent for sodium.

While the two reagents mentioned above are quite sensitive toward sodium, they possess the disadvantage of giving precipitates with potassium when moderate amounts of this ion are present in the solution tested,

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[1] A. Streng, *Z. wiss. Mikroskop.*, **3**, 129–130 (1886); *Chem. Zentr.*, **17**, 488 (1886).

[2] A. Blanchetière, *Bull. soc. chim.*, **33**, 807–818 (1923).

[3] I. M. Kolthoff, *Pharm. Weekblad*, **60**, 1251–1255 (1923).

[4] E. Crepaz, *Ann. chim. applicata*, **16**, 219–224 (1926).

[5] A. A. Noyes and W. C. Bray, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Company, New York, **1927**, pp. 258 and 472.

[6] I. M. Kolthoff, *Z. anal. Chem.*, **70**, 397–400 (1927).

so that when using gram samples, as is usual in qualitative analysis, these reagents cannot be used safely without effecting a separation of the two elements before applying the test for sodium. It has been found that a cobalt–uranyl acetate reagent of the above type is sufficiently sensitive toward sodium for the ordinary purposes of qualitative testing and yet is less sensitive toward potassium than the reagents containing zinc or magnesium, so that it may be safely used for detecting sodium in the presence of potassium when prepared and applied in the manner described below.

Preparation of Cobalt–Uranyl Acetate Reagent.—It was found that the most suitable manner of preparing the reagent is in two portions as follows.

Solution A		Solution B	
Crystallized uranyl acetate	40 g.	Crystallized cobalt acetate	200 g.
Glacial acetic acid	30 g.	Glacial acetic acid	30 g.
Distilled water to	500 cc.	Distilled water to	500 cc.

Each solution is separately warmed to about 75° until all of the salts are in solution and then the two solutions are mixed at this temperature and allowed to cool to 20°. The vessel containing the mixed reagent is then placed in water at 20°, and held at this temperature for an hour or two until the excess of salts has crystallized out. The reagent is finally filtered through a dry filter into a dry bottle. The solution thus prepared keeps indefinitely.

Experimental Part

General Technique.—In common with the triple acetates containing magnesium and zinc, the triple acetate containing sodium, cobalt and uranyl exhibits a marked tendency to form supersaturated solutions. This tendency is readily overcome by shaking the reagent vigorously with the test solution used. For qualitative purposes it was found that the most satisfactory procedure was to mix the reagent and the solution to be tested in a test-tube and then to stopper the tube and shake vigorously for two to three minutes, finally setting aside for five minutes before making the observation. In the following experiments, standard solutions of pure salts were prepared and tested in this manner. The precipitates formed with this reagent are best observed by holding the test-tube above the level of the eye and then looking at the bottom of the tube, by which means the heavy yellow precipitate that settles to the bottom of the tube may readily be seen in contrast to the deep red reagent.

Reactions of Cobalt–Uranyl Acetate Reagent with Pure Sodium Chloride Solutions.—Table I shows the results of a series of experiments made on solutions of pure sodium chloride.

It will be seen that two milligrams of sodium give an immediate precipitate with the reagent, while one milligram may, with certainty, be detected by allowing the mixture of reagent and sodium solution to stand for an hour or two. The results also indicate the necessity of keeping the volume of sodium solution down to a minimum so as not to dilute the reagent unduly and lead to the non-separation of the triple acetate.

TABLE I

REACTIONS OF COBALT–URANYL ACETATE REAGENT WITH PURE SODIUM CHLORIDE SOLUTIONS

Reagent, cc.	Sodium soln., cc.	Sodium present, g.	Ppt. after shaking and standing for 5 min.	Ppt. after one hour
10	1	0.0020	Marked	Heavy
10	2	.0020	None	Slight
20	1	.0030	Heavy	Heavy
20	1	.0020	Marked	Heavy
20	2	.0020	None	None
20	1	.0015	Slight	Marked[a]
20	1	.0010	None	Slight[b]
20	1	.0005	None	None[c]

[a] Marked ppt. in ten minutes. [b] Marked ppt. after several hours. [c] No ppt. in 24 hours.

The reason for using relatively large volumes of reagent appears under the experiments on potassium solutions.

Reactions with Potassium Chloride Solutions.—Table II shows the results obtained in a similar series of experiments in which one cc. of potassium solution was used in each case.

TABLE II

REACTIONS OF COBALT–URANYL ACETATE WITH POTASSIUM CHLORIDE SOLUTIONS

Reagent, cc.	Potassium present, g.	Ppt. after 5 min.	Ppt. after 1 hour	Ppt. after 24 hours
5	0.0500	None	None	....
5	.1000	Heavy	Heavy	....
10	.0500	None	None	....
10	.1000	None	None	Slight
10	.1500	Heavy	Heavy	....
20	.1000	None	None	None
20	.1500	None	None	Slight
20	Sat. KCl soln.	None	Slight	Heavy
20	Sat. K_2SO_4 soln.	None	None	None
10	Sat. K_2SO_4 soln.	None	None	....

It is evident from these results that the use of sufficiently large volumes of reagent favors the non-precipitation of the triple acetate of potassium, cobalt and uranyl. Evidently the concentration of potassium in the total volume of reagent plus solution governs the amount of precipitation and not the concentration of potassium in the original test solution. These experiments showed that a saturated solution of potassium sulfate gives no precipitate with 20 cc. of this reagent and that even a saturated solution of potassium chloride gives no immediate reaction.

Experiments on Precipitating Sodium in the Presence of Potassium.—To determine whether or not the presence of potassium would reduce the sensitivity of the reagent toward sodium, pure sodium and potassium chloride solutions were mixed, evaporated until their total volume was reduced to 1 cc. and then tested with 20 cc. of the reagent in the usual manner. Table III shows the results.

TABLE III

DETECTION OF SODIUM IN THE PRESENCE OF POTASSIUM WITH COBALT–URANYL ACETATE REAGENT

Sodium present, g.	Potassium present, g.	Ppt. after shaking and standing for 5 min.	Ppt. after 15 min.
0.0010	0.0500	Slight	Fair
.0010	.1000	Slight	Fair
.0010	.1500	Slight	Fair
.0020	.1000	Fair	Good
.0030	.1000	Heavy	Heavy

It was therefore concluded that the presence of potassium does not decrease the sensitivity of the reagent toward sodium. If anything, the presence of potassium appears to tend to increase the rapidity of the formation of the sodium–cobalt uranyl triple acetate.

Reaction of Cobalt–Uranyl Acetate Reagent with Various Ions.—Solutions of salts of lithium, ammonium, magnesium, calcium, barium and strontium, known to be free from all but traces of sodium, were also tested with the reagent. It was found that the reagent gave no reaction with these ions with the exception of lithium. Even in the case of lithium it is much less sensitive than the corresponding reagents containing zinc and magnesium since 10 mg. of lithium in 1 cc. of solution gave no precipitate and even 20 mg. gave only a faint precipitate after standing for several hours. For the usual student courses in qualitative analysis, the behavior toward lithium is, of course, of no significance. It has been found that most heavy metals give no reaction with this reagent. Phosphates and other anions that would precipitate the metallic constituents of the reagent must be absent, a condition that is automatically provided for in systematic qualitative analysis.

Quantitative Possibilities of this Reagent.—Several experiments were also directed toward determining the possibility of using this reagent for the quantitative determination of sodium, but it is apparently not suited to this purpose. Several analyses of the triple acetate precipitates obtained by this reagent showed that they approximate the composition represented by the formula $3UO_2(C_2H_3O_2)_2 \cdot Co(C_2H_3O_2)_2 \cdot NaC_2H_3O_2 \cdot 6H_2O$. It was found, however, that they tend to vary in composition so much that they are worthless for quantitative purposes.

Application to the Usual Scheme for Qualitative Analysis.—In applying this reagent to the usual plan for the qualitative analysis of the common metals it is preferable to precipitate magnesium along with barium, calcium and strontium according to the well-known procedure of Noyes.[7]

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[7] A. A. Noyes, "Qualitative Chemical Analysis," The Macmillan Company, 1920, 8th ed.

The filtrate resulting from the ammonium carbonate group may then be treated as follows.

Modified Procedure for the Alkali Group

Acidify the filtrate from Group IV with dilute sulfuric acid and evaporate carefully to dryness in a porcelain dish, finally heating to expel ammonium salts. After cooling treat the residue with 2 cc. of cold distilled water and stir for several minutes to bring the sulfates into solution. Finally filter through a small filter. Divide the filtrate into two equal parts.

Part I.—Test for potassium in the usual way with sodium cobaltinitrite, confirming by means of the flame test.

Part II.—Add 10–20 cc. of cobalt–uranyl acetate reagent, stopper the test-tube and shake thoroughly for two to three minutes. Allow the mixture to stand for at least five minutes. The formation of a yellow precipitate indicates the presence of sodium.

Notes on the Procedure

1. In case large amounts of these alkalies are present the sulfate residue will not all go into solution. This is no disadvantage since the usual tests will be obtained.
2. Care must be taken to use not more than 1 cc. of solution for the sodium test.
3. The amount and speed of formation of the triple acetate precipitate in the test for sodium afford a valuable indication of the probable amount present.

Summary

1. There has been described a new qualitative reagent for sodium composed of a solution of uranyl and cobalt acetates in normal acetic acid.

2. The application of this reagent in the qualitative scheme for the common metals has been indicated.

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[Contribution from the Department of Chemistry of Stanford University]

THERMAL DATA ON ORGANIC COMPOUNDS. V. A REVISION OF THE ENTROPIES AND FREE ENERGIES OF NINETEEN ORGANIC COMPOUNDS

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Received December 10, 1928 Published July 5, 1929

In four preceding papers[1] the entropies and free energies of eighteen organic compounds have been calculated from heat capacity data by means of the third law of thermodynamics. In these calculations the entropy increase for each compound between zero absolute and 90°K. was obtained by use of the "n formula" of Lewis and Gibson,[2] as in most cases the heat capacity data did not go much below the latter temperature. This formula was recognized as being only a rough first approximation but its simplicity and ease of application justified its use for comparative purposes.

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[1] Parks, This Journal, **47**, 338 (1925); Parks and Kelley, *ibid.*, **47**, 2094 (1925); Parks and Anderson, *ibid.*, **48**, 1506 (1926); Parks and Huffman, *ibid.*, **48**, 2788 (1926).

[2] Lewis and Gibson, *ibid.*, **39**, 2565 (1917).