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CHAPTER I

THE ORGANIC ACIDS

Many organic compounds exhibit acidic properties, but in this section only those are included which contain the carboxyl group. These substances are especially valuable in neutralization reactions and in the preparation of buffer solutions, but many possess additional properties which make them useful in analytical chemistry. For example, certain carboxylic acids are used for the precipitation of insoluble normal salts, such as the oxalates of calcium, barium and strontium, and also for the conversion of certain ions into soluble complexes, such as that of aluminum with tartaric acid. Some organic acids are also useful as reducing agents, such as oxalic acid in the reaction with the permanganate ion. Properties of precipitating action, complex formation and reduction are more or less specific for individual members of the group of acids, but the so-called acidic properties are to some extent common to all.

The effective use of organic acids in the control of acidity in analytical procedures requires a general knowledge of the fundamental concept of acids and bases. While it is impossible here to develop in detail the theory of acidity, a review of a number of the more important principles will prove helpful in providing the basis for many useful practical calculations.

An acid may be defined as a substance which yields protons or hydrogen ions. A great many dissimilar substances fall into this classification, such as the ammonium ion, hydrogen chloride, acetic acid, the hydronium ion and the bicarbonate ion. While these substances differ markedly from one another in their general properties, they all exhibit the characteristics of acids because of their common tendency to yield hydrogen ions in solution.

Acids differ widely in the extent to which they are ionized in aqueous solutions. Many, such as hydrogen chloride, hydrogen bromide, hydrogen iodide, perchloric acid, nitric acid, sulfuric acid, hydroferricyanic acid and the organic sulfonic acids are completely ionized with negligible quantities, if any, of the unionized molecular compound remaining. These are termed *strong acids*. Others, which include the organic acids, are only slightly ionized in aqueous solution, and are called *weak acids*.

Available evidence indicates that the hydrogen ion in solution is solvated to form what might be termed a solvonium ion. Thus, in an aqueous solution of an acid the hydrogen ion is hydrated to form the hydronium (or oxonium) ion, H_3O^+ , and it is this ion which is responsible for the so-called acidic properties. For simplicity in the following discussion, however, the classical symbol for the hydrogen ion, H^+ , is used with the understanding that it is always present in the hydrated form in aqueous solution.

The organic acids, as well as other weak electrolytes, ionize reversibly according to the equation



where HA is the acid and A^- the anion of the acid. Applying the principle of equilibrium and the law of mass action, the following equation is obtained

$$\frac{[\text{H}^+] \times [\text{A}^-]}{[\text{HA}]} = K_A \quad (2)$$

in which $[\text{H}^+]$ and $[\text{A}^-]$ represent the molar ionic concentration of the hydrogen ion and anion respectively and $[\text{HA}]$ is the molar concentration of the unionized molecules. K_A is a constant at any definite temperature.

Since the magnitude of K_A is determined by the concentration of the ions and unionized molecules, this value is a most useful index of the extent of ionization of an acid. The ionization constants of a number of organic acids are shown in Table 1. Not only are these constants useful to indicate relative strengths of acids, but they are also valuable in the solution of a number of problems of practical importance in analytical chemistry.

The molar concentration of an organic acid in aqueous solution is quite different from the concentration of the hydrogen ion, since these acids are weak acids and only incompletely ionized. The actual hydrogen ion concentration may be determined experimentally by several methods, but in many cases it is helpful to calculate the ion concentration without employing the more difficult and time-consuming experimental procedure. From equation (1) it is seen that in a solution containing only an acid which yields one hydrogen ion and one anion upon the ionization of one molecule, $[\text{H}^+] = [\text{A}^-]$ and $[\text{HA}] = c - [\text{H}^+]$, where c is the molar concentration of the acid. Consequently equation (2) becomes

$$\frac{[\text{H}^+]^2}{[\text{HA}]} = K_A \text{ or } \frac{[\text{H}^+]^2}{c - [\text{H}^+]} = K_A \quad (3)$$

and

$$[\text{H}^+] = -\frac{K_A}{2} + \sqrt{\frac{K_A^2}{4} + K_A c} \quad (4)$$

For many weak electrolytes, $[\text{H}^+]$ is so small compared with c that $c - [\text{H}^+]$ becomes virtually equal to c ; hence, an approximate form for equation (4) can be written

$$[\text{H}^+]^2 = K_A c \quad (5)$$

or

$$[\text{H}^+] = \sqrt{K_A c} \quad (6)$$

This form of the equation can be used with negligible error if $[\text{H}^+]$ is less than about 5 per cent of c , but if $[\text{H}^+]$ is greater than 5 per cent of the acid concentration, the exact equation (equation (4)) should be used.

A careful control of the acidity of solutions is often important in precipitation reactions and in effecting many analytical separations. The optimum condi-

tions of acidity and alkalinity are generally expressed in terms of pH, which is defined by the equation

$$\text{pH} = -\log \text{H}^+ \quad (7)$$

TABLE 1.—IONIZATION CONSTANTS OF ORGANIC ACIDS (25° C.)

Acid	K (First Hydrogen)	K (Second Hydrogen)
Acetic	1.86×10^{-5}	
Alanine	9×10^{-10}	
Barbituric ...	1.05×10^{-4}	
Benzoic	6.6×10^{-5}	
Bromoacetic	1.38×10^{-3}	
α -Bromopropionic	1.08×10^{-3}	
β -Bromopropionic	9.8×10^{-5}	
Butyric	1.48×10^{-4}	
Chloroacetic	1.55×10^{-3}	
α -Chloropropionic	1.47×10^{-3}	
β -Chloropropionic	8.59×10^{-5}	
Citric	8×10^{-4}	
Crotonic	2.0×10^{-5}	
Formic	2.14×10^{-4}	
Fumaric	1×10^{-3}	3×10^{-5}
Hippuric	2.3×10^{-4}	
Isobutyric	1.5×10^{-5}	
Isovaleric	1.7×10^{-5}	
Lactic	1.55×10^{-4}	
Maleic	1.5×10^{-3}	2.6×10^{-7}
Malic	4×10^{-4}	9×10^{-6}
Malonic	1.61×10^{-3}	2.1×10^{-6}
Mandelic	4.29×10^{-4}	
Mucic	6.3×10^{-4}	
α -Naphthoic	2×10^{-4}	
β -Naphthoic	6.8×10^{-5}	
Nicotinic	1.4×10^{-5}	
Oxalic	3.8×10^{-2}	4.9×10^{-5}
Phthalic	1.26×10^{-3}	3.1×10^{-6}
Picolinic	3×10^{-6}	
Pyromucic	7.1×10^{-4}	
Salicylic	1.06×10^{-3}	1×10^{-12}
Succinic	6.6×10^{-6}	2.8×10^{-6}
Sulfamic	6.2×10^{-4}	
Tartaric	1.1×10^{-3}	6.9×10^{-5}
Tartronic	5×10^{-3}	
Trichloroacetic	2×10^{-1}	
Valeric	1.6×10^{-6}	

Since $[\text{H}^+] = \sqrt{K_{\text{AC}}}$, the pH of a pure aqueous solution of an organic acid may be calculated from the equation

$$\text{pH} = -\frac{1}{2} \log K_{\text{A}} - \frac{1}{2} \log c \quad (8)$$

where K_A is the ionization constant and c the molar concentration of the acid. Since c as used in this equation is the molar concentration of the acid and not the actual concentration of the unionized acid molecules, the value of $\bar{p}H$ so obtained is only approximate, but it is sufficiently accurate for most practical purposes if the degree of ionization does not exceed 5 per cent. This method also gives a fair approximation for dibasic acids if the first ionization is used.

Solutions used in most analytical procedures contain not only the free acid but also some of the salt of the acid. In this case $[H^+]$ and $[A^-]$ are not the same, but $[H^+]$ may be calculated by the equation

$$[H^+] = \frac{K_A c}{[A^-]} \quad (9)$$

and

$$pH = -\log K_A - \log c + \log A^-$$

An approximate value of pH may be calculated if c is taken as the molar concentration of the acid and $[A^-]$ as the concentration of the salt. This equation is very useful, since buffer solutions are very important in analytical chemistry. When c and $[A^-]$ are equal

$$pH = -\log K \quad (10)$$

Another problem of importance is the calculation of the approximate pH of a simple solution of a salt of a weak acid and a strong base. This may be obtained from the equation

$$[H^+] = \sqrt{\frac{K_w \times K_A}{[A^-]}}$$

in which K_w and K_A are the ionization constants of water and the weak acid respectively, and $[A^-]$ is the molar concentration of the salt. Then

$$pH = 7 - \frac{1}{2} \log K_A + \frac{1}{2} \log [A^-].$$

A description of a number of the more important organic acids is included in the following sections:

ACETIC ACID



Mol. Wt. 60.05

Beil. Ref. II, 96.



Use: Detection of beryllium and sodium.

Determination of aluminum, chromium, cobalt, iron, manganese, sodium, titanium and zirconium.

Acetic acid is a colorless liquid of pungent odor. Its sp. gr. is 1.049. It boils at $118.1^\circ C$. and solidifies at $16.7^\circ C$. It is miscible with water, alcohol, and ether, but it is insoluble in carbon disulfide and carbon tetrachloride. Its dissociation constant at $25^\circ C$. is 1.86×10^{-5}

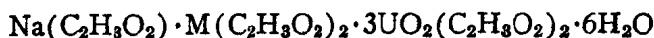
The most important use of acetic acid in analytical work is for the neutralization of solutions, and for the preparation of buffers. It is the most commonly used of all weak acids in laboratory procedures.

The basic acetate method for the separation of sesquioxides from protoxides in the third analytical group is also a very important use of acetic acid. Sodium acetate is an important reagent for the reduction of the hydrogen ion concentration of solutions of mineral acids through the conversion of highly ionized mineral acids to slightly ionized acetic acid.

Acetic acid is also an important solvent for many organic compounds in various analytical procedures. For example, diphenylamine, diphenylbenzidine, and 8-hydroxyquinoline are used in acetic acid solutions. Acetic acid is also used as a solvent in certain separations. For example, uranium dissolves in a mixture composed of 20 parts of acetic acid and 5 parts of nitric acid, while vanadium does not.¹⁹⁷ Many metals, antimony and tin excepted, and their alloys dissolve in 50 per cent acetic acid and 30 per cent hydrogen peroxide, and the resulting solutions are particularly well suited for further analytical treatment.¹⁹⁸

DETECTION AND DETERMINATION OF SODIUM

Under properly controlled conditions sodium can be precipitated as a slightly soluble triple acetate with the uranyl ion having the general formula:



in which M may be magnesium, zinc, nickel, cobalt, manganese and certain other divalent metals. The most satisfactory reagents for the sodium precipitation are formed with zinc and magnesium.¹⁸ Streng^{1,2} first discovered that sodium is precipitated with uranyl acetate, or as the triple salt of sodium magnesium uranyl acetate. Blanchetiere⁴ studied the work of Streng and determined the composition of the sodium salt formed with magnesium uranyl acetate. Kolthoff⁵ used this reaction as a qualitative test for sodium, and later Kling and Lassieur⁶ applied the reaction to a quantitative method for the determination of sodium. This method has been extensively studied and much of this work has been reported in a number of excellent reviews^{44,51,60,61,68,92,98,127,145,153,168,201}.

The following procedures, due to Kolthoff,^{5,75} illustrate the use of uranyl acetate reagents for the detection of sodium.

(a) Magnesium uranyl acetate:

Reagent. Dissolve 10 g. of uranyl acetate and 6 g. of 30 per cent acetic acid in water and dilute to 50 ml. Dissolve 33 g. of magnesium acetate and 6 g. of acetic acid in water and dilute to 50 ml. Mix the two solutions and allow to stand for several days. Filter and use the clear filtrate.

Procedure. Add 10 drops of the reagent and 2 ml. of alcohol to 2 ml. of the solution to be tested. A turbidity or precipitate forms within one hour if the concentration of sodium is greater than 50 mg. per liter.

(b) Zinc Uranyl acetate:

Reagent. Dissolve 10 g. of uranyl acetate and 6 g. of 30 per cent acetic acid in 34 g. of water. Heat, and mix the hot solution with a hot solution prepared by dissolving 30 g. of zinc acetate and 3 g. of acetic acid in 17 g. of water. Allow to stand one day and filter.

Procedure. Mix 4 ml. of the reagent with 0.5 ml. of the solution to be tested. A crystalline precipitate forms at once or after some time, depending on the amount of sodium present. The precipitate forms within 30 minutes with as little as 50 mg. of sodium per liter. The test is made more sensitive if alcohol is present.

A great many modifications of uranyl acetate reagent have been proposed from time to time in an effort to improve the sodium separation. The more important of these are listed in the following sections:

Magnesium uranyl acetate. Many investigators have employed magnesium uranyl acetate for the precipitation of sodium.^{1-22,29-31,36,37,42,45,49,63,65,69,127,225,226} Many have used the reagent originally proposed by Blanchetiere,^{4,6,7,9,14-16,19,127} which has the following composition:

Solution a

Uranyl acetate 100 g.
Glacial acetic acid 60 g.
Dilute with water to 1 liter

Solution b

Magnesium acetate 333 g.
Glacial acetic acid 60 g.
Dilute with water to 1 liter.

This reagent has been modified as follows:

- The same quantity of salts have been dissolved in sufficient water to form only one-half the final volume described above.^{5,11,49}
- The amount of crystalline uranyl acetate has been reduced to 85 g and the magnesium acetate increased to 500 g.^{17,18,20,22,36,42}
- The quantity of uranyl acetate dihydrate has been decreased to 90 g. and the magnesium acetate tetrahydrate has been increased to 600 g.^{21,80,81,65}
- The amount of magnesium acetate tetrahydrate has been increased to 700 g.²⁹
- A special reagent may be prepared by dissolving 25 g. of uranyl acetate, 150 g. of magnesium acetate and 780 ml. of glacial acetic acid. With this reagent it is claimed that there is no error due to potassium or lithium.^{40,127} This same reagent has been diluted with an equal volume of water.⁴⁴

The following special reagent has also been prepared: ¹²⁷

Solution a

Uranyl nitrate—10 g.
30% acetic acid—6 ml.
Dilute to 65 ml. with water.

Solution b

Magnesium acetate—30 g.
30% acetic acid—3 ml.
Dilute to 65 ml. with water.

This reagent gives a nitrate-free triple acetate.

Many authors have recommended the use of an alcoholic solution of magnesium uranyl acetate.^{23-25,27,28,32,33,35,39,41,48,50-52,55,57-59,66-68,70,127} The following reagent has been proposed by Kahane^{24,25}:

Uranyl acetate (cryst.)	32 g.
Magnesium acetate	100 g.
Glacial acetic acid	20 ml.
90% ethyl alcohol	500 ml.
Dilute with water to one liter.	

Liegeois¹²⁷ claims that in using this reagent for the determination of sodium an error occurs due to the precipitation of uranyl oxide. Caley and co-workers⁴⁸ have used a similar reagent containing 30 g. of uranyl acetate dihydrate, 150 g. of magnesium acetate tetrahydrate and an equal quantity of 95 per cent ethyl alcohol. Canessa⁴⁷ has increased the uranyl acetate to 35 g. and magnesium acetate to 150 g. Nydahl⁵⁹ recommends the following formula for the sodium reagent:

Uranyl acetate	19 g.
Magnesium turnings	25.5 g.
Glacial acetic acid	85 ml.
6 N Hydrochloric acid	165 ml.
95% Ethyl alcohol	500 ml.
Dilute with water to 1 liter.	

Zinc uranyl acetate. Many analysts have proposed formulas for the uranyl acetate reagent in which zinc is substituted for magnesium.^{3,26,44,46,73-77,79-82,84,86-88,90,91,98-96,98,101-106,108,112-114,116-120,123-125,127-129,131,133-145,148,149,151,153,154,156,157,161-164,166-168,170,171,173,174,204-206,227} The following reagent has been proposed by Barber and Kolthoff,⁷⁶ and others:

Solution a

Uranyl acetate dihydrate—10 g.
30% acetic acid—6 g.
Dilute with water to 65 g.

Solution b

Zinc acetate trihydrate—30 g.
30% acetic acid—3 g.
Dilute with water to 65 g.

The following modifications of this reagent have been proposed:

- Some authors recommend the addition of 50 ml. of water instead of diluting to 65 g.^{74,79,141,162,167,174}
- The quantity of zinc acetate may be increased by about 50 per cent¹¹⁷ and the uranyl acetate by approximately 20 per cent.^{88,113,116}
- The amount of acetic acid may be increased to 60 ml. and the quantity of water to 320 ml.¹³⁷ In this formula the glacial acetic acid may be reduced to 20 ml.¹²³

- (d) A similar reagent may be prepared containing 1.5 per cent alcohol with a final volume of only 50 ml.⁸⁵
- (e) Broadfoot and Browning¹⁸⁸ add 15 ml. of nitric acid to each 100 ml. of reagent to reduce coprecipitation.
- (f) The reagent of Barber and Kolthoff may be used after diluting with an equal amount of alcohol.^{98,99,100,109}
- (g) Sassier¹⁸² has used a reagent similar to that of Kahane's.

DETERMINATION OF SODIUM

The methods used for the final determination of sodium with the aid of uranyl acetate are very numerous, but all of these depend upon the precipitation of sodium from an aqueous solution as the slightly soluble triple acetate. The sodium precipitate may be weighed directly after drying or upon ignition as a gravimetric procedure, or it may be determined titrimetrically or colorimetrically.

(a) **Gravimetric determination.** The quantity of water of hydration contained in the triple acetate precipitate has been the subject of considerable controversy. Some state that the magnesium precipitate contains 9 molecules of water, while others claim that when an alcoholic solution of the reagent is used only 8 molecules of water are present. Six molecules is the number usually employed in the calculation, although according to some the number is more nearly 6.5.

The water content of dried sodium zinc uranyl acetate is slightly greater than that corresponding to the hexahydrate. Schoorl⁶⁷ reports that the amount of water depends upon the humidity of the atmosphere in which the precipitate is dried. The water content reported after drying in air at various humidities and at room temperatures is given in Table 2. The water of hydration of the triple acetate is not expelled when the precipitate is heated at 110° C.

TABLE 2.

Relative Humidity Per Cent	Moles of H ₂ O in Precipitate
0.	617
0.34	645
0.68	653
0.94	664
0.98	680

The precipitate is weighed in the air-dry state as the hexahydrate. The slight error which results from regarding the precipitate as the hexahydrate is compensated by small solubility losses in the procedure.

The solubility of sodium zinc uranyl acetate is 5.85 g. per 100 ml. of solution at 21° C., and this is fairly high for a quantitative precipitation. Special precaution, therefore, must be taken to insure the complete separation of sodium. This can be accomplished by adding a comparatively large volume of a concentrated solution of zinc uranyl acetate, which is saturated with the sodium salt, to a very small volume of the solution of the sodium salt. Precipitation occurs immediately, but the mixture should be allowed to stand for an hour or more with occasional stirring to insure quantitative separation. After collecting the precipitate on a filter crucible, it is washed with successive small portions of the reagent solution that has been saturated with the triple salt. The wash solution is then removed with 95 per cent alcohol that is saturated with sodium zinc uranyl acetate, and finally the precipitate is washed with acetone or ether to remove the alcohol. The sodium factor is 0.01495. The smallness of the factor is a great advantage when a small quantity of sodium is determined, but it limits the weight of sample that can be used when sodium and potassium are present in similar quantities. The following procedure is recommended by Barber and Kolthoff,⁷⁶ and this may be taken as typical of the gravimetric sodium procedures:

Reagent. *Zinc uranyl acetate.* *Solution a:* Mix 10 g. of uranyl acetate, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, 6 ml. of 30 per cent acetic acid and 50 ml. of water and warm until solution is complete.

Solution b: Mix 30 g. of zinc acetate, $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, 3 ml. of 30 per cent acetic acid and 50 ml. of water and warm until all the solid has dissolved.

Mix equal volumes of solutions *a* and *b* and allow the mixture to stand for 24 hours. If a precipitate forms, due to the presence of small quantities of sodium salts, filter and store the solution in a pyrex bottle. If no precipitate forms, add a small quantity of sodium chloride in order to saturate the solution with the sodium salt. Filter and store in a pyrex bottle.

Procedure. Dissolve a sample containing not more than 8 mg. of sodium and 25 mg. of potassium in 1 ml. of water and add 10 ml. of the zinc uranyl acetate solution. Mix and allow to stand for one hour. Stir occasionally to insure complete precipitation. Filter through a filtering crucible, and remove as much of the solution as possible with suction. Wash the beaker in which the precipitation was carried out, the crucible and the precipitate with five to eight 2-ml. portions of the reagent and allow the precipitate to drain each time. Then wash five times with 2-ml. portions of 95 per cent alcohol that has been saturated with sodium zinc uranyl acetate at room temperature, and then wash with a few small portions of ether or acetone. Draw air through the crucible for a few minutes to remove the ether or acetone and place the crucible in the balance case. Allow to stand for 10-15 minutes and weigh. Allow to stand in the balance case for an additional 10 minutes and again weigh to be sure the weight is constant. The weight of sodium is found by multiplying the weight of the precipitate by 0.01495. This method is accurate to about 0.5 per cent.

When the precipitates are ignited and weighed the following factors are used: ¹²⁷

Ignited Precipitate	Sodium Per Cent	Na ₂ O Per Cent
(U ₃ O ₇ Mg) ½ (U ₃ O ₇ Na ₂)	2.474	3.334
(U ₃ O ₇ Zn) ½ (U ₃ O ₇ Na ₂)	2.369	3.193

Lithium interferes in the above determination, since this metal also forms a slightly soluble triple acetate. Caley and Rogers ²⁰⁹ have prepared a reagent which is not very sensitive toward lithium, but which unfortunately is not very sensitive toward sodium. This reagent has the following composition:

Uranyl acetate (UO₂(C₂H₃O₂)₂·2H₂O) 88 g.
 Cupric acetate (Cu(C₂H₃O₂)₂·2H₂O) 88 g.
 Glacial acetic acid 60 ml.
 Sufficient water to make 1 liter of solution.

Better results are obtained by replacing a part of the water with ethyl alcohol. The best mixture for use in the presence of lithium has the following composition:

Uranyl acetate (UO₂(C₂H₃O₂)₂·2H₂O) 40 g.
 Cupric acetate (Cu(C₂H₃O₂)₂·2H₂O) 20 g.
 Glacial acetic acid 100 ml.
 Ethyl alcohol 500 ml.
 Water 450 ml.

The precipitate formed with this reagent appears to have the composition: 3UO₂(C₂H₃O₂)₂·Cu(C₂H₃O₂)₂·NaC₂H₃O₂ + approx. 5H₂O + 1.5 C₂H₅OH. From 1-50 mg. of sodium can be determined satisfactorily by assuming that the precipitate dried at 60° C. contains 1.45 per cent sodium. Lithium causes a slight positive error.

Potassium does not interfere except when present in relatively large quantities. Dworzak and Liebenberg ⁵⁸ say that the limit of allowable potassium is 2:1. Others ^{88, 95, 107} place the limit at 20:1, while Japhe ¹³⁶ states that this may be as high as 100:1. Mulwani and Pollard ¹³⁰ say that the ratio of potassium to sodium may be 12:1 for titrimetric methods but only 4:1 for colorimetric methods.

Phosphates yield precipitates with the reagent and must be removed. Protein, albumin and other organic materials may also interfere. Ammonium salts, magnesium, calcium and barium may be present in moderate quantities without interference although strontium causes high results. Chromium may interfere. Antimony, mercury and silver, as well as oxalates and arsenates also interfere. Aluminum, lead, manganese, cobalt, cadmium, nickel, cesium and rubidium do not interfere. Molybdate interferes with the formation of precipitates with zinc uranyl acetate reagents. The error is sometimes positive and sometimes

negative depending upon whether the precipitate is retained on the filter or not. By the addition of tartaric or citric acid, however, a complex anion containing molybdenum is formed which does not contaminate the sodium precipitate noticeably.

Sulfate must be absent when potassium is simultaneously present, since potassium sulfate is only slightly soluble in the reaction mixture.

Titrimetric determination of sodium. Many investigators have determined sodium titrimetrically after precipitating as sodium zinc (or magnesium) uranyl acetate ^{10,20,23-25,31,34,48,51,52,59,70,84,88-90,96,99,100,104,106,109,110,113,115-117,119,120,122,127,130,132,135,139,142,143,147,149,172}. Many of these methods are based upon the reduction of hexavalent uranium in the precipitate to the tetravalent state, and the subsequent titration of U(IV) \rightarrow U(VI) with the aid of various oxidizing agents. Potassium permanganate, ^{10,23-25,31,34,51,52,59,90,96,116,119,120,127,135,149} ceric sulfate, ^{81,59,110,122,139} and potassium dichromate ^{104,117} have been used as the oxidizing agents.

Blenkinsop ⁸⁴ recommends adding potassium thiocyanate to the uranium solution that has been reduced with titanium trichloride, and titrating the excess titanium trichloride with ferric potassium sulfate to a red end-point.

An iodometric method has been employed which is based upon the following steps: Dissolve the precipitate, add ammonium sulfate, sulfuric acid, potassium iodide, and starch and then gradually add potassium ferricyanide, and finally titrate the liberated iodine with a standard thiosulfate solution. ¹⁰⁶

Caley ²⁰ dissolved the precipitate in acetic acid and titrated the uranium with a standard disodium phosphate solution. This method has been modified by adding an excess of standard disodium hydrogen/phosphate and back titrating the excess with uranyl acetate, ^{99,100,108} using cochineal as indicator.

Arnoux and Coulomb ⁷⁰ dissolved the sodium precipitate in a sodium acetate solution, heated the mixture to boiling and then precipitated the uranium as red $\text{UO}_2(\text{C}_6\text{H}_5\text{NO})_2 \cdot \text{C}_6\text{H}_5\text{NOH}$ with the aid of 8-hydroxyquinoline. This precipitate was then dissolved in dilute hydrochloric acid, an excess of standard potassium bromate added and the excess determined by the addition of potassium iodide and subsequent titration with standard thiosulfate.

Dulac and Bouat ⁴⁸ determined sodium indirectly by estimating the amount of acetate in the sodium precipitate. They treated the sodium precipitate with tartaric acid, removed the acetic acid by steam distillation and titrated the distillate with barium hydroxide. The acetate content of the precipitate may also be determined by adding an excess of standard sodium hydroxide to the precipitate and titrating the excess with standard hydrochloric acid to an end-point with phenolphthalein. ^{88,116,132} Several investigators have recommended titrating the precipitates directly with standard sodium hydroxide. ^{89,113,115,142,143,172}

Colorimetric determination of sodium. Many methods have been proposed for the colorimetric determination of sodium after precipitation as the triple acetate. ^{15,18,22,25,26,36,38,49,69,72,74,81,85,93,97,101,108,111,114,125,130,134,137,141,153,154,156,157,170,182,184}

One of the most widely used methods for the development of a color in solutions of the sodium precipitate is based upon the conversion of the uranyl

radical to reddish-brown uranyl potassium ferrocyanide ($\text{UO}_2\text{K}_2\text{Fe}(\text{CN})_6$) by the addition of potassium ferrocyanide. This reaction has been studied by many investigators.^{15,25,26,38,74,81,85,93,101,108,111,114,130,141,153,158,157,170} The color is independent of acidity in solutions ranging from 0.4 to 5.0 per cent acetic acid. A 2 per cent acetic acid concentration has been recommended.^{111,153} The reaction does not take place in an alkaline medium. An optimum color is developed with a 0.2 per cent solution of a uranium salt and a 1 per cent solution of potassium ferrocyanide.¹⁵ With greater quantities of potassium ferrocyanide, the color is increased.⁸³ The color is proportional to the sodium content of the solution within a range of 50 per cent variation between the standard and sample solution.

Ernst and Barasits⁸¹ recommend adding an excessive quantity of acetic acid to stabilize the color. Tissier and Benard¹⁵ claim that with high concentrations of potassium ferrocyanide a precipitate may form. Marenzi and Vilallonga¹⁷⁰ report that a turbidity may result with the ferrocyanide method, and suggest using a 1 per cent solution of sodium bisulfate as a stabilizing agent.

The following method may be used for the determination of small quantities of sodium.

Procedure. Dissolve the precipitate of sodium zinc uranyl acetate, formed as described above, in 10 ml. of water and transfer to a 25-ml. volumetric flask. If the sodium concentration is relatively large, the sample solution should be diluted to a larger volume. In a similar flask, place the precipitate which is formed from 1 ml. or more of a standard sodium chloride solution, and to both sample and standard add 1 drop of glacial acetic acid and 0.5 ml. of 20 per cent potassium ferrocyanide for each 25 ml. of final volume. Dilute to the mark, mix well, and compare the resulting colors after three minutes.

In the presence of large quantities of potassium, dilute the solution of the sample so that the potassium content does not exceed 0.3 mg. per ml. Then add 0.5 ml. of 7 per cent potassium ferrocyanide and 1 drop of glacial acetic acid to each 7.5 ml. of the sample solution. The resulting color is compared with a standard similarly prepared.

The standard sodium solution is prepared by dissolving 0.1271 g. of pure sodium chloride in water and diluting the resulting mixture to 1 liter. Add a few ml. of chloroform as a preservative. One ml. of this solution contains 0.05 mg. of sodium.

A number of methods are based upon the use of the normal color of the sodium triple salt for comparisons against standards.^{18,22,36,89,97} Standards are prepared in the same manner as the unknown, and are stable for about one month.³⁶ In making the comparison, the temperature of the sample and the standard must be the same.¹⁸ Alcohol must not be added to the final solution in making the color comparison, since otherwise an error results due to precipitation of the triple salt.^{22,97}

The following procedure may be used for the direct comparison:

Procedure. Dissolve the precipitate of the sodium triple salt by adding water warmed to 60-70° C. in 2-ml. portions until solution is complete. Collect

the solution in a comparison tube and allow to cool. Dilute to a standard volume, depending upon the intensity of the color, and compare with a standard similarly prepared, using 2 ml. of standard sodium chloride solution. If more than 5 mg. of sodium is present in the sample, the colorimetric method should not be used, but rather the sodium should be determined gravimetrically.

When sodium zinc uranyl acetate is dissolved in a solution of sodium or potassium citrate, the extinction coefficient of the resulting yellow solution may be determined in a step photometer.¹³⁷

Hoffman and Osgood¹³⁴ have used an aqueous solution of ammonium thiocyanate to stabilize the color of the triple acetate against temperature change. Sumuleanu and Bottezatu¹²⁵ recommend dissolving the sodium zinc uranyl acetate precipitate in water and adding pyrocatechol and sodium hydroxide for the color comparison. They used permanent standards prepared from Bismarck brown. Sodium salicylate has been used to develop the color of aqueous solutions of the triple acetate.^{49,153} Sulfosalicylic acid has also been used to develop the color with uranium in the triple acetate precipitate.¹⁵⁴ This color is stable against time and temperature. Ishibishi and Kishi⁶² have used thorium B as a radio active indicator of the uranium content of sodium magnesium uranyl acetate. Goto¹⁵⁵ has studied the fluorescence of sodium zinc uranyl acetate as a basis for the sodium determination. Fredericq²²⁸ determined sodium after precipitating with magnesium uranyl acetate by measuring the violet color given by treating the dissolved precipitate with alizarin.

Other uranyl acetate reagents. A number of uranyl acetate reagents containing bivalent metals other than zinc and cadmium have been proposed for the sodium precipitation. These reagents have been of value only in qualitative analysis. Among the metal acetates that have been used are cadmium^{176,177,183}; nickel;^{98,176-178,180,183} manganese;^{176,178,181-184} cobalt;^{176,178-180,183} copper and iron;^{175-178,183,209} and lead.⁵⁸

BASIC ACETATE SEPARATIONS

A number of important separations are based upon the fact that ferric, aluminum and titanium acetates are hydrolyzed in hot dilute solutions much more readily than the acetates of the bivalent metals. Upon the hydrolysis of ferric acetate, acetic acid is formed according to the equation



and this tends to reverse the reaction due to the solvent effect of the hydrogen ion upon the basic ferric acetate. The concentration of the hydrogen ions may, however, be reduced by the addition of sodium acetate to insure the reaction running to completion. Among the metals from which iron, aluminum and titanium may be separated are manganese, nickel, cobalt and zinc. Ferric iron may be quantitatively precipitated by adjusting the pH of the solution to 5-6 with acetic acid and sodium acetate and heating. The following procedure may be

used for the separation of iron, aluminum and titanium from manganese, cobalt, nickel and zinc: 211-214

Procedure. To a slightly acid solution containing the chlorides of the metals, add a solution of sodium carbonate until a slight permanent opalescence appears. Add a few drops of dilute hydrochloric acid to redissolve the precipitate. In a large round-bottomed flask prepare a dilute solution of sodium or ammonium acetate which contains for each 0.1-0.2 g. of iron or aluminum, 1.5-2 g. of the acetate and 300 ml. of water. Heat the acetate solution to boiling and remove the burner. Then add the solution to be analyzed and replace the burner and boil the mixture for 1 minute. Discontinue the heating and allow the precipitate to settle. Filter while hot and wash 3 times by decantation with boiling water containing sodium or ammonium acetate. Transfer the greater part of the precipitate to a porcelain dish and dissolve the remainder from the paper by alternately treating with hot 3 N hydrochloric acid and hot water. Evaporate the resulting solution almost to dryness on a water-bath and repeat the precipitation as described above. Then dissolve the filtered and washed precipitate in hydrochloric acid and separate the iron and aluminum according to the usual methods. Manganese, nickel, cobalt and zinc may be determined in the combined filtrates.

The above method is especially suited for the separation of iron and titanium from the other metals, but the method is usually less satisfactory with aluminum. Some manganese may precipitate during the basic acetate precipitation, and so it is necessary to dissolve the precipitate and carry out the precipitation a second time.

Iron may be separated from manganese in the absence of other metals by the following method, which requires but a single precipitation.²¹⁵⁻²¹⁷

Procedure. To the acid solution containing not more than 0.3 g. of iron, add 0.35 g. of potassium chloride for each 0.1 g. of iron. Evaporate to dryness on a water-bath and break up the residue with the aid of a stirring rod. Heat for an additional 5 or 10 minutes and dissolve the residue in 10-20 ml. of water. Now add 1.5 g. of sodium acetate for each 0.1 g. of iron present, and dilute with boiling water to a volume of 200 ml. for each 0.1 g. of iron present. Heat to boiling with stirring and remove the burner. Allow the precipitate to settle, decant the solution through a filter, and wash the precipitate with hot water. Dissolve the precipitate in a minimum quantity of hydrochloric acid and precipitate iron with ammonium hydroxide. Filter, dry, and ignite to Fe_2O_3 .

The following method for separating iron and manganese has been proposed by Mittasch.²¹⁸

Procedure. Neutralize the slightly acid solution, containing not more than 0.3 g. of iron and having a volume not greater than 100 ml., by adding a 20 per cent ammonium carbonate solution from a buret while stirring constantly. When a precipitate is formed which dissolves only very slowly with stirring, complete the neutralization by adding a more dilute solution of am-