

XI. Methods of Analysis

Methods are based upon analytical procedures as performed at the Muscle Shoals Plant Laboratory. Some variations are included and alternatives are discussed.

DETERMINATION OF POTASSIUM CARBONATE

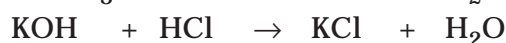
(Total Alkalinity as Potassium Carbonate and/or Potassium Oxide)

PURPOSE AND THEORY

The alkaline strength of potassium carbonate is determined through titration with hydrochloric acid using modified methyl orange as the indicator.

Potassium carbonate with either potassium bicarbonate or potassium hydroxide present reacts with the acid to produce potassium chloride, water, and carbon dioxide.

The alkaline strength of the sample is computed from the volume of acid required for the titration and may be reported as either percent potassium carbonate or potassium



oxide. When required, the exact amount of potassium carbonate can be determined by subtracting that portion of the acid required to neutralize the potassium hydroxide or potassium bicarbonate that is present in the sample.

PROCEDURE

This procedure should be performed as rapidly as possible to prevent adsorption/absorption of atmospheric CO_2 .

1. Weigh a 4.000 to 6.000 gram sample of anhydrous potassium carbonate into a glass weighing bottle. For 47% potassium carbonate solution, use a 8.000 to 10.000 gram sample.
2. Transfer quantitatively the weighing bottle into a 250 milliliter erlenmeyer flask. Add approximately 100 ml of distilled water and four drops of the modified methyl orange indicator.
3. Titrate with standardized 1 N hydrochloric acid using a Class A 100 milliliter buret until the color of the solution changes from green to a steel gray.
4. Record the required volume of acid used to the nearest 0.1 milliliter.

CALCULATIONS

Report total alkalinity as potassium carbonate and/or potassium oxide to the nearest 0.01%.

Let: W = Weight of sample (grams)
 V = Volume of HCl required (milliliters)
 N = Concentration of HCl (Normality)

$$\% \text{ Total Alkalinity as } \text{K}_2\text{CO}_3 = \frac{(V)(N)(6.91)}{W}$$

$$\% \text{ Total Alkalinity as } \text{K}_2\text{O} = \frac{(V)(N)(4.71)}{W}$$

REAGENTS

Hydrochloric Acid, Standardized, 1 N Solution
 Indicator, Modified Methyl Orange.

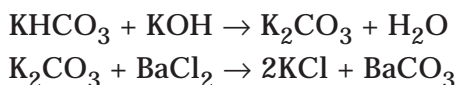
NOTE:
 An automatic titrator may be utilized for ease of analysis, especially if this test is performed often. Contact Technical Service for further information concerning automatic titration.

DETERMINATION OF POTASSIUM BICARBONATE OR POTASSIUM HYDROXIDE

PURPOSE AND THEORY

The bicarbonate (HCO_3) and hydroxide (OH) of potassium cannot co-exist in solution.

- ◆ If hydroxide is present, carbonate is precipitated by the addition of barium chloride. The hydroxide is determined by titration with standardized hydrochloric acid.
- ◆ If bicarbonate is present, it is converted to carbonate by the addition of an excess of standardized caustic soda solution. The carbonate is precipitated by the addition of barium chloride solution. The excess caustic soda is determined by titration with standardized hydrochloric acid.



PROCEDURE

This procedure should be performed as rapidly as possible to prevent adsorption/absorption of atmospheric CO_2 .

A. Sample

1. Weigh a 2.000 to 3.000 gram sample of anhydrous potassium carbonate into a weighing bottle and seal with the cover. For 47% K_2CO_3 solution use a 4.000 to 6.000 gram sample. Record as "W".
2. Transfer quantitatively the contents of the weighing bottle into a 500 ml erlenmeyer flask. Rinse bottle into the flask using distilled water and cover carefully. Add approximately 200 ml of distilled water and 4 to 6 drops

of phenolphthalein indicator.

3. Add 10 ml of 0.1 N sodium hydroxide solution and 100 ml of a 10% barium chloride solution to the flask.
 4. Titrate with 0.1 N hydrochloric acid until the pink color is just discharged. Record milliliters of 0.1 N HCl used as Titer "A".
- B. Blank
1. To a 500 ml erlenmeyer flask, add approximately 200 milliliters of distilled water. Add 4 to 6 drops of phenolphthalein indicator.
 2. Add 10 ml of 0.1 N sodium hydroxide solution and 100 ml of a 10% barium chloride solution to the flask.
 3. Titrate with 0.1 N hydrochloric acid until the pink color is just discharged. Record milliliters of 0.1 N HCl used as Titer "B".

CALCULATIONS

KOH is present if "A" is greater than "B".

KHCO_3 is present if "A" is less than "B".

Only K_2CO_3 is present if "A" equals "B".

$$\% \text{ KOH} = \frac{(\text{ml "A"} - \text{ml "B"})(\text{N})(5.61)}{\text{W}}$$

$$\% \text{ KHCO}_3 = \frac{(\text{ml "B"} - \text{ml "A"})(\text{N})(10.01)}{\text{W}}$$

REAGENTS

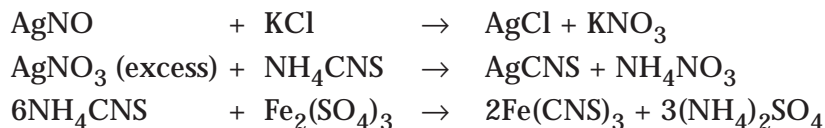
Barium Chloride, 10 % solution
 Hydrochloric Acid, 0.1 N,
 Standardized
 Sodium Hydroxide, 0.1 N,
 Standardized
 Phenolphthalein Indicator

DETERMINATION OF POTASSIUM CHLORIDE

PURPOSE AND THEORY

This method for determination of chloride is referred to as either the Volhard or Thiocyanate-Ferric Alum method. It is applicable to the titration of chloride in acid solutions. When an acidic silver ion solution and an alkali thiocyanate are mixed in the presence of a ferric salt, the thiocyanate has a selective action toward silver, resulting in silver thiocyanate. Any excess of thiocyanate required by the silver reacts with ferric salt to form reddish-brown ferric thiocyanate, indicating the completion of the reaction.

An excess of silver nitrate is added to a nitric acid solution containing chloride and ferric indicator. The excess silver nitrate is titrated with ammonium thiocyanate.



PROCEDURE

1. Weigh a 40 gram sample of anhydrous potassium carbonate into a 250 ml erlenmeyer flask. For 47% solution, use a 50 gram sample.
2. Make up to 100 ml with distilled water and neutralize sample with 1:1 nitric acid using litmus paper as indicator. Caution: Neutralize carefully - the sample will effervesce during neutralization.
3. Add one milliliter of ferric indicator.
4. Add 20 ml of 0.05 N silver nitrate.
5. Titrate to reddish-brown endpoint with 0.05 N ammonium thiocyanate. Endpoint should hold for at least 15 seconds.

NOTE:

An automatic titrator may be utilized for ease of analysis, especially if this test is performed often. Contact Technical Service for further information concerning automatic titration.

6. Minimum volumes of AgNO_3 and NH_4CNS should be 10 ml and 5 ml, respectively.

CALCULATIONS

Let: W = Weight of sample (grams)

N_1 = Concentration of AgNO_3 used (Normality)

T_1 = Volume of AgNO_3 required (milliliters)

N_2 = Concentration of NH_4CNS used (Normality)

T_2 = Volume of NH_4CNS required (milliliters)

$$\% \text{KCl} = \frac{(T_1 N_1 - T_2 N_2)(7.455)}{W}$$

REAGENTS

Ammonium Thiocyanate, 0.05 N,

Standardized

Silver Nitrate, 0.05 N, Standardized

Ferric Indicator

Nitric Acid, 1:1 Solution

DETERMINATION OF SODIUM

PURPOSE AND THEORY

Sodium content in potassium carbonate is determined with an atomic absorption (AA) spectrophotometer. The sample is diluted to maintain total dissolved solids at an acceptable level for proper operation of the burner-aspirator system. An air-acetylene flame is utilized.

Sodium in parts per million (Na, ppm) is determined through a standard additions methodology. The diluted sample is analyzed along with additional sample aliquots which are 'spiked' with known amounts of sodium. Most atomic absorption instrumentation includes built-in programs to calculate standard addition results. If appropriate software is not available, raw sample results may be plotted manually and the content of the original sample may be extrapolated from the curve. If manual calculation is necessary, curves should be prepared daily. If a large number of samples is to be analyzed, it may be sufficient to prepare only one or two sets of standard additions. The slope of the resulting curve(s) will be suitable for analysis of additional samples providing all sample matrices are similar.

ANALYSIS

1. Weigh 10 grams of potassium carbonate into a 100 ml volumetric flask. Dilute the flask to volume with deionized water and assure that the entire sample is dissolved.
2. Into each of three 100 ml volumetric flasks, pipet 0.5 ml of the diluted sample.
3. For the first flask, merely dilute to volume with deionized water. Mark this flask ADD0.
4. To the second flask, pipet 1 ml of a 100 ppm sodium standard. Mark this flask ADD1. To the third flask, pipet 2 ml of the 100 ppm sodium standard. Mark this flask ADD2. Dilute both of these flasks to volume with deionized water.
5. Set up and optimize your AA according to the manufacturer's specifications. Analyze all three samples using the standard additions mode on your AA.
 - a) ADD 0 is obviously the zero addition.
 - b) ADD1 is an addition of 1 ppm or, if you prefer, an addition of 2000 ppm if the sample dilution is taken into account.
 - c) ADD2 is an addition of 2 ppm or 4000 ppm if the sample dilution is taken into account.
6. If your instrument does not automatically calculate results for standard additions, record the instrument readout and plot the results manually. If information is needed concerning manual calculation of standard additions, you may wish to consult an analytical chemistry textbook.
7. If additions were considered as 2000 and 4000 ppm, results obtained are the ppm sodium in the original sample. If additions were considered as 1 and 2 ppm, multiply the result by 2000 to obtain the ppm sodium in the original sample.

REAGENTS

Standard Sodium Solution, 100 ppm

NOTE:
Other techniques, including ICP-AES may be utilized. Direct analysis, rather than standard additions, is possible if matrix matched standards are utilized. Contact Technical Service for further information concerning these other options.

DETERMINATION OF IRON

PURPOSE AND THEORY

The thiocyanate method is used for the determination of small amounts of ferric iron. Ferric iron and potassium thiocyanate in an acidic solution form a red-colored species. The intensity is proportional to the quantity of iron present.



A visual comparison may be made between a prepared sample and a standard. The color intensity of the standard is adjusted to match that of the sample by adding a solution containing a known amount of iron. The volume of standard iron solution required is used to calculate the quantity of iron in the sample.

More commonly, especially if iron is determined routinely, a spectrophotometer is utilized. A calibration curve is constructed for the instrument using solutions of known iron concentration.

PROCEDURE

1. Weigh 10 grams of anhydrous potassium carbonate into a 100 ml volumetric flask. For 47% K_2CO_3 solution, use a 20 gram sample.
2. Add 25 ml of distilled water and neutralize with 6.5 N HCl using litmus paper as indicator and add 6 ml HCl in excess.
Caution: Neutralize carefully - the sample will effervesce during neutralization.
3. Cool in water bath.
4. Add one drop hydrogen peroxide (H_2O_2) and mix well.
5. Add 10 ml of 1.5 N potassium thiocyanate solution and dilute to volume with distilled water. Mix well.

NOTE:
Other techniques, including ICP-AES may be utilized. Contact Technical Service for further information.

6. Measure absorbance on a Beckman "B" spectrophotometer (or equivalent instrument) using a wavelength of 480 millimicrons and a sensitivity setting of "2". Zero instrument with a reagent blank using 50 ml cells. Read within 15 minutes.
7. A calibration curve is prepared by using iron standards in an equivalent potassium chloride concentrated solution. Then, starting with Step 4, the same procedure is followed.

CALCULATION

$$\text{Weight of Fe (grams)} = \frac{\text{Microgram Fe from Curve}}{10^6}$$

$$\% \text{ Fe} = \frac{(\text{Weight Fe})(100)}{\text{Weight of Sample}}$$

REAGENTS

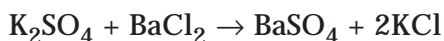
Hydrogen Peroxide, 30% solution
Potassium Thiocyanate,
1.5N solution (146 g/L)
Hydrochloric Acid, 6.5 N

DETERMINATION OF SULFATE

PURPOSE AND THEORY

The addition of a barium chloride solution to a slightly acidic solution containing sulfate ion results in the precipitation of barium sulfate.

Under specified conditions, the precipitation may be regarded as quantitative. The barium sulfate is recovered and weighed. The sulfate content of the sample is then computed and reported as percent K_2SO_4 .



PROCEDURE

1. Weigh a 50.0 gram sample in a 600 ml beaker, or 100.0 grams of 47% solution. Add 300 ml of distilled water and 3-4 drops of methyl orange indicator.
2. Add concentrated hydrochloric acid; 1 ml in excess of that required to change the solution color from yellow to red.
Caution: Neutralize carefully - the sample will effervesce during neutralization.
3. Filter through a No. 42 Whatman filter paper and wash filter paper with two washes of hot distilled water, collecting the filtrate in a 600 ml beaker.
4. Heat the filtrate to boiling, add 10 ml of barium chloride solution slowly with constant stirring. Continue to boil gently for 3-5 minutes. Allow precipitate to stand in a warm place for three hours or at room temperature overnight.
5. Filter off the precipitate (cold) on a Whatman 42 filter paper, use a rubber policeman to free any solids sticking to the beaker.
6. Wash the precipitate with suc-

cessive small portions of cold distilled water until a small test portion of the wash water does not become cloudy with the addition of 1-2 drops of silver nitrate.

7. Transfer precipitate and filter paper to a tared 15 ml crucible (heated 15 minutes at 1000°F and cooled in a desiccator). Cautiously char filter paper by tilting the crucible on a triangle over a controlled Fisher burner, then heat to about 1000°F for one-half hour.
8. Transfer the crucible to a desiccator, cool to room temperature then weigh. Record weight to nearest 0.0001 gram.

CALCULATIONS

Report the results as K_2SO_4 to the nearest 0.0001%.

Let: W_1 = Sample Weight (grams)

W_2 = Tared Crucible Weight (grams)

W_3 = Tared Crucible Weight plus precipitate (grams)

$$\% K_2SO_4 = \frac{(W_3 - W_2)(74.65)}{W_1}$$

REAGENTS

Barium Chloride, 10% Solution
Hydrochloric Acid, Concentrated
Silver Nitrate Solution, 5%

DETERMINATION OF HEAVY METALS (as Pb)

PURPOSE AND THEORY

Metals, such as lead, zinc, tin and copper, in low concentrations are precipitated as colloidal sulfides in weakly acidic solution. The turbidity of the precipitated sample is compared with that of a standard lead solution treated in an identical manner.

PROCEDURE

1. Weigh a 20.0 ± 0.1 gram sample in a small beaker and transfer to a 100 ml volumetric flask with water. For a 47% solution, weight 40.0 ± 0.1 grams of solution into a 100 ml volumetric flask.
2. Transfer a 10.0 ml aliquot to a 100 ml beaker. Neutralize with 1.0 N acetic acid to a pH of 3.0 to 4.0. Transfer quantitatively to a 50 ml Nessler tube.
3. To a second 50 ml Nessler tube pipet 2 ml of the standard lead solution prepared as given below. Dilute to 25 ml with water and adjust to a pH of 3.0 - 4.0 as in Step 2.
4. Dilute both tubes to about 35 ml with water and add 10 ml of freshly prepared hydrogen sulfide solution then fill to 50 ml volume with water. Mix well and allow to stand for five minutes.
5. Compare the sample tube with the standard by viewing downward over a white surface. The sample should be no darker than the standard. The standard solution contains 10 ppm heavy metals as lead. For other lead limits, change the size of aliquot taken from lead standard.

NOTES:

Hydrogen sulfide is a poisonous, flammable gas. Commercially available saturated hydrogen sulfide solution may be purchased to avoid the hazards of handling hydrogen sulfide gas.

REAGENTS

Acetic Acid, 1 N Solution

Heavy Metals Standard, 10

Microgram of Lead per Milliliter

Hydrochloric Acid, Concentrated

Hydrogen Sulfide, Saturated
Solution

DETERMINATION OF MOISTURE

PURPOSE AND THEORY

Two methods may be used to determine moisture in potassium carbonate. If a relatively complete analysis of the sample is made, then water can be calculated by difference. If the moisture content is desired quickly, then the oven loss method can be used. In this method, care must be taken in sample handling since potassium carbonate is deliquescent. When potassium bicarbonate is present, a correction for its volatile decomposition products equivalent to 0.3 of the determined potassium bicarbonate should be subtracted from the oven loss to give free moisture.



PROCEDURE

1. Weigh a 5.000 gram sample in an aluminum dish.
2. Dry for two hours at 250°C.
3. Sample should be placed in a desiccator for no more than 10 minutes. Weigh sample warm, but not at the elevated drying temperature. Potassium carbonate is deliquescent and will pick up moisture even in a desiccator.

CALCULATIONS

Let: W = Sample Weight (grams)
 A = Oven Loss Weight (grams)
 B = Potassium Bicarbonate Concentration (%)
 0.3B = Concentration of Potassium Bicarbonate Volatiles (%); when KHCO_3 is small or missing, this term is very small or zero.

$$\% \text{H}_2\text{O} = \frac{(A)(100) - (0.3B)}{W}$$

PREPARATION OF SPECIAL AND STANDARD SOLUTIONS

Acetic Acid, 1N: Dilute 60 ml of glacial acetic acid to one liter with water.

Ammonium Thiocyanate, Standardized, 0.05N: Dissolve 3.8062 grams of NH_4CNS in water and dilute to a liter. It is standardized against a standard silver nitrate solution, using a ferric alum indicator.

Barium Chloride, 10%: Dissolve 120 grams of reagent-grade $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 880 ml of distilled water.

Ferric Indicator: A saturated solution of reagent-grade $\text{FeNH}_4(\text{SO}_4)$ in distilled water.

Hydrochloric Acid, Standardized, 1N: Add 83 ml of concentrated HCl to a one liter volumetric flask containing distilled water, dilute to mark and mix well. (This solution is also available commercially.) Standardize with 5.0 grams of freshly prepared anhydrous sodium carbonate. Use primary standard analytical reagent grade Na_2CO_3 . Heat 10 to 20 grams of sodium carbonate in a weighing bottle at 250°C for one hour.

Hydrochloric Acid, Standardized, 0.1N: Dilute exactly 100 ml of 1N standardized hydrochloric acid solution at 20°C to one liter with distilled water in a volumetric flask and mix thoroughly.

Hydrochloric Acid, 6.5N: Add 540 ml of concentrated hydrochloric acid to a one liter volumetric flask containing distilled water and dilute to the 1000 ml mark.

Hydrogen Sulfide Saturated Solution: Prepare fresh solution daily. Bubble hydrogen sulfide through 250 ml of distilled water for 15 minutes in a hood. Hydrogen sulfide is very toxic. (A saturated solution is available commercially.)

Iron Standard Solution: Dissolve 0.7022 grams of reagent-grade ferrous ammonium sulfate crystals, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, in 50 ml of 5N nitric acid. Dilute to 500 ml in a volumetric flask with distilled water and mix well. Dilute 10 ml of this solution to 1 liter in a volumetric flask and mix thoroughly. One ml equals 20 micrograms of Fe.

Lead Standard Solution: Dissolve 0.1598 grams of lead nitrate, $\text{Pb}(\text{NO}_3)_2$, in 100 ml of water containing one ml of concentrated nitric acid. Solution A: dilute to one liter for 100 micrograms per ml. Solution B: dilute 10 ml of solution A to 100 ml for 10 micrograms per ml. Prepare solutions daily.

Modified Methyl Orange Indicator: Dissolve 0.14 grams of methyl orange and 0.12 grams of xylene cyanolle FF in deionized water and dilute to 100 ml.

Phenolphthalein Indicator: Dissolve 1 gram of phenolphthalein in 100 ml of methanol.

Potassium Chloride, 20%: Dissolve 200 grams of reagent-grade potassium chloride in 800 ml of distilled water.

Potassium Thiocyanate, (~ 1.5N solution): Dissolve 146 grams of reagent-grade potassium thiocyanate in one liter of distilled water.

Silver Nitrate, Standardized, 0.05N: Weigh out about 8.55 grams of silver nitrate and dissolve in a liter of distilled water. Standardize against a standard sodium chloride solution by the method of Mohr, Volhard or Fajous.

Silver Nitrate, 5%: Dissolve 5 grams of reagent grade silver nitrate in 95 ml of distilled water.

Sodium Hydroxide, Standardized, 0.1N: Dissolve about 6 grams of caustic soda in a half-liter of distilled water and add enough BaCl_2 to precipitate any carbonate that may be present. Allow BaCO_3 to settle, then filter into a liter flask and dilute to mark with CO_2 -free water. Standardize with hydrochloric acid using phenolphthalein as indicator. To prevent CO_2 from entering the bottle, the incoming air is filtered through a guard tube containing ascarite.

Sodium Standard Solution: ASTM certified standard atomic absorption sodium solution.