# Rapid Determination of Moisture in Ammonium Nitrate

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A rapid, accurate method for the determination of moisture in ammonium nitrate utilizes Karl Fischer reagent for the direct determination of water in the nitrate and substitutes a volumetric measurement of the nitrate for analytical weighings. An accuracy within ±0.05% may be obtained for the range of 0 to 1.0% moisture. A brief description is also given for the other methods studied during this investigation.

To MONITOR THE MOISTURE CONTENT of ammonium nitrate during the manufacturing process a rapid and accurate method was needed. Ammonium nitrate, manufactured for fertilizer use, is usually pelleted and coated with a diatomaceous earth. This coating acts as a deterrent of the caking of the pellets during storage in sealed bags. However, its effectiveness is dependent upon the moisture content of the prills—that is, the higher the moisture content, the greater is the tendency of the nitrate to cake in storage. The range of particular interest in this problem is from 0 to 1.0% moisture with an accuracy within ±0.05%.

Attempts to correlate capacitance, conductivity, and high frequency measurements with the moisture content of coated and uncoated ammonium nitrate prills were unsuccessful. Jensen, Kelly, and Burton (2) determined moisture in ammonium nitrate crystals by a high-frequency method. This involved extraction of the moisture from the crystals with a methanol-dioxane mixture and a subsequent measurement of the physical change in the solvent resulting from differences in water content. In this investigation a commercially made high-frequency oscillometer was used, and erratic results were obtained both for solid ammonium nitrate and methanol-dioxane solutions. These erratic results were attributed to the variable size and density of the prills, the presence of air bubbles in the prills, and the effect of the inert material used to coat the prills. The same difficulties prevailed for capacitance and conductance measurements.

Two well-known drying methods have been used extensively for this analysis in control laboratories. One of these is the vacuum-oven drying method in which the sample is dried for 3 hours under vacuum at 60° C., and the moisture content determined by weight loss. The other is the Moisture Teller method. The Moisture Teller, manufactured by the H. W. Dietert Co., dries the nitrate for 10 minutes in a stream of air warmed to 238° F. (114.4° C.). When analytical weighings before and after drying are considered, the analysis time is about 30 minutes. Good results can be obtained by these two methods. However, two factors that render most drying methods unsuitable for monitoring the moisture content of ammonium nitrate are thermal instability of the nitrate, and analysis time.

The method recommended in this paper utilizes Karl Fischer reagent for the direct determination of water in the prills and substitutes a volumetric measurement of the prills for analytical weighings. Using an automatic titrator, the time for an analysis is about 5 minutes.

## Reagents

Sodium Tartrate. Merck c.p. sodium tartrate ($Na_2C_4H_4O_6.2H_2O$) was found to be very satisfactory for standardization of the Karl Fischer reagent.

Iodine. Reagent grade, resublimed iodine should be used. It is advisable to crush as finely as possible before dissolution in methanol.

Methanol. Anhydrous methanol must be used.

Pyridine. Reagent grade pyridine prepared specifically for Karl Fischer reagent is available commercially.

Sulfur Dioxide. Cylinder sulfur dioxide is used.

## Preparation of Karl Fischer Reagent

Karl Fischer reagent is prepared in the following manner: Solution A is made by dissolving 320 grams of finely crushed iodine in 2.5 liters of anhydrous methanol. The bottle is sealed well and stored in a dark place. Solution B is made by slowly adding 242 grams of liquid sulfur dioxide from an inverted cylinder into 1 kg. of cooled pyridine. This is done by fitting the bottle with a rubber stopper containing a vent tube and a delivery tube reaching into the pyridine. By taring the bottle with pyridine on a suitable scale, the addition of the sulfur dioxide can be simplified. This solution is also sealed and stored in a dark place.

The final reagent is made by adding solution B to solution A and mixing well. The reagent should stand 24 hours before using. The individual solutions are very stable; but the mixed Karl Fischer reagent gradually loses its titer. It is recommended, therefore, that not over a 2 weeks' supply be made at one time by mixing proportionate quantities of the two solutions.

The Fischer Scientific Co. has available a stabilized, one-solution Karl Fischer reagent. This reagent has been used and found to be very satisfactory from the standpoint of stability. The

only deterring factor with the reagent was the high titer (about 6.9 mg. of water per ml. of reagent) when used for substances with low moisture content. However, Fisher Scientific now has available a diluent which is not supposed to affect the reagent stability, but does extend its usefulness to lower titers.

## Procedure

All moisture determinations were performed with a Beckman Model KF-2 Aquameter. Before any titrations are made the instrument is always balanced with Karl Fischer reagent and methanol. To standardize the reagent, weigh accurately about 200 mg. of sodium tartrate. When this has dissolved completely in the reaction vessel, titrate to the end point. The titer is calculated as follows:

$$\frac{\text{g. H}_2\text{O}}{\text{ml. K.F.}} = \frac{(\text{g. tartrate}) (0.1566)}{\text{ml. K.F. reagent}}$$

The value 0.1566 is the weight in grams of water per gram of the sodium tartrate primary standard. A titer range of 0.0025 to 0.0035 gram of water per ml. of Karl Fischer reagent was found to be suitable for this work.

To determine the moisture content of ammonium nitrate, the instrument is balanced and the nitrate sample quickly added. As soon as it has dissolved, the solution is titrated to the end point. Volume of reagent is entirely dependent on the water content of test sample. Methanol merely balances the Aquameter to zero water content and this volume is irrelevant to the moisture determination. The moisture content is calculated as follows:

% moisture =

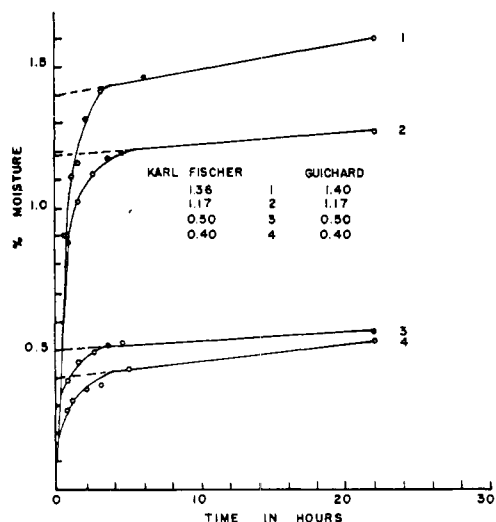$$\frac{(\text{ml. K.F. reagent}) (\text{titer})}{\text{sample weight}} \quad (100)$$



KARL FISCHER | GUICHARD
1.36 | 1 | 1.40
1.17 | 2 | 1.17
0.50 | 3 | 0.50
0.40 | 4 | 0.40

**Figure 1. Moisture in ammonium nitrate**

## Table I. Prill Uniformity

| Sample Number | Vial A[a] | | | Vial B | | |
|---|---|---|---|---|---|---|
| | Sample wt. | H₂O by K.F., % | | Sample wt. | H₂O by K.F., % | |
| 1 | 3.020 | 0.30 | (0.29) | 3.139 | 0.31 | (0.31) |
| 2 | 3.174 | 0.29 | (0.29) | 3.290 | 0.26 | (0.27) |
| 3 | 3.041 | 0.36 | (0.34) | 3.221 | 0.36 | (0.36) |
| 4 | 3.166 | 0.41 | (0.41) | 3.307 | 0.42 | (0.43) |
| 5 | 3.254 | 0.28 | (0.28) | 3.297 | 0.27 | (0.27) |
| 6 | 3.125 | 0.34 | (0.34) | 3.246 | 0.30 | (0.30) |
| 7 | 3.187 | 0.20 | (0.20) | 3.264 | 0.24 | (0.25) |
| 8 | 3.114 | 0.36 | (0.35) | 3.249 | 0.39 | (0.39) |
| 9 | 3.246 | 0.29 | (0.30) | 3.314 | 0.26 | (0.27) |
| 10 | 3.106 | 0.34 | (0.33) | 3.229 | 0.33 | (0.34) |
| 11 | 3.161 | 0.31 | (0.31) | 3.270 | 0.29 | (0.30) |
| 12 | 3.195 | 0.33 | (0.33) | 3.251 | 0.34 | (0.35) |
| 13 | 3.143 | 0.35 | (0.34) | 3.295 | 0.37 | (0.38) |
| 14 | 3.029 | 0.35 | (0.33) | 3.074 | 0.36 | (0.35) |
| 15 | 3.155 | 0.35 | (0.35) | 3.321 | 0.36 | (0.38) |
| 16 | 3.134 | 0.31 | (0.31) | 3.249 | 0.30 | (0.30) |
| 17 | 3.121 | 0.40 | (0.39) | 3.231 | 0.37 | (0.38) |
| 18 | 3.129 | 0.29 | (0.29) | 3.305 | 0.29 | (0.30) |
| 19 | 3.190 | 0.32 | (0.32) | 3.288 | 0.31 | (0.32) |
| 20 | 3.141 | 0.23 | (0.23) | 3.186 | 0.22 | (0.22) |

| | |
|---|---|
| Average sample weight, grams | 3.196 |
| Minimum sample weight (vial A, sample 1), grams | 3.020 |
| Weight error, % | 5.8 |
| Maximum sample weight (vial B, sample 15), grams | 3.321 |
| Weight error, % | 3.8 |

[a] Values in parentheses are the % moisture as calculated from average sample weight.

In all titrations care must be taken to eliminate, as much as possible, any air contact with the titrating solution.

The subsequent discussion describes a volumetric method for sampling that eliminates sample weighing.

## Discussion

The Karl Fischer titration was studied both with regard to accuracy and to the time per analysis. The range of interest in this problem was from 0.0 to 1.0% water with an accuracy within ±0.05%. The accuracy of this method was determined by a drying experiment similar to that used by Guichard (7). The samples were dried in a vacuum oven at 60° C. for an extended period of time. Periodically these samples were weighed to determine weight loss. The drying curves so obtained are shown in Figure 1. The flat portion of these curves represents the decomposition of ammonium nitrate. Theoretically, when this is extrapolated to zero time, the absolute moisture content of the sample is obtained. As may be seen from the inset, the Karl Fischer value is in excellent agreement with the extrapolated value.

The time for an analysis by the Karl Fischer titration was shortened by the elimination of weighing. A simple calculation shows that a weighing error as much as 5% may be tolerated. For example, with a sample that has a moisture content of 1%, a 5% weighing error would introduce an error of only ±0.05% in the moisture content. For this reason volumetric measurements of the prills were made rather than conventional analytical weighings.

To illustrate the consistency of volume measurement, 20 samples were taken individually in three 15 × 45 mm. screw-cap vials and weighed. No special precautions were taken in filling them other than filling them level with the top each time and screwing the plastic lid back on. Random packing was used throughout; no tapping or pressing was done. Once the samples had been weighed, the moisture content was determined on the Aquameter.

Table I shows the results of this experiment. The values in parentheses are the per cent moisture as calculated from the average sample weight. In no instance do the values in parentheses vary more than ±0.02 unit from the true value. As seen from this table, the observed maximum and minimum sample weights resulted in an average weight error of about 5.0%. A similar experiment was performed with 20 vials and three different samples to check vial uniformity. Again the average maximum and minimum weight error was no greater than 5.0%. With weighing eliminated, the time for one analysis is approximately 5 minutes.

## Literature Cited

(1) Guichard, M., Compt. rend. 215, 20 (1942).
(2) Jensen, F. W., Kelly, M. J., Burton, M. B., Jr., Anal. Chem. 26, 1716 (1954).