



Determination of Moisture of Fertilizers

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Executive Summary

The IFA Method Harmonization Working Group's evaluation of analysis methods to determine "Moisture" content in fertilizers has determined that the following methods can be considered to be preferred or best practice methodology for use in international commercial fertilizer trade.

- Karl Fischer for Nitrogen and Potassium based Fertilizers.
- Low Temperature Vacuum Gravimetric for Phosphorus and Potassium Chloride based Fertilizers.

The following are deemed to be the determining factors in developing this recommendation for bulk shipments of fertilizers:

Karl Fischer

- The method is the globally recognized official method for use with nitrogen and potassium commercial fertilizers.
- This methodology has been proven to be statistically-sound, yielding precise and accurate results repeatedly and consistently.
- The method has been determined to be fast, relatively simple cost-effective and requires only moderately expensive laboratory equipment.
- The method is the only approved direct measurement technique where water molecules are titrated to an end point.
- The method would be used in an arbitration case where moisture content of nitrogen and potassium fertilizers is in dispute.

Gravimetric

- Low Temperature Gravimetric methods are commonly used to accurately analyze phosphate type fertilizers (EN 12049, AOAC 965.08B and GOST 14879-77).
- Methods are officially recognized for use.
- In phosphate fertilizers low temperature is required to prevent volatilization of non water molecules and waters of hydration.
- This methodology has been proven to be statistically-sound, yielding precise and accurate results repeatedly and consistently.
- The method has been determined to be fast, relatively simple cost-effective and requires only moderately expensive laboratory equipment.
- The method would be used in an arbitration case where moisture content of phosphate or potassium chloride fertilizers is in dispute.

Determination of Moisture in Fertilizers

1. Introduction

Moisture content is one of the most commonly measured properties of fertilizers. It is important to customers, manufacturers, regulatory officials, formulators, and farmers for a number of different reasons:

- *Legal and Labeling Requirements.* There are legal limits to the maximum or minimum amount of water that must be present in certain types of fertilizer.
- *Economic.* The grade of many fertilizers depends on the amount of water they contain.
- *Quality of Product.* Significant product quality issues will arise if moisture levels in fertilizers exceed manufacturer recommended levels.

It is therefore important for analysts to be able to reliably measure moisture content. A number of analytical techniques have been developed for this purpose, which vary in their accuracy, cost, speed, sensitivity, specificity, ease of operation, etc. The choice of an analytical procedure for a particular application depends on the nature of the fertilizer being analyzed and the reason the information is needed.

The most important techniques developed to measure the moisture content are discussed below and summarized in **Appendix I**.

2. Water in Fertilizer

A number of analytical techniques commonly used to determine the moisture content of fertilizers are based on direct and indirect determinations of the mass of water present in a known mass of sample.

Historically indirect moisture analysis was done by evaporation/gravimetric methods. These methods presented a number of practical problems that made highly accurate, timely determinations of moisture content difficult and limited their use for certain applications. To address these issues, a number of analytical methods were developed to measure the moisture content of specific fertilizers under vacuum and low temperature. AOAC method 965.08 was developed to address these issues. The method uses a combination of low temperature, vacuum and time to remove surface water from fertilizer samples.

In 1935 a classical titration, direct method was introduced. The early Karl Fischer methods involved handling and preparation of hazardous, volatile organic solvents with pungent odours. The method was also complex with various hoses and tubes to contain the reagents and exclude outside sources of moisture. As such the method was relegated to those most in need – namely the nitrogen fertilizer industry. With advances in electronics and simplification of reagents the Karl Fischer method re-emerged as a viable cost effective direct measurement technique used in both Nitrogen and Potassium fertilizer labs.

Phosphate based fertilizers are more complex and contain waters of hydration that would be extracted and analyzed, giving an erroneously high result. In addition some phosphate compounds and or coatings may react with the Karl Fischer Reagents. As such the low temperature vacuum gravimetric method is recommended for phosphate fertilizers.

Most of these methods are described in section 4 and 5 of this report.

3. Terms of Reference Moisture

Despite having the same chemical formula (H₂O) the water molecules in a fertilizer may be present in a variety of different molecular environments depending on their interaction with the surrounding molecules. The water molecules in these different environments normally have different physicochemical properties. These properties, as described by various regulatory bodies, are summarized in **Table 1**.

Table 1. Terms of Reference Moisture.

European	North American
<p>3.1 Essential water – water in stoichiometric quantities, that forms an integral part of the molecular or crystal structure.</p> <p>3.2 Water of crystallisation. essential water present in a stable solid hydrate</p> <p>3.3 Water of constitution essential water that is released when the solid decomposes.</p>	<p><i>Chemically bound water.</i> Some of the water molecules present in a fertilizer may be chemically bonded to other molecules as water of crystallization or as hydrates, e.g. CaSO₄.2H₂O. These bonds are much stronger than the normal water-water bond and therefore chemically bound water has very different physicochemical properties to bulk water, e.g., lower melting point, higher boiling point, higher density, lower compressibility, higher heat of vaporization, different electromagnetic absorption spectra.</p>
<p>3.4 Non-essential water – water in non-stoichiometric quantities, that is retained as a consequence of physical forces.</p>	<p><i>Physically bound water.</i> A significant fraction of the water molecules in many fertilizers are not completely surrounded by other water molecules, but are in molecular contact with other constituents. The bonds between water molecules and these constituents are often significantly different from normal water-water bonds and so this type of water has different physicochemical properties than bulk water e.g., melting point, boiling point, density, compressibility, heat of vaporization, electromagnetic absorption spectra.</p>
<p>3.5 Adsorbed water non-essential water that is retained on the surface of solids in a humid environment.</p> <p><i>NOTE: The amount of water that is adsorbed depends on the fertilizer type, humidity, temperature and the specific surface area of the solid</i></p> <p><i>The term "free water" is often used to describe non-essential water and best correlates to the physical properties and bulk behaviour.</i></p>	<p><i>Bulk water.</i> Bulk water is free from any other constituents, so that each water molecule is surrounded only by other water molecules. It therefore has physicochemical properties that are the same as those of pure water, e.g., melting point, boiling point, density, compressibility, heat of vaporization, electromagnetic absorption spectra. Bulk water/moisture can also be broken into crude moisture on un-ground samples and free moisture on ground samples (where "crude moisture" determination as being surface moisture of unground product).</p> <p>Hydroscopic moisture (also known as "residual moisture" or "moisture in the general analysis sample") and this moisture is normally determined by drying a portion of the test sample at about 104°C for a designated period in a designated crucible.</p>

3.6 Absorbed water non-essential water that is held as a condensed phase in the capillaries of the solid.

3.7 Occluded water - liquid water entrapped in microscopic pockets throughout solid crystals.

NOTE: The quantity contained in the solid is greatly dependent upon temperature and humidity.

Capillary or trapped water. Capillary water is held in narrow channels between certain material components because of capillary forces. Trapped water is held within spaces within a granule that are surrounded by a physical barrier that prevents the water molecules from easily escaping, e.g., encapsulated slow release granule or a coating for dust control. The majority of this type of water is involved in normal water-water bonding and so it has physicochemical properties similar to that of bulk water.

Fertilizers can be heterogeneous materials that contain different proportions of chemically bound, physically bound, capillary, trapped or bulk water. In addition, fertilizers may contain water that is present in different physical states: gas, liquid or solid. The fact that water molecules can exist in a number of different molecular environments, with different physicochemical properties, can be problematic for the analyst trying to accurately determine the moisture content. Many analytical procedures developed to measure moisture content are more sensitive to water in certain types of molecular environment than to water in other types of molecular environment. This means that the measured value of the moisture content of a particular fertilizer may depend on the experimental technique used to carry out the measurement. Sometimes analysts are interested in determining the amounts of water in specific molecular environments (e.g., physically bound/non essential water), rather than the total water content.

4. Sample Preparation

Selections of a representative sample, and prevention of changes in the properties of the sample prior to analysis, are two major potential sources of error in any fertilizer analysis procedure. When determining the moisture content it is important to prevent any loss or gain of water. For this reason, exposure of a sample to the atmosphere, and excessive temperature fluctuations, should be minimized. When samples are stored in containers it is common practice to fill the container to the top to prevent a large headspace, because this reduces changes in the sample due to equilibration with its environment.

Commercial fertilizer samples can be analyzed for moisture on the ground or un-ground sample. Although un-ground analysis minimizes the potential for moisture uptake or loss during handling and grinding, some minimal precautions while grinding can prevent moisture loss/uptake or sample degradation while still generating comparable results.

The low temperature vacuum gravimetric method yields crude moisture data for un-ground and free moisture data on ground samples (where crude moisture" determination as being surface moisture of unground product). The Karl Fischer method gives total moisture on both un-ground and ground samples.

5. Evaporation (Indirect) Methods

These methods rely on measuring the mass of water in a known mass of sample. The moisture content is determined by measuring the mass of a sample before and after the water is removed by evaporation:

$$\% \text{Moisture} = \frac{M_{\text{INITIAL}} - M_{\text{DRIED}}}{M_{\text{INITIAL}}} \times 100$$

To obtain an accurate measurement of the moisture content or total solids using evaporation methods it is necessary to remove all of the adsorbed water molecules that were originally present without changing the mass of the matrix. This is often extremely difficult to achieve in practice because the high temperatures or long times required to remove all of the water molecules would lead to changes in the mass of the matrix, *e.g.*, due to volatilization or chemical changes of some components. For this reason, the drying conditions used in evaporation methods are usually standardized in terms of temperature and time so as to obtain results that are as accurate and reproducible as possible given the practical constraints. Some methods employ low temperature and vacuum to assist in removal of surface water only.

Using a standard method of sample preparation and analysis helps to minimize sample-to-sample variations within and between laboratories.

5.1 Evaporation/Gravimetric Methods

The thermal energy used to evaporate the water from a sample can be provided directly (*e.g.*, transfer of heat from an oven to) or indirectly (*e.g.*, conversion of electromagnetic radiation incident upon a sample into heat due to absorption of energy by the water molecules). A few of these methods are described below. Care should be taken with samples that contain volatile materials other than water.

Convection and forced draft ovens. Samples are placed in an oven for a specified time and temperature (*e.g.* 2 hours at 105°C) and their dried mass are determined, or they are dried until they reach constant mass. Due to the elevated temperature and risk of sample decomposition, samples that contain significant quantities of nitrogen based fertilizers should not be dried in convection or forced draft ovens at these temperatures.

Vacuum oven. Weighed samples are placed under reduced pressure (typically 25-100 mm Hg) in a vacuum oven for a specified time and temperature and their dried mass is determined. Lower temperatures can be used to remove the moisture (*e.g.* 50°C instead of 100°C), and so problems associated with degradation of heat labile substances can be reduced.

Microwave oven. Weighed samples are placed in a microwave oven for a specified time and power-level and their dried mass is weighed. Alternatively, weighed samples may be dried until they reach a constant final weight. The major advantage of microwave methods over other drying methods is that they are simple to use and rapid to carry out. Nevertheless, care must be taken to standardize the drying procedure and ensure that the microwave energy is applied evenly across the sample.

Infrared lamp drying. The sample to be analyzed is placed under an infrared lamp and its mass is recorded as a function of time. One of the major advantages of infrared drying methods is that moisture contents can be determined rapidly using inexpensive equipment, *e.g.*, 10-25 minutes. IR drying methods are not officially recognized for moisture content determinations because it is difficult to standardize the procedure. Even so, it is widely used in industry because of its speed and ease of use.

Although many official methods of analysis are based on the above indirect methods, these methods typically restrict their use for samples that contain volatile materials other than water.

5.2 Advantages and Disadvantages of Evaporation/Gravimetric Methods

Advantages:

- Relatively cheap.
- Easy to use.
- Officially sanctioned at low temperature and vacuum.
- Many samples can be analyzed simultaneously.

Disadvantages: The outcome of these methods is inferred, as results are based on weight loss of water and possibly other unknown compound(s). The method can be:

- Can be thermally destructive and as such unsuitable for some types of fertilizers. **For example excess temperatures can release compounds other than water.**
- Time consuming, time for heating ranges from 2-5 hours.
- Most fertilizers require different drying temperatures. There is no one temperature for mixed fertilizers.
- No clear lines to define what waters are removed and what is remaining.
- The rate and extent of moisture removal depends on the size and shape of the sample, and how finely it is ground.
- In samples with high moisture content product tends to clump together or form a semi-permeable surface crust during the drying procedure. This can lead to erroneous and irreproducible results.

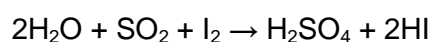
6. Chemical Reaction (Direct) Methods

Reactions between water and certain chemical reagents can be used for determining the concentration of moisture in fertilizers. In these methods a chemical reagent is added to the fertilizer that reacts specifically with water to produce a measurable change in the properties of the system, e.g., mass, volume, pressure, pH, color, conductivity. Measurable changes in the system are correlated to the moisture content using calibration curves. To make accurate measurements it is important that the chemical reagent reacts with all of the water molecules present, but not with any of the other components in the matrix. A method that is commonly used in the fertilizer industry is the *Karl-Fischer titration* method.

Chemical reaction methods do not usually involve the application of heat and so they are suitable for fertilizers that contain thermally labile substances.

6.1 Karl-Fischer Method

The Karl-Fischer titration is often used for determining the moisture content of fertilizers that have low water contents. It is based on the following reaction:



This reaction was originally used because HI is colorless, whereas I₂ is a dark reddish brown color, hence there is a measurable change in color when water reacts with the added chemical reagents. Sulfur dioxide and iodine are gaseous and would normally be lost from solution. For this reason, the above reaction has been modified by adding solvents (e.g., C₅H₅N) that keep the SO₂ and I₂ in solution, although the basic principles of the method are the same. The fertilizer to be analyzed is placed in a beaker containing solvent and is then titrated with *Karl Fischer reagent* (a solution that contains iodine).

While any water remains in the sample the iodine reacts with it and the solution remains colorless (HI), but once all the water has been used up any additional iodine is observed as a dark red brown color (I₂). The volume of iodine solution required to titrate the water is measured and can be related to the moisture content using a pre-prepared calibration curve. The precision of the technique can be improved by using electrical methods to follow the end-point of the reaction, rather than observing a color change. Relatively inexpensive commercial instruments have been developed which are based on the Karl-Fischer titration, and some of these are fully automated to make them less labor intensive.

6.2 Advantages and Disadvantages of Karl Fischer Method

Advantages:

- Relatively cheap; Officially sanctioned for many applications; Many samples can be analyzed sequentially.
- Samples that contain volatile materials other than water can be analyzed using this technique.
- The direct H₂O measurement method would be easier to defend in arbitration.
- Method is specific to water.

Disadvantages:

- More complex.
- Requires more elaborate lab equipment.
- Some hazardous chemicals used.
- Extractant needs to be specific for the fertilizer to be analyzed.
- Sealed titration chambers required to reduce analyst exposure.
- Phosphate compounds and or coatings may react with the Karl Fischer Reagents.
- Sulphur coatings on sulphur coated urea may react with the Karl Fischer Reagents.

7. Summary and Conclusions

Based on the findings of this report, two methods are recommended for the analysis of moisture in fertilizers. The Karl Fischer method is recommended for surface water analysis on Nitrogen and Potassium based bulk commercial fertilizers. The low temperature vacuum gravimetric method is recommended for surface water analysis on Phosphate based bulk commercial fertilizers.

- The Low temperature vacuum gravimetric method would be used in an arbitration case where moisture content in Phosphate or Potassium Chloride based fertilizer is in dispute.
- The Karl Fischer method would be used in an arbitration case where moisture content in Nitrogen and Potassium based fertilizers is in dispute.
- The Karl Fischer method is the only approved direct measurement technique where water molecules are titrated to an end point.
- Both methods are:
 - Recognized official methods for use with commercial fertilizer. The methods are accepted in NA, Europe, Russia, India, China, Africa and South America.
 - Have been proven to be statistically-sound, yielding precise and accurate results repeatedly and consistently.
 - Determined to be fast, relatively simple cost-effective and requires only moderately expensive laboratory equipment.

Appendix I. Existing Standard Methods.

Method	Regulatory Agency	Applicable to (for example)	Not applicable to	Forms of Water
Thermo-gravimetric at ca 65-100 C	EN 12048 AOAC 950.01 AFPC IX, No. 2 GOST 20851.4-75 P1 ES ISO 8190-2001 SPPA	-solid siliceous liming materials - solid carbonic liming materials - potassium chloride - solid phosphatic fertilizers of type: * super phosphate * natural phosphates *ground phosphates *partially solublized rock phosphates	- hydrated or burnt lime - ammonium compounds - magnesium sulphates - fertilizer containing volatiles other than water – excludes fertilizers with organic coatings	Not defined
Vacuum Thermo-gravimetric at ca 25 C	EN 12049 AOAC 965.08A GOST 20851.4-75 P1 ES ISO 8189-2001	Mono-ammonium phosphate, di-ammonium phosphate, potassium chloride	Fertilizers and liming materials containing: *Calcium nitrate *calcium hydroxide * calcium sulphate containing less than two molecules of crystal water *magnesium sulphate containing one to seven molecules of crystal water *salts which effloresce readily at ambient temperatures or which absorb water	Not defined
Vacuum Thermo-gravimetric at ca 50 C	EN 12049 AOAC 965.08B GOST 14879-77	Mono-ammonium phosphate, di-ammonium phosphate, potassium chloride	Fertilizers and liming materials containing: *Calcium nitrate *calcium hydroxide * calcium sulphate containing less than two molecules of crystal water *magnesium sulphate containing one to seven molecules of crystal water *salts which effloresce readily at ambient temperatures or which absorb water	Not defined
Karl Fischer Methanol extraction	EN 13466-1 GOST 20851.4-75 P4 GOST 14870-77 ES ISO 8190-2001 SPPA	All solid mineral fertilizers except Mono-ammonium phosphate, di-ammonium phosphate	Possible interferences with product treatment coatings	Includes “free water” and extracted water of crystallization of a number of components possibly present in fertilizers

Method	Regulatory Agency	Applicable to (for example)	Not applicable to	Forms of Water
Karl Fischer Propanol extraction	EN 13466-2	All solid mineral fertilizers except Mono-ammonium phosphate, di-ammonium phosphate	Possible interferences with product treatment coatings	Includes “free water” and extracted water of crystallization of a limited number of components, possibly present in fertilizers
Karl Fischer Dioxane Extraction	AOAC 972.01	All solid mineral fertilizers except Mono-ammonium phosphate, di-ammonium phosphate	Possible interferences with product treatment coatings	Includes “free water” and extracted water of crystallization of a limited number of components, possibly present in fertilizers