WHITE PAPER

Multiparameter analysis in fertilizers: Fast and easy via thermometric titration

Estimates show that approximately half of the world's population could not be supported without the usage of fertilizers [1]. Agriculture at significant scale without fertilizers is thus no longer possible in the modern world.

To grow a sufficient amount of produce for nearly 8 billion people as well as for domesticated animals and industrial uses, fertilizers of different nutrient compositions are available to cater to the unique needs of various soil types. To select the ideal fertilizer for a specific soil, information on the fertilizer's composition (e.g., total nitrogen, phosphorus, and potassium) is given.

Conventionally these constitutents are determined either gravimetrically (e.g., phosphorus, potassium, or sulfate) [2–4] or with ICP-OES (e.g., phosphorus or potassium) [5]. These methods either have the disadvantages of long analysis times combined with laborious sample preparation (gravimetry), or require expensive instrumentation with high running costs (ICP-OES).

This White Paper elaborates how thermometric titration is a fast and inexpensive alternative method to provide information on the content of various nutrients in different fertilizers.

Metrohm

FERTILIZER COMPOSITION FOR DIFFERENT NEEDS

The main nutrients in fertilizers, known as «macronutrients», are nitrogen, phosphorus and potassium. Other nutrients are «secondary macronutrients» (e.g., sulfur) or «micronutrients» (e.g., boron). Macronutrients in particular are essential in particular for plants, as they are needed for leaf growth, development of seeds and fruits, and for water transport within the plant.

Fertilizers are most often classified by their nutrient composition. Besides single nutrient or straight fertilizers (e.g., ammonium nitrate or single superphosphate), multi-nutrient fertilizers consisting of two or more nutrients are common, such as mono- and di-ammonium phosphate (MAP and DAP) or NPK (nitrogen-phosphate-potassium) fertilizers.

Aside from classification according to their nutrients, fertilizers can also be categorized into «inorganic mineral fertilizers» and «organic fertilizers» [2]. Organic fertilizers, as their name implies, consist of organic matter derived from plants and/or animals, such as dung. In contrast, inorganic fertilizers do not contain carbon-based materials, with the exception of urea. This white paper will focus mainly on inorganic fertilizers.

CONVENTIONAL DETERMINATION OF NUTRIENT COMPOSITION

Regardless of the fertilizer composition, it is important to know about the nutrient content. Without this information, too much fertilizer might be distributed to plants, resulting in undesirable fertilizer burns and environmental pollution. Fertilizer producers are therefore required to specify the amount of nutrients within their products, and various norms from **ISO**, **EN**, and **AOAC** exist for the standardized determination of these nutrients.

However, some of the proposed analysis techniques are very time-consuming, or the methods require expensive equipment. For example, potassium, phosphorus, and sulfur are usually determined gravimetrically or by using ICP-OES. Meanwhile, Kjeldahl digestion is usually required to determine nitrogen components with a subsequent acid-base titration.

Thermometric titration provides an inexpensive alternative solution for the analysis of potassium, phosphorus, sulfur, ammoniacal nitrogen, and urea without any time-consuming steps. Before elaborating on the analysis of these specific nutrients by thermometric titration, the general principle of thermometric titration is presented.

PRINCIPLE OF THERMOMETRIC TITRATION

Titration is an established analysis method, where the content of a species (analyte) is determined by adding a reagent solution (titrant) which reacts stoichiometrically with the analyte. By determining the required titrant volume for the reaction, the analyte content can be reliably determined. The required titrant volume can be determined using a suitable indication method.

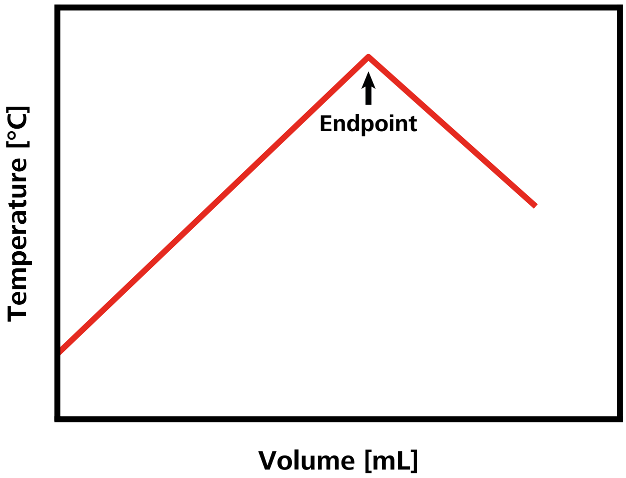

Figure 1. Idealized titration curve for an exothermic titration reaction. In this example, as long as analyte is present, the temperature increases with the titrant addition. When all analyte is consumed, the temperature decreases again as the solution equilibrates with the atmospheric temperature and/or due to the dilution of the solution with titrant. This temperature decrease results in an exothermic endpoint.

Thermometric titration uses the principle of the reaction enthalpy to indicate the endpoint of the titration. Titrant and analyte react with each other either exothermically (increase in temperature) or endothermically (decrease in temperature). When the titrant is added at a constant rate, the temperature in the titration vessel increases or decreases also at a constant rate. When the endpoint of the titration is reached, heat is no longer produced nor consumed, and a sharp break in the temperature curve can be observed, indicating the reaction endpoint (Fig. 1) [3].

Thermometric titrations use a thermistor, able to detect the smallest temperature change, to indicate the endpoint of a titration (Fig. 2). These sensors are capable of measuring temperature differences of less than 0.001 °C, and allow the collection of a measuring point every 0.3 seconds. In comparison to other sensors used in titration, they are nearly maintenance-free and can be used to determine various analytes. In the next section, the applicability of thermometric titration for the analysis of various nutrients in fertilizers will be demonstrated.

Figure 2. The Metrohm Thermoprobe is capable of measuring temperature changes of less than 0.001 °C, and allows the collection of a measuring point every 0.3 seconds.

APPLICABILITY OF THERMOMETRIC TITRATION FOR FERTILIZERS

– PHOSPHORUS

Phosphorus in fertilizer is usually present as phosphate. Being a macronutrient, it is not only present in multi-nutrient fertilizers (e.g., DAP, MAP, and NPK-fertilizers), but also as straight fertilizer in the form of superphosphates.

Historically, total phosphorus content is measured by gravimetric analysis. Alternatively, spectrophotometric analysis or ICP-OES may be used for the determination. These methods all require time-consuming sample preparation steps or regular calibrations.

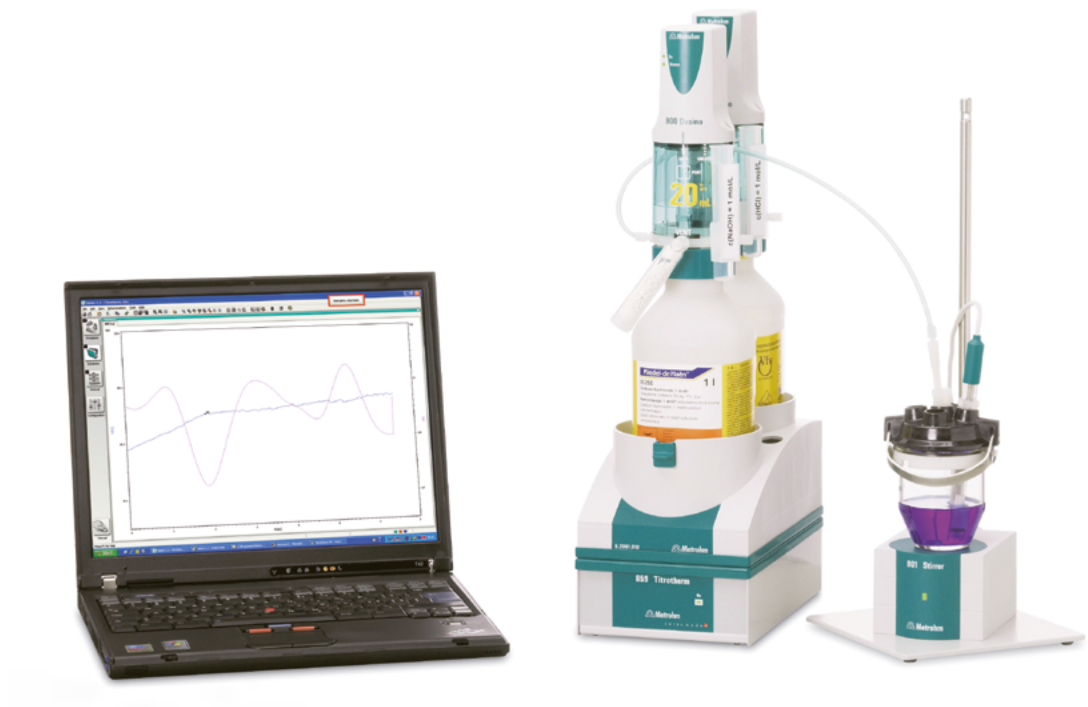

Figure 3. Thermometric titration system consisting of a Metrohm 859 Titrotherm equipped with a Thermoprobe for the indication and two 800 Dosinos for the titrant and addition of auxiliary solution. The system is controlled via the Metrohm ***tiamo***™ software.

The thermometric titration is based on the exothermic formation of insoluble struvite ($MgNH_4PO_4 \cdot 6\,H_2O$) in alkaline media according to the following reaction equation:

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} \longrightarrow MgNH_4PO_4$$

For the titration, magnesium nitrate is used as titrant in an alkaline NH_3/NH_4Cl buffer solution. The titration is thus an adoption of a classical gravimetric procedure. However, using thermometric titration, results for the phosphate content can be obtained within 5 minutes without any additional steps such as filtering, washing and drying.

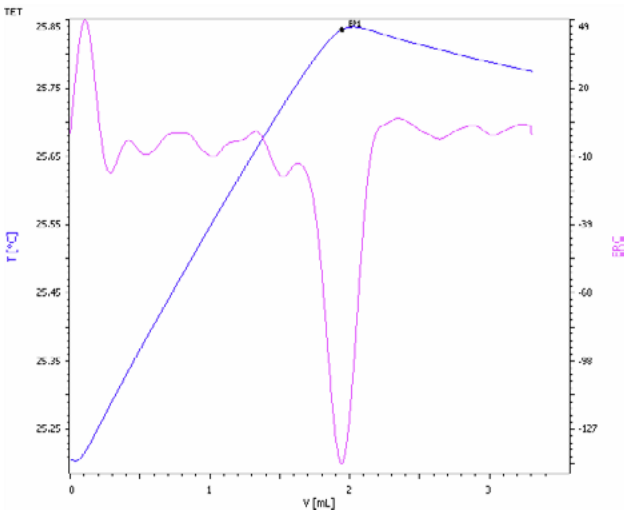

Figure 4. Exothermic titration curve of the phosphate determination in an NPK fertilizer by precipitation with magnesium ions in the presence of an ammonia/ammonium chloride buffer (blue = titration curve, pink = second derivative showing the endpoint).

Another important parameter in the phosphoric acid manufacturing process is the ratio of $H_2PO_4^{-}$ and HPO_4^{2-}. In a potentiometric acid-base titration, it usually not possible to distinguish these two species because of the leveling effects of water. However, thermometric titration is not restricted by this problem. Therefore, it is possible to simply determine the ratio using sodium hydroxide as titrant. If phosphoric acid is titrated, it becomes possible to observe all three endpoints (Fig. 5).

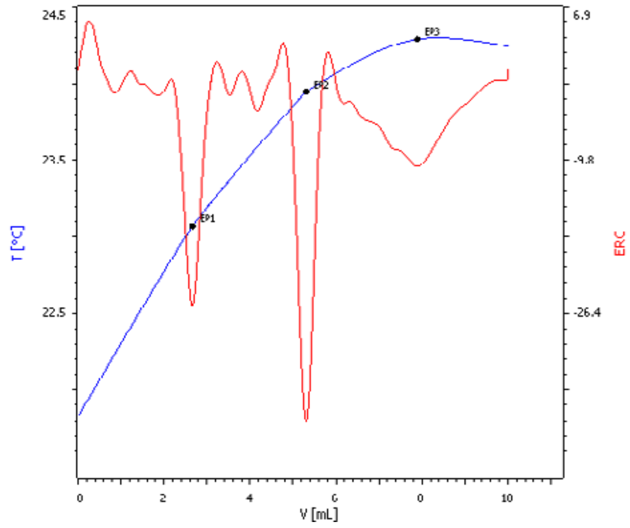

Figure 5. Exothermic titration curve of phosphoric acid titrated with NaOH. Here, all three deprotonation steps can be clearly distinguished (blue = titration curve, red = second derivative showing the endpoints).

– POTASSIUM

Potassium is a primary macronutrient for plants, as it plays an important role in water regulation as well as plant growth. For this reason, it is available as a straight fertilizer in the form of potash, as well as in multi-nutrient fertilizers such as potassium dihydrogen phosphate (MKP) or NPK fertilizers.

Traditionally, potassium is determined gravimetrically. More recently, ICP-OES or flame photometry is used. Using the precipitation reaction of potassium with sodium tetraphenyl borate (STPB), potassium can also be determined by titration.

A reliable determination of potassium using thermometric titration gives a result in approximately 5 minutes. Because of this benefit as well as the low costs per analysis and minimal sample preparation, this titration method is already incorporated into the Chinese recommended professional standard **HG/T 2321** on the analysis of fertilizer grade potassium dihydrogen phosphate [6].

If the fertilizer contains ammonium, this must be removed as ammonia prior to the titration, as it would otherwise precipitate concurrently with STPB and therefore interfere with the determination.

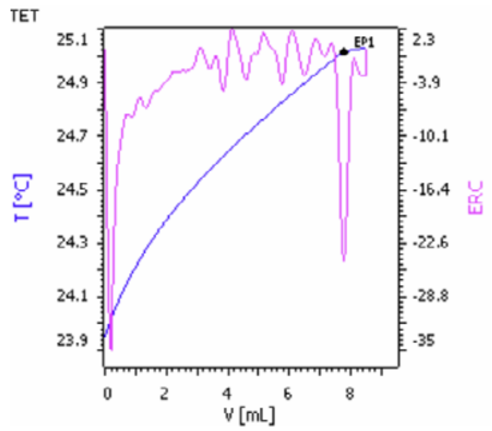

Figure 6. Exothermic titration curve of the potassium determination in potash by precipitation with STPB (blue = titration curve, pink = second derivative showing the endpoint).

– SULFATE

Sulfur is a secondary macronutrient for plants and is essential for chloroplast growth and function. In fertilizers, sulfur is usually provided in the form of sulfate. It is also present during the wet phosphoric acid production process. For an optimal production process, the sulfuric acid content within phosphoric acid as well as within final products (e.g., MAP, DAP, TSP, and NPK fertilizers) should be known.

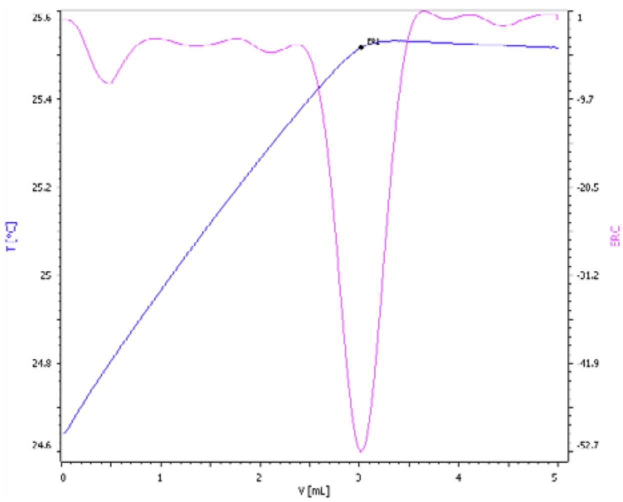

Figure 7. Exothermic titration curve of the sulfate determination in a NPK fertilizer spiked with sulfuric acid for enhanced method sensitivity (blue = titration curve, pink = second derivative showing the endpoint).

Sulfate content is conventionally determined gravimetrically by precipitation with barium. The same reaction principle is used for the thermometric titration and results can be obtained within 3 minutes, with only minimal sample preparation.

To increase the sensitivity of the method, the samples can be spiked with a standard sulfuric acid solution, which is then considered when calculating the result. Calcium (e.g., from CAN fertilizers) can interfere with this determination by forming insoluble calcium sulfate. It therefore must either be removed prior to the titration using cationic exchange resins, or precipitated with excess oxalate.

– AMMONIACAL NITROGEN AND UREA

Nitrogen is the third significant macronutrient which plants require, and represents by far the largest product group of fertilizers. Nitrogen in fertilizers can be present in several forms including ammonium, nitrate, or urea.

Ammonia is usually determined after alkaline distillation by acid-base back-titration, while other nitrogen species are usually first converted to ammonia by digestion prior to analysis. For the thermometric titration, a different approach is used to determine ammonia content. Ammonium ions react exothermically with hypochlorite in a redox reaction. This reaction is further catalyzed in the presence of bromide ions in slightly alkaline solution, where the more reactive species hypobromite is formed, which then reacts with ammonium to form nitrogen.

$$3\ OCl^- + 3\ Br^- \longrightarrow 3\ OBr^- + 3\ Cl^-$$

$$2\ NH_3 + 3\ OBr^- \longrightarrow N_2 + 3\ Br^- + 3\ H_2O$$

$$3\ OCl^- + 2\ NH_3 \longrightarrow N_2 + 3\ Cl^- + 3\ H_2O$$

This titration approach allows results after an analysis time of 2 minutes without any prior distillation step.

Among straight fertilizers which contain nitrogen, urea has the highest nitrogen concentration. Urea is produced from ammonia and carbon dioxide. The production process is influenced by the amount of ammonia present. During the process, it is thus necessary to know the ratio of ammonia and urea present [7].

With the aforementioned titration approach for ammoniacal nitrogen, it is possible to not only determine ammoniacal nitrogen in the sample, but also urea as well. This is possible due to the fact that urea also reacts with hypobromite, but with a slower reaction rate. Using an appropriate dosing rate of titrant, separation of ammonium and urea content in a single titration becomes possible. For a better separation of both endpoints, the fertilizer can be spiked with some urea.

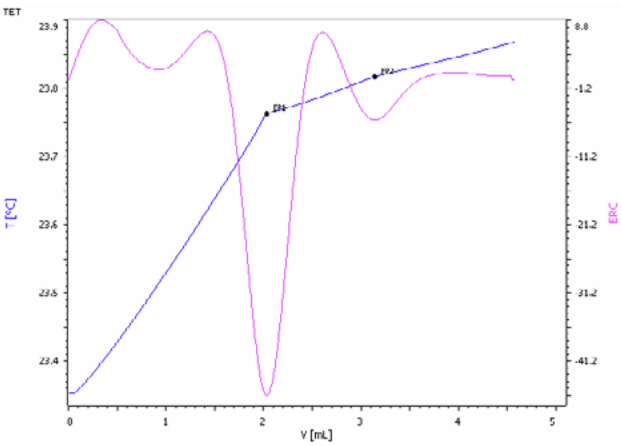

Figure 8. Exothermic titration curve of the ammoniacal nitrogen and urea determination in a NPK fertilizer. The first endpoint corresponds to the ammonia and the second to urea (blue = titration curve, pink = second derivative showing the endpoint).

THERMOMETRIC TITRATION: THE IDEAL SOLUTION TO ANALYZE FERTILIZERS

Thermometric titration is an inexpensive alternative method to analyze the key substances within fertilizers, or during their production processes. Furthermore, time-consuming sample preparation and analysis steps can be omitted, enabling analysts to obtain results within minutes. This in turn allows plant operators to more quickly optimize process settings. This greatly improves the efficiency of the production plants, while at the same time liberating chemists and lab technicians to carry out other tasks.

Further related Metrohm literature

This section contains a list of further in-depth Metrohm literature on the analysis of fertilizers by thermometric titration with more detailed analysis procedures. They can be found for free to download at **www.metrohm/com/applications**.

LIQUID PHOSPHORIC ACID

Application Bulletin AB-308

Determination of sulfate in phosphoric acid (liquid fertilizer samples) with 859 Titrotherm

Application Bulletin AB-316

Determination of phosphoric acid in liquid fertilizer with 859 Titrotherm

Application Bulletin AB-314

Determination of total phosphate in phosphoric acid and phosphate fertilizers with 859 Titrotherm

Application Note AN-H-116

Determination of sulfate in phosphoric acid through the standard addition of sulfuric acid

PHOSPHATE FERTILIZERS

Application Bulletin AB-307

Determination of sulfate in granular phosphate fertilizers with 859 Titrotherm

Application Bulletin AB-314

Determination of total phosphate in phosphoric acid and phosphate fertilizers with 859 Titrotherm

Application Note AN-H-008

Determination of phosphate by magnesium titration

Application Note AN-H-071

Determination of ammonium ions by titration with hypochlorite

NPK FERTILIZERS

Application Note AN-H-035

Phosphate in fertilizers – Rapid and reliable determination by thermometric titration

Application Note AN-H-145

Sulfate in fertilizers – Rapid and reliable determination by thermometric titration

Application Note AN-H-146

Ammonium and urea nitrogen in NPK fertilizers – Fast, simultaneous determination of both components by thermometric titration

Application Note AN-H-147

Potassium in fertilizers – Rapid and reliable determination by thermometric titration

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