



Review of Analytical Methods for Slow- and Controlled- Release Fertilizers

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Summary

The methods used for the analysis of slow- and controlled-release fertilizers are reviewed in this article. The methods are generally developed for nitrogen fertilizers, but some do have the potential to be used for other fertilizer elements. For slow release fertilizers like urea condensates, suitable methods are available to determine the amount of water insoluble nutrient by extraction methods or to determine the chemical composition by chromatographic techniques. For controlled release fertilizers, typically coated fertilizers, good testing methods for the initial release and release over time are available. Unfortunately, the “golden method” which enables fast screening of all materials and determines all the critical parameters does not exist. The proposed AOAC method by Medina, consisting of a sequential extraction cascade is a step into this direction, but still requires considerable time and effort to execute.

Review of Analytical Methods for Slow- and Controlled-Release Fertilizers

1. Introduction

The world population is growing rapidly and it reached 7 billion people in 2012. The Green Revolution enabled a steady increase in the yield per acre of farming land. Without a doubt, part of the increase was due to improved fertilization of arable land. The current prospect of larger population and changing diets calls for even more food and feed production. Coupled with an increased interest for biofuels and renewable sources for all kind of (agri) chemicals, it is clear that we will have to continue to increase agriculture production in a sustainable way (Sutton M.A., 2013). Also from a social and environmental perspective, there are clear limits to the amount of land that we can convert for agriculture purposes. Therefore, a further increase of the agriculture efficiency is needed. It is likely all available tools like better genetics of crops, integrated pest management, tailoring fertilizer use, and an efficient water use will be required to meet the challenging future demands.

The need for efficient fertilizer comes from multiple directions. Except for nitrogen, all the other nutrient sources are mined and limited in the amounts available. The limitations for phosphate are well known and estimations of the global reserves range typically in the order of a few hundred years (K. Salazar, 2013; Dawson & Hilton, 2011; European Commission, 2013). The second driver for efficient fertilizer use is that fertilizers can create pollution of soils, surface and ground water by overuse and/or adverse climatological conditions. Runoff to the surface water can cause eutrophication of rivers and coastal zones. Furthermore, high usage combined with high rainfalls can cause leaching to the groundwater. In some parts of the world, like in Europe, restrictions to fertilizer use are enforced. The fertilizer industry is endorsing best practices for the use of fertilizers and has defined the 4R principle: Use the right fertilizer, in the right dose, at the right place, and at the right time (IFA, 2009). Using adequate fertilization will enhance the security of food in the world. Another important driver for nutrient efficiency is a –potential- economic benefit for both farmers and consumers. Improved nutrient efficiencies lead to lower (operational) costs. Efficient fertilization is thus beneficial for people, planet, and profit, which in a general sense are the key considerations for sustainable growth.

In the search for highly efficient fertilization Slow- and Controlled-release fertilizers play an important role. Due to a vast amount of different products and testing methods an overview of the categories and testing method was required. In this paper we first discuss the aim and give some general background on different slow- and controlled-release fertilizers. Subsequently some general and more specific methods are described and some guidance how to analyses an unknown slow or controlled release sample is given. Finally we conclude with some recommendations.

1.1 Aim

Over the last decades new classes of fertilizers like slow- and controlled-release fertilizers have been developed. They are widely used in many different applications. Due to the plurality of the products and testing methods the IFA recognized the need to review the existing methods and develop a recommendation. Therefore, the IFA started a working group to report on the available methods and review their merits for testing slow- and controlled-release fertilizers.

There are many unpublished proprietary methods used by different manufacturers for either quality control or product development purposes. However, since there is no public record of these methods describing the principle, performance, and accuracy, we did not consider these methods in this review.

All slow- and controlled-release products have specific properties when applied to crops under certain conditions. There is no accepted test yet to compare the performance of a slow or controlled release fertilizer under the field conditions with a certain crop. In general, the producers of the products have done a considerable research and know exactly how and when to use a certain product. Furthermore, a wealth of knowledge is published in the literature. For this study, we concentrate on the published methods which are executed under controlled - laboratory- conditions.

1.2 Stabilized, slow- and controlled-release fertilizers

One of the methods for improving the efficiency of fertilizers is releasing the nutrients slowly over time. There are basically four different systems used nowadays: stabilizing agents for controlling the conversion of nutrients in the soil, nutrient sources which need to degrade before they are available to the plants, nutrient sources which are less soluble, and finally coated fertilizers where the coating governs the release. The names of the different products are given in **Table 1**. In the sections below, a short explanation of the different technologies is given. The publication by Trenkel (Trenkel, 2010) and an earlier publication by Goertz (Goertz, 1993) give a good overview of the field.

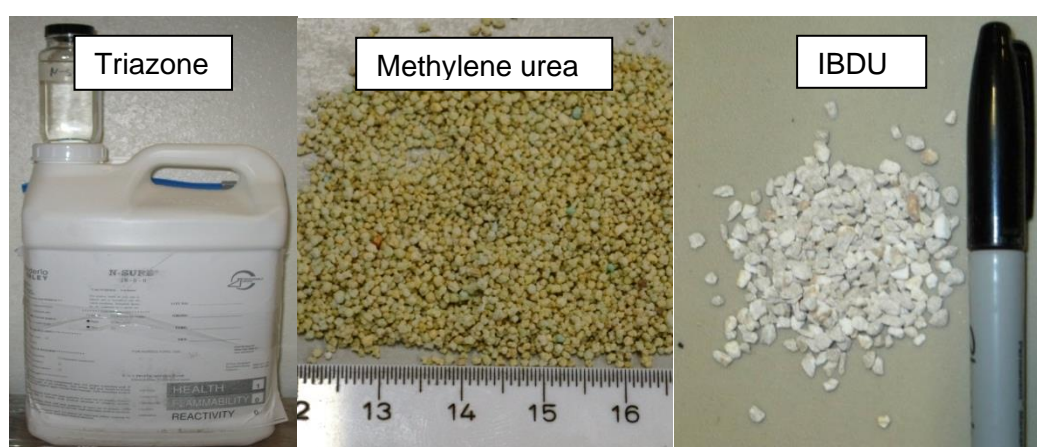
Plants take up different nitrogen sources from the soil for their growth. Ammonia and nitrates can be taken up by their root system. In soil, ammonia can be converted to nitrate and if not taken up by the roots, it is immobilized by the soil micro flora or can eventually leach out of the root zone into the deeper soil layers. Therefore, stabilizing agents can be added to ammonia containing fertilizers to prevent or slowdown of this process. The authors do not consider urea to be a slow release fertilizer even though it needs to be hydrolyzed in the soil. Urea is quickly hydrolyzed to ammonia and unless the ammonia is moved in the deeper surface layers in the soil by placement or by water, a fraction can volatilize. Also stabilizing agents for urea have been developed. Stabilizing agents reduce the conversion of the urea to the ammonia. Trenkel (Trenkel, 2010) mentions in his paper the most important nitrification and urease inhibitors. In this paper, we do not discuss the analytical methods for identification and quantification of these types of nitrogen stabilizing agents. For these types of products, specific methods are available or are in development to quantify the amount of inhibitor. Methods for this category are described elsewhere. (European Norm EN16328; European Norm EN 15688, 2008; European Norm EN15905, 2010; European Norm EN 16024, 2011; European Norm EN 16075, 2011) . They are outside the scope of the current study.

The first slow release products were the reaction products of urea and formaldehyde which were recognized in 1948 as slow release fertilizers by USDA. The urea-formaldehyde (UF) grades were sold in 1955 (Goertz, 1993). These products are also known as Methylene Urea (MU) products. The composition of the UF/MU fertilizer is basically dependent on the ratio of urea to formaldehyde but also on the condensation conditions, and different amounts of oligomers, i.e., MDU (methylene diurea), DMTU (dimethylene-triurea), TMTU (trimethylene-tetraurea) etc. are formed as the ratio changes. As the length of the oligomers increases, the water solubility decreases. The amount and their distribution determine the slow release properties of the product in the field (Goertz, 1993). The slow release properties of UF/MU products are caused by the microbiological degradation and hydrolysis in the soil. For these types of products, methods have been developed to test the amount of product soluble in cold water and hot water. Furthermore, chromatographic methods to determine the different compounds are also available and described in this paper. In addition to these solid urea-formaldehyde materials, liquid products are commercially available. The most important class of these liquid products are made by a condensation reaction of urea, formaldehyde, and ammonia, yielding mainly a six membered ring known as triazone ring (Clapp 2001). There are small amounts of methylene urea compounds present in these products as well. The slow release nitrogen in Triazone type fertilizers is made available to the plants by hydrolysis and microbiological degradation similar to other UF/MU products. See **Table 1** for further details.

More condensation products of urea with other aldehydes also exist and are commercially available (see **Table 1**). CDU (Crotonylidene diurea) is used as a slow release fertilizer and is produced by the condensation of either crotonaldehyde or acetaldehyde with urea. It is a ring type compound and the solubility is low. The slow release N in CDU is made available to the plants by hydrolysis and microbiological degradation. Another commonly available product is IBDU (Isobutylidene diurea) which forms by the reaction of isobutyraldehyde and urea. Compared to UF/MU products, IBDU (and CDU) are relatively pure compounds and not mixtures of several chemical compounds. The nitrogen in IBDU becomes available to the plants by hydrolysis and microbiological degradation of the sparingly soluble IBDU. Particle size has a significant effect on hydrolysis and conversion rate and governs the slow release properties of both IBDU and CDU products.

Some of the solid and liquid commercially available urea condensate fertilizers are shown in **Figure 1**.

Figure 1. Some of the commonly used slow release fertilizers of the urea condensates family.



There are generally two classes of coated controlled release fertilizers: Sulfur coated urea (SCU) products were developed by the Tennessee Valley Authority starting in the 1960's. Sulfur was selected as a coating material because it is a low-cost material and (after oxidation) is useful as a secondary nutrient. Polymer coated –sulfur coated urea (PSCU) products were developed to seal the imperfections in the sulfur layer and to increase the control of the release. The primary release mechanism of the urea of SCU is due to water permeation through imperfections in the sulfur layer and the subsequent diffusion of the concentrated urea solution. In a later stage, also biological degradation of the sulfur layer can increase the release of nutrients. Due to better environmental control, the amount of sulfur deposition through atmospheric means is decreasing leading to sulfur deficiency in some regions. This aspect increases the interest in the application of sulfur containing fertilizers.

The second group of coated fertilizers is the polymer coated fertilizers. In the mid 1960's, the first polymer coated controlled release fertilizers (CRF) were developed. By coating of granular fertilizers, it became possible to control the release of the nutrients for an extended period of time. Polymer coating is an advanced way to control the release properties of the nutrients in the soil. Currently very thin coating layers are used to meter out the nutrients over a period ranging from about 3 weeks to about 2 years. Coating thicknesses in the range of 50 micrometer are common nowadays. The release of CRF's is measured mostly by specific methods at constant temperatures under laboratory conditions. Based on experience and modeling, the release measured under controlled conditions is used to predict the performance under practical field conditions. The use of CRF products is becoming more accepted. The first user groups were growers of nursery plant, but nowadays CRF products are also used on the turf market and in agriculture applications.

Generally the release of CRF's are tailored to fit a specific plant or crop and the product is applied once per growing cycle. Furthermore, CRF products are also popular for consumer applications because of the ease of use and one time application. Some coated fertilizers are shown in **Figure 2**.

Figure 2. Some examples of coated fertilizers.

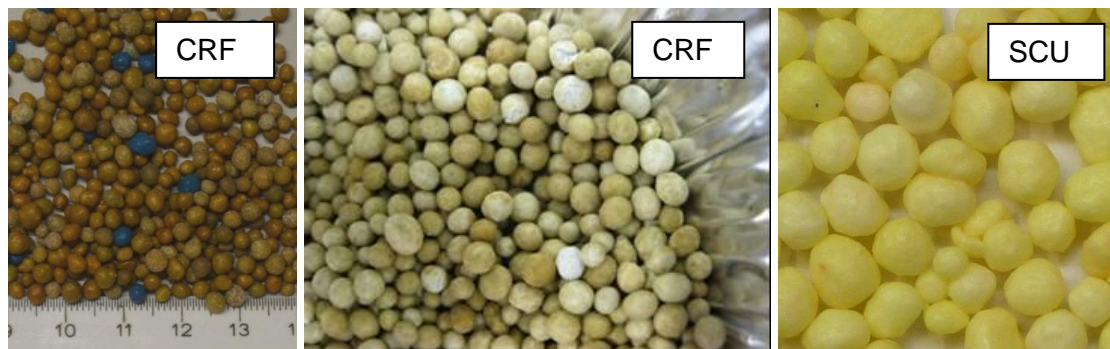


Table 1. Definitions of Slow- and Controlled-Release Fertilizers. Definitions are taken from (ISO/TC134, ISO_CD 8157 Fertilizers and soil conditioners Vocabulary, 2013).

Term	Definition	Technology	Example of product
Controlled Release Fertilizer (CRF)	Fertilizer in which nutrient release is controlled, meeting the stated release rate of nutrient and the stated release time at a specified temperature.	Fertilizer coated with a polymeric coating	Osmocote, Agroblen, Sierrablen (Everris) ESN (Agrium), Duration, POLYON (Koch Agronomic Services) Multicote (Haifa) Nutricote (JCAM Agri) Apex (Simplot)
Slow Release Fertilizer (SRF)	Fertilizer, of which, by hydrolysis and/or by biodegradation and/or by limited solubility, the nutrients available to plants is spread over a period of time, when compared to a "reference soluble " product e.g. ammonium sulphate, ammonium nitrate and urea.	Use of less water-soluble nutrients and/or compounds which are degraded in soil over time	N-Sure (Tessenderlo Kerley) Sierraform (Everris) Nitroform (Koch Agronomic Services) Floranid (IBDU) (Compo) IBDU (JCAM Agri) Sazolene and Sirflor (Sadepan Chimica) CDU (JCAM Agri)

2. Method Selection and General Comments

In the search of methods, we have reviewed the methods available by AOAC International (AOAC, accessed in 2013), standards available in the European Union, China, Japan, United States, Russia, and open literature. To be able to review the methods, selection criteria are needed. The IFA is using a fixed set of criteria for evaluation of a method. These criteria range from the status to safety of the method and include evaluation of repeatability, reproducibility, complexity, time and investment needed.

The methods can be divided into two groups. One which is applicable to any slow or controlled release product (described in paragraph 3), and more specific methods for either slow or controlled release fertilizers (described in paragraph 4 and 5). Almost all methods have one thing in common; the methods describe how the nutrient release properties are determined. However, they generally do not describe the analytical method for the exact nutrient analysis. Thus these methods need to be supplemented by commonly known methods, for instance determination of the total nitrogen by Kjeldhal (European Norm EN 15604, 2009). For the current study, we assume that the reader is familiar with such methods and is able to execute these.

For the evaluation of the performance of the methods we used the HorRat method (Horwith & Albert, 2006). The HorRat ratio is developed as an indicator for the reproducibility of inter laboratory testing. Furthermore the method can also be used as an indicator for the repeatability (single lab studies). Unfortunately for some of the methods described in this paper, the measured property is what the method defines (like for instance the hot water insoluble nitrogen method, AOAC method 955.05 (2.4.19)) and therefore the HorRat method is used more qualitatively.

3. General Methods for Slow- and Controlled-Release Fertilizers

The methods described in the paragraph can be used for any solid fertilizer sample regardless whether it is a slow or a controlled release fertilizer. Furthermore, although it is not explicitly mentioned, these methods can be used to determine the extraction behavior of nitrogen compounds, phosphate and potassium (and even micronutrients) in water. Most of the methods were developed for nitrogen based fertilizers, however when the final analytical methods are adjusted to determine the amount of soluble/insoluble material, these methods can be applied more widely.

The most relevant methods are compared in **Table 2**. In these methods, a sample is placed in a column and leached over an extended time with water. AOAC method 970.04 (2.4.15) (Horwitz W., 2000) is the simplest test in which 3 g of the fertilizer is placed in a column and extracted with water. The nutrients remaining in the column after extraction with 250 ml water are determined. Methods FM-701 (Florida Department of Agriculture, 2003) is closely related to the AOAC 970.04 method. The same extraction column, sample and water volume is used. However the gravity feed is exchanged by a pump controlling the water flow, which is a weak point of the 970.04 method. Repeatability (S.E. Katz C. F., 1970) and reproducibility (S.E. Katz C. F., 1973) of the method are acceptable given the complexity of the method (extraction and N analysis with Kjeldahl).

The method developed by Medina (Medina C., 2011; Medina L. C., Sartain, Obreza, Hall, & Thieux, 2014) is more elaborate and uses a series of extractions of a larger sample in a column (30 g). The sample is extracted with water at 25 °C (for 2 hours), 40 °C (2 hours), 20 hrs at 55 °C, 50 hrs at 60 °C, and 94 hrs at 60 °C. Thus a full extraction takes about one week. This is shorter than some real time release measurements (see paragraph 5), however longer than other methods like the AOAC method 970.04. The larger sample size is definitely an advantage, since some complex blends of uncoated/CRF and uncoated/SRF are used in the market place. This method becomes particularly useful by comparing the release properties of a product with a known reference. Medina also studied the nitrogen release of 8 different materials in soil under controlled conditions and correlated the lab extraction method with the soil release profiles (Medina L. C., Sartain, Obreza, Hall, & Thieux, 2014) (Medina L. C., Sartain, Obreza, Hall, & Thieux, 2014).

Table 2. Comparison table of general methods for Slow- and Controlled-Release Fertilizers.

	AOAC 970.04 (2.14.15)	AOAC 2015.15 (Medina)
Scope/Applicability	For coated fertilizers and urea condensates	All slow- and controlled-release fertilizers
Type of result	Insoluble Nitrogen Content	Accelerated release profile
Method Status	Accepted by AOAC	Published
Use/General acceptance	Global	Developed at University of Florida, some application in US
Repeatability (single lab)	Acceptable	Moderate
Performance (inter-laboratory)	Acceptable	Inter laboratory study will be organized
Dynamic range	Relatively large (3 g sample)	Large sample (30 g)
Complexity	Low	Complex set up
Time	0,5 day	One week
Cost/Availability	Cheap	Moderate
Health/Environment	Water extraction, low risk	Water extraction, low risk

4. Methods for Slow Release Fertilizers

In general, the methods developed for slow release fertilizers are all targeted to determine the amount and/or composition of urea condensates. The methods are targeted for methylene urea, triazone, CDU and IBDU type products. However they are inadequate to test products which are for instance sparingly soluble like slow release potassium products (Everris, 2013, p. SILK) and for products containing magnesium ammonium phosphate.

The methods for the solid slow release fertilizers can be divided into two categories: extraction techniques like AOAC method 945.01 (2.4.14) (Horwitz W., 2000) and AOAC method 955.05 (2.4.19) (Horwitz W., 2000) which yield information on the relative solubility of methylene urea products. Furthermore, advanced chromatographic techniques are used to identify and quantify the different methylene urea compounds and purity of CDU and IBDU products.

It is important to notice that the methods described in **Table 3** are laboratory techniques and that the slow release behavior needs to be tested in field trials to fully understand their working behavior as a fertilizer. Conversion of laboratory data into the field performance is not straight forward. For the solid products, physical properties like particle size are important. For the whole group of slow release fertilizers, environmental and soil parameters (soil type, temperature, available water, pH, etc.) are important and have influence on how long they provide nutrients to the plants. Typically, the working action of the slow release products is between several weeks to a few months.

AOAC method 945.01 is relatively simple and quick. Extract 1 g of (a methylene urea containing) product in water at room temperature for 15 minutes, filter and test the nitrogen content of the residue with a total nitrogen determination technique like Kjeldhal. This method yields the total amount of nitrogen fertilizer compound not soluble at room temperature. Subsequently a second test (AOAC method 955.05) can be used to determine the amount which is insoluble at 100 °C. An extraction at 100 °C for 30 minutes in a phosphate buffer is used in this test. From these combined measurements the activity index can be determined. The activity index is the fraction of the methylene urea product which is %water insoluble (WIN) - %hot water insoluble (HWIN) x100/%WIN. There is also a Chinese standard (HG/T 4137-2010 "Urea aldehyde slow release fertilizer", 2010) based on the same principle.

A whole range of chromatographic techniques have been developed for solid and liquid urea-condensate products:

The EN 15705 (European Norm 15705, 2010) describes how the amount of MDU, DMTU and TMTU can be determined in presumably solid UF products. The method also describes how the CDU and IBDU content in these slow release fertilizers can be determined. It is a HPLC method and by comparison with known standards the quantity of the different components can be determined. The method gives good separation of the individual peaks enabling good quantification.

AOAC method 983.01 (2.4.21) (Horwitz W., 2000) also describes the use of HPLC for the testing urea and methyleneureas (water-soluble) in fertilizers products for determination of the urea, MDU and DMTU contents. The differences between the two methods are columns/detection, and mobile phase. EN 15705 uses a NH₂, Diode array detection at 200 nm, and acetonitrile/water (85/15) as a mobile phase. AOAC method 983.01 uses a reverse phase column, refractive index detector and water as a mobile phase. Based on the statistical data the AOAC method is more accurate (single lab and inter lab) than the EN 15705 method for MU products. It is important to notice that the required pure standards are more difficult to obtain. This was recognized by industry and a company in Italy started cooperation with an university, which developed a lab methodology to synthesize MDU, DMTU and TMTU.

Method 959.03, First Action 1959, Final Action 1960, was proposed for the determination of Urea in Fertilizers based on the reaction of Urease Enzyme with the available urea in the fertilizer. This method works rather well with urea solutions and simple urea containing fertilizers, although the method is very much dependent to the enzyme activity, and to the type of enzyme source. The older/simple fertilizers that the 959.03 method works well were either straight urea or blends of urea with other fertilizers. These older fertilizers did not create any inaccuracy when 959.03 was applied to them for the determination of their urea contents.

Nowadays, there exist more complex fertilizers in the market. Urea-Formaldehyde Fertilizer products such as methylene urea contain adducts of urea and formaldehyde (ureaforms) that are straight chain adducts. Based on the mode of preparations, whether acid catalyzed or based catalyzed, these chains are small chains (monomethylol, dimethylol, triurea, methylenediurea, etc.) or polymeric chains (Dimethylenetriurea, Trimethylenetetraurea, etc.) as well as the small chains. There is always some unreacted urea with these adducts. These adducts are slow release N fertilizers, but the free urea is not and the N from the free urea is readily available. One has to accurately determine the amount of the free urea in this class of fertilizers to accurately claim the readily available N from the slow release N. Unfortunately, AOAC Official Method 959.03 does not work for this class of fertilizers due to the interference of the ureaforms with the urease enzyme (Hojjatie, M & Abrams, D: Journal of AOAC International Vol. 98, No. 6, 2015 1475).

Some of these fertilizers are solid and one could use AOAC Method 945.01, AOAC 970.04, and AOAC 955.05, although these methods have limitations as well and dependent on the size of the granulate products. If these are liquids, these methods do not apply.

There are yet other class of more complex urea fertilizers, namely Urea-Triazone water soluble fertilizers which form by the action of urea, formaldehyde, and ammonia. The compositions of these fertilizers are made of unreacted urea, ureaforms, and the triazone ring. These are totally water soluble and AOAC Method 945.01, AOAC 970.04, and AOAC 955.05 are not applicable for them. AOAC Official Method 959.03 is also not suitable for these fertilizers due to the interference of some these adducts with the urease enzyme (Hojjatie, M & Abrams, D: Journal of AOAC International Vol. 98, No. 6, 2015 1475). The results for the free urea in these fertilizers by this method are inaccurate due to this interference.

AOAC Official Method 988.01 was offered in 1988 for the determination of Triamino-s-Triazine in fertilizer mixes. However due to the use of WATER as mobile phase, this method is not able to separate all the components such as urea, biuret, triuret, and ureaforms from each other in these fertilizers and again the result is erroneous.

AOAC Method 2003.14 works well to achieve the accurate analyses of these fertilizers for their urea, biuret, and some of the ureaforms. The main goal with analyses of these fertilizers (methylene ureas, and Urea-Triazones) is to accurately report the amount of their free urea (readily available N) from the rest of the components (slow release N) for accurate reporting and claims. AOAC Method 959.03 and 988.01 could not accurately achieve this, but AOAC Method 2003.14 does.

It is advisable (Rodriquez & Hojjatie, 2013) to use a related HPLC technique to determine the amount of free (unreacted) urea without interference from other components. AOAC method 2014 (Hojjatie, Abrams, & Parham, 2004) describes the determination of urea. This method can also be used to determine biuret in urea containing fertilizers, liquid Urea-Triazone Fertilizers, and for the detection of different urea condensates (monomethylol urea, dimethylol urea, MDU, hexamethylenetetramine and triazone ring) in these products (Hojjatie M., 2012). The six-membered triazone ring is an important liquid slow release fertilizer. This method uses a propyl amine column with UV detection at 195 nm with acetonitrile/water (85:15) as mobile phase.

When using the urease digestion described in the AOAC method 959.03, and in the Chinese standard method, there is a –possibly- theoretical risk that reaction products of urea with formaldehyde (e.g. methylolureas) can also be digested by the urease enzyme and therefore yielding a biased urea content.

The details for the different methods are described in **Table 3**.

Table 3. Comparison table of general methods for fertilizers containing urea condensates.

	AOAC 945.01 (2.4.14)	AOAC 955.05 (2.4.19)	Urea Aldehyde Slow Release Fertilizer HG/T 4137-2010	EN 15705	AOAC 983.01 (2.4.21)
Scope/Applicability	Urea formaldehyde fertilizers	Urea formaldehyde fertilizers	Urea condensates	Urea condensates	Methylene urea condensates
Type of result	Insoluble Nitrogen	Hot water insoluble nitrogen	Insoluble Nitrogen and hot water insoluble nitrogen	Composition	Determination of urea, MDU and DMTU
Method Status	Accepted by AOAC	Accepted by AOAC	Chinese standard	European standard	Accepted by AOAC
Use/General acceptance	Global	Global	China	Europe	Commonly in US
Repeatability (single lab)	No data	No data	No data	Good for IBDU and CDU, reasonable for MU products	Good
Performance (inter-laboratory)	Good	Moderate	No data	Acceptable for IBDU and CDU, moderate for MU products	Good
Dynamic range	Small sample (1-1.4 g)	Small sample (0,12 WIN)	Small sample	Small sample	Small sample (2 g)
Complexity	Low	Low	Low	Moderate (HPLC Unit)	Moderate (HPLC Unit)
Time	0,5 day	One day	One day	0,5 day	0,5 day
Cost/Availability	Low	Low	Low	Moderate	Moderate
Health/Environment	Water extraction, low risk	Water extraction, low risk	Water extraction, low risk	Moderate (Acetonitrile)	Water, low risk

5. Methods for Controlled Release Fertilizers

The methods for controlled release fertilizers should be divided into two classes: methods for sulfur coated fertilizers and methods for polymer coated fertilizers. The release mechanism is different for these products and this is reflected in the available methods. For the sulfur coated fertilizers, the release is partly dependent on the degradation of the sulfur layer, while for polymer coated fertilizers the coating acts as an inert material and its physical state is not influenced by the environment. The methods for the sulfur coated products are discussed in paragraph 5.1. The testing methods for polymer coated fertilizers are discussed in paragraph 5.2.

5.1 Testing methods for Sulfur coated controlled release (nitrogen) fertilizers

As described previously, the release mechanism of the sulfur coated fertilizers is determined by small imperfections in the coating and diffusion of concentrated nutrient solutions through these imperfections. Furthermore, biological degradation of the sulfur layer can play a role, which is more difficult to harmonize and test under controlled conditions. Therefore the testing of sulfur coated products has been focused on determination of the initial release since this is both relevant for the quality of the product and its safety for plant growth. The method described in ISO/WD 17322 and 17323 (ISO/TC134, 2013; ISO/TC134, 2013) is closely related to the testing methods developed by TVA and are specific for sulfur coated urea products. The ISO/WD 17322 and 17323 are currently being drafted.

In principle, 20 g of a sulfur coated product is placed in water at 38 °C for 24 hours and seven days and the release in water is determined by total nitrogen determination (Kjeldahl) or by refractive index. The method is relatively accurate and easy to execute. Unfortunately, the translation to performance in the field needs to be determined by separate testing since there is no easy way to convert lab data to the practice.

Although the methods are developed for sulfur coated urea, the same principle (release testing in water) can be used for other sulfur coated products, like for instance sulfur coated potassium chloride. Only the testing methods of the nutrients need to be adjusted to be able to determine the amount which is released in 24 hours and after 7 days.

Table 4. Method for measuring sulfur coated Controlled Release Fertilizers.

	ISO/WD 17322:2015
Scope/Applicability	Sulfur coated fertilizer (urea)
Type of result	Initial release
Method Status	ISO standard 17322:2015
Use/General acceptance	ISO Standard
Repeatability (single lab)	Acceptable
Performance (inter-laboratory)	Moderate
Dynamic range	Large sample (20 g)
Complexity	Low
Time	Lengthy, 7 days
Cost/Availability	Simple equipment, moderately labor intensive
Health/Environment	Generally low except for CS ₂ extraction

5.2 Testing methods for Polymer coated controlled release fertilizers

The principle of all the methods for the polymer coated fertilizers is the same. A certain amount of the polymer coated product is placed in water at a certain temperature, typically 25 °C or 30 °C and the release into the water is followed as a function of time. The difference between the European method EN 13266 (European Norm EN 13266, 2001), the Japanese method 5.28 (Official analysis of fertilizers, 1987) and the Chinese method (Slow release fertilizer HG/T 23348-2009, 2009) are small. They place around 10 or 12.5 gram of fertilizer in 200-500 ml water at a temperature between 25-30 °C and determine the amount of nutrients released in water over time. Currently a ISO standard ISO/DIS 18644 for controlled release fertilizers is under development (ISO/TC 134).

The methods are presumably quite accurate as is documented in the EN 13266 (European Norm EN 13266, 2001) and yield information how the release evolves over time. Unfortunately, these measurements are real time measurements. Since the release of the polymer coated products is sensitive to temperature (higher temperatures yield faster release), it is logical that by increasing the temperature, the testing can be accelerated. An accelerated test is described in method EN 13266. Accelerated testing is commonly used in the industry.

The advantage of these elaborate release measuring methods is that they can be more readily translated to the release under field conditions, since the polymer coated products are only sensitive to temperature and the availability of water. Therefore, these measurements are used to define the longevity of a product. This is generally the time to release 75-80% of a certain nutrient at a certain temperature. When evaluating the longevity of CRF's, the temperature must be considered. Furthermore, it is important to note that an excess of water does not influence the nutrient release from the coated granules.

For non-urea containing coated fertilizers, the determination of the nutrients can be simplified by using the electrical conductivity in the solution as an indicator for the nutrient concentration. Although this approach is less accurate on an individual nutrient level since the EC behaves more like an average over the nutrients, its simplicity and speed of testing is advantageous for some systems like coated NPK granules based on ammonium nitrate as a main nitrogen component.

Table 5. Comparison of methods for Polymer Coated fertilizers.

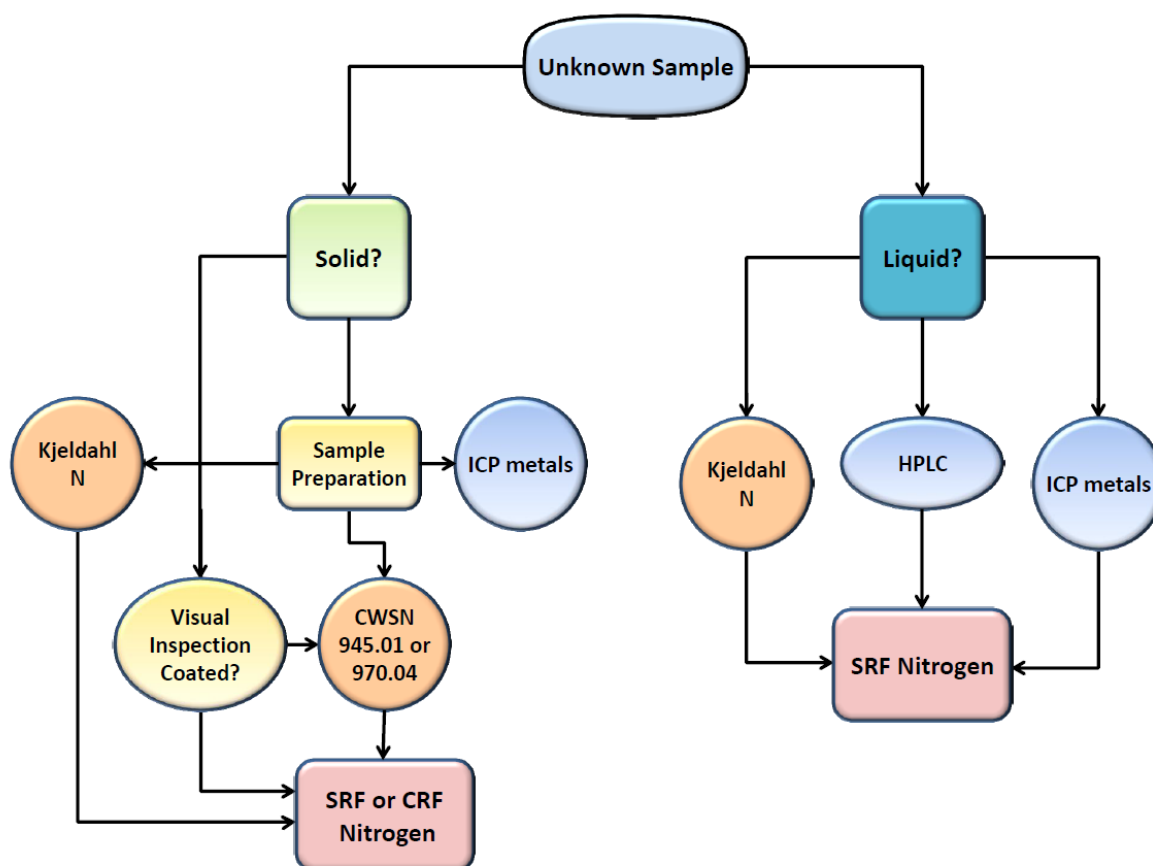
	HG/T 4215-2011 ¹	EN 13266	Method 5.28 Japan
Scope/Applicability	Controlled-release fertilizers	Coated fertilizers	Coated fertilizers
Type of result	Release profile	Release profile	Release profile
Method Status	Used in China, proposal for adopting as ISO norm	European standard	Official method in Japan
Use/General acceptance	China	Europe	Japan
Repeatability (single lab)	No data	Acceptable	No data
Performance (inter-laboratory)	No data	Acceptable	No data
Dynamic range	Large sample (10 g)	Large sample (10 g)	Large sample (12.5 g)
Complexity	Low	Low	Low
Time	Real time measurement	Real time measurement	Real time measurement
Cost/Availability	Simple equipment, labor intensive	Simple equipment, labor intensive	Simple equipment, labor intensive
Health/Environment	Water extraction, low risk	Water extraction, low risk	Water extraction, low risk

¹China also have GB/T 23348-2009 “Slow Release Fertilizer” and GB 29401-2012 “Sulfur Coated Urea”.

6. How to Analyze an Unknown SRF or CRF Sample

For an unknown slow- or controlled-release fertilizer sample, a flowchart is presented in **Figure 3** as a possible and preliminary approach to analyze such a sample. After a visual inspection to determine whether the unknown sample is a liquid or a solid, further analysis can be done. As far as the authors are aware, the liquid fertilizers can be divided into either conventional fertilizers (containing no slow release properties) or urea condensates in liquid form.

Figure 3. Analytical schedule for testing an unknown fertilizers sample which could contain slow or controlled release properties.



If the product is liquid, then the composition of the fertilizer sample could be determined by a combination of analytical methods. For example, the total nitrogen content can be determined by the Kjeldahl method. The phosphate, potassium, the secondary elements and the micronutrients content of the fertilizer sample can be determined by Inductively Coupled Argon Plasma (ICAP) in combination with an appropriate chromatographic technique like EN15705 (European Norm 15705, 2010) or AOAC method 983.01 (2.4.21) (Horwitz W. , 2000) for Methylene Urea type products. For triazone containing products a different method is required (Hojjatie, Abrams, & Parham, 2004). Although the method was described for urea, the same principle will work for triazone containing liquids.

For a solid fertilizer, the presence of a coating can sometimes become clear from a further visual inspection. The chemical composition can be determined the same way as for the liquid sample. However, comparing a ground sample versus the original sample (as received) in an extraction test like 945.01 or 970.04 can clearly indicate whether or not some slow release properties are present. For coated fertilizers, the slow release properties are completely lost by grinding. For slow release fertilizers, this is much less pronounced. For conventional fertilizers, comparisons of both ground and the original sample will show no difference.

7. Conclusions

In general, good testing methods exist for slow- and controlled-release fertilizers. Due to the intrinsic nature of these products, it is not always possible to test the release under controlled –laboratory- conditions in such a way that a release properties under the field conditions can be automatically determined or predicted.

It is important to know what product and property needs to be tested so that the appropriate test can be selected. There are some good general methods available, like the AOAC method 970.04, which describe a simple extraction that will work for all products regardless of the technology. The method described by Medina is also generally applicable to solids, yields more information, and can be used for “fingerprinting” a certain product by comparing to reference products.

For the urea condensates fertilizers such as methylene urea products and triazone products, good methods based on the chromatographic techniques (HPLC) are available to determine the composition quantitatively. Furthermore, some simple water extraction techniques are available for the methylene urea condensate products to quantify the amount of methylene urea which can be dissolved in water (cold and hot water soluble). These properties are sometimes required by law on the label of a product.

The controlled release fertilizers should be divided in sulfur coated and polymer coated fertilizers. For the sulfur coated products only the initial release over 1 and 7 days can be determined and this is due to the release mechanism. For the polymer coated fertilizers good methods are available which yield valuable information on the release profile over time. A serious disadvantage of the methods for the polymer coated products is that they are real time measurements and thus take considerable time to determine the release. Method EN13266 mentions the use of an accelerated test in its appendix, however further work is needed to make the testing applicable to all kind of fertilizers.

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