Applied methodologies for measuring nutrient release of slow and controlled release fertilizers

Leon Terlingen (Everris Int, Netherlands, leon.terlingen@everris.com)
Michael Hojjatie (Tessenderlo Kerley, USA, mhojjatie@tkinet.com)
Fred Carney (Agrium Advanced Technologies, USA, fcarney@agriumat.com)
March 2013

on behalf of IFA

Content

- Introduction
- Methods for urea condensates
- Methods for sulfur coated urea
- Methods for coated fertilizers
- General methods
- How to analyze an unknown sample
- Conclusions and next steps

Aim of the study

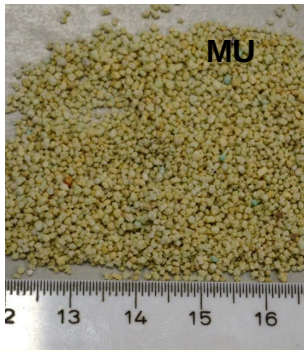
- Review the methods available for slow and controlled release technologies and if possible recommend the best available techniques

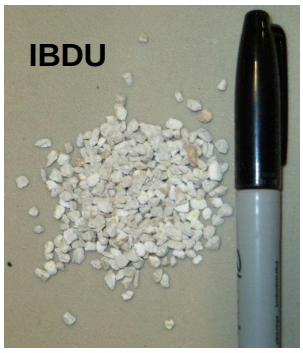
Definitions: Slow Release fertilizers (SRF)

- Slow release fertilizers: Fertilizer, of which, by chemical compound action or physical action of the nutrients, the nutrient availability to plants is spread over a period of time
- From a technology point of view: Generally products based on reduced solubility and/or (microbiological) degradation
- Products can be either solid or liquid

Examples of SRF

- Urea condensates like: Urea Formaldehyde (UF), (Triazone, Methylene Urea (MU)), Crotonylidene diurea (CDU), Isobutylidene diurea (IBDU)

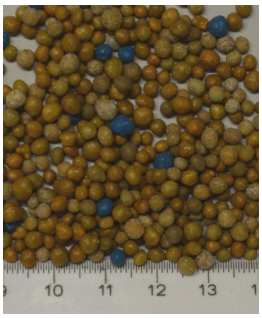




Definitions: Controlled Release Fertilizer (CRF)

- Fertilizer in which nutrient release is controlled, meeting the stated release rate of nutrient and the stated release time.
- From a technology point of view: Coated fertilizers.
- Two types: sulfur coated and polymer coated products

Examples of CRF



Selection of methods

- Only methods available in the literature, norms and legislation are considered
- No company specific methods because of IP consideration
- Only lab methods are considered. Agronomic testing of SRF and CRF is outside the scope

Coated fertilizer in EN13266 test

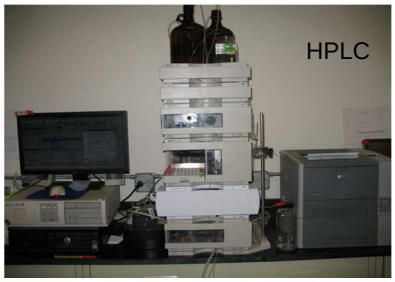
Techniques to test urea condensates

Extraction techniques

Determine soluble nutrients at a certain time

Chromatographic techniques

Identify and quanitify components by comparison with known standards



Methylene Urea methods

- **Extraction tests:**
  AOAC 945.01/955.01

  Detemination of the amount of cold water soluble, hot water soluble and hot water insoluble nitrogen.

  N determination by Kjeldhal

Immerse 1 g in 20 ml water at room temperature and filter subsequently. Test N in residue

Extract 0,12 HWIN in phopshate buffer for 30 min at 100 ºC. Filter and test N in residue

Chromatographic methods for urea condensates

- For MU (also called urea formaldehyde):EN 15705
  Test will give amount of urea oligomers:MDU, DMTU, TMTU
- For IBDU: EN 15705
  Test will yield IBDU content
- For CDU: EN 15705
  Test will yield CDU content
- Determination of free urea with AOAC 2003-14
  To determine free urea content in liquid MU

Dissolution of MU oligimers (0,5 g samples in 1 L boiling water for 30 min). Test vrs standards on HPLC

IBDU, CDU. Dissolve 1 g in water and test vrs standards on HPLC.

Free urea, test 0,001 g directly on HPLC

Techniques to test Sulfur Coated Urea

- From Chinese standard HG/T 3997-2008 and ISO norm proposals ISO 17322/17323

Amount of urea released after 24 hr and 7 days in water at 38 ^{o}C

Immerse 20 g in mesh bag in 200 ml for 24 hours or 7 days in water at 38 ^{o}C. Determine N in solution by Kjeldhal or refractometer

Techniques to test coated fertilizers

1. European method EN13266*
2. Chinese method: HG/T 23348-2009*
   Initial release, release period up for which 75-80% is released
3. Japanese method (Official method 1997)
   Differential release rate determination

10 g in 500 ml water at 25 °C under stirring. (EN method)
Immerse 10 g in mesh net in 200 ml water at 25 °C. (Chinese method)
12,5 g in 250 ml water at 30 °C. (Japanese method)

All methods: Change water and measure nutrients

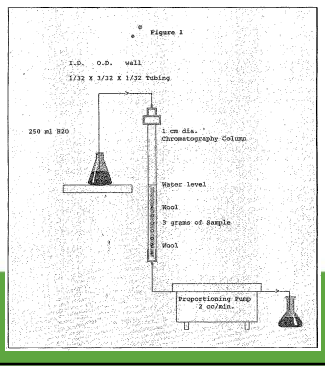
*Both methods describe the use of higher water temperature for release testing

General methods for testing

- AOAC 970.04 and FM-701
  Determination of the water insoluble part

3 g of product is placed in column and is being extracted with 250 ml of water under constant flow of 2 ml/min. Determine N content of residue with Kjeldhal.

FM method uses pump instead of gravity feed.

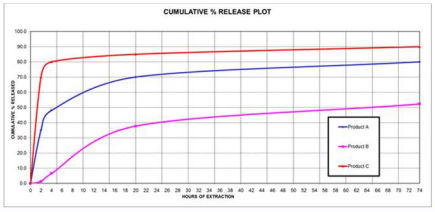


General methods for testing

- Accelerated Nutrient Extraction Method

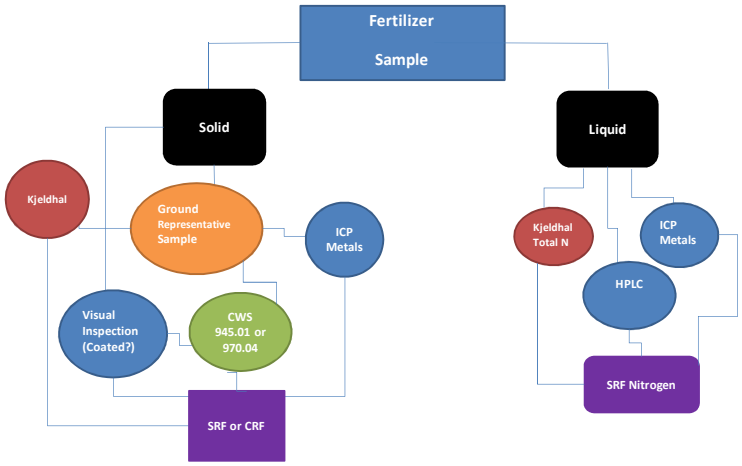
  AOAC proposal by Medina and Hall

  Release profile at higher temperature



30 g in column is extracted by a sequence of 2 hrs at 25 ºC, 2 hrs at 40 ºC, 20 hrs at 55 ºC, 50 hrs at 60 ºC, 94 hrs at 60 ºC. Determination of nutrients in extract

How to analyze an unknown sample



Conclusions

- Good chromatographic techniques available for urea condensates
- Method need to be selected in relation to the property that needs to be measured.
  - Simple methods generally yield indication of soluble part of nutrients
  - Release testing of coated fertilizers even with accelerated methods is time/labor intensive.

Next steps

- Draft paper reviewing the methods currently available and publish via IFA.

Acknowlegdements:

- IFA, Everris Int, Tessenderlo Kerley, Agrium Advanced Technologies for supporting this work