Determination of Urea in Fluid Fertilizers Containing Water-Soluble Urea-Formaldehyde Reaction Products

A liquid chromatographic method has proved successful for over a decade in determining amount of urea in a class of fluid fertilizers.

Dr. Michael Hojjatie, Dean Abrams

The Fluid Journal • Official Journal of the Fluid Fertilizer Foundation • Early Spring 2011 • Vol. 19, No. 2, Issue #72

Summary: *A liquid chromatographic method (using a different column, eluent, and operational parameters from AOAC Method 983.01) was developed and has been used for over a decade for the determination of urea in a class of liquid fertilizers noted as not being suitable for urea analyses by present official methods. It was judged a suitable candidate for a collaborative study to provide a methodology for use in cases where present methods are unsuitable. Tessenderlo Kerley, Inc. of Phoenix, Arizona, in collaboration with ten other laboratories (five commercial and five state labs), developed a method based on liquid chromatography. It separates efficiently, clearly, and calculates the amount of unreacted urea from other N-containing compounds present in solution that could be used to determine the amount of control release nitrogen (CRN)/slow release nitrogen (SRN) in solution.*

Urea is one of the most widely used nitrogen-release fertilizers. More than 90 percent of the world's urea production is used as fertilizer. Soil bacteria containing urease enzyme catalyzes the conversion of urea to ammonia and carbon dioxide via ammonium carbonate formation and decomposition. Nitrogen (N) from urea can be lost to the atmosphere if fertilizer urea remains on the soil surface for extended periods of time during warm weather. Urea breakdown can begin as soon as it is applied to the soil. In the presence of the enzyme urease and a small amount of soil moisture, urea hydrolyses occurs and N is lost due to ammonia volatilization (Figure 1).

Techniques applied

Several techniques have been applied in order to prevent loss of N from urea due to ammonia volatilization. Sulfur-(S) coated urea and polymer-coated urea have been used to prevent hydrolyses of urea and to slowly release N from urea to the soil, hence the term slow release fertilizer has been introduced. Slow Release Nitrogen is a measurable quantity and is defined as that portion of N in a fertilizer that slowly releases to the soil. Slow Release Nitrogen is dependent on soil pH, soil moisture, and on soil temperature. There is no standard method yet to determine the SRN in solid slow-release fertilizers. The slow-release committee of the American Association of Plant Food Control Officials (AAPFCO) has been working on a method that could be used universally for this purpose.

Controlled release nitrogen fertilizers were formed by incorporating urea in chemical reactions forming bonded urea products that slowly break down in the soil, releasing its N content. Typically, these fertilizers are either solid or liquid products. Triazone-CRN fertilizers are an example of fluid fertilizers formed by the chemical reaction of urea. The term CRN is a measurable quantity and is defined as that portion of N in the fertilizer that releases in the soil over time. It is also dependent on soil properties. Unlike the solid slow-release fertilizers and solid control-release fertilizers, there is a method to quantitatively measure the amount of controlled release N in the liquid-controlled released N fertilizers. This method has been approved by the AOAC International and AAPFCO.

Delayed release N fertilizers are another term for those fertilizers releasing their N content over time.

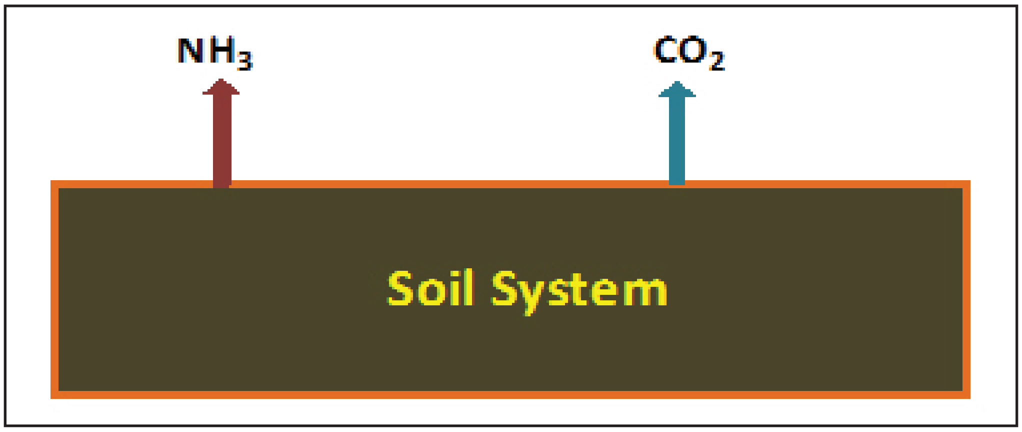


Figure 1. Environmental losses of N from urea.

These three terms have been used synonymously.

Urea-formaldehyde condensation products, commonly known as "ureaforms," have been used for many years as the source of controlled-release N fertilizers for plants. In commercial fluid fertilizers derived from reaction of urea and formaldehyde, unreacted urea is always a substantial component of such products and is quantitatively claimed on the registration labels. These classes of products also contain a substantial component of water-soluble urea-formaldehyde reaction products. Due to the presence of these co-products, quantitative determination of the claimed urea content is important.

Urea and formaldehyde react with each other under acidic or basic conditions to produce ureaform products, including dimethylolurea (DMU), methylenediurea (DMU), and dimethyltriurea (DMTU). A based catalyzed reaction of urea and formaldehyde is shown in Figure 2.

Under acidic conditions, urea and formaldehyde react according to the chemical reaction shown in Figure 3. Ureaforms have been used as CRN fertilizers.

Controlled reaction of urea, formaldehyde, and ammonia forms a six-member ring that contains a high percentage of CRN (Figure 4).

Triazone. According to the definition by AAPFCO (Official Publication No. 63, 2010), Urea-Triazone Solution (UTS) is a stable solution resulting from controlled reaction in an aqueous medium of urea, formaldehyde, and ammonia, which contains at least 25 percent N. The solution shall contain no more than 40 percent, no less that 5 percent of total N from unreacted urea and not less than 40 percent from Triazone. All other N shall be derived from water-soluble, dissolved reaction products of the above reactants. It is a source of slowly available N. Figure 5 shows the N release pattern from urea and Triazone.

Due to the presence of some unreacted urea in Triazone products, not all of the N content of these fertilizer solutions is slow release. Accurate reporting of the urea from N (fast release) and other available N contents (control-release/slow release) should be accounted for and conform to the label.

A typical chromatographic fingerprint of a Triazone fertilizer solution (UTS) shows the presence of untreated urea, Triazone six-member ring, and ureaform constituents. A typical high-performance liquid chromatographic (HPLC) fingerprint of a Triazone fertilizer solution (UTS) is shown in Figure 6.

The two larger adsorption peaks at around 3 min and 6 min are due to free urea and Triazone, respectively. The smaller peaks are the urea-formaldehyde adducts (ureaforms). The N from free urea shall not be claimed as CRN/SRN and an accurate method is needed to account for these.

Questionable techniques

AOAC International currently has two official methods--959.03 (Urease Method) and 983.01 (Liquid Chromatographic Method). Both methods suffer from interference of these co-products. One or more of these substances makes Method 959.03 unreliable by hampering action of the urease enzyme. The liquid chromatography in Method 983.01 suffers from co-elution of some of these substances in some occasions. No suitable method currently exists for regulatory analyses of urea (or urea N) in these products.

Urea-formaldehyde. It also has long been determined that 959.03, the method most commonly used for regulatory urea determination in fertilizers, is not reliable for the determination of urea in a certain class of urea-containing fluid fertilizers that also contain a substantial component of water soluble urea-formaldehyde reaction products. Test data indicate that one or more substances from this UF-derived component inhibit the action of the urease enzyme upon which action

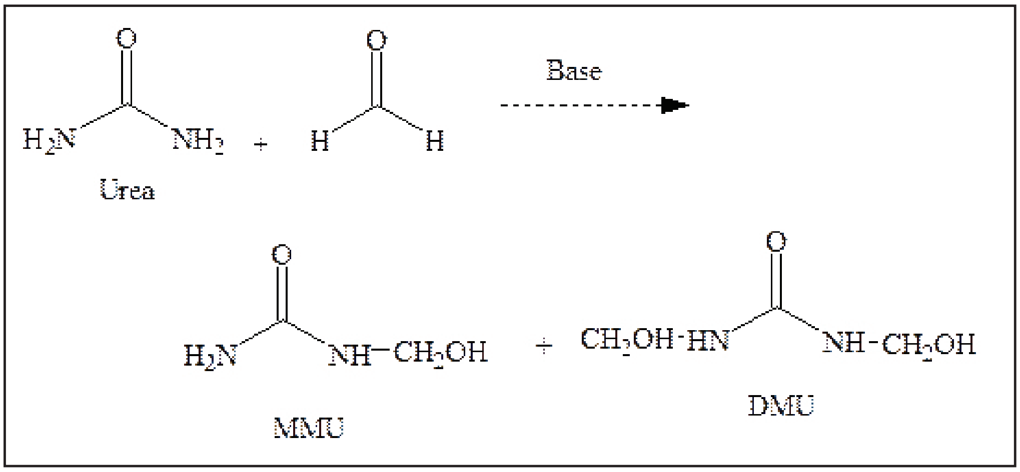


Figure 2. A based catalyzed reaction of urea and formaldehyde.

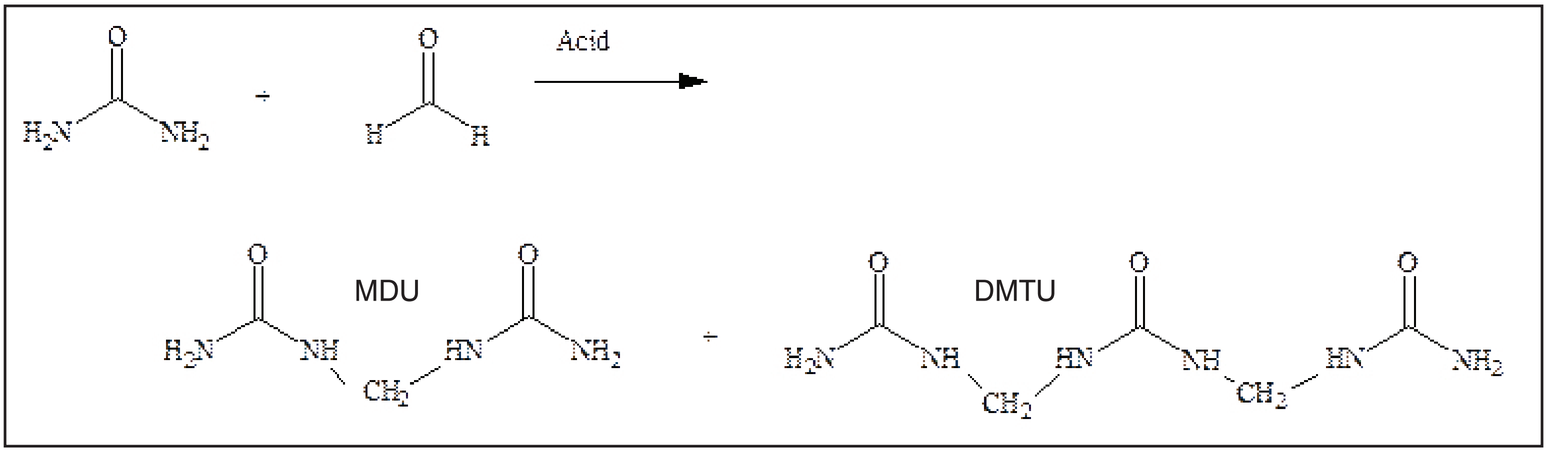


Figure 3. Reaction of urea and formaldehyde under acidic conditions.

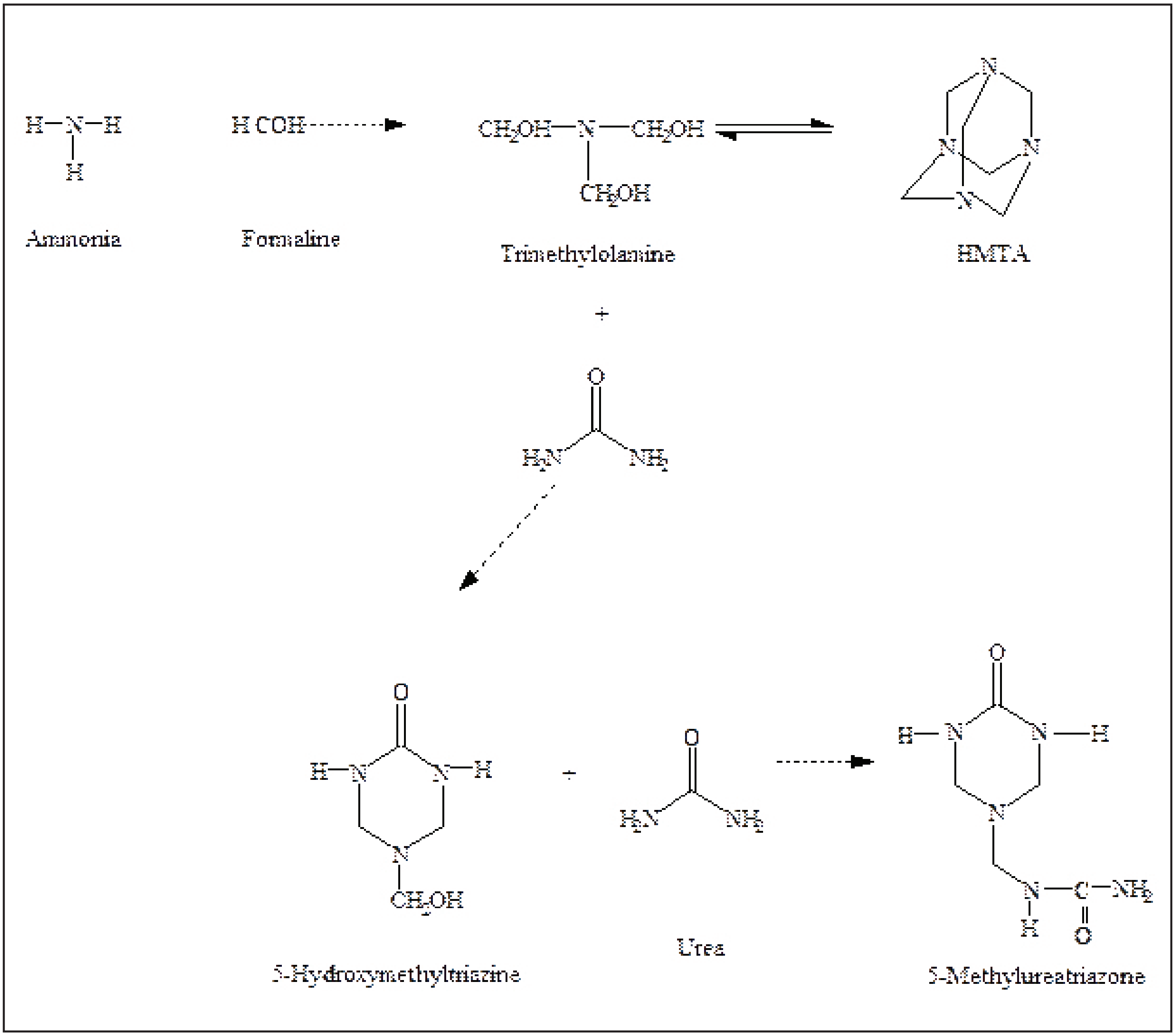


Figure 4. *Controlled reaction of urea, formaldehyde, and ammonia*

Method 959.03 is dependent. Method 983.01, a liquid chromatographic method, also is not reliable for determination of urea in the cited class of fertilizers because in most, if not all cases, there is co-elution of a non-urea peak with the urea peak.

As a consequence, there presently exits no official method suitable for regulatory analysis for urea (or urea N) in commercial fluid fertilizers containing the described urea-formaldehyde reaction products even though dissolved, unreacted urea is always a substantial component of such products and is quantitatively claimed on the registration labels thereof.

A better way?

A liquid chromatographic method from a proposed collaborative study (using a different column, eluent, and operational parameter from 983.01) has been developed and in industry use for over a decade for the determination of urea in the class of fluid fertilizers noted here as not being suitable for urea analysis by present official methods. It would seem to be a suitable candidate for the collaborative study to provide an official method for use in the cases cited here where present official methods are unsuitable.

The liquid chromatographic method was developed by Tessenderlo Kerley, Inc. of Phoenix, Arizona, in collaboration with ten other laboratories of which five were commercial labs and the other five were state labs. This method is based on liquid chromatography that separates efficiently and clearly and calculates the amount of unreacted urea from the other N-containing compounds present in the solution that could be used to calculate the amount of CRN/SRN in solution. Using an accurate methodology to determine the amount of CRN/SRN in solution prevents inaccurate and false reporting. This method has been approved by the AOAC International and adopted by the Association of Plant Food Control Officials (AAPFCO). It can also be used for the determination of CRN/SRN in fluid fertilizers containing water-soluble, urea-formaldehyde reaction products. It also covers urea-containing N fluid fertilizers and, in particular, aqueous urea solution. The method is quantitative and applicable to the determination of urea (usually expressed as urea N) in commercial water-soluble urea-formaldehyde products, urea-containing fluid N fertilizers, and aqueous urea solutions. It could also be used for the determination of biuret contents in urea solutions.

A comparison of the determination of SRN in different commercially available fluid fertilizers containing water-soluble urea-formaldehyde reaction products is shown in Table 1. Urease methodology does not accurately account for the free urea in these fluid fertilizers. To determine the CRN/SRN contents of these fertilizers one has to know the amount of free urea accurately. The reasons are:

- SRN/CRN coming from the cyclic Triazone moiety and from the ureaform constituents
- Free urea not providing slow-release N.

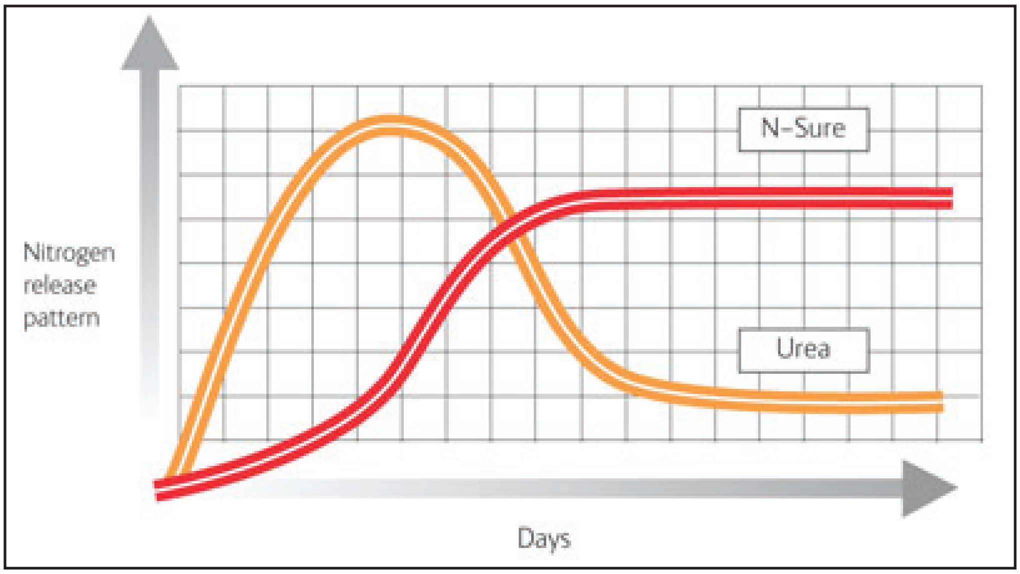
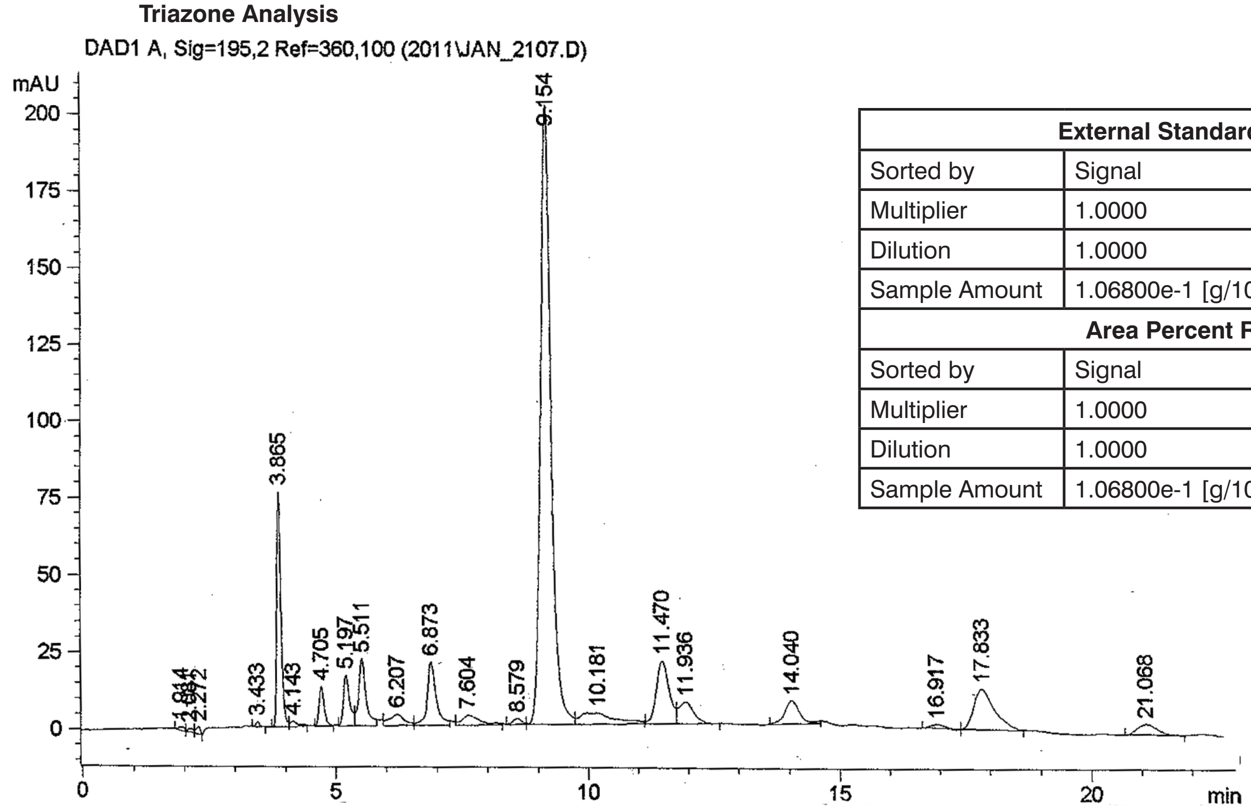


Figure 5. *Nitrogen release pattern from urea and Triazone.*

	Method	
	HPLC (%)	Urease (%)
N-SURE 28-0-0 **(72% SRN claimed)**	72	88
FORMOLENE-PLUS 30-0-0 **(60% SRN claimed)**	60	77
N-SURE-PRO 30-0-0 **0-0-0(50% SRN claimed)**	50	68
CoRoN 28-0-0 **(70% SRN claimed)**	50	70
NITRO-30 30-0-0 **(85% SRN claimed)**	46	*

**Not determined by urease*

Table 1. *A comparison of the determination of SRN in different commercially available liquid fertilizers containing water-soluble urea-formaldehyde reaction products.*



External Standard Report	
Sorted by	Signal
Multiplier	1.0000
Dilution	1.0000
Sample Amount	1.06800e-1 [g/100ml] (not used in calc.)
Area Percent Report	
Sorted by	Signal
Multiplier	1.0000
Dilution	1.0000
Sample Amount	1.06800e-1 [g/100ml] (not used in calc.)

Figure 6. *Typical high performance liquid chromatographic fingerprint of a Triazone fertilizer.*

Dr. Michael Hojjatie is R&D Director, and Dean Abrams is senior chemist with R & D Laboratories, Tessenderlo Kerley, Inc, Tucson, AZ.