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Research Paper

New Methods for Determination of Composition of Urea-Ammonium Nitrate Solution - Control Of the Final Product

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Abstract: *UAN- urea-ammonium nitrate solutions are called the fertilizers of the 21st century. The product contains all available forms of nitrogen: nitrate (-NO_3), ammonium (-NH_4) and amide (-NH_2). Using this kind of fertilizer fulfills the need of plants for nitrogen even they are in a dormant state. The new process needs tight analytical control of the process which is essential for the final product to be of the right quality. The research was dedicated to finding new, better and easier methods compared with methods described in* EU ordinance. *TOC total organic carbon and method of refraction and density were checked. The first one - analysis of total organic carbon, which is converted to the content of the amide nitrogen, by using the addition of acid and oxidizer during analysis allows the determination of content in the sample up to 100% ± 0.5%. Results for the second method - correlation between refraction-density in dependence on concentration, allow the analysis of the composition of the content of the amide nitrogen, and the sum of nitrate and ammonium nitrogen in the sample. New analytical methods were developed and implemented in the production process.*

Keywords: Fertilizers, TOC total organic carbon, Method of refraction-density.

Introduction

In recent years, there has been a significant increase in demand for liquid fertilizers containing nitrogen in all available forms i.e. nitrate (-NO_3), ammonium (-NH_4) and amide (-NH_2). UAN (urea-ammonium nitrate solution) is a solution of urea and ammonium nitrate in water, the range the most commonly used grade of these fertilizer solutions is 28% N - 32% N also known as UN28 (UN-28) - UN32 (UN-32)[1]. Using this kind of product fulfills the need of plants for nitrogen during the growing season, the liquid form allows an even and faster distribution of the substance and better assimilation under normal conditions or in periods of drought compared to solid fertilizers. The next advantage is related to the economic efficiency of the fertilizer due to the lower price of the principal component - nitrogen. Each technological process is also associated with a number of laboratory tests, the task of which is to ensure continuous monitoring during production and of the final product. Certain technical conditions for the final UAN product must be met if it is to conform to the regulations of the European Parliament and of the Council relating to fertilizers[2]. This document defines the method for the determination of ammonium, nitrate, and urea nitrogen content. These methods are based mostly on distillation i.e. methods of Ulsch, Arnd, and Devard[3-6], which were developed in the 19th and 20th century, during this time the technical progress in the field of new equipment has been very significant. Distillation is relatively cumbersome as a repetitive unit operation. Due to sample preparation (digestion) and the time required to reach the boiling point of the examined substance. What is more, mentioned methods need the addition of metal or metallic alloy and standard sulphuric acid solution and a standard solution of sodium or potassium hydroxide, what produce a lot of waste and increase the price of the experiment. As an example, in

Arnd's method reduction of nitrates to ammonia is conducted by means of a metallic alloy composed of 60 % Cu and 40 % Mg in the presence of magnesium chloride ($MgCl_2$). The next step is a distillation of the ammonia, and determination of the yield in a known volume of standard sulphuric acid solution. Titration of the excess sulphuric acid by means of a standard solution of sodium or potassium hydroxide. Another fundamental disadvantage is the low repeatability of the experiments. Accordingly, there is a need to develop new, faster and easier methods which will be effective for urea-ammonium nitrate solutions (UAN). The aim of the study was to develop and implement in the production process and quality control of two methods of analysis: the method of refraction-density and method for determination of total organic carbon (TOC). The team of Sloan[7] describes the approaches for determination of refractive index, and specific gravity and their correlations in the UAN solutions. Progressive development in equipment and spreadsheet program allowed to improve this method. The second one is the method used to determinate the quality of microelectronics, pharmaceutical, and drinking water[8]. The application described in this work is trailblazing due to the matrix of samples which is inorganic salt. The mentioned methods besides speed, are environmentally friendly and much cheaper in comparison to methods described in regulations of European Parliament.

Material and Methods

All starting materials and reagents were purchased from commercial sources and were used as received: urea 99.5% analytical grade (Acros), ammonium nitrate 99% analytical grade (AnalaR NORMAPUR® ACS). As a solvent used demineralized water with electrical conductivity < 0.5 µS/cm.

TOC – determination of total organic carbon

Standard solutions with known values of the various forms of nitrogen, wherein the amount of nitrate and ammonium was constant (8% NO_3-N, 8% NH_4-N) and the amide nitrogen content varied: 15%, 15.5%, 16%, 16.5% N -NH_2 (m/m) were prepared.

General procedure: To the measuring flask (500 mL) was added 2g (accurate to 0.01 g) UAN (urea-ammonium nitrate solution) containing a known amount of each form of nitrogen. Next, 100 mL of water was added and mixed together, then further water was added to bring the total volume to 500 mL, stoppered and mixed again. Measurements were conducted on Analyzer Sievers Laboratory InnovOx + GE Autosampler. This method consists in the oxidation of organic substances contained in the sample to carbon dioxide (CO_2) under supercritical water, which then is converted into the organic carbon content. Supercritical water condition is determined by two parameters: temperature above 374 °C and pressure above 218 atm[9]. The water in such a state has specific properties that make oxidation of the organic substances contained in the sample easier. Due to the low polarity, organic material dissolves much more easily in supercritical water. Inorganic compounds are almost passive and do not consume any oxidizer[10,11]. The oxidation takes place in a titanium reactor which is provided with a platinum catalyst. Apart from the sample, a suitable amount of oxidizer and acid are added to the reactor, allowing inorganic carbon to be removed before analysis. The acid is 42.5% orthophosphoric acid, and the oxidizer is 30% (m/v) solution of sodium persulfate[8].

$$organic\ carbon + S_2O_8^{2-} + heat + pressure \rightarrow CO_2 + H_2O + SO_4^{2-}$$

The kind of used analyzer is dedicated to analyzing of a sample of water where the matrix does not contain a lot of salts. The research looked at the application of TOC analysis to the control of the production process itself and the final UAN product, which is characterized by a large amount of inorganic salt – ammonium nitrate. The twin objectives are the determination of the urea content in the liquid fertilizer and choosing appropriate measuring parameters (amount of acid and oxidizer) and sample preparation to optimize the efficiency of the process. A mathematical model can then be developed to convert TOC content values into urea content and consequently the amount of amide nitrogen.

The content of total organic carbon in the sample:

$$TOC[mg\,C/g] = \frac{C - C_0}{m} \cdot V$$

C - read value from the analyzer for the sample [mg L^{-1}]
C_0 - read value from the analyzer for the blank [mg L^{-1}]
m - the weight of sample taken for the analysis [g]
V - flask capacity [L]

The content of urea:

$$content\ of\ urea\,[\%] = \frac{TOC}{1000 \cdot M\,mol\,C} \cdot M\,mol\,(\mathrm{NH_2})_2\mathrm{CO} \cdot 100$$

TOC – content of total organic carbon [mg C/g]
M mol C - molar mass of carbon [g mol^{-1}]
M mol $(NH_2)_2CO$ - molar mass of urea [g mol^{-1}]

The content of amide nitrogen:

$$content\ of\ amide\ nitrogen\,[\%] = \frac{content\ of\ urea}{46.412} \cdot 100$$

Method of refraction-density

Standard solutions with known values of total nitrogen (27%, 28%, 29%, 30%, 31%, 32% and 33%) wherein the correlation between amide nitrogen and the sum of ammonium and nitrate nitrogen was 1:1, were prepared. Measurements were conducted on Densimeter DMA

4100M Anton Paar and Refractometer RX-5000A Atago.

Results and Discussion

TOC – determination of total organic carbon

A number of experiments were conducted for a set of prepared standards with a known content of urea (16% NH_2-N) and ammonium nitrate (8% NH_4-N, 8 % NO_3-N). An appropriate amount of sample, what is described in part Materials and Methods, allowed to avoid the problems with a matrix of the sample and was suitable in the range of calibration curve. Each measurement was repeated 3 times. Table 1 shows the average of obtained results.

Table 1: The content of total organic carbon converted to amide nitrogen, depending on the measurement parameters

Sample	Acid [%]	Oxidizer [%]	Mass of UAN [g]	The content of C [ppm]	Recovery of NH_2-N [%]
1.	2	20	2.08	279	97.31
2.	2	22	2.08	277	96.61
3.	2	24	2.08	280	97.65
4.	2	26	2.08	279	97.31
5.	2	28	2.08	278	96.96
1.	4	20	2.03	277	99.00
2.	4	22	2.03	275	98.05
3.	4	24	2.03	282	100.55
4.	4	26	2.03	279	99.59
5.	4	28	2.03	279	99.59
1.	6	20	2.05	278	98.38
2.	6	22	2.05	277	98.02
3.	6	24	2.05	279	98.73
4.	6	26	2.05	278	98.38
5.	6	28	2.05	277	98.02

The conducted experiments showed directly that the best results were obtained by using the addition of 4% acid and 24% oxidizer. To test the versatility of the most effective parameters of acid and oxidizer new standards with different contents of amide nitrogen (15%, 15.5% and 16.5% NH_2-N) were prepared. Measurements of three replicate analyses were conducted. The results are shown in Table 2.

Table 2: Content of total organic carbon converted to amide nitrogen in measurements with standards with different amide nitrogen content

Sample NH_2-N	Acid [%]	Oxidizer [%]	Mass of UAN [g]	The content of C [ppm]	Recovery of NH_2-N [%]
15.0%	4	24	2.01	261	100.18
15.5%	4	24	2.00	266	99.62
16.5%	4	24	2.06	292	99.51

Method of refraction-density

For urea-ammonium nitrate solutions, nitrogen concentration can be determined by measurements of density and refraction index due to good linear correlations between total N and these parameters (Figure 1 and 2).

This relationship was checked in two parallel experiments using a series of standard solutions with concentrations of total nitrogen in the range of 27-33% there were 1% apart. The ratio of percentages of the various forms of nitrogen i.e. amide (-NH_2) and the sum of ammonium (-NH_4) and nitrate (-NO_3) was 1:1. The next research step was the investigation of the influence of varying ratio of the specific forms of nitrogen on density and refraction. Seven series of standards with total nitrogen concentration in the range of 27-33% were prepared.

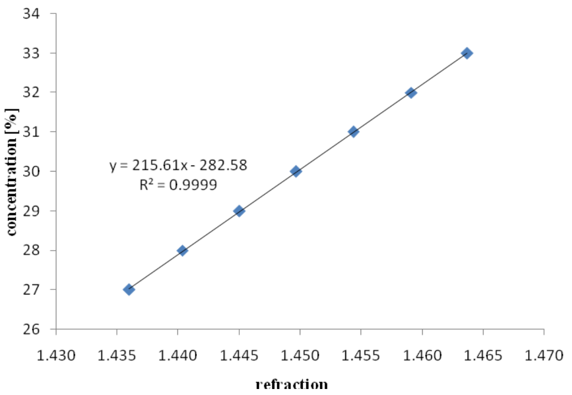

Figure 1: The dependence of refraction on concentration of the UAN solution

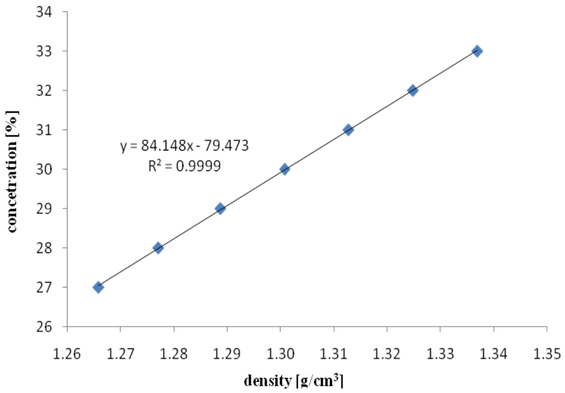

Figure 2: The dependence of density on the concentration of the UAN solution

For each concentration prepared solutions with ratio of percentages of amide nitrogen (-NH_2) to nitrogen in the ammonium nitrate (AN): N_{AN} + 2%; N_{AN} + 4%; 1:1; N_{amide} + 2%; N_{amide} + 4%.

The results obtained allow the preparation of a table containing density, refraction, total nitrogen content and content of nitrogen in all forms: NH_2 and sum of -NH_4 and -NO_3 (part of the table is shown in Table 3).

Then, as a result of interpolation, 2500 correlations of density-refraction depending on the concentration of the various forms of nitrogen were obtained. It allowed preparing special function in Excel Microsoft Office to find adequate contents.

Table 3: Content of total organic carbon converted to amide nitrogen, depending on the measurement parameters

Density [g cm^{-3}]	Refraction	N Total [%]	NH_2-N [%]	N(-NH_4 and -NO_3) [%]
1.3542	1.46254	33.0	14.50	18.50
1.3456	1.46238	32.9	14.45	18.45
1.3463	1.46257	32.9	14.55	18.35
1.3462	1.46276	32.9	14.65	18.25

Conclusion

The research demonstrated that two fully effective methods of determination the composition of urea-ammonium nitrate solution UAN had been developed. The first one - analysis of total organic carbon, which is converted to the content of the amide nitrogen, by appropriate amount of sample (2 g of UAN solution on 500 ml of water) and by using the addition of 4% orthophosphoric acid and 24% oxidizer during analysis allows the determination of content in the sample up to 100% ± 0.5%. Results for the second method - correlation between refraction-density in dependence on concentration, allow the analysis of the composition of the content of the amide nitrogen, and the sum of nitrate and ammonium nitrogen in the sample with better accuracy due to development in equipment and spreadsheet. Both presented methods have a crucial advantage over existing methods, which is speed and repeatability of analyses. What is more, the developed methods were checked with real product from the production installation.

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