DETERMINATION OF NITROGEN USING A PERMEATION DEVICE

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ABSTRACT

The authors present a system to analyze nitrogen, presents as ammonium or nitrate ion, at concentration level of percent. The device can be easily converted into a FIA assembly and, consequently, can be used to improve the analytical frequency at a quality control laboratory. The determination is based on measurement of conductivity and standard addition method. A sample of commercial potassium nitrate, sold as fertilizer, was analyzed with good agreement with AOAC method, either using ammonium chloride or potassium nitrate as standard solutions, showing the robustness of the system. The detection limit, based on standard deviation of the blank, is 65.1×10^{-6} and 69.5×10^{-6} mol L^{-1} for ammoniacal and nitric nitrogen, respectively.

KEYWORDS: Conductivity. Devarda´s Alloy. Fertilizer. Standard Addition Method.

DETERMINAÇÃO DE NITROGÊNIO UTIIZANDO UM DISPOSITIVO DE PERMEAÇÃO

RESUMO

Os autores apresentam um sistema para analisar nitrogênio, presente na forma nítrica ou amoniacal, em altas concentrações. O sistema proposto pode ser usado para análise por injeção em fluxo (FIA) e, conseqüentemente, ser usado para aumentar a freqüência analítica em laboratórios de controle de qualidade. A determinação está baseada na medida de condutividade e no método de adição de padrão. Uma amostra de nitrato de potássio comercial, vendido como fertilizante, foi analisado com boa concordância entre os resultados ao serem comparados pelo método AOAC, tanto quando foi usada solução padrão de cloreto de amônio quanto com nitrato de amônio, demonstrando a robustez do sistema. O limite de detecção, baseado no critério dos três desvios padrão do branco, é 65.1×10^{-6} and $69.5\ 10^{-6}$ mol L^{-1} para nitrogênio amoniacal e nítrico, respectivamente.

PALAVRAS-CHAVES: Fertilizante. Condutividade. Método Padrão de Adição. Liga de Devarda.

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1. INTRODUCTION

The necessity to know the nitrogen content is justified by the importance that this element has to the live, prior to vegetal and finally to all organisms that occupied upper levels in trophic chain. Nitrogen cycle has been studied for long time and is usually used to understand an environment [1]. Thus, to explain if some event is caused by natural or anthropogenic phenomena [2], environmental researchers frequently determine the concentration of ammonia, nitrite and nitrate, i.e., adopt the speciation of nitrogen. On the other hand, nitrogen can be determined in several matrixes, such as in biological fluids [3], fresh waters [1, 4, 5], seawater [6, 7, 8], wastewaters [1, 2, 9], food [10, 11], sediment/soil [12] and fertilizer [13, 14]. Considering fertilizer industry, the amount of nitrogen is used as a parameter to measure the efficiency of production and to assure the product quality. The analytical method used to determine the concentration of nitrogen in different matrixes must be selected based on chemical composition of the sample, on its concentration, on necessity to know the speciation, etc. Thus, in environmental studies, instrumental methods would be used because the analyte usually is present at low level and there are a great number of samples to be analyzed, but if nitrogen is present in high concentration, at percent level, classical methods are preferred.

Nowadays, it is not possible to maintain the level of the crops, and consequently to feed world population, without using fertilizers. In a great number of countries the quality control of fertilizer production, as well as the definition of the soil fertilization rate, is mainly based on classic nitrogen analysis [14]. The regulation in this subject varies from country to country, but usually it is not expressed the chemical speciation of nitrogen [14-17]. In Brazil, for example, the quality of the fertilizer, regarding nitrogen content, is given by total amount of this nutrient, regardless its source [18].

The cost of nitrogen and the process variables will define the raw used to produce the fertilizer. So, ammonia anidra is always used when it is possible, but urea, nitrates and different ammonium salts also can be used in granulation units [14]. The preferences to use ammonia anidra are associated with its low cost and the paper it plays in granulation process. Consequently, two-thirds of nitrogen presents in the granulated fertilizer is in ammoniacal form [14]. The quality control in fertilizer industry, with respect nitrogen, is mainly done with the alkaline distillation of the sample [13, 19]. But, if the fertilizer has been made with nitrate, this procedure does not assure all nitrogen is measured. In this case, a specific reducing agent to assure the total conversion at ammonium form must be used and the reducing agent most used is Devarda’s alloy. This reagent is a solid mixture of copper (50%), aluminum (45%) and zinc (5%), that in high alkaline solution reduces nitrate to ammonium ions and soon after in ammonia, that is distilled, collected and measured [13]. FIGURE 1 presents a scheme of classic nitrogen analysis, considering nitrogen in nitric and ammoniacal forms.

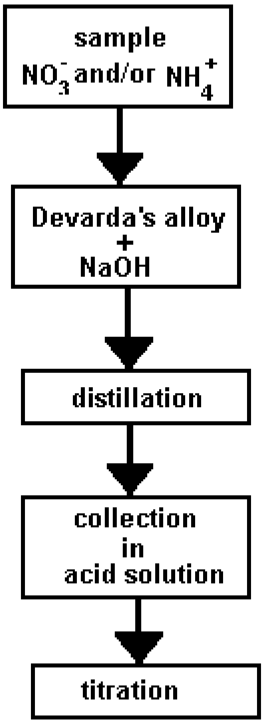

Figure 1 – Scheme of classic nitrogen analysis.

Devarda's alloy can be used just to reduce nitric nitrogen, but there are several ways to reduce the other nitrogen forms to ammonium ion. For example, salicylic acid in presence of sodium sulfate and zinc metallic, in anhydrous medium, or catalytic Raney's powder in sulfuric acid also can be used. [13]. After all, nitrogen is reduced to ammonium ion (NH_4^+) and this ion is converted in ammonia gaseous (NH_3) that volatilizes from alkaline solution, as shown in Equation (1). By heating the alkaline solution, ammonia is completely removed from the solution and quantitatively absorbed into acid solution.

$$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O \qquad (1)$$

The time consumed in an analytical determination maybe a key factor to assure the quality of a product. In this way, Flow Injection Analysis (FIA) is a powerful tool since it reduces analytical time. There are several FIA methods described in literature to analyze nitrogen [3, 4, 10, 20-25] and even commercial device to do that. But, the price of the equipments and necessity of skilled operators, make this option less attractive to be adopted in fertilizers industries in the Latin America, for example.

Thus, the quality control in fertilizers industries of South America continues to be done by classic methods, i.e., sample distillation in high alkaline medium followed by titration.

It is presented a robust device to determine nitrogen (in ammoniacal or nitric form), in percent range, that is suitable to analyze fertilizers. The proposed system is good to be converted in automatic one and so, to be used to reduce analytical time and can be built everywhere spending few money and time. The improvement of the analytical frequency can give information that will help to reduce production costs and to improve the productivity of fertilizers industries.

2. MATERIAL AND METHODS

2.1 Analytical system

It was developed a system determines the nitrogen based on variation of conductivity of a solution, due to absorption of ammonia that was evaporated from a high alkaline solution. The system, schematically presented in FIGURE 2, can be seen as two different chambers: the reaction (**R**) and the sampling (**C**) chamber. These chambers were made of 10 mL disposable pipette. The alkaline solution (**S1**) was heated by an electric coil (**H**), positioned at the bottom of the chamber **R**. Different aliquots of the nitrogen standard solution, or of the sample, were injected by the duct (**A**). The chambers **R** e **C** are separated by Teflon® film (**M**), through which ammonia permeates and is absorbed by the solution (**S2**). Two stainless steal cylindrical electrodes (**E**) are immersed into solution (**S2**). The diameter of the electrodes is ca. 0.4 mm and they are separated by 1 mm and are connected to conductivimeter DIGIMED CD20. The ammonia evaporated from chamber **R** permeates through the membrane **M** and is absorbed by **S2**, modifying the conductivity of this solution.

The aliquots are injected in chamber **R** using a peristaltic pump (MILAN BP 204) and a flow injector homemade (not shown in FIGURE 2), being the volume of the aliquot adjusted by selection of adequate sample loop.

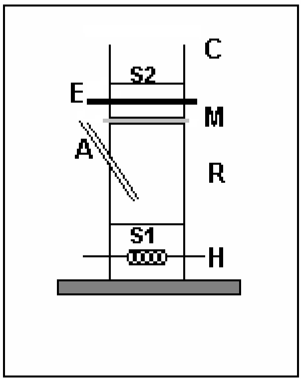

Figure 2 – Proposed system. All parts are described in the text.

2.2 Analytical Procedure

The proposed method is based on chemical property of ammonium ion (NH_4^+) to be converted in gaseous ammonia (NH_3) in alkaline medium, as previously discussed. The alkaline solution **S1** (1 mL) is fed to the chamber **R**, followed by adjusting the membrane **M** and the positioning of sampling chamber **C**, as showed in FIGURE 2. The absorbent solution (1.5 mL) is transferred to the chamber **C**, at the same time the conductivity of the solution **S2** is measured and the solution **S1** is maintained under heating. The conductivity read at this moment will be considered as base line, i.e., the zero system.

The standard addition method is used. So, 100 μL aliquots of solution containing nitrogen (sample and standard) are successively injected on reaction chamber that contains heated alkaline solution followed by injection of 100 μL of 10 g L^{-1} Devarda's alloy suspension, prepared in distilled water. At the end of 5 min, the conductivity is read and the process is repeated at least three times. If the sample has only ammoniacal nitrogen, the addition of Devarda's alloy can be suppressed.

2.3 Solution to be analyzed

Samples of fertilizer were grounded (dp <0.5 mm), the mass weighted according to nitrogen content, transferred to 250 mL volumetric flask, which volume was adjusted with distilled water. The flasks were put in a mixer (Wagner's type) and maintained under revolution for 30 min.

Standard solutions of different ammonium salts were prepared by weighting and diluting convenient mass of them, using distilled water.

3. RESULTS

The system was previously evaluated by the blank of the method. The test is done injecting ten 100 μL aliquots of distilled water under analysis conditions. The results are acceptable, since the signal is less than 0.1% of the signal generated by injecting an aliquot of 2 10^{-3} mol L^{-1} nitrogen solution.

3.1 Definition of operational system conditions and detection limit

a) Alkaline solution heating

The heat from alkaline solution can be transferred to the absorbent solution and, consequently, changing the conductivity. However, tests have demonstrated that heating the alkaline solution for 30 min at 90ºC, temperature higher that to be used during analysis, the variation of the conductivity was less than 1%, what is acceptable.

b) Concentration of alkaline solution

Different calibration curves, using 0.10, 0.20 and 0.45 g mL^{-1} sodium hydroxide solutions, were made injecting five 100 μL aliquots of 10^{-2} mol L^{-1} NH_4Cl solution. The mathematical equations and Pearson's coefficient (r) for interpolates lines, using least square method, are shown in TABLE 1.

Table 1: Mathematical equation of the calibration curves for different NaOH concentration.

	Equation	r
0.10	L = 0.048*cnc – 10.20	0.9994
0.20	L = 0.044*cnc – 7.65	0.9983
0.45	L = 0.051*cnc – 14.09	0.9996

L is mean conductivity (μS cm^{-1}), cnc is nitrogen concentration (10^{-6}mol L^{-1}) in alkaline solution, r is Pearson´s coefficient. NaOH, g mL^{-1}

The results are consistent, regarding the intercept, the slope and correlation coefficient, and there is no significant difference between results got using solutions with different concentrations of NaOH. For the following experiments it was chosen NaOH 0.45 g mL^{-1} solution, because it is the commonest used. These results show the robustness of the system.

c) Signal and nitrogen concentration

It was investigated if conductivity is linearly related to nitrogen concentration. The experiments were done with standard solutions containing nitrogen in ammoniacal or nitric form. For Ammoniacal nitrogen: the calibration curves were done injecting five aliquots of

NH_4Cl 18.7×10^{-3} mol L^{-1} and 1.87×10^{-3} mol L^{-1} standard solutions. Mathematical equations of the interpolating lines are shown on TABLE 2. The conductivity used to obtain the equations show on TABLE 2 is the mean of three readings done in different days.

Table 2 – Mathematical equations of the calibration curve.

	Equation	r
18.7	L = 0.0408 cnc – 43.16	0.9956
1.87	L = 0.1244 cnc – 5.46	0.9970

where L is the conductivity (μS cm^{-1}), cnc is the nitrogen concentration (10^{-6} mol L^{-1}) in alkaline solution. Standard solution, 10^{-3} mol L^{-1}

The intercept of the lines shown on TABLES 1 and 2 makes clear the influence of the quality of absorbent solution over the results or the conditions in that the system is operated. The slope using 18.7×10^{-3} mol L^{-1} solutions (first equation in TABLE 2) is very similar those observed in TABLE 1.

For Nitric nitrogen: the determination of nitric nitrogen was done using Devarda's alloy, as reducing agent. At moment the Devarda's alloy reaches the heated alkaline solution hydrogen (H_2) is liberated, so it is expected the internal pressure in reaction chamber (R) increases and membrane to expand. Depending on extension of that, alkaline solutions could reach the chamber C. However, it was not observed in the experiments and the blank tests gave satisfactory results. Five calibration curves were done injecting KNO_3 1.87×10^{-3} mol L^{-1} standard solution and the equation of the interpolated line that correlates the readings to nitrogen concentration is the following:

$$L = 0.1422cnc - 8.27 \qquad (r = 0.9992) \qquad (2)$$

When the slope of the second equation shown on TABLE 2 (ammoniacal nitrogen) is compared to the slope of the Equation (2) (nitric nitrogen), it is not observed significant difference between them. Higher sensitivity for nitric nitrogen analysis could be expected as a function of increasing internal pressure in the chamber R, due to hydrogen evolution, with increasing the ammonia permeation through the membrane. But it did not occur, because almost all of the ammonium ions have been evaporated, as ammonia, and the increasing pressure has little effect on method sensitivity.

d) Absorbent solution

It was tested distilled water, 10^{-3} and 10^{-2} mol L^{-1}potassium chloride as absorbent solution. Best results are obtained with distilled water.

e) Detection limit

The detection limit calculated by the criterion of three standard deviation of blank was 65.1×10^{-6} and 69.5×10^{-6} mol L^{-1}, using the analytical procedure for ammoniacal and nitric forms, respectively.

3.2 Commercial sample analysis

A commercial fertilizer sample, containing nitric nitrogen, was bought in local store and analyzed. To test the robustness of the method, it was done two determinations: the first using KNO_3 as standard solution; and the second using NH_4Cl as standard solution (remember it is used standard addition method). The mean recovery (n=3) for the sample, comparing with the result obtained by AOAC method [13], was 97.1% when it was used KNO_3 solution, and 95.4% when used NH_4Cl solution. Both results show to be acceptable, once more showing the robustness of the system.

4. CONCLUSIONS

The proposed system has demonstrated to be adequate to analyze nitrogen in high concentration, either in nitric or ammoniacal form. This characteristic makes the proposed device very suitable to analyze the solution of fertilizer that would be used to determine potassium in flame photometer. Other important characteristic of this method is that it can be easily converted into a FIA method to analyze fertilizers, for example, and in this way improve the quality control of the production process.

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