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TOTAL NITROGEN DETERMINATION IN AMMONIACAL, AMIDIC AND NITRATE NITROGEN CONTAINING FERTILIZERS BY THE RANEY CATALYST METHOD

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ABSTRACT

This paper presents the optimized conditions for the determination of total nitrogen in ammoniacal, amidic, and nitrate nitrogen containing fertilizers by the Raney catalyst method using a Buchi K-436 speed digester and a Buchi K-360 distillation unit.

Keywords: Fertilizers, nitrogen, raney, ammonical, amidic, nitrate

INTRODUCTION

Nitrogen is one of the nutrients that mostly limit plant growth. Therefore, fertilizers normally contain at least one form of nitrogen, mainly ammoniacal, amidic, or nitrate nitrogen, as exemplified in Table 1.

Table 1. Some types of nitrogen used in fertilizers

	Type	Examples
N-NH_4^+	Ammoniacal	Monoammonium phosphate ($NH_4H_2PO_4$) (MAP) Ammonium sulfate (NH_4SO_4)
N-amidic	Amidic	Urea ($CO(NH_2)_2$)
N-NO_3^-	Nitrate	Calcium nitrate ($Ca(NO_3)_2$) (CN)
N-NH4+/ N-NO3-	Ammoniacal + nitrate	Ammonium nitrate (NH4NO3) (AN) Calcium ammonium nitrate (5Ca(NO3)2.NH4NO3.10H2O) (CAN)

In the soil, the amidic nitrogen (N-amidic) has to be hydrolyzed to ammoniacal nitrogen (N-NH4+), which then suffers nitrification by bacteria to the nitrate form (N-NO3-). Only nitrate is taken up by plants, rapidly and at high rates. Nitrate-based fertilizers have been considered the most efficient nitrogen sources, since they are immediately available as nutrients for plant uptake and cause less acidification of the soil than urea or ammonium-based fertilizers. However, granular nitrates absorb water from air and ammonium nitrate (AN) is a detonable substance, which has caused several disasters through the 20th century (BRABAUSKAS, 2016).

The analysis of total nitrogen is usually carried out by the Kjeldahl method (1883), which starts by the digestion of nitrogen-containing compounds in the presence of a catalyst (such as Hg, Cr, Ni-Al alloy, or Cu) and sulfuric acid, which is a weak oxidant (KIRK, 1950; SÁEZ-PLAZA et al., 2013). Potassium sulfate is used to raise boiling point (ABRAMS et al., 2014; CAMPBELL & HANNA, 1937; HILLER et al., 1948) and the rate of digestion (KIRK, 1950). The quantity of sulfuric acid has to exceed the amount of K_2SO_4 to prevent ammonia losses, and the usual acid and salt contents (15 mL H_2SO_4 and 15 g K_2SO_4, which is divided in two portions, 7.5 g K_2SO_4 dissolved in the acid, and 7.5 g K_2SO_4 added later as powder) produce a digestion temperature of about 380 ºC, without reaching 400 ºC, which may lead to pyrolityc loss of nitrogen (SÁEZ-PLAZA et al., 2013). The use of a high K_2SO_4 to H_2SO_4 ratio will cause loss of ammonia (BARKER & VOLK, 1964). After digestion, nitrogen is reduced to ammonia and presented in the form of ammonium sulfate (MACKENZIE, 1994). The next step is the alcalinization and distillation of ammonia, which is collected in an acidic solution. Finally, an acid-base titration determines the amount of ammonia and consequently the nitrogen content.

The Manual of Oficial Analytical Methods for Fertilizers and Correctives of the Brazilian Ministry of Agriculture, Livestock and Food Supply (MAPA, 2017a, b) addopts the Raney catalyst method (BRABSON & BURCH, 1964; BRABSON & WOODIS, 1969) for nitrogen determination, presented as macro- and micromethods. Among the Raney catalyst powders (alloys of aluminum with other metals), the alloy containing Ni and Al is the most efficient reductant of nitrates in acid medium (BRABSON & BURCH, 1964), usually in the proportion 50 % Ni : 50 % Al (JOHNSON & MILLER, 1974). Nascent hidrogen is generated by reaction of Al with the acid and reduces nitrate to ammonia (BRABSON & BURCH, 1964). The accurracy of the reaction increases when carried out in a solution containing sulfuric acid and part of the potassium sulphate (BRABSON & WOODIS, 1969). In the nitrate analysis using the Raney catalyst method, the maximum amount 42 mg nitrate is set (BRABAUSKAS, 2016; BRABSON & BURCH, 1964; MAPA 2017a, b) in order to ensure that at least 1.5 g Raney alloy is available to reduce 42 mg nitrate (BRABSON & WOODIS, 1969). The reduction of nitrate to ammonia can also be carried out using salicilic acid (DICKINSON, 1954; RANKER, 1926; SAH, 1994) using for instance HgO or metallic Hg (AOAC 955.04-D method) or using $CuSO_4.5H_2O$ (MAPA, 2017a, b), however the method fails in the presence of chloride and is not suitable for liquid fertilizers (BRABSON & BURCH, 1964).

In the LFDA/PA fertilizers laboratory, since 2019 the amount of nitrate fertilizers received for analysis has increased considerably. Usually the samples are sent for analysis without description of the fertilizer nitrogen type. Therefore, the analysis is initially carried out by the Raney macromethod and then, if necessary, it is repeated by the same method with reduced sample uptake or the analysis is performed by the Raney micromethod. This article describes the optimized conditions to carry out the Raney catalyst macro- and micromethods in ammonical, amidic, and nitrate containing fertilizers using a Buchi K-439 SpeedDigester and a Buchi K-360 distillation unit.

MATERIALS AND METHODS

Instruments and apparatus

Samples and standards were weighed in Sartorius Cubis MSA analytical balances (Sartorius, São Bernardo do Campo, Brazil). The digestion was carried out in a Buchi K-436 SpeedDigester (Buchi, Valinhos, Brazil), connected to a Buchi scrubber K-415, while the distillation was performed using a Buchi KjelFlex K-360 distillation unit. For the acid-base titration, calibrated digital Titrette burettes (Brand, Wertheim, Germany) or glass burettes were used.

Reagents and chemicals

Ultrapure water (resistivity 18.2 MΩ cm) was obtained from a Milli-Q Integral 15 purification system (Merck Millipore, São Paulo, Brazil) and used throughout. Potassium sulfate (Merck, Rio de Janeiro, Brazil), sulfuric acid (Merck Millipore, São Paulo, Brazil), Raney catalyst (50 % Ni and 50 % Al) (Dinâmica, Indaiatuba, Brazil), copper sulfate pentahydrate (Merck, São Paulo, Brazil), sodium thiosulfate (Sigma-Aldrich, São Paulo, Brazil), sodium hydroxide (Dinâmica, Indaiatuba, Brazil), boric acid (J. T. Baker, Phillipsburg, Brazil), methyl red (Sigma-

Aldrich, São Paulo, Brazil), bromocresol green (Neon, Suzano, Brazil), and potassium nitrate 99 % (Química Moderna, Barueri, Brazil) were chemical grade. Kjeldahl tablets were Merck (Merck Millipore, São Paulo, Brazil) and consisted of a mercury- and selenium-free catalyst containing 47.7% Na_2SO_4, 47.7% K_2SO_4, 2.8% TiO_2, and 1.8% $CuSO_4$. Ammonium sulphate, MAP, and urea were obtained as fertilizer raw materials, analyzed by the Raney catalyst micromethod, and validated in our laboratory for homogeneity and stability in order to be used as quality control samples. The nitrate fertilizer standard reference material was SRM NIST 193 (NIST, Gaithersburg, United States) and contained 13.84 % w/w of nitrogen. The K_2SO_4-H_2SO_4 solution was prepared using 20 % V V^{-1} H_2SO_4 and 10.67 % w V^{-1} K_2SO_4.

Fertilizers analysis

The analysis of fertilizers was performed as summarized in Figure 1. The samples and reagents listed in Table 2 were added to 300-mL Buchi SpeedDigester sample tubes and the digestion was performed according to the conditions of Table 3. After the mixtures were cooled down, the distillation was carried out as shown in a Buchi K-360 distillation unit using the parameters of Table 4. Finally, the distilled solutions were titrated using 0.25 M sulfuric acid (macromethod) or 0.1 sulfuric acid (micromethod) using methyl red and bromocresol green as indicators.

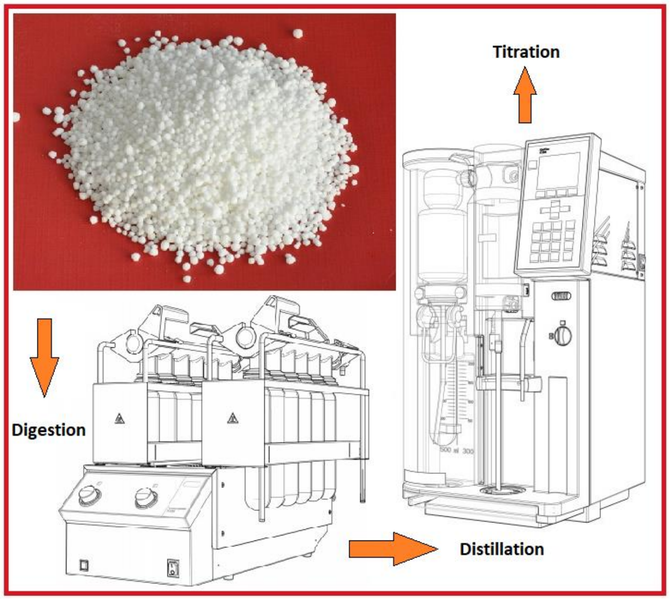

Figure 1. Determination of total nitrogen in ammoniacal, amidic and nitrate nitrogen containing fertilizers by the Raney catalyst method using a Buchi K-436 SpeedDigester and a Buchi K-360 distillation unit.

Table 2. Fertilizers preparation for digestion.

	Raney macromethod			Raney micromethod
Fertilizer / nitrogen type	Granular, not nitrate	Granular, nitrate	Liquid, not nitrate	Granular and liquid, nitrate and non-nitrate
Sample mass	0.5 g sample	Equivalent to 21 mg $N\text{-}NO_3^-$ (1)	2.5 g sample	1.0 g sample
Water	-	-	250 mL	250 mL
Aliquot	-	-	Equivalent to 10 mg to 40 mg N	Equivalent to 2.5 mg to 15 mg N
Raney catalyst	0.85 g	0.85 g	0.85 g	0.70 g
H_2SO_4 - K_2SO_4 solution	75 mL (2)	75 mL (2)	75 mL (2)	-
$CuSO_4.5H_2O$	0.5 g (3)	0.5 g (3)	-	-
K_2SO_4	7.5 g (3)	7.5 g (3)	7.5 g (3)	-
H_2SO_4	-	-	-	5 mL
Water	-	-	-	From the aliquot

(1) In case of KNO_3 (13.72 % N) and NIST 193 (13.84 % N), sample uptake was 0.15 g (equivalent to 42 mg nitrate).

(2) 75 mL of K_2SO_4-H_2SO_4 solution contains 15 mL H_2SO_4 and 8.0025 g K_2SO_4, which corresponds to 20 % V V^{-1} H_2SO_4 and 10.67 % w V^{-1} K_2SO_4.

(3) Alternatively, K_2SO_4 and $CuSO_4.5H_2O$ were replaced by one Merck Kjeldahl tablet.

Table 3. Digestion conditions at the Buchi K-436 SpeedDigester.

Raney macromethod	Raney micromethod
Preheat: 370 ºC	
Step 1: 370 ºC 1 min	Preheat: 370 ºC
Step 2: 350 ºC 13 min (1)	Step 1: 370 ºC 45 min
Step 3: 370 ºC 60 min	Step 2: 50 ºC 0 min
Step 4: 50 ºC 0 min	

(1) 13 minutes corresponds to 3 minutes necessary to drop the temperature from 370 ºC to 350 ºC, followed by 10 minutes at 350 ºC.

Table 4. Distillation conditions for the Buchi KjelFlex K-360 distillation unit.

Reagents / Distillation parameters	Use	Raney macromethod	Raney micromethod
Water	Added to sample tube	50 mL	50 mL
$Na_2S_2O_3.5H_2O$ 8% w/V	Added to sample tube	3 mL	-
NaOH 32% w/V	Added to sample tube	78 mL	35 mL
H_3BO_3 40% w/V	Added to collector flask	50 mL	5 mL
Water	Added to collector flask	-	40 mL
Reaction time	-	5 s	5 s
Steam power	-	100 %	100 %
Distillation time	-	300 s	300 s

RESULTS AND DISCUSSION

Sample preparation, digestion and distillation methods

The macro- and micromethods of the Raney catalyst used in the study are based on the Manual of Official Analytical Methods for Fertilizers and Correctives of the Brazilian Ministry of Agriculture, Livestock and Food Supply (MAPA, 2017a, b). However, due to the use of Buchi equipment (K-436 SpeedDigester and K-360 distillation unit), some adjustments were necessary, as summarized in Tables 2, 3 and 4 and discussed below.

Raney catalyst macromethod: digestion temperature

Regarding the digestion temperature, the Buchi conditions were first set for N-NO_3^- containing fertilizers, whose digestion parameters are the most difficult to optimize. Once these conditions were set (Table 2), they were satisfactorily tested for the other nitrogen forms (ammoniacal and amidic). The MAPA manual describes the use of an initial digestion temperature that brings 100 mL water to boiling in 5 minutes, which should then be reduced to a temperature that brings 100 mL water to boiling in 10 minutes, and finally be raised again to the initial temperature, which shall be kept until H_2SO_4 white fumes cease and the mixture becomes clear. In the K-439 Buchi SpeedDigester, the temperature of 350 ºC brings water to boil in 10 minutes, however the temperature ramp developed by this digester is not quick enough to bring water to boil in 5 minutes, no matter how high the initial temperature is set. Therefore, the best digestion condition was obtained using a preheat to the initial temperature of 370 ºC (this step usually takes

11 minutes), which was kept for 1 minute (step 1), then the temperature was reduced to 350 ºC and kept for 10 minutes (step 2, 13 minutes in total), and finally the temperature was raised again to 370 ºC and maintained until the white fumes ceased (step 4, 60 minutes), which serves as an indication that the digestion of ammoniacal, nitrate, and urea nitrogen was completed (BRABSON & WOODIS, 1969; MAPA, 2017a, b).

A longer digestion method, in which the step 3 at 370 ºC was increased from 60 to 90 minutes, was also tested, in order to extend the digestion by 30 minutes after the white fumes ceased, as recommended by Brabson & Woodis (1969), however no improvements in nitrogen recoveries were observed. Additionally, a two-step digestion method was also tested, as nitrogen digestion is usually carried out (addition of Raney catalyst, H_2SO_4, and half of K_2SO_4 and heating, prior to the addition of $CuSO_4.5H_2O$ and of the remaining K_2SO_4). In order to do this using the Buchi equipment, steps 1 and 2 of the digestion method (Table 2) were performed without the suction module of the SpeedDigester, and then $CuSO_4.5H_2O$ and the remaining K_2SO_4 were added and the digestion proceeded according to step 3 (Table 2) using the suction module. Since no recovery improvements were obtained, the method was kept as shown in Table 2, with the addition of all reagents, connection of the Buchi suction module, and start of the Buchi method.

Raney catalyst macromethod: catalysts

According to the MAPA manual, the macromethod requires sample masses up to 2.0 g, as well as 1.7 g of Raney catalyst and 150 mL of H_2SO_4-K_2SO_4 solution (equivalent to 15 mL H_2SO_4 and 8.0025 g K_2SO_4). Additionally, 1.0 g $CuSO_4.5H_2O$ and 15 g K_2SO_4 are also required in case of granular fertilizers (Chapter I of the Manual), while only 15 g K_2SO_4 (without copper) are added in case of liquid fertilizers (chapter II of the Manual). For nitrate containing fertilizers, it is essential to keep a proportion of 1.7 g (or at least 1.5 g) of the Raney catalyst to 42 mg nitrogen (BRABSON & WOODIS, 1969; JOHNSON et al., 1974). In the Buchi SpeedDigester, it was more convenient to use half of the masses and volumes described in the MAPA manual, in order to ensure that the volume inside the digestion tube is less than 1/3 of its volume, as recommended in the Buchi manual.

It was observed that K_2SO_4 and $CuSO_4.5H_2O$ (whenever used) can be substituted by one Merck Kjeldahl tablet. These tablets contain 47.7% Na_2SO_4, 47.7% K_2SO_4, 2.8% TiO_2 and 1.8% $CuSO_4$. Since each tablet weights approximately 5 g, it corresponds to 2.385 g Na_2SO_4, 2.385 g

K_2SO_4, 0.14 g TiO_2, and 0.09 $CuSO_4$ (equivalent to 0.1407 g $CuSO_4.5H_2O$). Although the addition of $CuSO_4$ to the analysis of liquid fertilizers strongly reduces the recovery of nitrogen, the use of the Merck Kjeldahl tablet containing $CuSO_4$ did not affect significantly the nitrogen recovery in liquid fertilizers. The tablet also contains TiO_2, and the combination of $CuSO_4$ and TiO_2 was already reported to make protein digestion feasible in 40 minutes instead of 90 minutes in case only $CuSO_4$ was used (KANE, 1986).

Raney catalyst macromethod: distillation

After digestion and cool down, water and NaOH are added, in order to neutralize the acid and generate an excess of NaOH (basic conditions). The addition of thiosulfate is based on its capacity to precipitate mercury, catalyst in the original method (BRABSON & WOODIS, 1969), and to allow the liberation of ammonia by boiling (HILLER et al., 1948). We tested the use of 3 mL and 12.5 mL of a 8 g/L solution of $Na_2S_2O_3.5H_2O$ for the macromethod and, since no recovery differences were observed, the volume of 3 mL was maintained (Table 3).

Nitrogen recoveries

Table 5 shows the nitrogen recoveries obtained using the optimized experimental conditions summarized in Tables 2, 3 and 4. The KNO_3 recovery using the micromethod was the reference used during the optimization of the macromethod for KNO_3 and NIST 193.

Table 5. Nitrogen recoveries.

Experimental conditions							Nitrogen content					
Method	N type	Sample uptake	Raney catalyst (g)	H_2SO_4 K_2SO_4 sol. (mL)	K_2SO4 (g)	$CuSO_4$. $5H_2O$ (g)	Declared amount (% w/w)	Obtained amount (% w/w)	f_{REC} (%)	Obtained amount (% w/w) average	f_{REC} (%) average	CV (%)
Micro method	KNO_3	1 g in 250 mL, aliquot 25 mL	0.7	-	-	-	13.72	12.37	90.16	13.38	97.50	5.21
							13.72	12.72	92.71			
							13.72	13.40	97.67			
							13.72	13.22	96.36			
							13.72	13.46	98.10			
							13.72	13.11	95.55			
							13.72	14.10	102.77			
							13.72	14.72	107.29			

Experimental conditions							Nitrogen content					
Method	N type	Sample uptake	Raney catalyst (g)	H_2SO_4 K_2SO_4 sol. (mL)	K_2SO4 (g)	$CuSO_4.5H_2O$ (g)	Declared amount (% w/w)	Obtained amount (% w/w)	f_{REC} (%)	Obtained amount (% w/w) average	f_{REC} (%) average	CV (%)
							13.72	13.29	96.87			
Macro method	MAP	0.5 g	0.85	75	7.5	0.5	11.40	11.98	105.06	11.77	103.19	2.89
							11.40	12.04	105.58			
							11.40	11.29	99.01			
							11.40	11.76	103.13			
Macro method	Urea	0.5 g	0.85	75	7.5	0.5	46.30	44.50	96.12	44.62	96.37	0.23
							46.30	44.49	96.09			
							46.30	44.76	96.68			
							46.30	44.67	96.48			
							46.30	44.64	96.42			
							46.30	44.64	96.42			
Macro method	N-NH_4^+	0.5 g	0.85	75	7.5	0.5	20.75	20.76	100.04	20.80	100.24	0.30
							20.75	20.72	99.85			
							20.75	20.88	100.62			
							20.75	20.82	100.33			
							20.75	20.83	100.38			
Macro method	KNO_3	0.15 g KNO_3 (21 mg N)	0.85	75	7.5	0.5	13.72	13.30	96.94	13.12	95.64	1.74
							13.72	12.38	90.23			
							13.72	13.27	96.72			
							13.72	13.29	96.87			
							13.72	13.28	96.79			
							13.72	12.94	94.31			
							13.72	13.10	95.48			
							13.72	13.31	97.01			
							13.72	13.15	95.85			
							13.72	12.98	94.61			
							13.72	13.16	95.92			
							13.72	13.25	96.57			
							13.72	13.27	96.72			
							13.72	13.11	95.55			
							13.72	13.02	94.90			
							13.72	13.30	96.94			
							13.72	12.89	93.95			
							13.72	13.19	96.14			

Experimental conditions							Nitrogen content					
Method	N type	Sample uptake	Raney catalyst (g)	H_2SO_4 K_2SO_4 sol. (mL)	K_2SO_4 (g)	$CuSO_4.5H_2O$ (g)	Declared amount (% w/w)	Obtained amount (% w/w)	f_{REC} (%)	Obtained amount (% w/w) average	f_{REC} (%) average	CV (%)
Macro method	NIST 193 (N-NO_3^-)	0.15 g KNO_3 (21 mg N)	0.85	75	7.5	0.5	13.84	13.22	95.52	13.14	94.97	2.07
							13.84	13.47	97.33			
							13.84	12.46	90.03			
							13.84	13.31	96.17			
							13.84	13.08	94.51			
							13.84	12.78	92.34			
							13.84	12.91	93.28			
							13.84	13.40	96.82			
							13.84	13.13	94.87			
							13.84	13.19	95.30			
							13.84	13.15	95.01			
							13.84	13.16	95.09			
							13.84	12.85	92.85			
							13.84	13.66	98.70			
							13.84	13.35	96.46			
							13.84	13.16	95.09			
							13.84	13.18	95.23			
							13.84	13.14	94.94			

CONCLUSION

The determination of nitrogen in fertilizers containing nitrogen nitrate (N-NO_3^-) demands some attention concerning the digestion temperature, sample uptake, and exposure to humidity. The Raney macromethod was optimized for the main fertilizers nitrogen types (ammoniacal, amidic, and nitrate) using Buchi equipment in order to reach similar recoveries obtained using the Raney catalyst micromethod.

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