

Determination of Ammonium-Nitrogen by Molecular - Emission Spectroscopy in Premixed Cool flames

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Nitrogênio-amônio é determinado pela emissão quimiluminescente a 336,0, 500,0 e 388,3 nm para as espécies NH, NO-O e CN respectivamente, que geram amônia em solução alcalina. É usado um queimador circular capilar. As determinações para nitrogênio-amônio em concentrações acima de 20 mg/l no extrato de solo, mostram-se rápidas, exatas e precisas.

Ammonium-nitrogen was determined using the chemiluminescence emissions at 336.0, 500.0 and 388.3 nm of the species NH, NO-O and CN respectively produced when ammonia gas generated from alkaline samples solutions is introduced in various flames. A Circular Capillary burner was used. The main band heads of the emission spectra from ammonia using hydrogen/air/nitrogen, acetylene/air/nitrogen and propane/nitrogen flames were used to obtain calibration graph of ammonium-nitrogen vs emission intensity over wide concentration ranges. The determination above of 20 mg l⁻¹ of ammonium-nitrogen in soil extracts have been found to be accurate rapid and precise.

Key words: ammonium; nitrogen; molecular emission spectrometry; soil analysis.

Introduction

Ammonium-nitrogen (AN) is found in soils, waters, biological substances, and other materials. The determination of nitrogen in this particular chemical form is of importance because it is an important micronutrient in the wood, oceans and soils¹. Various analytical spectrometric methods for the determination of AN have been discussed in the literature with regard to precision and sensitivity. Although most spectrometric methods are highly sensitive, special precautions are required when applying them to samples of coloured solutions or suspensions². In contrast, the flame emission or absorption methods are fast and are not affected by the colour of the solution³⁻⁸. In this paper, the spectrophotometric determination of ammonium-nitrogen by molecular emission after its liberation as ammonia from strongly alkaline sample solution is described. An all gas premixed circular burner was used to generate the flames. The emission from several molecular species in hydrogen/air/nitrogen (NH and NO-O species), acetylene/air/nitrogen and propane (NH and CN species) flames were used in the determination.

Experimental

Burner design. Fig. 1 shows the burner system used in this work. The various gases are premixed and the flame stabilized at a circular burner head constructed from stainless steel capillary tubing were a closed hexagonally packing is ob-

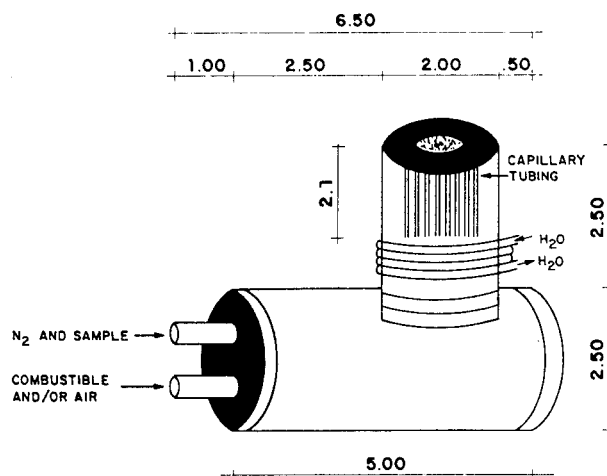


Figure 1. Burner design. Numbers indicate dimensions in cm.

tained. The diameter of the burner head (0.75, 1.0 and 1.5 cm i.d.) and of the stainless steel tubes (1.3 and 2.2 mm e.d.), the length (2.1 and 2.8 cm), and the number of these tubes (from 30 to 98) were optimized based on flame stability, sensitivity and safety. The smaller diameter tubing (1.3 mm e.d.) shows a very stable flame and the emission intensities of the molecular species were higher with the 0.75 cm i.d. burner head. The length of tubing did not influence the flame stability of the sensitivity. For safety reasons, the ignition and extinction of the different flames with various fuel-oxidant flow ratios were examined. In some cases explosive flashback of the hydrogen and acetylene flames was observed. This could be due to overheating of the burner head or to an inappropriate burning/gas flow ratio^{9,10}. This unsafety was prevented by incorporating a water cooling device which consisted of a 3.0 mm i.d. copper tube coiled below of the burner head and optimizing the gases flow ration (*see below*).

Apparatus. An schematic diagram of the employed instrumentation and gas generations system is shown in Fig. 2. The spectrometer was a modified atomic absorption spectrometer (Varian-Techtron LTD, Melbourn, Australia, Model AA-1475) arranged to permit flame emission spectrometry. The used cell-teflon reaction vessel (RV) system was the same as described previously¹¹. A magnetic-stirrer-hot plate was used to heat and to mix the RV. A two-ways valve was connected to the system, as shown in Fig. 2, to allow the nitrogen carrier-gas to pass to the flame without passing through the reactor, so as to give a constant background before and after sweeping through the evolved ammonia.

Reagents. All reagents were of analytical-reagent grade. Deionized/distilled water was used throughout. A stock solution of 10 mg ml⁻¹ ammonium-ion was prepared by dissolving ammonium sulfate in water and lower-concentration solutions were prepared daily.

Recommended procedure. Use the optimized instrumental conditions summarized in Table 1. Turn the two-ways valve to allow the nitrogen carrier gas to flow directly into the flame. Transfer 0.5-0.6 g (about three pellets) of solid sodium hydroxide into the reaction chamber of the RV system. De-aerate the RV for 20 s with nitrogen and then switch the valve to its initial position. Inject exactly 1.0 ml of the sample solution through a silicon septum into the reaction chamber and wait for 3 min. Then, direct the carrier gas to the RV by switching the two-ways valve (in this way the ammonia gas

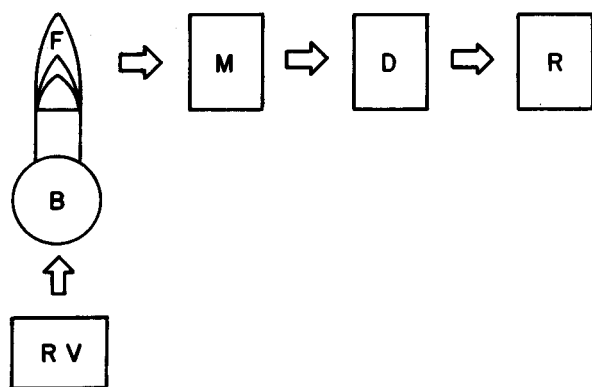


Figure 2. Schematic diagram of the instrumentation. RV: reaction vessel, B: burner, M: monochromator, F: flame and R: recorder.

Table 1. Details of optimum experimental conditions*.

Gas-generation conditions	
Sample volume, ml	1
Sodium hydroxide amount, g	0.5 - 0.6
RV temperature, °C	70
Tubing from RV to burner, cm	11
Tubing temperature, °C	80
Hydrogen flame composition	
NH species determination	
H ₂ flow, l/min	2.20
Air flow, l/min	0.78
N ₂ flow, l/min	0.23
NO-O species determination	
H ₂ flow, l/min	1.34
Air flow, l/min	2.70
N ₂ flow, l/min	0.23
Acetylene flame composition	
CN and NH species	
Acetylene flow, l/min	0.25
Air flow, l/min	2.00
N ₂ flow, l/min	0.06
Propane flame composition	
CN and NH species determination	
Propane flow, l/min	0.50
N ₂ flow, l/min	0.19

* Measurements for the species NH, NO-O and CN were made at 336.0, 500.0 and 388.3 nm respectively. In either case, the burner distance below the optical path of the detector view was of 2.0 mm.

generated is swept into the flame). The emission intensity is recorded as a function of time. For the determination of exchangeable AN content in soil, samples were first air-dried at 25°C and then the ammonium ion was extracted from the soil by the method described by Adams and Stevenson¹².

Optimization of flame and spectrometer operating conditions. The emission spectra obtained in this work using the hydrogen/air/nitrogen, acetylene/air/nitrogen and propane/nitrogen flames were similar to those reported previously¹³⁻²¹. In these relatively cool flames, no emission due to NH, NO-O or CN species were observed when the spectrum of either flame alone was recorded. Besides, the emission measurements were taken close to the top of the burner head level, in the coolest region of the flame, where its thermal energy is insufficient to breakdown the N₂ molecules of the carrier gas. However, when the ammonium-nitrogen flame it generated the NH and NO-O band emission with main band heads at 336.0 and 500.0 nm, respectively. Whereas, by using acetylene/air/nitrogen and propane/nitrogen flames the main emitting species was CN with a maximum wavelength emission at 388.3 nm. Particularly, in the last two flames the OH 306.4 nm band head is strongly degraded to the red and causes sufficient background emission to make the detection of low emission intensity from NH species very difficult, and therefore was not further studied.

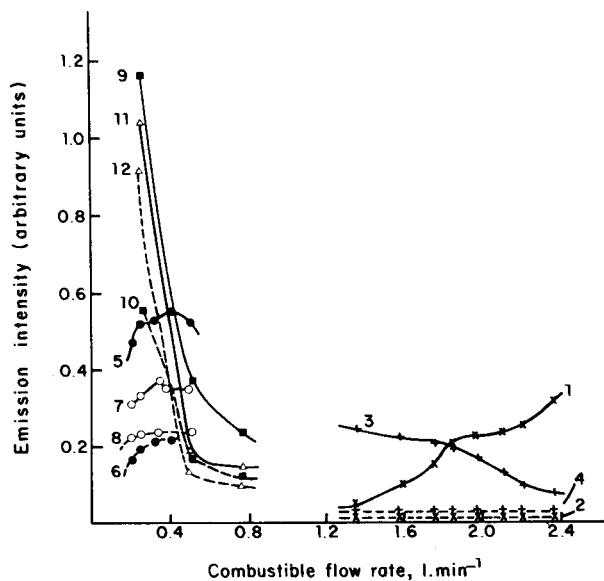


Figure 3. Effect of combustible flow rates on the emission intensity. $H_2/air/N_2$ flame: emission (1) and background (2) from NH and emission (3) and background (4) from NO-O. Propane/ N_2 flame: emission (5) and background (6) from CN and emission (7) and background (8) from NH. Acetylene/ air/N_2 flame: emission (9) and background (10) from CN and emission (11) and background (12) from NH. Experimental conditions as specified in Table 1. Flame backgrounds are indicated in dashed lines.

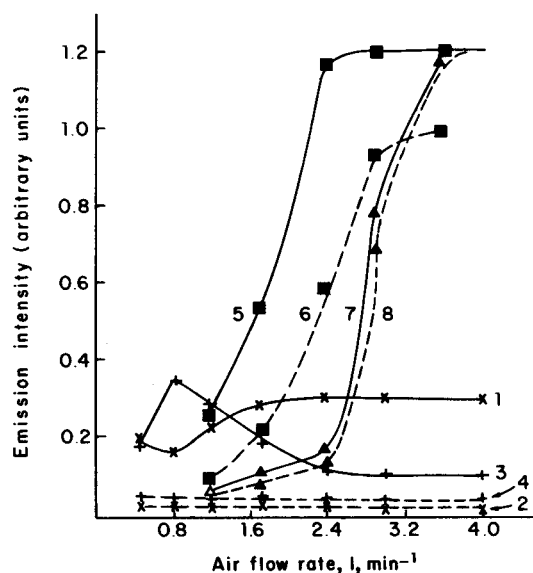


Figure 4. Effect of air flow rate on the emission intensity. $H_2/air/N_2$ flame: emission (1) and background (2) from NH and emission (3) and background (4) from NO-O. Acetylene/ air/N_2 flame: emission (5) and background (6) from CN and emission (9) and background (10) from NH. Experimental conditions as specified in Table 2. Flame backgrounds are indicated in dashed lines.

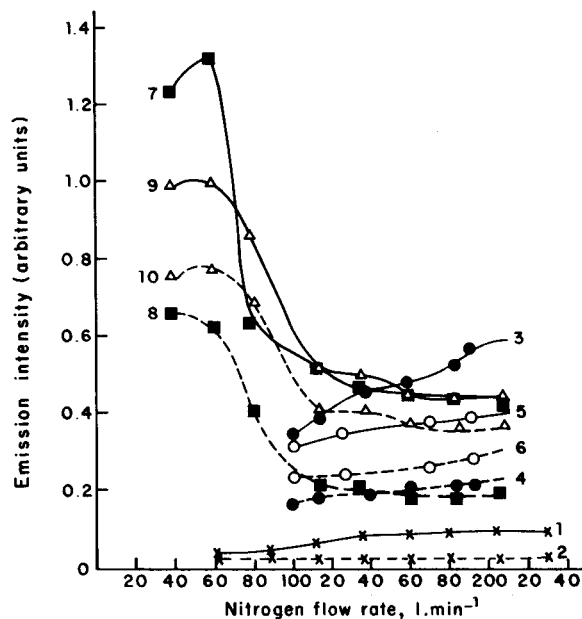


Figure 5. Effect of nitrogen flow rates on the emission intensity. $H_2/air/N_2$ flame: emission (1) and background (2) from NH./Propane/ N_2 flame: emission (3) and background (4) from CN and emission (5) and background (6) from NH. Acetylene/ air/N_2 flame: emission (7) and background (8) from CN and emission (9) and background (10) from NH. Experimental conditions as specified in Table 1. Flame backgrounds are indicated in dashed lines.

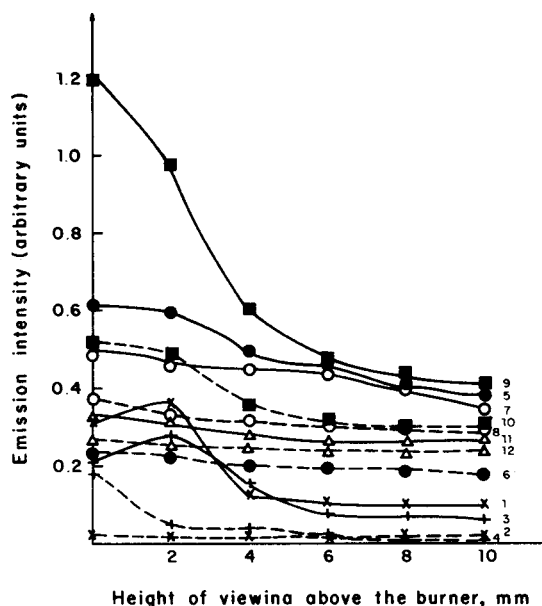


Figure 6. Effect of height of viewing above the burner on the signal intensity. $H_2/air/N_2$ flame: emission (1) and background (2) from NH./Propane/ N_2 flame: emission (3) and background (4) from CN and emission (5) and background (6) from NH. Acetylene/ air/N_2 flame: emission (7) and background (8) from CN and emission (9) and background (10) from NH. Experimental conditions as specified in Table 1. Flame backgrounds are indicated in dashed lines.

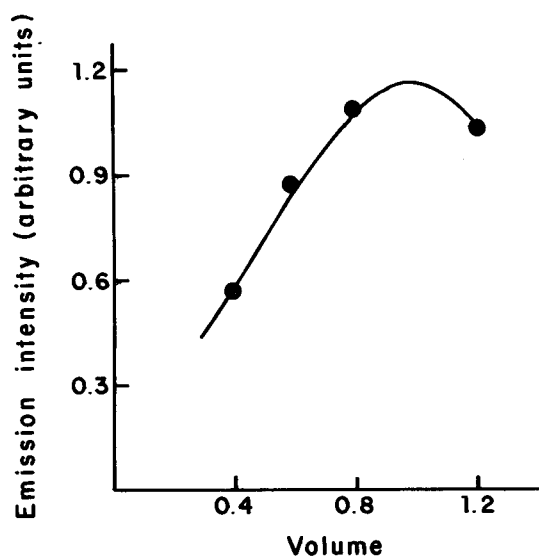


Figure 7. Effect of sample volume on the emission intensity of the NH signal using a H_2 /air/ N_2 flame. Experimental conditions as specified in Table 1.

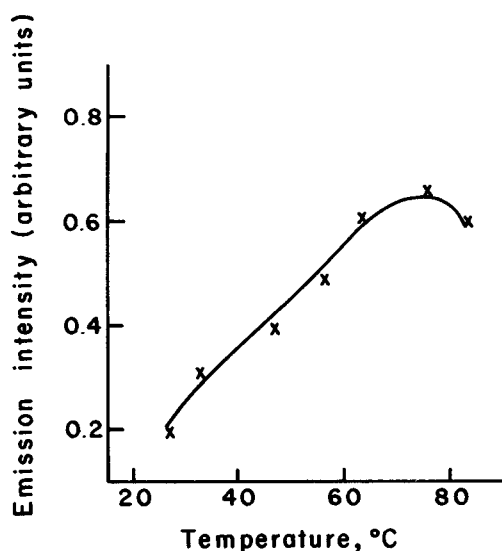


Figure 8. Effect of reaction vessel temperature on the emission intensity from NH using a H_2 /air/ N_2 flame. Other experimental conditions as specified in Table 1.

The effect of the variation of combustible, air and nitrogen flow-rates and height of viewing above the burner on the signal and background emission intensities at each respective maximum wavelength intensity for the different emitting species was investigated. The results are shown in Figs. 3-6. These results were obtained, when signals from solutions containing 100 mg l^{-1} of ammonium ion were recorded using the finally adopted (Table 1) experimental conditions, together with the obtained integrated background intensities. In either case, the best signal to background intensity ratio was

Table 2. Analytical figures of merit.

Flame	Specie	Linear Range mg/l	Slope	Intersection on Y axis	Coeff. Regress.	Limit of Detection mg/l
H_2 /air N_2	NH	30-700	0.031	0.034	0.998	20
	NO-O	100-700	0.007	0.85	0.9837	90
C_2H_2 /air N_2	CN	20-500	0.570	1.73	0.9991	20
C_3H_8 / N_2	CN	20-50	0.367	11.52	0.9929	20

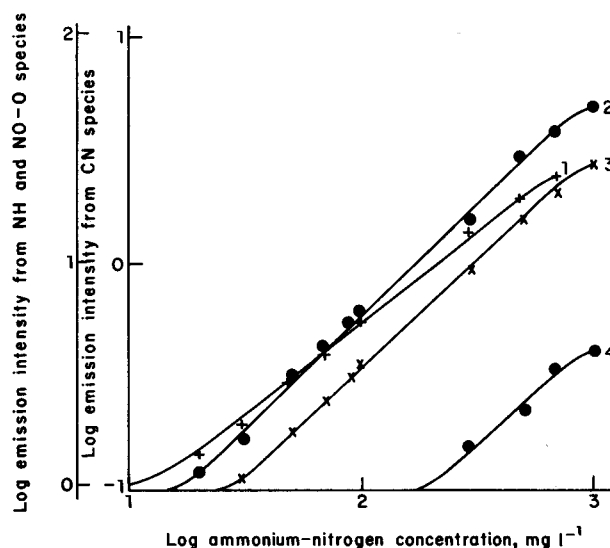


Figure 9. Effect of ammonium-nitrogen on maximum emission intensity. (1) CN emission in propane/ N_2 flame; (2) CN emission in acetylene/air/ N_2 flame; (3) NH emission in H_2 /air/ N_2 flame and (4) NO-O emission in H_2 /air/ N_2 flame. Experimental conditions as specified in Table 1. 1,2 scale a and 3,4 scale b.

chosen as the optimum flame operating conditions (Table 1). In the case of hydrocarbon flames, the background is relatively high because of the presence of unstable radicals, such as CH , C_2 and HCO , etc, besides the OH band also present in the hydrogen flame²². These species give a *quasi-continuum* in the visible and near ultra-violet regions. The addition of oxygen to either kind of flame could favour the formation of the NO-O species, but diminishes the intensity of the NH and CN species. However, the introduction of an additional stream of oxygen increases the temperature of the flame above 3,000 K and significantly increases the flame background. These observations and the additional difficulty in dealing with dangerous mixtures of gases prevented us of using oxygen.

Optimization of the gas-generation technique for ammonia. The effect of sample volume, amount of sodium hydro-

Table 3. Precision (%) for the determination of 30, 100 and 500 mg N/l by using the various flames.

Flame	Specie	AN, mg/l		
		30	200	500
H ₂ /air/N ₂	NH	5.0	3.1	2.3
	NO-O	--	5.1	3.7
C ₂ H ₂ /air/N	CN	3.8	2.5	1.8
C ₃ H ₈ /N ₂	CN	7.7	2.6	2.1

xide, nitrogen flow rate supplied to the RV, reaction time and RV temperature was investigated. In order to optimize the required volume of analyte for each injection, different volumes, containing 0.5 mg l⁻¹ of AN were injected in the reaction chamber containing 0.5-0.6 g of sodium hydroxide. Fig. 7 shows that a sample volume of 1.0 ml gives maximum emission intensity.

It was visually observed that when three pellets (about 0.5-0.6 g) of sodium hydroxide were used small amounts of the pellets were still present at the end of the reaction in the RV. It was noticed that fast and reproducible (coefficient of variation of ca. 1.1%) signals were obtained if an excess of sodium hydroxide was used. Therefore, it was decided to use three pellets of sodium hydroxide per measurement.

The heat generated by the dissolution of the alkali hydroxide speeds up the volatilization of the ammonia^{4,14}. Therefore, the effect of the temperature during the accumulation of ammonia in the reactor was investigated. The results are shown in Fig. 8. An increase in the emission intensity with the RV temperature was observed and a temperature of 70 °C was used for all subsequent measurements. The generation of ammonia was completed after 3 minutes at 70 °C. Therefore, the generated gas was introduced into the flame, 3 min after mixing the sample and sodium hydroxide.

The use of a magnetic follower and a stirrer motor beneath the RV was necessary. The efficient generation of ammonia required efficient stirring to obtain the maximum rate of renewal of the solution surface and a large surface area of the solution in comparison to the 8 ml dead volume of the generator above the liquid. The distance of the tubing from the generator to the burner was kept as short as possible (11 cm) in order to achieve higher sensitivity. In order to avoid condensation of the ammonia on the interface tubing walls, the tube was wrapped with a heating tape kept at ca. 80 °C.

Analytical performance. Using the recommended procedure previously described and the optimal operating conditions specified in Table 1, calibration graphs were prepared (Fig. 9) for evaluating the emission intensities from the species NH and NO-O (using the hydrogen/air/nitrogen flame) and CN (using acetylene/air/nitrogen and propane/nitrogen flames). The analytical figures of merit are presented in Table 2. They demonstrate that AN can readily be determined over wide concentration ranges as the calibration graphs for AN (peak height) were linear for 30 - 700, 100 - 700, 20 - 500 and 20 - 500 mg N/l by evaluating the emission from NH, NO-O (with a hydrogen/air/nitrogen flame), CN

(with an acetylene/air/nitrogen flame) and CN with a propane/nitrogen flame), respectively. The coefficients of variation (CV) for the determination of 30, 100, and 500 mg N/l (10 determinations) are given in Table 3. The best precision was obtained by using the propane/nitrogen flame (CV from 1.8 or 3.8). In all cases the precisions when 30 mg N/l was determined were poor, whereas they improved to acceptable values for the determination of 100 and 500 mg N/l (commonly about 2.5%). The limits of detection (signal of twice the background noise) were 20 mg N/l in all cases using either aqueous standard or soil extract solutions except for the NO-O emission with the hydrogen/air/nitrogen flame, which was 90 mg N/l.

Recoveries of N added to two soil samples that contained known amounts of N ranged from 94 to 104% in either case. As well, there were no interference in the determination of 100 µg N/l from a 9-fold amounts of Na⁺, K⁺, Ca²⁺, Mg²⁺, CO₄²⁺, Cu²⁺, Hg²⁺, Pb²⁺, Ni²⁺, Cd²⁺, Zn²⁺, Fe³⁺, Mn²⁺, Al³⁺, SO₄²⁻, Cl⁻, PO₄³⁻ and NO₃⁻.

As an application, NV contents of two local uncertified and fertilized soil samples were determined (Table 4). These results show a good agreement among the values, which is an indication that the accuracy by evaluating the NH (with a hydrogen/air/nitrogen flame) and CN (with acetylene/air/nitrogen and propane/nitrogen flames) emission is satisfactory. However, the NV content could not be evaluated in these samples by measuring the NO-O emission intensity generated in the hydrogen/air/nitrogen flame as its concentrations were below the working ranges.

Table 4. NV content in Mérida's unfertilized and fertilized soil samples*.

Flame	Specie	NV, mg g ⁻¹ of dry soil	
		Unfertilized soil	Fertilized soil
H ₂ /air/N ₂	NH	0.150 ± 0.004	0.728 ± 0.004
C ₃ H ₈ /NB	CN	0.143 ± 0.003	0.715 ± 0.003
C ₂ H ₂ /air/N ₂	CN	0.144 ± 0.004	0.737 ± 0.005

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