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Title: Development of an original and easy method for Isocyanic acid (HNCO) calibration on FTIR Spectrometer

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Abstract: HNCO is a harmful gaseous molecule presents in atmosphere and in many gaseous effluents such as automobile exhaust gases and waste biomass burning processes. Nevertheless, no commercial standard gas is available making analyzers calibration impossible, for FTIR spectrometry which is the most common method used for on-line measurements of isocyanic acid. The release of HNCO from the depolymerization of cyanuric acid by pyrolysis at 450°C and 550°C has been investigated, using a tubular reactor coupled with an infrared spectrometer. Under these conditions, gaseous HNCO is the major product (50% < HNCO < 80%), all other gas species (CO₂, CO, NH₃) being identified and well quantified. The coefficient of a cubic calibration equation between HNCO area FTIR spectrum and HNCO gas content are calculated by assuming the same quantity of HNCO given by mass balance and by FTIR measurement. Additional tests were performed to assume the reliability of the performed calibration.

Keywords: infrared spectroscopy, FTIR Calibration, pyrolysis, isocyanic acid, cyanuric acid.

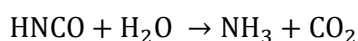
1. INTRODUCTION

Our research focuses on the quantification of HNCO during wood waste pyrolysis. One of the interests of wood waste pyrolysis is to remove an important proportion of adhesives from wood wastes. These glues are mainly produced from urea and thus contain large quantities of nitrogen [1–3]. The nitrogen contained in the resins is released into three main gases during thermal degradation: hydrogen cyanide (HCN), ammonia (NH₃) and isocyanic acid (HNCO) [1–6]. Isocyanic acid (HNCO) was identified and characterized in the 19th century by Liebig and Wöhler [7]. It is known to be present in interstellar environments [8–10] and has recently been measured in atmosphere [11–14]. It is mainly produced in automobile exhaust gases [11,15–20] and in biomass burning emissions [21]. Different thermochemical processes conduct also to the production of isocyanic acid such as pyrolysis of coal [4,22], pyrolysis of biomass [5,6,23,24] and pyrolysis of wood waste such as particleboard [1–3]. The quantification of such a gas is therefore essential to study the fate of fuel nitrogen during pyrolysis of waste and for N-mass balance establishment.

The quantification of HNCO in the ambient air and its fate in the atmosphere has been recently investigated by Borduas and al. [14] and Leslie and al. [11]. HNCO has been identified as a toxic and harmful gas for human health. Borduas and al. [14] assessed the lifetime of HNCO against hydrolysis ranges from a few seconds to years depending on the temperature, the pH and its location:

- Cloud water: from 10 hours to 20 days ($3 < \text{pH} < 6$, in the troposphere)
- Ocean water: 1-2 years if no other reactive chemistry is taking place ($T < 30^\circ\text{C}$, $\text{pH} = 8$)
- Human blood: several months (at physiological pH and temperature)

Leslie and al. [11] reviewed biochemical publications related to the toxicity of the OCN⁻ ion and induced reactions in the human body. The OCN⁻ ion is potentially dangerous to humans because it can induce changes in proteins through a carbamylation reaction. Carbamylation alters the structure of proteins and leads to complications such as renal failure, cardiovascular disease, cataracts, and rheumatoid arthritis. The removal of HNCO is achieved by a reaction of hydrolysis to make it harmless, converting HNCO into ammonia and carbon dioxide [5,14,25]:



Borduas and al. [14] showed that the solubility of HNCO in aqueous solution, which is directly related to the hydrolysis of HNCO, depends on pH and temperature. An acidic pH and a high temperature of an aqueous solution seems to favour a rapid hydrolysis of HNCO.

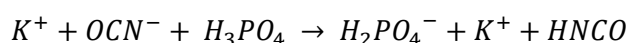
Its quantification in gas phase is possible regarding different methods described in literature. Firstly, by indirect method by sampling gas in impingers containing different types of solvent, solvent being afterwards analyzed. Two major indirect methods are described: sampling in aqueous acidic solvent (5E-3 M NaH₂PO₄ in water adjusted to pH 7 with LiOH [18,19], 1.7E-3 M HNO₃ in water [5]; 0.1 M H₂SO₄ in water [6]; 0.02 M CH₃SO₃H (methanesulfonic acid) [24]) and analyze by ionic chromatography or sampling in 0.01 M di-n-butylamine (DBA used as derivative agent) in toluene [12,13] and analyze by LC-MS. In-line measurement methods are also available such as Proton Transfer Reaction Mass Spectrometry (PTR-MS) [11,25,26], Chemical-ionization mass spectrometry (CIMS) [11–14,21], ammonia ion sensitive electrode (ion meter) after HNCO hydrolysis in acidic conditions [20] and Fourier transformed infrared (FTIR) analysis [4,9,15,16,23,25,27–33], FTIR being the most cited one.

Classical indirect methods do not need any calibration but do not allow differentiation between NH₃ and HNCO since the two gases are hydrolyzed in water into NH₄⁺ [5,6]. The latter are therefore not suitable to study processes where NH₃ and HNCO are both produced which is often the case for

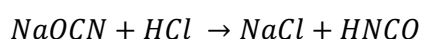
waste pyrolysis of N-fuel [1–4,22]. It still exists a method described by Kröcher and al. [20] which allows the distinction between NH₃ and isocyanic acid after dissolving in an adsorption solution. Nevertheless, this one has not been considered since pyrolysis of waste wood could also produce a significant amount of N-Tars [1] which may interfere with the method proposed. These N-Tars are also partly insoluble in water conducting to problems of plugging of sampling device. That is why only quantification methods on gas phase were only considered for this work.

In-line measurements on gas phase (without any dissolving step) are therefore more suitable but need to be calibrated with gas standards. Nevertheless, HNCO standards are not commercially available [1–4,9,11,23] as it polymerizes at high concentrations [2,11,13] in cyanuric acid and other species such as cyamelide [14].

Regarding FTIR analysis, calibration is described following two major ways. The first one consists to use established HNCO spectra available in literature [4,16,22,23] or synthetic calibration spectra computed with the use of the program MALT (Multiple Atmospheric _Layer _Transmission), including environmental (pressure, temperature, pathlength, etc.) and instrumental (resolution, line shape, wavenumber shift) effects in the calculation [34]. Nevertheless, these methods have limitations. Indeed, in order to match real spectra closely, instrumental characteristics such as wavelength scale shift, poor phase correction and line shape, effective resolution, and detector nonlinearity must be known. If the spectrometer is not well aligned or is otherwise not operating ideally, some independent determination of these parameters must be made [34]. That is why these methods are not so accurate than the one which consists to produce HNCO in well-known quantities and to dilute it in a flow of gas stream such as nitrogen [12–14]. The production of HNCO has been largely commented in literature and different ways are described. Firstly, by chemical reactions. Ashby and Werner [30] proposed a method for the production of HNCO using potassium cyanate (KOCN) and phosphoric acid (H₃PO₄) in solution. The reaction processes as follows:



In their work, Lowenthal and al. [29] used gaseous chloric acid with sodium cyanate to produce pure HNCO. The reaction equation is as follows:



Fujimoto and al. [35] also used sodium cyanate but with stearic acid. The HNCO used was prepared by heating a vacuum-desiccated mixture of KCNO and stearic acid in vacuum approximately 90°C. The HNCO was then collected at -196°C and distilled trap-to-trap between -60°C and -120°C to remove impurities.

In a second way, HNCO could also be synthesized by thermal degradation of urea [18,25,31,36] or of cyanuric acid [9,11,14,21,25,27,28,30,33,37], sometimes followed by a purification step [9,11,27,29,30,35]. Since some by-products are also synthesized (biuret, cyanuric acid and ammeline from urea [31,36] ; CO₂, NH₃, HCN from cyanuric acid [27]), a second step of purification could be needed. Concerning degradation of cyanuric acid, Liebig and Wohler's method [7] has been further developed, to give a purer product and better yield, by Linhard [37] and by Herzberg and Reid [27]. Cyanuric acid, on being heated, tends to sublime without reaction. In order to achieve depolymerization, heat must first be applied to the solid to vaporize it and then the resulting vapour must be heated still further. Herzberg and Reid gave the cyanuric acid a preliminary heating in vacuum to 200°C in order to remove water and avoid the production of NH₃ [27]. The solid was then volatilized slowly in vacuum at 450°C and the gas stream was passed through a tube furnace at 700°C. The bulk of the HNCO was collected in a trap at -80°C. After oxidation by Ag₂O of any HCN present,

drying with P₂O₅, and distillation at -30 °C, a product considered to be better than 99.5% pure was obtained. Different works presented in literature describe the calibration method for their analysers using the way of HNCO production [12–14] but the way precisely used are really complex.

The aim of this work is therefore to find and to describe clearly an easier method to calibrate a FTIR spectrometer. The production of HNCO through thermal degradation processes is firstly studied regarding preliminary tests. After the choice of the more convenient method to produce isocyanic acid, the ways to assume a precise monitoring of HNCO concentration as well as the numerical calibration are highlighted.

2. EXPERIMENTAL SECTION

2.1 Apparatus

The experiments were carried out in a refractory steel tubular reactor placed in a horizontal furnace (i.e Figure 1). The sample boat enables the introduction of samples in variable positions in the reactor by the insertion axis. The sample boat is equipped with a thermocouple to measure the sample temperature. The variation of the sample boat position in the reactor enables to control the sample temperature without changing furnace temperature. It allows therefore the use of only one furnace. A gas flow controlled by a numerical flow controller supplied the reactor with the required gas mixture (nitrogen in this work).

Figure 1. Sketch of the laboratory study device

The resulting gases (mix of carrier gas and produced gases) pass through a glass tube and two glass coils cooled at 0°C to trap non-depolymerized cyanuric acid at the outlet of the reactor. Indeed, some deposit of cyanuric acid has been detected on the heated gas-cell of the FTIR spectrometer. In order to avoid the problem and to assume a better mass balance, glass coils have been added. The advantage of glass is that it is possible to check visually if the length of the coil is enough to assume that all non-depolymerized cyanuric acid residue has been trapped. A part of produced gases is then collected by a dilution system equipped with a sonic orifice, supplied by a nitrogen stream of 5 L/min at STP. The dilution system creates a depression to always collect the same amount of gas, independently from the incoming flow of gas. The dilution system is heated to 320°C in order to avoid deposits of condensable and of polymerized cyanuric acid and assumes a stable dilution rate close to 100.

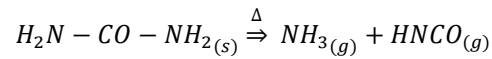
Diluted gases resulting from the pyrolysis of cyanuric acid are then sent through FTIR spectrometer (Bruker Equinox 55) equipped with a heated multiple-path gas cell (2.4m path length) and a liquid-nitrogen-cooled MCT detector. Gases were analysed in a semi-continuous way (20 s. of sampling time (16 scans), resolution of 1 cm⁻¹). The FTIR spectrometer configuration (Opus software) allows the qualitative and quantitative analysis of many compounds: carbon dioxide and monoxide, methane, N-compounds (ammonia, isocyanic and hydrocyanic acid), methanol, formic and acetic acid. The spectrometer calibration includes the dilution probe and sampling.

Taking into account HNCO toxicity [11,14], the outlet gas stream pass through a bubbler filled with an acidic pH solution and a temperature above 30°C. This enable the hydrolysis of HNCO and avoid any risk related to its dissemination in the atmosphere

2.2 Preliminary tests for HNCO production

2.2.1 Thermal degradation of urea

The pyrolysis of wood wastes releases a high amount of HNCO mainly due to the presence of aminoplast based resins (melamine – urea – formaldehyde monomers) in the waste composition [1–3,38]. As a first step, urea pyrolysis was investigated as a source of HNCO. It was hypothesized that urea degrades by heating to form HNCO as well as ammonia according to the following reaction equation [18,25,36]:



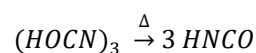
Some urea pyrolysis tests have been carried out to check the hypothesis that urea decomposes into HNCO and NH₃. During tests, further compounds were observed on infrared spectrums. Figure 2 shows two infrared spectra illustrating the peaks of the compounds obtained during the pyrolysis of a urea sample.

Figure 2. Two Infrared spectra illustrating the peaks obtained during the pyrolysis of a urea sample.

The compounds produced, in addition to HNCO (2285, 2252 cm⁻¹ on red curve), CO₂ (2364, 2332 673 cm⁻¹) and NH₃ (clusters of peaks around 3334, 1629, 965-930 cm⁻¹ on blue curve), correspond to compounds mentioned in the literature [31,36]: biuret (1081 cm⁻¹), cyanuric acid (1778, 1703, 1053, 764 cm⁻¹) and ammelide (1073 cm⁻¹). However, the laboratory does not have the ability to quantify the compounds produced. As a result, the generation of HNCO by thermal degradation of urea has been rejected.

2.2.2 Thermal degradation of cyanuric acid

Considering HNCO production through cyanuric acid thermal degradation, the method published by Herzberg and Reid in 1950 [27] has been approximately followed. The thermal depolymerization of cyanuric occurs above 330°C and gives the following reaction equation:



Herzberg and Reid described the method to produce HNCO in their work [27]:

- The cyanuric acid is preliminary heated at 200°C under vacuum to remove water and avoid the hydrolysis of produced HNCO into NH₃ during the experiment.
- The cyanuric acid is sublimated slowly at 450°C. The gas stream pass through a hotter tube furnace at 700°C to depolymerize the cyanuric acid. Herzberg and Reid report that cyanuric acid have a tendency to sublime without depolymerization.
- The major part of the HNCO produced was collected in a trap maintained at -80°C. The CO₂ was trapped in a second guard trap cooled by liquid nitrogen to reduce the fractionation time required to obtain a pure product. The product was finally purified by the Linhard method [37] (oxidation of HCN by Ag₂O, followed by drying with P₂O₅ and a distillation from a bath at -30°C). Herzberg and Reid assumes that the produced HNCO had a purity higher than 99.5%.

Preliminary experiments were performed to determine the best conditions to product isocyanic acid i.e. which:

- improve the gas production
- improve the HNCO proportion in gases

- assume that all by-products gases to be quantifiable by FTIR spectrometer

The cyanuric acid (Figure 3) used in this work was supplied by Sigma-Aldrich and 98% pure. Cyanuric acid is a nontoxic white powder.

Figure 3. Cyanuric acid (HNCO)₃ - 1,3,5-triazine-2,4,6-triol.

Cyanuric acid was oven-dried at $103 \pm 5^\circ\text{C}$ before tests to prevent HNCO hydrolysis during the decomposition of cyanuric acid and potential NH_3 production afterwards as commented by Herzberg and Reid [27].

Four parameters can be controlled in the tests: the pyrolysis temperature (final sample temperature in the sublimation area), the furnace temperature (depolymerization area), the N_2 gas flow and the quantity of cyanuric acid to be degraded in the reactor.

The mass of inserted dry acid cyanuric was between 0.4g and 1.4g, the flow of nitrogen stream between 0.5 and 1 L/min at STP, temperature of furnace between 350°C and 650°C and position of sample (after insertion) to reach a final sample temperature between 350°C and 500°C . Tests started with a flow of 1 L/min at STP, a cyanuric acid mass of 0.5g and a pyrolysis temperature of 350°C following the degradation temperature of cyanuric acid.

The pyrolysis temperature was gradually adjusted to 450°C , allowing a faster degradation and thus a higher peak area on FTIR spectrometer. The furnace temperature, and therefore the depolymerization area, has been adjusted to 550°C . At lower temperature, cyanuric acid is not completely depolymerized and traces of cyanuric acid are visible on the recorded FTIR spectra. Insufficient temperature generated a lot of condensate throughout the device as well as in the infrared spectrometer cell. Therefore, glass coils were added just after the reactor to avoid cyanuric acid deposit along the transfer line and in the FTIR gas cell as well as to improve mass balance.

The gas flow was adjusted to 0.5 L/min at STP because a too high gas flow decreased the signal of the infrared spectrometer (already decreased by the dilution system). In addition to this, it can be supposed that a lower gas flow allows a longer residence time of the generated gases in the reactor and thus a better depolymerization of cyanuric acid.

The preliminary tests performed on the degradation of cyanuric acid show encouraging outcomes. Cyanuric acid degradation conducts to a gas and solid phase production. The gas phase, mainly constituted of HNCO, represents approximately 90 wt% of the degradation products. Figure 4 shows two infrared spectra (from the test 21_1.2g available in results part):

- The first in red was taken at the beginning of a test of cyanuric acid degradation when only NH_3 , CO and CO_2 are produced. Some traces of HCN are also observed but in so low quantities that it has been neglected. This spectrum corresponds also to the time when NH_3 and HCN production is maximum.
- The second one in black was taken when the HNCO production is at the maximum of the test.

Figure 4. Two Infrared spectra illustrating the peaks obtained during the pyrolysis of a cyanuric acid sample (21_1.2g).

HNCO (2284, 2251, 670 cm^{-1}) seems to be the major gas product only by comparing areas on FTIR spectra (Figure 4). A small amount of NH_3 and CO (peaks around 2040-2220 cm^{-1}) is produced at the beginning of the test as can be seen on red curve as well as HCN in really low quantities (band between 3200 and 3350 cm^{-1} and peak at 712 cm^{-1}). Moreover, all gases produced (CO, CO_2 , NH_3), except for HNCO, are well calibrated on the FTIR spectrometer. HCN was neglected because of its really low concentration. The first step of preheating at 200°C under vacuum (avoiding NH_3 production) and the last step of gas purification (elimination of by-products i.e. CO_2 , CO) through method proposed by Herzberg and Reid [27] are therefore unnecessary.

This method was chosen for the next part of this work. The experimental device, the method used and the established equation for the infrared spectrometer calibration will be presented.

2.2.3 Experimental protocol

In a first step, cyanuric acid is oven-drying. The required quantity of cyanuric acid is weighed into a glass recipient and placed in the sample boat of the experimental device (Figure 1). The glass recipient and the glass coils are also weighed in order to determine precisely the amount of deposit remaining after pyrolysis. ($m_{\text{glass coil}}$ and m_{residue}). The sample boat is then placed at the beginning of the reactor in order to inert reactor and assumes a reaction in pyrolysis conditions. The reactor is set at 550°C and closed after the sample insertion. The inerting is achieved by the supplying of a nitrogen flow (2 L/min at STP) through the reactor. The composition of the gases coming out of the reactor is monitored by the infrared spectrometer until only N_2 is detected.

After that, the pyrolysis step is launched. The nitrogen flow is adjusted to 0.5 L/min at STP. Infrared spectrums are recorded. The sample boat is moved to the determined position to reach 450°C.

Finally, the experiment is stopped when the entire amount of cyanuric acid is degraded and the infrared spectrometer do not detect any gases. During the tests, the generated gases only consist of NH_3 , CO_2 , HNCO and CO. The glass vessel and the glass coils are weighed after the test.

2.3 Calculations procedures

2.3.1 FTIR quantitative analysis

A quantitative analysis method has been developed to quantify the volume of CO, CO_2 and NH_3 produced during experiments. The FTIR spectrometer is regularly calibrated for CO, CO_2 between 0-10% and NH_3 between 0-5% volume. The characteristic frequencies used for the quantitative analysis was 2170–2174 cm^{-1} for carbon monoxide, 665–672 cm^{-1} for carbon dioxide, 954–970 cm^{-1} for ammonia, and, finally 696-702 cm^{-1} for isocyanic acid (HNCO).

The values of concentrations of the different gases in function of time was recorded in an excel table. The volume of CO, CO_2 and NH_3 produced during experiments was obtained with the following expression 1:

$$V(X) = \sum_i^n \left(\frac{C_i(X) + C_{i+1}(X)}{200} Q_{gas_i} * t \right) \quad (1)$$

Where $V(X)$ is the volume of the gas X produced during the experiment (NL), n the number of measures during the experiment, $C_i(X)$ the concentration of the gas X for the i th measure given by FTIR spectrometer (%), Q_{gas_i} the flow of gases (L/min at STP) (sum of produced gases and nitrogen

flow) and t is the sampling time (sec). Q_{gas_i} was calculated for each measure following the expression (2):

$$Q_{gas_i} = Q_{N_2} * \left(1 + \sum_j \frac{C(j)}{100}\right) \quad (2)$$

Where Q_{N_2} is the nitrogen flow (L/min at STP) and $C(j)$ the concentration of the component j .

The volume percentage of each gas is calculated with equation (3):

$$\%V(X) = \frac{V(X)}{\sum V} * 100 \quad (3)$$

Where $\%V(X)$ is the volume percentage of the gas X produced (%v), $V(X)$ is the volume of the gas X produced (NL) and $\sum V$ is the sum of the gas volumes produced (CO, CO₂, NH₃ and HNCO) during the experiment.

2.3.2 Mass balance calculation

The only compound in the experiment that cannot be directly quantified is HNCO. Thus, mass balance makes the quantification of produced HNCO possible following expression 4. The mass balance is equal to 1 because it's assumes that there are no leaks all over the reactor and that all deposits are precisely weighed.

$$MB = \frac{m_{gases} + m_{glass\ coil} + m_{residue}}{m_{cyanuric\ acid}} = 1 \quad (4)$$

Where m_{gases} is the sum of the produced gas masses, calculated by the expression (5) and (6):

$$m_{gases} = m_{NH_3} + m_{CO_2} + m_{CO} + m_{HNCO} \quad (5)$$

$$m_X = \frac{V(X) * M_X}{V_m} \quad (6)$$

Where m_X is the mass of the X gas (g), $V(X)$ is the produced volume of the X gas (NL), M_X is the molar mass of the X gas (g.mol⁻¹) and V_m is the molar volume of a perfect gas (= 22,4 NL.mol⁻¹).

Glass coils were weighed before and after tests to measure the mass of deposits lodged in the coils during a test. The sample recipe was also weighed before and after tests to measure the mass of the residue after pyrolysis (expression 7).

$$m_i = m_{i_{after}} - m_{i_{before}} \quad (7)$$

Where m is the collected mass obtained after the pyrolysis (g), i refers to the glass coil deposits or to the sample recipe residue, $m_{i_{before}}$ is the mass before the test (g) and $m_{i_{after}}$ is the mass after the test (g).

Finally, the expected total mass of produced HNCO is calculated by using the mass balance expression (4):

$$m_{HNCO_{expected}} = m_{cyanuric\ acid} - m_{glass\ coil} - m_{residue} - (m_{NH_3} + m_{CO_2} + m_{CO}) \quad (8)$$

The mass percentage of each gas is calculated with equation (9):

$$\%m(X) = \frac{m_x}{m_{gases}} * 100 \quad (9)$$

Where $\%m(X)$ is the mass percentage of the gas X produced (wt%), m_x is the mass of the gas X produced (NL) and m_{gases} is the sum of the produced gas masses (CO, CO₂, NH₃ and HNCO) during the experiment.

2.3.3 Cubic equation determination

The infrared spectrometer calibration method uses the peak area of the molecule in the infrared spectrum. The peak area at each measurement point is then used to calculate the concentration of HNCO through a cubic calibration equation (10). Cubic equation has been used since it is used also for other gases.

$$y = a * x^3 + b * x^2 + c * x + d \quad (10)$$

Where a , b and c are the parameters of the cubic equation, y is the HNCO concentration (%) and x is the area of the HNCO given by FTIR software. d is equal to 0 because the HNCO detection area is zero when no HNCO is detected.

The values of the 4 parameters of the calibration cubic equation are afterwards determined using Excel solver assuming that mass balance is complete (i.e. MB (calculated through equation 4) is equal to 1).

3. RESULTS AND DISCUSSION

3.1 Calibration curve

The calibration curve that has been chosen is the cubic curve that is mainly used for the calibration of gaseous compounds on FTIR. The parameters of a cubic equation have been determined independently for all the 26 tests with the Excel solver. These 26 tests were summarized on the same Microsoft Excel file. Following this independent determination of cubic equation parameters, a global optimization is performed by averaging the parameters obtained from the 26 tests. Excel solver is then re used to find a global cubic calibration equation by minimizing a global error, evaluated as the sum of independent error functions given in Table 1. The final and global equation's parameters obtained are as follows to quantify a concentration of HNCO between 0 and 5.6% (which correspond to the highest concentration on a spectrum of all tests):

$$\begin{aligned} a &= 0.07195282 \\ b &= 2.86502064 \\ c &= 17.9512677 \\ d &= 0 \end{aligned}$$

The HNCO concentration of each spectrum was calculated with the calibration equation determined previously and spectra were put into the infrared spectrometer software to calibrate HNCO.

Table 1. Results obtained after degradation of cyanuric acid.

HNCO was quantified with the cubic calibration equation on the 26 cyanuric acid degradation tests. The quantity of pyrolysed cyanuric acid varies between 0.4g and 1.4g. The obtained results are summarized in Table 1. It can be seen in Figure 5 that the production of HNCO is much higher than

the other gases. Figure 5 shows the produced gases as a function of time for the test 21_1.2g. This graph shows the typical appearance of product gases during the pyrolysis of cyanuric acid. The HNCO curve was obtained by using the cubic HNCO calibration equation.

Figure 5. Typical gas distribution of cyanuric acid pyrolysis (test 21_1.2g) as a function of time.

CO₂, NH₃ and CO are first generated and then HNCO becomes fastly the major product.

Figure 6. Concentration of HNCO as a function of time for the degradation of different masses of cyanuric acid.

Figure 6 shows the concentration of HNCO as a function of time for 6 increasing masses of cyanuric acid. When the mass of cyanuric acid increases, the test duration increases as well as the maximum peak height. Therefore, a larger mass of cyanuric acid generates a higher peak of HNCO for the calibration.

3.2 Distribution of (HNCO)₃ pyrolysis products

Figure 7 shows the weight distribution of the generated products by the pyrolysis as a function of the cyanuric acid mass. The three products correspond to the residues contained in the sample boat, the residues collected in the glass coils and the gases generated by the pyrolysis.

Figure 7. Pyrolysis products distribution as a function of cyanuric acid mass.

It can be seen that the major product generated by the degradation of cyanuric acid is gases, with about 80-90% for all masses of isocyanic acid. The proportion of residues recovered from glass traps (sum of glass coil and glass tube residues) seems to decrease with increasing mass of cyanuric acid, from around 15% to 10% between 0.4g and 1.4g. Residues collected in sample boat are negligible since they represent less than 1% by mass of the pyrolysis products. These results allow to validate the production of gases from cyanuric acid because they represent the largest part of pyrolysis products.

3.3 Distribution of generated gases

Figure 8 shows the volume distribution of generated gases as a function of the mass of degraded cyanuric acid. As mentioned in the experimental part, the gases are detected by infrared (HNCO, CO₂, CO and NH₃) and are quantified volumetrically by FTIR. The total gas volume is then estimated and the volume proportion of each gas is calculated.

Figure 8. Volume distribution of generated gases as a function of cyanuric acid mass.

Figure 8 shows that the volume percentage of HNCO increases from about 55%v to 85%v from 0.4g to 1.4g. The part of CO₂ decreases from about 30%v to 12%v and the part of CO decreases from about 13%v to less than 3%v from 0.4g to 1.4g. A small amount of NH₃ is detected and therefore quantified but remains relatively low (<2%v).

The volume of produced gases was multiplied to the molar mass and divided by the molar volume to give the mass percentage of each gas. The mass percentage of HNCO is between 60 wt% and 85 wt% from 0.4g to 1.4g. The content of CO₂ decreases from around 35 wt% to 12 wt% as well as the part of CO decreases from around 12 wt% to 2 wt% from 0.4g to 1.4g. The amount of NH₃ remains relatively low (<1 wt%).

It can then be stated that, in conditions tested in this work, the mass conversion rate of cyanuric acid into HNCO is between 45 wt% and 75 wt%.

3.4 Error on HNCO quantification

The error on mass balance for each test is detailed in Table 1. The maximum error on the mass balance is 6% with the previously determined calibration equation. This value is relatively good but don't give the maximal error that can be made on the HNCO measurement.

The calculation of the real error on HNCO measurement implies the calculation of the systematic error of each step of the calibration procedure:

- Weighing of initial and residual masses (given by the precision of the balance (0.1 mg));
- CO, CO₂ and NH₃ quantification method (given by spectrometric analysis precision (0.1 %));
- Control of the N₂ flows (carrier gas and dilution gas) assumed by a numerical mass flow controller (1% of the read value);
- Cyanuric acid purity (98%).

Beyond the difficulties faced to determine latter systematic errors, some others are impossible to evaluate such as:

- Precision of the sealing of the reactor;
- Precision regarding the flow sampled through the sonic orifice of the diluting system;
- Precision regarding the collection of the solid deposits along the piping wall at the outlet of the reactor.

That is why, the precise assessment of the error on HNCO has not been calculated.

Nevertheless, an apparent error has been quantified based on the following equation:

$$Error_{HNCO} = \frac{|m_{HNCO_{FTIR}} - m_{HNCO_{expected}}|}{m_{cyanuric\ acid}} * 100 \quad (11)$$

Where:

- $m_{HNCO_{FTIR}}$ is the mass of HNCO given by FTIR measurements;
- $m_{HNCO_{expected}}$ is the expected mass of HNCO based on global mass balance following the equation (8);
- $m_{cyanuric\ acid}$ is the initial mass of cyanuric acid.

Figure 9 presents the absolute value of the error on HNCO as a function of the cyanuric acid mass.

Figure 9. Error on HNCO as a function of the mass of cyanuric acid.

As it can be seen on Figure 9, the maximum error is about 10% and seems to decrease as the mass of isocyanic acid increases. The error standard deviation for all the tests is about 5.2%.

3.5 Calibration reliability control through nitrogen mass balance

A nitrogen mass balance is carried out on a couple of tests to check the isocyanic acid calibration via the nitrogen quantity contained in the different compounds resulting from the thermal degradation of cyanuric acid. Tests were performed with 1.2g of cyanuric acid: without (ssp) and with gas trapping (avp) to trap produced HNCO in a bubbler with H₂SO₄ at 0.1 mol.l⁻¹ (placed just after glass coils on the laboratory device available on Figure 1). Each produced compound during thermal decomposition was collected:

- Sample boat residue: sampling of cyanuric acid residues contained in the sample boat.
- Glass coil residue: glass coils were filled with water and placed in an ultrasonic apparatus (cleaner) to collect the maximum amount of residues, diluted in water.
- Glass tube residue: collect the maximum amount of residues with a metal rod.
- Gases: quantification of gases by FTIR analysis (and gas trapping in a bubbler with H₂SO₄ at 0.1 mol.l⁻¹ for required tests)

Compounds collected resulting from the thermal degradation of cyanuric acid were analyzed by Kjeldahl method. Kjeldahl method is a global well-known method which has been used to quantify nitrogen contained in different materials [39–41]. The masses of the different products, their nitrogen content given by Kjeldahl analysis, and the corresponding nitrogen mass are given in Table 2 as well as nitrogen balance also presented in Figure 10 to be more readable.

Table 2. Nitrogen balance of cyanuric acid thermal degradation: 2 tests without and with gas trapping in a bubbler.

It is noticeable that NH₃ only represents less than 0.5% of the global mass (only 1 % of the nitrogen mass) which confirms that the contribution of HCN, which is in lower quantity than NH₃, on the global and on the nitrogen mass balance is negligible.

Figure 10. Nitrogen balance of cyanuric acid degradation with and without gas trapping.

As it can be seen in Figure 10, the difference with the initial nitrogen mass contained in cyanuric acid and the sum of nitrogen contained in the produced compound is between -3.4% and +2.2%, with or without gas trapping. Regarding the low error on N-mass balance, it can be assumed that FTIR quantification method is accurate and that method proposed in this work is suitable for HNCO calibration on FTIR spectrometer.

CONCLUSION

To conclude, this work allowed us to calibrate isocyanic acid (HNCO) on our infrared spectrometer. In our case, the method that has been chosen to produce HNCO in large quantities is the depolymerization of cyanuric acid in a tubular reactor. This technique is based on the literature and has

been modified and adapted to the available laboratory equipment. As a first step, preliminary tests were carried out to determine the parameters favoring the production of HNCO. In a second step, 26 cyanuric acid depolymerization tests (between 0.4g and 1.4g) were carried out in order to calibrate the infrared spectrometer. The area of the peak on the infrared spectrum was extracted in order to determine a cubic equation, using the Excel solver. This allowed the calibration of the infrared spectrometer between 0 and 5.6%v. The accuracy of the quantification method has been evaluated. The error on the mass balance does not exceed 6%. By considering that the error only comes from the quantification of HNCO (without considering the errors on the residues weighing), the maximum achievable error is about 10%, while the standard deviation on the errors is 5.2%. Additional tests performed show a N-mass balance error between -3.4% and +2.2% assuming the accuracy of the quantification method.

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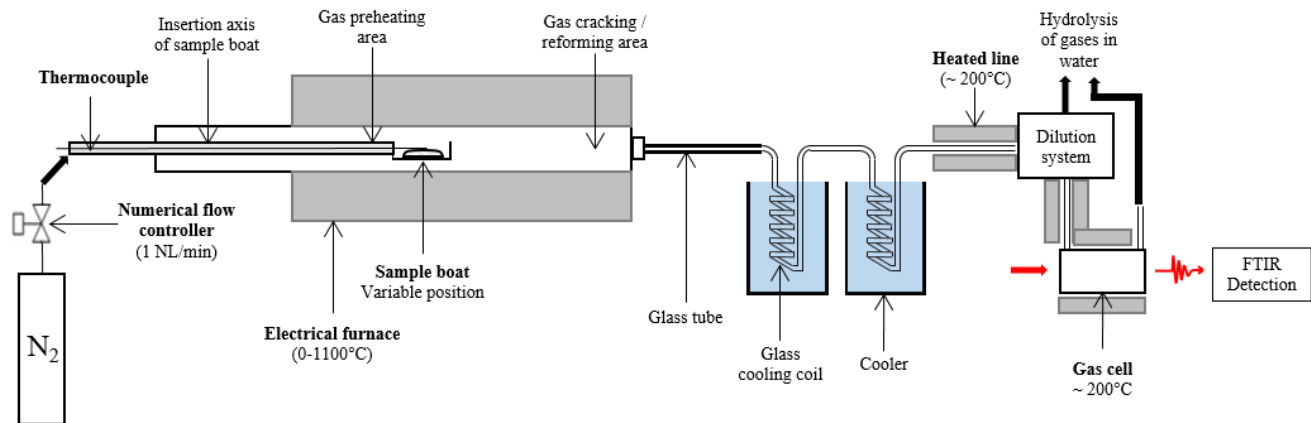


Figure 1. Sketch of the laboratory study device

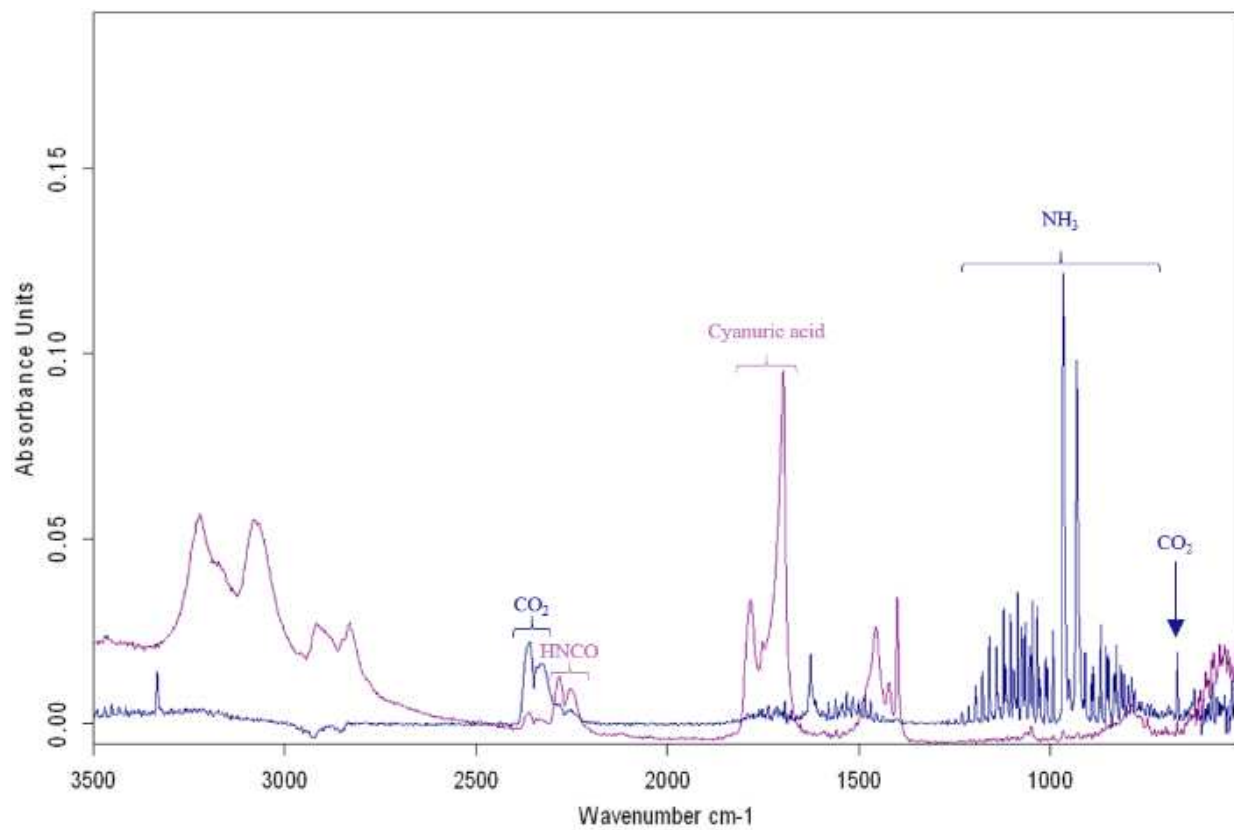


Figure 2. Two Infrared spectra illustrating the peaks obtained during the pyrolysis of a urea sample.

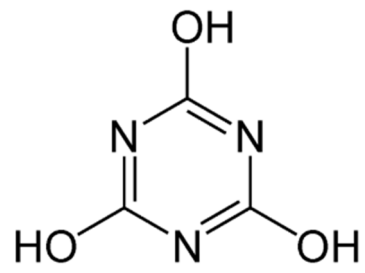


Figure 3. Cyanuric acid (HNCO)₃ - 1,3,5-triazine-2,4,6-triol.

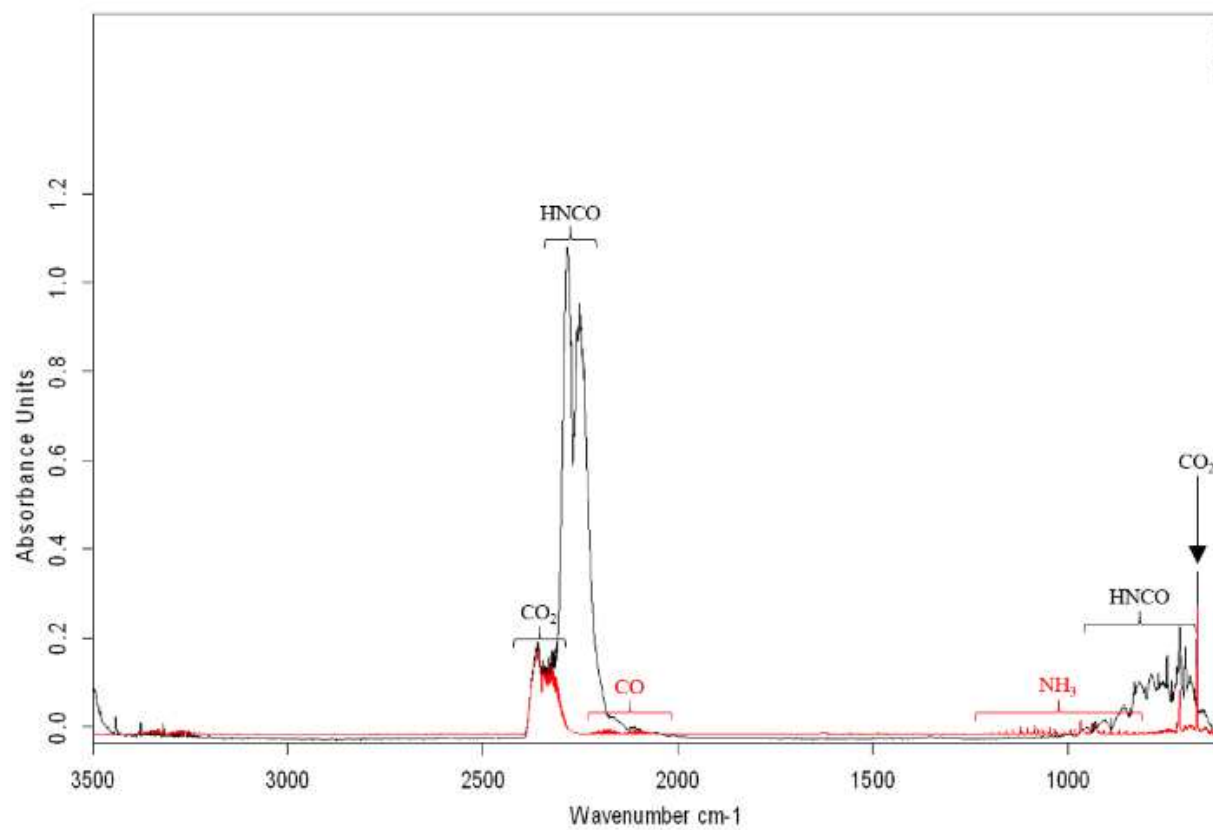


Figure 4. Two Infrared spectra illustrating the peaks obtained during the pyrolysis of a cyanuric acid sample (21_1.2g).

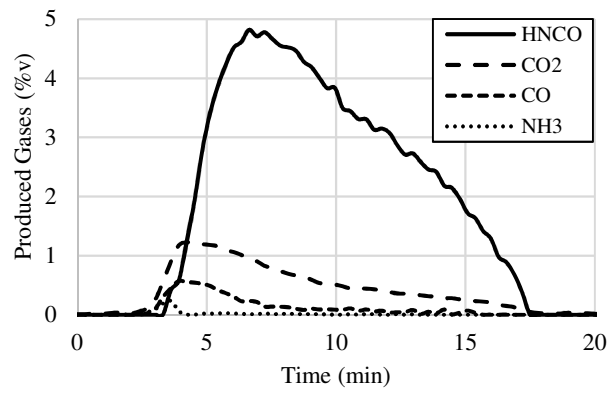


Figure 5. Typical gas distribution of cyanuric acid pyrolysis (test 21_1.2g) as a function of time.

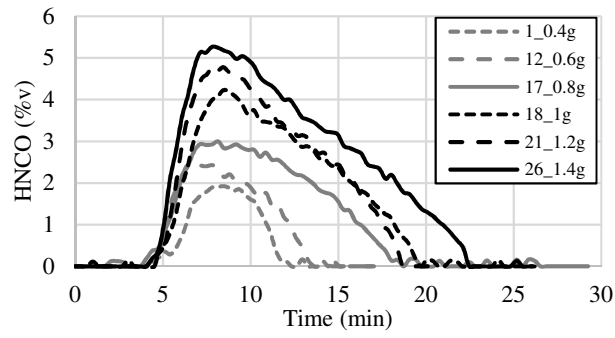


Figure 6. Concentration of HNCO as a function of time for the degradation of different masses of cyanuric acid.

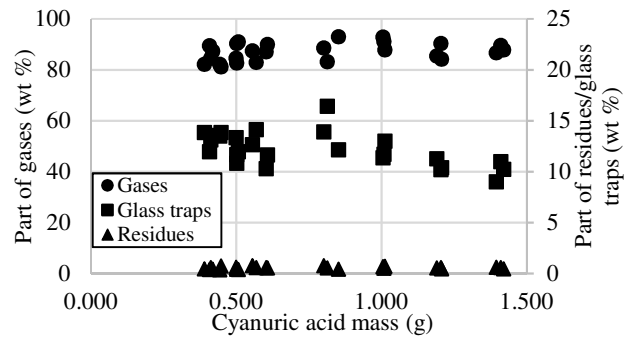


Figure 7. Pyrolysis products distribution as a function of cyanuric acid mass.

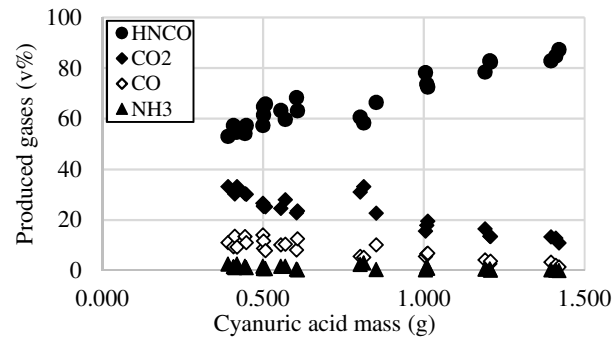


Figure 8. Volume distribution of generated gases as a function of cyanuric acid mass.

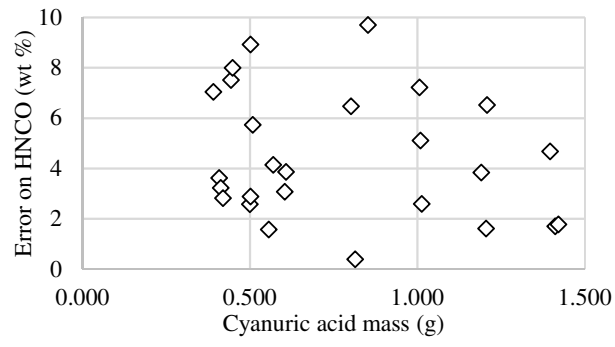


Figure 9. Error on HNCO as a function of the mass of cyanuric acid.

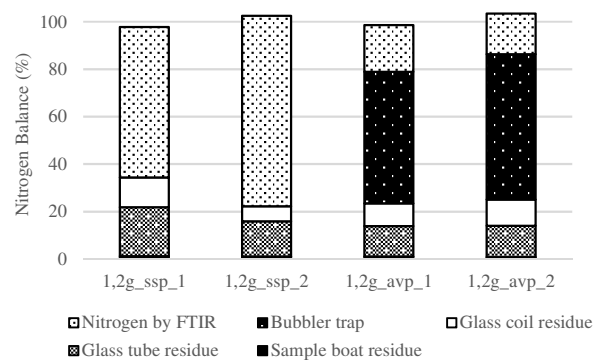


Figure 10. Nitrogen balance of cyanuric acid degradation with and without gas trapping.

Table 1. Results obtained after degradation of cyanuric acid.

Test	m _{cyanuric acid} (g)	Gases (%)	m _{produced isocyanic acid} (g)	sample boat residues (%)	Tube residues (%)	glass coil residues (%)	Gas composition (v %)				Error (%)	
							CO ₂ (%)	CO (%)	HNCO (%)	NH ₃ (%)	Error on HNCO (%)	Error on matter balance (%)
1_0.4g	0,3900	82,2	0,18	0,5	10,3	3,6	33,3	11,1	53,0	2,6	7,0	3,5
2_0.4g	0,4071	89,5	0,22	0,4	8,4	3,6	31,5	9,5	57,4	1,6	3,6	1,9
3_0.4g	0,4115	84,6	0,20	0,6	9,8	3,4	30,4	13,7	54,7	1,2	3,2	1,6
4_0.4g	0,4185	87,3	0,21	0,5	8,7	4,8	33,2	9,4	54,7	2,6	2,8	1,4
5_0.45g	0,4429	82,3	0,21	0,4	9,7	3,8	30,5	13,5	54,2	1,8	7,5	3,8
6_0.45g	0,4470	81,2	0,22	0,8	10,6	3,3	30,3	11,1	57,4	1,3	8,0	4,2
7_0.5g	0,4991	84,6	0,26	0,6	9,5	3,9	26,7	14,1	57,3	1,8	2,6	1,4
8_0.5g	0,5009	90,4	0,30	0,5	8,6	2,3	25,4	8,9	64,8	0,9	2,9	1,7
9_0.5g	0,5010	82,7	0,27	0,4	8,8	2,9	25,7	11,7	61,6	1,1	8,9	5,2
10_0.5g	0,5071	91,0	0,31	0,4	9,3	2,7	25,3	8,0	65,9	0,9	5,7	3,3
11_0.55g	0,5550	87,5	0,32	0,8	9,6	3,1	24,7	10,2	63,4	1,7	1,6	0,9
12_0.6g	0,5686	83,0	0,29	0,6	11,0	3,1	28,0	10,5	59,8	1,7	4,2	2,2
13_0.6g	0,6031	87,2	0,37	0,6	7,6	2,7	22,8	8,2	68,4	0,6	3,1	1,9
14_0.6g	0,6067	90,0	0,4	0,6	8,4	3,3	23,7	12,7	63,2	0,4	3,9	-2,2
15_0.8g	0,8013	88,6	0,44	0,8	11,2	2,8	31,1	5,7	60,7	2,5	6,5	3,4
16_0.8g	0,8129	83,3	0,41	0,6	11,5	5,0	33,2	5,3	58,3	3,1	0,4	0,3
17_0.8g	0,8519	93,1	0,55	0,4	8,8	3,3	22,8	10,2	66,5	0,5	9,7	5,7
18_1g	1,0051	92,9	0,74	0,7	8,3	3,1	15,7	5,7	78,3	0,4	7,2	5,0
19_1g	1,0084	91,1	0,70	0,5	8,9	2,9	18,0	6,7	73,7	1,6	5,1	3,4
20_1g	1,0120	87,9	0,66	0,7	9,6	3,4	19,6	6,9	72,6	1,0	2,6	1,7
21_1.2g	1,1904	85,4	0,81	0,6	8,9	2,3	16,5	4,3	78,5	0,6	3,8	2,7
22_1.2g	1,2046	90,4	0,91	0,6	7,2	3,0	13,6	2,7	82,9	0,7	1,6	1,2
23_1.2g	1,2070	84,2	0,85	0,5	8,1	2,3	13,6	3,8	82,4	0,3	6,5	4,9
24_1.4g	1,3954	86,8	1,02	0,6	7,2	1,8	13,3	3,4	82,9	0,3	4,7	3,6
25_1.4g	1,4106	89,7	1,08	0,6	8,1	3,0	12,8	2,1	84,8	0,2	1,7	1,3
26_1.4g	1,4201	87,9	1,09	0,5	7,2	3,0	11,0	1,6	87,4	0,1	1,8	1,4

Table 2. Nitrogen balance of cyanuric acid thermal degradation: 2 tests without and with gas trapping in a bubbler.

		ssp_1			ssp_2			avp_1			avp_2		
		Mass (mg)	Nitrogen content (%)	Nitrogen mass (mg)	Mass (mg)	Nitrogen content (%)	Nitrogen mass (mg)	Mass (mg)	Nitrogen content (%)	Nitrogen mass (mg)	Mass (mg)	Nitrogen content (%)	Nitrogen mass (mg)
Initial mass of Cyanuric acid		1194.8	32.2	384.5	1219.9	32.2	392.6	1197.2	32.181	385.3	1207.3	32.181	388.5
Residue analysis	Sample boat residue	9.1	52.2	4.7	7.8	52.1	4.1	8.3	46.2	3.8	6.3	48.8	3.1
	Glass tube residue	160.9	49.2	79.1	135.5	43.1	58.5	112.5	44.1	49.6	118.4	43.4	51.4
	Glass coil residue	98	49.3	48.3	54.8	44.8	24.5	80.6	45.7	36.8	91	47.1	42.9
	Bubbler trap	0	0	0	0	0	0	64 682	0.33	213.8	72 618	0.33	237.8
		Volume (L at STP)	Mass gas (mg)	Nitrogen mass (mg)	Volume (L at STP)	Mass gas (mg)	Nitrogen mass (mg)	Volume (L at STP)	Mass gas (mg)	Nitrogen mass (mg)	Volume (L at STP)	Mass gas (mg)	Nitrogen mass (mg)
Gas analysis	HNCO	0.38	735.7	239.5	0.50	952.9	310.2	0.11	213.2	69.4	0.10	188.6	61.4
	NH ₃	0.0066	5.0	4.1	0.0081	6.1	5.0	0.0105	8.0	6.6	0.0084	6.4	5.2
		Total mass (mg)	Δ mN (mg)	Δ mN (%)	Total mass (mg)	Δ mN (mg)	Δ mN (%)	Total mass (mg)	Δ mN (mg)	Δ mN (%)	Total mass (mg)	Δ mN (mg)	Δ mN (%)
Balance		375.9	8.6	2.2	402.3	-9.8	-2.5	380.1	5.2	1.3	401.8	-13.3	-3.4