



*Cent. Eur. J. Energ. Mater.* 2020, 17(3): 362-383; DOI 10.22211/cejem/127713

Article is available in PDF-format, in colour, at:

[http://www.wydawnictwa.ipo.waw.pl/cejem/Vol-17-Number3-2020/CEJEM\\_01138.pdf](http://www.wydawnictwa.ipo.waw.pl/cejem/Vol-17-Number3-2020/CEJEM_01138.pdf)



Article is available under the Creative Commons Attribution-Noncommercial-NoDerivs 3.0 license CC BY-NC-ND 3.0.

*Research paper*

## Nitration of $\gamma$ -Cyclodextrin

Pawel Maksimowski\*, Agnieszka Janson

*Warsaw University of Technology, Faculty of Chemistry,  
The Division of High Energetic Materials, 3 Noakowskiego Street,  
00-664 Warsaw, Poland*

\*E-mail: pmaksimowski@ch.pw.edu.pl

**Abstract:** A number of  $\gamma$ -cyclodextrin ( $\gamma$ -CD) nitration reactions were conducted with different times, temperatures and types of nitrating mixtures. The degree and yield of  $\gamma$ -CD nitration ( $\gamma$ -CDN) depended on the  $\text{HNO}_3$  concentration, the type of nitrating mixture, the nitration time and, to a lesser extent, the temperature. 100%  $\text{HNO}_3$  proved to be the finest nitrating agent. By nitrating  $\gamma$ -CD in this system, a degree of nitration of 1, as well as a yield of 90-99% were obtained. An examination of the properties of the resulting  $\gamma$ -CDN served to conclude that the density and sensitivity to mechanical stimuli (friction and impact) depend on the degree of substitution of the  $-\text{OH}$  groups with  $-\text{ONO}_2$  groups. The higher the degree of  $\gamma$ -CD nitration, the greater the density and sensitivity to external stimuli. Thermal analysis of the  $\gamma$ -CDN obtained at various nitration levels demonstrated that  $\gamma$ -CDN with a high degree of substitution decomposes in one exothermic stage, at temperatures of approximately 184-250 °C. The lower the degree of  $\gamma$ -CDN nitration, the lower is the thermal effect of decomposition, with the maximum exothermic peak being shifted increasingly towards a higher temperature.

**Keywords:**  $\gamma$ -cyclodextrin,  $\gamma$ -cyclodextrin nitrate, nitration

### Nomenclature:

- A Number of esterified  $-\text{OH}$  groups in  $\gamma$ -CD
- CD Cyclodextrin
- CDN Cyclodextrin nitrate ester

$F$	Friction sensitivity [N]
$I$	Impact sensitivity [J]
$T$	Reaction temperature [ $^{\circ}$ C]
$t$	Reaction time [min]
$W$	Yield, expressed as the percentage of the mass of solid product obtained in relation to the initial $\gamma$ -CD mass [%]

## 1 Introduction

Cyclodextrins (CDs) belong to the group of cyclic oligosaccharides, which contain glucopyranose units connected with  $\alpha$ -1,4-glycosidic bonds. They are formed by the enzymatic action of glucotransferase (CGTase) on starch [1]. The most popular CDs are  $\alpha$ -,  $\beta$ - and  $\gamma$ -CD, containing 6, 7 and 8 glucose units, respectively [2, 3]. A principal feature of CDs is their ability to form inclusion complexes with many solid, liquid or gaseous compounds. This is possible due to an hydrophilic layer allowing CDs to be water soluble as well as due to their hydrophobic interior. CDs are produced globally by environmentally friendly technologies, in thousands of tons per year; therefore they have become major substances for forming inclusion complexes with other compounds. CDs find wide application in industry, being components of medicines, foods and cosmetics. They are also used in the chemical, biochemical and rocket engineering industries [1, 4-7].

Obtaining new, as well as improving already existing high energy materials, remains the focus of the defense and civil industries, which require novel materials characterized by a higher energy yield and lower sensitivity. The discovery of new high energy materials or composites could have a positive impact on the production of propulsion materials, propellants and gunpowders, whilst increasing their safety or lowering their production costs. Nitro derivatives of CDs could potentially play such a role. Due to the large number of hydroxyl groups in a CD molecule, it is possible to modify the structure of a CD molecule and add new properties to its inclusion complexes by replacing hydroxyl groups with other functional groups, *e.g.*  $-\text{NO}_2$  [8, 9]. Although data on CDs are quite extensive, studies on cyclodextrin nitrate esters (CDN) are relatively scarce.

CDs are similar to cellulose in composition and their nitrates are comparable to cellulose nitrates. In order to ensure the repeatability of the production of high energy materials (gunpowders, rocket fuels and propellant systems), research on the substitution of nitrocellulose by other synthetic polymers of high repeatability has been conducted. Therefore, as reported in several publications [10-12] and patents [13-16], it is quite common to undertake attempts to use CDN in the same

applications as nitrocellulose. In particular, it has been demonstrated that the formation of CD inclusion complexes and CD nitrates with such explosive molecules as nitroglycerin, 1,1,1-trimethylolethane trinitrate and 1,2,4-butanetriol trinitrate enhances the stability and decreases the sensitivity of such energy materials [13, 17].

Maksimowski *et al.* [18, 19] described research allowing a 1:1  $\gamma$ -CD/CL-20 complex to be obtained, as well as a Cl-20/ $\gamma$ -CDN inclusion complex. The formation of both complexes has been confirmed by a number of examinations, including FTIR spectroscopy,  $^1\text{H}$  NMR, as well as measurement of the density of the resulting complexes.

Depending on the type of CD and the number of hydroxyl groups to be nitrated, different nitrating agents can be used. The literature reports mainly on nitration of  $\beta$ -CD with  $\text{HNO}_3$  and  $\text{HNO}_3/\text{H}_2\text{SO}_4$  nitrating mixtures. Deshmukh *et al.* [8] used nitrated  $\beta$ -CD as a nitrating agent in NTO synthesis.  $\beta$ -CD was nitrated using fuming  $\text{HNO}_3$  for 1 h at 10–20 °C. The reaction yield was 88%. Luppi *et al.* [9] nitrated  $\beta$ -CD using a 1:1 mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  for 60 min at a temperature below 10 °C and obtained a yield of 90%. Additionally, the authors described difficulties resulting from the release of sulfate esters during the nitration reaction, which prevented the reaction from being completed in less than 60 min. Ruebner *et al.* [14] nitrated various types of CD polymers with 98%  $\text{HNO}_3$ , at 10 °C for 30 min, and obtained various degrees of nitration of the –OH groups in polycyclodextrins from 9.5 to 19% nitrogen content. With regard to patent [13], three different methods for nitrating  $\beta$ -CD were demonstrated. In the first method, 90%  $\text{HNO}_3$  was used as the nitrating agent. CD was dispersed in  $\text{HNO}_3$  at approximately 30 °C. After the entire amount of CD had been added, the system was cooled to 0 °C and subsequently water was slowly added while stirring thoroughly. In the second method,  $\beta$ -CD was added slowly to 90%  $\text{HNO}_3$  at a constant temperature of 30 °C. Then, oleum (30 °C) was slowly added to the stirred solution. Additional amounts of oleum were added in order to precipitate the product from the solution. In the third method,  $\beta$ -CD was slowly dispersed in a stirred solution of 90%  $\text{HNO}_3$  with  $\text{H}_2\text{SO}_4$  (at 30 °C). After 2–3 h of reaction, water was added slowly to cause the product to precipitate. Under these conditions, 18 out of 21 hydroxyl groups were successfully nitrated.

In the patent [20],  $\gamma$ -CD was nitrated with both  $\text{N}_2\text{O}_5$  and anhydrous  $\text{HNO}_3$  using  $\text{L-CO}_2$  as the solvent. In the first example, CD was nitrated with  $\text{N}_2\text{O}_5$  with a 10% excess of nitrating agent at –10 °C and under a pressure of 68 atm in  $\text{L-CO}_2$  as the solvent; the yield was 45%. In the second example, the same conditions and corresponding nitrating mixture were employed, but additionally sodium fluoride was used during the nitration, which increased the reaction yield to 91%. In the next example, CD was nitrated in the same way as in the first example, however with

anhydrous  $\text{HNO}_3$  as the nitrating agent, and resulted in a reaction yield of 12%; when sodium fluoride was additionally used, the yield increased to 85%. In the following study [21],  $\text{HNO}_3$  of various concentrations was used as the nitrating agent. Dried  $\beta$ -CD was dispersed in  $\text{HNO}_3$  at 3–5 °C. After the entire amount of  $\beta$ -CD had been added, the resultant solution was stirred until 20 °C was reached. Depending on the acid concentration, the authors managed to nitrate from 2 to 20 –OH groups in  $\beta$ -CD.

The aim of the present research was to study the nitration reaction of  $\gamma$ -CD using various nitrating mixtures. Hitherto,  $\gamma$ -CD nitration has not been widely described in the literature.  $\gamma$ -CD nitrate esters ( $\gamma$ -CDN), with varying degrees of substitution of the –OH groups with –NO<sub>2</sub> groups, are the products of such reactions. The resulting  $\gamma$ -CDNs were tested for their thermochemical properties and sensitivity to external stimuli, friction and impact.

## 2 Experimental

### 2.1 Materials and analytical instruments

$\gamma$ -CD (purity 98.4%) was obtained from Baoji Guokang Bio-Technology Co., Ltd. Other reagents and chemicals were of AR grade. Infrared spectroscopic analysis (FTIR) was performed at room temperature by means of Nicolet 6700 Thermo Scientific spectrophotometer with an ATR attachment.

<sup>1</sup>H NMR spectra were generated in a Varian NMR System 500 MHz instrument. The samples were dissolved in deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>). Density measurements were carried out by means of a Micromeritics Accu Pyc II 1340 helium gas pycnometer. The measurements were made with an accuracy of 0.01 g/cm<sup>3</sup>. Thermogravimetric measurements were conducted using an SDT Q600 (TA Instruments) instrument in a flow of nitrogen. The final temperature of the measurements was 550 °C, at 10 °C/min increase.

The friction sensitivity of the samples was determined with a BAM friction apparatus until no explosion/ignition in six consecutive test samples at that weight were observed. The lower limit of sensitivity is defined as the lowest load at which the result “explosion” is obtained from at least one out of six trials. Impact sensitivity tests were performed with a BAM Fallhammer apparatus with a load weight of 2 kg. The sensitivity was defined as the lower limit of sensitivity (maximum height, at which one explosion occurred).

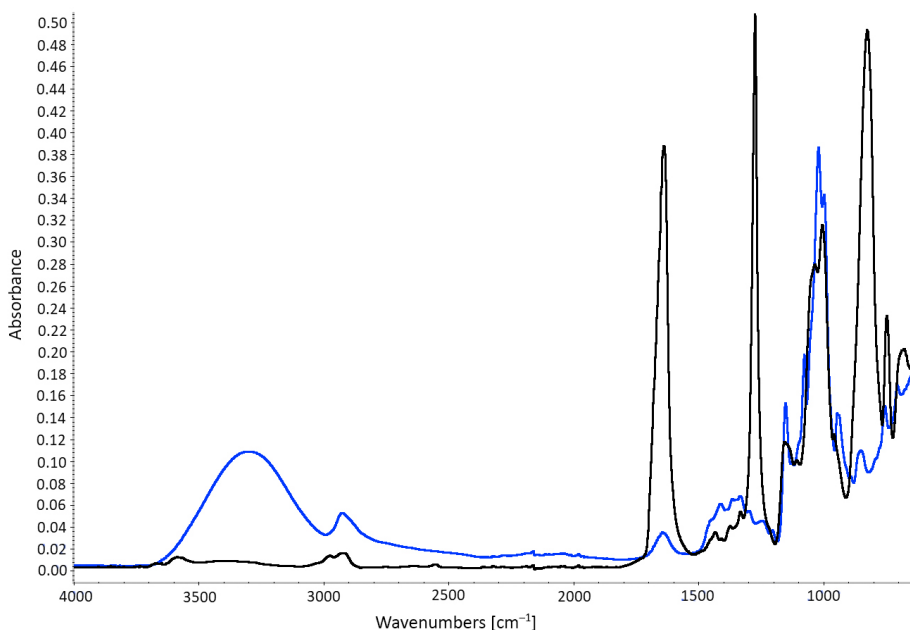
### 2.2 Illustrative description of a $\gamma$ -cyclodextrin nitration reaction

$\text{HNO}_3$  (50 mL) was placed in a three-necked flask (100 mL) fitted with a thermometer and mechanical stirrer. Subsequently,  $\gamma$ -CD (10 g, 0.0077 mol) was

added with stirring at 0-5 °C, then the contents were stirred at that temperature for a further 30 min. The post reaction mixture was then poured as a small stream into a beaker containing distilled water with ice (approximately 400 mL). The resulting precipitate was filtered off and dissolved in acetone. The acetone  $\gamma$ -CDN solution was then slowly added dropwise, with stirring, to 1% sodium bicarbonate solution. The precipitate was filtered off and washed three times with distilled water to pH 6.5-7.0, and then dried to a solid at 60 °C.

### 3 Results and Discussion

A number of  $\gamma$ -CD nitration reactions were carried out where the time, dosing and conditioning temperatures, as well as the type of nitrating mixture, were changed. The formation of  $\gamma$ -CDN was confirmed by infrared spectroscopy. In order to compare the signals occurring in  $\gamma$ -CD and its nitro derivatives, overlapped FTIR spectra of the initial  $\gamma$ -CD and its nitro derivative with a nitration degree of 1 are presented in Figure 1.



**Figure 1.** Overlapping FTIR spectra of  $\gamma$ -CD (blue) and  $\gamma$ -CDN (black) with a degree of nitration equal to 1

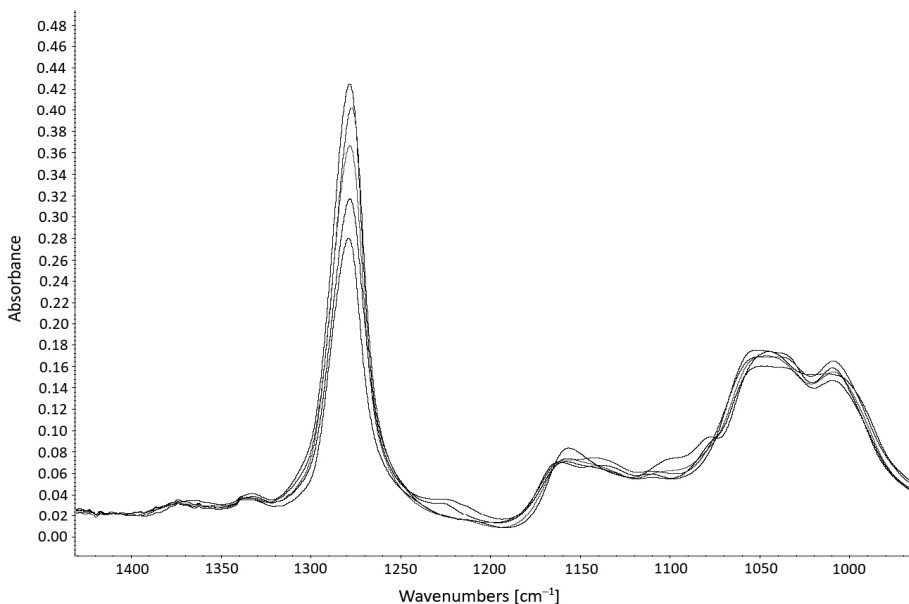
The bands characteristic for  $\gamma$ -CD are:

- 3650-3000  $\text{cm}^{-1}$  – stretching vibrations of  $-\text{OH}$  groups,
- 2926  $\text{cm}^{-1}$  – C–H stretching vibrations of  $-\text{CH}_2$  and  $-\text{CH}-$  groups,
- 1030  $\text{cm}^{-1}$  – C–O stretching vibrations.

For CDN the following bands were observed:

- 1639  $\text{cm}^{-1}$  – the additional band of asymmetrical stretching vibrations,
- 1274  $\text{cm}^{-1}$  – symmetrical N=O stretching vibrations,
- 826  $\text{cm}^{-1}$  – O–N stretching vibrations.

A procedure for determining the degree of  $\gamma$ -CD nitration was developed using infrared spectroscopy (FTIR). The FTIR spectra of  $\gamma$ -CD and its nitro derivatives with different degrees of substitution with  $-\text{NO}_2$  groups were compared. The degrees of nitration of the  $\gamma$ -CD nitro derivatives were verified by elemental analysis and  $^1\text{H}$  NMR spectroscopy. The peak at approximately 1274  $\text{cm}^{-1}$  was selected to determine the number of substituted  $-\text{NO}_2$  groups, as it corresponds to symmetrical N=O stretching vibrations and changes in intensity corresponding to the number of  $-\text{NO}_2$  groups; this peak is not exhibited by  $\gamma$ -CD and does not overlap with other signals in the spectrum. Another peak was one at approximately 1030  $\text{cm}^{-1}$  corresponding to C–O bond stretching vibrations, whose intensity does not change with the number of substituted  $-\text{OH}$  groups.

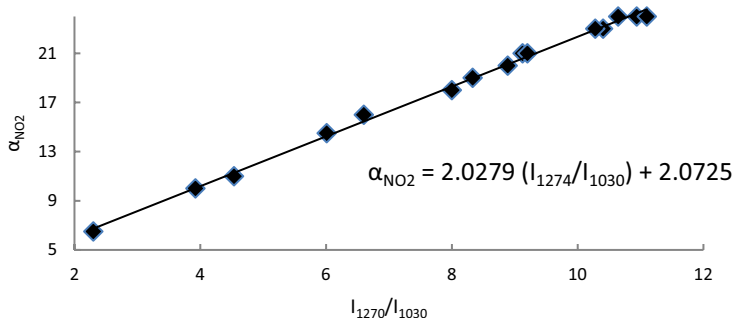


**Figure 2.** Overlapping  $\gamma$ -CDN spectra of various degrees of nitration, in the range of 1430-960  $\text{cm}^{-1}$

Figure 2 shows the overlapped spectra of  $\gamma$ -CD nitro derivatives with approximately 6, 10, 15, 20 and 24 –OH groups having been nitrated. It was found that the degree of  $\gamma$ -CD nitration corresponds with the increase in the intensity of bands responsible for the symmetrical N=O stretching vibrations.

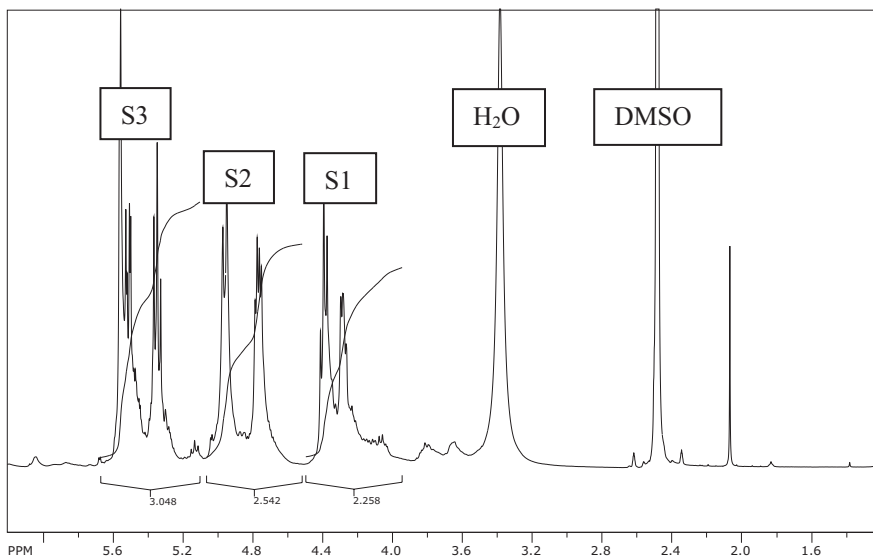
In order to plot a calibration curve, the intensity factor of  $I_{1274}/I_{1030}$  was used as determined by measuring the relative peak heights. Figure 3 shows the calibration curve obtained from 15  $\gamma$ -CDN samples of different degrees of nitration. The data were used to obtain an equation for the determination of the number of nitrated –OH groups ( $A_{NO_2}$ ) in  $\gamma$ -CDN:

$$A_{NO_2} = 2.0279 (I_{1274}/I_{1030}) + 2.0725 \quad (1)$$

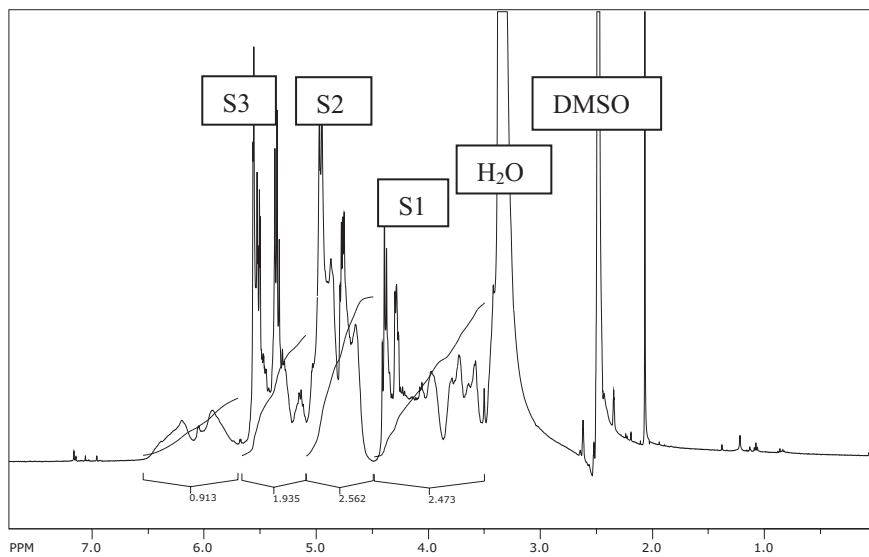


**Figure 3.**  $I_{1274}/I_{1030}$  intensity factor vs. the number of nitrated –OH groups in  $\gamma$ -CD

$^1\text{H}$  NMR spectroscopic analysis was also used to determine the number of nitrated –OH groups in  $\gamma$ -CDN. For this analysis, the method described by Romanova *et al.* [21] was used, where the authors describe a procedure for determining the degree of nitration of CD nitrates by  $^1\text{H}$  NMR spectroscopy. In this procedure, determination of integrals in specific areas of the spectrum allows the amount of substituted nitrate groups and the degree of nitration of the initial CD to be established. Figure 4 shows examples of the  $^1\text{H}$  NMR spectra of  $\gamma$ -CDN samples with different degrees of esterified –OH groups. Table 1 lists the collated results of  $\gamma$ -CD nitration with 100%  $\text{HNO}_3$ ;  $\gamma$ -CD (10 g) and 100%  $\text{HNO}_3$  (50 mL) were used in these reactions.

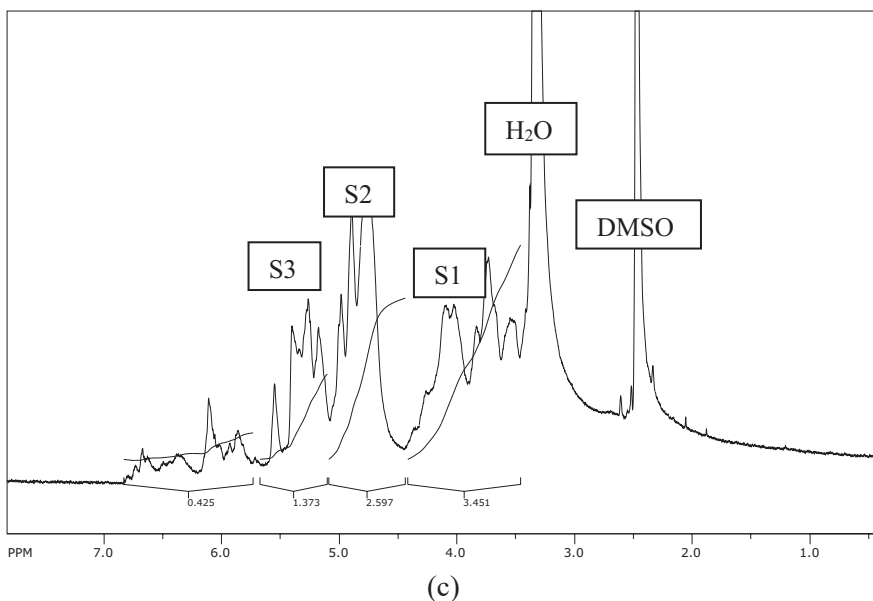


(a)



(b)





**Figure 4.**  $^1\text{H}$  NMR spectra of  $\gamma$ -CDN representing various degrees of nitration: (a) 1, (b) 0.67 and (c) 0.33

**Table 1.** The results of  $\gamma$ -CD nitration with 100%  $\text{HNO}_3$

$T$ [°C]	$t$ [min]	$W$ [%]	$d$ [g/cm <sup>3</sup> ]	$A$		Nitrogen [%N]	$F$ [N]	$I$ [J]
				$^1\text{H}$ NMR	FTIR			
(-5)-(-10)	60	94	1.777	24.0	24.0	14.1	117-126	5.2
0-5		99	1.775	24.0	24.0	14.1	117-126	5.2
20-25		98	1.777	24.0	24.0	14.0	117-126	5.2
(-5)-(-10)	30	90	1.767	23.5	24.0	14.0	117-126	5.2
0-5		92	1.766	24.0	24.0	14.1	117-126	5.2
20-25		95	1.767	24.0	24.0	14.1	117-126	5.2
(-5)-(-10)	10	61	1.646	20.1	20.8	12.8	158	6.4
0-5		66	1.649	20.4	21.2	12.9	158	6.4
20-25		73	1.666	22.0	21.5	13.5	142-158	5.8

The  $\gamma$ -CD nitration reaction with 100%  $\text{HNO}_3$  proceeded smoothly, no rapid temperature increases being observed when adding the  $\gamma$ -CD to  $\text{HNO}_3$ . In the temperature ranges of 0-5 °C and 20-25 °C,  $\gamma$ -CD dissolved in the acid almost immediately, whereas at (-5)-(-10) °C it took 10 min more to complete the process.

The highest yields, calculated in % of the solid product mass obtained versus the initial mass of  $\gamma$ -CD, were observed for  $\gamma$ -CD nitrated for 30 and 60 min; these yields fluctuated within the range 90-99%. A minor relationship between the yield and the nitration temperature in the tested range may be noted, *i.e.* the higher the temperature, the greater the yield. Furthermore, a slight decrease in yield for a nitration time of 30 vs. 60 min, amounting to several percent, was observed. A significant decrease in the reaction yield was observed for the samples nitrated for 10 min, where the yields amounted to 60-70%. For this nitration time, an increase in the temperature of nitration also produced an increased yield.

The degree of nitration was found to be highest for  $\gamma$ -CD nitrated in the range of 30-60 min regardless of temperature and practically amounted to 1, *i.e.* each hydroxyl group in  $\gamma$ -CD was esterified by  $\text{HNO}_3$ , as confirmed by  $^1\text{H}$  NMR, FTIR and elemental analysis. The theoretical content of nitrogen in a completely nitrated  $\gamma$ -CDN would be 14.14%. For a nitration time of 10 min, a lower degree of  $\gamma$ -CD nitration was obtained, and amounted to 0.84-0.92. The higher the nitration temperature, the higher the degree of substitution was observed. Based on density measurements, it was found that the greater the number of substituted nitrate groups in  $\gamma$ -CDN, the higher was the density value. The highest density was obtained for  $\gamma$ -CD nitrated for 60 min and was equal to 1.777 g/cm<sup>3</sup>.

The tests for sensitivity to mechanical stimuli demonstrated that friction and impact sensitivities depend on the degree of substitution of  $-\text{OH}$  groups with  $-\text{ONO}_2$  groups in  $\gamma$ -CDN. The samples which proved most sensitive to friction and impact were the ones having the highest number of nitrate groups, their sensitivity to friction being in the range 117-126 N, whereas their impact sensitivity was 5.2 J.

Table 2 summarizes the results of nitration of  $\gamma$ -CD with 98%  $\text{HNO}_3$ ;  $\gamma$ -CD (10 g) and 98%  $\text{HNO}_3$  (50 mL) were used in these reactions. The  $\gamma$ -CD nitration reaction with 98%  $\text{HNO}_3$  proceeded smoothly as in the case of nitration with 100%  $\text{HNO}_3$ , no rapid temperature increases being observed when adding the  $\gamma$ -CD to nitric acid. After the  $\gamma$ -CD had been added to  $\text{HNO}_3$ , it became dissolved over a certain period of time. In this case, as for  $\gamma$ -CD nitrated with 100%  $\text{HNO}_3$ , the same relationship was observed regarding the degree of nitration and reaction yield. In this particular case however, slightly lower yields and a lower degree of nitration were obtained. The highest yield was 95%, whilst the greatest number of nitrated  $-\text{OH}$  groups was equal to 23.5. A corresponding relationship was demonstrated in the results for density measurements as well as for the friction and impact sensitivity tests.

$\gamma$ -CDN with the highest degree of esterification with HNO<sub>3</sub> was characterized by the highest density, 1.766 g/cm<sup>3</sup>, and additionally the highest sensitivity to friction (117-126 N) and impact (5.2 J).

**Table 2.** Results of  $\gamma$ -CD nitration with 98% HNO<sub>3</sub>

<i>T</i> [°C]	<i>t</i> [min]	<i>W</i> [%]	<i>d</i> [g/cm <sup>3</sup> ]	<i>A</i>		Nitrogen [%N]	<i>F</i> [N]	<i>I</i> [J]
				<sup>1</sup> H NMR	FTIR			
(-5)-(-10)	60	91	1.766	23.5	23.1	14.0	117-126	5.2
0-5		90	1.758	23.5	23.1	13.8	117-126	5.2
20-25		95	1.743	23.1	23.2	13.9	117-126	5.6
(-5)-(-10)	30	90	1.746	23.2	22.9	13.5	117-126	5.6
0-5		91	1.743	23.1	23.0	13.7	126	5.6
20-25		94	1.666	22.8	23.0	13.6	126	5.6
(-5)-(-10)	10	51	1.619	19.6	20.0	12.4	158	6.4
0-5		55	1.635	19.8	20.2	12.5	158	6.4
20-25		68	1.636	21.3	21.1	12.9	158	6.4

Table 3 summarizes the results for nitration of  $\gamma$ -CD using 91% HNO<sub>3</sub>;  $\gamma$ -CD (10 g) and 91% HNO<sub>3</sub> (50 mL) were used in these reactions. During the addition of  $\gamma$ -CD and the reaction course, no rapid increases in temperature were observed. The reactions were carried out in the same manner as for the nitrations with 100 and 98% HNO<sub>3</sub>.

**Table 3.** Results of  $\gamma$ -CD nitration with 91% HNO<sub>3</sub>

<i>T</i> [°C]	<i>t</i> [min]	<i>W</i> [%]	<i>d</i> [g/cm <sup>3</sup> ]	<i>A</i>		Nitrogen [%N]	<i>F</i> [N]	<i>I</i> [J]
				<sup>1</sup> H NMR	FTIR			
(-5)-(-10)	60	90	1.665	22.1	21.7	13.1	142-158	5.6
0-5		95	1.658	21.8	21.5	13.1	158	5.8
20-25		91	1.666	22.5	22.0	13.3	142	5.6
(-5)-(-10)	30	85	1.643	20.6	20.9	12.7	158	5.8
0-5		90	1.665	22.5	22.0	13.5	142	5.6
20-25		91	1.667	22.9	22.5	13.6	142	5.6
(-5)-(-10)	10	53	1.568	16.6	17.3	11.6	184	8.4
0-5		60	1.636	19.2	19.8	12.6	165	6.4
20-25		78	1.599	18.6	19.0	12.1	165	7.6

The highest yield obtained during nitration with 91% HNO<sub>3</sub> was 95% and was close to the level of yields obtained when nitrating with 100 and 98% HNO<sub>3</sub> within 60 min. No significant relationship between the temperature and the degree of  $\gamma$ -CD nitration was observed in this case, however the longer the reaction time, the more –OH groups could be successfully esterified. When compared to nitrations with higher concentrations of HNO<sub>3</sub>, a slightly lower degree of nitration was obtained.

Corresponding to the previous cases, the highest density of 1.667 g/cm<sup>3</sup> was obtained for  $\gamma$ -CDN with the highest degree of nitration. Similarly, in the tests for sensitivity to mechanical stimuli, the sensitivity to friction and impact was the highest and amounted to 142 N and 5.6 J, respectively, for  $\gamma$ -CDN with the highest degree of substitution with nitrate groups.

Table 4 summarizes the results of  $\gamma$ -CD nitration using conventional HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> nitrating mixtures with volume ratios of 1:1, 1:2 and 2:1;  $\gamma$ -CD (10 g) and 98% HNO<sub>3</sub> (75 mL) and 96% H<sub>2</sub>SO<sub>4</sub> (75 mL), 98% HNO<sub>3</sub> (50 mL) and 96% H<sub>2</sub>SO<sub>4</sub> (100 mL), 98% HNO<sub>3</sub> (100 mL) and 96% H<sub>2</sub>SO<sub>4</sub> (50 mL) were used in these reaction. While adding the  $\gamma$ -CD to the acids, the formation and caking of sulfate esters (insoluble in acids) was observed when nearly half of the amount had been added, which hindered both stirring and the reaction process. After some time, the precipitated sulfate esters redissolved in the acids and the solution became clear. Furthermore, the reaction was less smooth than during nitration with HNO<sub>3</sub> alone, as there were temperature fluctuations.

**Table 4.** Results of  $\gamma$ -CD nitration with HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> nitrating mixture

HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub> v/v	<i>T</i> [°C]	<i>t</i> [min]	<i>W</i> [%]	<i>d</i> [g/cm <sup>3</sup> ]	<i>A</i>		<i>F</i> [N]	<i>I</i> [J]
					<sup>1</sup> H NMR	FTIR		
1:1	(-5)-(-10)	60	88	1.733	23.7	23.5	126	4.2
	0-5		85	1.766	24.0	23.8	126	4.2
	20-25		83	1.667	22.7	22.1	126	4.2
1:2	(-5)-(-10)		89	1.666	22.1	22.0	126	4.4
	0-5		82	1.696	23.1	22.7	126	4.4
	20-25		85	1.666	22.3	22.1	142	4.8
2:1	(-5)-(-10)		80	1.666	22.4	22.0	142-158	4.8
	0-5		87	1.650	21.4	21.8	142-158	5.2
	20-25		82	1.640	20.7	21.0	142-158	5.2

HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub> v/v	T [°C]	t [min]	W [%]	d [g/cm <sup>3</sup> ]	A		F [N]	I [J]						
					<sup>1</sup> H NMR	FTIR								
1:1	(-5)-(-10)	30	80	1.559	16.4	16.8	184	8.6						
	0-5		77	1.587	17.1	17.2	184	8.6						
	20-25		74	1.580	18.0	17.9	165	8.4						
1:2	(-5)-(-10)		70	1.636	19.5	19.7	165	5.2						
	0-5		71	1.590	17.9	17.3	184	8.6						
	20-25		67	1.641	20.5	20.0	165	5.2						
2:1	(-5)-(-10)		No reaction											
	0-5		82	1.608	18.9	19.2	165	8.4						
	20-25		75	1.560	16.8	16.4	212	9.6						
1:1	(-5)-(-10)	10	No reaction											
	0-5													
	20-25													
1:2	(-5)-(-10)													
	0-5													
	20-25													
2:1	(-5)-(-10)													
	0-5													
	20-25													

The highest yields were recorded for  $\gamma$ -CD nitrated for 60 min, regardless of the temperature and acids ratio; the yields fluctuated in the range 80-89%. For  $\gamma$ -CD nitrated for 30 min, lower yields were observed, in the range of approximately 67-80%, regardless of the temperature and acids ratio.  $\gamma$ -CD nitrated at (-5)-(-10) °C with a HNO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub> ratio of 2:1 was exceptional in that no precipitate was formed after pouring onto ice.  $\gamma$ -CDN was probably formed, but characterized by a low degree of substitution with nitrate groups and was soluble in the diluted post-nitration acids. Additionally, no precipitation took place after pouring  $\gamma$ -CD nitrated with the mixture of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, with volume ratios of 1:1, 1:2 and 2:1, for 10 min onto the ice. The highest degree of nitration (0.92-1) was obtained for the mixtures of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> in 1:1 and 1:2 ratios and a reaction time of 60 min. The temperature in the range tested had no significant effect on the yield or the degree of nitration of  $\gamma$ -CD.

When a greater number of substituted -OH groups occurred in  $\gamma$ -CDN, a higher density was obtained, the highest value being 1.733 g/cm<sup>3</sup>. Likewise, a higher degree of CD nitration gave greater sensitivity to mechanical stimuli. The highest sensitivity to friction was 126 N, whereas the sensitivity to impact

was 4.2 J. Impact sensitivity was slightly higher (with the corresponding degree of nitration) than in the case of  $\gamma$ -CDN obtained during nitration of  $\gamma$ -CD with  $\text{HNO}_3$  alone, which is probably caused by trace amounts of  $\text{H}_2\text{SO}_4$  that had not been washed away during the de-acidification procedure.

By comparing these observations with the results obtained in the nitration of  $\gamma$ -CD with  $\text{HNO}_3$ , it may be concluded that nitration with the mixtures of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  for 60 min produces comparable degrees of substitution of  $-\text{OH}$  groups as with 100 and 98%  $\text{HNO}_3$ , however at the same time it gives lower yields. On the other hand, when nitrating for less than 60 min,  $\gamma$ -CDN with a significantly lower degree of substitution and yield was obtained than in the cases of samples nitrated with  $\text{HNO}_3$  for comparable times and with the above mentioned concentrations.

Table 5 summarizes the results of nitration of  $\gamma$ -CD with mixtures of 98%  $\text{HNO}_3$  and 85%  $\text{H}_3\text{PO}_4$  of volume ratios 1:2 and 1:3;  $\gamma$ -CD (10 g) and respectively 98%  $\text{HNO}_3$  (50 mL) and 85%  $\text{H}_3\text{PO}_4$  (100 mL), 98%  $\text{HNO}_3$  (50 mL) and 85%  $\text{H}_3\text{PO}_4$  (150 mL) were used in these reactions. During the reaction, an extended time for dissolution of the  $\gamma$ -CD in the nitrating mixture was observed. The reactions occurred with no significant increase in temperature.

**Table 5.** Results of nitration of  $\gamma$ -CD with  $\text{HNO}_3/\text{H}_3\text{PO}_4$  mixture for  $t = 60$  min

$\text{HNO}_3/\text{H}_3\text{PO}_4$	$T$ [°C]	$W$ [%]	$d$ [g/cm <sup>3</sup> ]	$A$		$F$ [N]	$I$ [J]
				<sup>1</sup> H NMR	FTIR		
1:3	(-5)-(-10)	51	1.525	4.9	5.0	284	19.0
	0-5	50	1.531	7.3	6.4	248	17.6
	20-25	47	1.535	9.6	9.2	237	15.2
1:2	(-5)-(-10)	No reaction					
	0-5	52	1.533	9.0	8.5	237	15.2
	20-25	50	1.546	11.5	10.8	237	14.0

The yields for  $\gamma$ -CD nitrations with  $\text{HNO}_3/\text{H}_3\text{PO}_4$  mixtures were comparable and were approximately 50%, except when  $\gamma$ -CD was nitrated with  $\text{HNO}_3/\text{H}_3\text{PO}_4$  with a 1:2 acid ratio at 0-5 °C for 60 min. In that case, no precipitate was formed after pouring the reaction mixture onto ice. The degree of nitration of the resulting  $\gamma$ -CDN was low and was in the range of approximately 0.2-0.5. The higher the nitration temperature, the higher the degree of  $\gamma$ -CD substitution with nitrate groups was observed. As in the previous cases, the density increased, whereas the sensitivity to mechanical stimuli decreased with an increase in degree of  $\gamma$ -CD nitration. When comparing these findings with the results discussed earlier,

it may be concluded that mixtures of  $\text{HNO}_3$  and  $\text{H}_3\text{PO}_4$ , nitrates  $\gamma$ -CD to a lesser degree than  $\text{HNO}_3$  and the mixtures of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ .

Table 6 summarizes the results of nitration of  $\gamma$ -CD with 98%  $\text{HNO}_3$ ,  $\text{P}_2\text{O}_5$  and 85%  $\text{H}_3\text{PO}_4$ ;  $\gamma$ -CD (10 g), 98%  $\text{HNO}_3$  (50 g),  $\text{P}_2\text{O}_5$  (42.8 g) and 85%  $\text{H}_3\text{PO}_4$  (57.2 g) were used in these reactions. The nitration of  $\gamma$ -CD with  $\text{HNO}_3/\text{P}_2\text{O}_5/\text{H}_3\text{PO}_4$  mixtures proceeded smoothly with no high increases in temperature.  $\gamma$ -CD dissolved poorly in this mixture and more time was required to obtain a clear solution, as in the case of the mixtures of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . The yields of  $\gamma$ -CDN obtained with the  $\text{HNO}_3/\text{P}_2\text{O}_5/\text{H}_3\text{PO}_4$  mixture were comparable and were approximately 60%. It has been observed above that the higher the nitration temperature, the higher is the degree of  $\gamma$ -CD substitution with nitrate groups. The highest degree of  $\gamma$ -CDN substitution was reported from nitration at 20–25 °C and was 18 esterified –OH groups. That particular  $\gamma$ -CDN was also characterized by the highest density (1.580 g/cm<sup>3</sup>) and the highest sensitivity to friction (165 N) and impact (8.4 J).

**Table 6.** Results of nitration of  $\gamma$ -CD with  $\text{HNO}_3/\text{P}_2\text{O}_5/\text{H}_3\text{PO}_4$  mixture for  $t = 60$  min

$T$ [°C]	$W$ [%]	$d$ [g/cm <sup>3</sup> ]	$A$		$F$ [N]	$I$ [J]
			<sup>1</sup> H NMR	FTIR		
(–5)–(–10)	57	1.551	14.8	13.9	212	13.0
0–5	57	1.560	15.9	14.5	212	10.0
20–25	61	1.580	18.0	17.9	165	8.4

Table 7 lists the results of  $\gamma$ -CD nitration with a mixture of 98%  $\text{HNO}_3$  and  $\text{CH}_3\text{COOH}$  with a 1:1 volume ratio;  $\gamma$ -CD (10 g), 98%  $\text{HNO}_3$  (75 mL) and  $\text{CH}_3\text{COOH}$  (75 mL) were used in these reactions.  $\gamma$ -CD did not dissolve in the  $\text{HNO}_3/\text{CH}_3\text{COOH}$  nitrating mixture at (–5)–(–10) °C, dissolved poorly at 0–5 °C, but became effectively dissolved at 20–25 °C. No temperature increase was noted during the addition of  $\gamma$ -CD. The highest yield obtained for  $\gamma$ -CDN was 62%, where the conditioning and dispensing time amounted to 60 min, and the temperature was maintained at 0–5 °C. At the low temperature of (–5)–(–10) °C,  $\gamma$ -CD could not be nitrated successfully. The resulting yields were low and the degree of nitration was approximately 0.3.

**Table 7.** Results of  $\gamma$ -CD nitration with  $\text{HNO}_3/\text{CH}_3\text{COOH}$  mixture for  $t = 60$  min

$T$ [°C]	$W$ [%]	$d$ [g/cm <sup>3</sup> ]	$A$		$F$ [N]	$I$ [J]
			<sup>1</sup> H NMR	FTIR		
(-5)-(-10)	No reaction					
0-5	62	1.523	6.5	6.0	248	16
20-25	43	1.537	9.4	8.3	248	19

Table 8 summarizes the results of  $\gamma$ -CD nitration with a mixture 98%  $\text{HNO}_3$  and acetic anhydride ( $\text{Ac}_2\text{O}$ ) with a volume ratio of 1:1;  $\gamma$ -CD (10 g), 98%  $\text{HNO}_3$  (75 mL) and  $\text{Ac}_2\text{O}$  (75 mL) were used in these reactions. When adding  $\gamma$ -CD to the nitrating mixture, rapid temperature increases were observed and the reaction was strongly exothermic.  $\gamma$ -CD dissolved well in the mixture. The resulting yields were in the range 55-68%, and the degree of nitration was high, in the range of 0.8-0.97. The higher the reaction temperature, the higher the degree of nitration was observed.  $\gamma$ -CD could not be nitrated in less than 60 min.

**Table 8.** Results of  $\gamma$ -CD nitration with  $\text{HNO}_3/\text{Ac}_2\text{O}$  mixture for  $t = 60$  min

$T$ [°C]	$W$ [%]	$d$ [g/cm <sup>3</sup> ]	$A$		$F$ [N]	$I$ [J]
			<sup>1</sup> H NMR	FTIR		
(-5)-(-10)	55	1.647	19.4	19.7	165	3.4
0-5	68	1.666	22.0	21.8	142-158	3.2
20-25	63	1.733	23.3	22.9	117-126	3.2

The highest density, *i.e.* 1.733 g/cm<sup>3</sup>, was obtained for the sample with the highest degree of nitration.  $\gamma$ -CDN with 23.3 esterified -OH groups turned out to be most sensitive to friction and impact; its sensitivity to friction was 117-126 N and to impact was 3.4 J. It should be noted that the samples nitrated with the  $\text{HNO}_3$  and  $\text{Ac}_2\text{O}$  mixture exhibited the highest impact sensitivity, of the  $\gamma$ -CDNs obtained with the other nitrating mixtures. By nitrating with this mixture, lower yields were obtained than in nitrations with  $\text{HNO}_3$  and with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  mixtures. On the other hand, the degrees of nitration obtained were similar to  $\gamma$ -CD nitrated with  $\text{HNO}_3$  and the mixtures of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , nitrated for 60 min.

Table 9 lists the results of nitration of  $\gamma$ -CD with the mixture of dinitrogen pentoxide in methylene chloride (5%  $\text{N}_2\text{O}_5$  solution in  $\text{CH}_2\text{Cl}_2$ ) and  $\text{HNO}_3$  (17.3%  $\text{N}_2\text{O}_5$  solution in  $\text{HNO}_3$ );  $\gamma$ -CD (10 g) and  $\text{N}_2\text{O}_5$  (20 g),  $\text{CH}_2\text{Cl}_2$  (380 g) and  $\text{N}_2\text{O}_5$  (13.1 g), 100%  $\text{HNO}_3$  (62.9 g) were used in these reactions. No difficulties were encountered in conducting  $\gamma$ -CD nitration reactions with  $\text{N}_2\text{O}_5/\text{CH}_2\text{Cl}_2$

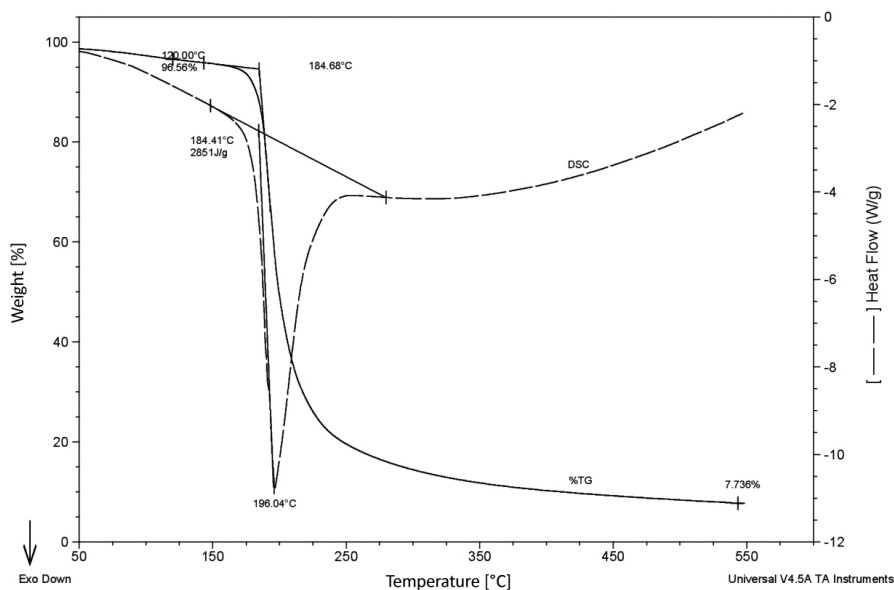


and  $\text{N}_2\text{O}_5/\text{HNO}_3$  mixtures. In both cases, the  $\gamma$ -CD dissolved in the mixtures and after adding the entire amount of  $\gamma$ -CD the solution became clear. In the case of the  $\text{N}_2\text{O}_5/\text{HNO}_3$  mixture, a rapid increase in temperature was observed when starting the  $\gamma$ -CD addition. Nitration reactions were conducted at 0-5 °C and for 60 min. During the nitration of  $\gamma$ -CD with  $\text{N}_2\text{O}_5/\text{CH}_2\text{Cl}_2$ , a yield of 66% and a degree of nitration of 0.78 were obtained. In the case of nitration with the  $\text{N}_2\text{O}_5/\text{HNO}_3$  mixture, the results obtained were similar to those obtained when nitrating  $\gamma$ -CD with 100%  $\text{HNO}_3$ . A completely nitrated  $\gamma$ -CDN was obtained with a yield of 99%.

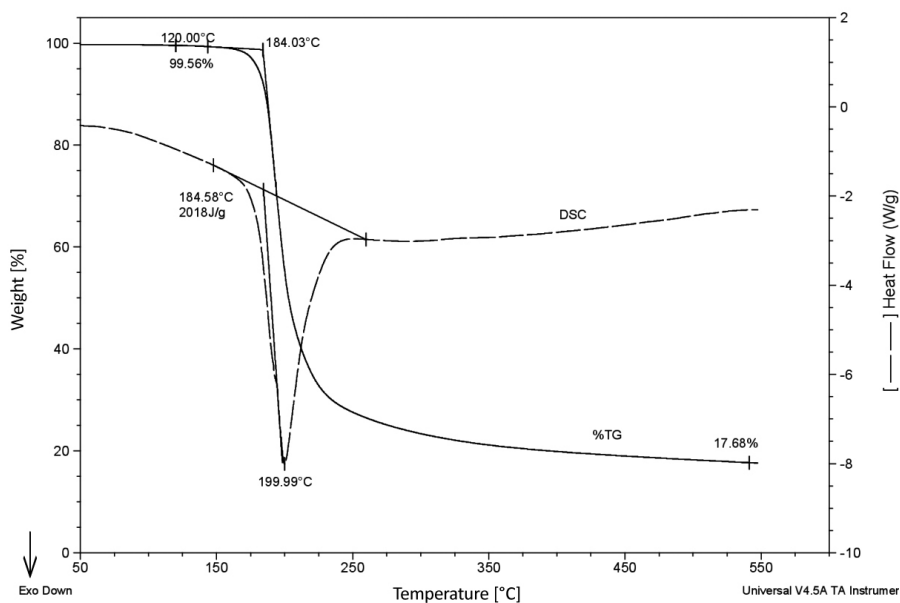
**Table 9.** The results of  $\gamma$ -CD nitration with  $\text{N}_2\text{O}_5/\text{CH}_2\text{Cl}_2$ ,  $\text{N}_2\text{O}_5/\text{HNO}_3$  mixtures for  $T = 0-5$  °C and  $t = 60$  min

Nitrating mixture	$W$ [%]	$d$ [g/cm <sup>3</sup> ]	$A$		$F$ [N]	$I$ [J]
			<sup>1</sup> H NMR	FTIR		
$\text{N}_2\text{O}_5/\text{CH}_2\text{Cl}_2$	66	1.615	18.6	19.0	165	7.6
$\text{N}_2\text{O}_5/\text{HNO}_3$	99	1.775	24.0	24.0	117-126	5.2

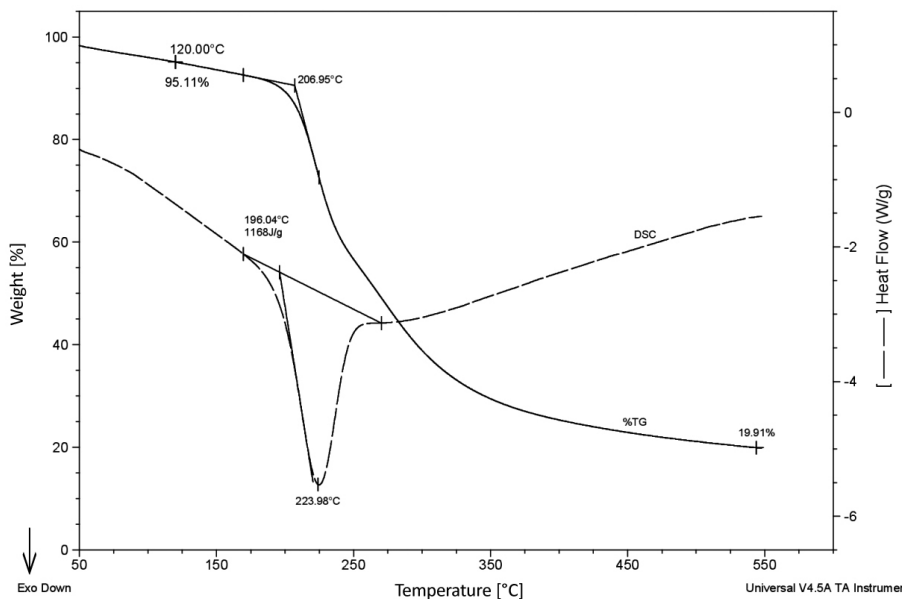
The  $\gamma$ -CDNs obtained were analyzed by thermogravimetric measurements. Figures 5-7 present selected thermograms for  $\gamma$ -CDN of varying degrees of nitration (1, 0.89, 0.68). A weight loss in the temperature range of approximately 184-250 °C is visible in the TGA curve for  $\gamma$ -CDN with a degree of nitration of 1 and 0.89 (Figures 5 and 6). The DSC curves exhibit the exothermic effect of decomposition of  $\gamma$ -CDN in both cases. The heat effect amounts to approximately 2851 J/g for  $\gamma$ -CDN with a degree of nitration of 1 and approximately 2018 J/g for  $\gamma$ -CDN with a degree of nitration of 0.89. The maximum exothermic peak for  $\gamma$ -CDN with the degree of nitration of 1 was at 196 °C, and for  $\gamma$ -CDN with the degree of nitration of 0.89 at 200 °C. The  $\gamma$ -CDN sample with a degree of nitration of 1 does not decompose completely; at approximately 550 °C nearly 7.7% of the initial mass of the sample was left, and in the case of  $\gamma$ -CDN with the degree of nitration of 0.89 nearly 17.7% of the initial sample mass remained. Figure 7 presents the TGA and DTA curves for  $\gamma$ -CDN with a nitration degree of 0.68. The TGA already shows a two-stage weight loss in the temperature range of approximately 206-350 °C. The exothermic effect of  $\gamma$ -CDN decomposition is visible on the DSC curve. The heat effect was approximately 1168 J/g, with the exothermic peak at 224 °C. The sample does not decompose completely; at approximately 550 °C nearly 20% of the sample mass was left.



**Figure 5.** TG/DTA curves of  $\gamma$ -CDN obtained with 100%  $\text{HNO}_3$ , at 0-5 °C, after nitration for 60 min (degree of nitration 1)



**Figure 6.** TG/DTA curves of  $\gamma$ -CDN obtained with  $\text{HNO}_3/\text{H}_2\text{SO}_4$  2:1, at 0-5 °C, after nitration for 60 min (degree of nitration 0.89)



**Figure 7.** TG/DTA curves of  $\gamma$ -CDN obtained with  $\text{HNO}_3/\text{H}_2\text{SO}_4$  1:1, at 0-5 °C, after nitration for 30 min (degree of nitration 0.68)

Based on the TGA/DSC measurements, it may be observed that the lower the degree of  $\gamma$ -CDN nitration, the smaller is the thermal effect of decomposition, the maximum of the exothermic peak being shifted increasingly towards a higher temperature.

## 4 Conclusions

A range  $\gamma$ -CD nitration reactions was conducted, with different times, addition and conditioning temperatures, as well as types of nitrating mixtures used. Nitrating mixtures such as:

- nitric(V) acid of various concentrations,
- nitric(V) acid/sulfuric(VI) acid mixtures,
- nitric(V) acid/acetic anhydride mixtures,
- nitric(V) acid/phosphoric acid mixtures,
- nitric(V) acid/acetic acid mixtures,
- nitric(V) acid/phosphorus(V) oxide/phosphoric(V) acid, and
- nitric(V) oxide in methylene chloride and in nitric(V) acid.

The nitration reactions were carried out at three different temperature ranges:  $(-5)$ - $(-10)$  °C,  $0$ - $5$  °C,  $20$ - $25$  °C and for periods of 10, 30 and 60 min. The formation of  $\gamma$ -CDN was confirmed by FTIR,  $^1\text{H}$  NMR spectroscopy and elemental analysis.

The  $\gamma$ -CD nitration reactions with  $\text{HNO}_3$  proceeded smoothly, no rapid temperature fluctuations were observed when adding the  $\gamma$ -CD to  $\text{HNO}_3$ . The highest yields were reported for  $\gamma$ -CD nitrated with 100%  $\text{HNO}_3$  for 30 and 60 min and were approximately 90-99%, with the highest degree of nitration of 1. The degree of nitration of  $\gamma$ -CDN and reaction yield depend on the  $\text{HNO}_3$  concentration, the nitration time and, to a lesser degree, on the temperature.

During the  $\gamma$ -CD nitration reaction with  $\text{HNO}_3/\text{H}_2\text{SO}_4$ , the precipitation of sulfate esters was observed, which hindered the reaction. In addition, the reaction proceeded less smoothly than during nitration using  $\text{HNO}_3$  alone, due to temperature fluctuations. By comparing these results with those obtained in  $\gamma$ -CD nitration reactions with  $\text{HNO}_3$ , it may be concluded that nitration with  $\text{HNO}_3/\text{H}_2\text{SO}_4$  mixtures for 60 min produces comparable degrees of  $\gamma$ -CDN nitration, as in the cases of 100 and 98%  $\text{HNO}_3$ , however it entails lower yields. On the other hand, nitration for less than 60 min results in  $\gamma$ -CDN with a significantly lower degree of substitution and yield than in the cases of  $\gamma$ -CDN nitrated with  $\text{HNO}_3$  for the same period of time and in the quoted concentrations.

During the  $\gamma$ -CD nitration reaction with  $\text{HNO}_3/\text{H}_3\text{PO}_4$ , a quite extensive dissolution time of  $\gamma$ -CD in the nitrating mixture was observed. The reaction proceeded with no significant temperature increases. The resulting yields were around 50% and the degree of nitration was low, in the range 0.2-0.5. The higher the nitration temperature, the higher the degree of  $\gamma$ -CDN substitution with nitrate groups was observed.  $\gamma$ -CD could not be successfully nitrated in less than 60 min.

Nitration of  $\gamma$ -CD with a  $\text{HNO}_3/\text{P}_2\text{O}_5/\text{H}_3\text{PO}_4$  mixture proceeded smoothly with no significant temperature increases, but the  $\gamma$ -CD dissolved poorly in this nitrating mixture. Lower yields and lower degrees of nitration were obtained as compared to  $\gamma$ -CD nitrated with  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$  in  $\text{HNO}_3$ ,  $\text{HNO}_3/\text{H}_2\text{SO}_4$  mixtures or  $\text{HNO}_3/\text{Ac}_2\text{O}$  mixtures. The highest degree of  $\gamma$ -CDN nitration obtainable was 0.75.

$\gamma$ -CD did not dissolve in the  $\text{HNO}_3/\text{CH}_3\text{COOH}$  nitrating mixture at  $(-5)$ - $(-10)$  °C, and dissolved poorly at  $0$ - $5$  °C, however the most effective dissolution occurred at  $20$ - $25$  °C. No temperature increase was noted during the addition of  $\gamma$ -CD. The resulting reaction yields were low. The degree of nitration was approximately 0.3. When comparing this nitrating mixture with the other nitrating mixtures,  $\text{HNO}_3/\text{CH}_3\text{COOH}$  was found to be the least effective.

$\gamma$ -CD nitration with the  $\text{HNO}_3/\text{Ac}_2\text{O}$  mixture proceeded less smoothly. When adding  $\gamma$ -CD to the nitrating mixture, rapid temperature increases were observed, and the reaction was strongly exothermic.  $\gamma$ -CD dissolved well in the mixture. When nitrating with this mixture, lower yields were obtained than in the case of nitration with  $\text{HNO}_3$  or with the  $\text{HNO}_3/\text{H}_2\text{SO}_4$  mixture, however similar values of the degrees of nitration of  $\gamma$ -CDN were obtained.

No difficulties were encountered when conducting  $\gamma$ -CD nitration reactions with  $\text{N}_2\text{O}_5/\text{CH}_2\text{Cl}_2$  and  $\text{N}_2\text{O}_5/\text{HNO}_3$  mixtures. In both cases, the  $\gamma$ -CD dissolved in the nitrating mixtures. In the case of nitration with  $\text{N}_2\text{O}_5/\text{HNO}_3$ , the results obtained were comparable to those obtained when nitrating  $\gamma$ -CD with 100%  $\text{HNO}_3$ . Completely nitrated  $\gamma$ -CDN was obtained with a yield of 99%.

An analysis of the properties of  $\gamma$ -CDN served to demonstrate that the density and sensitivity to mechanical stimuli (friction and impact) depend on the degree of substitution of  $-\text{OH}$  groups with  $-\text{ONO}_2$  groups in  $\gamma$ -CDN. The highest density  $1.777 \text{ g/cm}^3$  was exhibited by  $\gamma$ -CDN with the highest degree of esterification with  $\text{HNO}_3$ . Samples having the largest number of nitric groups and whose sensitivity to friction was in the range 117-126 N and sensitivity to impact was 5.2 J, were the most sensitive ones to friction and impact.

Thermal analysis of the resulting  $\gamma$ -CDNs with different degrees of nitration demonstrated that for  $\gamma$ -CDN with a high degree of substitution, decomposition takes place in one exothermic stage, in the temperature range of approximately 184-250 °C. The lower the degree of  $\gamma$ -CDN nitration, the lower the thermal effect of decomposition was observed, whereas the maximum of the exothermic peak was shifted increasingly towards higher temperatures.

## Acknowledgements

This work was financially supported by Warsaw University of Technology.

## References

- [1] Del Valle, E.M.M. Cyclodextrins and Their Uses: A Review. *Process Biochem.* **2004**, 39(9): 1033-1046.
- [2] Szejtli, J. Introduction and General Overview of Cyclodextrin Chemistry. *Chem. Rev.* **1998**, 98(5): 1743-1754.
- [3] Szejtli, J. *Cyclodextrin Technology*. Kluwer Academic Publishers, Dordrecht/Boston/London, **1988**, pp. 6-7; ISBN 978-90-481-8427-9.
- [4] Bender, M.L.; Komiyama, M. *Cyclodextrin Chemistry*. Springer-Verlag, Berlin/Heidelberg/New York, **1978**; ISBN 978-3-642-66844-9.
- [5] Śliwa, W.; Girek, T. *Cyclodextrin, Properties and Applications*. Wiley-VCH Verlag

- GmbH & Co. KGaA, Germany, **2017**; ISBN: 978-3-527-33980-8.
- [6] Singh, R.; Bharti, N.; Madan, J. Characterization of Cyclodextrin Inclusion Complexes – A Review. *J. Pharm. Sci. Technol.* **2010**, *2*(3): 171-183.
- [7] Szejtli, J. Past, Present, and Future of Cyclodextrin Research. *Pure Appl. Chem.* **2004**, *76*(10): 1825-1845.
- [8] Deshmukh, M.B.; Wagh, N.D.; Sikder, A.K.; Borse, A.U. Cyclodextrin Nitrate Ester/H<sub>2</sub>SO<sub>4</sub> as a Novel Nitrating System for Efficient Synthesis of Insensitive High Explosive 3-Nitro-1,2,4-triazol-5-one. *Ind. Eng. Chem. Res.* **2014**, *53*: 19375-19379.
- [9] Luppi, F.; Cavaye, H.; Dossi, E. Nitrated Cross-linked  $\beta$ -Cyclodextrin Binders Exhibiting Low Glass Transition Temperatures. *Propellants, Explos., Pyrotech.* **2018**, *43*(10): 1023-1031.
- [10] Consaga, J.P.; Gill, R.C. Synthesis and Use of Cyclodextrin Nitrate. *Int. Annual Conf. ICT, Proc., 29<sup>th</sup>*, Karlsruhe, **1998**, V5/1-V5/6.
- [11] Statton, G.L.; Kosowski, B.M. Synthesis of Cyclodextrin Polymer (Poly CD), a Raw Material for Insensitive, High Energy and Shock Survivable Explosives. *Int. Annual Conf. ICT, Proc., 29<sup>th</sup>*, Karlsruhe, **1998**, P46/1-P46/12.
- [12] Ruebner, A.; Statton, G.L.; Meyers, C.; Kosowski, B.M.; Robitelle, D. Cyclodextrin Polymer Nitrate. *Int. Annual Conf. ICT, Proc., 31<sup>st</sup>*, Karlsruhe, **2000**, V12/1-V12/10.
- [13] Consaga, J.P.; Collignon, S.L. *Energetic Composites of Cyclodextrin Nitrate Esters and Nitrate Ester Plasticizers*. Patent US 5114506, **1992**.
- [14] Ruebner, A.; Statton, G.L.; Consaga, J.P. *Polymeric Cyclodextrin Nitrate Esters*. Patent US 6527887B1, **2003**.
- [15] Consaga, J.P. *Complexed Liquid Fuel Compositions*. Patent US 6110306, **1992**.
- [16] Consaga, J.P. *Chemically Reactive Fragmentation Warhead*. Patent US 6293201, **2001**.
- [17] Akito, E.; Nakajima, Y.; Horioka, M. *Nitroglycerine Inclusion Compounds with Cyclodextrin and Composition Containing the Same*. Patent US 4073931, **1978**.
- [18] Maksimowski, P.; Rumianowski, T. Properties of the Gamma-Cyclodextrin/CL-20 System. *Cent. Eur. J. Energ. Mater.* **2016**, *13*(1): 217-229.
- [19] Maksimowski, P.; Grzegorzczak, A.; Cieślak, K.; Gołofit, T.; Chmielarek, M.; Tomaszewski, W.; Pawłowski, W.  $\gamma$ -Cyclodextrin Nitrate/CL-20 Complex: Preparation and Properties. *Propellants, Explos., Pyrotech.* **2019**, *44*(2): 207-216.
- [20] Naufflett, W.G.; Farncomb, E.R. *Nitration of Organics in Carbon Dioxide*. Patent US 6177033, **2001**.
- [21] Romanova, L.B.; Barinova, L.S.; Lagodzinskaya, G.V.; Kazakov, A.I.; Mikhailov, Yu.M. Preparation and NMR Analysis of  $\beta$ -Cyclodextrin Nitrates. *Russ. J. Appl. Chem.* **2014**, *87*(12): 1884-1889.

Received: April 17, 2020

Revised: September 21, 2020

First published online: September 28, 2020