

## Stability of solid amine sorbents for CO<sub>2</sub> capture from air

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UNIVERSITY OF LIEGE  
FACULTY OF APPLIED SCIENCE



# Stability of solid amine sorbents for CO<sub>2</sub> capture from air

by  
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Thesis presented for obtaining the Master's degree in  
**Chemical and Materials engineering**

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# Asbtract

Since the beginning of industrialisation, the energy consumption in the world increased tremendously. As a consequence of the use of fossils fuels as main source of energy, the release of CO<sub>2</sub> and other greenhouse gases (GHG) increased as well. Therefore, the concentration of CO<sub>2</sub> increased from 280 ppm in the beginning of industrialisation to 400 ppm nowadays. This increase in atmospheric CO<sub>2</sub> concentration leads to an increase of the atmospheric temperature. Considering the energetic consumption in the world, it is not realistic to imagine a near future without the use of fossil energies to limit the Global Warming. So, it is important to develop some methods to limit CO<sub>2</sub> release. CCS (Carbon Capture and Storage) and DAC (Direct Air Capture) are the main technologies that aim to reduce the CO<sub>2</sub> emissions. This thesis studies the DAC in two ways. At first, a review about the state of art about DAC is made. Then, the degradation of a particular amine-based solid sorbent, Lewatit®VP OC 1065 (Lanxess), is studied in a quartz tubular reactor regarding some main parameters : temperature in the reactor, duration of the experiment and composition of the feed gas of the reactor. The influence of these parameters is studied in order to characterise the degradation of the sorbent. The main results of the thesis are the impact of oxygen on the degradation, greater than the impact of temperature, the measurement of pure thermal degradation below 150 °C and the weak effect of water on the degradation.

## Résumé

Depuis le début de l'industrialisation, la consommation énergétique mondiale augmente de manière exponentielle. Les sources principales d'énergie étant les énergies fossiles, une quantité grandissante de CO<sub>2</sub> et autres gaz à effet de serre se retrouve dans l'atmosphère. En particulier, depuis le début de l'industrialisation et jusqu'à aujourd'hui, la concentration en CO<sub>2</sub> est passée de 280 ppm à 400 ppm. Cette augmentation de la concentration en CO<sub>2</sub> dans l'atmosphère mène à une augmentation de la température moyenne mondiale. Et, considérant les consommations énergétiques du monde moderne, il n'est pas imaginable de se passer de ressources fossiles pour atténuer ce phénomène de réchauffement climatique. Il est donc important de développer des méthodes capables de capturer le CO<sub>2</sub> afin de limiter les émissions de celui-ci. Les principales méthodes pour limiter ces émissions reposent sur la capture du CO<sub>2</sub> et sur son stockage. Dans cette thèse, les méthodes se focalisant sur la capture du CO<sub>2</sub> dans l'air ambiant sont considérées de deux manières. Premièrement, l'état de l'art des méthodes de capture du CO<sub>2</sub> dans l'air ambiant est décrit. Ensuite, la dégradation d'un sorbent solide aminé spécifique, Lewatit®VP OC 1065 (Lanxess), fut étudiée. Ce sorbent était dégradé dans un réacteur tubulaire en quartz et sa dégradation étudiée selon certains paramètres principaux : la température dans le réacteur, la durée de l'expérience et la composition du mélange gazeux entrant dans le réacteur. Le but de cette étude était de caractériser la dégradation de ce sorbent. Les résultats principaux de la thèse concernent l'influence de l'oxygène, démontrée comme plus importante que celle de la température, les mesures de dégradation thermique pure en dessous de 150 °C et le faible effet de l'eau sur la dégradation.



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# Abbreviations

<b>APS</b>	Aminopropyl Organosilanes
<b>AZ</b>	Aziridine
<b>BET</b>	Brunauer-Emmett-Teller
<b>CCS</b>	Carbon Capture and Storage
<b>DAC</b>	Direct Air Capture
<b>DETA</b>	Diethylenetriamine
<b>DT</b>	Diethylenetriamine Organosilanes
<b>ED</b>	Ethylenediamine Organosilanes
<b>FID</b>	Flame Ionization Detector
<b>GC</b>	Gas Chromatography
<b>GHG</b>	Greenhouse Gas
<b>GISS</b>	Global Institut for Space Studies
<b>IER</b>	Ion Exchange Resin
<b>IR</b>	Infrared
<b>LDHs</b>	Layered Double Hydroxides
<b>MAP</b>	Methylaminopropyl Organosilanes
<b>MCF</b>	Silica Mesocellular Foam
<b>MEP</b>	Methylaminopropyl Organosilanes
<b>MOFs</b>	Metal-Organic Framework
<b>MOPs</b>	Microporous Organic Polymers
<b>MS</b>	Mass spectrometer
<b>PAA</b>	Poly(Allylamine)
<b>PB</b>	Packed Bed
<b>PEG</b>	Poly(Ethylene Glycol)
<b>PEI</b>	Poly(Ethylenimine)
<b>PEHA</b>	Pentaethylenehexamine

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<b>RH</b>	Relative Humidity
<b>RT</b>	Retention Time
<b>SG</b>	Silica Gel
<b>TCD</b>	Thermal Conductivity Detector
<b>TEPA</b>	Tetraethylenepentamine
<b>TGA</b>	Thermogravimetry Analysis
<b>TPD</b>	Temperature-Programmed Desorption
<b>VOL</b>	Volumetric Method



# Chapter 1

## Introduction

Since the beginning of industrialisation, the energy consumption in the world increased tremendously. As a consequence of the use of fossil fuels as main source of energy, the release of CO<sub>2</sub> and other greenhouse gases (GHG) increased as well. Therefore, the concentration of CO<sub>2</sub> increased from 280 ppm in the beginning of industrialisation to 400 ppm nowadays. The major consequence of this increase in the atmospheric concentration of GHG's is the global warming. The GISS (Goddard Institut for Space Studies) evaluated with its last data that the temperature has increased of at least 0.8 °C since 1951 [6]. Some models evaluate that the temperature will increase of more than 2 °C before 2100. And with such an increase in temperature, the CO<sub>2</sub> which is trapped at this moment in the Arctic, in the permafrost, will be released. The tipping point is 2-4.5 °C of increase in the global temperature. [1] [2]

Considering the energetic consumption in the world, it is not realistic to imagine a near future without the use of fossil energies. So, it is important to develop some methods to limit CO<sub>2</sub> release. CCS (Carbon Capture and Storage) and DAC (Direct Air Capture) are the main technologies that aim to reduce the CO<sub>2</sub> emissions. The first one is more general, and considers among other post-combustion capture and DAC. DAC is therefore a particular part of CCS which is dedicated to the capture of CO<sub>2</sub> directly from the ambient air. So, DAC are negative CO<sub>2</sub> emissions process which aim to decrease the concentration in the atmosphere rather than limit the emission. Figure 1.1 lists the different main methods to capture CO<sub>2</sub>.

In this work, DAC is considered. More accurately, this thesis studies the degradation of a specific solid sorbent (Lewatit®VP OC 1065 [Lanxess]) provided by the group of Mister

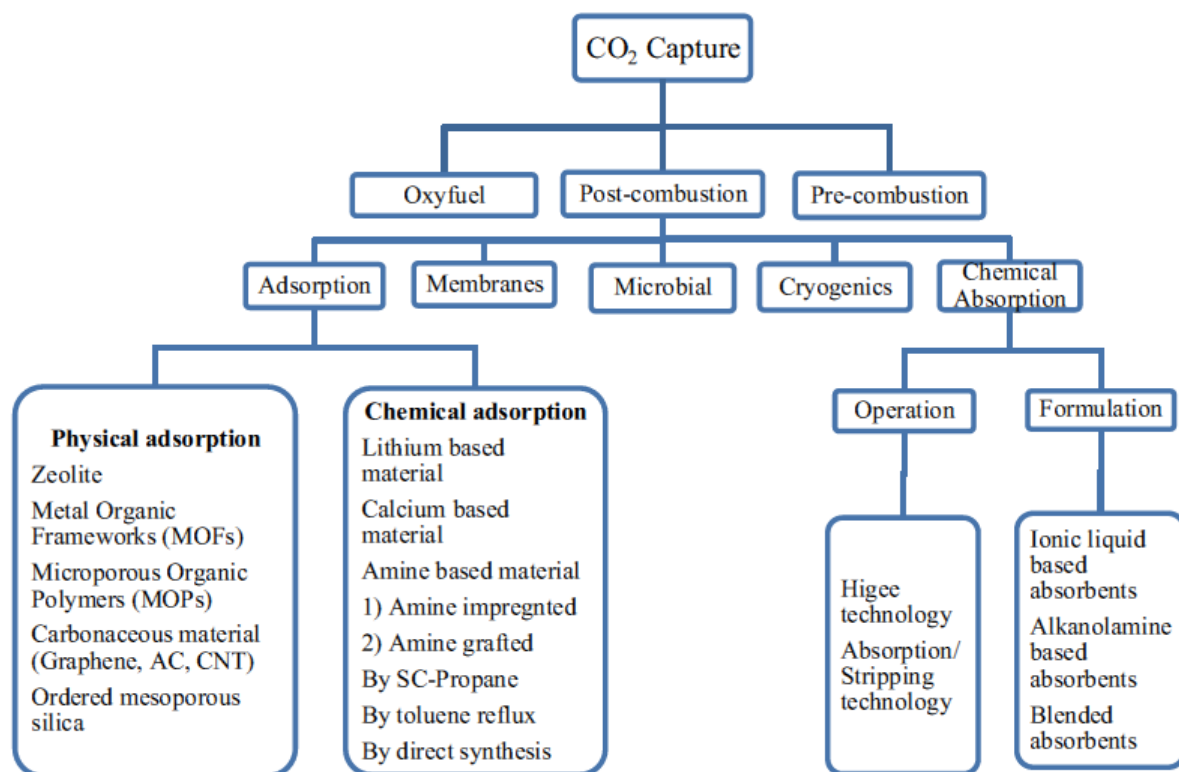


FIGURE 1.1: The different main methods to capture CO<sub>2</sub>. Reference : [1]

Brilman (University of Twente). For this purpose, an experimental setup, used before for test of catalytic reforming, was used to test the degradation of the sorbent under multiple conditions. The main parameters considered in this study will be the temperature, the duration of the test and the composition of the gas in contact with the sorbent. The purpose of this work is to study the degradation of this sorbent, to obtain information about the best conditions for it to be regenerated.

This thesis is made of several parts. The first part consists in a global review about the state of art of DAC. The different methods for DAC, their advantages, limitations, and so on, are presented as the generalities about DAC as a whole. The second part is the heart of this thesis and presents the experiments. The results are discussed in this same part. Finally, the last part concludes this work. This part discusses about the different ways the experiment could be improved for further investigation into this same subject.

## 1.1 Goal of the thesis

The goal of the thesis is to study the state of art about DAC and make a bibliographic review about it. But more than that, an experimental study was done to bring something new to the literature. This experimental work was the study of the stability of the sorbent Lewatit®VP OC 1065 (Lanxess) and its degradation. In this thesis, the uptake of CO<sub>2</sub> was not measured. Usually, the degradation is measured by difference in the uptake of CO<sub>2</sub> before and after the experimentation; it is not the case here. The degradation was studied with different characterisation methods in order to give a new overview of the effect of the degradation on the sorbent. The purpose was really to study and obtain a better understanding of the degradation of the chosen sorbent.

The main parameters considered were :

- Duration
- Temperature
- Gas composition (%N<sub>2</sub> %O<sub>2</sub> %CO<sub>2</sub> %H<sub>2</sub>O)

The different methods that were used to characterise the degradation were the following :

- Gas chromatograph : thermal conductivity detector (TCD) + flame ionization detector (FID)
- Thermogravimetry (TG) + mass spectroscopy (MS)
- Nitrogen adsorption-desorption measurements
- Helium pycnometry

## Chapter 2

# State of art

In this chapter, the state of art about Carbon Capture and Storage and Direct Air Capture will be summarised. At first, generalities about CCS and DAC will be presented, as well as a short listing of the several methods encountered in the literature. After that, some methods for DAC will be presented in more details, in regard to their mechanisms, advantages, disadvantages and limitations, that will be discussed.

### 2.1 Carbon Capture and Storage

CCS considers all the methods which capture  $\text{CO}_2$ . There is three major ways to proceed :

- Precombustion  $\text{CO}_2$  capture
- Oxyfuel combustion
- Postcombustion  $\text{CO}_2$  capture

#### 2.1.1 Precombustion $\text{CO}_2$ capture

The purpose of this method is to directly reduce the carbon content of the feed. The principal process that uses this method is the conversion of coal (or biomass) into syngas ( $\text{CO} + \text{H}_2$ ). After performing the gasification, steam is added to the gas mixture. Thanks to the water-gas shift reaction, the  $\text{CO}$  is converted into  $\text{H}_2$  and  $\text{CO}_2$  with a concentration of  $\text{CO}_2$  between 15 and 60%. At these concentrations, the  $\text{CO}_2$  can then be separated easily.

This leads to the formation of a gas mixture with a high concentration in  $H_2$ , which is a clean source of energy.

### 2.1.2 Oxyfuel combustion

Here, pure oxygen is used to perform the combustion. The volume of gas needed is then smaller thanks to the absence of nitrogen. The  $CO_2$  is recirculated in the combustion chamber to increase even more its concentration up to 90%. The real limitation of this method is its price because of the need of pure oxygen.

### 2.1.3 Postcombustion $CO_2$ capture

Postcombustion  $CO_2$  capture are the most used methods. Their principal advantage is the fact that they can be added on existing units unlike the others. In the other hand, they have plenty of disadvantages. The major drawback is that the concentration of  $CO_2$  in flue gas is between 4 and 12%.

The two major ways to perform postcombustion capture are by absorption or adsorption.

#### 2.1.3.1 Capture by absorption

Capture by absorption is generally performed using amine aqueous solutions. Different types of amine are currently used in industry, such as monoethanolamine (MEA), diethanolamine (DEA) or methyldiethanolamine (MDEA). The efficacy of these solutions is proven, but there is a lot of drawbacks in their use. The first and major one is the massive amount of energy needed to regenerate these solutions. Indeed, the regeneration is performed by heating the solution, but heating the bulk of water is expensive. There is a lost of amine within the operation and the contact area between liquid and gas is low. Moreover, the corrosive property of liquids amine that degrades the equipments is another important drawback.

#### 2.1.3.2 Capture by adsorption

The use of solid sorbents to capture the  $CO_2$  by adsorption is an alternative to bypass the problem of the bulk of water. The sorbents are easier to handle and they are not corrosive.

There are several types of sorbents to capture the CO<sub>2</sub>. The CO<sub>2</sub> can be adsorbed by physisorption or chemisorption. In physisorption, the CO<sub>2</sub> is linked by weak physical forces (electrostatic, dipole-dipole, Van Der Waals, ...) and the energy of cohesion is about 8-41 kcal/mol. In chemisorption, there are strong chemical bonds (ionic, covalent, metallic) and the cohesion energy is about 60-418 kcal/mol. These two types of adsorption have different properties because of their respective strength and weakness. In physisorption, the regeneration is easier than in chemisorption and can be performed with simple degassing, although the major drawback of physisorption is the lack of selectivity.

Several types of adsorbents are listed here for information [1] [7] :

- Low-temperature adsorbents :
  - Carbonaceous material-based adsorbents
  - Amine-based solid adsorbents
  - Dry alkali metal-based sorbents
  - Zeolites-based adsorbents
  - Metal-organic framework (MOFs)
  - Microporous organic polymers (MOPs)
- Medium-temperature adsorbent
  - Layered double hydroxides (LDHs)
- High-temperature adsorbents
  - Alkali ceramic based sorbent
  - Calcium-based sorbent

## 2.2 Direct Air Capture

DAC are negative CO<sub>2</sub> emission methods. They aim to capture CO<sub>2</sub> in the ambient air to reduce its concentration in the air. The first and more basic "process" of DAC is the natural cycle of the CO<sub>2</sub>. Plants capture the CO<sub>2</sub> directly from the air using the sunlight as an

energy source. Sending the biomass in process like gasification or biomethanisation leads to the formation of a fuel with a zero CO<sub>2</sub> balance; or combined with CCS to a negative CO<sub>2</sub> balance.

The main difference between DAC and the other methods of CCS is the concentration of the CO<sub>2</sub>. In the ambient air, the concentration is about 400 ppm, which is slower than in flue gas. Because of that, all the methods of postcombustion capture cannot be used. Indeed, a strong affinity for CO<sub>2</sub> is needed for a material to be effective at these concentration. More accurately, only the methods based on chemisorption are useful at such concentration. The others based on physisorption (such as the use of zeolites as adsorbent) show a bad CO<sub>2</sub> uptake and a low selectivity.

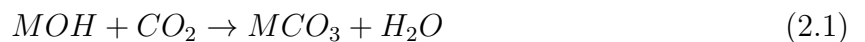
It can already be stated that increasing the basicity of a sorbent will lead to an improvement of the CO<sub>2</sub> capture capacity. Indeed, CO<sub>2</sub> is a Lewis acid; and because of that fact, the basicity of the sorbent will obviously increase its CO<sub>2</sub> affinity and so its capture capability.

### 2.2.1 Aqueous hydroxide sorbents

In DAC history, the first method designed for DAC capture was based on an aqueous hydroxide sorbent. This method was the first to consider DAC as a real measure for reducing atmospheric CO<sub>2</sub>. [2] [8]

Over the years, these techniques have been improved. But even today, they have the same main disadvantages that limit their viability for an intensive use. These disadvantages are mainly a high energy requirement and a high temperature (> 700 °C) for regeneration.

The main principle for every of these methods is the same and is quite simple. It considers to use of large "pools" of alkali hydroxide; the latter shows a strong affinity with carbon dioxide thanks to a chemical reaction that forms carbonate. The general and not balanced equation of this reaction is written below, where M is an alkaline or alkaline-earth metal.



The energy consumption of this process comes directly from the regeneration of the hydroxide. The other limitations of these techniques come from the liquid/gas mass transfer. To decrease these limitations, simple "pools" of hydroxide are not used anymore; the techniques are obviously evolving to maximise the contact surface between air and the sorbent at the lowest price.

### 2.2.2 Calcium hydroxide sorbent

This was the first method encountered in the DAC history which was proposed by Lackner in 1999.

Mechanisms :



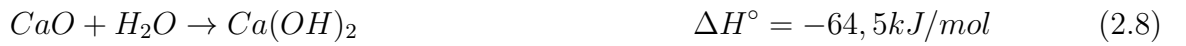
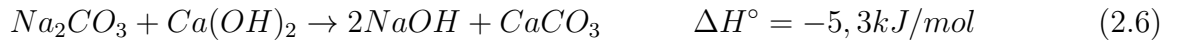
The first step of this method is to form calcium carbonate by reaction between the  $CO_2$  and the calcium hydroxide. The carbonate is then separated by precipitation in order to be regenerated. This last step is performed by calcination at high temperature ( $> 700^\circ\text{C}$ ) which produces calcium oxide and release the  $CO_2$ . The oxide obtained is then hydrated to complete the cycle.

The binding energy is strong and the major part of the energy needed is for the regeneration. This and the fact that calcium hydroxide is not very soluble in water (max. 1 mol/L to prevent precipitation of non-desired calcium hydroxide), which directly limit the possible adsorption, are the two major drawbacks of this method. And so, the energy penalty can be evaluated from the enthalpy of reaction. The minimum energy needed to convert calcium carbonate into calcium hydroxide is related to the first reaction, and is therefore of 109 kJ/mol, but the regeneration step needs 179.2 kJ/mol instead.



### 2.2.2.1 Sodium hydroxide solution

The problem of solubility of calcium from the last process previously mentioned can be bypass by using a sodium hydroxide solution instead. The mechanism is written below. This process is based on the Kraft methods from the paper industry.



The principle itself is simple : sodium hydroxide captures  $CO_2$  with the same efficiency as calcium hydroxide, with the advantage that sodium hydroxide is highly soluble (limited to 1 mol/L to prevent precipitation of non-desired calcium hydroxide). After that, the  $CO_2$  is transferred by precipitation of calcium carbonate and the sodium hydroxide is regenerated. This last step is referred as "causticization". The process is then the same as the previous method. So, the energy needed for the regeneration is the same; same for the energy penalty. But this method was innovative, and deletes one of the drawback of its predecessor. Figure 2.1 represents schematically this process and Figure 2.2 presents the enthalpy scale of the different steps.

Potassium hydroxide can be considered as well for this reaction instead of sodium hydroxide, but it is less frequent because of the higher cost of potassium hydroxide.

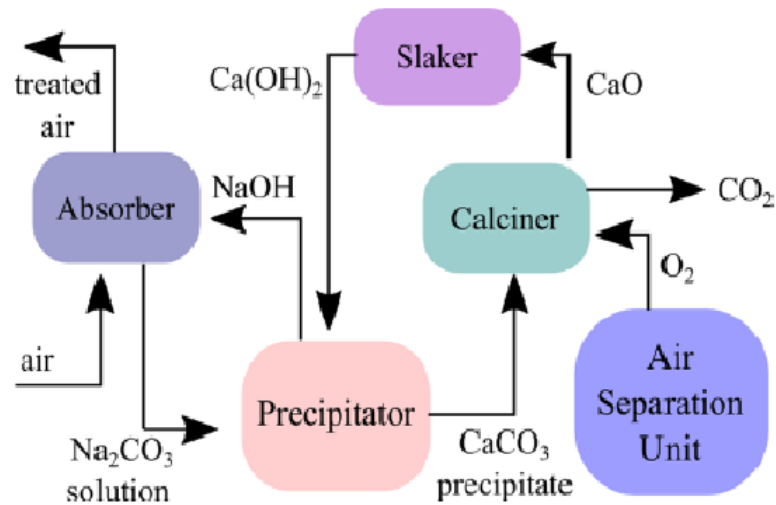


FIGURE 2.1: Schematic representation of the process using NaOH [2]

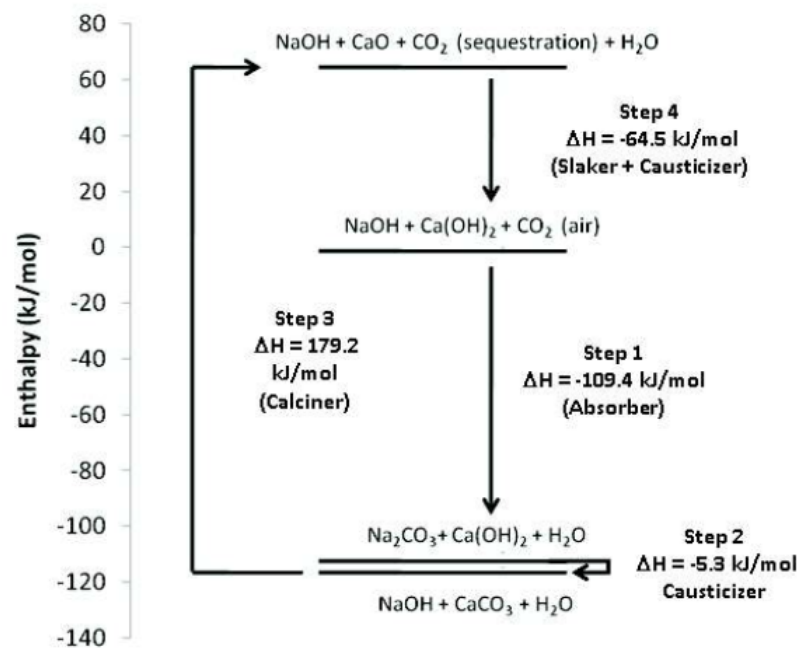
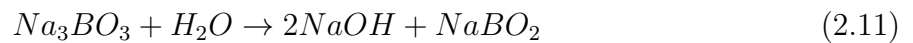
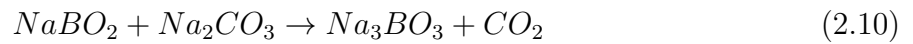
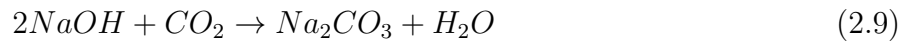


FIGURE 2.2: Enthalpy scale of the reactions [3]

### 2.2.2.2 Autocausticization

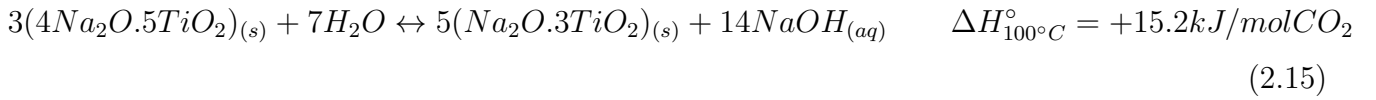
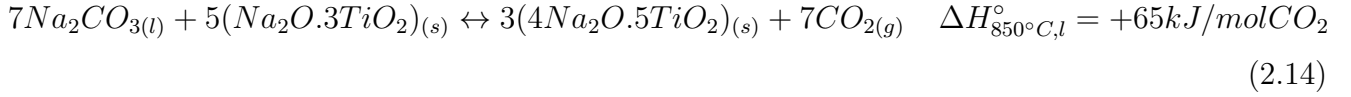
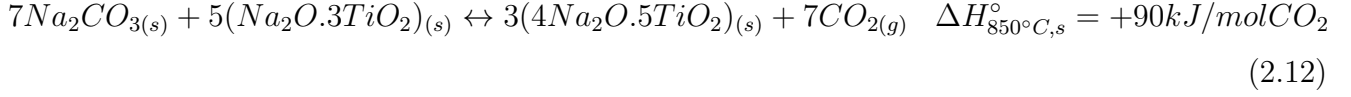
Always in the purpose to improve the method, another alternatives were developed. One of these methods is the autocausticization method [2]. The mechanism of an autocausticization method is written below.



The principle is to conserve a water soluble product during regeneration by using sodium metaborate; this way, there is no risk of precipitation of non-desired calcium hydroxide for example, and the NaOH concentration is no more limited at 1 mol/L. The main drawback of this method is that the high energy consumption and the high temperature requirement ( $\geq 900$  °C) remain, like for the two previous methods mentioned.

### 2.2.2.3 Direct Causticization

In this method, the decarbonizing agent is separated from the main cycle of the operations. This advanced causticization method uses titanium dioxide as reactant. And so, the main decarbonization reactions in direct causticization are those between  $Na_2CO_3$  and  $Na_2O \cdot 3TiO_2$  [8] [2].



The major difference of this process with the other methods is the need of pure dry sodium carbonate. Therefore, to apply this method it is needed to be able to extract the carbonate from the sodium hydroxide-sodium carbonate mix resulting from the very first step of the process (reaction 2.5). This add several steps of purification and extraction to the process. The extraction is performed using multi-steps crystallisation techniques.

Although temperatures as high as 800 °C are needed for this process, the heat requirement are comparatively slower than the previously presented methods : only 90 kJ/mol (reaction 2.12) instead of 179.2 kJ/mol (reaction 2.7).

Mahmoudkhani and Keith [8] studied this process and made an energy and exergy analysis of the whole process, taking the extraction step into account as well. This study reveals that this method has a heat requirement similar to the aqueous amine-based liquid postcombustion CO<sub>2</sub> capture process : about 130 kJ/mol CO<sub>2</sub>.

### 2.2.3 Supported alkali metal-based adsorbents



In this reaction, M is an alkali. In particular, sodium or potassium are the most common. The principle of this method is to capture CO<sub>2</sub> with the solid alkali sorbent thanks to the reaction 2.16. The regeneration is performed by using the same reaction in the opposite

way by increasing the temperature; indeed, above a certain temperature, the carbonate is more stable than the bicarbonate resulting in the release of both water and  $\text{CO}_2$  and the regeneration of the initial carbonate. The direct reaction is exothermic, and the regeneration is endothermic.

The preparation of such type of sorbent is usually made by impregnation of alkali precursor on a catalytic support. This support can be activated carbon,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{MgO}$  and zeolites. The big advantage of these supports is that they increase both the surface area and the porosity of the resulting material. And so, these two last properties are some major parameters in the efficiency of these materials and their enhancement will lead to an overall better sorbent. [1] [2] [7]

#### 2.2.4 Organic/inorganic hybrid sorbents

At the moment, the most widespread method to capture  $\text{CO}_2$  is by using aqueous amine solutions. But this method has its drawback such as a high energy requirement for the regeneration due to the bulk of water in the system. So, another approach is to use solid adsorbents containing amine groups to have the advantages of the amine group, like its high potential to capture  $\text{CO}_2$ , without the problem of the bulk of water that increases a lot the price of the regeneration. Over the past years, extensive researches have been made to find better adsorbents and amine-based adsorbents have been by far the most studied.

Amine groups are efficient for  $\text{CO}_2$  capture thanks to their chemical reaction with it. Due to this fact, amine and  $\text{CO}_2$  are linked with strong bonds, allowing significant uptake even at low  $\text{CO}_2$  partial pressure. Furthermore, the selectivity is better for these sorbents than for those which use physisorption. These are the main reasons why amine-based sorbents are so suitable for DAC and that most of the researches consider these sorbents.

Because of the presence of amine in the amine-based sorbents, the behaviour of these sorbents is different than other common sorbents such as microporous or macroporous materials. At first, these two last types of sorbents rely entirely on physisorption, while amine-based sorbents rely on a strong chemisorption. This provides a better specificity at low  $\text{CO}_2$  concentration for amine-based sorbents compared to the two others, as previously mentioned. For this same reason, the  $\text{CO}_2$  uptake is larger as well for amine-based sorbents comparatively to the two others. And because of these differences in the mechanisms, the main parameters

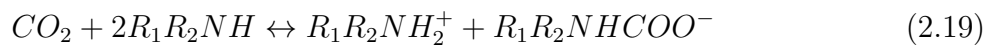
of the sorbents are not the same. For microporous materials, the main parameter is the pore diameter. For macroporous material, since the pore diameter is larger and the confinement effect smaller, both surface area and gas-surface interaction are the main parameters for a good capture. And finally, for amine-based material, the determinant parameter is the amine loading. [9] [2] [10]

One of the more important topic that is studied for sorbents is their stability. The latter strongly influences the price of the capture through the lifetime of the sorbents. The more adsorption/desorption cycles the sorbent can achieve without losing too much properties, the higher is the lifetime and the less is the cost per unit of CO<sub>2</sub> captured. The following formula can be used to assess the price of a sorbent per unit of CO<sub>2</sub> [11] :

$$\text{Cost of sorbent (€/ton CO}_2\text{)} = \frac{\text{€/ton sorbent}}{\text{Nb cycles} \times \Delta q\left(\frac{\text{ton CO}_2}{\text{ton sorbent}}\right)} \quad (2.17)$$

Currently, the price of CO<sub>2</sub> capture is too high. The price of the electricity would increase of about 83 and 43% for a new pulverized coal plant and a new natural gas combined cycle power plant respectively. Therefore, major improvements are needed to lower the price of CO<sub>2</sub> capture and find new interesting ways to use CO<sub>2</sub> as a resource. [12]

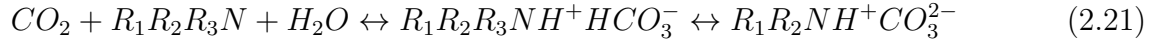
In anhydrous conditions, for primary and secondary amine, the mechanism of CO<sub>2</sub> capture by amine sorbent is the following :



Where R<sub>1</sub> and R<sub>2</sub> are carbon chains.

The maximum achievable amine efficiency, which is the measure of the efficiency of an amine sorbent, is 0.5 mol CO<sub>2</sub> / mol amine. This value is only in regard of chemisorption, and thus the total value can be greater if the physisorption on the support and the amine is high. These two reactions are not possible for tertiary amine, which do not react with CO<sub>2</sub> in anhydrous conditions.

When water is present, the mechanism is the following for secondary and tertiary amine :



Now, the amine efficiency is 1 mol CO<sub>2</sub> / mol N. So, the sorbent can be twice as efficient as in anhydre conditions. Reaction 2.21 is the only referred reaction that leads to a strong bond between tertiary amine and CO<sub>2</sub>. Indeed, in anhydre conditions CO<sub>2</sub> and tertiary amine do not react together. Although the reaction is possible if there is a protic molecule other than water, like alcohol, which is not frequent at all for DAC.

Amine sorbents are classified in three classes depending on their synthesis :

- Class 1 : Sorbent prepared by amine impregnation of a porous support;
- Class 2 : Amine tethered on the wall of the porous support through covalent bound;
- Class 3 : Polymerisation in-situ of monomer amine during the synthesis of the porous support;

It is possible to combine the two first class to form what can be defined as a fourth class : amine-tethered sorbent with amine impregnated added to enhance the properties. Hybrid materials are promising for further investigation in DAC.

The purpose of these classes is really to classify the amine. The class of a sorbent provides information about the methods of synthesis and about the interaction between the amine and the support. This classification gives an idea about the stability of the sorbent as well. Indeed, class 1 sorbent will be in general less stable than the others classes, because of weak physical interactions between amine and support for class 1 compared to covalent bonds for the others classes. The main advantage of class 1 sorbent is the fact that, because there is no chemicals bonds, it is possible to use a wide variety of both support and amine. Because each class has advantages and weakness, they are all studied in the literature. [2] [10]

The type of amine is really important too. There are three types of amine : primary amine, secondary amine and tertiary amine. For DAC, tertiary amine are not really desired. As it

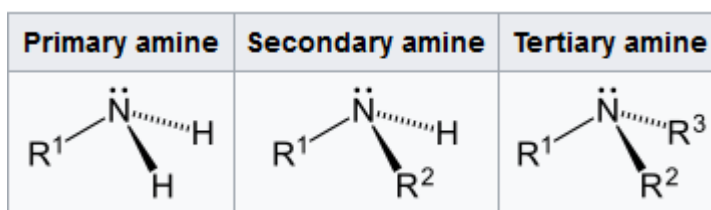


FIGURE 2.3: Schematic representation of primary, secondary and tertiary amine [4]

has been mentioned before, tertiary amine does not react with  $\text{CO}_2$  in anhydrous condition, and thus reducing the possibility for the capture. The three classes of amine are represented on Figure 2.3. The heat of  $\text{CO}_2$  adsorption is higher for primary amine, and thus leading to stronger bonds. Therefore, the regeneration is easier for secondary amine than for primary. And so, for some authors, even if primary amine are the best in term of reactivity (and thus the best for  $\text{CO}_2$  uptake) [2] [10] and the most important amine type for DAC in general, secondary amine are a good compromise between reactivity and ease of regeneration [2]. In term of stability, a study from 2011 showed that both primary and tertiary amine were more stable than the secondary amine when subjected to a long term effect of air at high temperature [11]. Jones and co-worker [13] investigated about the effect of amine type on the hydrophobic properties of class 2/3 amine sorbents. Therefore, primary amine were enhancing the hydrophobic properties of the material while secondary amine were decreasing it. Concerning the stability, the formation of urea can be problematic. Reference [14] and [11] made a summary of different references that study specifically urea formation. These researches find that there were two different ways to form urea under a pure  $\text{CO}_2$  gas flow at a wide range of temperature (50-160 °C). One of these mechanisms involve the formation of an isocyanate intermediate, which is only possible when primary amine are present. The second mechanism forms cyclic urea and is possible with both primary and secondary amine. But the first mechanism is the lowest energy route, and thus the primary amine is more able to form urea than the secondary amine. [14] and [11] found in the literature that the presence of water was sufficient to completely inhibit urea formation as well as regenerate the already formed urea for a poly(ethylenimine) (PEI) impregnated silica sorbent. But in their own experimental work using Lewatit (styrene-divinylbenzene with aminomethylene groups), the urea formation was not removed nor completely inhibited by the presence of moisture, meaning that water will not be sufficient to inhibit and remove urea for all amine-based sorbents.



#### 2.2.4.1 Class 1 - Amine impregnated sorbent

Now, in this section, the class 1 of amine-based sorbent will be discussed more in details.

To begin this section, the method of synthesis will be discussed. This method is a simple physical deposition of amine species onto porous support. Since this is really simple and does not imply any reaction, the synthesis is possible for a wide variety of both porous support and amine-containing species.

For practical uses, not all the amines are possible. Since the material must overcome regeneration and multiple adsorption/desorption cycle, it is better to use not too volatile amine species. Indeed, if the amine was too volatile, there will be more loss within the capture cycle and thus leading to an increase of the price of the whole process.

The most used amine-containing species for these sorbents is the branched poly(ethylenimine) (PEI) (primary amine), because of its high resistance to temperature swing adsorption and vacuum swing adsorption, temperature swing adsorption being the most used process for DAC with amine [15]. The other advantage of PEI was its high amine density, resulting in a better CO<sub>2</sub> uptake. Other amine species are used, for example tetraethylenepentamine (TEPA) and pentaethylenehexamine (PEHA), despite showing not negligible amine loss or leaching. [2] [16]

The possible supports for the amine are numerous. The support used in the literature are among others : commercial silica, fumed silica, mesocellular foam, Zr-SBA-15,  $\gamma$ -alumina and SBA-15. The difference in structure, pore diameter, pore volume, and so on of all these support play an active role in the amine efficiency.

In the literature, lots of ways to improve amine efficiency, CO<sub>2</sub> uptake and/or stability are considered, as for example, by adding poly(ethylen glycol) (PEG) to the amine in order to form a sorbent with enhanced properties [17] [18]. The substance added are not randomly chosen. They are for example well known to have a positive effect on postcombustion CO<sub>2</sub> capture or these components are simply added to enhance the basic properties of the sorbent (sorbent loaded with Zr, Al, Ti for example) to obtain, in principle at least, a better capture. To illustrate, PEG is added to amine based sorbent for postcombustion CO<sub>2</sub> capture. [17] studied this addition and tried to understand the mechanism to develop more effective sorbents. In one of their last IR studies, they find that adding PEG to amine/SiO<sub>2</sub> slowed

down the formation of a thermally degraded product (carboxylates species) during both adsorption (presence of air) and desorption (under argon).

Table 2.1 is a summary of several sorbent from the literature. This table was made by [2] and is just copied in this work to have a better overview of the sorbent encountered in the literature.

Temperature is one of the key parameters for the CO<sub>2</sub> capture. Generally, the amine-based sorbents show their better efficiency in adsorption at a higher temperature than expected. Indeed, the thermodynamic of the sorption favour adsorption at low temperature. But many studies showed that there was an actual maximum at a more elevated temperature (for example this temperature can be about 50 °C). This maximum results of an equilibrium between thermodynamic effects and kinetic effects (transfer of the CO<sub>2</sub> within the sorbent, speed of the reaction). [2]

Moisture is one of the important parameters to take into account in DAC like the temperature. And so, the hydrophobic/hydrophilic properties of the sorbents are important to obtain a good capture when there is moisture. Theoretically, adsorption is easier for hydrophilic materials since adsorbed water can play the role of a free base for deprotonation of the zwitterionic intermediate during CO<sub>2</sub> capture, increasing amine efficiency. However, the material can not be too hydrophobic. If it is the case, water will fill the pores and limit the access for the CO<sub>2</sub>, decreasing the efficiency. And each mole of water will have a cost when the sorbent will be regenerated by thermal swing adsorption [10]. For these reasons, the impact of moisture is studied for a wide variety of sorbents. However, the results obtained are different for one sorbent to another, and no general trends can be found. For some sorbents under certain conditions, water can be beneficial thanks to the formation of carbonate and bicarbonate. But for other sorbents or other conditions, the water can over saturate the pores, limiting the diffusion of CO<sub>2</sub> in the pores and reducing the amine availability. More studies are needed to obtain a better understanding of the behaviour of the amine sorbents under wet conditions. But this will not be an easy task since even for CO<sub>2</sub> capture from flue gas there is some wide difference for the impact of water for different materials.

Support	Amine	T (°C)	CO <sub>2</sub> (ppm)	Amine loading (mmol of N/g of sorbent)	Adsorption capacity (mmol of CO <sub>2</sub> /g of sorbent)	Amine efficiency (mmol of CO <sub>2</sub> /mmol of N)	Method
Commercial silica	PEI	25	400	10,5	2,36	0,22	TGA
	PEI+AP	25	400	10,7	2,26	0,21	TGA
	PEI+TP	25	400	10,5	2,19	0,21	TGA
MCF	PAA	25	400	7,24	0,86	0,12	TGA
	PEI	25	400	10,7	1,74	0,16	TGA
	PEI-InH	25	400	11,4	1,05	0,09	TGA
Zr-SBA-15	PEI	25	400	8,3	0,85	0,1	TGA
γ-alumina	PEI	25	400	11,2	1,74	0,16	TGA
SBA-15	PEI	25	400	9,2	1,05	0,11	TGA
Commercial silica	TEPA	35	400	10,1	2,5	0,25	TGA
fumed silica	PEI-H	25	420	33%	1,18		IR
		25	420	33%	1,77 <sup>a</sup>		IR
		25	420	50,00%	1,71		IR
		25	420	50,00%	1,41 <sup>a</sup>		IR
SBA-15	PEI	75	400		0,51		TPD
γ-alumina	PEI	30	400	8,5	1,96 <sup>b</sup>	0,25	IR
fumed silica	PEI-H+PEG	50	360	9,8	0,68	0,07 <sup>d</sup>	TGA
SBA-15	PEI+PEG200	30	400	5,75	0,79	0,14	TGA
fumed silica	PEI-In	25	400	50,00%	2,34		IR
	PEI	25	400	50,00%	2,44		IR
	PEI-M	25	400	50,00%	1,69		IR
	PEI-H	25	400	50,00%	1,67		IR
MCF, silica mesocellular foam; PEI, branched PEI (M <sub>w</sub> = 800 Da); PEI-M, branched PEI (M <sub>w</sub> = 1 800 Da); PEI-H, branched PEI (M <sub>w</sub> = 25 000 Da); PEI-In, linear PEI (M <sub>n</sub> = 423 Da); PEI-InH, linear PEI (M <sub>w</sub> = 2 500 Da); PAA, poly(allylamine); PEG, poly(ethylene glycol) (M <sub>w</sub> = 400 Da); TGA, thermogravimetric analysis; IR, infrared analyzer; TPD, temperature-programmed desorption							
<sup>a</sup> 67% relative humidity (RH) at 25°C <sup>b</sup> 50% relative humidity at 30°C <sup>c</sup> Amine efficiency calculated with equation given in the paper. Amine loading calculated from CO <sub>2</sub> uptake efficiency							

TABLE 2.1: Class 1 - amine-based sorbent [2]

#### 2.2.4.2 Class 2 & 3 - Amine tethered to porous support

For both last classes of amine-based sorbent, the synthesis is more complicated than previously. Now, the synthesis implies chemical bounds, more accurately the synthesis needs the creation of covalent bound between the amine and the support.

The support can be quite different. There are different classes of support. At first, the oxyde support, such as alumina. The most used amine for these sorbent with this type of support are the aminopropyl organosilanes (APS) and the diethylenetriamine organosilanes (DT). But other amine are encountered in the literature, such as methylaminopropyl organosilanes (MEP), ethylenediamine organosilanes (ED). The support are numerous too, and one can find in the literature PE-MCM-41, mesocellular foam, silica gel and SBA-15 for example. The purpose of all these supports is to maximize the amine efficiency; the surface area, pore volume and others structural properties being optimised to enhance the amine efficiency. [2] [19]

Table 2.2 is a summary of several sorbent from the literature. This table was made by [2] and is just copied in this work to have a better overview of the sorbent encountered in the literature.

The second possibility is to use organic supports. A lot of organic supports can be used to create sorbents. These support can be for example polymers, nanobrillated cellulose (NFC) or resins. Even carbon black can be another possibility. There are several ways to produce these materials. One of the simplest ways consists in functionalising high surface area polymers with amine. The functionalisation can be made by grafting for example. The purpose is the same than previously : enhancing the amine efficiency thanks to the structural properties of the support.

To illustrate these two classes of sorbent, an example can be discussed. For example, the sorbent that will be studied in this thesis, in the experimental part, is a member of these classes of sorbent. Lewatit®VP OC 1065 (Lanxess), is a commercial sorbent based on an ion exchange resin functionalised with amine groups. More accurately, it is made of styrene-divinylbenzene with aminomethylene groups (primary amine). This ion exchange resin (IER) based sorbent shows a high tolerance to water, high CO<sub>2</sub> capacity and fast kinetics. There are not a lot of studies concerning the stability of this IER, and this thesis is one of these. Qian Yu and co worker [11] studied the stability of this IER under several

Support	Amine	T (°C)	CO <sub>2</sub> (ppm)	Amine loading (mmol of N/g of sorbent)	Adsorption capacity (mmol of CO <sub>2</sub> /g of sorbent)	Amine efficiency (mmol of CO <sub>2</sub> /mmol of N)	Method
PE-MCM-41	DT	25	400	7,9	0,98	0,12 <sup>a</sup>	TGA
PE-MCM-41	DT	25	300	7,9	0,9	0,11 <sup>a</sup>	PB
PE-MCM-41	DT	25	300	7,9	1,19 <sup>b</sup>	0,15 <sup>a</sup>	PB
PE-MCM-41	DT	25	300	7,9	1,4 <sup>c</sup>	0,18 <sup>a</sup>	PB
PE-MCM-41	DT	30	400	7,9	0,61	0,08	TGA
PE-MCM-41	DT	30	400	7,9	0,54 <sup>d</sup>	0,07	TGA
PE-MCM-41	DT	(+5)-(-5)	400 <sup>e</sup>	7,9	1,16	0,15	TGA
MCF	APS	25	400	2,7	0,54	0,2	TGA
MCF	MAP	25	400	2,41	0,17	0,07	TGA
SG	ED	25	400-440	2,48	0,4	0,16	TGA
SG	ED	25	400-440	2,48	0,44 <sup>f</sup>	0,18	TGA
SBA-15	AZ	25	400	9,9	1,72 <sup>g</sup>	0,17	MS
SBA-15	LY	25	400	5,18	0,6	0,12	TGA

MCF, mesocellular foam; SG, silica gel; APS, aminopropyl organosilanes; MAP, methylaminopropyl organosilanes; ED, ethylenediamine organosilanes; DT, diethylenetriamine organosilanes; AZ, aziridine in situ polymerization; LY, Z-(L-lysine) in situ polymerization; TGA, thermogravimetric analysis; PB, packed bed.

<sup>a</sup>Amine efficiency calculated from amine loading and CO<sub>2</sub> uptake. <sup>b</sup>Relative humidity 26%. <sup>c</sup>Relative humidity 64%. <sup>d</sup>Relative Humidity 73%. <sup>e</sup>Outdoor air used. <sup>f</sup>Relative humidity 40%. <sup>g</sup>Fully humidified conditions.

TABLE 2.2: Class 2&amp;3 - amine-based sorbent on oxyde support [2]

conditions. Their degradation experiments show that the regeneration must be performed in absence of oxygen above 70 °C, and under 150 °C to avoid thermal degradation. Urea formation was detected when the CO<sub>2</sub> partial pressure was about 1 bar and the temperature higher than 200 °C. Even water was not able to completely avoid this urea formation. The sorbent was stable under wet conditions and moisture does not effect negatively its capture capacity. Finally, their conclusion was that steam stripping was promising for this sorbent as a regeneration method.

Further example can be found in Table 2.3. This table is, as the two previous ones, from [2].

The effect of water for this type of sorbent was tested too. From [2], the following conclusion can be written: in a lot of cases, the moisture increases the amine efficiency of the sorbents. And so, this increase is obviously a function of the nature of the amine or the support, but the amine loading is one of the main variables too. But as for class 1 materials, more researches are needed to find a clear trend and obtain a better understanding about the link between amine efficiency and moisture content in the air. In the last example presented (Lewatit), water was not detrimental to the adsorption or the stability.

Type	Support	Amine	T (°C)	CO <sub>2</sub> (ppm)	Amine loading (mmol of N/g of sorbent)	Adsorption capacity (mmol of CO <sub>2</sub> /g of sorbent)	Amine efficiency (mmol of CO <sub>2</sub> /mmol of N)	Method
polymers	PPN-6-CH <sub>2</sub> DETA	DETA	22	400		8,5	1,04 <sup>a</sup>	0,12 VOL
	CB-N-g-PCMS-OH-		15	400 <sup>b,c</sup>			0,14	IR
	CB-g-PCMS-OH-		15	400 <sup>b,c</sup>			0,14	IR
	PS-CC		15	400 <sup>b,c</sup>			0,57	IR
	Colloidal crystal		15	400 <sup>b,c</sup>			0,36	IR
	HIPE		15	400 <sup>b,c</sup>			0,5	IR
	Pick-20%-silica-2%		15	400 <sup>b,c</sup>			0,72	IR
	HP20/PEI-50	PEI	25	400		11,8	2,26	0,19 TGA
	Proprietary		25	440			0,86	IR
	AP-NFC	APS	25	506 <sup>d</sup>		4,9	1,39	0,28 IR
NFC	AP-NFC	APS	23	400		4,2	1,11	0,26 IR
NFC	AP-NFC	APS	23	400 <sup>e</sup>		4,2	2,13	0,51 VOL
	RFAS4	APS	30	400 <sup>f</sup>		8,07	1,69	0,21 IR
DETA, diethylenetriamine; PEI, poly(ethylenimine) (M <sub>n</sub> = 600 Da); APS, aminopropyl organosilanes; IR, infrared gas analyzer; VOL, volumetric method; TGA, thermogravimetric method								
<sup>a</sup> Adsorption capacities interpolated from IAST calculation from measured single-component CO <sub>2</sub> , O <sub>2</sub> , and N <sub>2</sub> isotherms. <sup>b</sup> Compressed laboratory air was used as gas feed. <sup>c</sup> Relative humidity 95%. <sup>d</sup> Relative humidity 40%. <sup>e</sup> Relative humidity 91%. <sup>f</sup> Relative humidity 4%.								

TABLE 2.3: Class 2&amp;3 - amine-based sorbent on organic support [2]

## Chapter 3

# Experimental

### 3.1 Materials and methods

#### 3.1.1 IER based sorbent

The sorbent material used in this thesis is Lewatit®VP OC 1065 (Lanxess), a commercial sorbent based on an ion exchange resin functionalised with amine groups. More accurately, it is made of styrene-divinylbenzene with aminomethylene groups (primary amine). The sorbent is made of small spherical shaped particles with a diameter between 0.3 and 1 mm. The surface area, the pore diameter and the pore volume of the beads are 50 m<sup>2</sup>/g, 25 nm and 0.27 cm<sup>3</sup>/g respectively according to the manufacturer. The molar concentration of amine is 7.5 mol/kg [20].

This material is well known to adsorb both CO<sub>2</sub> and water, water being more adsorbed than CO<sub>2</sub> (mass of the sorbent up to max. 65/70%wt water).

Fresh sorbent was given by the University of Twente, as well as degraded samples of this same sorbent.

#### 3.1.2 Experimental setup for degradation experiments

To perform the degradation of the samples in different conditions, the experimental setup showed on Figure 3.1 and 3.2 was used. It consists basically of a tubular oven made of inox (INOX 316 1/2") of about 72 mm of internal diameter, a mixing chamber and several gas





FIGURE 3.1: Experimental setup - view from entrance

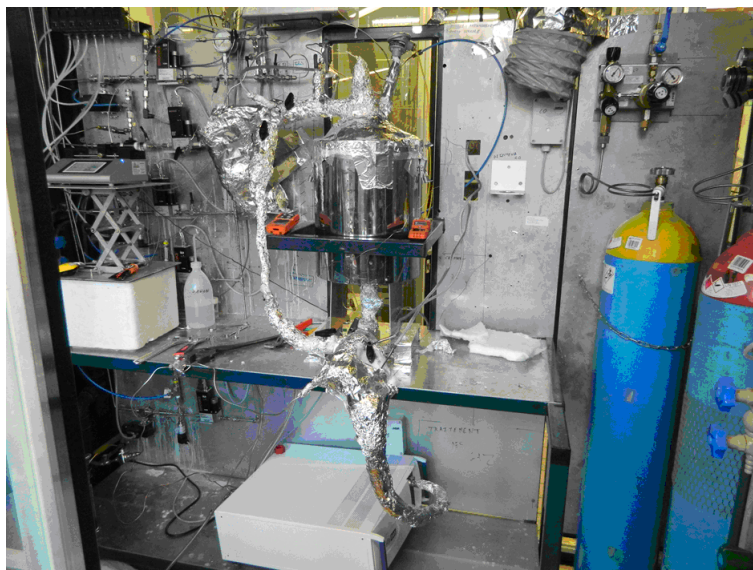


FIGURE 3.2: Experimental setup - view from inside

lines. A simplified scheme is presented in Figure 3.3; before the experiments, the air line was redirected into the mixing chamber, which is not correctly represented in the scheme. This experimental setup was initially used for catalytic test of tars reforming and was able to use a large variety of gases and water.

Figure 3.4 presents the temperature profile in the oven between 80 and 140 °C. As it can be seen, the working zone (in which the temperature is about the one set and almost constant) is about 15-25cm above the bottom of the oven. The placement of the sorbent in the oven was derived of this information.

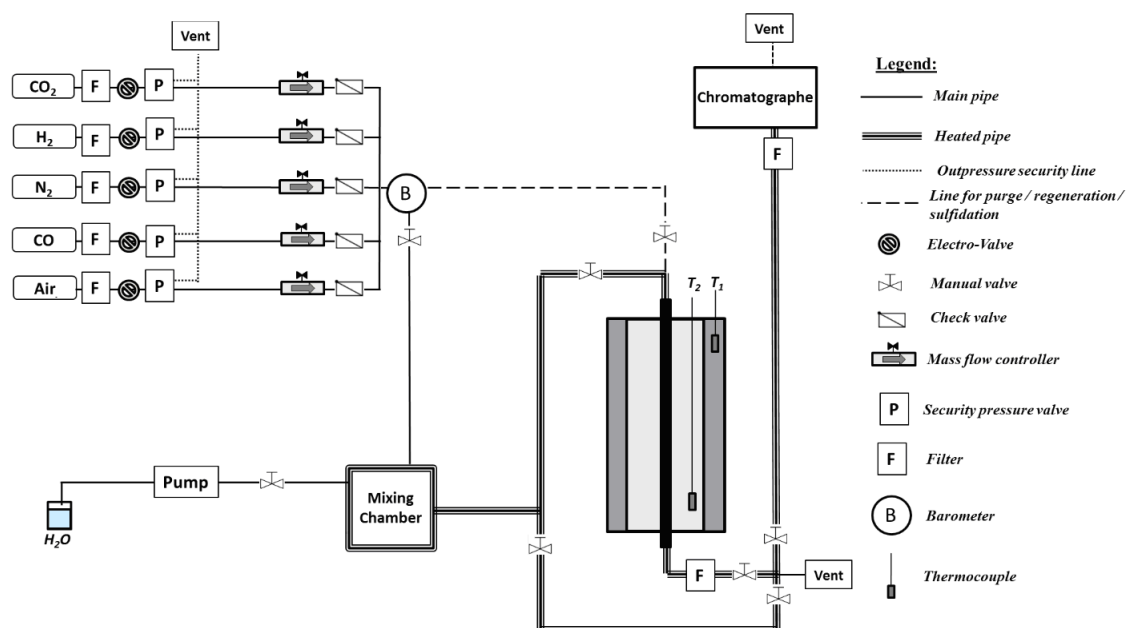


FIGURE 3.3: Experimental setup - schematic view

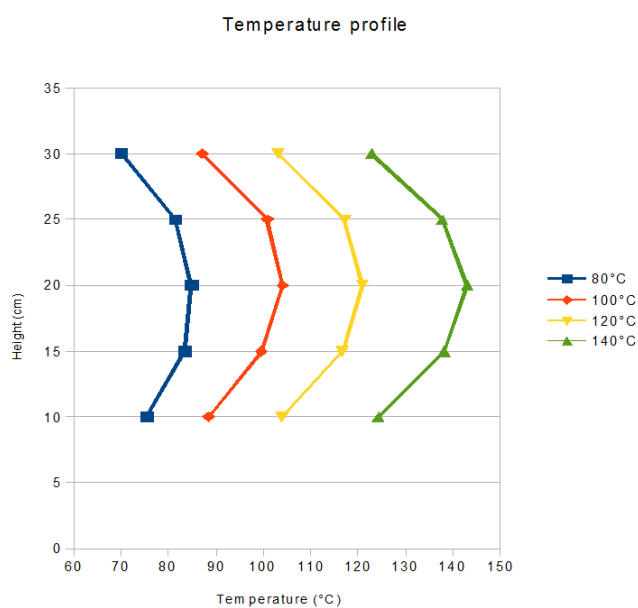


FIGURE 3.4: Temperature profile in the oven

The different lines can be at an accurate gas flowrate between 10 and about 160 mL/min. The CO<sub>2</sub> line can even be precise from 5 mL/min.

Water can go in the experimental setup thanks to a peristaltic pump. This last is an IPC-N (ISM935) from Ismatec that can impose an accurate flowrate between 0.0004 - 11 mL/min.

The experimental setup is connected to the chromatograph.

### 3.1.3 General implementation of degradation experiments

The reactor was a quartz tube of about 70 mm diameter. This tube was at first filled with about 1 cm of quartz wool at a height of 20 cm. The whole was then weighted and tared. The adsorbent was then introduced above the quartz wool, and a bed of about 4 cm height was inserted in. The mass of the bed was about 1g +/- 10%. After weighting exactly the bed mass, another centimetre of quartz wool was introduced in the tube. The whole tube was then weighted too. The tube filled is showed in Figure 3.5 and 3.6. The high of the bed in the tube is about 21 to 25 cm. This means that, because of the setting of the experimental setup, the bed will be at a height of 16 to 20 cm above the bottom in the oven. Therefore, the bed will be entirely in the 15-25 cm working zone.

The preparation being finished, the tube was then introduced in the oven. The latter was already at the working temperature and flushed with nitrogen. To insert the tube, the experimental setup was opened to ambient air, and so air (and oxygen) entered the oven. Before closing the oven, a Teflon band was tied up to the quartz tube to ensure the sealing. The duration of this operation was between 5 and 10 minutes. Therefore, the impact of air at working temperature in the oven during this operation can be neglected regarding the time of the experiment compared to these 5-10 minutes.

The next step was to perform a leak test of 10 minutes with nitrogen, after flushing the experimental setup with nitrogen to expel the air.

Finally, the gas flows were adjusted to the specificity of the test and the chromatograph was started.

If water was needed in the gas mixture, the water was send in the experimental setup at the moment of the beginning of the experiment, not before. So, a small time was needed for the experimental setup to reach the steady state concerning the inflow of water.



FIGURE 3.5: Quartz reactor filled with sorbent



FIGURE 3.6: Zoom on the sorbent in the reactor

For the test in which  $\text{CO}_2$  was sent to the reactor, a pretreatment was performed. The sample was put in the reactor at  $50\text{ }^\circ\text{C}$ . Then, after doing the leak test, a gas flow of  $100\text{ mL/min}$  was sent. The composition of the gas was  $20\%\text{ CO}_2$  and  $80\%\text{ N}_2$ . The pretreatment duration was about  $3\text{ h } 30$ . So, the sample was saturated in  $\text{CO}_2$  before the degradation experiment, and some water was already desorbed. The reason of this pretreatment will be explained later in this thesis.

### 3.1.4 Gas Chromatograph

For this thesis, a chromatograph CompactGC 4.0 was used.

The scheme of the chromatograph is represented in Figure 3.8. It is basically made of a TCD and a FID. But the system of valve and the different columns present in the chromatograph give it the possibility to allow water in the injection.

The characteristics of this chromatograph are listed in table 3.1.

The FID is able to measure organic compounds up to  $\text{C}_{40}$  and the TCD is able to measure various gas phases ( $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2$ , ... and even water). The limit of detection is  $100\text{ ppm}$ .



GC conditions			
Injector   Column channel 1 :			
Valve oven	100	°C	
Channel 1 carrier (He)	50	kPa	
Channel 1 split flow	5	mL/min	
Channel 1 column oven	60	°C	
FID :			
FID temperature	150	°C	
FID H2 flow	35	mL/min	
FID air flow	350	mL/min	
FID flame off level	0,5	pA	
FID detector	On		
FID flame	On		
Injector   Column channel 2/3 :			
Valve oven	150	°C	
Channel 2 carrier (He)	220	kPa	
Channel 3 carrier (He)	230	kPa	
Channel 3 backflush	5	mL/min	
Column oven 2	55	°C	
Column oven 3	110	°C	
TCD :			
TCD block temperature	110	°C	
TCD filament temperature	210	°C	
TCD reference flow	1	mL/min	
TCD detector	On		
Columns			
Column type	Length (m)	ID (mm)	OD ( " )
HS-N 60/80	0,5	1	1/16
HS-N 60/80	2	1	1/16
MS5A 60/80	2	1	1/16
Column type	Length (m)	ID (mm)	df (µm)
Rtx-1	15	0,32	0,25

TABLE 3.1: GC conditions and columns

For the TCD, the retention time (RT) of the important gases are :

- $N_2$  : 545 s
- $O_2$  : 530 s
- $H_2O$  : 320 s
- $CO_2$  : 95 s

It is important to note that, for each measurement with TCD, there are two artefacts that have no real meaning. These appear because of the switch of valves during the analysis. Figure 3.7 put these artefacts in evidence.

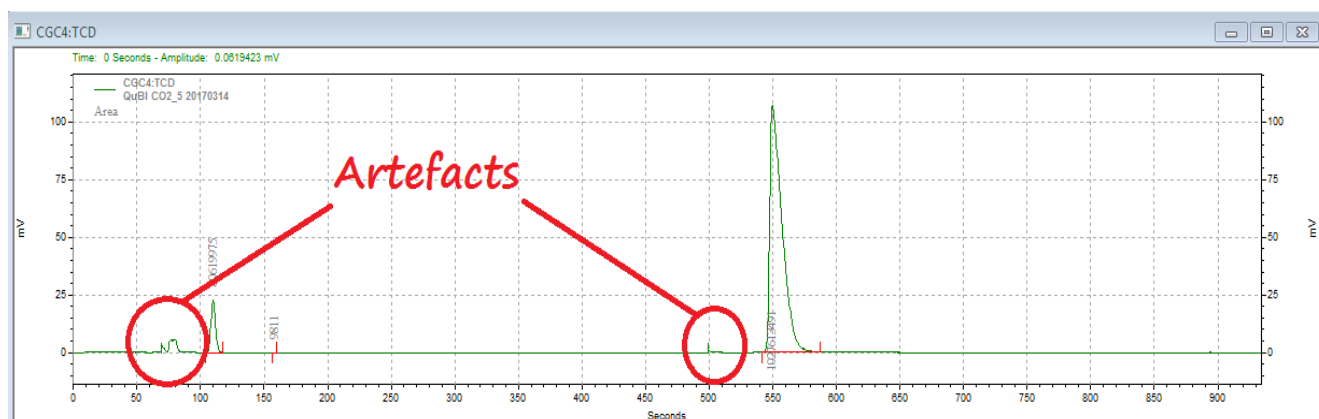


FIGURE 3.7: Artefacts of the TCD

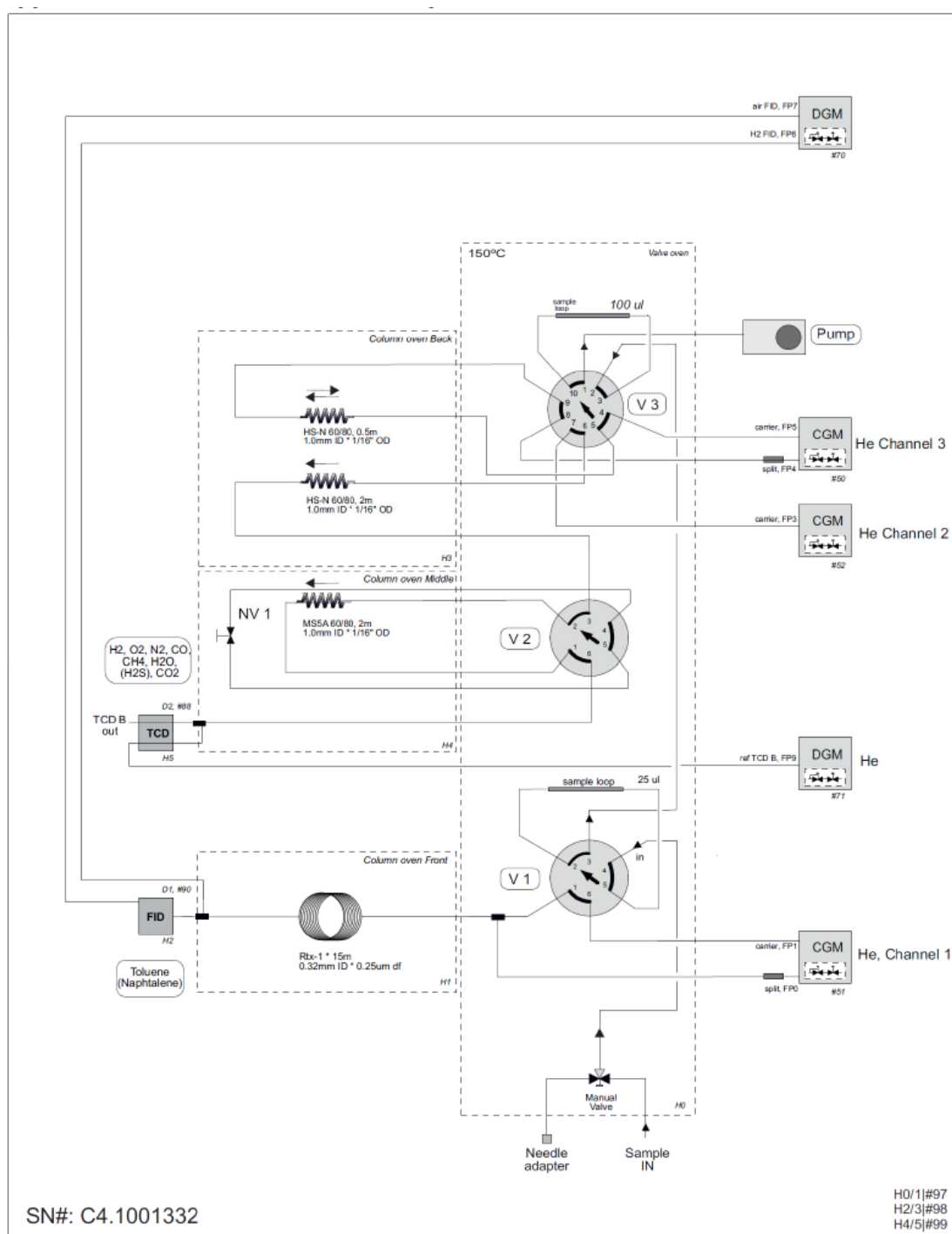


FIGURE 3.8: Schematic representation of the chromatograph



### 3.1.5 Thermogravimetry and Mass Spectrometry

A thermogravimeter (Sensys Evo - Setaram Instrumentation) linked to a mass spectrometer (OmniStar Pfeiffer Vacuum) was used for some tests. It can be seen in Figure [3.9](#)

The thermogravimeter, can used two types of gases, helium or air, but it can't mix them. The machine can continuously increase the temperature at a certain speed or keep the temperature constant depending on what is asked.

For the tests, temperature ramps from 20 to 300 °C were applied with an increase of temperature of 2 °C/min and with a flowrate of 20 mL/min of helium or air depending on the test. A purge of about 1 h was performed before the test at ambient temperature with helium or air depending the gas used in the test afterwards.

The information available at the end of such analysis are the mass loss, the heat flux and the mass spectrum in function of time/temperature.

It has to be noted that currently, the University had been using this MS for the first time since a long time. And so, it is not sure that it is well calibrated. The area under the peaks and the amplitude of the peaks are accurate, but the value on the scale are not.

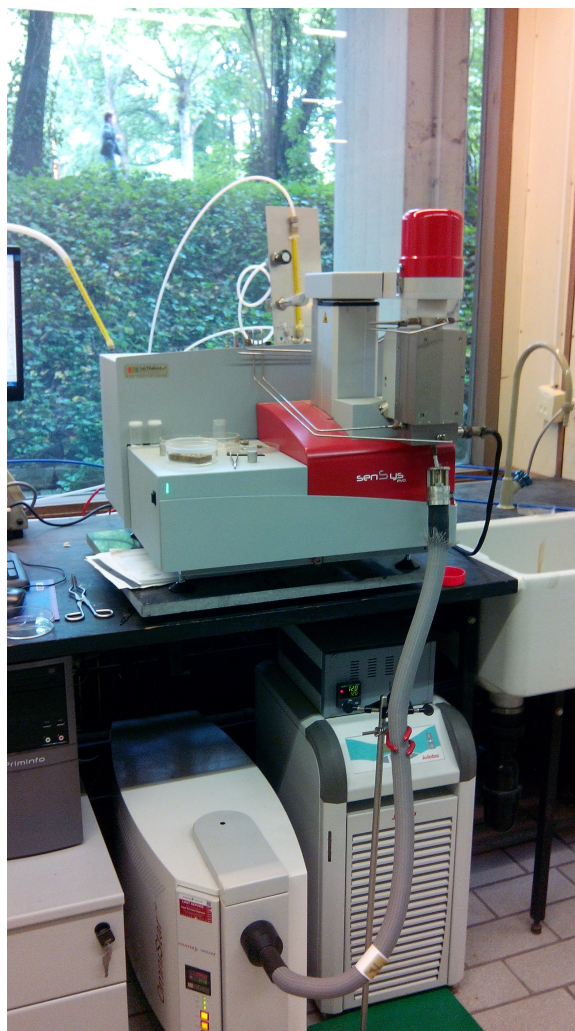


FIGURE 3.9: Photograph of the thermogravimeter (up) linked to the mass-spectrometer (down)

### 3.1.6 Nitrogen adsorption-desorption measurements

For the measurements of specific surface area of samples, nitrogen adsorption-desorption measurements were realized. The Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area and the porous volume of samples.

Because of technical problems, two different apparatus were used. The first one was a multi-analysis apparatus : ASAP 2420. The second one was a single-analysis apparatus : Sorptomatic 1990. The apparatus are showed on Figure 3.10 and 3.11. Figure 3.12 represents the outgassing unit used to outgas the samples before the BET measurements in Sorptomatic; the outgassing was performed by ASAP when the measurements were taken by ASAP. Experimental errors are in the range of  $2 \text{ m}^2/\text{g}$  for ASAP, and about  $5 \text{ m}^2/\text{g}$  for Sorptomatic. To obtain accurate results, it is recommended to put at least  $15 \text{ m}^2$  in ASAP and to use about  $0.3 \text{ g}$  for Sorptomatic.



FIGURE 3.10: ASAP 2420

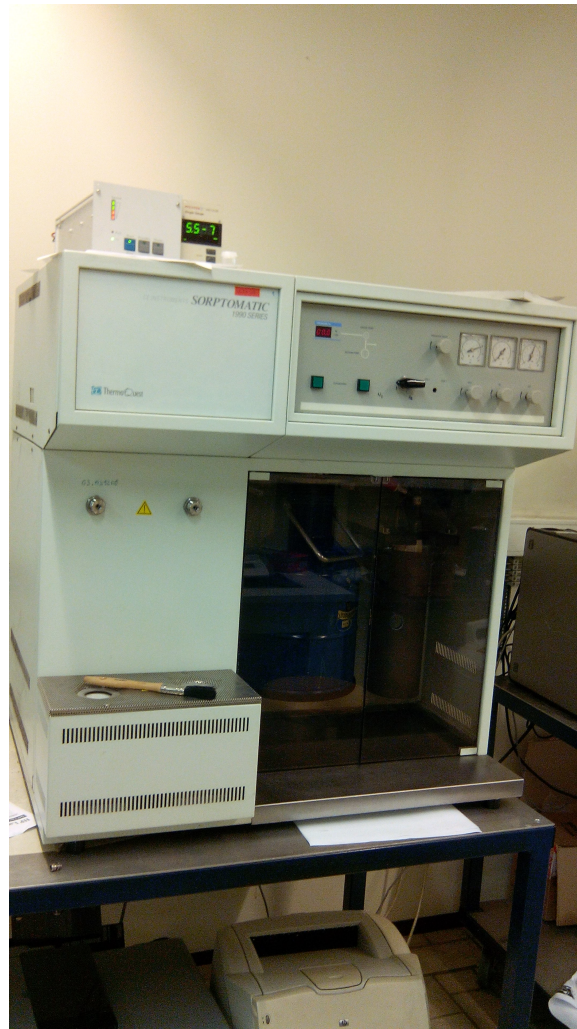


FIGURE 3.11: Sorptomatic 1990





FIGURE 3.12: External outgassing unit

### 3.1.7 Helium pycnometry

Helium pycnometry was performed in order to measure the density of the different samples with the apparatus Micromeritics AccuPyc 1330. The method consists in injecting helium into the sample and measuring the volume of helium that can be injected within the pore. The total volume of solid matter is then determined, and the density is calculated using the mass corresponding to this volume. It has to be noted that the total volume of solid matter contains the non-available pores. If the sample is saturated with water for example, helium can not fill the pores and then density is not correctly estimated. The estimated accuracy of this apparatus is about  $\pm 0.002 \text{ g/cm}^3$ .

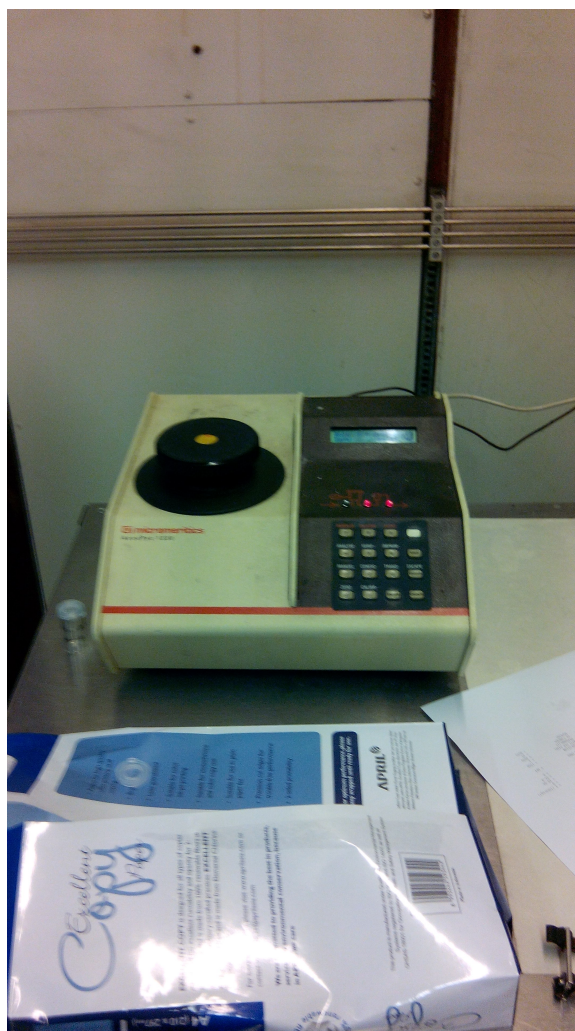


FIGURE 3.13: Pycnometer

## 3.2 Experimental design

The experimental design is presented in Table 3.2. The different conditions like temperature, duration, gas composition are listed in this table. The total flowrate for all the experiments was fixed at 100 mL/min. For the experiments with water, the pipes were heated up to 120 °C to ensure that no condensation occurs. For the other experiments, the pipes were just set to 100 °C.

Experimental design							
Name Exp.	%N2	%CO2	%H2O (gas)	%Air	%O2 (via air)	T° (°C)	Duration (h)
BaseCase	20	0	0	80	16,8	140	15
BaseCase-120T	20	0	0	80	16,8	120	15
BaseCase-15CO2	5	15	0	80	16,8	140	15
BaseCase-15CO2-Repet	5	15	0	80	16,8	140	15
BaseCase-2H2O	18	0	2	80	16,8	140	15
BaseCase-15CO2-2H2O	3	15	2	80	16,8	140	15
100N2-120T-7D	100	0	0	0	0	120	7
100N2-140T-7D	100	0	0	0	0	140	7
100N2-120T-15D	100	0	0	0	0	120	15
100O2-120T-15D	0	0	0	100	21	120	15
100O2-140T-15D	0	0	0	100	21	140	15
100O2-120T-7D	0	0	0	100	21	120	7

TABLE 3.2: Experimental design

The choice of the temperature in the oven was very important. It was desired to obtain sufficient degradation to be able to observe it. But, to be sure to be in conditions that can be extrapolated to regeneration conditions ( in the range of about 70-140 °C) this temperature can not be too high in order to avoid changes in the mechanisms of degradation. So, the four first experiments were there to obtain a first overview of the degradation at 120 and 140 °C. After observing the results of the BET measurements, these temperatures seemed to give measurable difference between fresh and degraded samples. At this moment, the base case was defined. The base case is the centre of the experimentation, and the others are made in order to be compared to this base case. And for this one, the temperature of 140 °C and the duration of 15 h were chosen to enlarge the potential difference in degradation between the different samples in the different conditions. Because, obviously, a longer time under certain conditions will lead to a higher effect of these conditions, and so it will potentially increase the measurable difference in term of degradation between one experiment and another.

The total gas flowrate of 100 mL/min (in normal conditions) was set. With 1 g, the bed is about 4 cm in height, so because of the diameter of about 70 mm of the reactor, the average residence time on the gas side is about 1 second at 140 °C and 1 atm. Doing it with less than 100 mL/min was not really possible because of the limitation in precision of the flowmeter

(10 mL/min at least - 5 mL/min for CO<sub>2</sub>). Due to this short residence time of 1 s, a bigger flowrate did not seem more suited for the test.



### 3.3 Results and discussion

#### 3.3.1 Fresh sorbent and degraded sorbent from Twente - TG/MS

##### 3.3.1.1 Fresh sorbent

In the beginning of this thesis, the first sample to be tested was the fresh sorbent. It was important to obtain more information about it and a better understanding of it to design accordingly the next steps.

The way to test the fresh sorbent was by using TG combined with MS. These two apparatus are able to give three different pieces of information, as listed in a previous section : the mass loss, the heat flux and the mass spectra. Such information will give a first overview of the degradation of the sorbent in term of mass (mass loss) and in term of degradation product (heat flux + mass spectra).

At first, Figure 3.14 and 3.15 can be observed. These are the same experiment with two different samples of fresh sorbent, in order to test the repeatability. The method applied was the following : helium purge for about 1 hour with a gas flowrate of 20 mL/min, then an increase in temperature of 2 °C/min until reaching 300 °C with the same helium flowrate. These two figures show similar tendencies as desired for repeatability.

As it can be seen in Figure 3.14 and 3.15, there is an important mass loss (about 40-45 %w) between 50 and 100 °C. After that mass loss, under helium, the mass is almost stable even until 300 °C. The heat flux related to the mass loss points out that the phenomenon observed is endothermic. This mass loss is possibly linked to water and CO<sub>2</sub> desorption since they are both adsorbed on the fresh sorbent. Indeed, the sorbent adsorb both CO<sub>2</sub> and water in the ambient air, and taking a sample from the bottle of fresh sorbent is sufficient for him to capture some water and CO<sub>2</sub>. To check this hypothesis, the mass spectrum can be used. For more simplicity, only the mass spectrum linked to Figure 3.14 will be used below in this current discussion, not those of Figure 3.15 that are quite similar (they are indeed in the Appendix for more information). Figure 3.16 and 3.19 are the reference MS spectra from [5] for water and CO<sub>2</sub> respectively. They show what are the most important peaks that appear when either water or CO<sub>2</sub> are detected. To begin with, one can prove that water is desorbed. Figure 3.17 and 3.18 are the major peaks for water and both are clearly detected within the range of temperature considered. Considering the fact that the sorbent is able

to capture up to 65%w of water, the first explanation of the mass loss is the desorption of water between 50 and 100 °C. But Figure 3.20, which is the major peak detected for CO<sub>2</sub>, can be observed too. And so, one can say that CO<sub>2</sub> is desorbed too in the range of temperature. More accurately, CO<sub>2</sub> is desorbed a bit later than water, so it is a bit later than 50 °C, more like 60 °C as can be seen on Figure 3.20 (or even more precisely on Figure A.27 in Appendix). Furthermore, the mass spectra shows that water was adsorbed in larger quantities than CO<sub>2</sub>, since the amplitude of the peaks detected were greater for the water. Other carbonaceous components are detected between 50 and 100 °C (Figure ?? and ??). These components are heavier and are made of small chains. It is possible that there was some volatile matter (for example residual monomer) in the pores, and that this matter is then detected in a similar range of temperature. The possibility of the presence of volatile matter in the pores of the sorbent will be discussed later regarding the results of the GC.

As a reminder, the University had been using this MS for the first time since a long time. And so, it is not sure that it is well calibrated. The area under the peaks and the amplitude of the peaks are accurate, but the value on the scale are not.

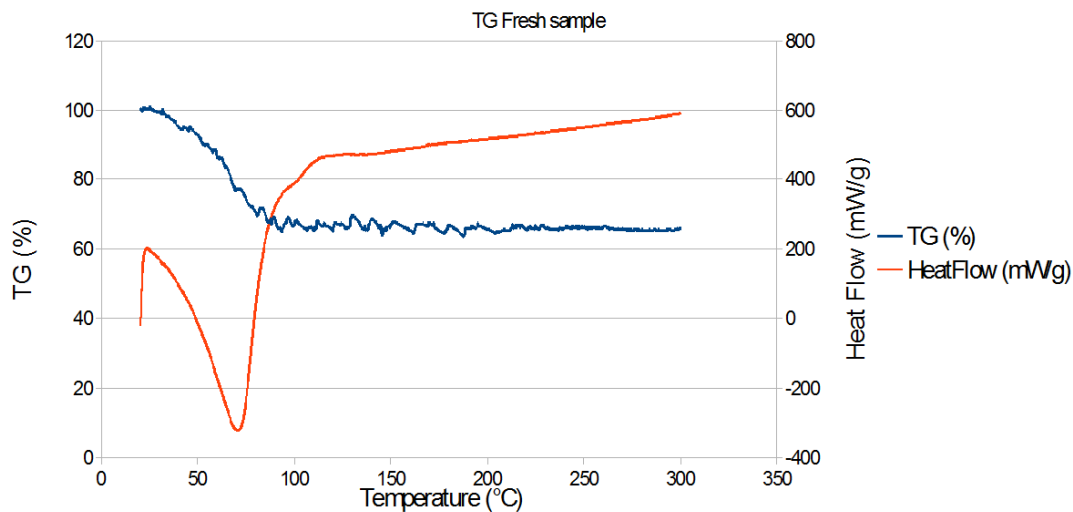


FIGURE 3.14: TG of fresh sorbent with helium

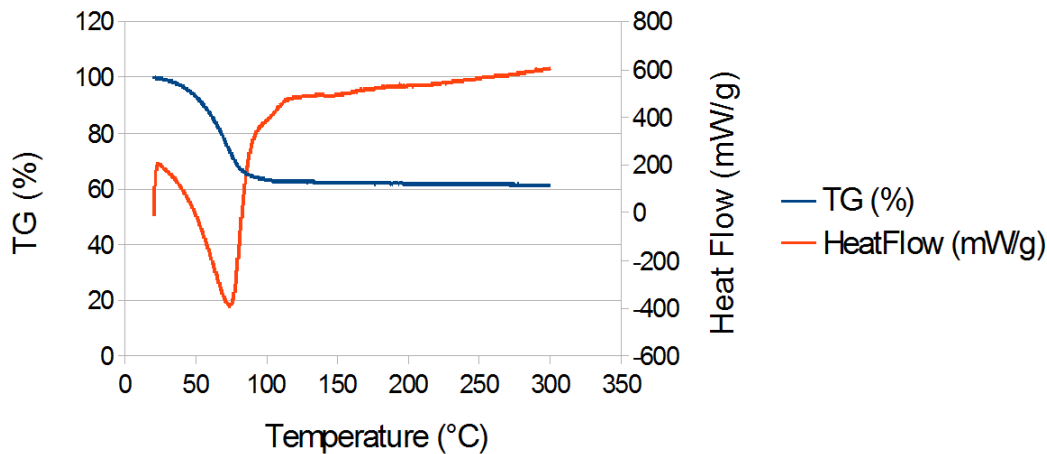


FIGURE 3.15: Second TG of fresh sorbent with helium

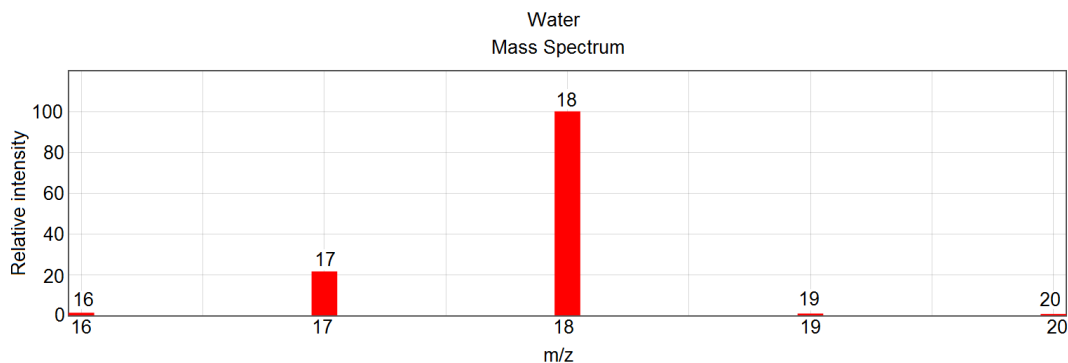


FIGURE 3.16: MS spectra for water from [5]

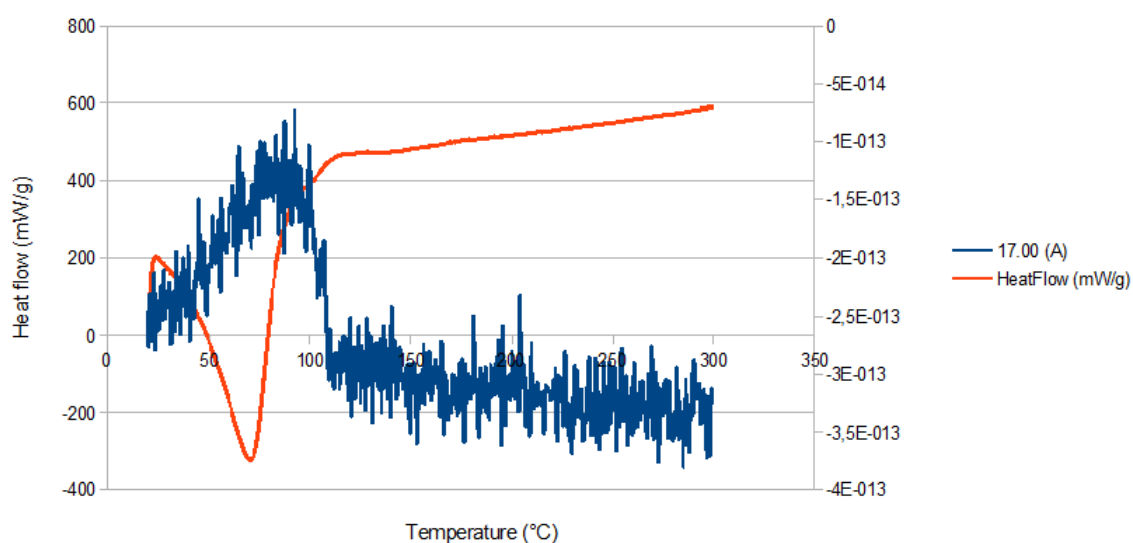


FIGURE 3.17: Peak 17 and heat flow

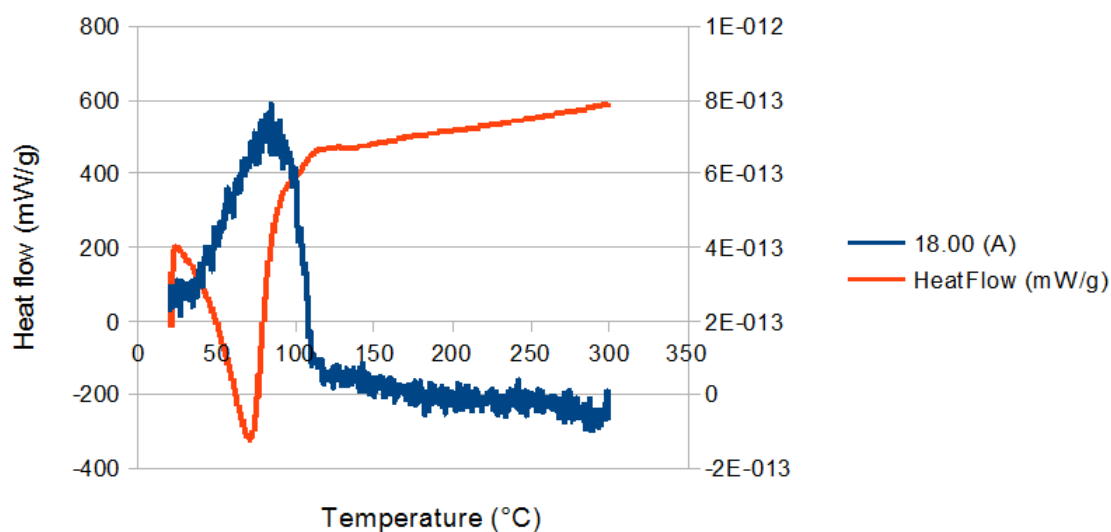


FIGURE 3.18: Peak 18 and heat flow

### 3.3.1.2 Degraded sorbent from Twente

The University of Twente sent some samples already degraded. So, to begin with, these sorbents were tested with the TG to check the information that can be obtained by this apparatus.

The results were not satisfying, and one is showed below in Figure 3.21. Indeed, degraded samples does not seem to give lots of information with the TG. Indeed, the mass loss is very

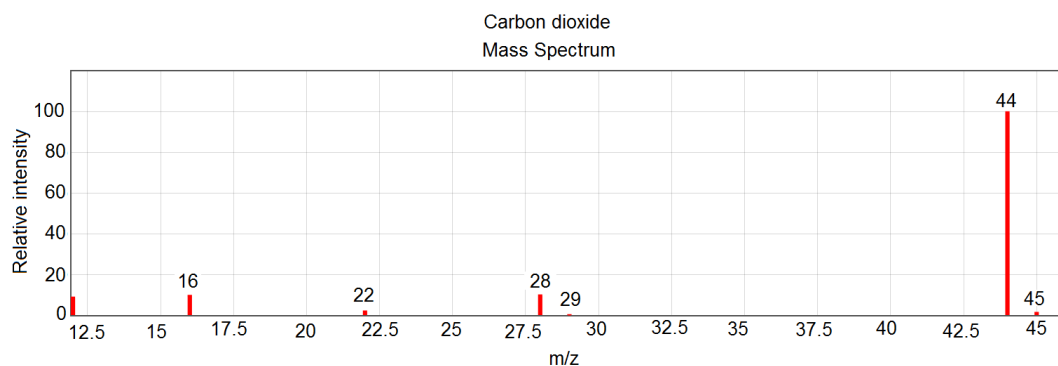
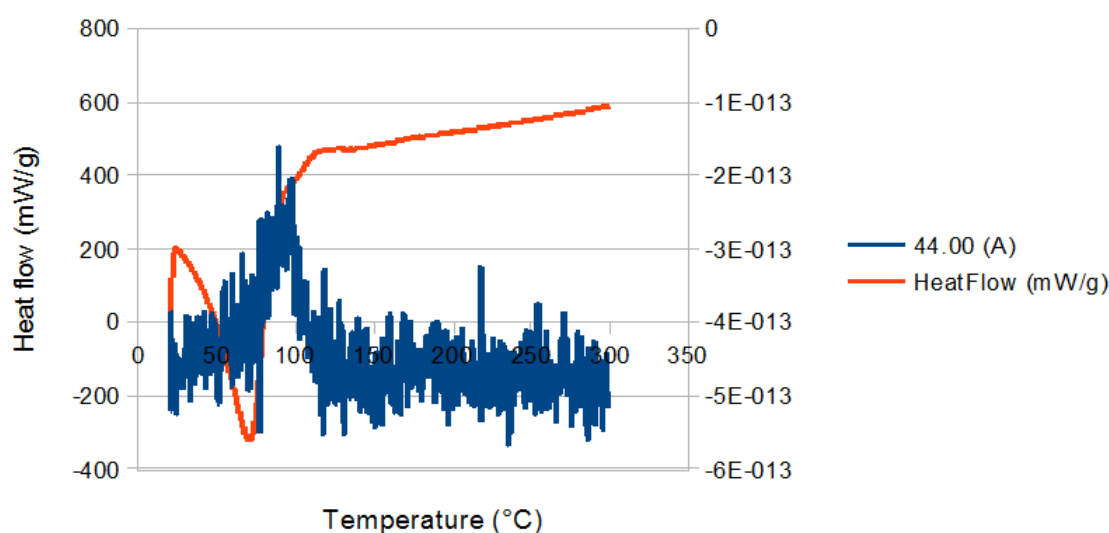
FIGURE 3.19: MS spectra for CO<sub>2</sub> from [5]

FIGURE 3.20: Peak 44 and heat flow

small and the heat flux do not shows a clear endothermic or exothermic reaction (no clear peak). Knowing that, it was established that for the next steps TG will not be considered anymore for the degraded sample as an useful characterisation method. The MS spectra were not more useful, given approximately the same information than for the fresh sorbent.

Then, the degraded samples were sent into the BET. The results are listed in Table 3.3 (A to M) that can be compared with the result of the fresh sorbent. But the analysis of these results will be done further in this work, to discuss them with those of the degraded samples produced in Liege.

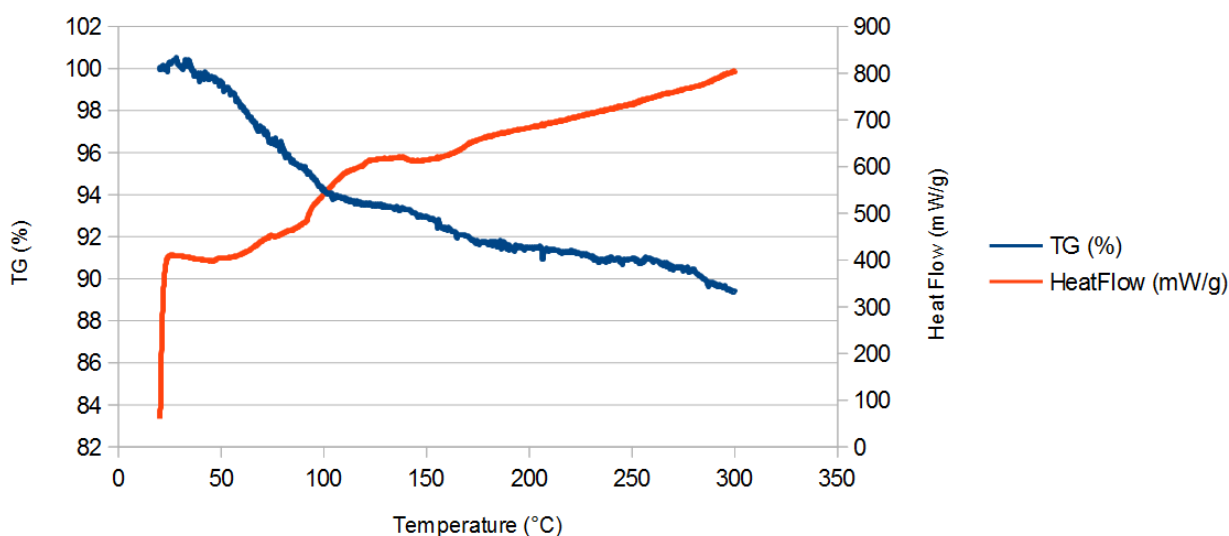


FIGURE 3.21: TG of the degraded sample "A" from Twente

### 3.3.2 Samples degraded at constant temperature in the experimental setup - GC/TCD/FID/He pycnometry

#### 3.3.2.1 Base case

To begin with, the base case can be analysed. The information provided by this experiment will be the basis of the comparison between the different experiments. Thanks to this base case, the effect of the different parameters will be checked.

At first, the results from the FID can be analysed. It is important to note that because no internal standards were used, these results are only qualitative. Figure 3.22 to 3.24 show the peaks obtained in the beginning, after about 250 minutes and at the end of the experiment. Figure 3.25 is the results of a GC without sample and with only 10 %CO<sub>2</sub> and 90 %N<sub>2</sub>. To begin with, it can be seen by comparing the three first figures with the last one that there is a real difference when there is some sorbent in the experimental setup rather than when there is nothing. Indeed, there is more peaks when there is sorbent than were there is not. The major peak at about 150 s of residence time does not exist when there is no sorbent in the experimental setup. And between about 200 and 250 s retention time, there is multiple peaks that appears when sorbent is in the experimental setup; these peaks appear clearly in Figure 3.22. Then, by comparing figures 3.22 to 3.24, it can be seen that the signal-to-noise ratio decreased with time. This means that there is less and less of the components

that are detected. Mixing these two information together, an hypothesis can be made : the signal given by the FID in the beginning comes from the volatile components that are inside the sorbent. The peaks are present even in the beginning of the experiment, and were observed for other tests even at ambient temperature. So, the best way to explain these is to consider that the sorbent contains some volatile matters within its pores. These matters comes probably from the synthesis of the sorbent. This is probably some residual monomers or small residual polymers with short chains which were trapped into the beads during the polymerisation and that are here driven to the FID by the gas flow.

Now, the results of the TCD can be analysed. The first important observation is that, by comparison between the same third figures than previously, the different components detected in FID are not detected in the TCD. Indeed, the peaks that are observed are only those of nitrogen (RT : 545 s) and oxygen (RT : 530 s). In the beginning, water (RT : 320 s) and CO<sub>2</sub> (RT : 95 s) can be seen too because they are desorbed of the sorbent. In fact, the only peaks different than those of the feed gases (N<sub>2</sub> and oxygen) are those of CO<sub>2</sub> and H<sub>2</sub>O that are desorbed in the beginning; so there are no amine species nor another species that are in sufficient quantity to be detected. This means that the degradation is not sufficient and that the conditions were not severe enough for the gas chromatograph to be useful. The amine groups, and more generally the sorbent, were able to endure 15 h at 140 °C at a concentration of about 16.8% O<sub>2</sub> (80% from 21%) with a resident time of about 1 s without generating gaseous amine species in measurable concentration (< 100 ppm).

Despite no oxidised species were detected by both FID and TCD, some degradation can be observed with BET. The results given by this last apparatus are listed below in Table 3.3. As it can be seen from this table, there is a clear and measurable difference between the fresh sorbent and the degraded sample of the base case. The structural properties decrease a lot as it can be seen by comparing the two different values. This information can be completed by checking Table 3.4. This last one can be used to compare the values obtained for fresh and degraded samples by the pycnometer. As it can be seen, the density of the beads increased after the experiment for the base case, which means that there is more mass in a same volume, meaning less pore volume. The data given by both BET and helium pycnometry can lead us to an hypothesis : the thermal treatment leads to a sintering of the beads and a following decrease of the structural properties. Visually, it is difficult to say if the beads are smaller than when the sorbent was fresh. No quantitative measurements of

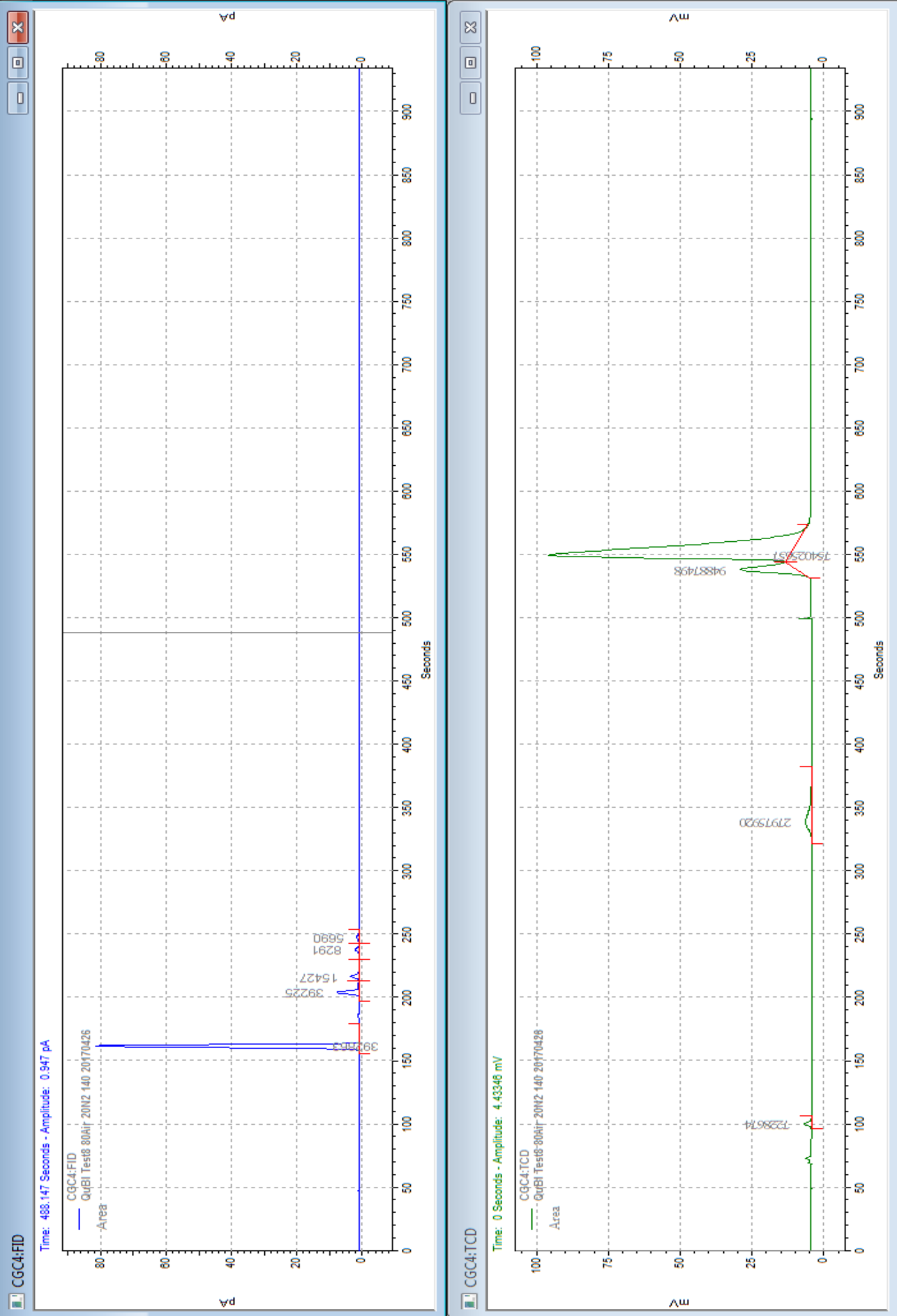


FIGURE 3.22: Base case : beginning



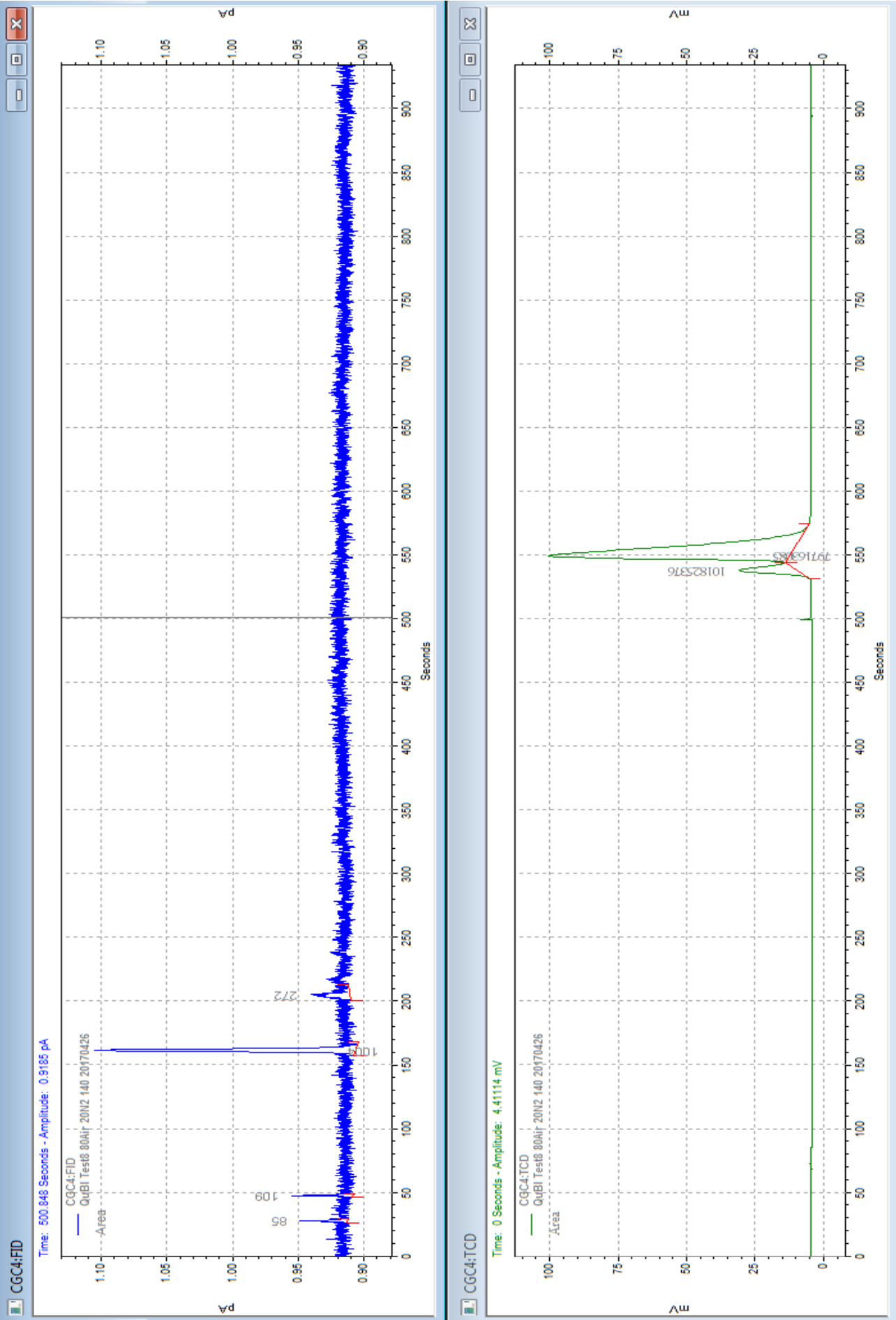


FIGURE 3.23: Base case : about 250 minutes after beginning

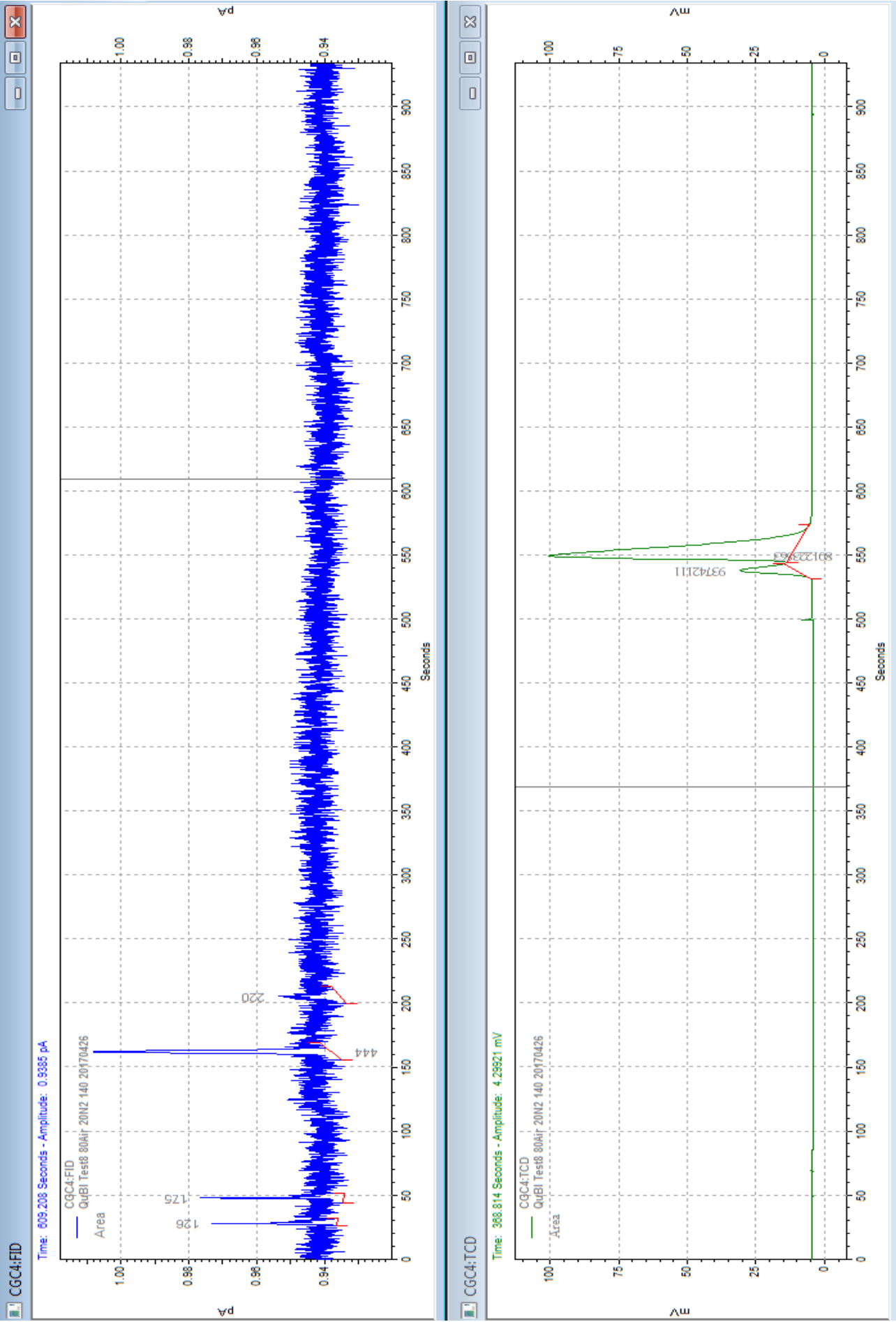


FIGURE 3.24: Base case : end

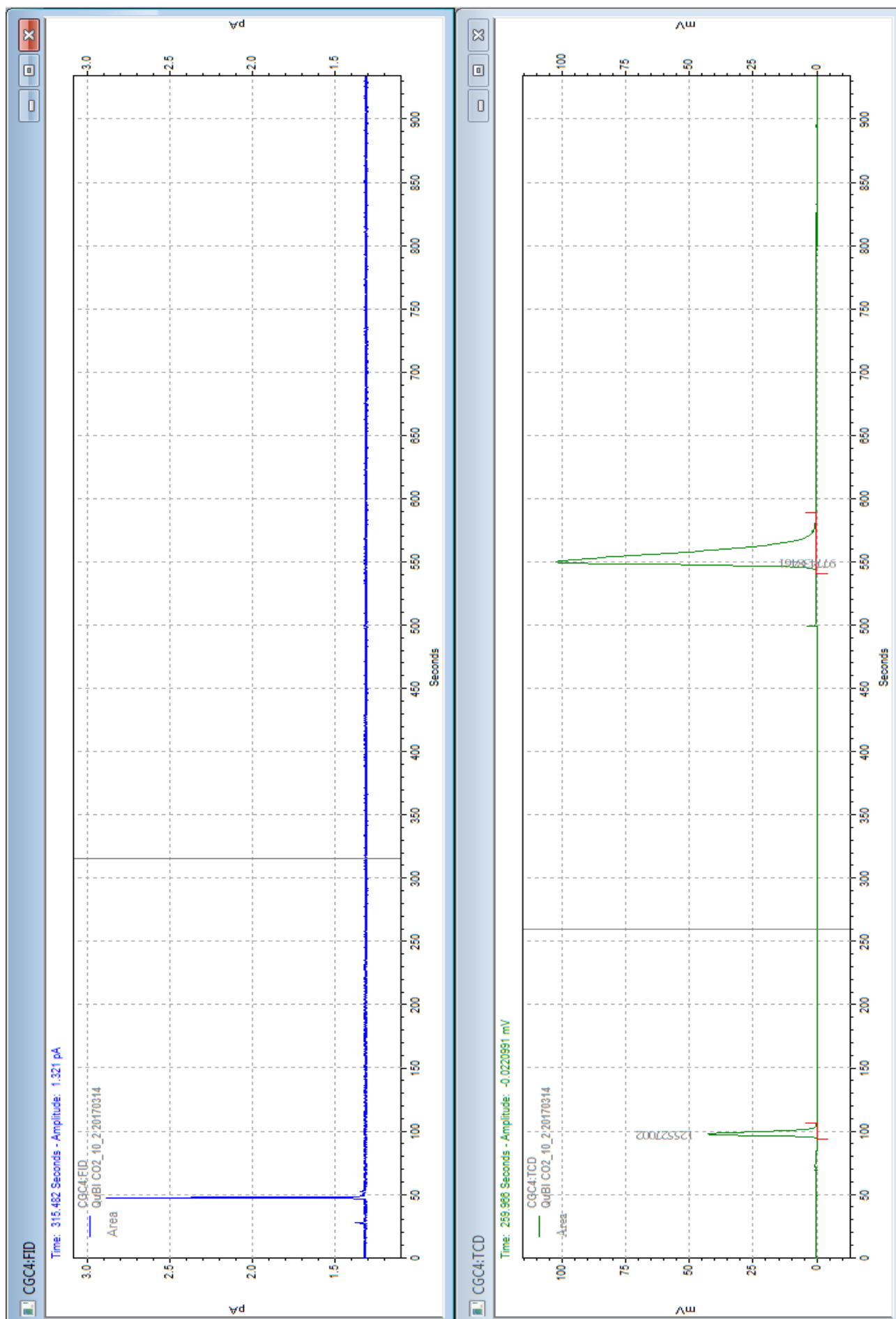


FIGURE 3.25: GC without sorbent for comparison

Fresh sample – BET					
Apparatus	Sample	Sample mass (g)	BET Surface Area (m <sup>2</sup> /g)	Total Surface Area (m <sup>2</sup> )	Pore specific volume (cm <sup>3</sup> /g)
Sorptomatic	Fresh sample	0,2723	57	16	0,31
ASAP	Fresh sample	0,9262	35	32	0,33
Supplier	Fresh sample	/	50	/	0,27
Degraded samples Twente – BET					
Apparatus	Sample	Sample mass (g)	BET Surface Area (m <sup>2</sup> /g)	Total Surface Area (m <sup>2</sup> )	Pore specific volume (cm <sup>3</sup> /g)
ASAP	A	0,2905	18	5	0,19
ASAP	B	0,3252	18	6	0,19
ASAP	C	0,2769	18	5	0,19
ASAP	D	0,4129	21	8	0,21
ASAP	E	0,3047	19	6	0,19
ASAP	G	0,1771	23	4	0,24
ASAP	H	0,4826	23	11	0,25
ASAP	I	0,4838	23	11	0,24
ASAP	J	0,5863	25	14	0,23
ASAP	K	0,6703	16	10	0,17
ASAP	M	0,1427	33	5	0,20
Base Case – BET					
Apparatus	Sample	Sample mass (g)	BET Surface Area (m <sup>2</sup> /g)	Total Surface Area (m <sup>2</sup> )	Pore specific volume (cm <sup>3</sup> /g)
Sorptomatic	Base Case	0,2521	27,5	7	0,43
Tests – BET					
Apparatus	Sample	Sample mass (g)	BET Surface Area (m <sup>2</sup> /g)	Total Surface Area (m <sup>2</sup> )	Pore specific volume (cm <sup>3</sup> /g)
Sorptomatic	BaseCase-120T	0,281	32	9	0,21
Sorptomatic	BaseCase-15CO <sub>2</sub>	0,2843/0,3034	49/35 <sup>a</sup>	14/11	0,17/0,38
Sorptomatic	BaseCase-15CO <sub>2</sub> -Repet	0,2784	33	9	0,26
Sorptomatic	BaseCase-2H <sub>2</sub> O	0,1236	25	3	0,41
Sorptomatic	BaseCase-15CO <sub>2</sub> -2H <sub>2</sub> O	0,2398	24	6	0,09
ASAP	100N2-120T-7D	0,5562	30	17	0,33
ASAP	100N2-140T-7D	0,4568	27	12	0,29
ASAP	100N2-120T-15D	0,4967	25	12	0,27
ASAP	100O <sub>2</sub> -120T-15D	0,587	21,5	13	0,22
Sorptomatic	100O <sub>2</sub> -140T-15D	0,2743/0,2389	6/24 <sup>a</sup>	2/6	0,11/0,22
Sorptomatic	100O <sub>2</sub> -120T-7D	0,2802	21	6	0,15

TABLE 3.3: BET results

size distribution were performed with both fresh and degraded samples to check a decrease in size of the beads. It would be one of the first ways to improve this work, and this way will be listed in the next chapter with other potential enhancement of this thesis.

Table 3.3 is really interesting for another reason : there are three quite different values for the specific surface for the fresh sorbent. At first, it seems that the two different apparatus of the laboratory, ASAP and Sorptomatic, give quite different results. The beads being the same, this difference comes from the methods employed for the analysis. For example, the outgassing was different for Sorptomatic than for ASAP, and that can play a part in this difference. For ASAP, the outgassing was made by ASAP itself at 50 °C for a duration of 6 hours. For Sorptomatic in the other hand, the first outgassing was at ambient temperature for a complete night with another outgassing unit. As showed previously by the TG of fresh sorbent, water and CO<sub>2</sub> were desorbed at about 50 °C and it is known that CO<sub>2</sub> and water are both chemisorbed and physisorbed on the sorbent. So, considering this information and the difference in results for the BET, an hypothesis can be made :

Fresh sample – Pycnometry		
Sample	Sample mass (g)	Density (g/cm <sup>3</sup> )
Fresh sample	1,7794	1,156
Base Case – Pycnometry		
Sample	Sample mass (g)	Density (g/cm <sup>3</sup> )
Base Case	0,3346	1,214
Tests – Pycnometry		
Sample	Sample mass (g)	Density (g/cm <sup>3</sup> )
BaseCase-120T	0,4667	1,189
BaseCase-15CO2	0	/
BaseCase-15CO2-Repet	0,3918	1,166
BaseCase-2H2O (wet)	0,7836	1,297
BaseCase-15CO2-2H2O (wet/outgassed)	0,6783/0,21	1,3069/1,1615
100N2-120T-7D	0,1869	1,405
100N2-140T-7D	0,3323	1,195
100N2-120T-15D	0,3827	1,167
100O2-120T-15D	0,4099	1,165
100O2-140T-15D	0,2279	1,163
100O2-120T-7D	0,2866	1,163

TABLE 3.4: Density Pycnometer

Sample from Twente : conditions				
Code	Sample description	Desorption time	Temperature (°C)	Note
A	O2 27/02/2015	72h	60	
B	O2 02/03/2015	72h	70	
C	O2 02/02/2015	72h	80	
D	Air H 26/03/2015	72h	100	with some humidity
E	Air H 02/04/2015	72h	120	with some humidity
G	Air (dry)	21h	120	
H	Run 1 Bed 3 006	120h (60 cycles 100min.)	80	
I	Run 1 Bed 2 005	120h (60 cycles 100min.)	100	
J	Run 1 Bed 1 004	120h (60 cycles 100min.)	120	
K	Sorbent 2/11/2016	?	Mainly 120	(with water)
M	Run 0 001	-	-	White powder

TABLE 3.5: Degraded samples from Twente : conditions of degradation

Because of the nature of the adsorption, a mix between both chemisorption and physisorption, the outgassing was probably one of the critical step to obtain good and repeatable results. And so, the outgassing done for the BET measurements were not well suited to the material. In the case of Sorptomatic, the outgassing was at ambient temperature. Such a simple outgassing is well known in the literature ([1]) to be insufficient to outgas a sorbent with chemisorption; but because of the long time of outgassing, one can say that the physically adsorbed components were almost entirely gone. In the other hand, for ASAP, the outgassing was performed at 50 °C, but during a shorter time by far. Because of the TG, one can say that 50 °C is a bit limited to outgas properly the sorbent. Indeed, the

desorption of both water and CO<sub>2</sub> begins at 50 °C or higher. And so, the temperature was just too short to obtain a good outgassing. Since the outgassing time was shorter, the outgassing was probably worse than the outgassing performed in the independent unit at ambient temperature; this leads to a lower surface area measured afterwards for the fresh sorbent.

It is obvious that the conditions in the TG and during the outgassing can not be compared directly like that; as the pressure for example is lower during an outgassing operation than during a TG at atmospheric conditions. So, nothing ensures that the desorption of CO<sub>2</sub> and water will be at the same temperature than during the TG. To test if the outgassing was really one of the steps that was not quite performed during the thesis, it would be simple : using the same outgassing at higher temperature (80 °C for example) for both apparatus. If the results obtained by both apparatus are closer (and closer to the value given by the supplier) with some repeatability, the problem was the outgassing as supposed here. If not, the problem is another thing. But in principle, because both apparatus are made to find the same value with a certain errors (2 m<sup>2</sup>/g for ASAP, 5 m<sup>2</sup>/g for Sorptomatic), the value given by both devices must be quasi identical and similar to the commercial value, either 50 m<sup>2</sup>/g.

The problem of the difference in measurement with the two different apparatus will be a recurring problem, that is it will not be relevant to compare values from one apparatus with some of the other. In the same way, there will be inaccuracies with the different measurements performed for the different samples, as well as problems of repeatability. Indeed, if the outgassing is not well designed for this actual sorbent, nothing guarantees the repeatability of the measurements, since the samples will not be in the same initial state before measurements. These problems of accuracy and repeatability will be discussed more in details in the section which is about the repeatability of the different experiments.

### 3.3.2.2 Density

Before speaking about the impact of the effect of the different parameters like the presence of water, the temperature or the duration, some general results can be observed.

At first, Table 3.4 can be observed with more accuracy. As it can be seen on this figure, lots of results are similar and about 1.6 g/cm<sup>3</sup>. As a reminder, the accuracy of the pycnometer

is about  $0.002 \text{ g/cm}^3$ , and so a lot of these results cannot be considered as different. But there is a general trend : for all the samples, the density is higher for the degraded samples compared to fresh sample. And so, as explained before, this means that there is more mass in the same volume than for the fresh sample, meaning the pore volume decreases with the thermal treatment. This decrease can be seen as a result of a sintering of the beads, which will result obviously in the reduction of the pore volume of the samples. So, it seems that in every conditions, the beads are subjected to a comparable sintering in view of the density. However, there is some difference between some samples.

At first, one will see that the sample "100N<sub>2</sub>-120T-7D" is higher in density than all the other samples. Since there is no reason for this difference, this is probably an aberrant value due to the low mass tested. And so, this result has probably no meaning. From `Tabletab:basePycn`, it can be seen that the samples which were wet show a high density as well. This is because there is water in the pores; in helium pycnometry, when water is saturating the pores, helium cannot enter them. And because of that, the density is overestimated. The sample "BaseCase-15CO<sub>2</sub>-2H<sub>2</sub>O" is perfect to see this difference between wet and outgassed samples. The outgassing for this sample was made with the external outgassing unit; this sample was the only one that was outgassed before He pycnometry, in order to see the difference between wet and outgassed. Then, there are three results that are significantly different from all the others : "Base Case", "BaseCase-120T" and "100N<sub>2</sub>-140T-7D". It is difficult to give a signification to these differences, since there is no real trend. Indeed, it would be surprising if the sample which undergoes the stronger conditions (100% air - 140 °C - 15 h) was showing a less important sintering than the base case for example. And so, because of that, there is no real conclusion that can be made about these differences.

### 3.3.2.3 Pore volume

The pore volume of the different samples will be discussed before speaking about the impact of the different parameters. This, because no major observation can be done, so that only general discussion is possible.

To begin with, Figure 3.26 to Figure 3.31 show the pore volume of the different samples (from Table 3.3) in function of the main parameters. There is only one trend that can be observed for all these graphs in Figure 3.28. It seems that the pore volume decreases with the duration of the experiment, which seems logical; if the degradation is longer, the

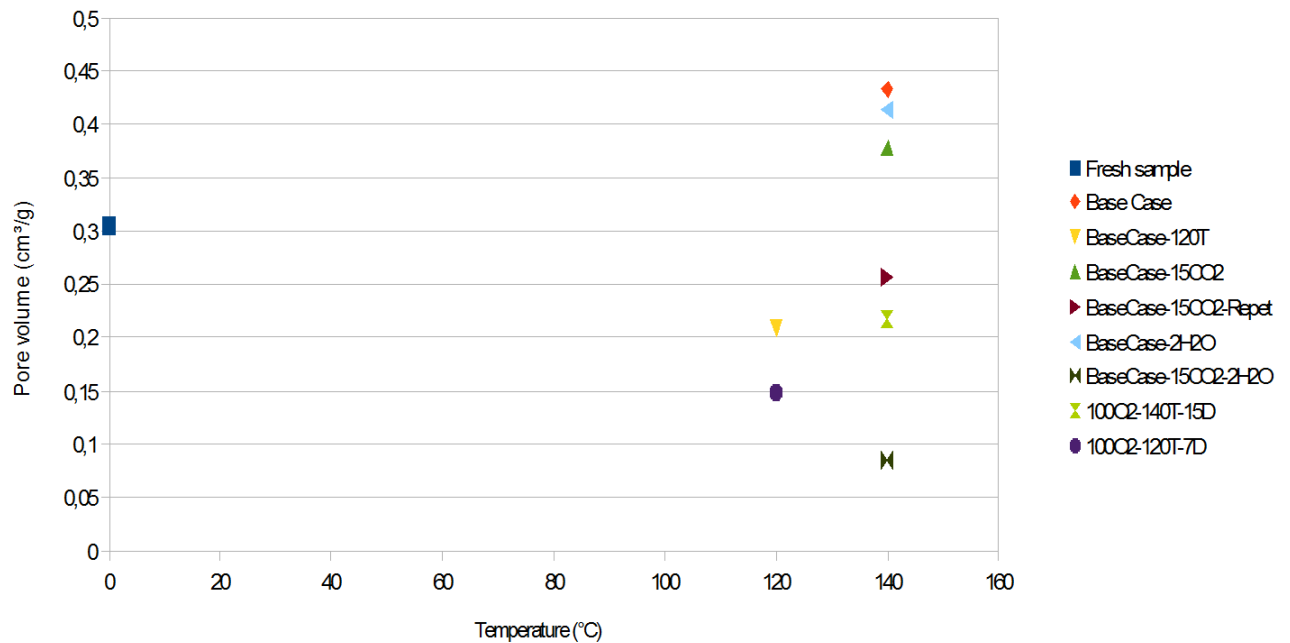


FIGURE 3.26: Pore Volume Sorptomatic - Temperature

structural properties must decrease more. But this is not the case when checking Figure 3.27, which plot the results from Sorptomatic. And so, there is no real general conclusion that can be made regarding pore volume.

The same can be said for the pore size distribution of samples. This one is almost the same for every samples. Figures 3.32 to 3.34 show distributions for quite different samples. The only different distribution was for the first measurement of "100O<sub>2</sub>-140T-15D" which was clearly an aberrant measurement.



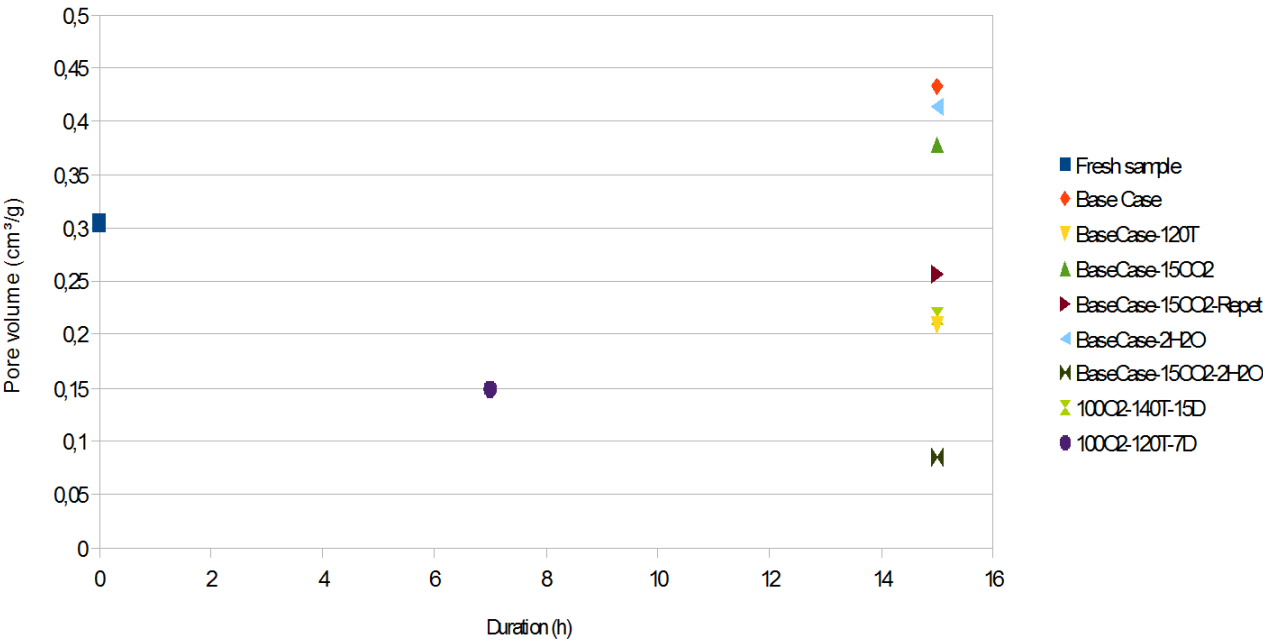


FIGURE 3.27: Pore Volume Sorptomatic - Duration

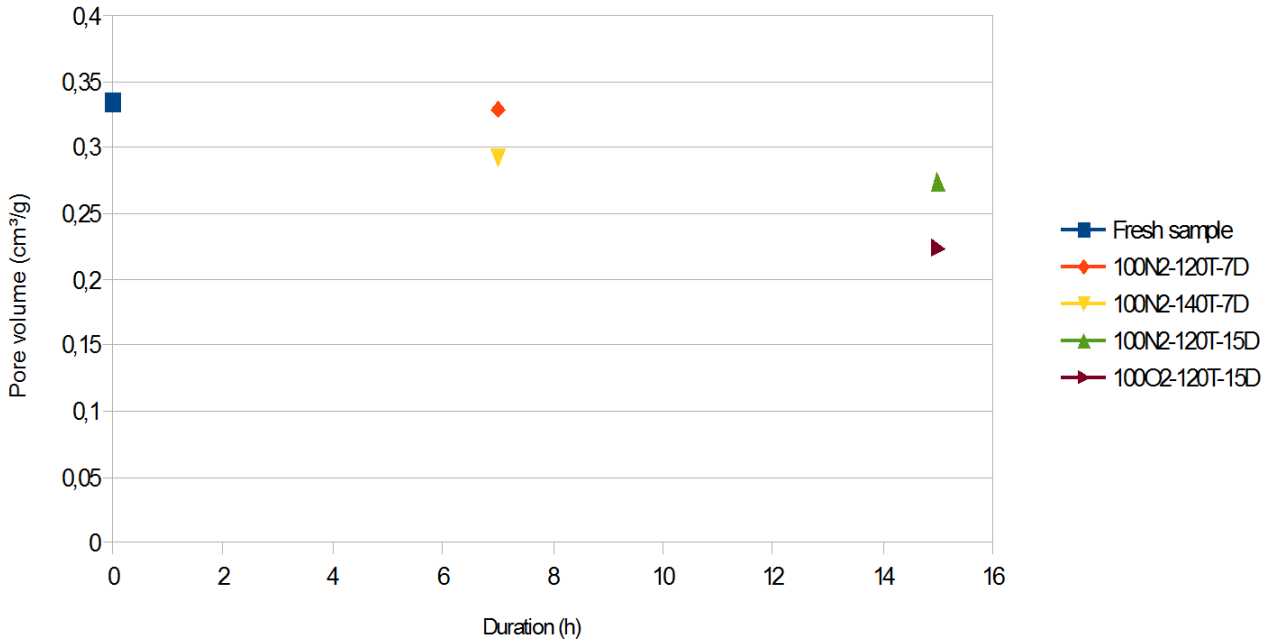


FIGURE 3.28: Pore Volume ASAP - Duration

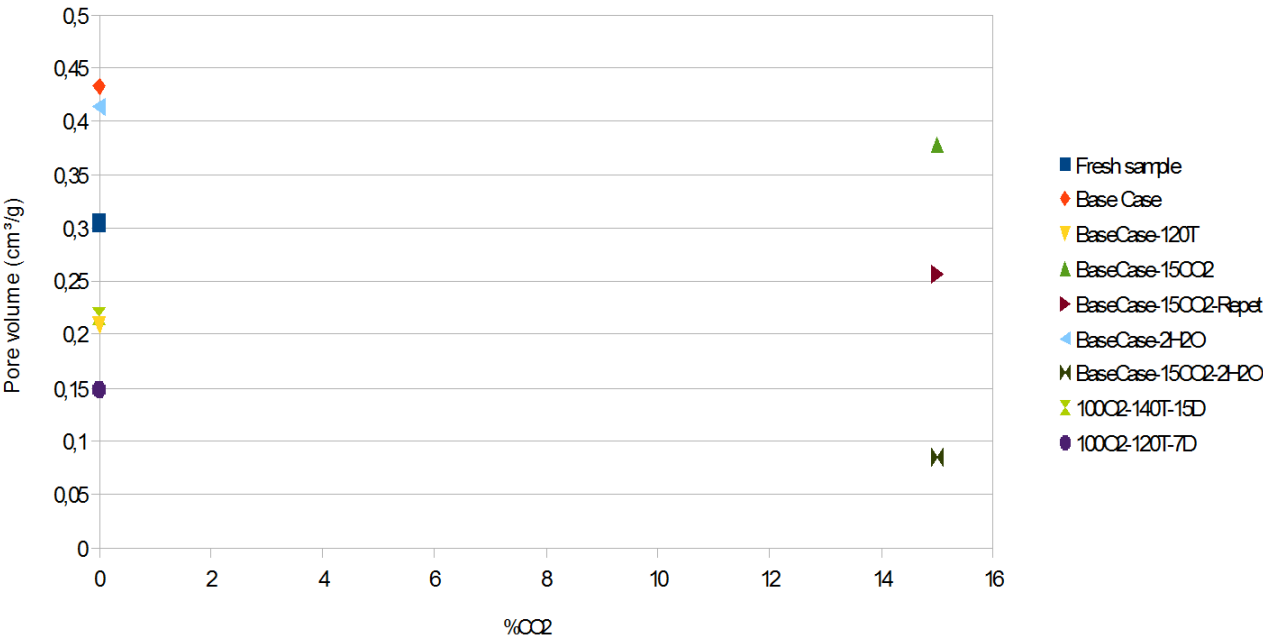


FIGURE 3.29: Pore Volume Sorptomatic - CO<sub>2</sub>

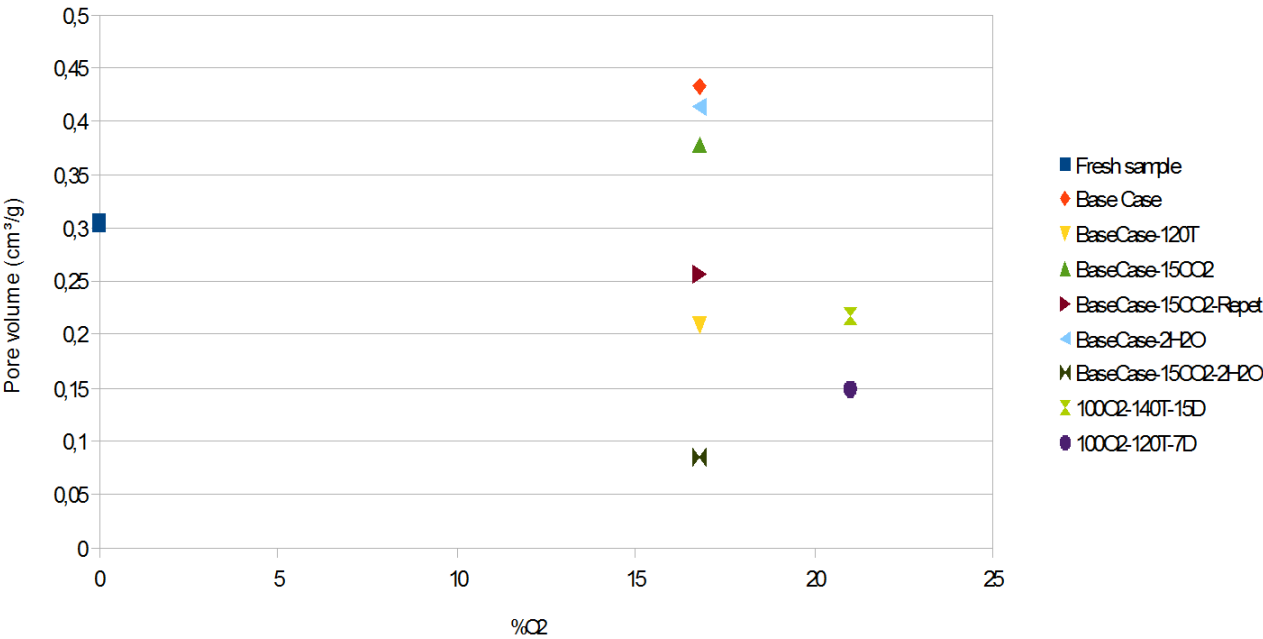


FIGURE 3.30: Pore Volume Sorptomatic - O<sub>2</sub>

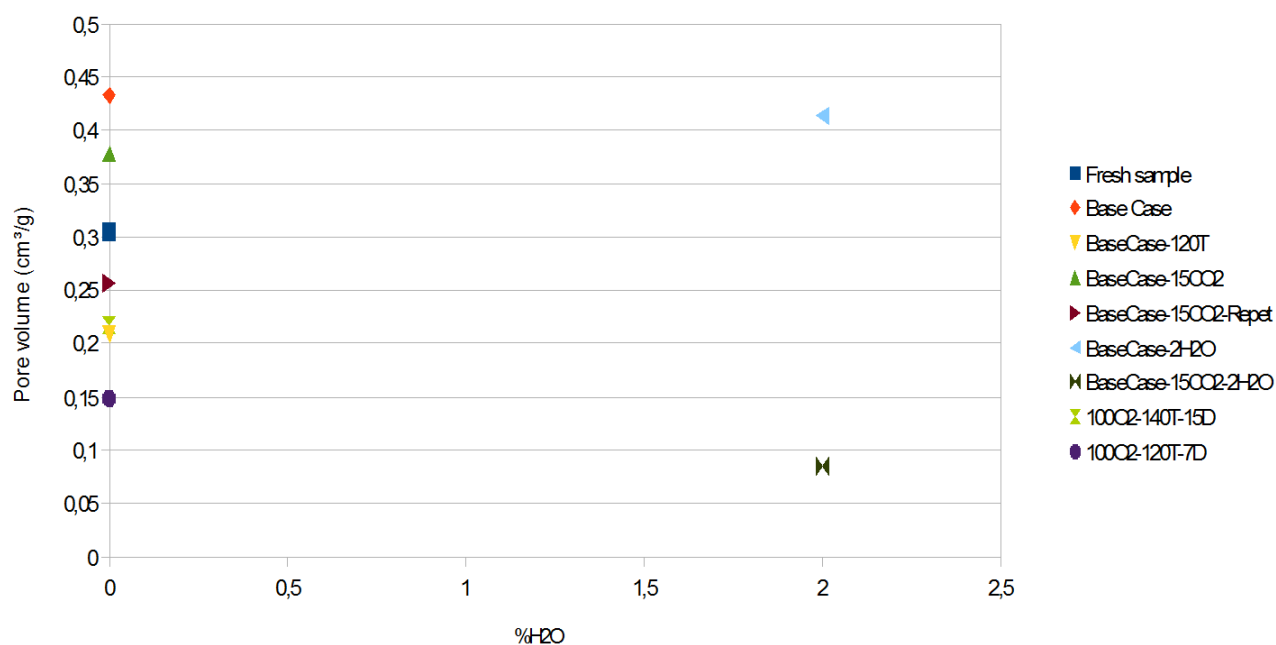


FIGURE 3.31: Pore Volume Sorptometric - Water

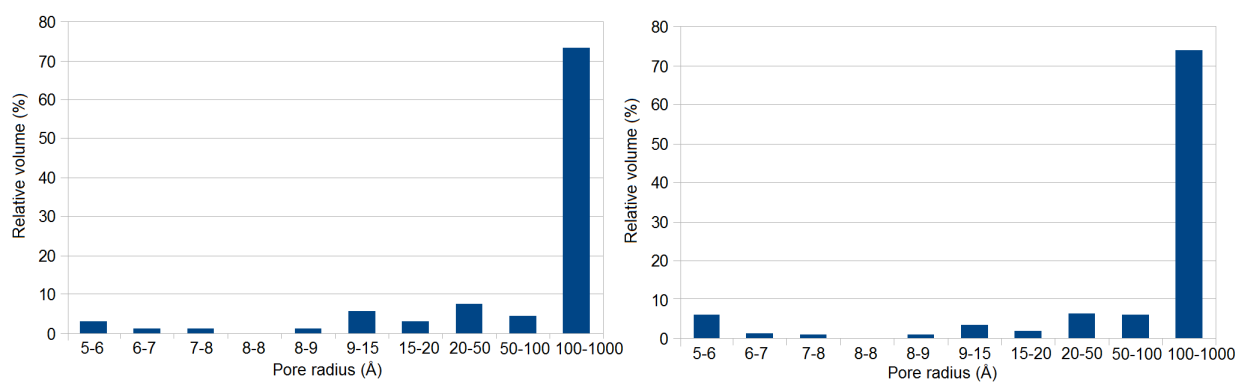
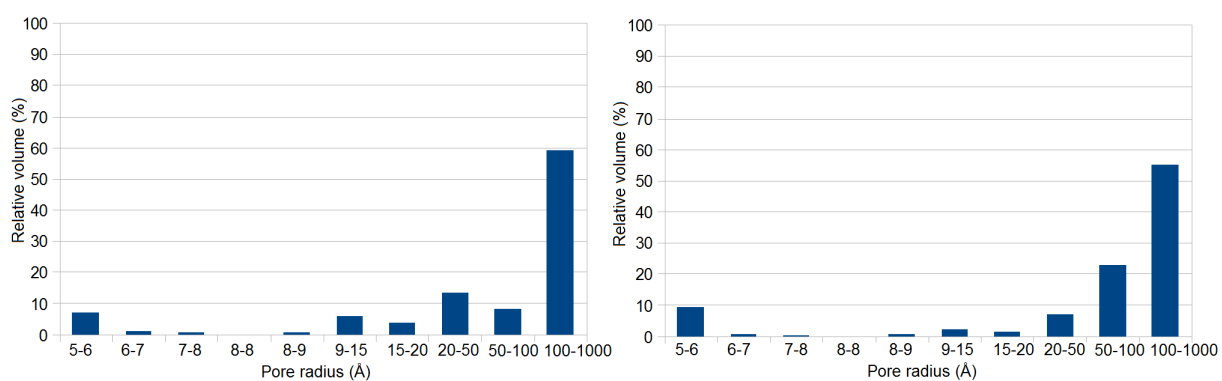


FIGURE 3.32: Pore Volume distribution - Left : Fresh - Right : Base Case

FIGURE 3.33: Pore Volume distribution - Left : "BaseCase-2H<sub>2</sub>O" - Right : BaseCase-15CO<sub>2</sub>-2H<sub>2</sub>O

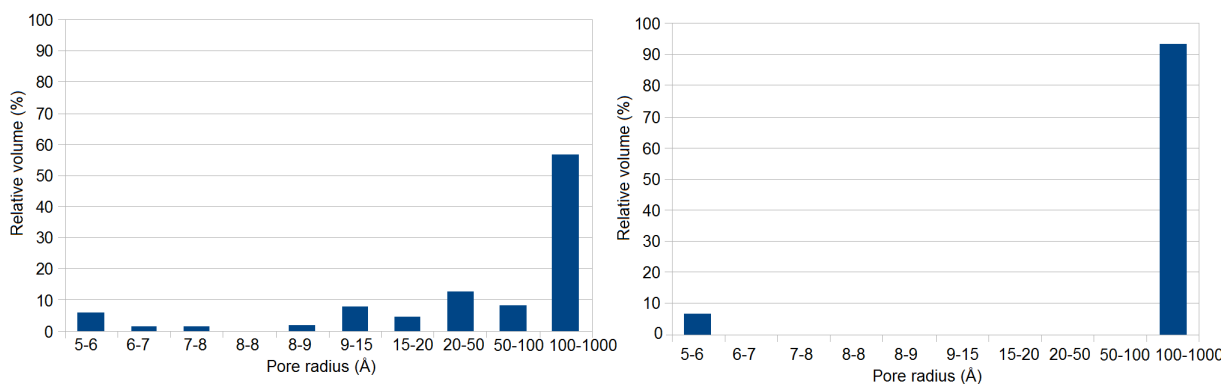


FIGURE 3.34: Pore Volume distribution - Left : "100O<sub>2</sub>-140T-15D" - Right : "100O<sub>2</sub>-140T-15D" aberrant

### 3.3.2.4 Impact of Duration

Two different duration were tested. In the beginning of all the experiments, 7 and 15 hours were considered. The results of the BET can be shown in Table 3.3 as well.

At first, Figure 3.35 plots the results of the BET in term of specific surface for the fresh sorbent (measured by ASAP), "100N<sub>2</sub>-120T-7D" and "100N<sub>2</sub>-120T-15D". Figure 3.35 seems to shows a trend : the higher the duration, the more the samples are degraded. This conclusion is logical and was expected. To be more accurate, as can be seen on Table 3.3, the difference between the two values is about 5 m<sup>2</sup>/g, which is more than twice the experimental error range for ASAP.

Two other samples can be compared to check the impact of duration, "100O<sub>2</sub>-120T-7D" and "100O<sub>2</sub>-120T-15D". They were not plotted because one was measured by ASAP, and the other one by Sorptomatic. And it was stated previously that the results of these apparatus will not be compared because of wide difference in term of results for the fresh sorbent, menaning that repeatability between the apparatus is not guaranteed.

The comparison can be extended with the results from GC. But as for the base case, there is nothing specific detected by both TCD and FID. So, for these reasons, these graphs are not in this section. One can check it in the Appendix, Figure B.17 compared to Figure B.21 and Figure B.23 compared to Figure B.27.

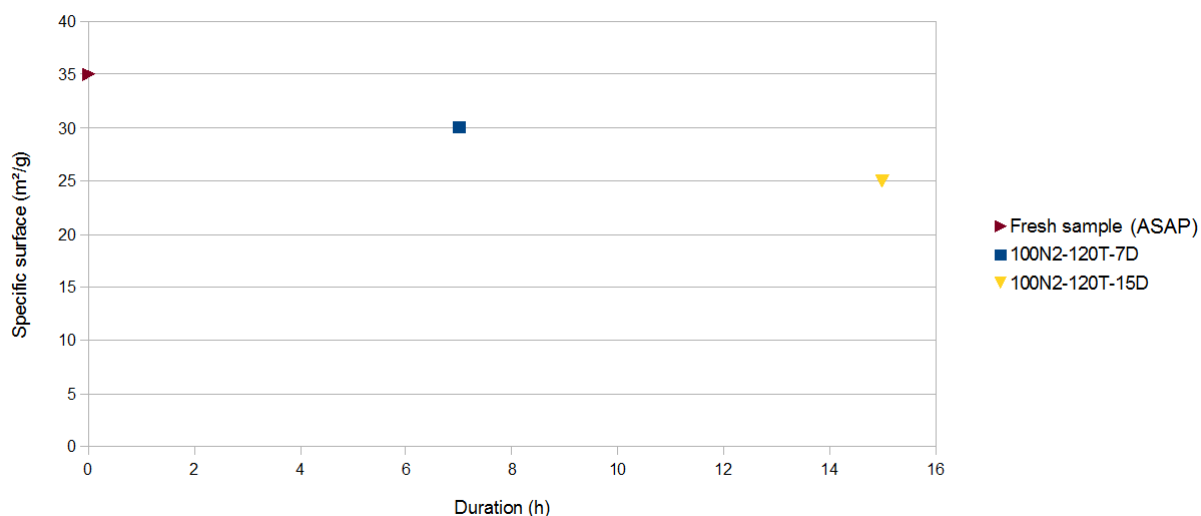


FIGURE 3.35: Specific surface in function of Duration

### 3.3.2.5 Impact of temperature

To check the impact of temperature, two different temperatures were tested.

To begin with, Figure 3.36 plots the results of the BET in term of specific surface for the fresh sorbent, "BaseCase", "BaseCase-120T", "100N<sub>2</sub>-120T-7D" and "100N<sub>2</sub>-140T-7D". There is two figures in this section ( a) and b) ) because the results from ASAP and Sorptomatic are separated on the figure (Sorptomatic : a) ; ASAP : b) ). The value plotted for the fresh sorbent is different for each graphs, since the value measured was different for ASAP and Sorptomatic.

For both figure a) and b), there is a clear trend. Indeed, the higher temperature leads to the lower specific surface. To be more accurate, the difference between the two values for "BaseCase" and "BaseCase-120T" is about 5 m<sup>2</sup>/g, which is the accuracy of Sorptomatic, and the difference between the two values for "100N<sub>2</sub>-120T-7D" and "100N<sub>2</sub>-140T-7D" is out of the error range of the ASAP. "100O<sub>2</sub>-120T-15D" and "100O<sub>2</sub>-140T-15D" can theoretically be compared. But in fact, they can not since the BET were performed with the two different apparatus.

In conclusion, an increase in temperature increase the degradation. This conclusion is not completely in agreement with the results reported by [11]. They studied the same sorbent (Lewatit) and plotted the results of long term experiments of degradation under pure N<sub>2</sub> exposure at 100, 150 and 200 °C, and pure thermal degradation was not detected for 100

and 150 °C. In this thesis, the comparison between "100N<sub>2</sub>-120T-7D" and "100N<sub>2</sub>-140T-7D", where only pure thermal degradation can occur since there is no oxygen, leads to the conclusion that there was more degradation at 140 °C than at 120 °C. If there was no thermal degradation under 150 °C, the structural properties of the sorbent would not change between 120 and 140 °C as observed in this thesis. Finally, in regard of this discussion, more tests of pure thermal degradation with the experimental setup of Liege would be interesting to check the results and make a proper conclusion.

Finally, the results from GC can be compared. But as for all the other samples, there is nothing detected, and so, the graphs are put in the Appendix if one wants to check that. The graphs of interest for this section are B.2 compared to B.4 and B.17 compared to B.19.

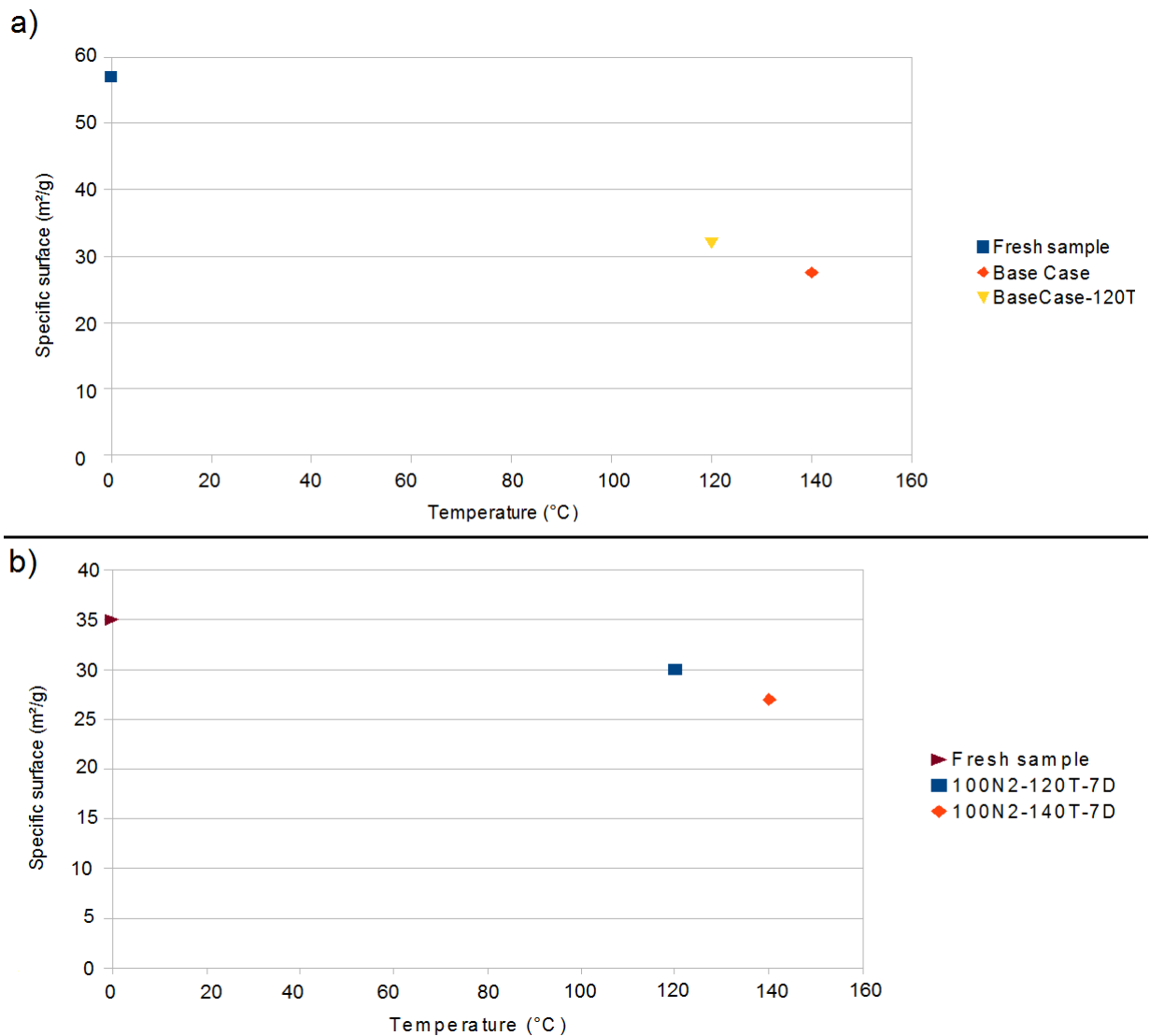


FIGURE 3.36: Specific surface in function of Temperature - a) Sorptomatic - b) ASAP

### 3.3.2.6 Impact of Oxygen

The gas composition was one of the main parameters that was changed. To begin with, the impact of the Oxygen content will be discussed here.

The first overview is given by Figure 3.37 which plots the specific surface of the fresh sample, "Base Case", "100O<sub>2</sub>-140T-15D", "100N<sub>2</sub>-120T-15D" and "100O<sub>2</sub>-120T-15D". The two graphs a) and b) are to separate the results of Sorptomatic ( a ) and ASAP ( b ). In Figure 3.37 a), it seems that there is a clear trend with oxygen content : the more oxygen there is, the more degraded are the samples. The same trend can be supposed in Figure 3.37 b), but there are not enough data to ensure that. The conclusion is simply that the content of oxygen, which is related to oxydative degradation, impacts negatively the structural properties of the sorbent. In other words, the more there is oxygen, the more there is structural degradation. This was something expected. From Table 3.3, one can see that the difference in surface between "Base Case" and "100O<sub>2</sub>-140T-15D" is about 3 m<sup>2</sup>/g, which is in the error range. The difference between "100N<sub>2</sub>-120T-15D" and "100O<sub>2</sub>-120T-15D" is out of the error range of ASAP. And the differences between all values ("Base Case", "100O<sub>2</sub>-140T-15D", "100N<sub>2</sub>-120T-15D" and "100O<sub>2</sub>-120T-15D") and the fresh sorbent are out of the error range for every samples.

Now, in this section, the previous BET results of the degraded samples from Twente can be analysed. The analyse of these results will lead to a similar conclusion : higher concentration of oxygen during the degradation will lead to a higher structural degradation. Indeed, by using Table 3.5, which list briefly the conditions encounter by these samples, and Table 3.3 (A to M), one can see that the samples degraded in pure oxygen (D, E, G) show a higher structural degradation than those degraded in air (A, B, C). And those degraded in air show higher degradation than those degraded without oxygen. Because of the differences in term of degradation conditions (duration, experimental setup), it is difficult to make a comparison between those values and the values of the degraded samples produced in Liege. But the general effect of oxygen is the same, and the general conclusion concerning the impact of oxygen is the same.

Figure 3.38 is a very interesting plot of every results in term of specific surface (results of Sorptomatic). Figure 3.38 a) shows the results in function of oxygen, and 3.38 b) do the same in function of the temperature.

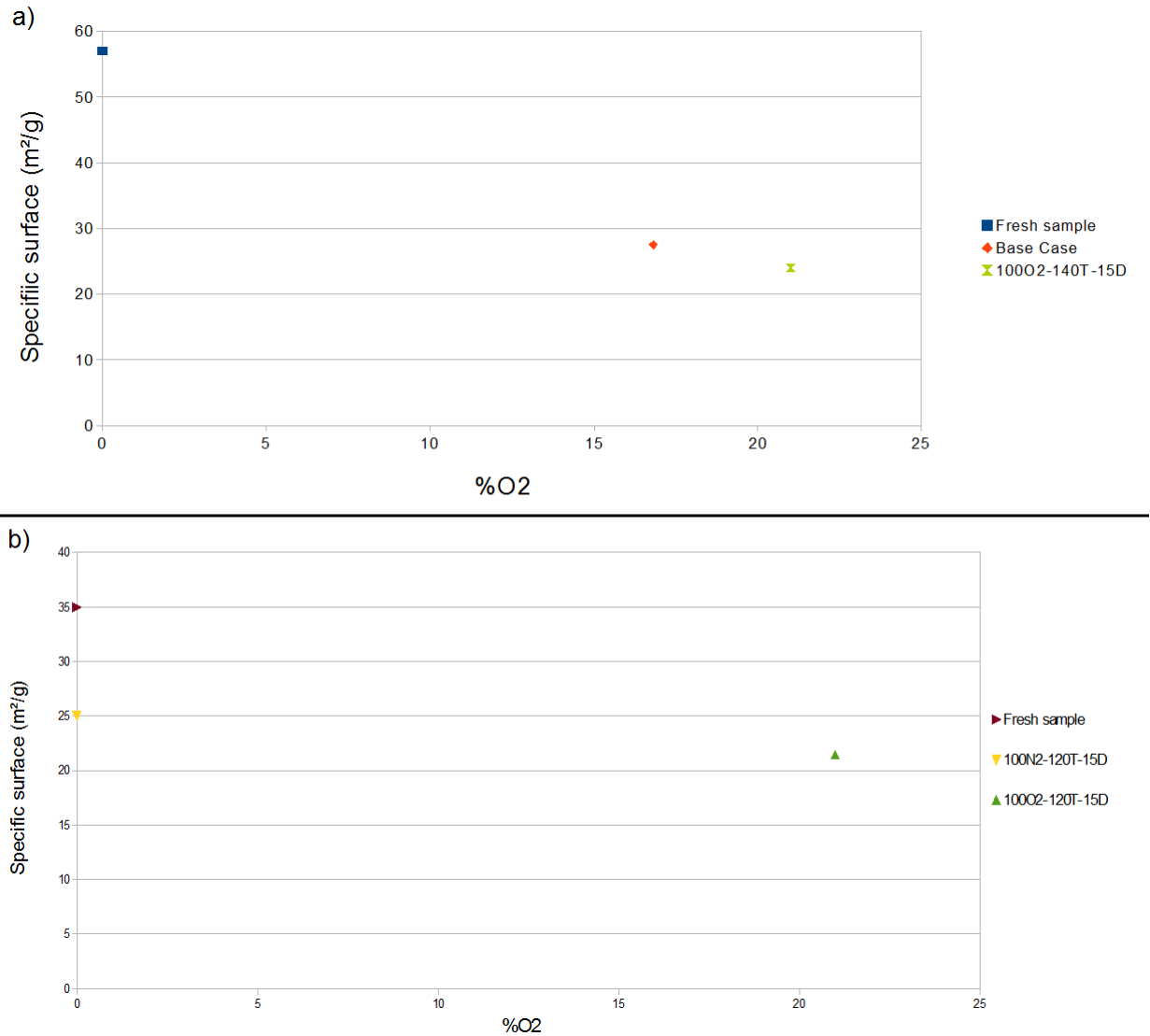


FIGURE 3.37: Specific surface in function of % Oxygen - a) Sorptomatic - b) ASAP

It is really interesting to see that a trend appears for Figure 3.38 a) only. It is like the samples are almost in a same range of values in function of the % O<sub>2</sub>. This means that the impact of oxygen is noticeable over all the other parameters. In others words, mixing all the samples (which undergo different conditions of degradation) in a same figure do not hide the effect of oxygen. The intensity of the impact of oxygen seems more important than the impact of all the others parameters. It is not the case for the temperature, Figure 3.38 b) do not shows any trend. And so, the impact of temperature is indeed smaller than the impact of oxygen. This underline a result of the literature : oxidative degradation is more important than thermal degradation for amine-based sorbents in regeneration conditions. Indeed, the thermal degradation is linked to the temperature which has a smaller effect than the oxygen, which is linked to the oxidative degradation. Obviously, the temperature increases the speed



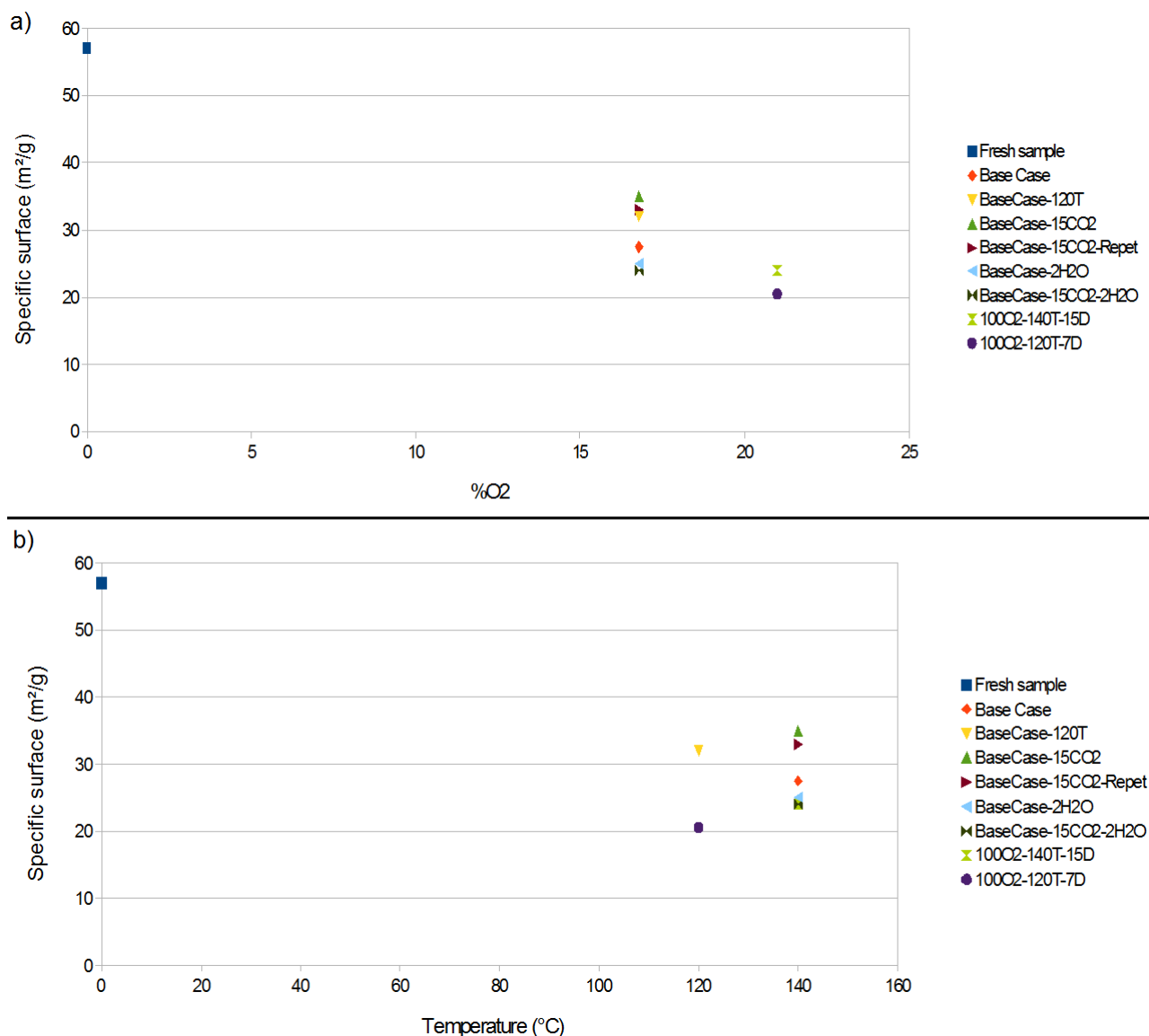


FIGURE 3.38: Specific surface in function of a) % Oxygen (Sorp-tomatic) - b) Temperature (Sorp-tomatic)

of oxidative degradation too; and the fact that temperature does not change the degradation in measurable and clear ways like the oxygen means that the oxidative degradation keeps the same mechanisms between 120 and 140 °C. If the mechanisms was changing between the two temperatures, the effect of temperature would be as important as the effect of oxygen, or even more, and Figure 3.38 b) would have probably shown a specific trend like 3.38 a).

The results of the GC can be analysed. But there is no clear differences. It has been stated that the main mechanism of degradation was oxidative degradation, but no oxidized species were measured, even when 100% air was used. And so, it can be clearly said that the concentration of oxidative species is smaller than the detection limit of the GC (100 ppm).

One can check the figures in the Appendix : Figure B.2 compared to Figure B.25 and Figure B.21 compared to Figure B.23.

### 3.3.2.7 Impact of Water

The water content was one of the operating variables. It was possible to add up to 2% (in volume) of water vapour during an experiment. It has to be noted that the experimental setup was not made to work with a lot of water, and because of the hydrophilic nature of the sorbent, there were some small problems during the experiments. The flux was not really constant at each moment, and the pressure was a bit higher than 0.

The first overview concerning the specific surface is given by Figure 3.39. The samples plotted are the fresh sorbent, "Base Case", "BaseCase-15CO<sub>2</sub>", "BaseCase-15CO<sub>2</sub>-Repet", "BaseCase-2H<sub>2</sub>O" and "BaseCase-15CO<sub>2</sub>-2H<sub>2</sub>O". The results obtained were in the lowest range of values for both experiments with water, around 25 m<sup>2</sup>/g. So, compared to the base case, these values are in the same order (difference between the values in the error range). The difference between "BaseCase-15CO<sub>2</sub>" / "BaseCase-15CO<sub>2</sub>-Repet" and "BaseCase-15CO<sub>2</sub>-2H<sub>2</sub>O" is out of the error range and the specific surface of "BaseCase-15CO<sub>2</sub>-2H<sub>2</sub>O" is clearly smaller than the specific surface of the two others samples. The result for "BaseCase-15CO<sub>2</sub>-2H<sub>2</sub>O" will be discussed in the next section with the impact of CO<sub>2</sub>.

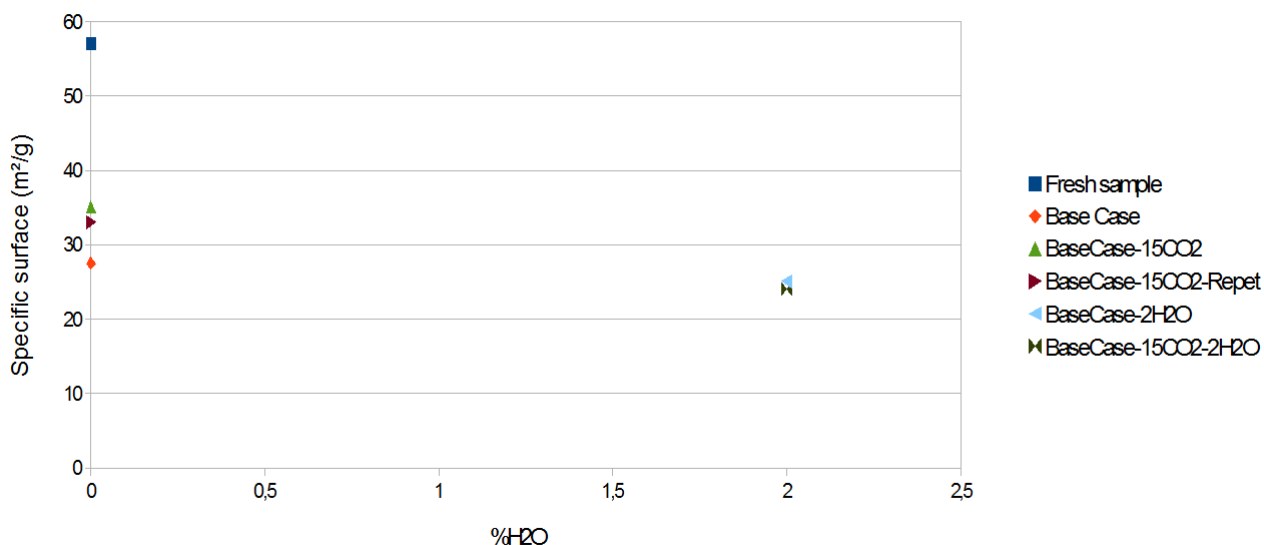


FIGURE 3.39: Specific surface in function of % Water

In the literature [14], it is known that water enhances the robustness of Lewatit thanks to the formation of bicarbonate. However, in our case, this piece of information is out of the context and cannot be used like that. Indeed, let's suppose that the sorbent was perfectly fresh, without any CO<sub>2</sub> or water adsorbed. In that case, the water will have no influence and no bicarbonate will be formed during the test, since there is no CO<sub>2</sub> in the feed gas during the base case. And therefore, the structural properties are not enhanced. In our case, it is even different. The sorbent was not really fresh, it had already adsorbed ambient water and CO<sub>2</sub>. And because of that fact, because of the presence of both water and CO<sub>2</sub>, there was already some bicarbonate formed within the sorbent. An hypothesis can be made : the formation of bicarbonate was probably not sufficient to leads to measurable differences in structural properties because there was already some bicarbonate in the sorbent. The conclusion is therefore simple, given that water does not seem to protect the sample when bicarbonate is present prior to the degradation, and so that the effect of water observed in the other study seems to be really due to the formation of bicarbonate. If there was another effect of the water for protecting the sample, regarding the conditions of the test in this study, there would have been probably a difference in structural properties.

The GC results can be analysed, but as in the previous section, no degraded substances were detected. One can check the figures in the Appendix : Figure B.2 compared to Figure B.12 and Figure B.6/B.8 compared to Figure B.15.

But the GC results can lead to two majors observations. At first, it is obvious that there was some inconsistency in the gas flux during the experiments regarding the GC results. Indeed, as can be seen in Figure 3.40, 3.41, 3.42 and 3.43, the TCD detects very different quantities of incoming gases at different moments, even when these moments are not separated by a lot of time. The second observation is that there is more noise in the FID than previously. The TCD does not detect other gases than the incoming ones for these experiments.

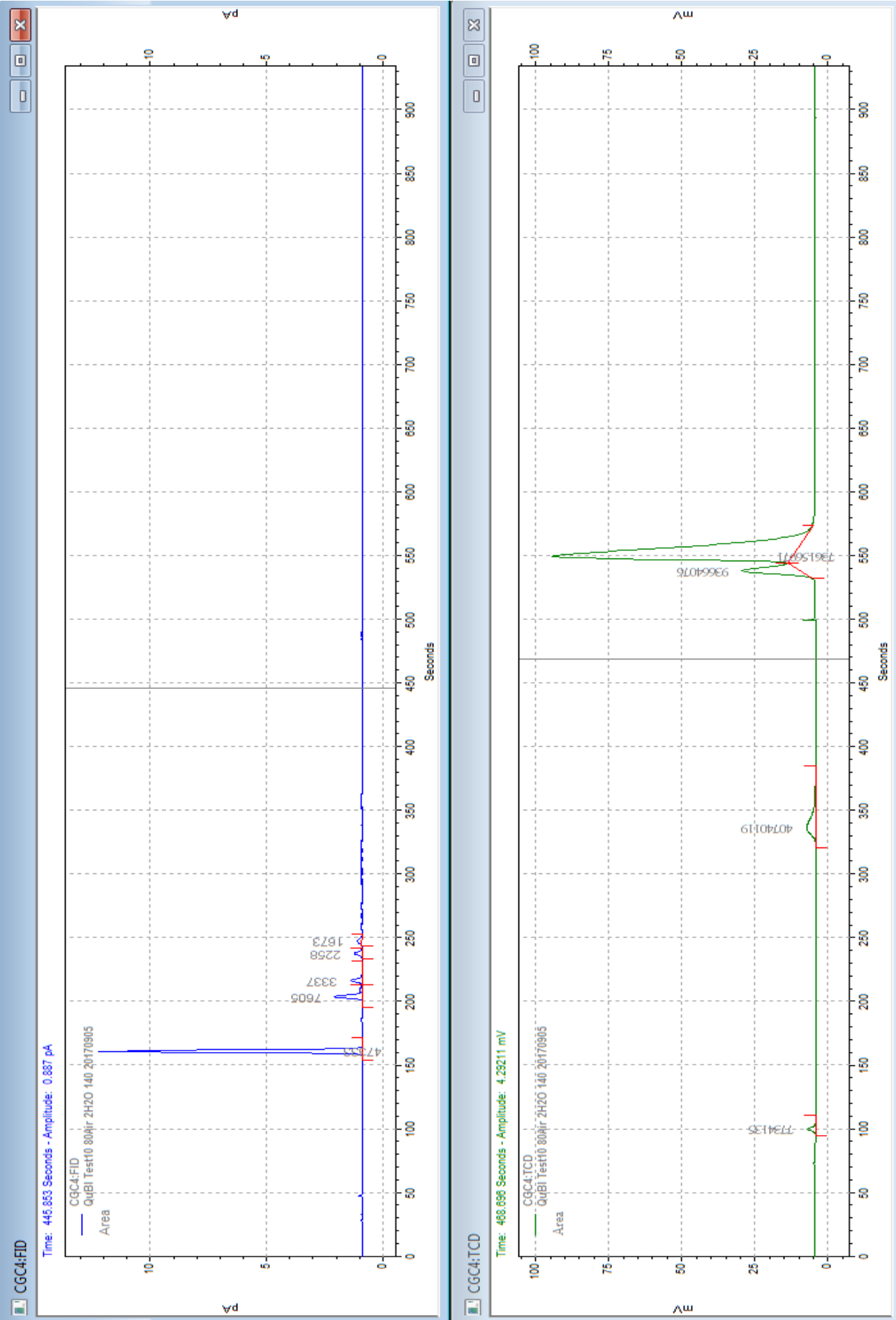


FIGURE 3.40: Gas chromatography "BaseCase-2H<sub>2</sub>O" - Beginning

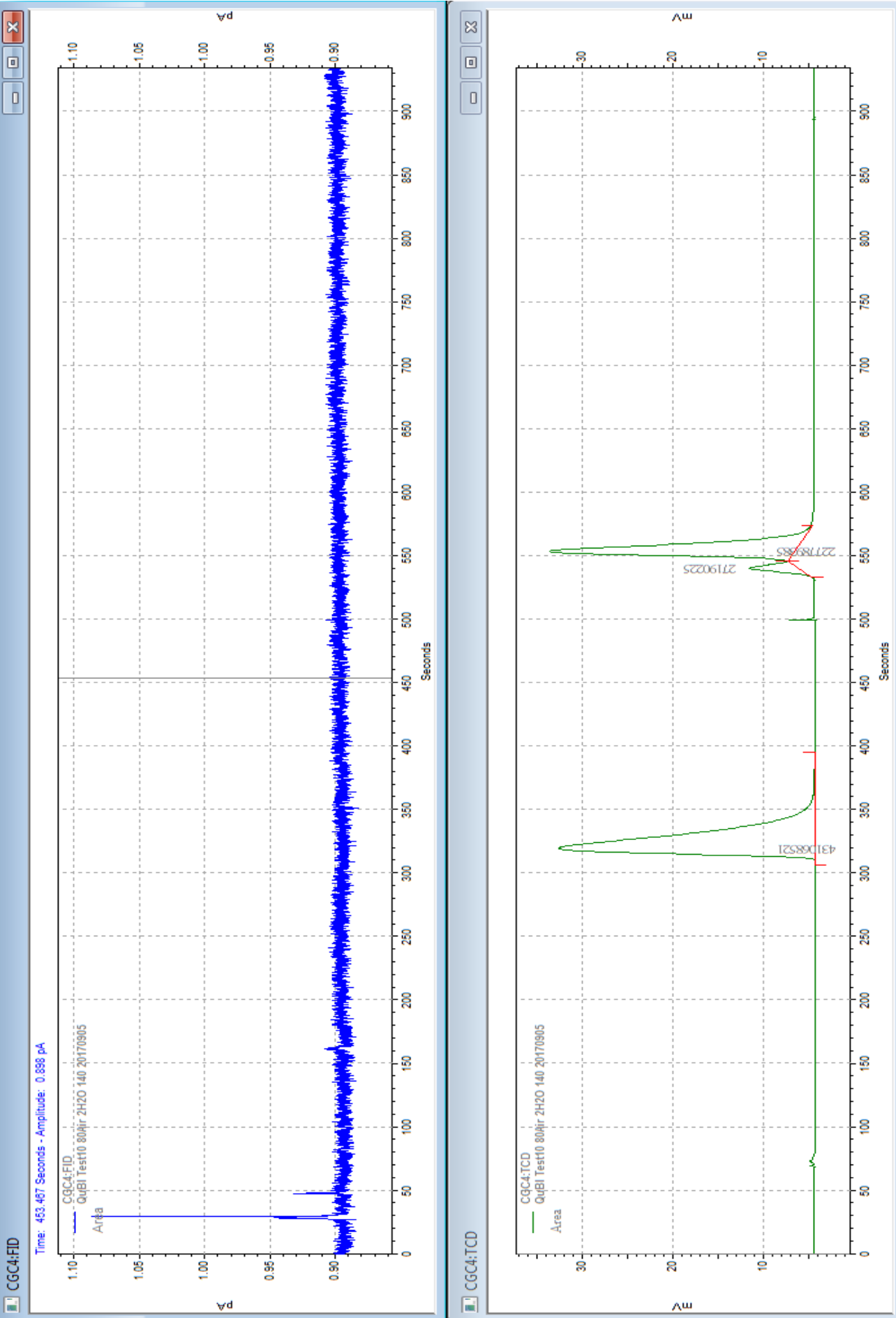


FIGURE 3.41: Gas chromatography "BaseCase-2H<sub>2</sub>O" - 270 minutes

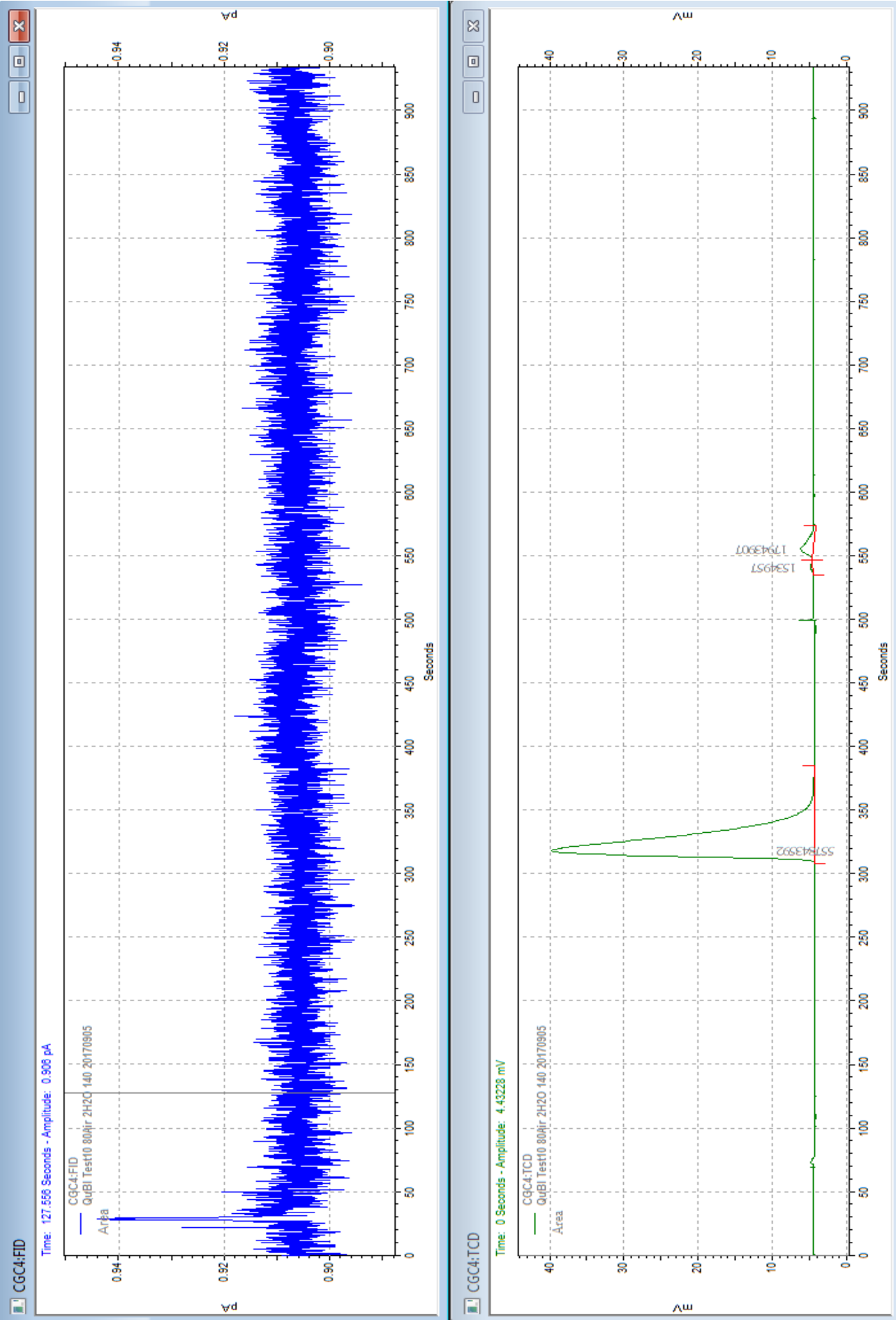


FIGURE 3.42: Gas chromatography "BaseCase-2H<sub>2</sub>O" - 810 minutes

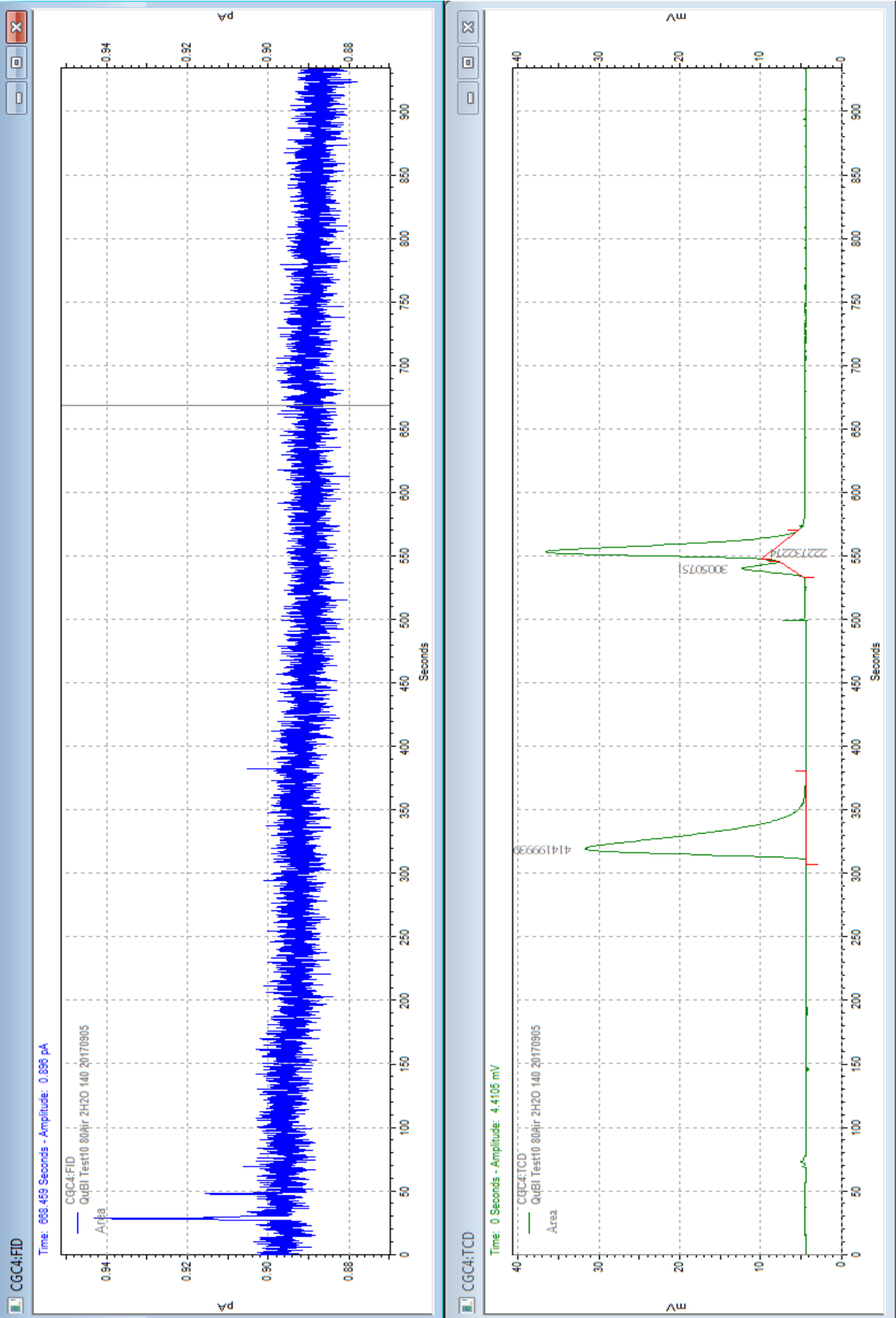


FIGURE 3.43: Gas chromatography "BaseCase-2H<sub>2</sub>O" - End

### 3.3.3 Impact of Carbon Dioxide

Before analysing the results, it is important to recall that samples subjected to  $\text{CO}_2$  in the gas mix were pretreated, unlike all the other samples. This pretreatment is already explained in detail in a previous section, but it is not the case of its purpose. This one was quite simple; the objective was to ensure that the sorbent was saturated with  $\text{CO}_2$  before the start of the degradation test. Therefore, in the beginning of the experiment, there was not any unknown quantity of  $\text{CO}_2$  that was adsorbed on the sorbent instead of flowing through the reactor. The drawback of that pretreatment is that the initial state of the sorbent is clearly different than for the other experiments, and so the comparison between the results can be harder.

The first result that can be observed is, as in the other section, the overview of the relative surface given by the BET and plotted in Figure 3.44. The samples considered are the fresh sorbent, "Base Case", "BaseCase-15 $\text{CO}_2$ ", "BaseCase-15 $\text{CO}_2$ -Repet", "BaseCase-2 $\text{H}_2\text{O}$ " and "BaseCase-15 $\text{CO}_2$ -2 $\text{H}_2\text{O}$ ". In fact, these samples are the same than those of the previous section. But here "Base Case" is compared to "BaseCase-15 $\text{CO}_2$ " / "BaseCase-15 $\text{CO}_2$ -Repet" and "BaseCase-2 $\text{H}_2\text{O}$ " is compared to "BaseCase-15 $\text{CO}_2$ -2 $\text{H}_2\text{O}$ ". And so, Figure 3.44 is here plotted in function of %  $\text{CO}_2$  rather than %  $\text{H}_2\text{O}$ .

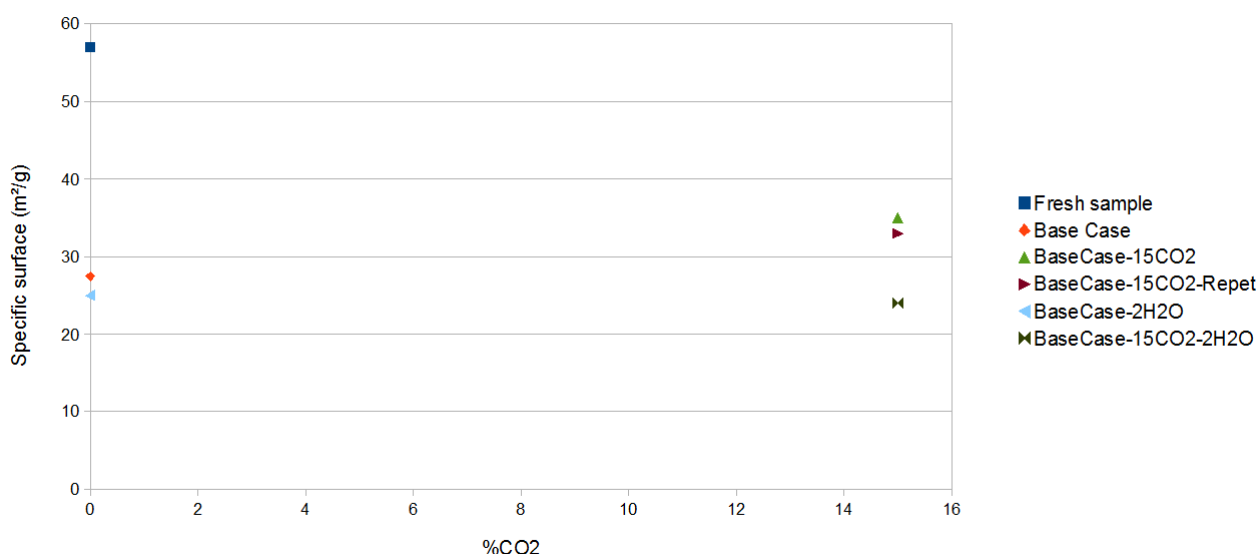


FIGURE 3.44: Specific surface in function of %  $\text{CO}_2$



Apparently, by seeing the results,  $\text{CO}_2$  protects partially the sorbent from structural degradation. The results for "BaseCase-15 $\text{CO}_2$ " / "BaseCase-15 $\text{CO}_2$ -Repet" are indeed in the upper range of relative surface measured, being comparable to "BaseCase-120". In the other hand, the last sample with  $\text{CO}_2$  "BaseCase-15 $\text{CO}_2$ -2 $\text{H}_2\text{O}$ " which was subjected to both water and  $\text{CO}_2$  shows a higher degradation. Indeed, the result obtained by the BET is smaller, and the range is about  $25 \text{ m}^2/\text{g}$ , similar to the base case. So, it seems that when there is water and  $\text{CO}_2$ , the positive effect of  $\text{CO}_2$  is dwarfed by the presence of water. The fact that  $\text{CO}_2$  seems to protect the sample can be explained with the following hypothesis :

Prior to the experiment, as stated in the previous section, the fresh sorbent was not out-gassed. And so, because of the presence of both water and  $\text{CO}_2$ , bicarbonate was formed. But no one will be able to say if the sorbent was at equilibrium or not. If it was not the case, the pretreatment with  $\text{CO}_2$  was able to saturate the sorbent. And because of the presence of water, even more bicarbonate were formed, reaching a new state closer to the equilibrium. This results globally in an increase of the structural properties. This hypothesis is interesting but does not explain why both water and  $\text{CO}_2$  do not increase the properties. If the hypothesis was correct, the mix of both water and  $\text{CO}_2$  would create more bicarbonate species, leading to an improvement of the structural properties. It would be interesting to perform the experiment with both water and  $\text{CO}_2$  another time to ensure the result obtained. It is possible that the result obtained is due to water saturating some pores. This will lead to a lower surface area. This hypothesis can be tested by using a well suited outgassing method prior to the BET measurements.

The GC results do not show anything interesting, as for the other experiments. One can check in the Appendix : Figure B.2 compared to Figure B.6/B.8 and Figure B.12 compared to Figure B.15. . For the sample with both water and  $\text{CO}_2$ , there was the same problem of variability of the gas flow rate than the one during the experiment when there was only water.

### 3.3.3.1 Repeatability

The repeatability is an important question. Both the characterisation methods and the degradation setup must be repeatable for the results to have a real and useful meaning.

During this thesis, there were several problems of repeatability or consistency that decrease the reliability of this work. In this section, these problems will be listed.

At first, the degradation setup can be considered. To promote repeatability, the preparation of the degradation experiments were all the same. But one element was not quite the same between the very first experiment and the last experiment for example. This was the real mass of the sample. In the beginning, the fresh sorbent was "more fresh", this freshness decreasing each time the bottle of sorbent was opened to ambient air. And because of that fact, the mass tested was changing with time, which is detrimental to the repeatability of the measurements. This difference is not evaluated, and there are no real ways with the data collected to assess the evolution of water in the fresh sorbent with time.

Two experiments show a very bad potential repeatability : the experiment with water and the experiment with both water and CO<sub>2</sub>. Indeed, as stated in a previous section, the gas flux when water was present was really not constant. The variability was really important and the pressure was higher than the other experiments. The last increase in pressure was not desired and not measured accurately. One would say that these experiments can not be repeatable with this less control of different parameters as important as the pressure or the incoming gas composition. And so, if one would try to repeat the results of these experiments, the variability of the operating conditions will be a real problem.

All the results in pycnometry excluding one are quite consistent. To check the repeatability, one would measure the same sample multiple times in a row and take the means. But in this work, this was not done. However, there is still three results that are different, difference that can not be explained, and one result that is probably aberrant. This last is probably due to the low mass tested as stated previously, meaning that this result is due to a bad use of the apparatus.

The thermogravimeter shows a good repeatability. Two similar experiments were performed in this thesis, both testing fresh sorbent in the TG, and the results were similar. The same can be said about the mass spectrometer.

One would say that gas chromatograph was quite consistent. The results were indeed quite consistent between each samples excepting those with water. The main problem with the GC was that nothing was detected.

The BET in the other hand shows several problems of repeatability and consistency.

There are different categories of problems : at first, problem of repeatability from one apparatus compared to the other one. Short reminder, because of a technical problem, ASAP was not available for all the measurements. For this last reason, Sorptomatic was used instead. But as it can be seen on Table 3.3, there was a huge difference between the result from ASAP and that of Sorptomatic for the fresh sorbent ( $57 \text{ m}^2/\text{g}$  for Sorptomatic compared to  $35 \text{ m}^2/\text{g}$  for ASAP). With this much difference, it was not really possible to compare the values from one apparatus with those of the other. These differences between the two experiments were assigned to the outgassing method which was not really suited for this type of samples.

The second type of problems is the problem of repeatability with the same sample. There is two examples in Table 3.3, "BaseCase-15CO<sub>2</sub>" and "100O<sub>2</sub>-140T-15D" where it can be seen that for both samples, two measurements lead to different values : 49 and 35  $\text{m}^2/\text{g}$  for "BaseCase-15CO<sub>2</sub>" and 6 and 24  $\text{m}^2/\text{g}$  for "100O<sub>2</sub>-140T-15D". The difference were clearly out of the error range for both of these samples. Both of these samples were sent to Sorptomatic, and these inaccuracies are the result of problems during the experiments. For example, for some samples, the nitrogen was condensing in the test tube instead of just filling the sample pores, resulting in the failure of the experiments. These problems come from a bad use of the apparatus considering the specificity (low surface area) of the samples.

Another reasons of the lack of repeatability for two measurements of the same sample is the mass send into the apparatus. For both ASAP and Sorptomatic, some samples were too small; therefore, the accuracy and the error range specified by the apparatus were not ensured.

## Chapter 4

# Conclusion

### 4.1 Conclusion of the experiments

In this section, the major results of the experimental section will be synthesised.

- Outgassing

Outgassing was defined as one of the determinant step to obtain repeatable and reliable results. Outgassing must be done at about 70 °C at least to desorb the chemisorbed species.

- Sintering

Degradation experiments put in evidence the possibility of the sintering of the beads. This must be checked accurately with a size distribution measurement of the beads.

- Impact of temperature

Structural degradation increases with temperature. Thermal degradation detected below 150 °C. Conclusion not in agreement with some results from [\[11\]](#). New tests of pure thermal degradation in the experimental setup would be interesting to conclude properly.

- Impact of oxygen

Oxygen is the major parameter. This parameter is more important than temperature. The mechanisms of oxidative degradation at 120 and 140 °C are the same. Structural degradation increases with oxygen.

- Impact of H<sub>2</sub>O

Water does not seem to have an effect. "Base Case" and "BaseCase-2H<sub>2</sub>O" had similar specific surface area.

Hypothesis 1 : when water and CO<sub>2</sub> are present in the sorbent prior to the experimentation, there is formation of bicarbonate. Then, the formation of more carbonate during the experiment do not change the structural properties in a measurable way.

Hypothesis 2 : since there is no influence of water when some bicarbonate are formed prior to the degradation compared to the base case where bicarbonate are formed prior to the degradation for the same reasons, this means that the only influence of water for Lewatit is the formation of bicarbonate species. If there was another influence of water, regarding the experimental conditions, the structural properties would have been different between the two experiments.

- Impact of CO<sub>2</sub>

CO<sub>2</sub> seems to stabilise the sorbent. Smaller structural degradation when CO<sub>2</sub> is present. Probably due to the formation of bicarbonate with the water present in the fresh sorbent prior to the experiments. When both water and CO<sub>2</sub> are used, no more positive effect of CO<sub>2</sub> on the properties. Need another experiment with both water and CO<sub>2</sub> to clarify this effect; and need to use a well suited outgassing method before BET measurements to ensure that this results is not due to water filling the pores.

## 4.2 Further improvements

At the end of this thesis, after the different discussions and considerations, it is obvious that a lot of improvements are possible for a future study on the same subject. In this section, several ways to improve this thesis will be listed.

- Characterisation methods

After the analysis of the results, it seemed that the different methods of characterisation were not all well suited to understand completely the degradation of the sorbent. Obviously, typical CO<sub>2</sub> adsorption measurement would give precious information concerning the degradation. This will not be a replacement method of those used in this thesis but rather a complementary tool. Indeed, the characterisation methods used were not that badly chosen. BET results are useful to observe the structural degradation and the state of the pores. But, in this thesis, they were not sufficient alone to understand fully the behaviour of the material under the test conditions. By simply testing the capacity of adsorption, one would be able to quantify with a value the loss in efficacy of the sorbent, the loss in CO<sub>2</sub> capacity of the sorbent.

For the same reasons, IR-measurement would be very good to check the evolution of the different bonds within the material, in particular the amine bonds. Finally it would be very interesting to measure the beads size distribution to evaluate the sintering of the beads.

- Thermogravimetry + Mass Spectrometry

The TG+MS used in this thesis have a real potential for degradation experiments. Indeed, the apparatus can continuously increase the temperature at a certain speed or keep the temperature constant depending on what is asked. And the mass spectrometer is linked in real time and analyses at each time and each temperature which chemical species are presents. With this apparatus, it is really possible to program a temperature profile for specific degradation experiments, and with the possibility to really have an insight into the experiment thanks to the mass spectrometer. There are nevertheless three major drawbacks to this new method. At first, the mass that can be send in the TG is quite low, the maximum being about 30mg with this sorbent. This limits the possible uses of the resulting degraded sorbent. For example, the ASAP would need about 0.6-1g of the sorbent to reach its specifications in term of specific surface to guarantee the reliability and repeatability of the measurement. Then, with long experiments, the mass spectra would possibly be really difficult to be analysed. Indeed, the mass of information for long experiments can be difficult because of the nature of the spectra combined to the mass of information (reminder : the species are broken and/or ionised and a specific mass on charge can be the same for different

species). And finally, the gases that can be send in the TG are quite limited, namely, pure air or pure CO<sub>2</sub>. This limits the possibilities in term of degradation experiments. In this thesis, the TG was not used for degradation experiments because of these limitations and because of a lack of time.

- Mass Spectrometer and Gas Chromatography

The experimental setup was linked to a gas chromatograph. But, instead of this GC, a mass spectrometer would have been a really powerful tool to obtain accurate results. In this thesis, the GC was not really useful and did not really detect anything, and so, the MS would have been an interesting alternative to obtain a better overview of the degradation.

- Outgassing

The outgassing was not well suited in this thesis. Indeed, using simply typical outgassing method at ambient temperature for this sorbent was a really bad idea. The inaccuracy of the results obtained are probably partially due to this bad outgassing method.

Another problem with outgassing was the absence of outgassing before the tests. This means that the real mass of sorbent was changing with time because of the decrease in freshness of the sorbent, and the natural variability of this non controlled adsorption.

### 4.3 Conclusion

This thesis as well as my master's degree come to an end. During this thesis, I had the opportunity to work on several different apparatus. I learnt a lot about these different techniques, and my technical skills increased a lot too. One of the major things I have learned from this master thesis is really what is called "systeme D" in french, which is an expression that expresses the resourcefulness. Indeed, during such a thesis, everything has not worked well every time.. And you do not have always the equipment needed for the task you are performing. And so, you need to think how to by pass the difficulty, you search other ways, ... In my thesis, I was mostly working alone and so I had really to go through the difficulties with my own strength. Of course, my promoter and co-promoter were there to help me when I was really struggling, for what I would really like to them a lot. The same for the technician Jeremy Geens who helped me a LOT too when I was really struggling and who gived answers to my very numerous questions.

This thesis was an opportunity for me to learn more about how to plan experiments too, to organise my days and weeks. I had to really organise myself because of the high duration of the experiments. I had to design my experiments, with my promoters'help as well as from Mister Brilman, from Twente. About that, this thesis was a possibility to have contact with another university. Indeed, this thesis has been made in collaboration with the University of Twente, with the group of Mister Brilman. It was interesting to have a contact with them to plan experiment and speak about the subject to go further. I thing that it would have been interesting to have more contacts with them, in order to increase the exchange between them and me and enhance the quality of my work with this share of information.

This thesis has been a very good experience. Unlike the beginning of this year, I really feel I am ready for the industrial world and to begin as an engineer in the active life.



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# Appendix A

## MS Spectra

In this chapter, the MS spectra obtained will be listed for one experiment with fresh sorbent. For the peaks 17, 18 and 44 ( $m/z$ ), those from a second experiment with fresh sorbent will be showed as well to check the repeatability.

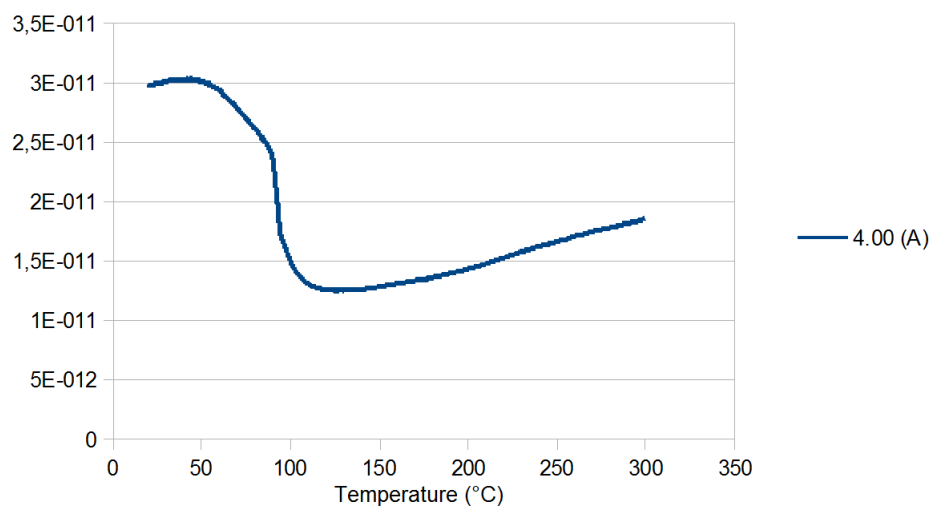
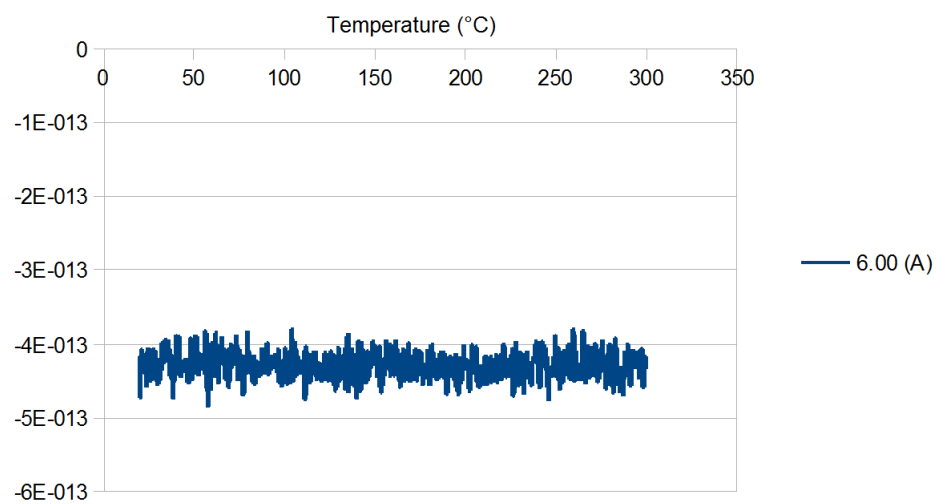
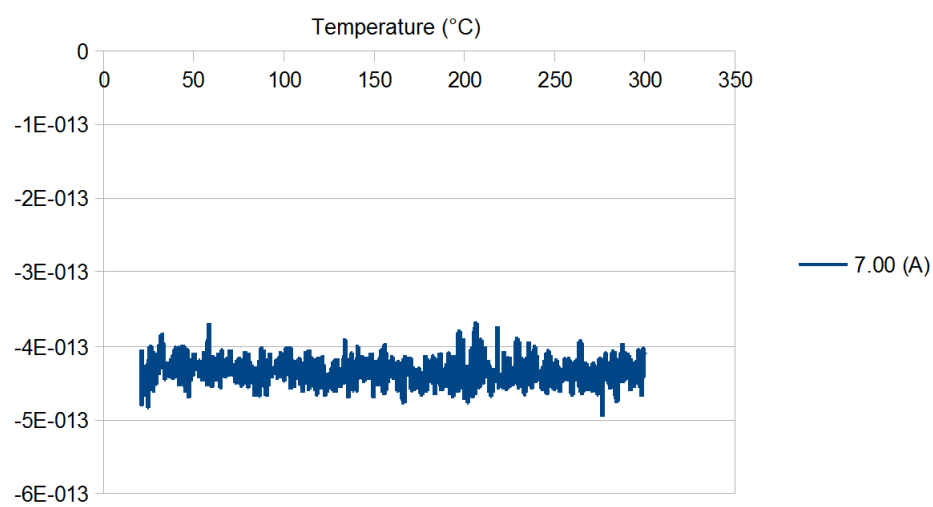
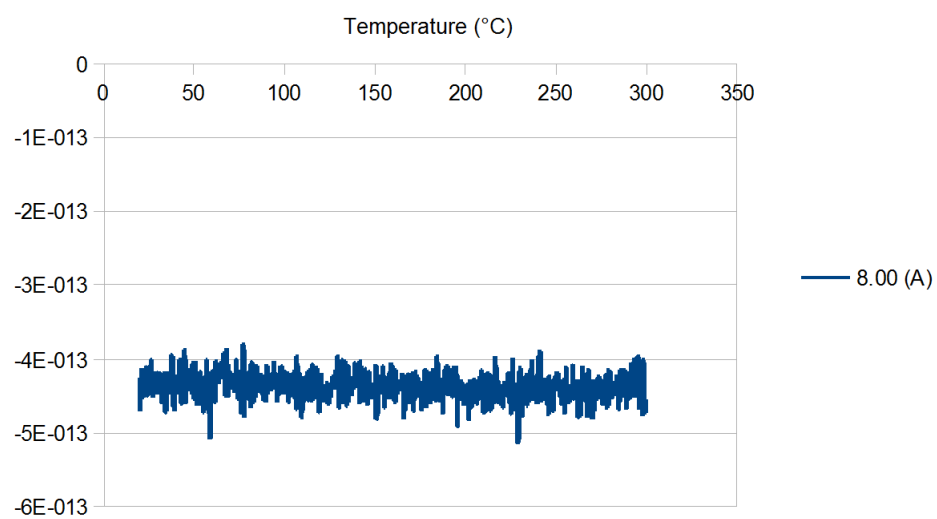
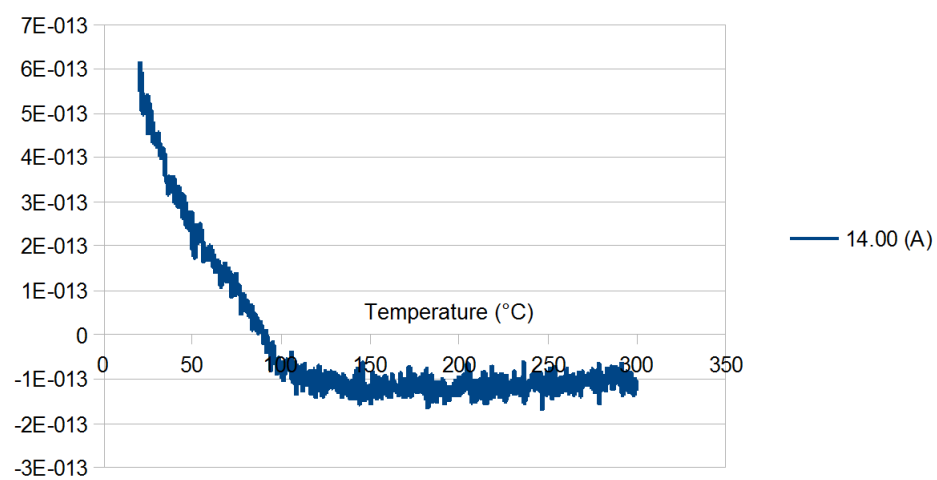


FIGURE A.1: MS spectra - 4.00 ( $m/z$ )

FIGURE A.2: MS spectra - 6.00 ( $m/z$ )FIGURE A.3: MS spectra - 7.00 ( $m/z$ )

FIGURE A.4: MS spectra - 8.00 ( $m/z$ )FIGURE A.5: MS spectra - 14.00 ( $m/z$ )

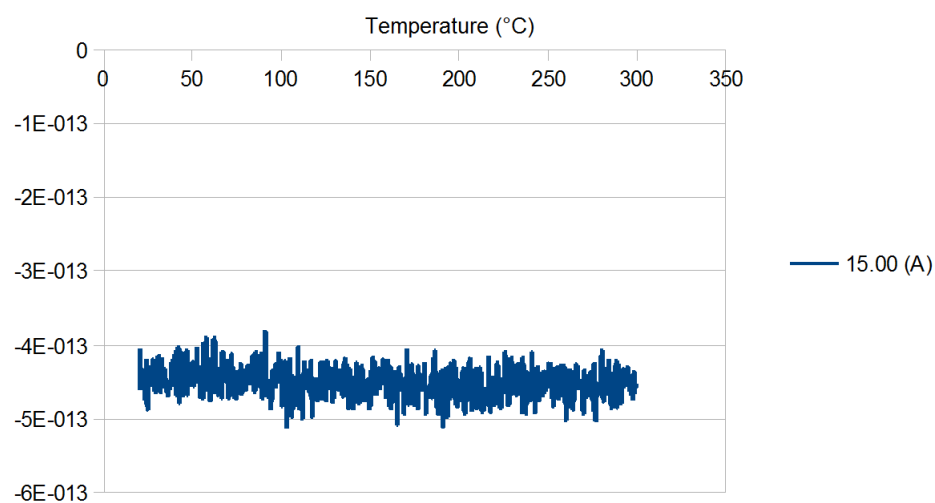


FIGURE A.6: MS spectra - 15.00 (m/z)

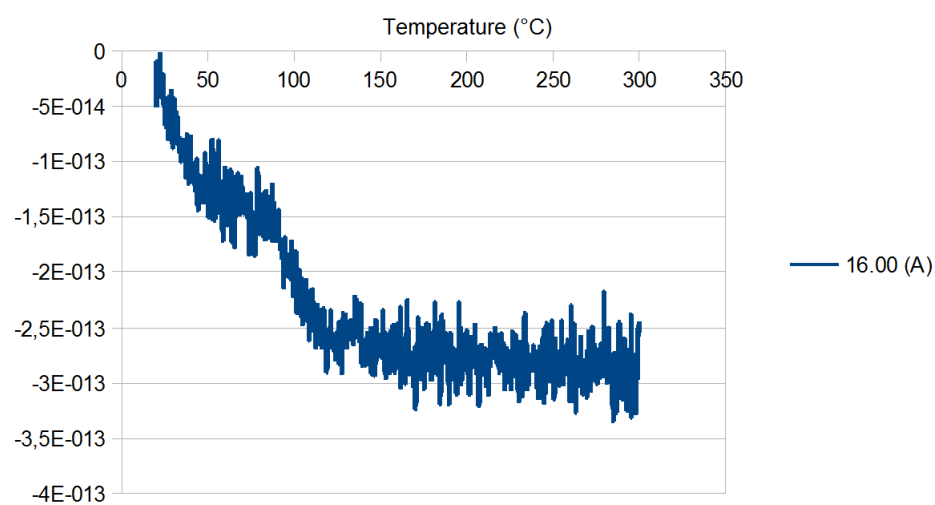


FIGURE A.7: MS spectra - 16.00 (m/z)

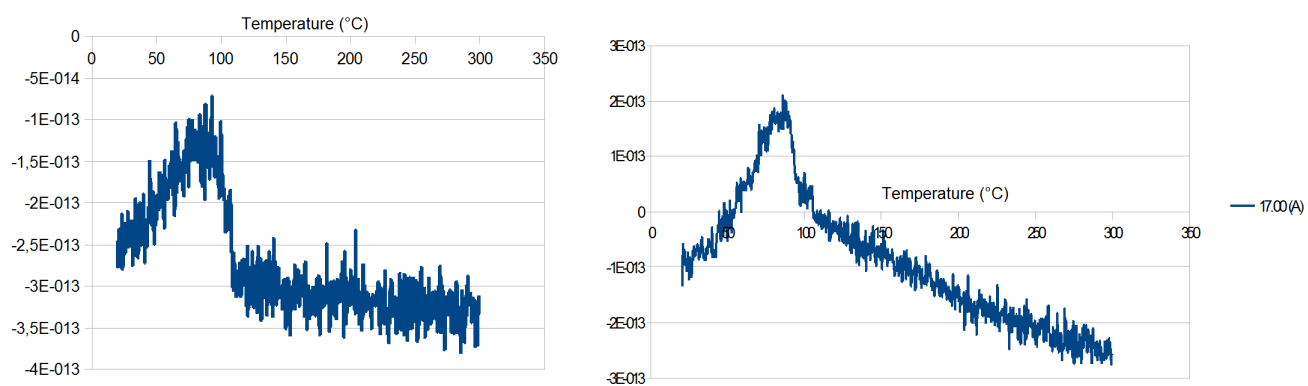


FIGURE A.8: Left : Second experimentation with fresh sorbent; Right : First experimentation

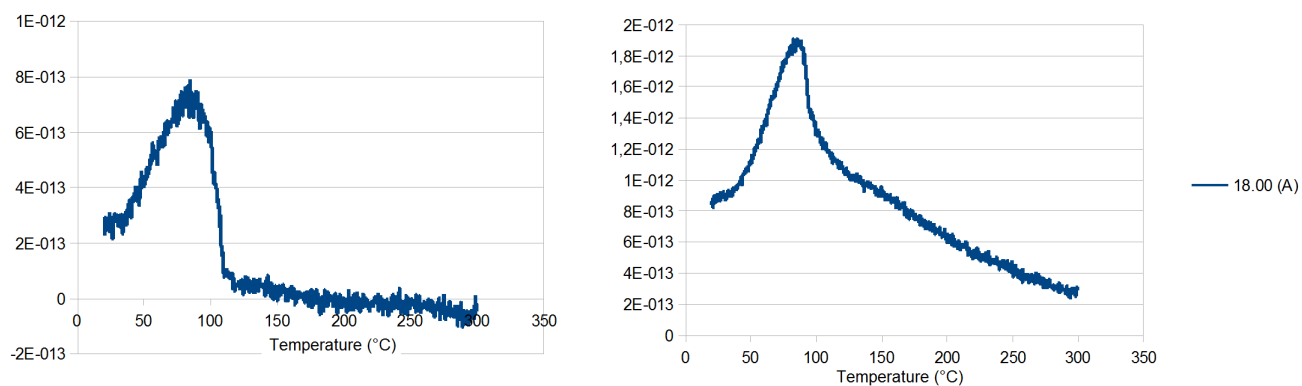


FIGURE A.9: Left : Second experimentation with fresh sorbent; Right : First experimentation

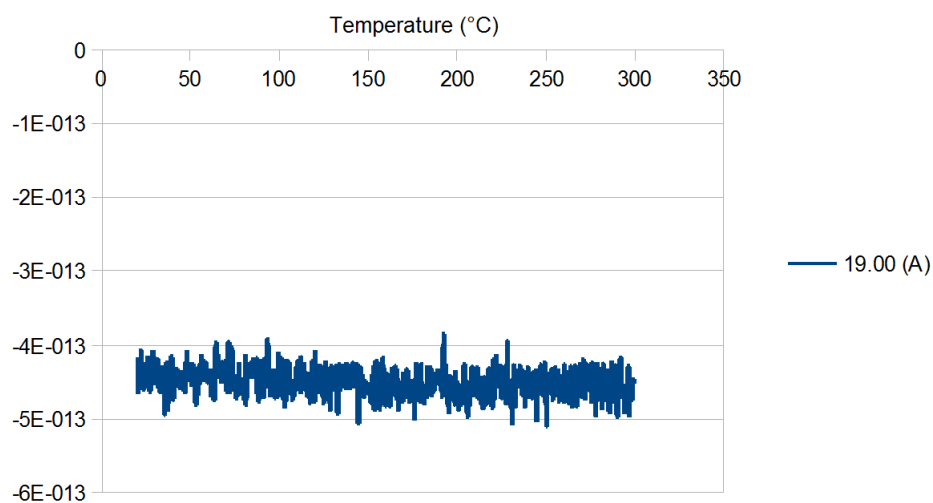


FIGURE A.10: MS spectra - 19.00 (m/z)

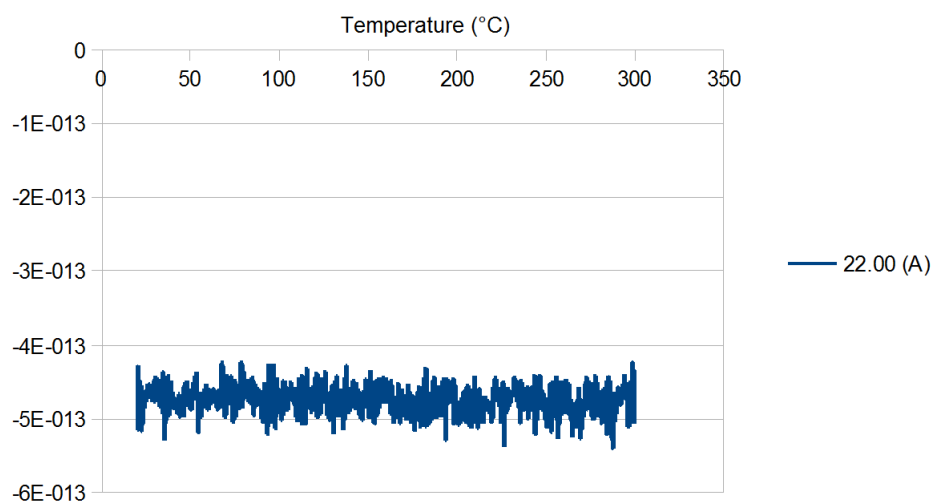
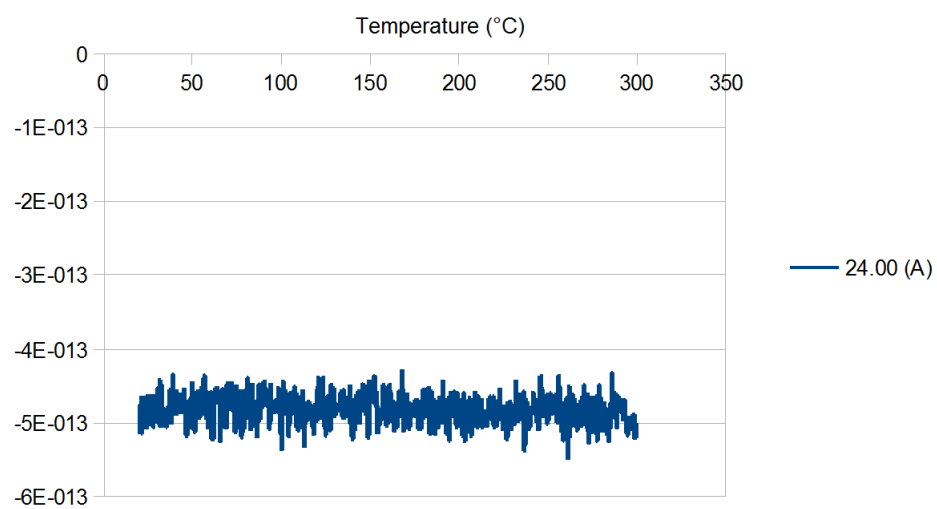
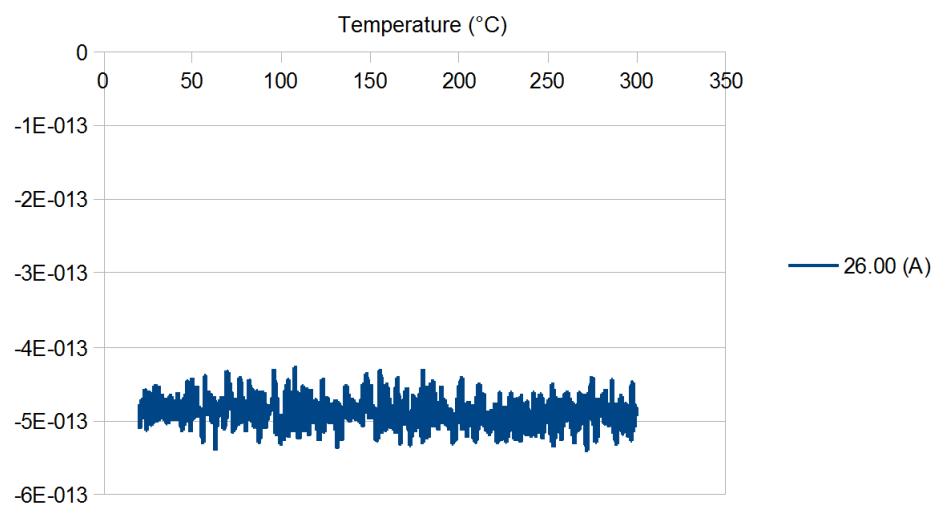
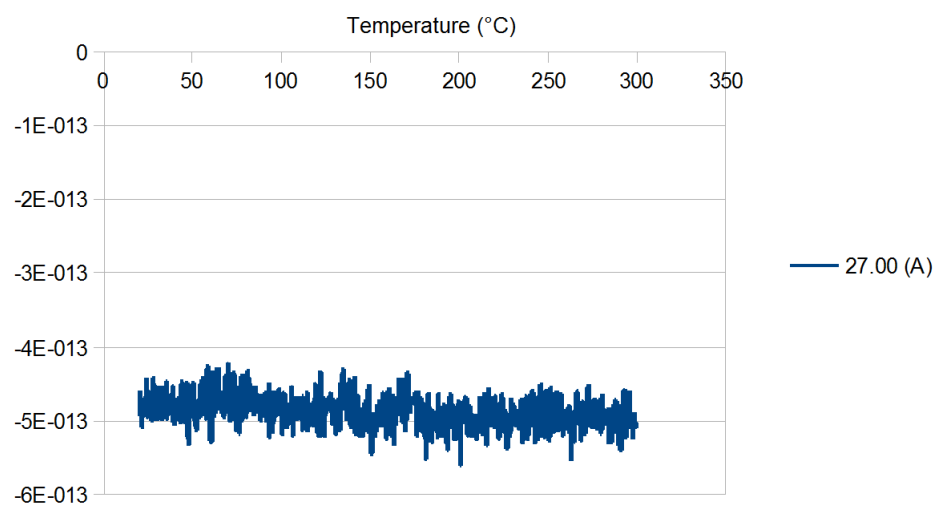
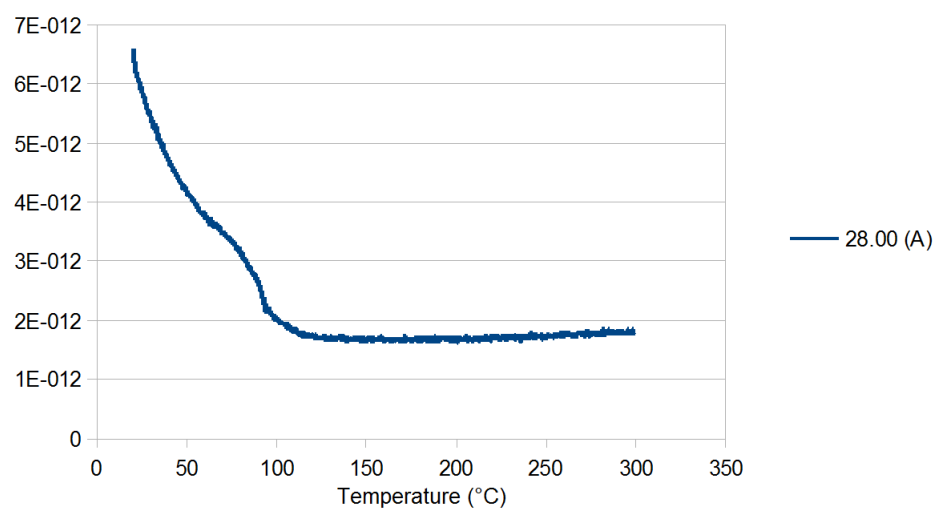
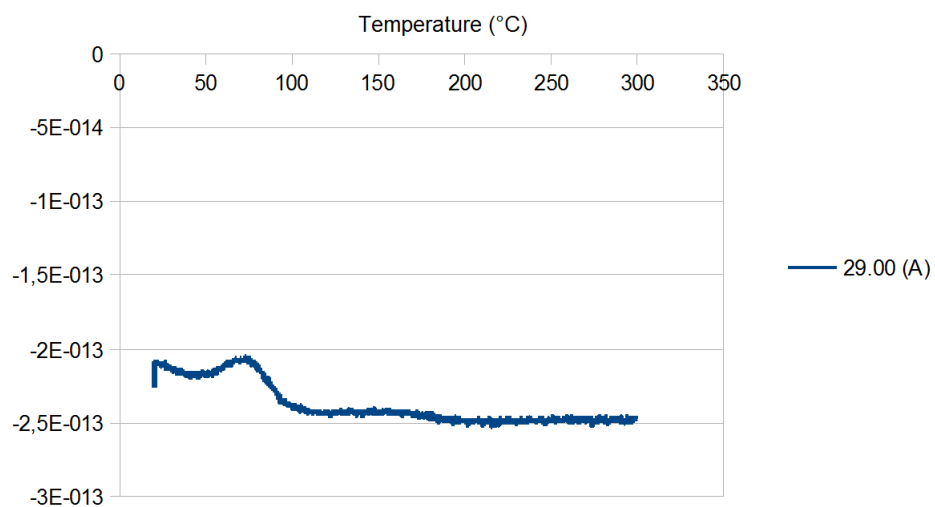
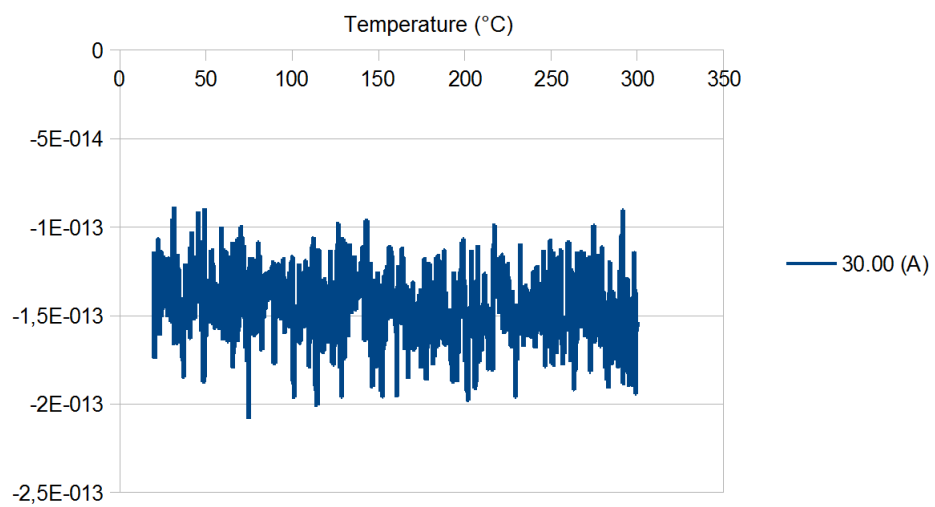


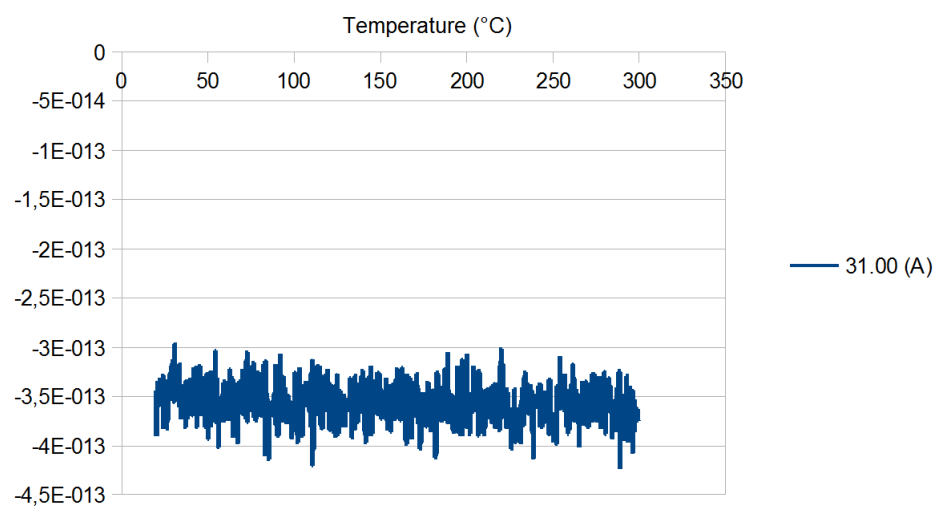
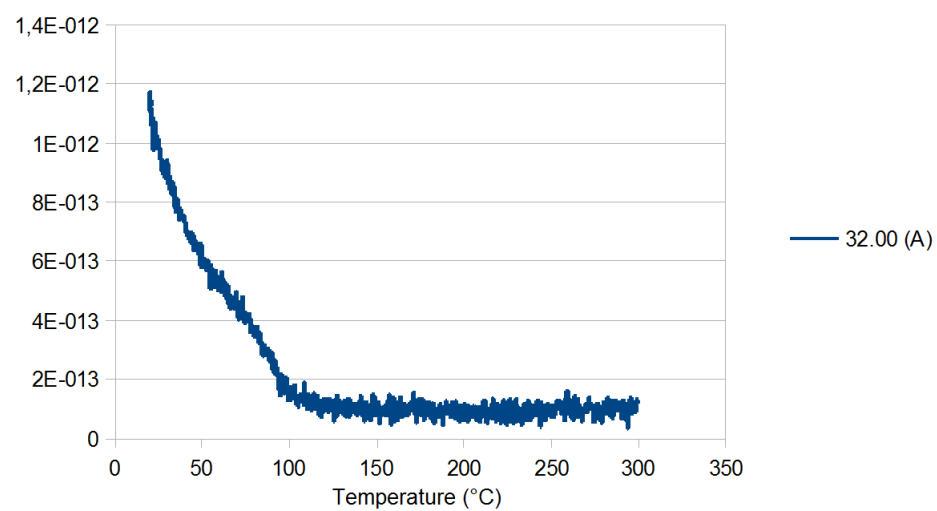
FIGURE A.11: MS spectra - 22.00 (m/z)

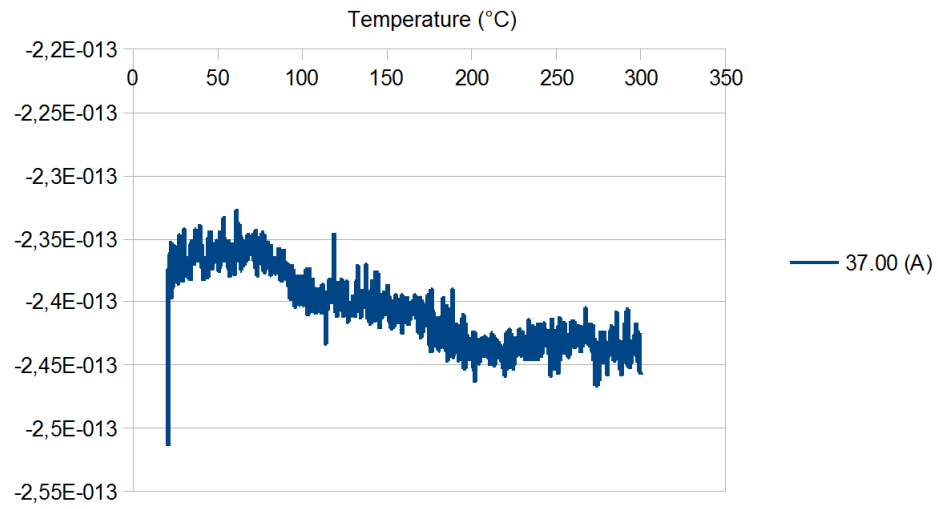
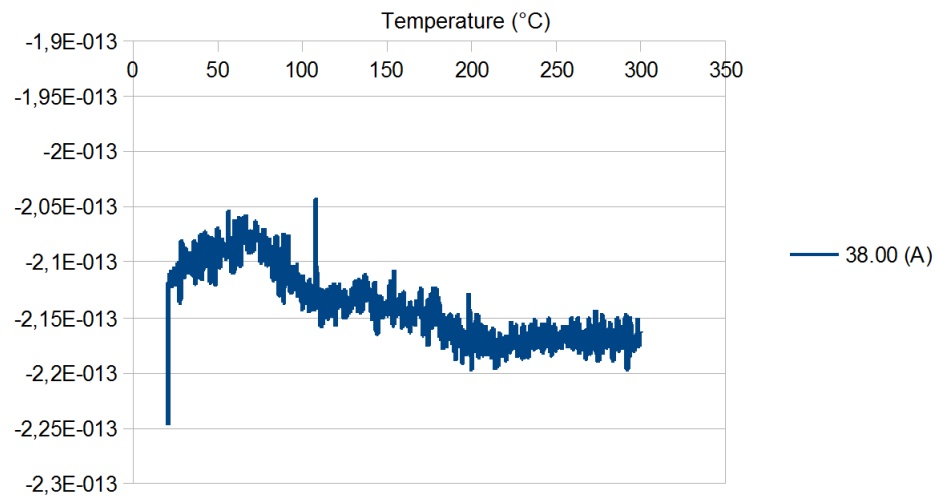


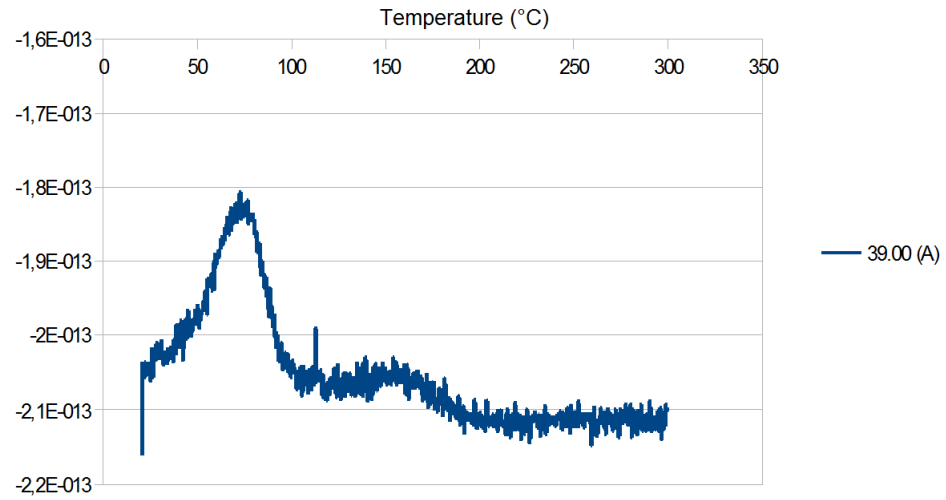
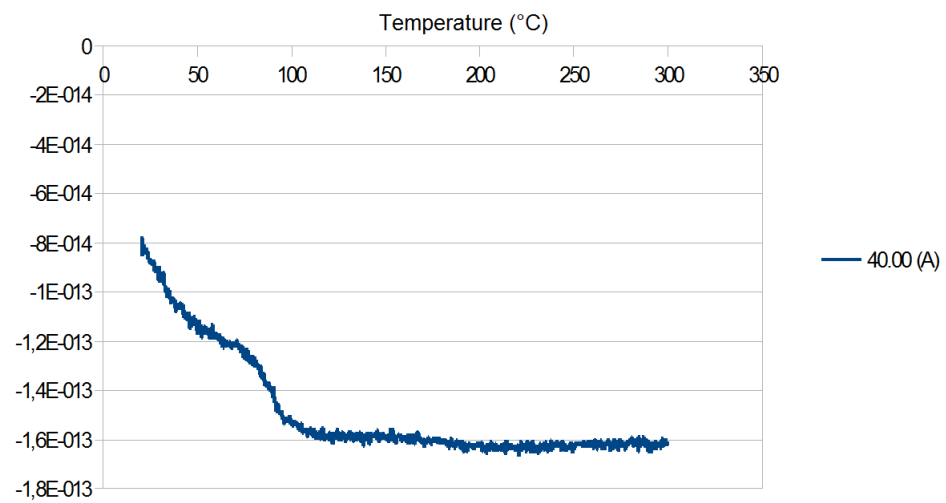
FIGURE A.12: MS spectra - 24.00 ( $m/z$ )FIGURE A.13: MS spectra - 26.00 ( $m/z$ )

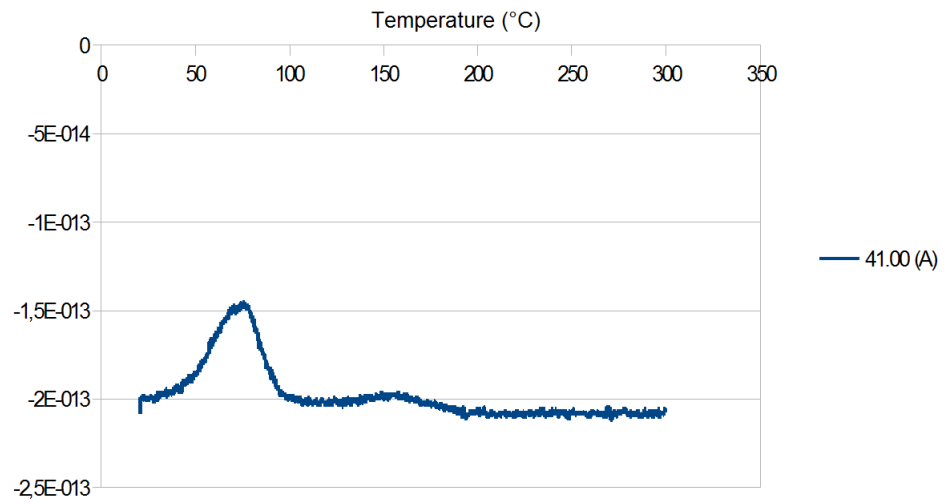
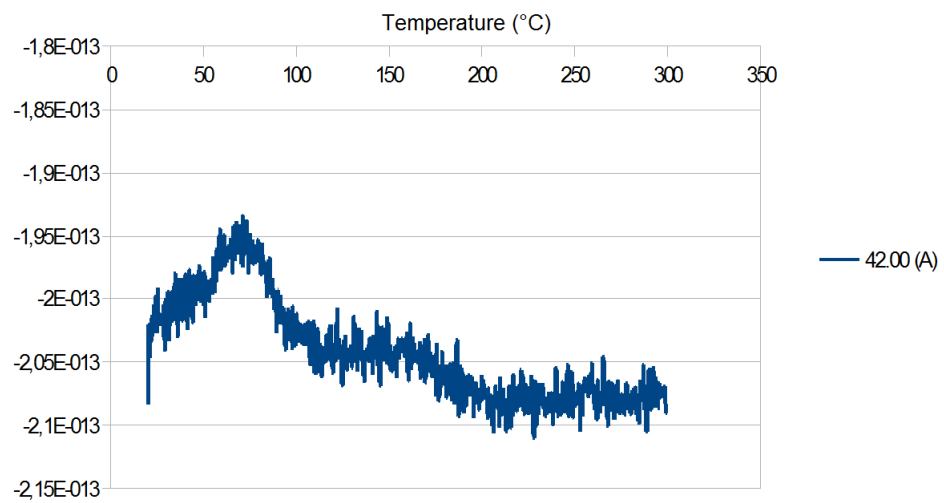
FIGURE A.14: MS spectra - 27.00 ( $m/z$ )FIGURE A.15: MS spectra - 28.00 ( $m/z$ )

FIGURE A.16: MS spectra - 29.00 ( $m/z$ )FIGURE A.17: MS spectra - 30.00 ( $m/z$ )

FIGURE A.18: MS spectra - 31.00 ( $m/z$ )FIGURE A.19: MS spectra - 32.00 ( $m/z$ )

FIGURE A.20: MS spectra - 37.00 ( $m/z$ )FIGURE A.21: MS spectra - 38.00 ( $m/z$ )

FIGURE A.22: MS spectra - 39.00 ( $m/z$ )FIGURE A.23: MS spectra - 40.00 ( $m/z$ )

FIGURE A.24: MS spectra - 41.00 ( $m/z$ )FIGURE A.25: MS spectra - 42.00 ( $m/z$ )

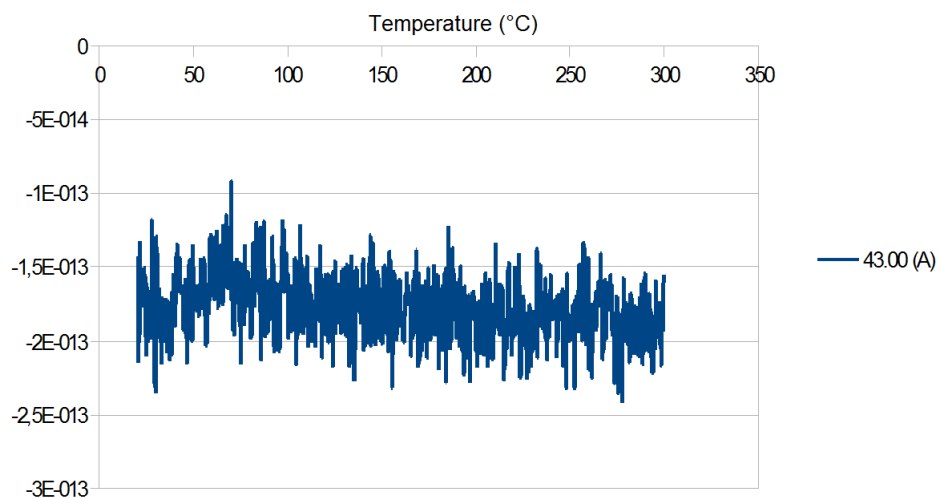


FIGURE A.26: MS spectra - 43.00 ( $m/z$ )

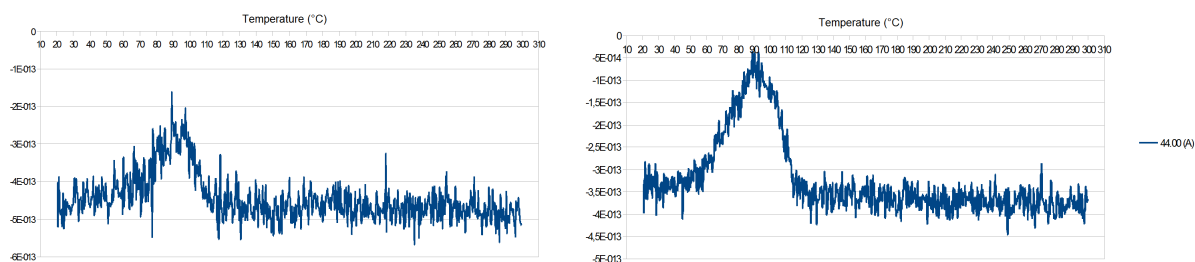


FIGURE A.27: Left : Second experimentation with fresh sorbent; Right : First experimentation

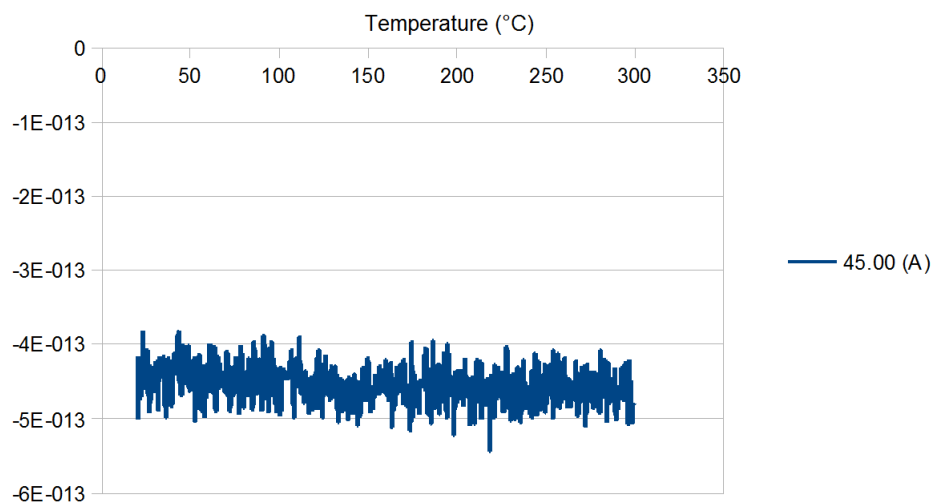


FIGURE A.28: MS spectra - 45.00 ( $m/z$ )



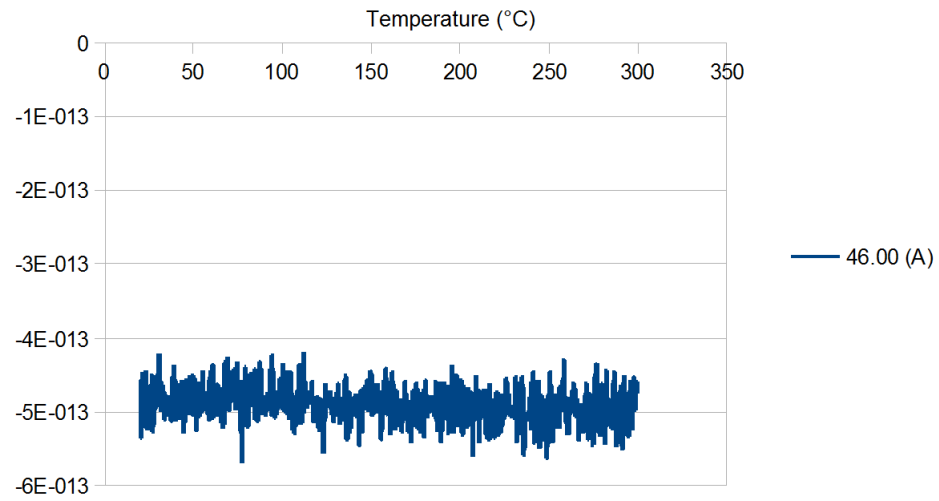


FIGURE A.29: MS spectra - 46.00 (m/z)

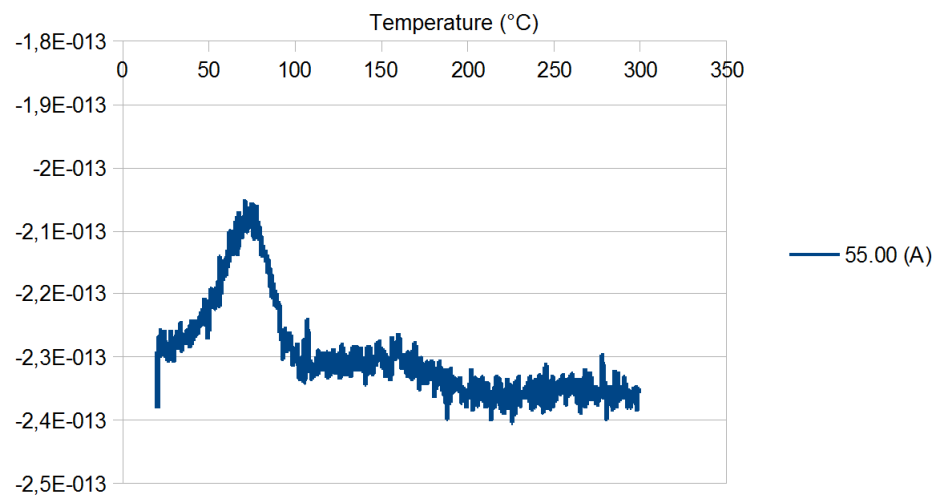


FIGURE A.30: MS spectra - 55.00 (m/z)

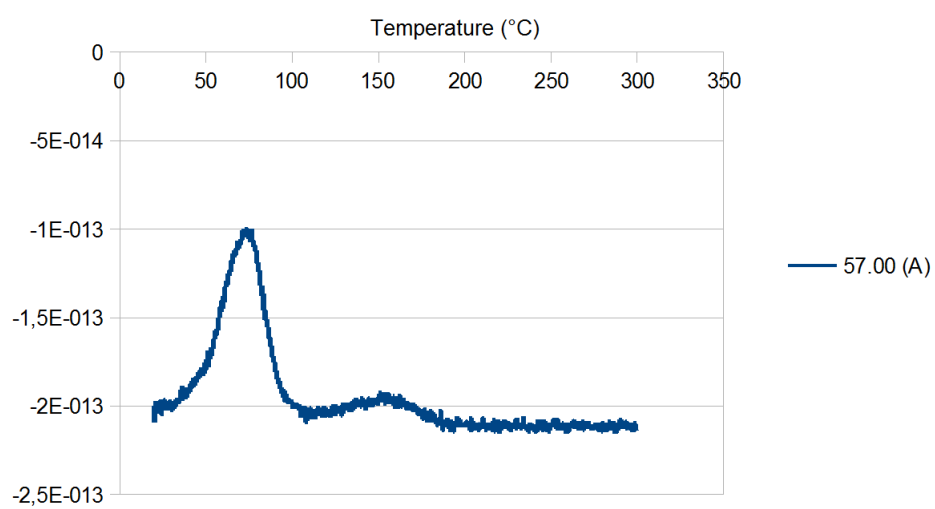


FIGURE A.31: MS spectra - 57.00 (m/z)

## Appendix B

### GC Results

In this section, major GC results will be plotted. In general, 2 figures for each experiments will be here. One at the beginning (20 minutes after beginning), the second at the end of the experiment. For the tests with water, more results are shown. It is to show the fact that the installation was not completely able to use so many water at the temperature of the test with the considered sorbent. The GC results show some big differences between one experiment to another. It was possible to see this instability during the experiments because there was a small increase in pressure, which means that the incoming gas did not flow perfectly.

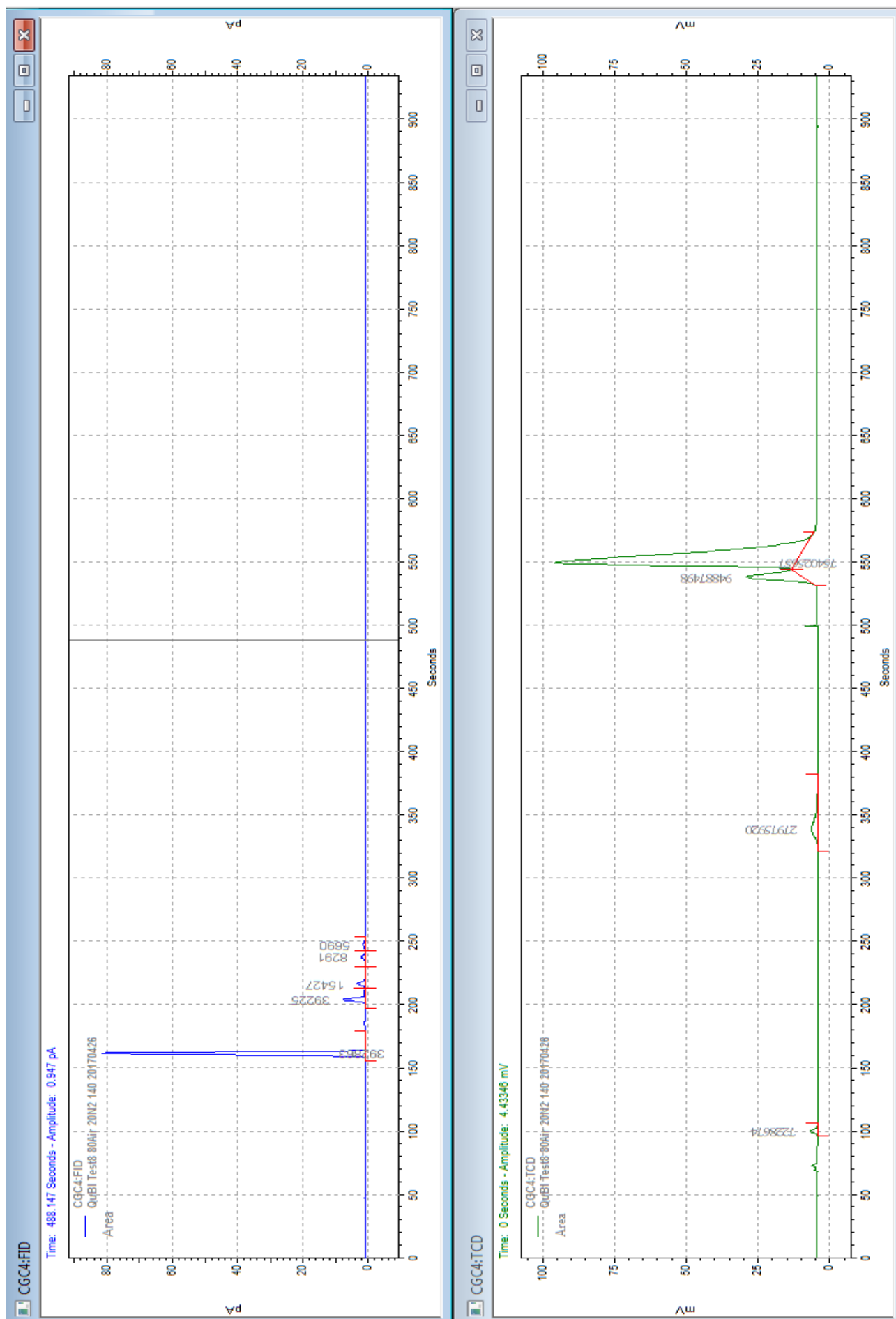


FIGURE B.1: Base Case - Beginning

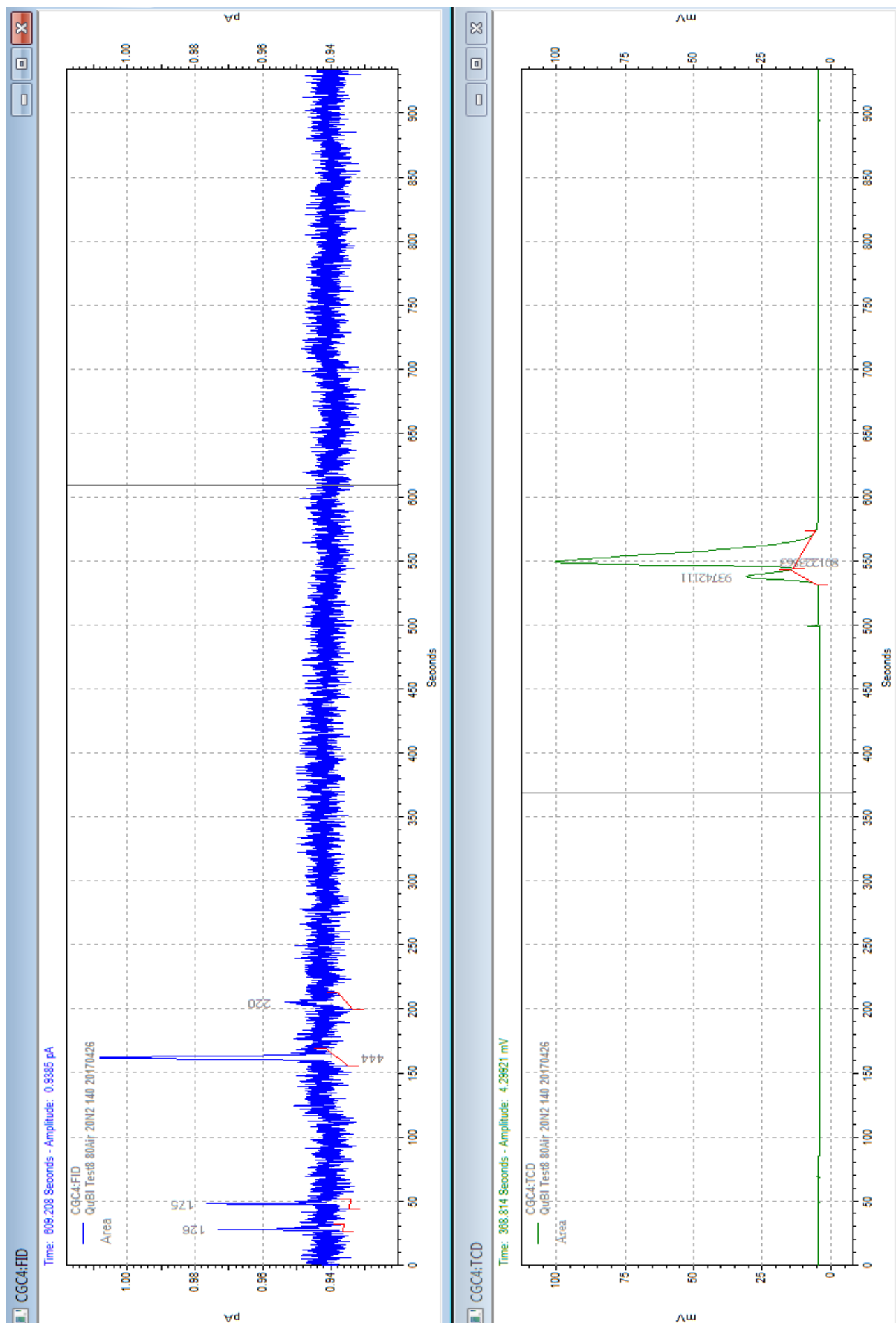


FIGURE B.2: Base Case - End

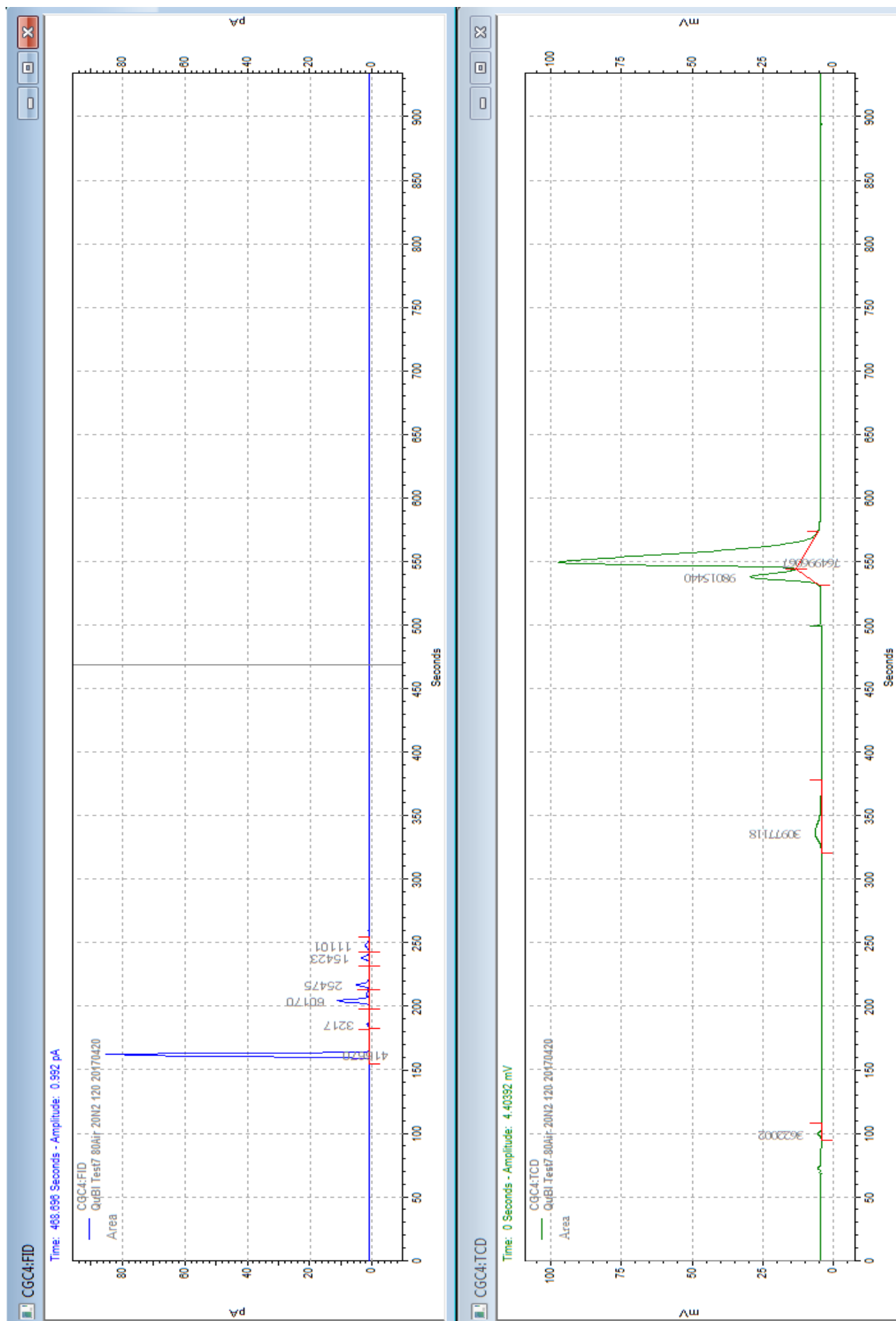


FIGURE B.3: BaseCase-120T - Beginning

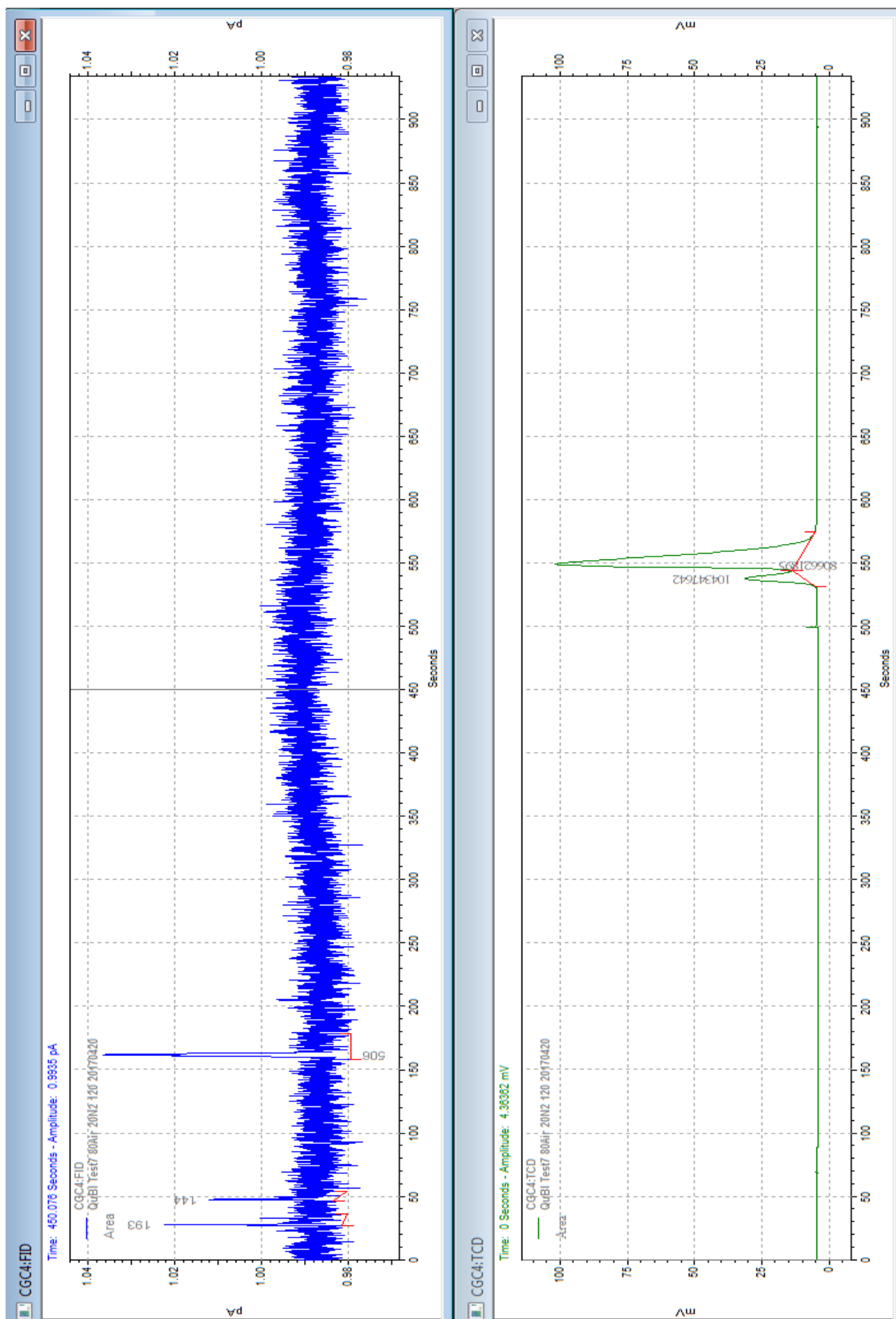


FIGURE B.4: BaseCase-120T - End

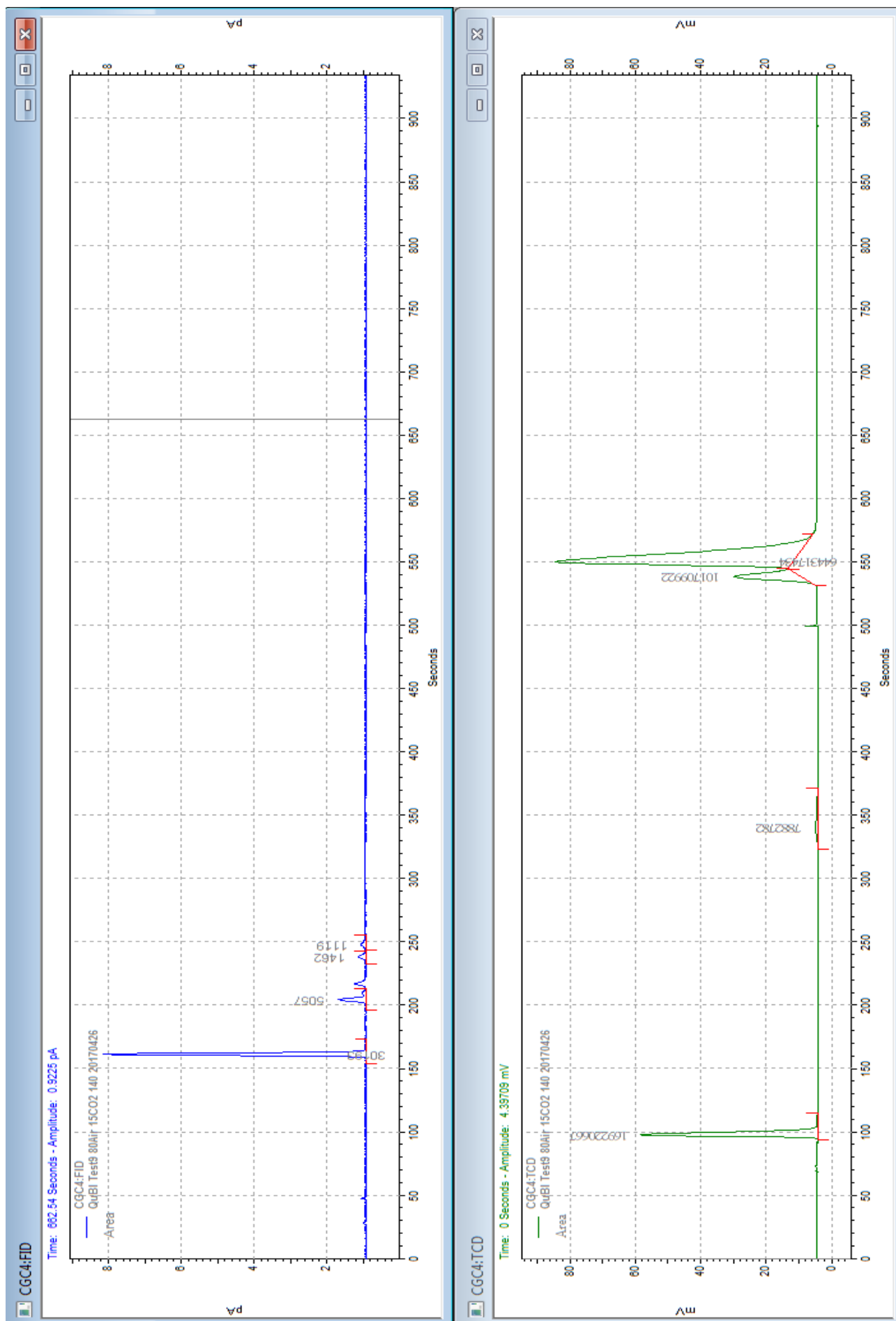


FIGURE B.5: BaseCase-15CO2 - Beginning



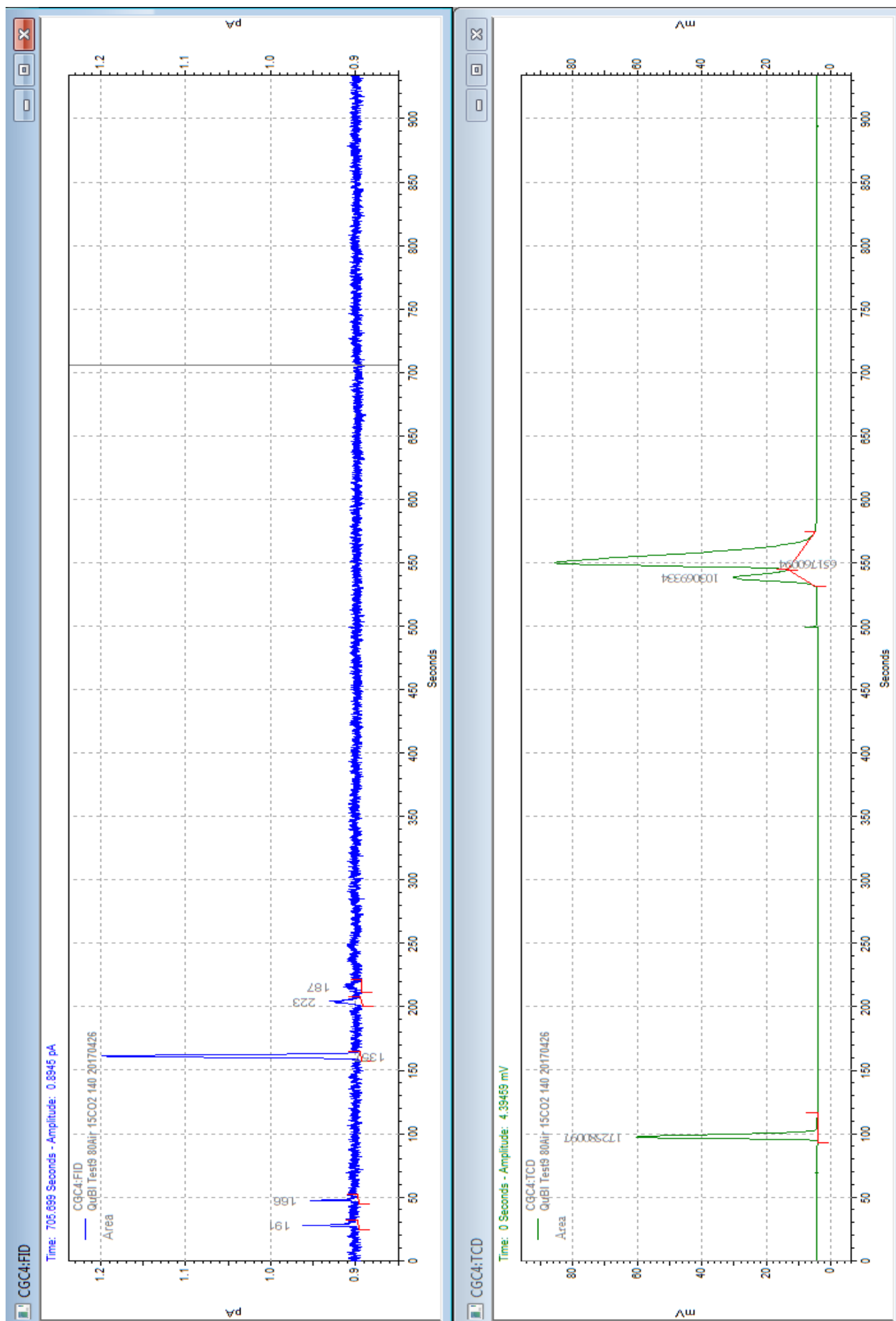
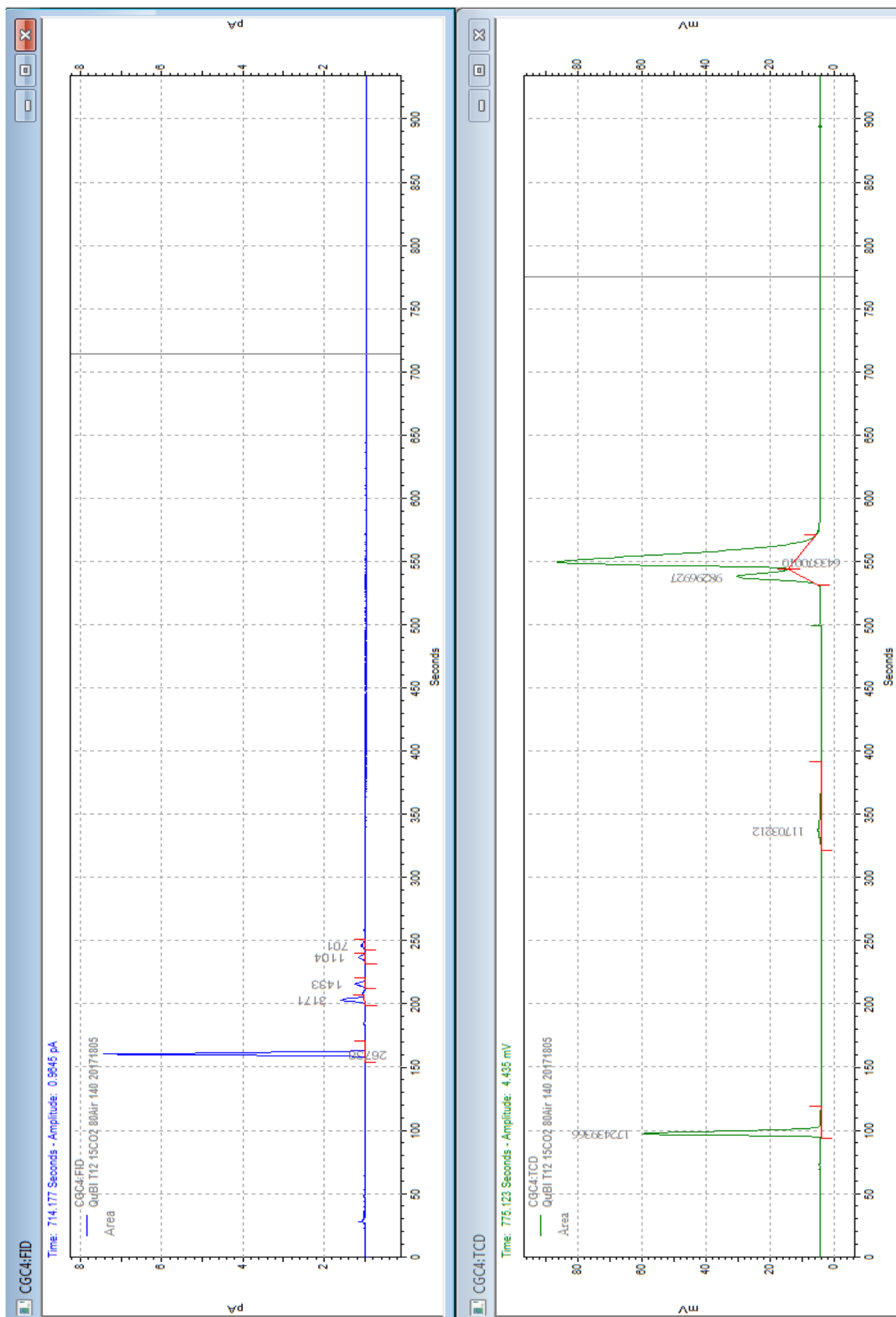
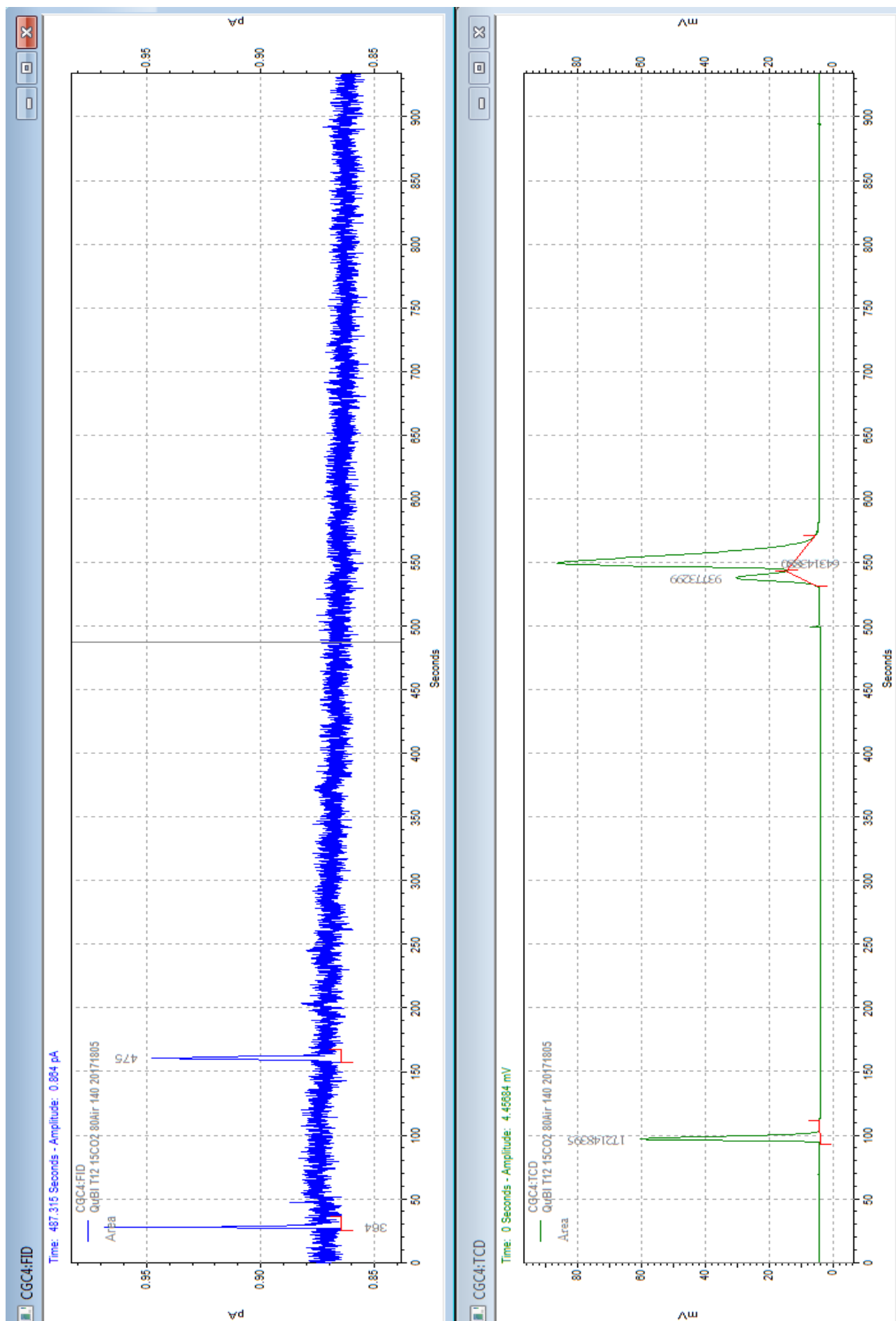


FIGURE B.6: BaseCase-15CO2 - End

FIGURE B.7: BaseCase-15CO<sub>2</sub>-Repet - Beginning

FIGURE B.8: BaseCase-15CO<sub>2</sub>-Repet - End

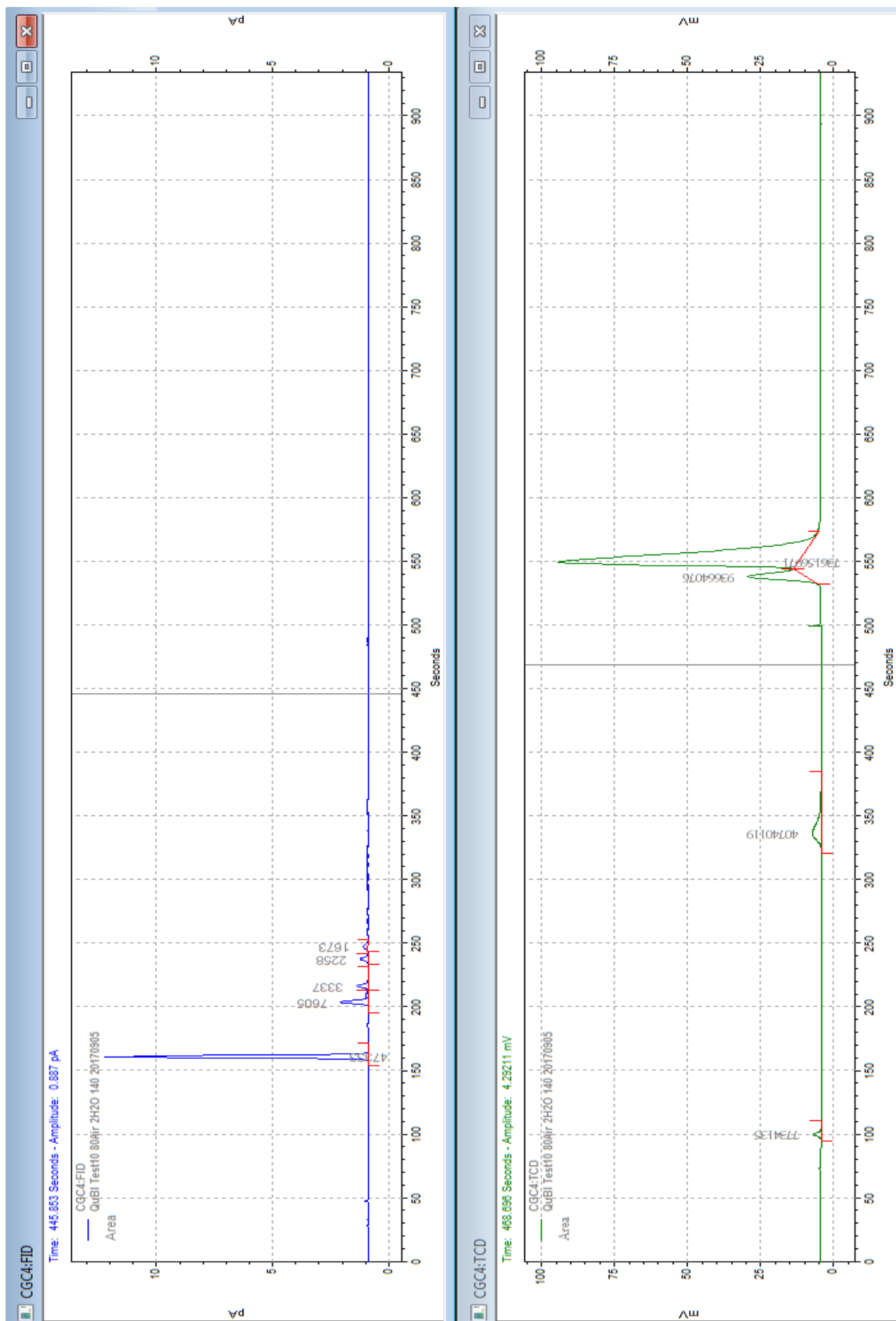


FIGURE B.9: BaseCase-2H2O - Beginning

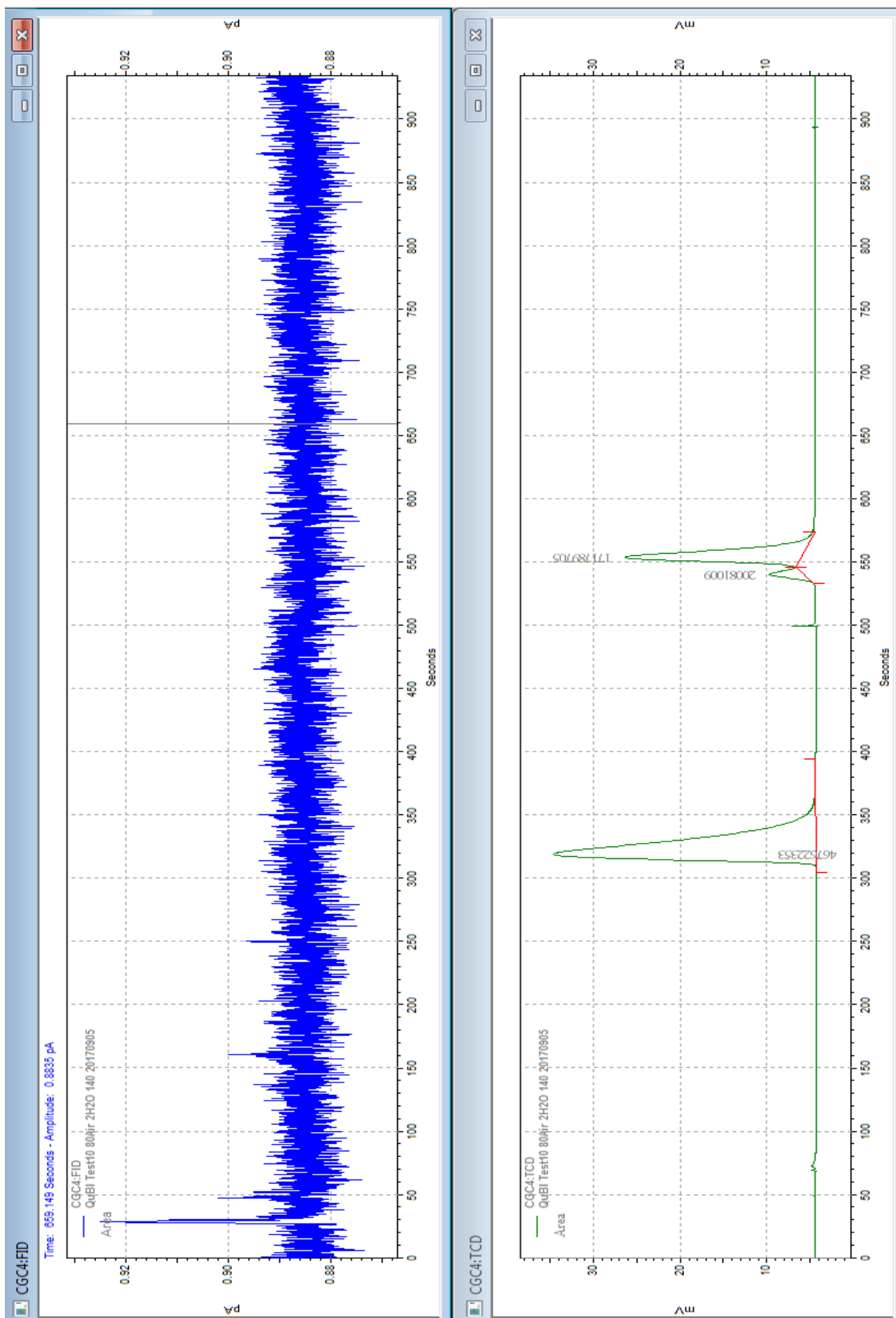


FIGURE B.10: BaseCase-2H2O - 180 minutes

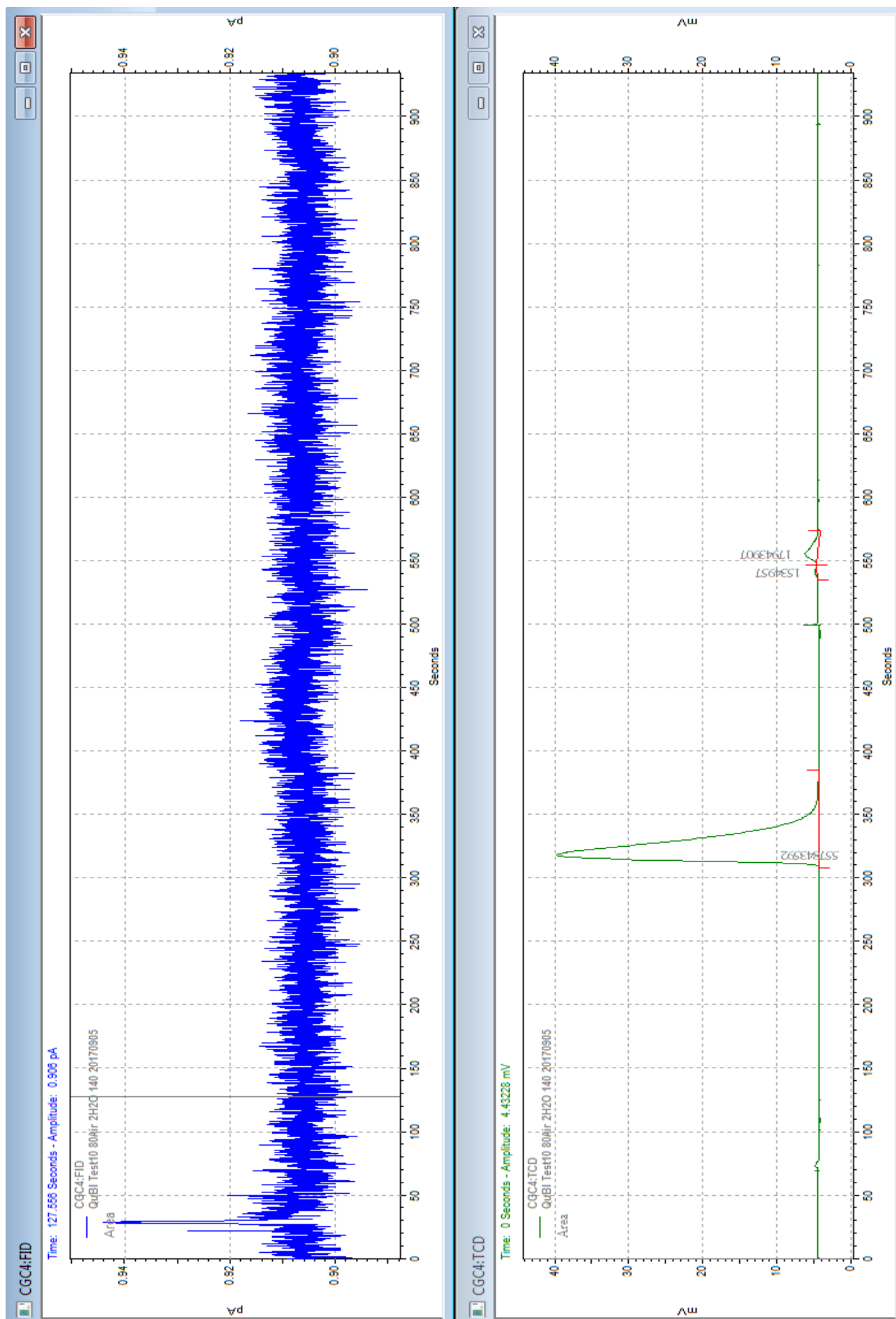


FIGURE B.11: BaseCase-2H2O - 810 minutes

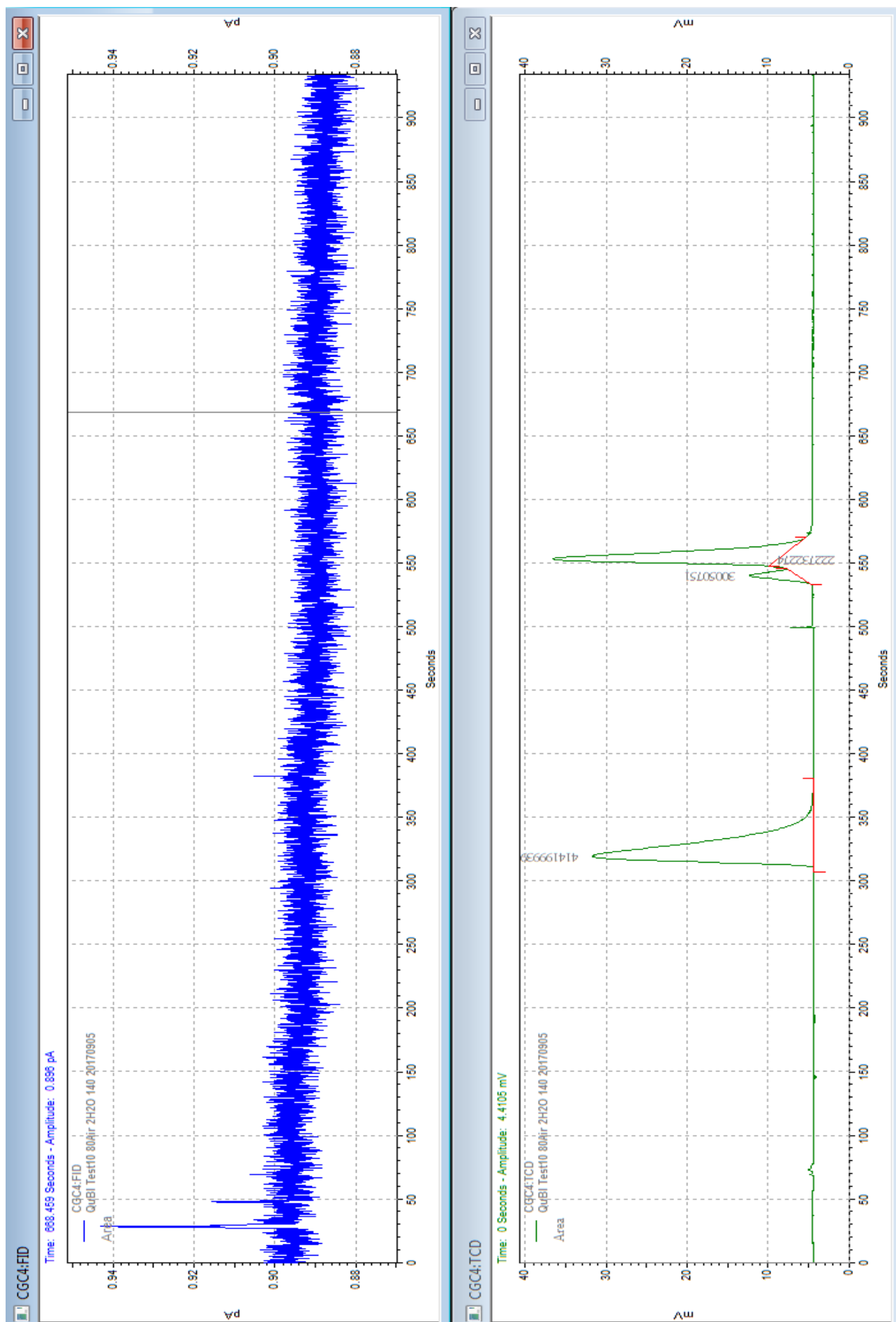


FIGURE B.12: BaseCase-2H2O - End

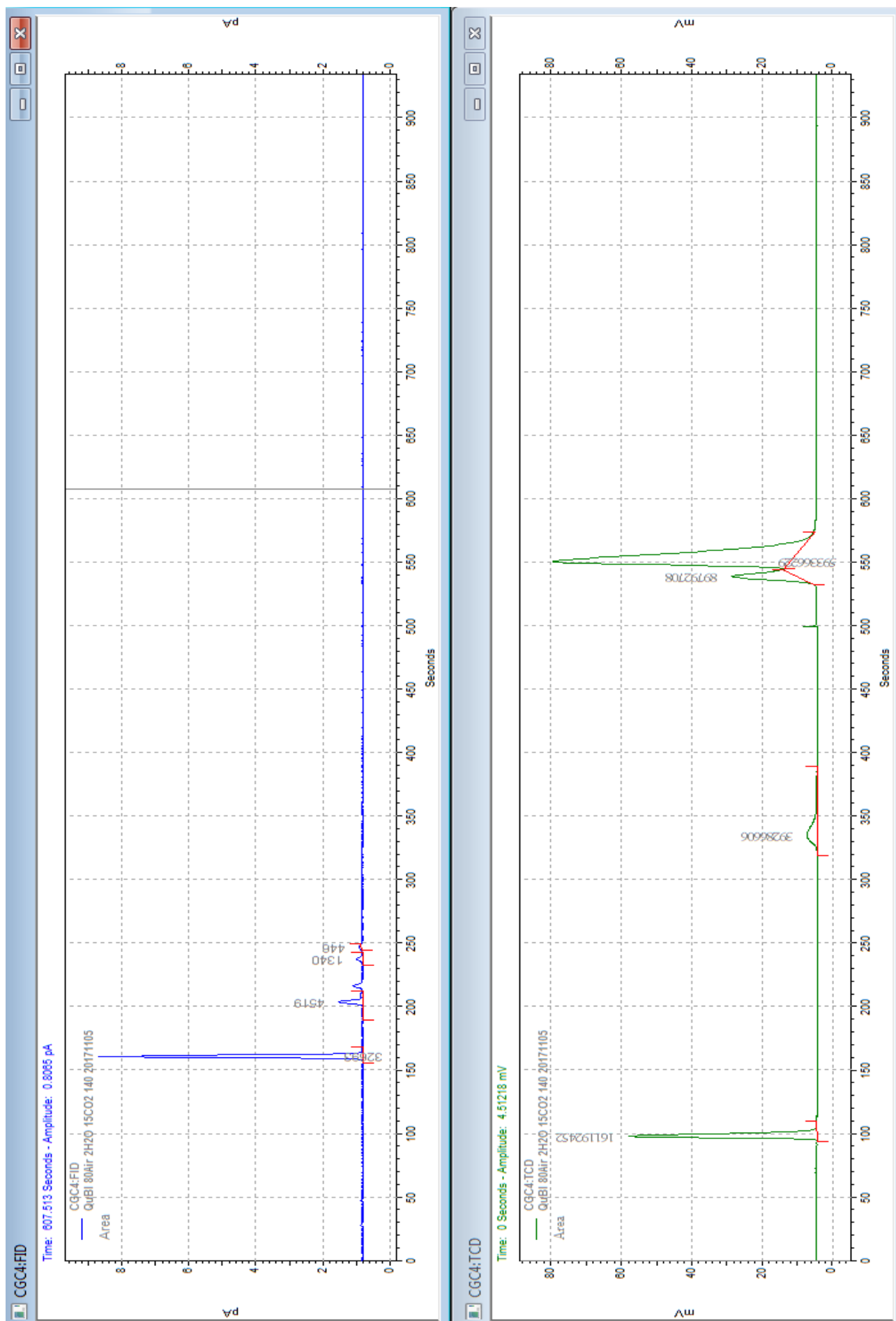


FIGURE B.13: BaseCase-15CO2-2H2O - Beginning



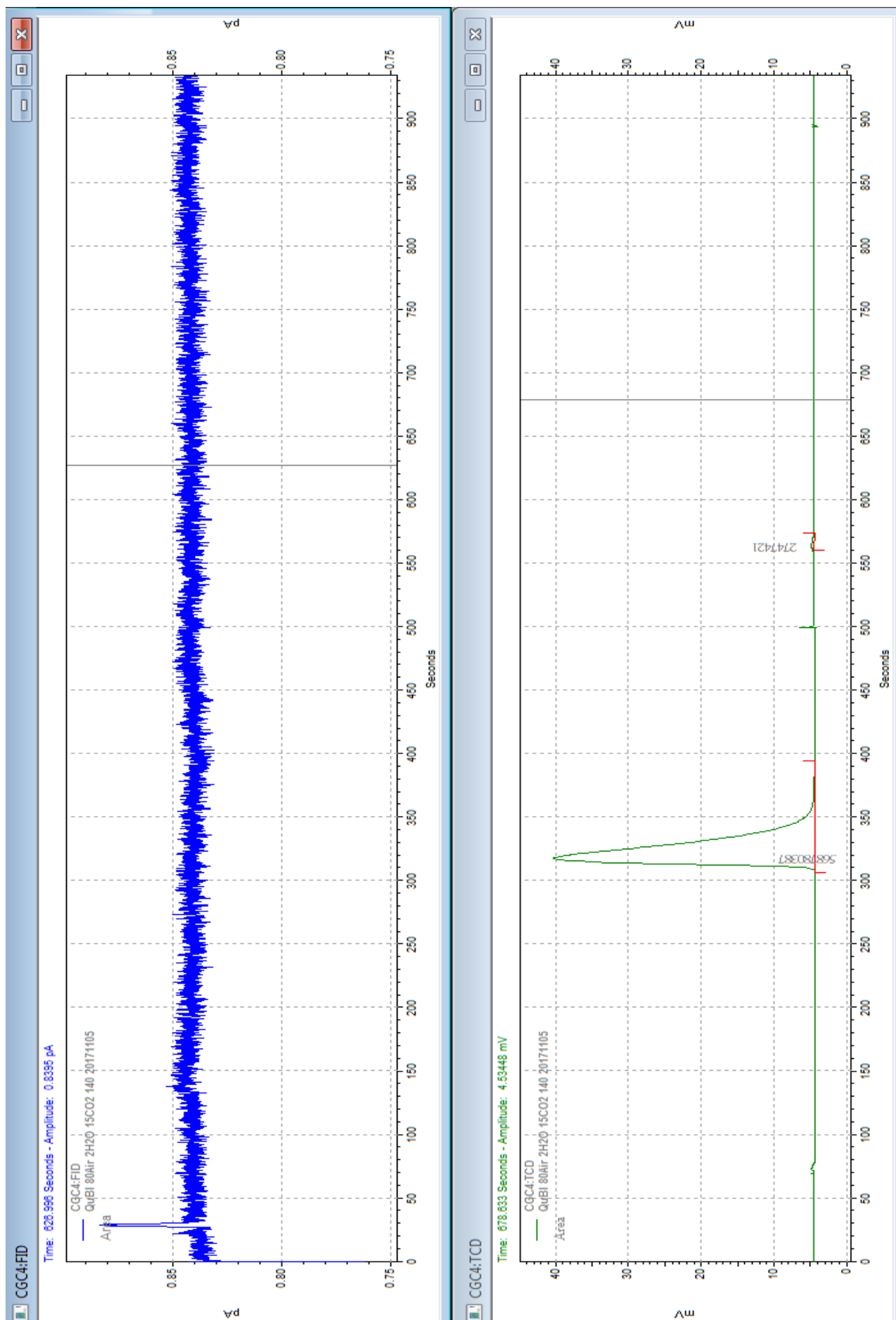


FIGURE B.14: BaseCase-15CO2-2H2O - 810 minutes

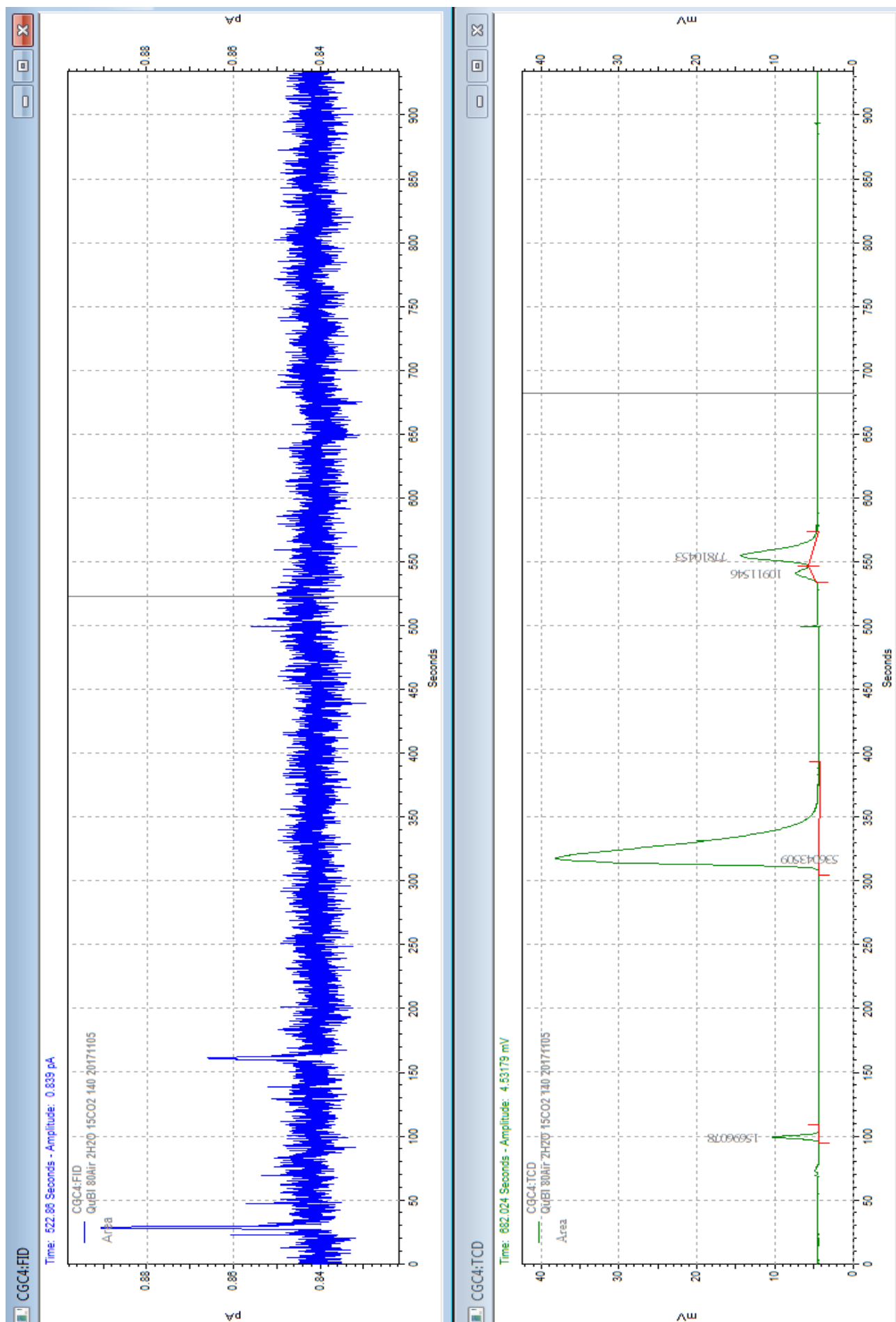


FIGURE B.15: BaseCase-15CO2-2H2O - End

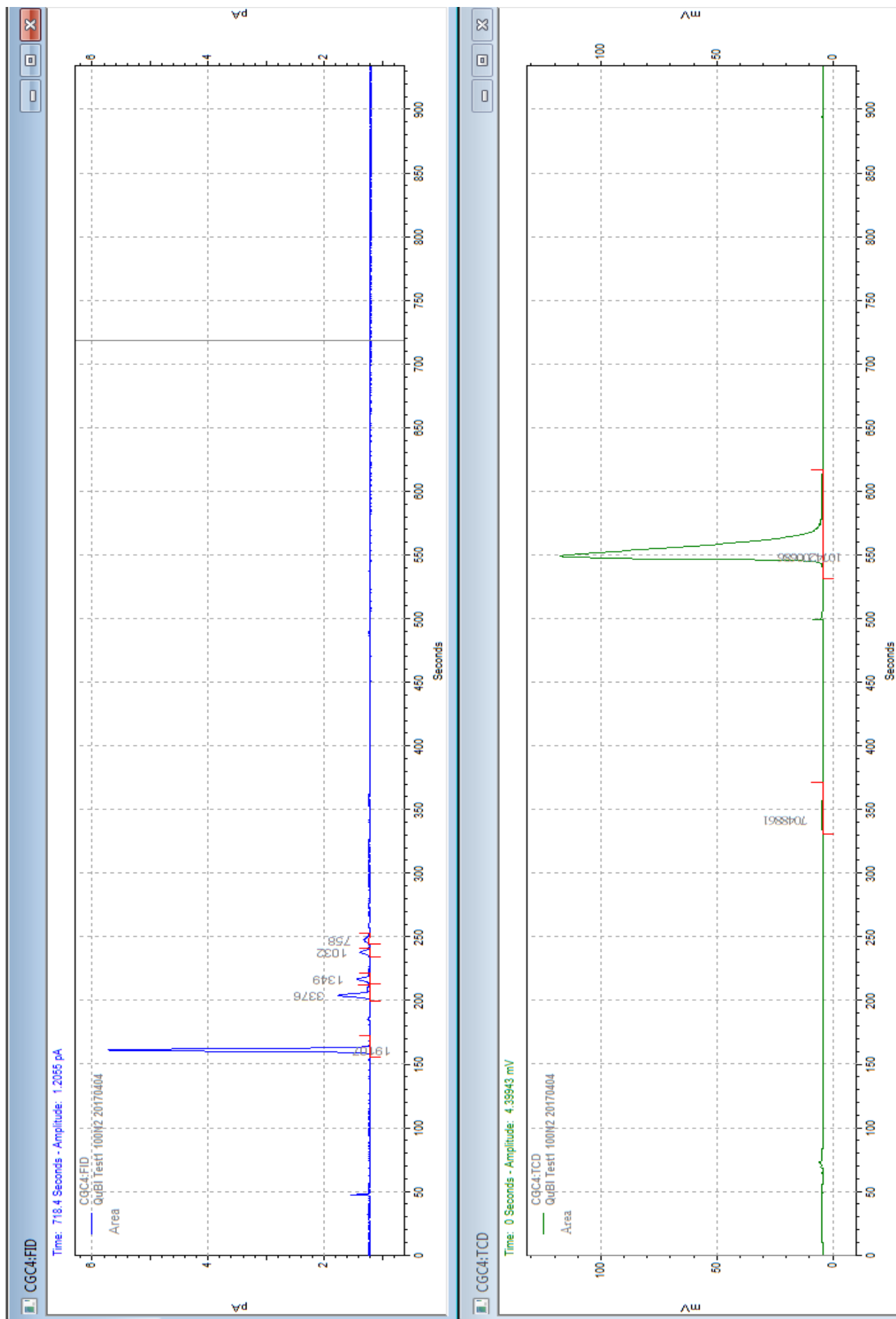


FIGURE B.16: 100N2-120T-7D - Beginning

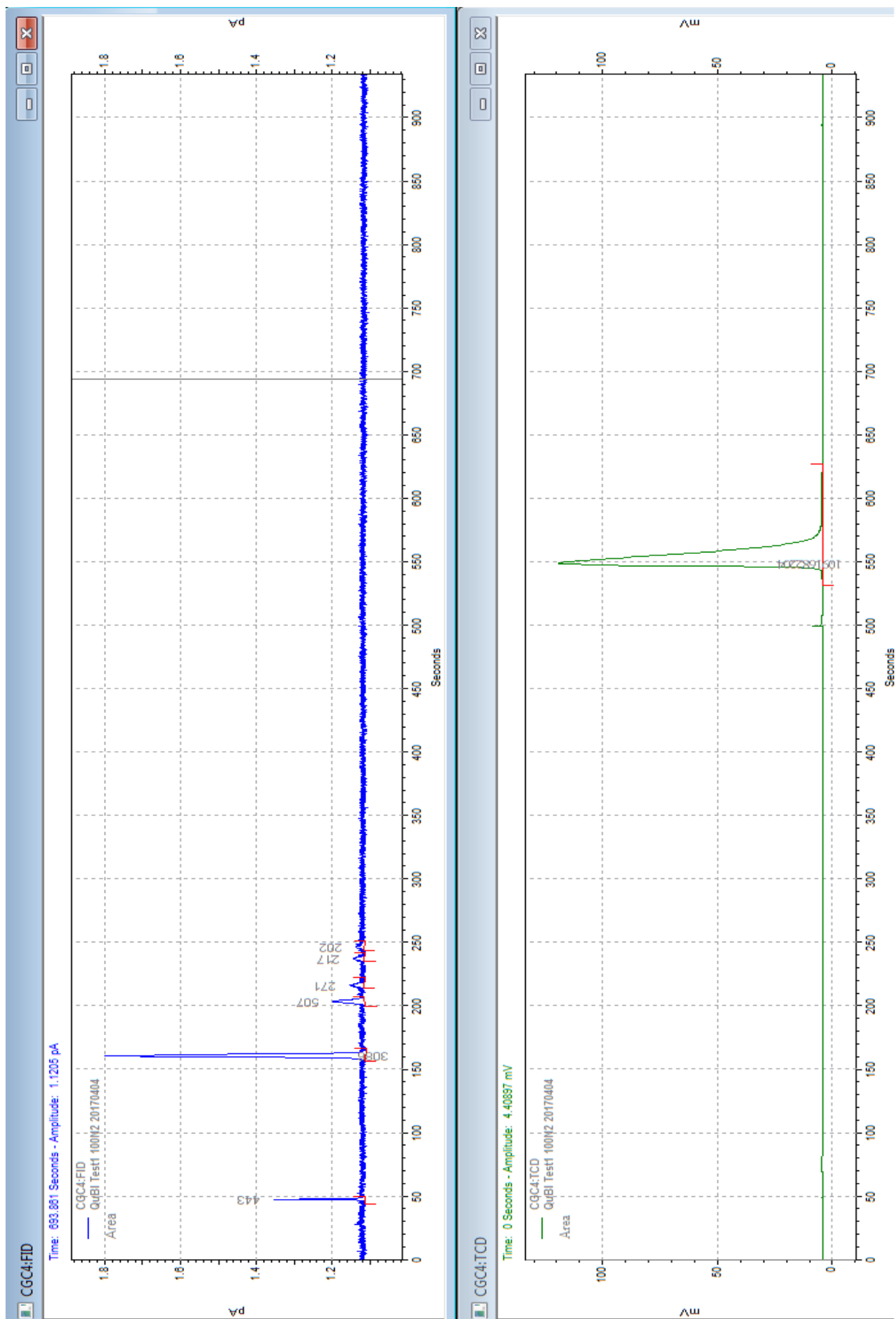


FIGURE B.17: 100N2-120T-7D - End

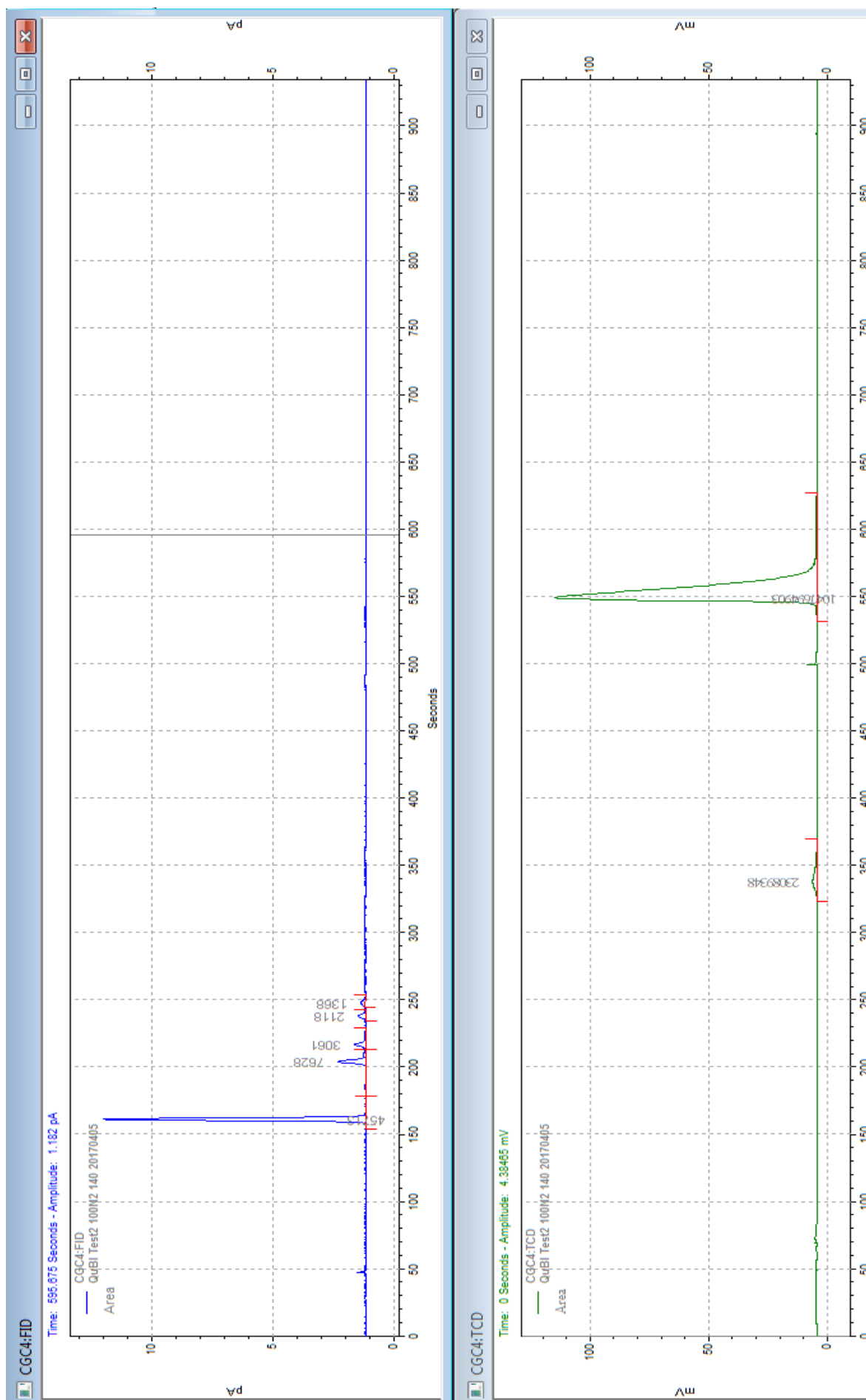


FIGURE B.18: 100N2-140T-7D - Beginning

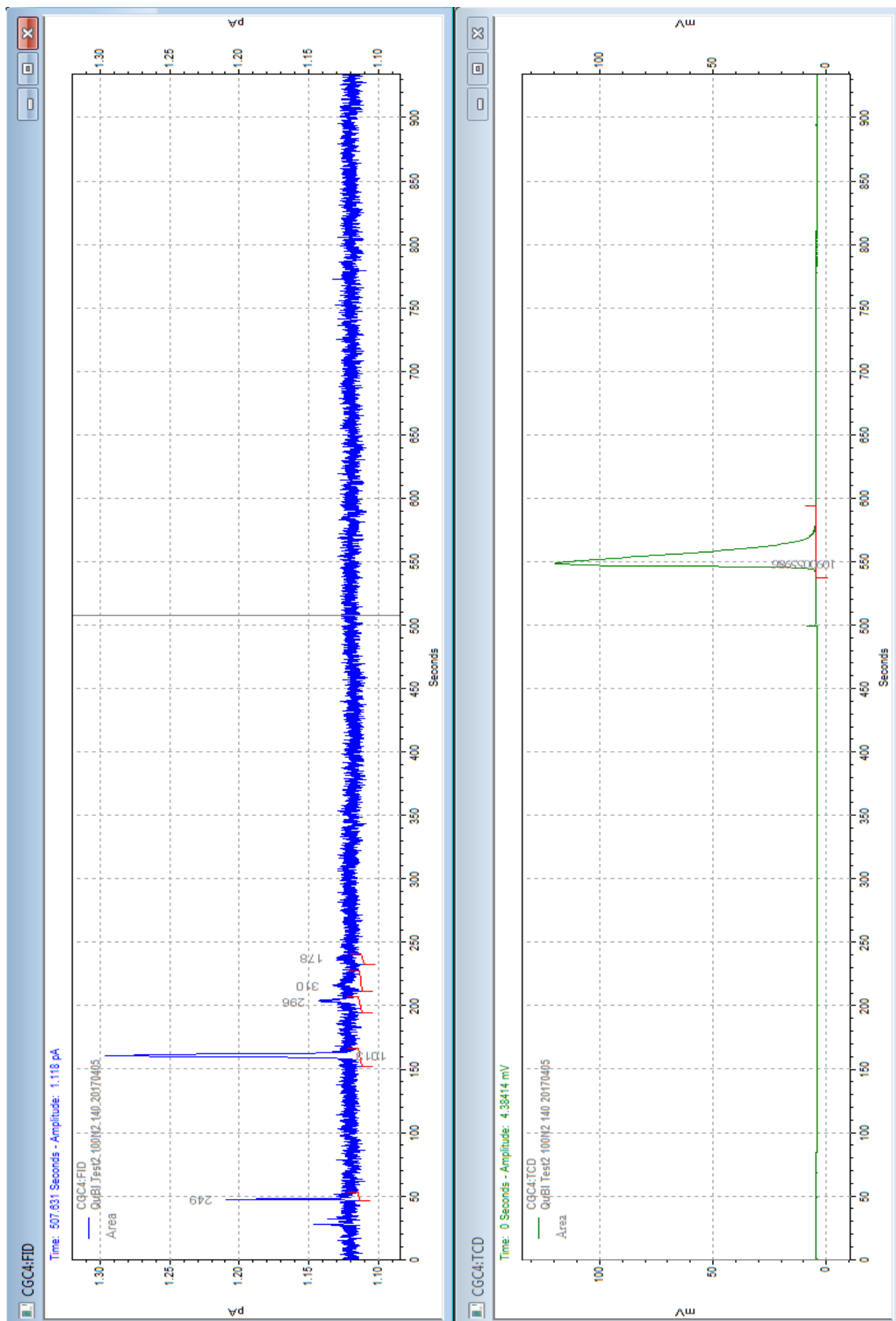


FIGURE B.19: 100N2-140T-7D - End

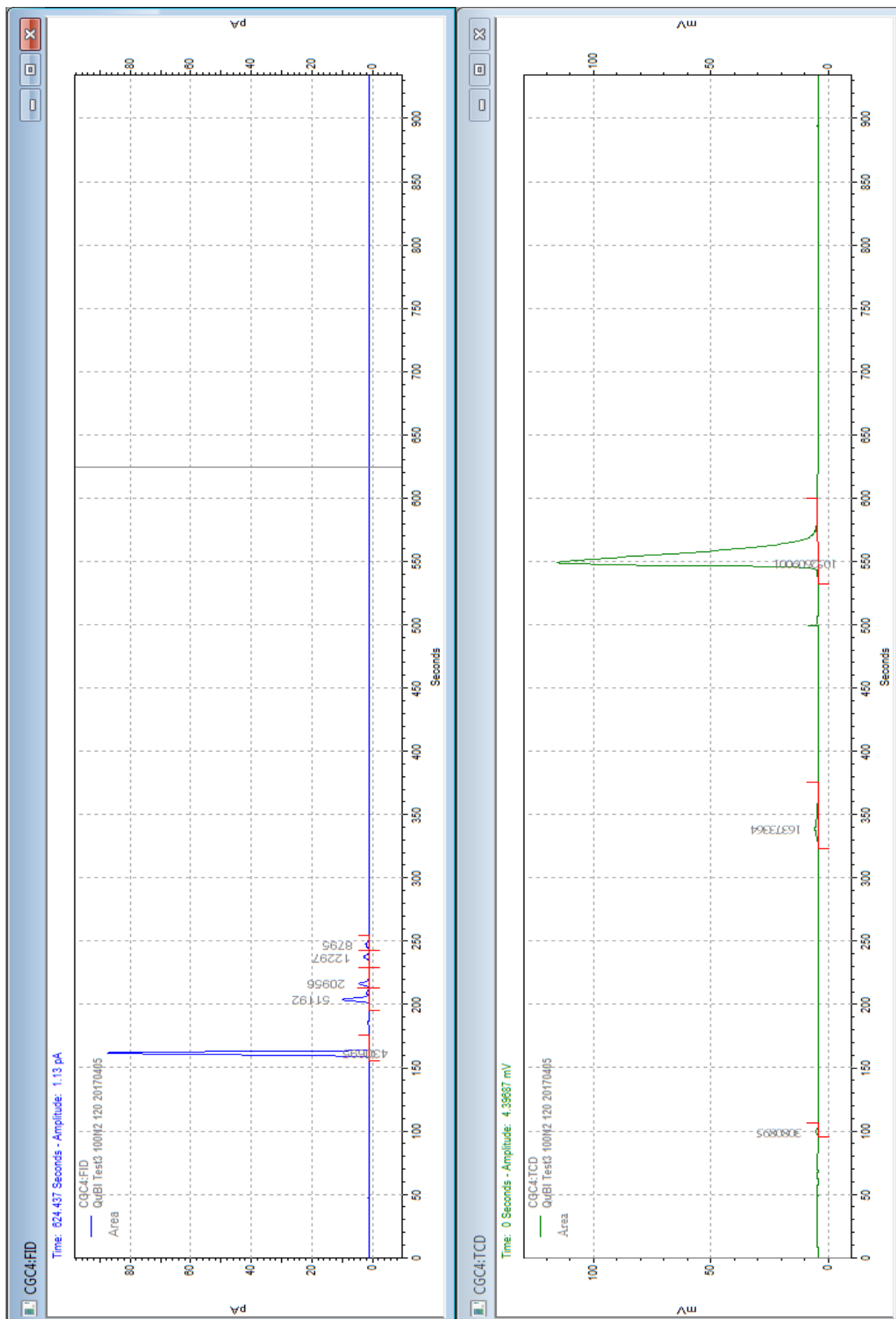


FIGURE B.20: 100N2-120T-15D - Beginning

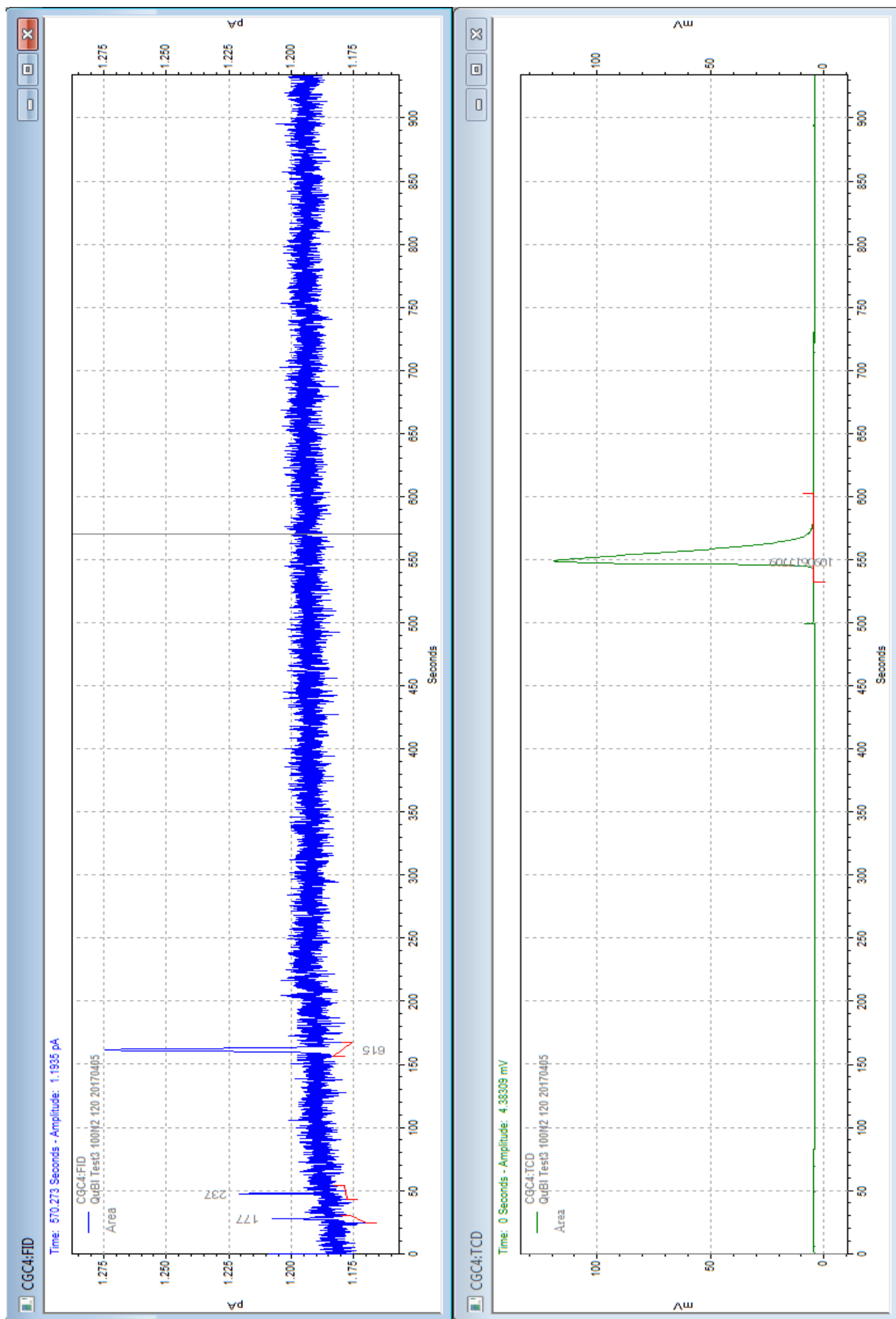


FIGURE B.21: 100N2-120T-15D - End



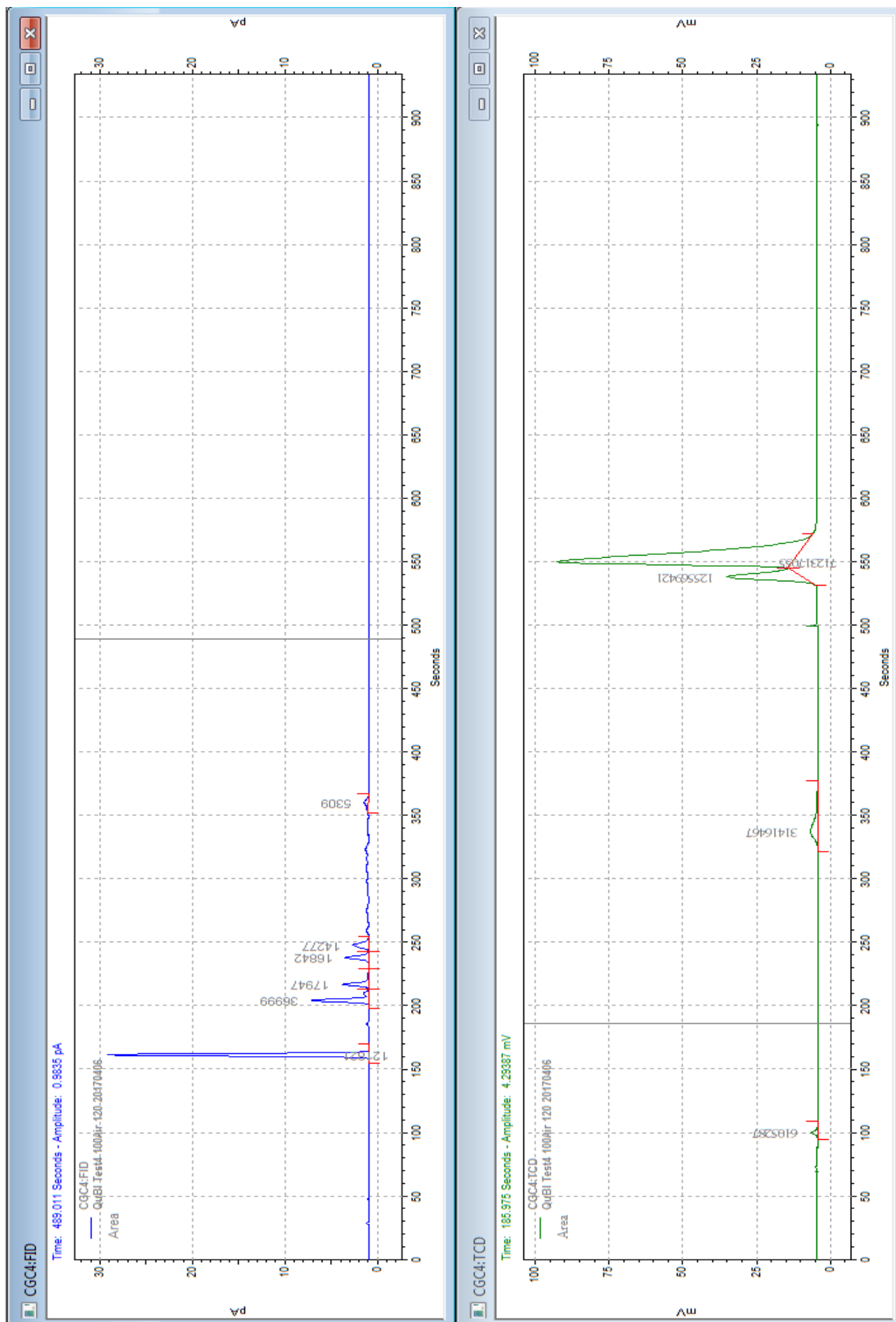


FIGURE B.22: 100O2-120T-15D - Beginning

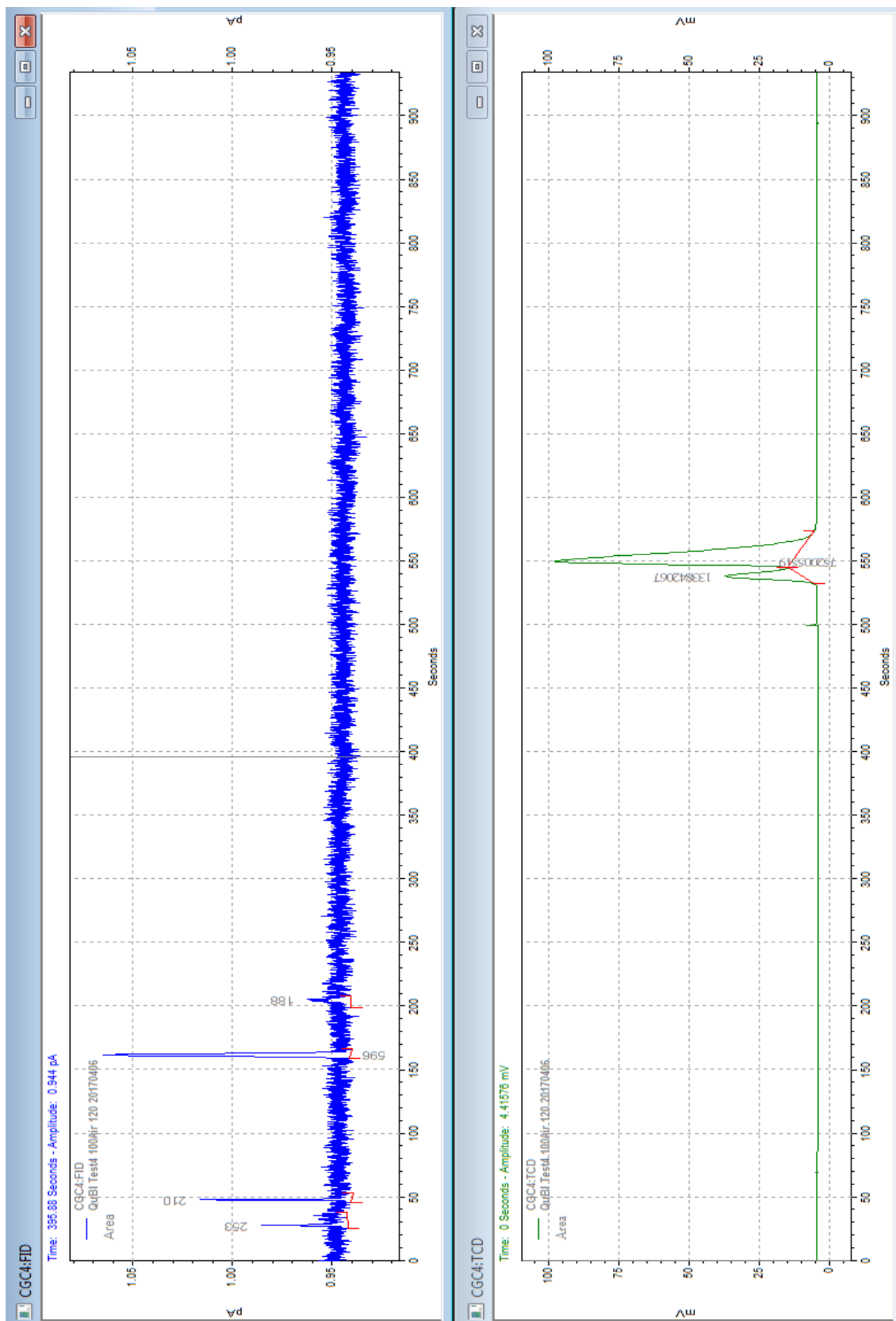


FIGURE B.23: 100O2-120T-15D - End

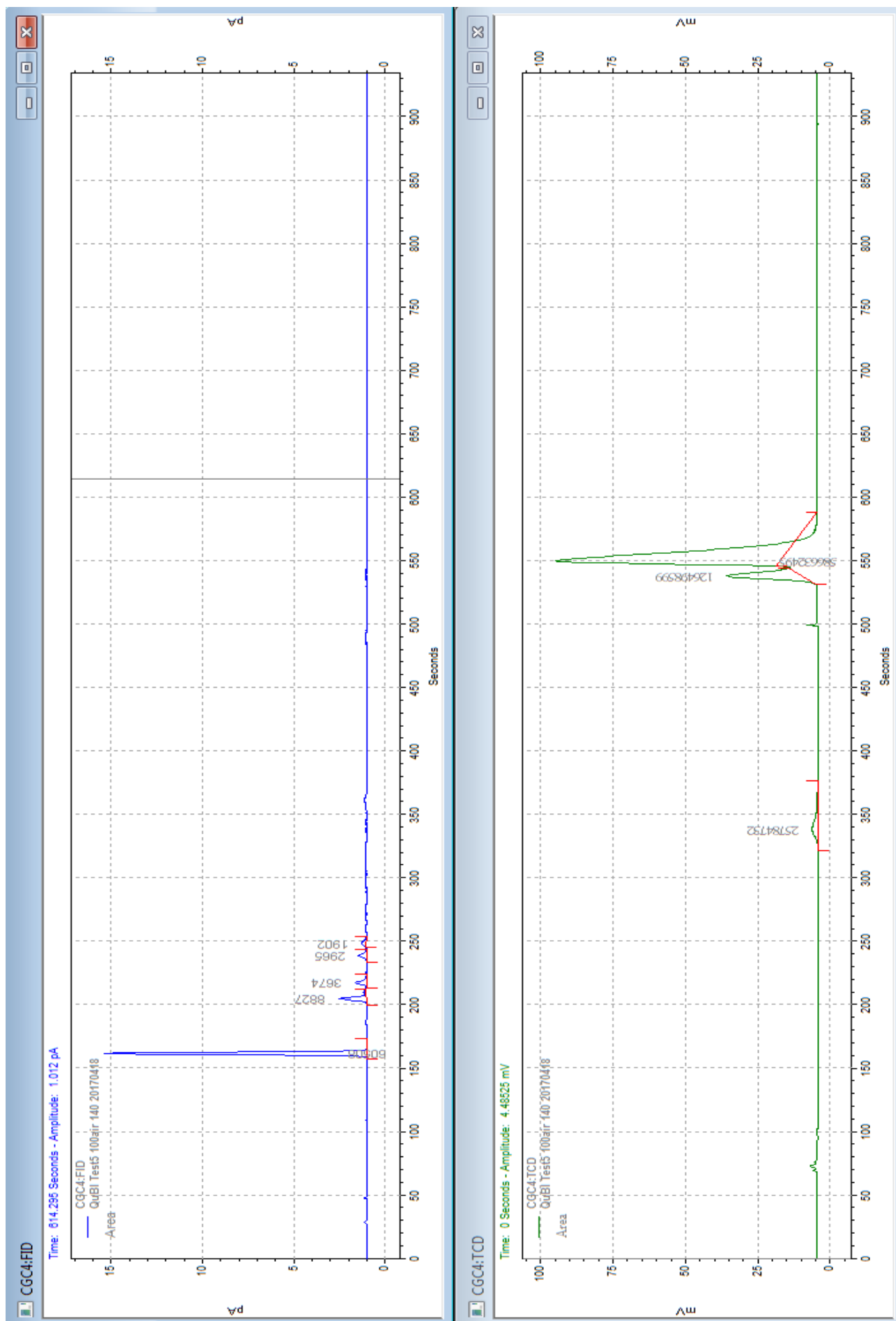


FIGURE B.24: 100O2-140T-15D - Beginning

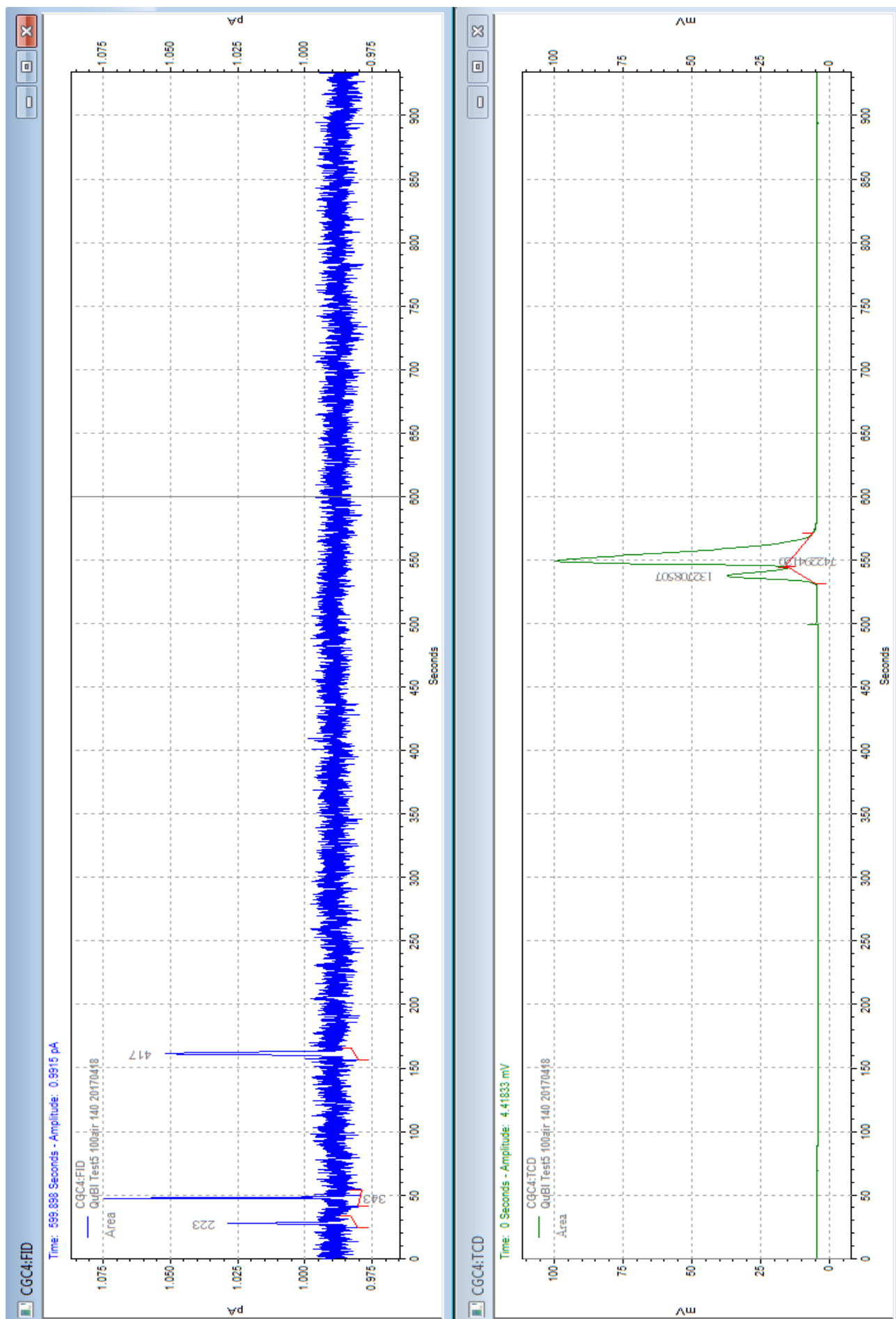


FIGURE B.25: 100O2-140T-15D - End

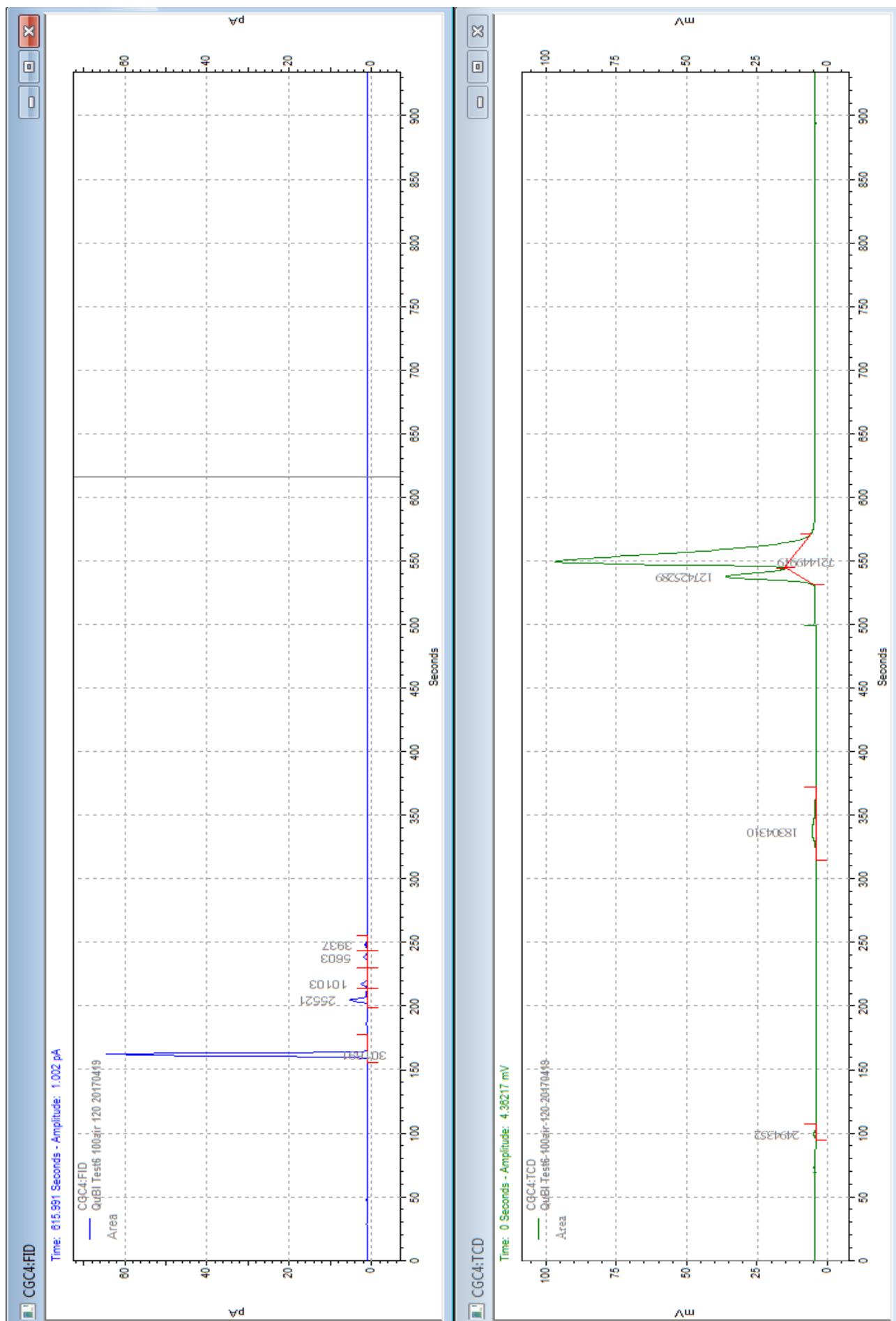


FIGURE B.26: 100O2-120T-7D - Beginning

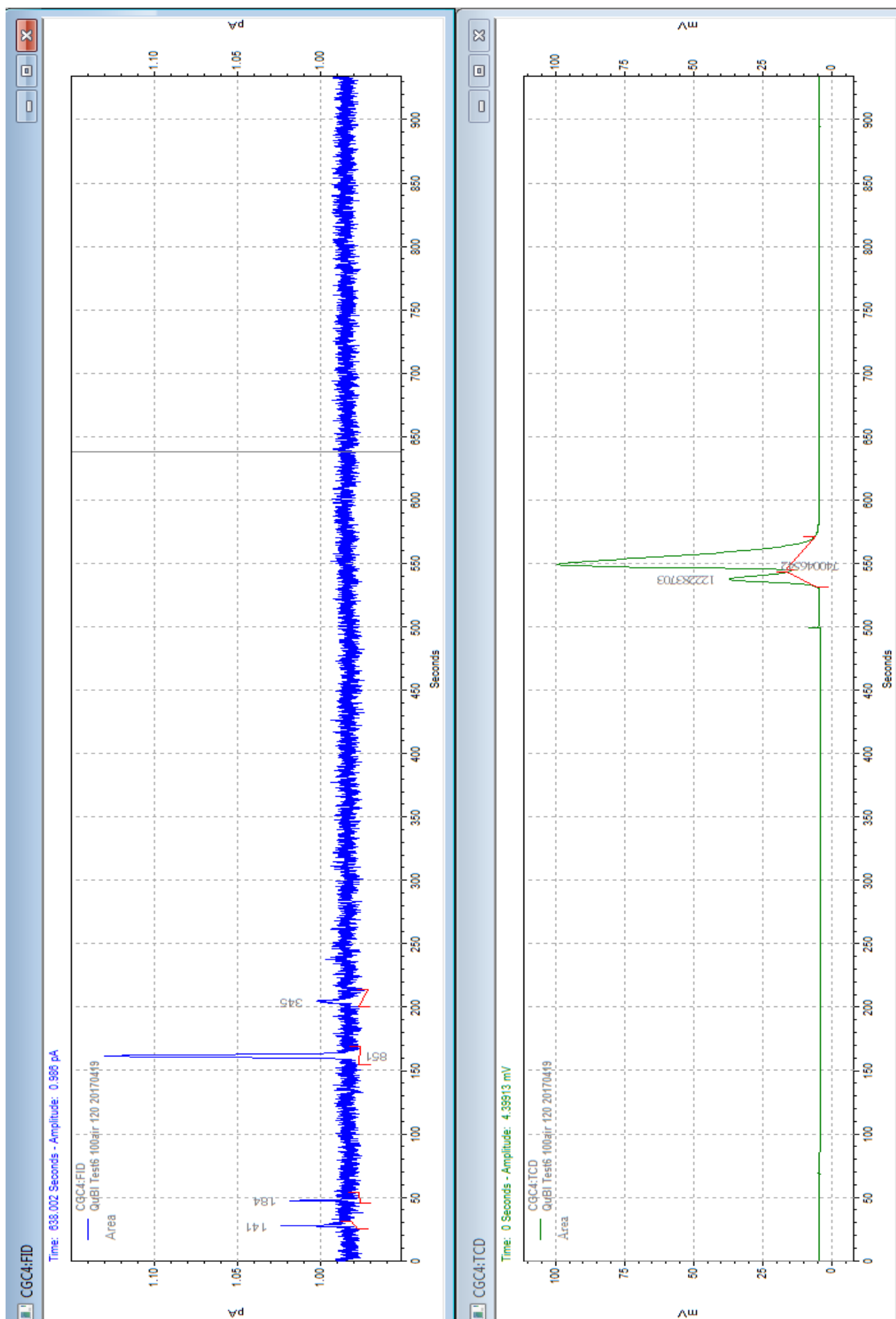


FIGURE B.27: 100O2-120T-7D - End