Characterization of the Atmosphere of the Fruit Conservation Chambers

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ABSTRACT

Pera *Rocha* do Oeste DOP is a pear variety native from Portugal. The fruits can be stored for several months during conservation, in different atmospheres, and physiological problems can occur, either due to their characteristics or the atmospheres used, such as internal browning and superficial scald. The objective of this work is to identify and quantify the volatile compounds (VOCs) produced by the Rocha pears throughout their permanence in the conservation chambers, and to associate them with the physiological state of the fruits. The identification and quantification were carried out using a gas chromatograph, with a mass spectrometry detector (GC-MS) and with a flame ionization detector (GC-FID). Physical-chemical characterization of the fruits was carried out, both at the harvester and at the end of the storage period, after being subjected to different conservation atmospheres. The VOCs produced by pears were analyzed not only in the shelf-time period, in a desiccator after removal from conservation, but also in a chamber throughout the conservation period. The analyses carried out by GC-MS allowed to identify 29 different compounds, eight of which belong to the alcohols group, six to aldehydes, five to ketones, and three to esters, among others. Alcohols were the most abundant compounds, with relative abundances higher than 70% in all analyses performed. Monitoring of ethylene concentration in different chambers throughout the conservation period was also carried out by GC-FID. The ethylene concentrations obtained in the 2021/2022 harvest are lower than those obtained in the 2020/2021 harvest since one analysis was carried out at the end of the conservation period and another at the beginning of it.

Keywords: Rocha Pear, volatile compounds, GC-MS, GC-FID, conservation atmospheres, 1-MCP, zeolites, shelf-life, NaY, 5-A, CBV 10-A.

1. INTRODUCTION

Pera *Rocha* do Oeste, *Pyrus communis* L., is a DOP (Denomination of Protected Origin) pear from the western region of Portugal. It is the fourth cultivar in Europe and the main cultivar in Portugal [1].

Rocha pear, after being harvested, must be stored and preserved using different technologies, so that it can be available for consumption in the following months, maintaining its characteristic qualities. This is achieved by using different post-harvest technologies, which aim to reduce the metabolic processes of the fruit without affecting its desired qualities [2].

There are several types of atmospheres for pear storage. Cold storage in a normal atmosphere (NA) is the most traditional method, but the fruits can only be stored for a maximum period of five months. The control of the partial pressure of atmospheric gases (CA), combining cold temperatures and high relative humidity inside the chambers, allows storage for up 10 months, by reducing ripening, ethylene production, respiration rate, and microbial activity [3]. However, long-term storage can lead to the development of physiological problems. Superficial scald (SS) can develop during NA-storage, and internal browning (IB) in CA-storage [4], [5].

Ethylene plays an important role in pear ripening because it accelerates ripening and senescence, reducing postharvest life [6]. The application of 1-methylcyclopropene (1-MCP) can bind to the ethylene receptors, such that ethylene cannot bind to them. In addition to delaying ethylene production ([7]), 1-MCP can also reduce the incidence of SS and IB during long-term NA-storage and in the *shelf-life* period. The *shelf-life* period corresponds to the period in which the fruits are placed at a normal atmosphere and room temperature, to simulate the conditions that they are subjected to during the distribution to the consumer.

VOCs are produced through metabolic and ripening processes and are strongly influenced by

storage conditions [8]. Several authors noticed that there is a decrease in the production of VOCs in CA and *ultra-low oxygen* (ULO) and in fruits treated with 1-MCP [9]–[12]. Gomes *et al.* [13] observed that esters were the most abundant VOCs in fresh-cut *Rocha* pear. Esters are formed through an esterification reaction between alcohols and catalyzed by the enzyme alcohol acetyltransferase [14]. On the other hand, Barbosa [15] observed that the alcohols were the most abundant VOCs in *Rocha* pear, stored for five months. Ethanol and acetaldehyde are associated with anaerobic processes and also with IB incidence [16], [17].

The objective of this study is the identification and quantification of VOCs produced by *Rocha* pears throughout the conservation period. To achieve that, the production of compounds was analyzed by gas chromatography, using mass spectrometry detection (GC-MS) and flame ionization detection (GC-FID).

2. EXPERIMENTAL PROCEDURES

2.1. Samples

The *Rocha* pears used as samples in this work refer to the end of the storage period of the 2020-2021 campaign (harvest in August 2020), and to the beginning of storage in the 2021/2022 campaign (harvest in August 2021). They came from three different orchards in the West region. The fruits were placed in RochaCenter conservation chambers. Pears were stored under four conditions: NA (20,80% O_2, 0,03% CO_2), CA (4,00% O_2, 0,50% CO_2), ULO (0,50% O_2, 0,50% CO_2), and CA+1-MCP (312 ppb). Due to the application of 1-MCP, there is a need for the chamber to remain 60 days in NA after the treatment. Thus, during the analysis of the 2021-2022 campaign, the chamber where was applied 1-MCP stayed at NA conditions.

2.2. Reagents

The reagents used in this work were: acetaldehyde (99% PS, Panreac Sintesis), ethyl acetate (95%, Fisher Scientific), n-butyl acetate (95%), 1-butanol (99,5%, Merck), ethanol (99,8%, puriss p.a., Riedel-de Haën), ethylene (4% v/v in nitrogen, Air Liquide and 100 ppm in nitrogen, Rivoira) and nitrogen (Rivoira).

Four zeolites were used: 5-A (Sigma Aldrich), CBV 10-A (Zeolyst), NaY (Grace Davidson), and NaY (UOP).

2.3. Physico-Chemical Characterization

Rocha pears were characterized by pulp firmness, total soluble solids (TSS), and starch regression rate (SRR). Three samples were used, each consisting of 20 fruits from each of the three orchards. On the arrival of the fruits to RochaCenter, firmness, TSS and SRR were measured, and the Streiff index was calculated. At the end of the storage period (10 months), firmness and TSS were determined, as well as the incidence of SS and IB.

The firmness was determined by a penetrometer (Turoni, Fruit Pressure Tester, model FT327). The results were expressed as kg/0,5cm^2. The TSS (%) were evaluated by a digital refractometer (Pocket refractometer, Atago, S7101033). The SRR was determined using an iodine solution, comparing to a reference chart [18].

2.4. VOCs Analysis

Due to the reduced concentration of VOCs in the conservation chambers, zeolites were used for the extraction and concentration of compounds. The adsorbents were placed in separate Petri dishes. Weekly, these dishes were placed in the different storage chambers, replacing those from the previous week. Regarding the 2020/2021 campaign, this sampling was carried out in eight consecutive weeks, starting on March 30th and ending on May 18th. For the 2021/2022 campaign, samples were taken for five weeks, starting on August 19th, and ending on September 16th.

To simulate the *shelf-life* period, 10 pears stored at ULO (eight months) + NA (two/three weeks) conditions and 10 pears stored under NA conditions were placed in two different desiccators, at laboratory room temperature (approximately 23 ºC) for one week.

The desorption method was optimized. For adsorption in desiccators, 50 mg of adsorbent were placed in a 10 mL vial, sealed with septum (18-MSC-ST3HT, Fisher) and an aluminum cap, at 200 ºC for 45 min. For adsorption in chambers, 100 mg of adsorbent were placed at the vial, at 200 ºC for 45 min. Then, 1mL of headspace gas was collected and injected into the GC.

2.5. Chromatographic Method

Samples were analyzed on a GC (Trace 1300 GC, ThermoFisher Scientific), coupled to an MS (ISQ QD Single Quadrupole MS, ThermoFisher Scientific), and to an FID. The chromatographic

column used in GC-MS was a TraceGold TG-WAXMS (ThermoFisher Scientific) (60m x 0,5 µm x 0,25 mm). The analysis method was optimized based on [15]. The injector and detector were maintained at 180 ºC. The column temperature program was as follows: 30ºC for 4,5 min, raised to 100 ºC at 20 ºC min^{-1}, holding for 1 min. Then, raise to 150 ºC at 2 ºC min^{-1}, holding for 2 min. The split mode was used, with a split ratio of 33,3. Helium was used as the carrier gas at a flow rate of 1 ml min^{-1}. Mass spectra were scanned in the range of *m/z* 33-150. The temperatures of the ion source and interface were set at 180 ºC.

The column used in GC-FID was a TracePlot TG-BOND (ThermoFisher Scientific) (30m x 10 µm x 0,53 mm). The analysis method was optimized, based on [19]. The injector and detector were maintained at 200 ºC and 250 ºC, respectively. The column temperature program was as follows: 50ºC for 2 min, raised to 200 ºC at 10 ºCmin^{-1}, holding for 3 min. The split mode was used, with a split ratio of 13. Helium was used as the carrier gas at a flow rate of 4 mlmin^{-1}. The flow rates of air, hydrogen and nitrogen were 350, 35, and 45 mLmin^{-1}, respectively.

2.6. Calibration Curves

With the analysis methods optimized, calibration curves were prepared for the quantification of VOCs, namely acetaldehyde, ethyl acetate, n-butyl acetate, 1-butanol, ethanol, and ethylene. For each one of them (except ethylene), the first dilution of a standard solution was performed, using distilled water. From this solution, different calibrators were prepared to be used, with different dilution factors. Regarding ethylene, the volume of a gas collection vial was measured by weighing the volume of distilled water. Then, the collection vial was filled with nitrogen, then opening it quickly, to release the excess nitrogen, without contamination by external gas, and the interior remain at atmospheric pressure. Different volumes of ethylene were then injected into the collection vial, to prepare different calibrators.

2.7. Statistical Analysis

Six replicate instrumental responses were obtained for each calibrator. The validation of the analytical method was performed by the Excel statistic spreadsheet by [20]. The linearity was evaluated by the ANOVA Lack-of-fit test, and the homoscedasticity by Levene's test. Outliers were identified by Grubbs' test. The confidence level used in all tests was 99%.

3. RESULTS AND DISCUSSION

3.1. Physico-Chemical Characterization

The evaluation of the quality parameters of *Rocha* pears was carried out to characterize them and the state of ripeness in which they were harvested (**Table 1**).

Table 1 – Results obtained for the physicochemical characterization analysis on the arrival to the RochaCenter.

Date	Firmness ($kg/0,5cm^2$)	TSS (%)	SSR	Streiff Index
08/2020	4,99	11,64	7,78	0,06
08/2021	6,32	11,60	6,65	0,08

Firmness decreases over time as the fruit ripens. The reference values used for *Rocha* pear at harvest are between 5,1 and 6,4 $kg/0,5cm^2$ [21]. So, it can be concluded that the fruits of the 2020/2021 campaign had an average firmness below the minimum value described and that the fruits from the 2021/2022 campaign presented a lower state of maturation. The TSS values are both within the mean values of reference at harvest and are not divergent [18]. Starch, during the maturation period, is transformed into sugar through hydrolysis reactions. It is advised that, at harvest, fruits present SSR between 5 and 7. Fruits with SSR values below 4 will hardly ripen, and those above 8 have to enter the commercial circuit as soon as possible [18], [21]. The SSR values obtained for the 2021/2022 campaign are lower than the aforementioned range. The Streiff comprises three good tests (pulp firmness, TSS, and SSR) and reference values at harvest are between 0,07 and 0,09 [18], [21].

It is verified that fruits from the 2021/2022 campaign were, at harvest, in an earlier stage of maturation compared to fruits of 2020/2021. This factor could be determinant in the analysis of volatile compounds. In fruits with a higher state of maturation, the number of ethylene receptors is higher, and therefore the production of this compound may be higher too, even using 1-MCP [11].

At the end of storage, fruits were also evaluated after zero and seven days of *shelf-life* (**Table 2**). Firmness values were similar at harvest and at the end of conservation. However, during the *shelf-life* period, firmness decreased, and fruits stored at NA conditions showed higher values compared to fruits stored in CA conditions. These observations were also verified by Galvis-Sánchez *et al.* [22]. Fruits stored in the chamber where 1-MCP was applied, on the other hand, showed higher firmness compared to the ones stored in other conditions.

Table 2 – Average results and standard deviation obtained for the physicochemical characterization analysis after zero and seven days of shelf-life.

Storage Conditions	Firmness (kg/0,5cm^2)		TSS (%)		SS Incidence (%)			
	Day 0	Day 7	Day 0	Day 7	Grade 0	Grade 1	Grade 2	Grade 3
CA+1-MCP	4,64 ± 0,45	4,67 ± 0,44	11,23 ± 1,06	15,59 ± 0,81	-	-	-	-
ULO	4,75 ± 0,38	1,17 ± 0,35	12,02 ± 1,21	13,32 ± 0,95	-	-	-	-
NA	4,36 ± 0,35	2,28 ± 0,53	10,59 ± 1,16	11,67 ± 1,26	32,50	20,00	20,00	27,50
CA	4,52 ± 0,42	1,66 ± 0,50	11,05 ± 1,24	13,07 ± 1,54	-	-	-	-

Saquet *et al*. [7], in a study with *Rocha* pear, also observed that treatment with 1-MCP prevented softening.

Pears stored in CA conditions, when moving to *shelf-life* conditions, have a metabolic increase caused by the increase in O_2 content, and by the increase of temperature, resulting in higher production of ethylene. In pears stored in NA, the metabolic increase is only enhanced by the increase of temperature. Thus, pears stored in CA and ULO will have lower firmness compared to pears stored in NA, after a *shelf-life* period.

In [5], [23] it was observed that TSS values increased during *shelf-life* and that there were no differences in values between fruits stored at 3 kPa and 0,5 kPa of O_2. In fact, from **Table 2**, it can be seen that fruits stored under ULO and CA did not obtain divergent TSS values. It was also observed that fruits stored in NA exhibit lower TSS values, also verified in [24].

SS is a physiological problem that occurs in fruits after long-term NA-storage conditions, at low temperatures. Confirming this statement, SS was verified only in fruit stored under NA conditions. About 50% of the analyzed fruits had moderate to severe SS. No IB was detected in any conservation chamber.

3.2. Shelf-life *period*

The air from each desiccator was analyzed. The baseline did not stabilize on the analysis of the desiccator with pears stored in ULO+NA, and therefore no compound could be detected. On the other hand, the air from the desiccator containing pears that were stored under NA conditions was analyzed. It was possible to identify seven compounds and to quantify some of them (**Table 3**).

Ethanol was the most abundant VOC. In this analysis, 3 esters were detected, but the most abundant group was the alcohols. Esters, which give fruity and flowery aromas, have been described as the most abundant family of compounds, particularly on *shelf-life* period [10], [25]–[27]. In Barbosa's [15] work, alcohols were the most abundant group. It should be noted, however, that the analysis of VOCs produced by different pear varieties and in different periods of storage conservation can give different results.

Table 3 – VOCs identified for Rocha *pears stored in NA conditions, after seven days of* shelf-life *(23 °C), by GC-MS. VOCs with respective retention time (RT), probability given by the software, area, % area, and % height of the peaks. Expanded uncertainty with* k=*2.*

RT	Compound	Prob. (%)	Area (%)	Concentration (ppm)
5,69	Acetaldehyde	85,50	0,44	5,54 ± 4,77
6,87	Octane	28,30	0,07	-
7,71	Methyl Acetate	89,60	0,30	-
8,68	Ethyl Acetate	94,40	20,62	41,83 ± 1,90
9,50	Ethanol	89,30	77,49	705,90 ± 124,50
12,03	Butyl Acetate	82,30	0,31	0,33 ± 0,20
13,43	1-Butanol	54,80	0,76	1,74 ± 0,69

Ethanol production can be enhanced by *shelf-life* conditions, as verified by Chervin *et al.* [28]. The abundance of ethanol may also be related to the possibility that the O_2 content inside the desiccator has decreased during *shelf-life* and to the increase in CO_2 content, which favors the transition from aerobic to anaerobic respiration. Gomes *et al.* [13] reported that ethanol and ethyl acetate concentrations increased due to stress caused by a lack of O_2. Ethyl acetate is often associated with an excessive state of maturation and/or with anaerobic metabolism [29]. Saquet *et al.* [30] also found that ethanol increased over the conservation and even more during *shelf-life*.

In the desiccator with pears stored at ULO+AN conditions, zeolites were placed in separate Petri dishes. After desorption, 1mL of headspace gas was collected and injected into the GC. It was possible to identify 20 compounds with NaY UOP, and NaY GD, 5-A, and CBV each detected seven compounds. It was possible to quantify some of them (**Table 4**).

In all of these analyses, alcohols were the majority group, and ethanol was the most abundant compound. Acetaldehyde was, in all analyses, the second most abundant compound.

The only analysis where esters were detected was using NaY UOP, but their relative abundance is quite low compared to other compounds. This result contradicts the conclusion of the study by Gomes et al. [13], who states that esters, especially acetates, were the most abundant family of compounds in their analyses with fresh-cut Rocha pear. 1-Butanol, characterized by a metallic aroma [1], was also detected only using the concentration by the CBV zeolite, and it is reported that this alcohol increases with maturation [29]. Butyl acetate, the main compound in several studies with Rocha pear [1], [15], [17] and characterized by a sweet aroma [1], [29], was not detected in any of the previous analyses. In all analyzes where the technique of concentration of volatile compounds through zeolites and its consecutive desorption was used, the compound trimethylsilanol was detected. Given its characteristics, it is considered to be caused by the deformation of the silicone in the septum, caused by exposure to high temperatures.

It was not possible to carry out a direct comparison between the results obtained by analyzing the desiccator air and those obtained by desorption of zeolites, since the pears were stored under different conditions. However, it is possible to observe that the adsorbent NaY UOP, subjected to the same conditions as the other zeolites, was the adsorbent that obtained the highest concentration of VOCs. This fact may be due to the higher affinity of zeolite NaY UOP to the compounds under the conditions studied, which confirmation should be carried out. As Kim *et al.* [31] noted, NaY zeolites had better ethanol adsorption capacities than CBV mordenite under the same conditions. These tests can allow the selection of zeolites for use in devices to be built and to be used in the optimization of the atmospheres of the conservation chambers.

Ethylene production was measured by analyzing the air from each desiccator (**Table 5**). It was determined that pears stored under ULO+NA conditions showed a higher concentration than those under NA conditions. In fact, Saquet *et al.* [19], in a work with *Rocha* pear in the shelf-life period, observed that the ethylene production rate was higher in the first days, decreasing afterward. They found out that pears preserved under ULO conditions had a higher rate of ethylene production. When the fruits are subjected to atmospheres that drastically reduced their metabolism, and when they are placed at room temperature and normal oxygen levels, their metabolic response is boosted. Pears stored in ULO conditions, when transferred to NA conditions, had a metabolic response boosted by the increase of oxygen content. Then, when the fruits were transferred from NA conditions to shelf-life conditions, there was a new metabolic response, boosted by the increase in temperature. For pears stored only at NA conditions, the metabolic response was only enhanced by the increase of temperature. Also in [5], it was verified that, in *Rocha* pears stored for more than eight months, there was a higher production of ethylene in the *shelf-life* of fruits stored in ULO conditions, compared to AC conditions. Thus, it is natural that pears stored at ULO+NA conditions have a higher ethylene production in *shelf-life*, compared to pears stored only in NA conditions.

Table 5 – Ethylene quantification for Rocha *pears stored in NA and ULO+NA conditions, after seven days of* shelf-life *(23 °C), by GC-FID.*

Storage Conditions	Concentration (ppm)
NA	111,72
ULO+NA	239,11

3.3. Conservation period

Three samples were collected from the chamber under CA+1-MCP conditions, two on April 6th with CBV and 5-A zeolites (**Table 6**), and one on April 13th with NaY UOP zeolite (**Table 7**). In both cases, the zeolites were placed in the chamber seven days before.

It was possible to identify 15 compounds using CBV and 16 using 5-A. The most abundant group is alcohols, followed by aldehydes. Similar results were obtained by Deuchand *et al.* [32], where they conclude that the lowering of oxygen content in the storage of *Rocha* pear drastically increases the concentrations of ethanol and acetaldehyde since they are products of anaerobic metabolism. However, in fruits where 1-MCP was applied, lower production of fermentative metabolites would be expected, as the ethylene receptors would be blocked, preventing physiological processes of ripening [33]. In works with kiwi fruit, for example, it was observed that the application of 1-MCP reduced the production of acetaldehyde and ethanol, inhibiting the activity of the enzymes responsible for the catalysis of their production [34].

Table 4 - VOCs identified for Rocha *pears stored in ULO+NA conditions, after seven days of* shelf-life *(23 °C), by GC-MS, using different adsorbers. VOCs with respective retention time (RT), probability given by the software, and % area of the peaks. Expanded uncertainty with* k=*2.*

RT	Compound	NaY UOP			NaY GD			CBV			5-A		
		Prob. (%)	Area (%)	Concentration (ppm)	Prob. (%)	Area (%)	Concentration (ppm)	Prob. (%)	Area (%)	Concentration (ppm)	Prob. (%)	Area (%)	Concentration (ppm)
5,61-5,65	Acetaldehyde	83,50	3,06	2013,34 ± 39,70	80,70	5,43	39,34 ± 4,76	80,00	12,45	69,77 ± 4,83	70,00	12,75	41,80 ± 4,76
7,00	Propanal	35,30	0,08	-	-	-	-	-	-	-	-	-	-
7,42-7,45	Acetone	89,80	2,31	-	84,00	3,61	-	81,20	3,56	-	88,30	6,48	-
7,87	Octene	-	-	-	-	-	-	16,00	0,52	-	-	-	-
8,41-8,44	Butanal	84,10	0,03	-	-	-	-	-	-	-	67,30	0,78	-
8,53	Methacrolein	53,50	0,02	-	-	-	-	-	-	-	-	-	-
8,60	Ethyl Acetate	92,40	0,02	1,46 ± 0,20	-	-	-	-	-	-	-	-	-
8,85-8,87	2-Butanone	65,40	0,45	-	58,30	1,11	-	-	-	-	69,20	0,91	-
9,28-9,29	Isopropyl Alcohol	43,80	0,17	-	19,10	0,59	-	-	-	-	-	-	-
9,42-9,45	Ethanol	59,90	91,78	37841,63 ± 2556,79	90,70	84,37	393,65 ± 127,91	91,80	78,70	281,36 ± 129,99	91,10	74,72	158,30 ± 132,76
10,12	Ethyl Nitrate	45,70	0,03	-	-	-	-	-	-	-	-	-	-
10,22	Butanal, 3-methyl	-	-	-	-	-	-	-	-	-	44,40	2,31	-
10,23	2-Pentanone	64,80	0,27	-	-	-	-	-	-	-	-	-	-
10,77-10,79	Trimethylsilanol	83,70	0,25	-	80,10	4,04	-	55,20	2,46	-	56,30	2,06	-
11,21	1-Propanol	92,10	0,07	-	-	-	-	-	-	-	-	-	-
13,34	1-Butanol	-	-	-	-	-	-	23,90	1,26	1,11 ± 0,70	-	-	-
13,49	Imidazole, 2-amino-5-[(2-carboxyl) vinyl]-	19,60	0,35	-	-	-	-	-	-	-	-	-	-
13,77	Nitromethane	82,10	0,20	-	-	-	-	-	-	-	-	-	-
14,26	2-Heptanone	11,90	0,02	-	-	-	-	-	-	-	-	-	-
15,18	Isoamyl Alcohol	64,50	0,50	-	-	-	-	-	-	-	-	-	-
16,38	1-Pentanol	29,90	0,04	-	-	-	-	-	-	-	-	-	-
18,35	Isohexanol	28,10	0,02	-	-	-	-	-	-	-	-	-	-
19,64-19,74	1-Hexanol	49,00	0,33	-	17,80	0,86	-	11,40	1,05	-	-	-	-

Table 6 - VOCs identified for Rocha *pears stored in CA+1-MCP conditions, by GC-MS, using CBV and 5-A zeolites (06/04/2021). VOCs with respective retention time (RT), probability given by the software, and % area of the peaks. Expanded uncertainty with* k=*2.*

RT	Compound	CBV			5-A		
		Prob. (%)	Area (%)	Concentration (ppm)	Prob. (%)	Area (%)	Concentration (ppm)
5.37	Hexane	-	-	-	23.20	0.19	-
5.64-5.67	Acetaldehyde	84.30	452	342.87 ± 7.89	83.30	8.96	524.25 ± 10.97
6.98-7.00	Propanal	49.80	0.07	-	46.70	0.29	-
7.44-7.47	Acetone	91.20	3.29	-	92.20	5.35	-
8.42-8.44	Butanal	37.50	0.07	-	77.20	0.26	-
8.52-8.54	Methacrolein	31.90	0.02	-	47.30	0.07	-
8.60	Ethyl Acetate	84.70	0.04	0.29 ± 0.21	-	-	-
8.86	2-Butanone	-	-	-	77.40	0.76	-
8.88	5,9-Dodecadien-2-one, 6,10-dimethyl-(*E*,*E*)	62.10	0.60	-	-	-	-
9.12	Butanal, 3-methyl	-	-	-	56.10	0.15	-
9.27-9.29	Isopropyl Alcohol	58.20	0.36	-	30.70	0.37	-
9.43-9.45	Ethanol	91.00	88.81	4235.83 ± 265.08	91.10	75.54	2778.10 ± 182.53
10.22-10.23	2-Pentanone	56.30	0.28	-	60.50	0.61	-
10.78-10.78	Trimethylsilanol	76.80	0.15	-	82.10	0.18	-
11.87	Butyl Acetate	34.70	0.06	0.30 ± 0.20	-	-	-
13.45	2-Butanol	-	-	-	60.90	6.37	-
13.48	1-Butanol	66.50	1.17	14.28 ± 0.85	-	-	-
13.94	Nitromethane	86.40	0.43	-	85.20	0.64	-
14.98	2-Heptanone	-	-	-	32.00	0.17	-
19.75	1-Hexanol	14.80	0.13	-	14.00	0.11	-

Table 7 – VOCs identified for Rocha *pears stored in CA+1-MCP conditions, by GC-MS, using NaY UOP zeolite (13/04/2021). VOCs with respective retention time (RT), probability given by the software, and % area of the peaks. Expanded uncertainty with* k=*2.*

RT	Compound	Prob. (%)	Area (%)	Concentration (ppm)
5,64	Acetaldehyde	84.80	11.03	695.34 ± 14,11
7.45	Acetone	90.80	4.27	-
7.98	2-Propenal	86.60	0.08	-
8,44	Butanal	33.10	0.06	-
8.52	Methacrolein	69.40	0.07	-
8.87	2-Butanone	40.10	0.62	-
9.29	Isopropyl Alcohol	65.40	0.18	
9,44	Ethanol	90.70	81.89	3243.60 ± 207.24
10.24	2-Pentanone	69.00	0.22	-
10.79	Trimethylsilanol	74.30	0.08	-
13,49	1-Butanol	54,70	0,74	7.54 ± 0,69
13.96	Nitromethane	90.80	0.77	-

However, it must be considering the long-term storage of pears under CA conditions, which leads to a higher production of fermentative metabolites. Although both zeolites were placed in the same atmosphere for the same period, their adsorption capacity was different. The use of different zeolites can affect the characterization of the same atmosphere.

It was possible to identify 12 compounds using NaY UOP. The most abundant group is alcohols, followed by aldehydes. No esters were detected. That can be caused by 1-MCP. It has already been described that this antagonist reduces the production of this group of VOCs [10]–[12].

Monitoring of the ethylene concentration in different chambers throughout the conservation period was carried out. Analyses were performed at the end of the 2020/2021 campaign (March to May 2021) and at the beginning of the 2021/2022 campaign (August and September 2021).

The ethylene concentrations produced by pears harvested in 2021 (**Figure 1**) are lower than those obtained in the 2020 campaign (**Figure 2**), since the fruits, in the period of analysis, were in different conservation states.

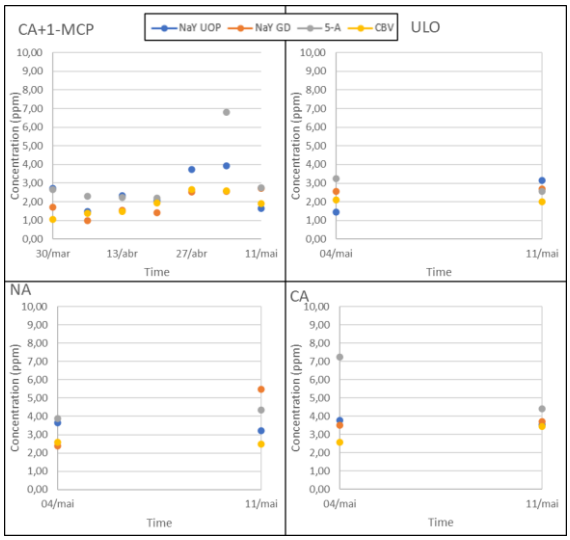

Figure 1 – Evolution of ethylene concentration in different conservation chambers, using different zeolites, by GC-FID. (2020/2021 campaign)

Evaluating the same period (May 4th to 11th), it is observed that the fruits stored at NA and CA conditions produced higher concentrations of ethylene (**Figure 1**). In ULO storage, having a higher oxygen content than CA storage, fruits produced less ethylene. This fact is due to the application of 1-MCP at the beginning of the conservation period, confirming the action of this post-harvest product in inhibiting and blocking ethylene receptors [11].

In **Figure 2**, it was verified that chambers under NA and AC storage conditions, which contains higher oxygen contents, revealed a lower ethylene concentration than the ULO chamber, with lower oxygen. It was observed that the chamber where 1-MCP was applied had a higher ethylene concentration, comparing to the chamber under NA conditions. These results are contradictory and can be caused by errors in the atmosphere control system or originated during analysis. Thus, it is not possible to conclude from these results regarding ethylene production.

In these analyses, it was possible to verify that NaY UOP is the adsorbent that concentrated higher ethylene concentrations. It was also concluded that the CBV will not be a good choice for ethylene removal from the chambers, since, with few exceptions, it was the adsorbent that least concentrates this compound.

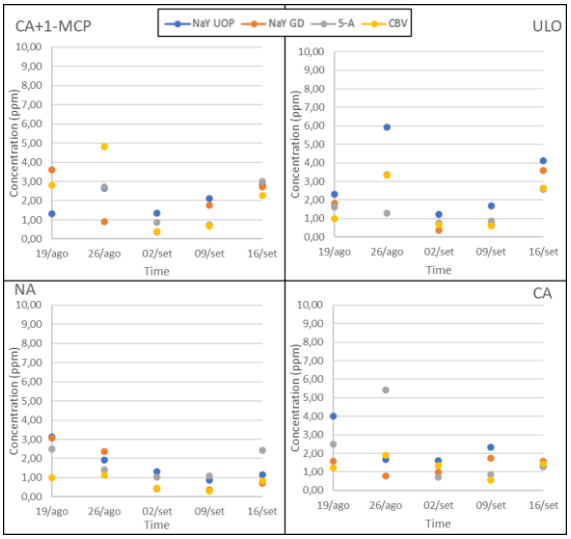

Figure 2 – Evolution of ethylene concentration in different conservation chambers, using different zeolites, by GC-FID. (2021/2022 campaign)

4. CONCLUSIONS

The analyses carried out by GC-MS allowed to identify 29 different compounds, eight of which belong to the alcohols group, six to aldehydes, five to ketones, and three to esters, among others. Alcohols were the most abundant compounds, with relative abundances higher than 70% in all analyses performed.

It was possible to observe that the adsorbent NaY UOP, subjected to the same conditions as the other zeolites, was the adsorbent that obtained the highest concentration of VOCs and ethylene. This fact may be due to the higher affinity of zeolite NaY UOP to the compounds under the conditions studied, which confirmation should be carried out in future studies. It was also concluded that the CBV will not be a good choice for ethylene removal from the chambers, since, with few exceptions, it was the adsorbent that least concentrates this compound.

This work can be the starting point of the development of external devices for monitoring the concentration of VOCs inside the conservation chamber and systems for ethylene removal.

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