VOLATILE AND SEMIVOLATILE COMPOUNDS QUANTIFICATION IN RECYCLED PLASTIC BY THERMAL DESORPTION COUPLED TO GAS CHROMATOGRAPHY AND MASS SPECTROMETRY

BACHELOR'S THESIS

MENCIÓN DUAL EN RAVAGO PLÁSTICOS

BACHELOR'S DEGREE IN CHEMISTRY

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Summary

Plastics are one of the fundamental bases in our daily life, constituting one of the most important industries worldwide. Due to do the new politics regarding pollution and sustainability, many companies have decided to reshape their production strategy, making use of resources that were considered waste: recycled material, especially in automotive production. One of the main disadvantages from the usage of recycled material is the corresponding increase in volatile organic compounds (VOC) emission, as the polymer and the additives suffer from multiple degradations during the consecutive production processes. These compounds migrate from the surfaces of the plastic components and come to contact with people, compromising their health.

In this work, the concentration of VOC in plastic samples sourcing from recycled materials are analyzed by TD-GC-MS in order to determine the effectivity of a silo implemented in the production process for emissions reduction. This installment has resulted successful for two out of the four grades examined, reducing significantly their VOC emission.

El plàstic és un dels materials fonamentals de la nostra vida quotidiana, constituint una de les indústries més importants a nivell mundial. A causa de la nova política en matèria de contaminació i sostenibilitat, moltes empreses han decidit remodelar la seva estratègia de producció, fent ús de recursos que es consideraven residus: material reciclat, especialment en la producció d'automoció. Un dels principals inconvenients de l'ús de material reciclat és el corresponent augment de l'emissió de compostos orgànics volàtils (COV), ja que el polímer i els additius pateixen múltiples degradacions durant els processos de producció consecutius. Aquests compostos migren des de les superfícies dels components plàstics i entren en contacte amb les persones, comprometent la seva salut.

En aquest treball s'analitza la concentració de COV en el proveïment de mostres de plàstic a partir de materials reciclats per TD-GC-MS per determinar l'eficàcia d'una sitja implementada en el procés de producció per a la reducció d'emissions. La implementació de la sitja ha resultat exitosa per a dos dels quatre tipus examinats, reduint significativament la seva emissió de COV.

1. Objective

The objective of this thesis is to implement a method for volatile and semi-volatile organic compounds determination sourcing from recycled polymers in order to determine whether the installment of a silo is successful for decreasing their concentration in the final product, as a constant exposure to these compounds can be harmful to the health and a control is becoming a requirement for automobilist customers.

To achieve this, the following steps were taken: sampling of polymer and air from the silo under specified conditions; analysis by thermal desorption coupled to gas chromatography and mass spectrometry; and chemometric data analysis in order to extract meaningful conclusions.

2. Introduction

In this section, a brief introduction to all the topics related to the project is done: to the company that suggested the thesis and their business idea and objective, to the polymeric background of the polymeric samples that were analyzed and to the analytical basics for the sample analysis understanding.

2.1. Polymeric background

2.1.1. The company: Ravago Plásticos

Ravago is a Belgic company founded in 1961 with the aim of creating a new polymer manufacturing from petrochemical production waste. The company came to Vilallonga del Camp in 1979, stablishing their first headquarters in Spain (Figure 1), to a strategical position near a petrochemical center close to the Mediterranean Sea with the objective of expanding the business with new plastic applications and utilities mainly destined to automotive, household and electrical components.

The objective of this company is to create new materials with smaller environmental footprint and costs but achieving the same quality as a prime polymer. Because of this reason,

the company decided to invest into the development of a project destined for automobile industry, with the objective of decreasing the volatile and semivolatile organic compounds concentration and their consequently odor that is sourced from plastic reprocessing, as they support a health hazard under long-term exposure.

Figure 1. First installations of Ravago Plásticos (Vilallonga, Spain) in the 80s [1]

2.1.2. Upcoming regulations

The interest in Ravago for increasing and improving their recycled material is promoted by the actions of the European Automobile Manufacturers' Association (ACEA) [2], who is in process of implementing a plan determining that, with prospect for 2030 and in order to reduce waste coming from automobile production, the recycled material used in the production of vehicles should reach a minimum percentage, both from recycled pre-consume plastics and from post-consume, which should contain a certain percentage of ELV (end-of-life vehicles), promoting circularity and sustainability in automobile creation. The percentages have not yet been defined, but the general overview suggests around a 20%, in order to reduce the environmental impact and energy consumption.

2.1.3. Problematic

One of the main issues from the usage of plastics and, furthermore, recycled plastics, is their release of volatile organic compounds (VOC) and semivolatile organic compounds (FOG or sVOC). Both VOC and FOG may come from additives and components of polymers that migrate to the surface and remain in gaseous state or condensate, respectively, in the automobile compartment due to the easy increase in temperature and the consequent desorption

(mainly in summer time), concentrating in a small confined space, as illustrated in Figure 2.[3,4] By this effect, FOG, of a higher molecular weight, lead to deposition in windscreens, producing a "fogging" effect and reducing transparency, therefore their name. These molecules can be easily detected by the odor they emit, with a response proportional to their concentration and intensity.[5,6]

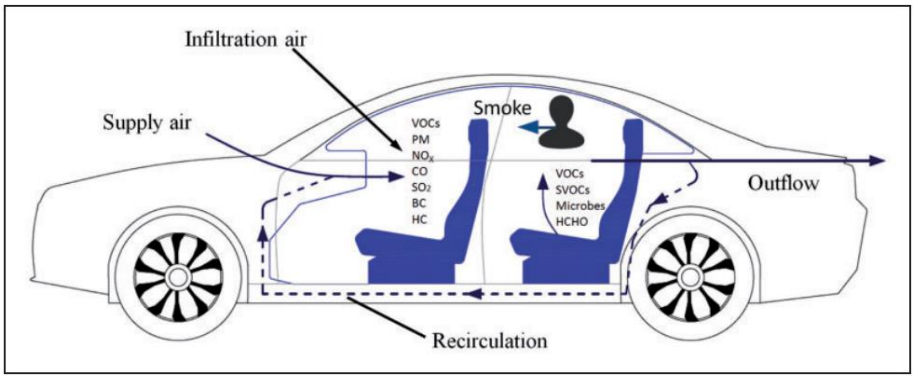


Figure 2. Schematic representation of in-cabin air pollutant sources and transport.[7]

In the last decade, multiple studies have shown the relationship between air pollution and adverse health effects: eyes and throat irritation, allergic reactions, headaches and tiredness[6]. Some of these harmful pollutants are, among other substances, particulate matter (PMs), inorganic oxides, aromatic hydrocarbons and carbonyls, VOC and FOG. The main concern regarding permanent health issues is related to VOCs, which contain substances classified as "possibly carcinogenic" or "carcinogenic" by the World Health Organization (WHO) and the International Agency for Research on Cancer (IARC), as well as leading to morbidity and adverse respiratory, cardiovascular and neurological effects.[5,7]

Due to this problematic, the voluntary program for the European Automotive Industry (VDA) has declared their intention on defining limits for VOC and FOG concentration in the interior of vehicles. One of the designed tests for testing is the Method VDA-278[8] for semiquantitative determination of emissions from nonmetallic molded materials used in automotive industry under dynamic conditions. [9]

The project Ravago has implemented for VOC and FOG concentration reduction in recycled plastic consists of the installment of a silo (Figure 3) in which the material, immediately after production, will undergo an air flow of determined temperature and pressure in order to heat the material and promote the extraction of VOC and FOG. This silo has a capacity of 25 tons but, to ensure that the plastic was properly heated by the air flow, it was

only filled up to 5 tons. As for the project approach, samples of the material will be taken before and after the silo with different residence times in order to determine an effective residence time for VOC and FOG reduction in the final material. This material will be analyzed by following the directions stated in the VDA 278 and then compared among grades and residence times to find the optimal procedure for reduction of odor and organic compounds.

Figure 3. Silo installment: the hot air is introduced through the circular bottom tubes.

2.2. Analytical background

TD-GC-MS (Thermal Desorption coupled to Gas Chromatography and Mass Spectrometry) is widely used for determination of multiple substances. They are coupled as shown in Figure 4 to allow a more precise and accurate identification of the substances, as well as to decrease the limits of detection and quantification of the desired compounds [10]. As it is shown, the desorption tube containing the sample is connected to the cryogenic trap, in which the analytes are focused, and then transferred to the chromatographic column inside the oven. Lastly, these compounds exiting the column arrive to the detector of the mass spectrometer, and the results are obtained as a chromatogram and the corresponding mass spectra. As represented in the left of the figure, all this analyte transfer is performed by a carrier inert gas.

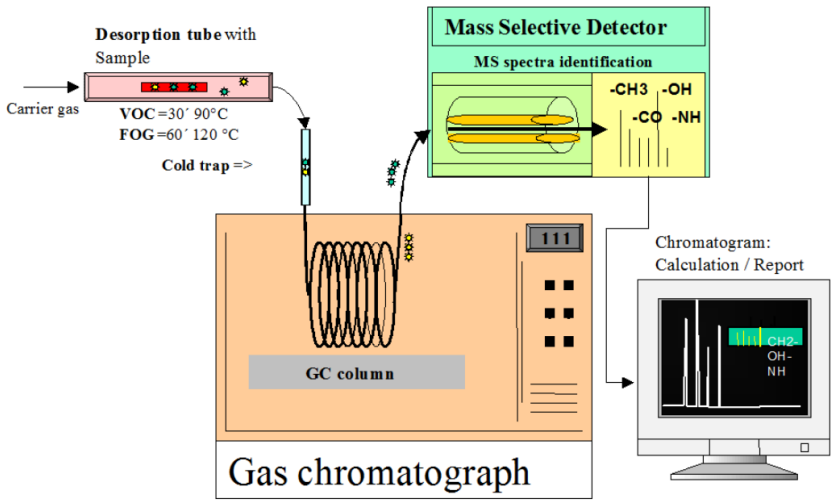


Figure 4. TD-GC-MS set-up. [8]

2.2.1. Thermal desorption

Thermal desorption is a technique usually combined with gas chromatography for monitoring of traces and analysis of solid samples or analytes sourcing from liquid or gas samples that have been previously extracted and trapped in a solid sorbent, by volatilization of their components. The analytes are desorbed from the sample and transferred to the cold trap, in which they are trapped by condensation, as well as by the action of a sorbent if the trap has. One of the advantages is that there is no need for using any organic solvent for desorption, which reduces the environmental impact of the analysis overall.[11]

The cold trap enables the compounds to reach the chromatographic column by a focusing step, which results in narrower peaks and therefore, higher sensitivity. As well, high selectivity is obtained as the desired compounds are retained in the cold trap and unwanted substances (solvents, gases) can be purged both by the desorptions of the tube and the cryogenic trap by applying the *split* mode. That allows the extraction from complex solid, liquid and gas samples, mainly for volatile and semivolatile organic compounds. Another characteristic of this techniques is that is can be combined with real time sensors, such as the eNose, an ensemble of sensors that recognize odors and process their intensity to relate them to volatile organic compounds concentrations.

The solid sample or the retained analytes are placed in the desorption unit and conducted to the desorption process, which is divided in two steps (Figure ***5***). In the first one the desorption tube is heated at high temperatures, extracting the compounds from the adsorbent of from the solid sample and are directed by an inert gas flow to the cold trap. Once

the analytes are retained in the cold trap, the second step begins, in which the compounds are now desorbed from the cold trap into a transfer line to finally reach the chromatographic column, also by using high temperatures and an inert gas flow.

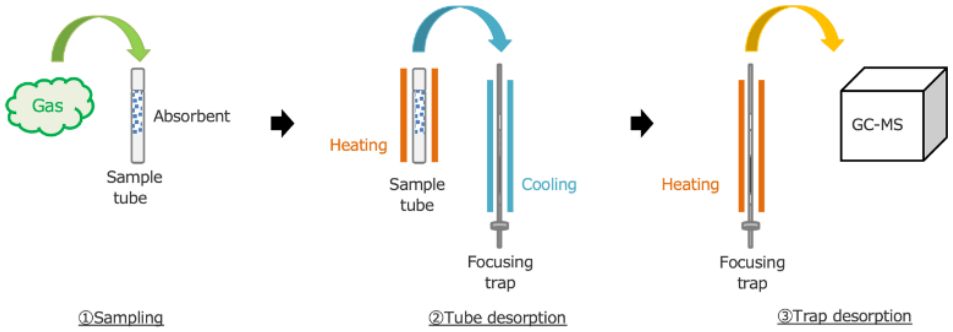


Figure 5. Thermal desorption main steps scheme [12]

2.2.2. Gas chromatography and mass spectrometry

In gas chromatography the desorbed components of the sample are separated in a chromatographic column according to their affinity to the stationary phase and push with a flow of an inert gas, called the mobile phase or the carrier gas. For the analysis of VOC and FOG usually open tubular well coated columns (WCOT) that are apolar are used as they provide a good separation in their range of compounds at the stablished temperatures[13]. Due to the complexity of the sample and considering the volatility of these compounds an oven temperature gradient from 40 to 280ºC should be used.

Mass spectrometry (MS) is one of the most frequently used detectors after the chromatographic step, a block diagram of the process is represented by Figure 6.

The ionization source is of electronic impact (EI), in which the molecules are bombarded with a beam of electrons creating ionized molecules represented by their m/z (mass charge ratio), in which z usually equals one[14]. The mass analyzer allows the separation of the different ions that arrive by a quadrupole: four parallel rods create electric fields that allows a single ion to pass through and reach the detector [15.] The mass detector consists of a transducer, also considered an electron multiplier, that transforms and enhances the ions into an electric signal, allowing the ionic signals to be recorded.

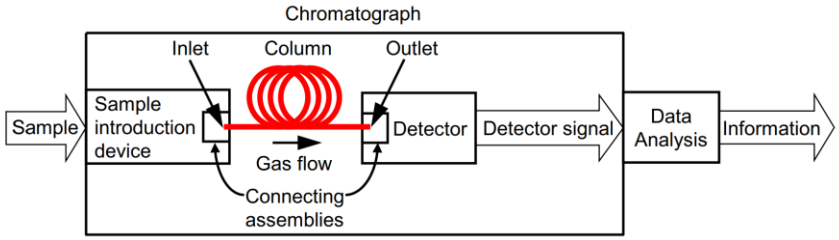


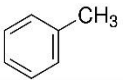
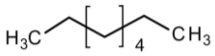
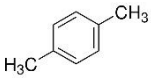
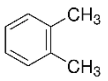
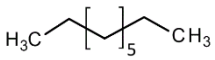
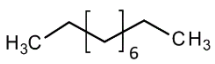
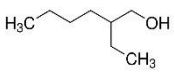
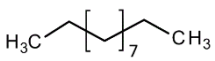
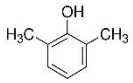
Figure 6. Block diagram of a gas chromatograph coupled to a mass spectrometer detector.[13]

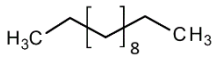
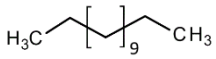
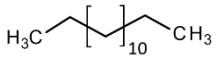
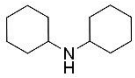
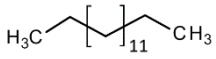
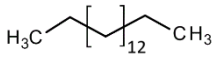
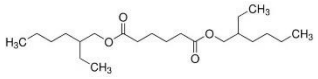
3. Experimental part

3.1. Reagents and standards

The standards used for the analysis of plastics were 18 VOC and FOG (Sigma-Aldrich, Steinheim, Germany): benzene, n-heptane, toluene, n-octane, p-xylene, o-xylene, n-nonane, n-decane, 2-ethylhexanol-1, n-undecane, 2,6-dimethylphenol, n-dodecane, n-tridecane, n-tetradecane, dicyclohexylamine, n-pentadecane, n-hexadecane and bis(2-ethylhexyl) adipate, bought as GC individual reference substances of purities higher than 98%. In Table 1 the main chemical properties such as the molecular weight, structure and CAS number are stated for these 18 compounds. A control stock solution was prepared with the 18 compounds, with an approximate concentration of 45000 µg mL^{-1}. From there, a working solution of 110 µg mL^{-1} was prepared in methanol suitable for GC analysis (Carlo Erba, Sabadell, Spain) and stored in the freezer at -19ºC.

Table 1. Target analytes and chemical properties.

Compound	MW ($g\ mol^{-1}$)	CAS No.	Formula	Structure
Benzene	78,11	71-43-2	C_6H_6	
n-Heptane	100,2	142-82-5	C_7H_{16}	
Toluene	92,14	108-88-3	C_7H_8	
n-Octane	114,23	111-65-9	C_8H_{18}	
p-Xylene	106,17	106-42-3	C_8H_{10}	
o-Xylene	106,17	95-47-6	C_8H_{10}	
n-Nonane	128,26	111-84-2	C_9H_{20}	
n-Decane	142,28	124-18-5	$C_{10}H_{22}$	
2-Ethylhexanol-1	130,23	104-76-7	$C_8H_{18}O$	
n-Undecane	156,31	1120-21-4	$C_{11}H_{24}$	
2,6-Dimethylphenol	122,16	576-26-1	$C_8H_{10}O$	

n-Dodecane	170,33	112-40-3	$C_{12}H_{26}$	
n-Tridecane	184,36	629-50-5	$C_{13}H_{28}$	
n-Tetradecane	198,39	629-59-4	$C_{14}H_{30}$	
Dicyclohexylamine	181,32	101-83-7	$C_{12}H_{23}N$	
n-Pentadecane	212,41	629-62-9	$C_{15}H_{32}$	
n-Hexadecane	226,44	544-76-3	$C_{16}H_{34}$	
Bis(2-ethylhexyl) adipate	370,57	103-23-1	$C_{22}H_{42}O_4$	

For VOC and FOG quantification of the plastic samples calibration solutions of toluene and n-hexadecane, respectively, were prepared in methanol (Carlo Erba) and also stored in the freezer.

Regarding the air samples, standard commercial mixtures EPA 592/594 Volatile Organic Calibration Mix (Supelco, Bellefonte, USA) and individual standards of 1,3-butadiene, i-pentane, n-pentane, 2-pentene, isoprene, 1-hexene, n-hexene, n-octane and 1,2,3-trimethylbenzene (Aldrich, St. Louis, USA), 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene, 1,3-diethylbenzene, 1,4-diethylbenzene (Fluka, Buchs, Switzerland) and 2-methylnaphthalene (Riedel-de Häen, Seelze, Germany) were bought. In total, the compounds determined in air samples were 108.

For the chromatographic analysis helium and nitrogen (Carburos Metálicos, Tarragona, Spain) of 99.999% purity were used.

3.2. Sampling and sample treatment

The polymeric samples were collected in pellet shape by the production personnel from Ravago Plásticos into five-liter low density polyethylene bags and stored closed with tape until their pretreatment. To homogenize the samples, the pellets were shaped by an injection machine (Allrounder 320c Golden Adition, Arburg S.A., Spain) with standardized conditions such as temperature and pressure specified in Table 2 and before and after the injection the

machine was cleaned. The mold used was UL94 1.6/3.2MM Mould insert (Axxicon B.V., The Netherlands) (Figure 7) and the resulting probes (Figure 8) were of dimensions 1.6 x 10 x 100 mm. Each of the samples was individually wrapped in aluminum foil, carried to the university and stored in a polyethylene bag until the analysis.

Table 2. Injection conditions for the probes

	Zone 1 Material entry	**Zone 2**	**Zone 3**	**Zone 4**	**Zone 5 Material exit**
Temperature	155 ± 10	170 ± 20	180 ± 20	190 ± 20	200 ± 10
		Injection	**Post-Pressure**		
	Pressure (bar)	1100	200	250	25
Pressure	Time (s)	-	0.30	17.00	0.10
	Required volume (cm^3)	**Extrusion speed ($cm^3\ s^{-1}$)**	**Extrusion pressure (bar)**	**Commutation volume (cm3)**	**Dosing volume (cm^3)**
Dosing	39.000	5.0	1100	13.000	39.000

Figure 7. Mold used for probe injection

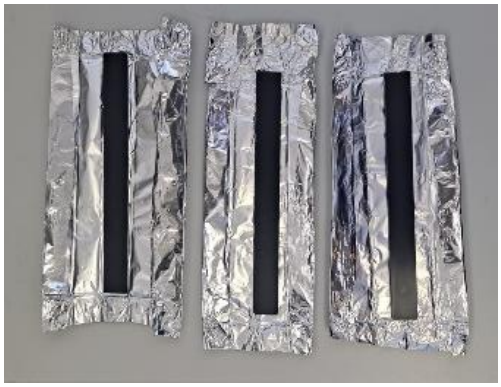


Figure 8. Probes obtained by pellet injection

The samples of the air inside the silo were taken with an active sampler, Markes ACTI-VOC Pocket Sized Sampling pump For Thermal, attached to stainless steel tubes with 600 mg Carbopack X adsorbent, of 9 cm length, 6.35 mm and 4.5 mm outer and inner diameters (Supelco, Bellefonte, USA). The tube, attached to the pump as shown in Figure 9, was placed

in a designated hole in the upper part of the silo and sampled at a flow of 50 ml min^{-1} for 5 minutes.

Figure 9. Active sampling probe.

3.3. Analysis procedure

The plastic samples were left uncovered for seven days to simulate the production process. Then, they were cut by using a paper-cutter, achieving a surface as smooth and consistent among samples as possible. To reach the required 30 ± 5 mg required by the VDA 278, the initial probes were cut in strips of 1.6 x 10 x 1.8 mm approximately, considering a general density of 1.05 g cm^{-3}. Immediately after, each piece was placed in an empty glass desorption tube of 6 cm length and 5mm and 4.8 mm outer and inner diameters (Markes International, Cardiff, United Kingdom) (Figure ***10***) and carried to the instrument.

Figure 10. Desorption tubes containing plastic samples.

They were desorbed by an ULTRA TD autosampler coupled to a UNITY 2 thermal desorber (Markes International). The cryogenic tramp, hydrophobic focusing trap of quartz, with 60 mm of sorbent, bought also in Markes International was newly installed for this method. A new analytical column HP Ultra 2 (50m x 0,32mm x 0,52µm) of (5%-phenyl)-methylpolysiloxane (Agilent Technologies, Santa Clara, California, USA), was also installed in a 7890A gas chromatograph system, coupled to a 5975C inert mass spectrometer with Triple-Axis Detector (Agilent Technologies).

As indicated in the VDA, there are three different TD methods (shown in Table ***3***): for volatile organic compounds, semivolatile organic compounds and calibration solutions; and two different GC-MS methods (shown in Table ***4***): one for volatile organic compounds and calibration solutions and another for semivolatile organic compounds.

Table 3. Parameters for TD analysis of plastic samples.

Unit	**Parameters**	**VOC**	**FOG**	**Calibration & control**
Thermal desorption unit	Tube desorption t.:	90 ºC	120 ºC	300 ºC
	Tube desorption time:	30 min.	60 min.	10 min.
	Flow path t.:	200 ºC		
	Trap flow:	42 mL min^{-1}.		
	Split flow (inlet/outlet):	42 mL min^{-1}.		
Cold trap	Cold trap low t.:	-30 ºC		
	Cold trap high t.:	300 ºC		
	Cold trap hold time:	3 min.	5 min.	10 min.
	Trap heat rate:	> 60 K s^{-1}		

Table 4. Parameters for GC-MS analysis of plastic samples.

Unit	**Parameters**	**VOC**	**FOG**
Gas chromatograph	Flow	1.3 mL min^{-1} (He)	
	Temperature program	40ºC for 2 min.	50ºC for 2 min.
		3 ºC min^{-1} to 92ºC	25ºC min^{-1} to 160ºC
		5 ºC min^{-1} to 160ºC	
		10 ºC min^{-1} to 280ºC	10 ºC min^{-1} to 280ºC
		Hold for 10 min.	Hold for 10 min.
Mass spectrometer	Start of data capture	3 min.	
	Scan mode	29-450 amu, >3 scans s^{-1}	
	MS threshold	50	

For the plastic sample analysis, the standard procedure stablished by the VDA, stated in Table 5, should be followed to ensure the proper functioning of the analysis. In our case, multiple replications of each sample were analyzed in order to check for repeatability among samples by the repetition of steps 5-7, as it is recommended.

Table 5. Analysis procedure scheme.

No.	Type	Sample	Tube	TD	GC
1	Blank	-	Glass	Calibration	VOC
2	Control	Control standard	Tenax TA	Calibration	VOC
3	Calibration	Toluene standard	Tenax TA	Calibration	VOC
4		Hexadecane standard	Tenax TA	Calibration	FOG
5	Blank	-	Glass	VOC	VOC
6	Samples	Sample portion 1	Glass	VOC	VOC
7		Sample portion 2	Glass	VOC+FOG	VOC+FOG
8	Calibration	Toluene standard	Tenax TA	Calibration	VOC
9		Hexadecane standard	Tenax TA	Calibration	FOG
10	Control	Control std.	Tenax TA	Calibration	VOC

The air samples were analyzed in a gas chromatograph 7890A (Agilent Technologies, Palo Alto, U.S.A.), with a capillary column ZEBRON ZB-5 (Phenomenex, Torrance, CA, U.S.A.), and helium 99.999% purity as the carrier gas. The detection was done by a mass spectrometer 5975C (Agilent Technologies, Palo Alto, U.S.A.), in full scan mode, and the splitless desorption took place in a Unity 2 system (Markes International Limited, Llantrisant, UK). The instrument parameters for the TD-GC-MS analysis are collected in Table 6.

Table 6. Parameters for TD-GC-MS analysis of active air samples.

Unit	Parameters	Active samples
Thermal desorption unit	Tube desorption t.:	330 ºC
	Tube desorption time:	10 min.
	Trap flow:	20 ml min^{-1}.
	Split flow (inlet/outlet):	Splitless
Cold trap	Cold trap low t.:	-30 ºC
	Cold trap high t.:	330 ºC
	Cold trap hold time:	10 min
	Trap heat rate:	> 60 K s^{-1}

Gas chromatograph	Flow	1.2 ml min^{-1} (He)
	Temperature program	40 ºC for 5 min. 6 ºC min^{-1} to 140 ºC 15 ºC min^{-1} to 220ºC Hold for 8 min.
Mass spectrometer	Start of data capture	3 min.
	Scan mode	35 - 280 amu

3.4. Calibration

To ensure the chromatographic separation worked properly during the whole analysis of the plastic samples, a control solution had to be spiked before and after each analysis.

To check the chromatographic separation, 4 µL of the control solution of 110 µg mL^{-1} were spiked into a Tenax® TA tube, stainless-steel mesh with Tenax TA adsorbent (particle size 35/60 mesh), of 6 cm length, and 5 mm and 4,8 mm outer and inner diameters (Markes International) using a 10 µL syringe and the sandwich technique (placing air before and after the sample) which was then purged on a calibration loading ring (Markes International Limited) for 5 minutes at 100 ml min^{-1} of helium in order to evaporate the methanol.

For the quantifications of the samples an external calibration curve was created by standard solutions of toluene and hexadecane in methanol. Tenax® TA sorbent tubes were spiked with 1 µL of each solution using a 10 µL syringe and the sandwich technique, and the same purge method as before. Both standard solutions of toluene and hexadecane were prepared to achieve between 10 and 1000 ng of compound in the tubes. As recommended, linearities were checked to be $R^2 \geq 0.99$.

The calibration for the air samples was already done by the group CROMA, following their usual procedure by spiking the mentioned standards in Carbopack X tubes and allowing the determination of 108 compounds. Therefore, no other calibration procedure was required for these samples.

3.5. Quantification of the samples

The quantification of the plastic samples is done accordingly to a response factor proportional to the areas of the calibration solutions of toluene (for volatile organic compounds) and hexadecane (for semivolatile organic compounds). By Equation 1 the response factor (Rf) is obtained and by Equation 2 the proportional emission of VOC or FOG is obtained.

$$R_f = \frac{\mu g \text{ Toluene / Hexadecane}}{\text{Peak area}} \cdot 1000000 \qquad \text{Equation 1}$$

$$\text{Emission } [\mu g\ g^{-1}] = R_f \text{ (Toluene/Hexadecane)} \cdot \frac{\text{Sum of peak area}}{1000 \cdot \text{test portion sample (mg)}} \qquad \text{Equation 2}$$

The quantification of the air samples is done taking into account the sampling time (5 minutes) and the air flowrate (50 ml min^{-1}). The mass is obtained by the substitution of the area obtained for each compound in their corresponding calibration curves. To consider the air flow, Equation 3 allows the change from mass to concentration.

$$C\ (\mu g\ m^{-3}) = \frac{m_d - m_b}{Ru_T \cdot t} \cdot 10^6 \qquad \text{Equation 3}$$

The parameters mentioned in this equation correspond to:

m_d (µg): mass of analyte obtained from the sample analysis

m_b (µg): mass of analyte obtained from the blank

Ru_T (ml min^{-1}): adsorption for each analyte under sampling time. This value had already been calculated for each analyte

t (min): sampling time

3.6. Chemometric data analysis

To extract conclusions from the obtained data by the chromatographic analysis chemometric analysis is done for the interpretation of the data and achievement of factual conclusions. For these tests, the population is assumed to have a normal distribution, and the values are calculated considering a confidence interval of 95%. The analysis is divided in two different categories.

Firstly, the detection of possible outliers among the sample measurements, in order to achieve unbiased conclusions. In Europe, according to the ISO normative, the recommended test for outlier detection is Grubb's test[16]. For the test, the $G_{calculated}$ (Equation 4) is compared to the $G_{critical}$, considering the size (N) of the matrix (Equation 5).

$$G_{calculated} = \frac{\left|x_{suspected} - \bar{x}\right|}{s} \quad \text{Equation 4}$$

$$G_{critical} = \frac{(n - 1) \cdot t_{crit}\left(\frac{\alpha}{n}, n - 2\right)}{\sqrt{n \cdot \left(n - 2 + \left(t_{crit}\left(\frac{\alpha}{n}, n - 2\right)\right)^2\right)}} \quad \text{Equation 5}$$

Then, the average values of the concentrations of different samples are compared in order to determine whether there are significant differences among them, for that a t-test is done. To determine whether the variances of these samples are comparable or not and decide which type of t-test to apply, a F test is required.[17] For the variance comparison the following $F_{calculated}$ (Equation 6) is compared to the corresponding tabulated $F_{critical}$.

$$F_{calculated} = \frac{{s_1}^2}{{s_2}^2} \quad \text{Equation 6}$$

For the comparison of the mean value by a t-test the $t_{calculated}$ value is obtained from Equation 7. In the case of comparable standard deviations, a pooled estimate of s is calculated by Equation 8 and the degrees of freedom by Equation 9. In the case of non-comparable standard deviations, the individual deviations are used, and the number of degrees of freedom is calculated by Equation 10, approximated to an integer.

$$t_{calculated} = \frac{\left|\overline{x_1} - \overline{x_2}\right|}{\sqrt{\frac{{s_1}^2}{n_1} + \frac{{s_2}^2}{n_2}}} \quad \text{Equation 7}$$

$$s = \frac{(n_1 - 1){s_1}^2 + (n_2 - 1){s_2}^2}{(n_1 + n_2 - 2)} \quad \text{Equation 8}$$

$$dof = n_1 + n_2 - 2 \quad \text{Equation 9}$$

$$dof = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\frac{s_1^4}{n_1^2\,(n_1 - 1)} + \frac{s_2^4}{n_2^2\,(n_2 - 1)}}$$ Equation 10

The parameters mentioned in these equations correspond to:

x: average value of the samples

s: standard deviation of the samples

s^2: variance of the samples

n: number of values per sample

α: significance level (0.05)

dof: degrees of freedom

4. Results and discussion

One important consideration in this project is that, as the plastics to be analyzed were very complex samples, in cases that there were areas without a regular baseline the individual integration of these peaks was not recommended, but rather the integration of this area as a whole, determining any peaks above the baseline. For peaks with well-defined starting and ending points, regular individual integration was performed.

The materials chosen for the project were four grades destined for automotive production: three partially recycled polypropylene rich in talc (named Talc1, Talc2 and Talc3) and one fully recycled polypropylene rich in fiber (named Fiber). The characteristics of these materials are specified in Table 7.

Table 7. Characteristics of the materials to be analyzed

Material	**Recycled (%)**	**Filler**	
		(%)	**Characteristics**
Talc1	40	11.5	Lamellar
Talc2	35	16	Compacted
Talc3	30	10	Compacted
Fiber	77	20	-

4.1. Chromatographic separation and calibration results

As mentioned in the previous sections, the analytes were analyzed according the VDA and then identified in order to find the corresponding retention times. For this identification, as shown in Table 8, each of the resulting peaks from the mass spectrometric step had some characteristic ions (and relative abundancies of each): the main ion was used for quantification of the analyte and the next three of mayor abundancy (with respect to the quantifier ion) to distinguish among compounds. Additionally, these spectrometric data was compared to a data library available in the equipment to verify that our analytes had similar spectra to the bibliography. Figure 11, which consists on the chromatogram of all the analytes used for the control solution, shows the proper separation of the analytes in narrow peaks, as well as the retention times for each of them.

Table 8. Retention times and ions of analytes (relative abundance in brackets)

Analyte	**t_R (min)**	**Quantifier ion**	**Qualifier ions**		
Benzene	6.337	78	77 (23%)	51 (15%)	52 (15%)
n-Heptane	7.344	43	71 (67%)	41 (56%)	57 (56%)
Toluene	9.934	91	92 (60%)	65 (11%)	39 (8%)
n-Octane	11.283	43	85 (60%)	41 (48%)	57 (46%)
p-Xylene	14.793	91	106 (49%)	105 (24%)	77 (13%)
o-Xylene	16.006	91	106 (48%)	105 (20%)	77 (12%)
n-Nonane	16.247	43	57 (98%)	41 (50%)	85 (41%)
n-Decane	21.428	57	43 (82%)	71 (44%)	41 (42%)
2-Ethylhexanol-1	22.729	57	41 (37%)	43 (30%)	55 (29%)
n-Undecane	25.724	57	43 (74%)	71 (51%)	41 (41%)
2.6-Dimethylphenol	26.066	122	107 (94%)	121 (33%)	77 (32%)
n-Dodecane	29.306	57	43 (70%)	71 (59%)	41 (38%)
n-Tridecane	32.441	57	43 (69%)	71 (63%)	85 (40%)
n-Tetradecane	35.051	57	43 (67%)	71 (66%)	85 (42%)
Dicyclohexylamine	35.739	138	56 (28%)	55 (13%)	181 (12%)
n-Pentadecane	37.044	57	71 (68%)	43 (65%)	85 (44%)
n-Hexadecane	38.686	57	71 (68%)	43 (65%)	85 (45%)
Bis(2-ethylhexl) adipate	47.696	129	57 (40%)	55 (30%)	70 (29%)

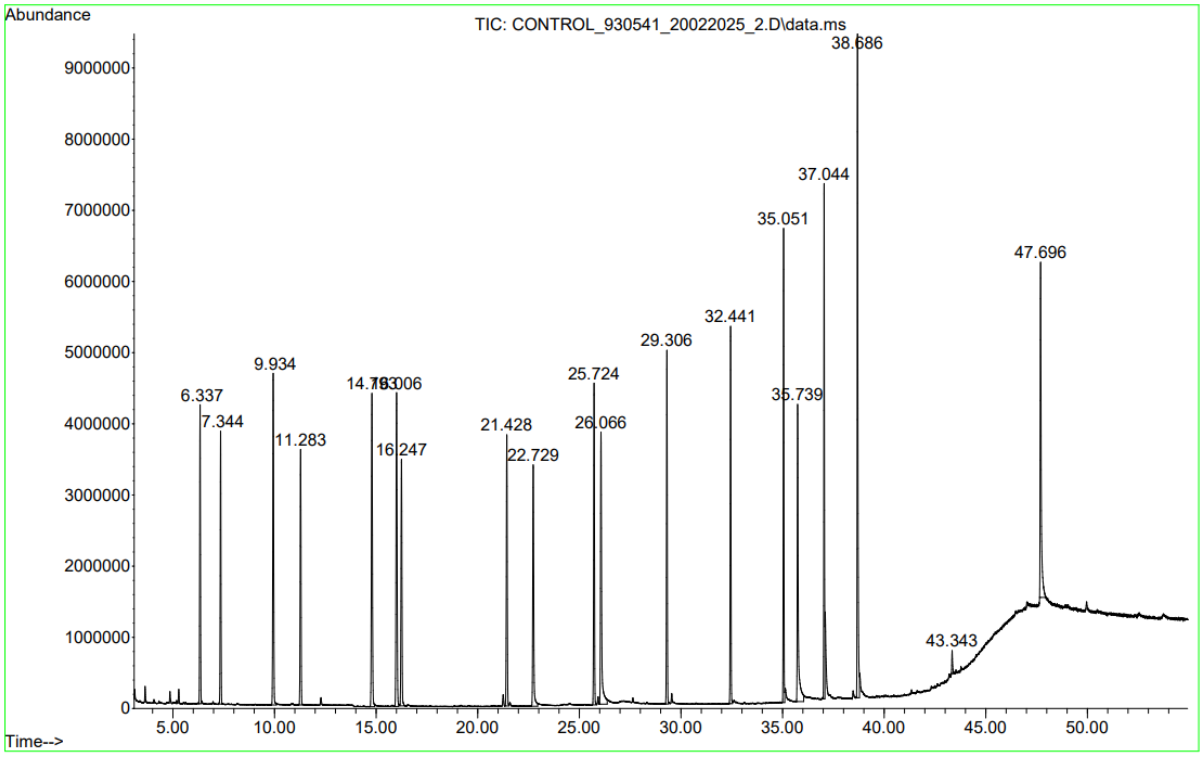


Figure 11. Chromatogram of control solution.

With respect to the external calibration curves of toluene and hexadecane in methanol, the obtained linearities were y = 7E+07x – 485721 with R^2 = 0.9988 for toluene and, for hexadecane, y = 9E+07x + 3E+06 with R^2 = 0.9948.

As previously mentioned, the calibration for the air samples was already done, and the previous values were used.

4.2. Preliminary analysis

As a first approach to the project, it was decided to gather material previously produced in order to achieve an approximation of the initial values of VOC and FOG compounds that would be expected and what could achieve. For this, three different materials out of the four to be analyzed were sampled: Fiber, Talc1, and Talc2. The samples were analyzed, as stated in the norm, twice for VOC and once for FOG. According to the stated results, the Fiber material had a lower VOC and FOG concentration (in the order of 50 and 150-200 µg g^{-1} respectively) than both materials containing talc (with concentrations of 250-300 and higher than 300 µg g^{-1}, respectively), shown in Figure 12.

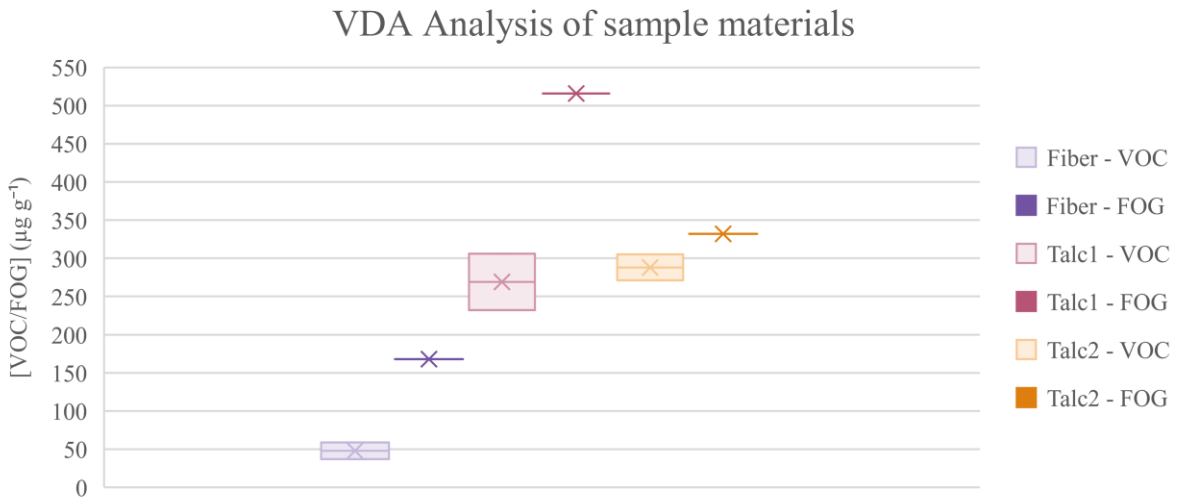


Figure 12. Box and whisker chart of initial VOC and FOG concentrations of three different materials.

Multiple outliers were detected at the beginning due to improper closure of the desorption tubes, which led to leaks during the thermal desorption step and loss of organic compounds concentration. As that situation was noticed, the taps were reconditioned and in the following analysis no more leaks were detected when the final samples were analyzed.

4.3. First productions

The next step was to sample these materials in the following productions once the silo was working according to the recommended conditions: incoming air at 80ºC, air flowrate of 1000 $m^3\ h^{-1}$ during 8 hours; and compare the concentrations obtained from the raw material and the material after the treatment. As an additional measure, some materials were given a longer residence time, in order to deduce its effects.

For each of the samples multiple analyses were performed in order to guarantee repeatability and reproducibility along the tests, as well as to have additional values in case outliers were detected. Figure 13 and Figure 14 represent the obtained results: for Talc2 and Talc1 the samples were analyzed before the silo and after eight hours, and the values were around 300 and 150 µg g^{-1} for VOC and around 200 µg g^{-1} in FOG; in the other hand, the Fiber sample was done before the silo, and after eight, twelve and sixteen hours, and the values for all these variations are within 50 µg g^{-1} for VOC and FOG. As a general conclusion from the figures, no difference in concentrations can be observed among samples at different residence times in the silo.

A t-test performed to the data obtained, represented in Table ***9***, showed that there was no significant difference in the mean of any of these productions, suggesting that the silo was not working as supposed to.

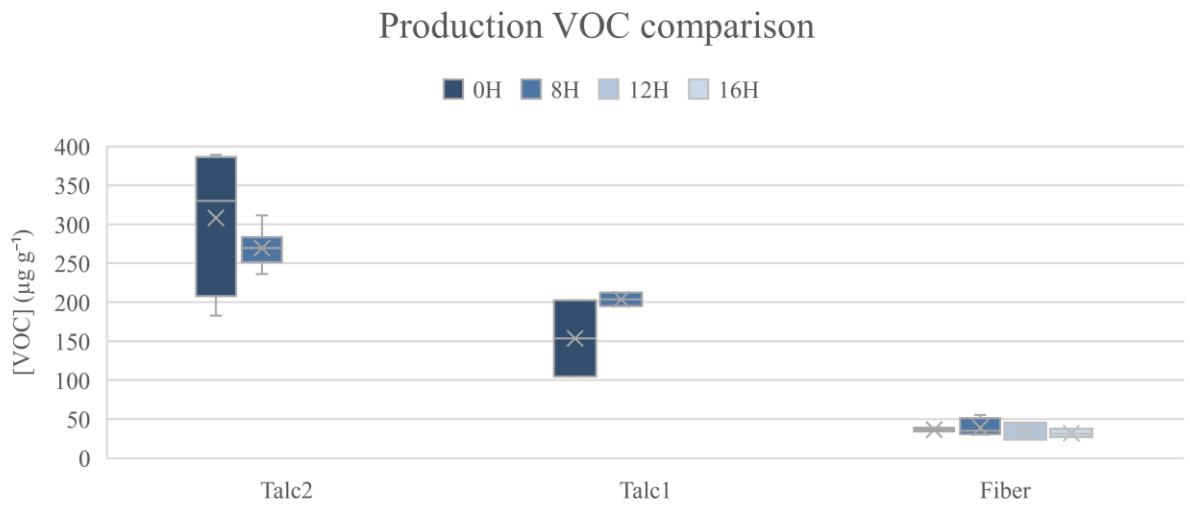


Figure 13. Box and whisker chart of VOC concentrations of three different productions depending on retention time in the silo.

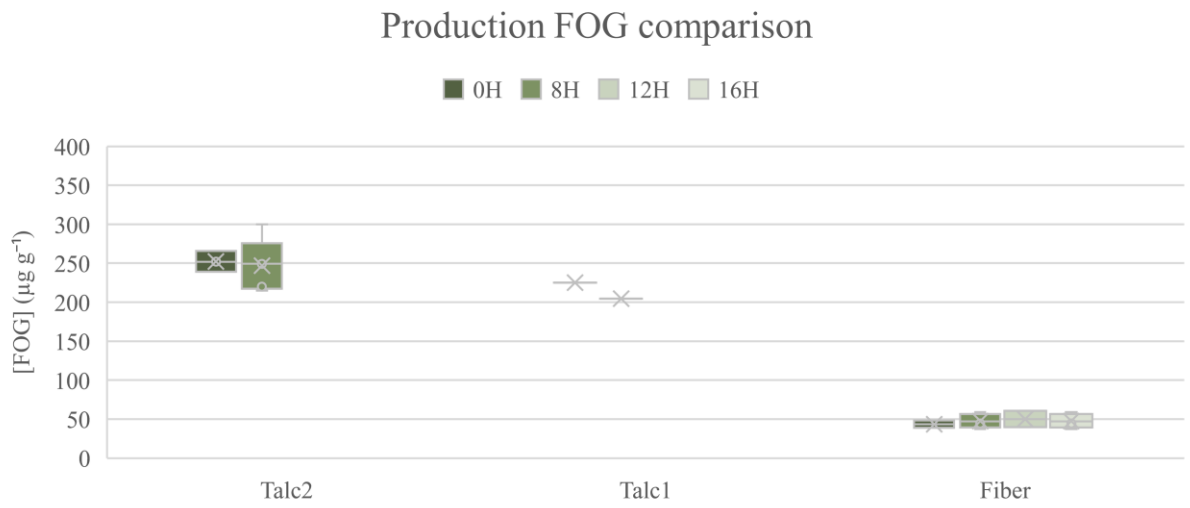


Figure 14. Box and whisker chart of VOC concentrations of three different productions depending on retention time in the silo.

Table 9. Chemometric t-test for mean comparison of first productions.

	Fiber			**Talc2**	**Talc1**
	Blank	8h silo	16h silo	Blank	Blank
8h silo	H_0 $\mu_1=\mu_2$			H_0 $\mu_1=\mu_2$	H_0 $\mu_1=\mu_2$
16h silo		H_0 $\mu_1=\mu_2$			
Blank			H_0 $\mu_1=\mu_2$		

In order to solve this issue, a further analysis was done by taking the blank sample of Talc2 and placing it in an oven for 8 hours at 80ºC, in order to simulate the working method of the silo and find the reason why no decrease on VOC and/or FOG concentration was observed. As in the previous case, the results were represented in Figure 15 and Figure 16, and a noticeable decrease in concentration of both VOC and FOG analysis is observed. In the sample after the silo, the concentration in the samples decreases to around 175 µg g^{-1} for both VOC and FOG. Another t-test was done comparing the three samples and the results, collected in Table 10, confirm that the conditions did work, but the silo did not.

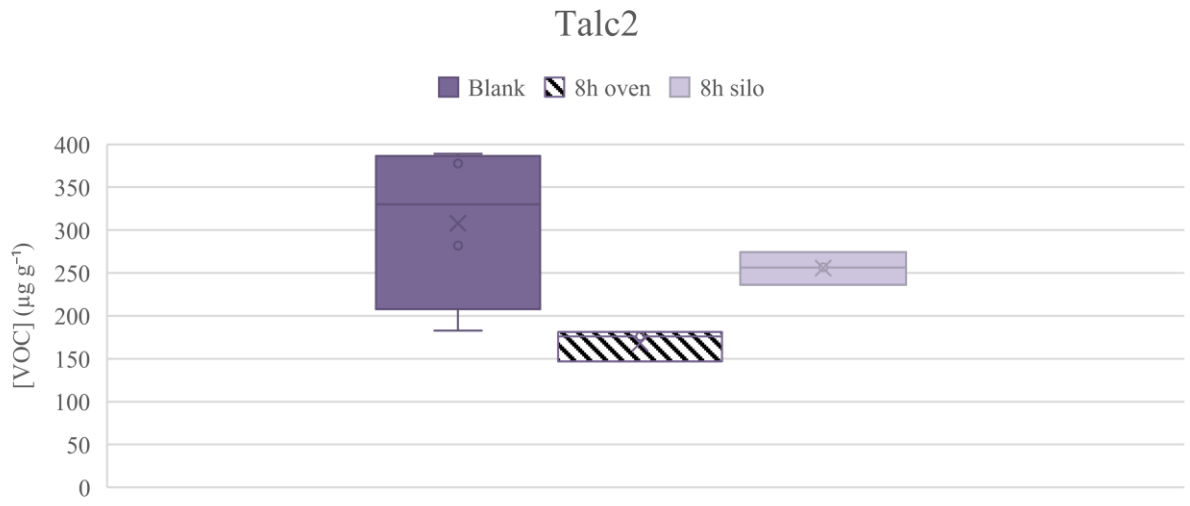


Figure 15. Box and whisker chart of VOC concentrations of Talc2 with the sample placed in the oven at 80ºC.

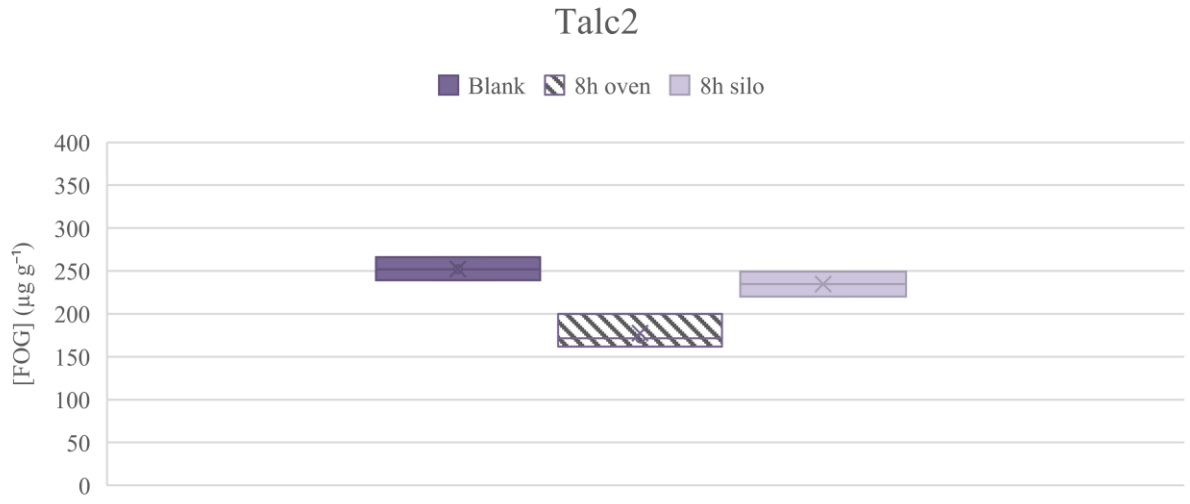


Figure 16. Box and whisker chart of VOC concentrations of Talc2 with the sample placed in the oven at 80ºC.

Table 10. Chemometric t-test for mean comparison of first productions

	Talc2		
	Blank	8h silo	8h oven
8h silo	H_0 $\mu_1=\mu_2$		
8h oven		H_1 $\mu_1\neq\mu_2$	
Blank			H_1 $\mu_1\neq\mu_2$

After considering all the variables in the silo, it was suggested that maybe the incoming air was not at the appropriate temperature. The engineering department was contacted and the installation was checked over, until a connection error was found in the blower. In order to avoid similar mistakes in the future a probe for temperature registration was installed in the

silo. Once the temperature and air flow were considered correct, four new productions were planned, one for each grade, in order to get accurate values. The previous trials were considered unprofitable as the material was not under the proper conditions.

4.4. Final productions

More trials were done for each of the four grades with an exhaustive control of the process conditions in order to guarantee the efficiency of the process. The graphical results are represented by Figure 17 and Figure 18. Additionally, in Annex 1 the chromatograms for all the samples are shown, one for each grade and containing the samples at all retention times in the silo.

As a general overview, it can be determined that the general tendency in Talc production is to have a higher VOC and FOG concentration than the Fiber: in Fiber in the range of 100 to 250 µg g^{-1} for VOC and in Talc around 50 µg g^{-1}. In addition, it can also be noticed a significant decrease for these compounds in the Talc1 and Talc2 productions, whereas in the Talc3 and Fiber productions the change is not so noticeable, a possibility it is due to the difference in the main materials that constitute them.

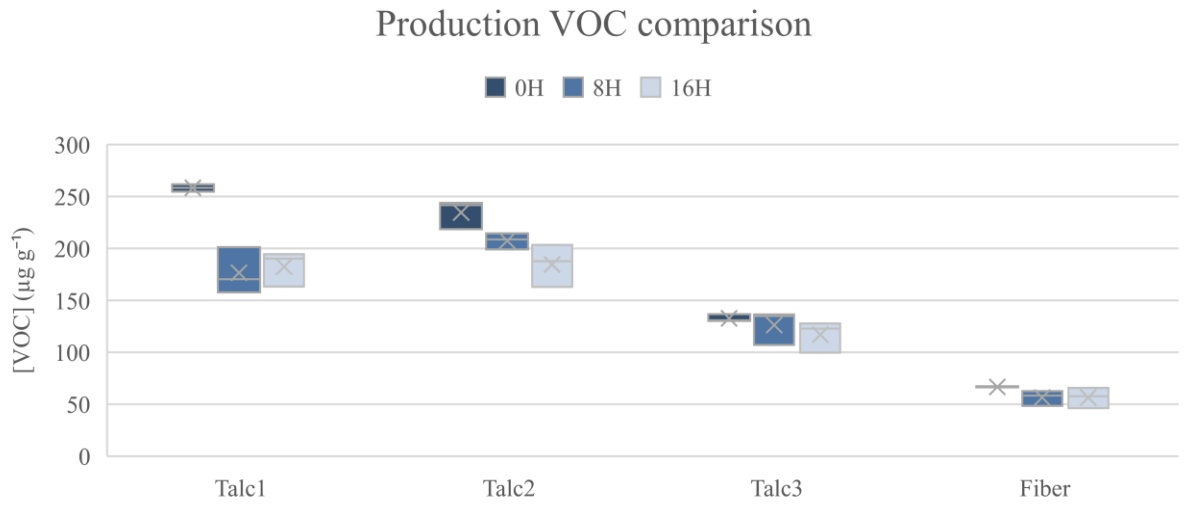


Figure 17. Box and whisker chart of VOC concentrations of the four productions at recommended conditions

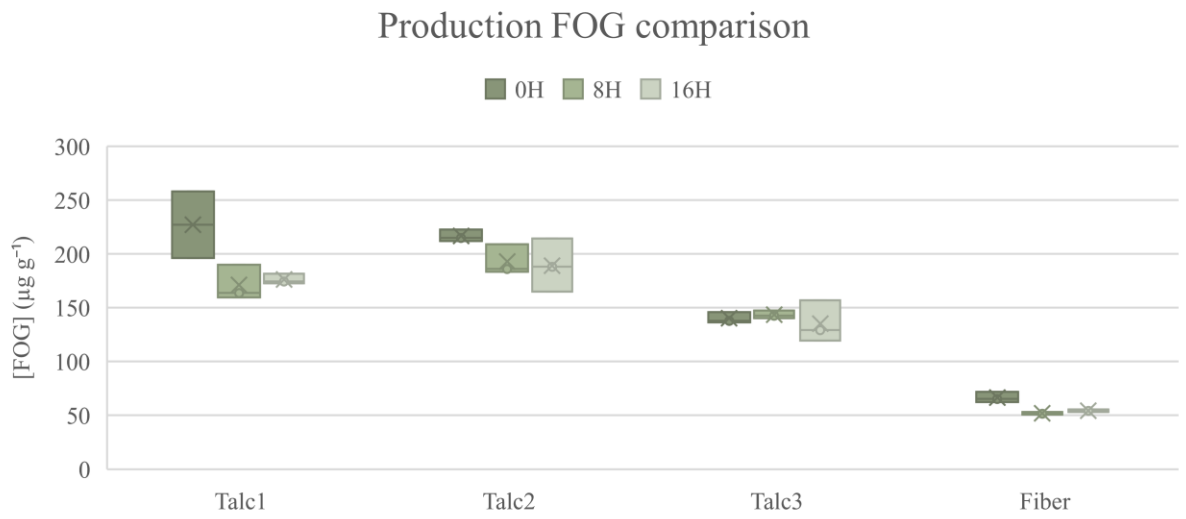


Figure 18. Box and whisker chart of FOG concentrations of the four productions at recommended conditions.

For these samples a more exhaustive data analysis is detailed, as these are considered the conclusive productions due to their correct fabrication. In Annex 2, the Grubb's test for outlier detection results are stated, proving the absence of outliers; in Annex 3, the F-test for variance comparison is done, in order to previously apply the proper t-test for each set of samples, represented in Annex 4.

Summarizing these analyses, for Talc1 and Talc2 productions, the average concentration values differ for blank versus 8h and 16h, whereas for 8h versus 16h no significant differences were found. The conclusion that can be extracted from these values is that the material significantly reduces its concentration during the first eight hours of the silo working but, after this time, no noticeable variation happens working under the specified conditions. In the other hand, for Talc3 and Fiber productions no noticeable variation happens not even among the blank sample or the 16h residence time.

4.5. Results from the air samples

The air sample were collected for two different productions: Fiber and Talc2. It would be important to mentioned that the sample for Fiber was taken before the silo was checked, and therefore the incoming air might not have been at the correct conditions. Talc2 was sampled afterwards, making sure the recommended conditions were followed.

For Fiber the analysis was done during eight hours and the results for the sum of identified VOC and for the sum of all compounds, represented in Figure 19 and Figure 20 respectively, as well as the tendency shown in the chromatogram, matched the expected ones: the initial amount of volatile compounds in the air, as well as the total area, increased along time until a maximum peak (at 2 hours) with corresponded to the silo being complete, and then decreased as the extraction of VOC and FOG from the material was maximum (at 8 hours).

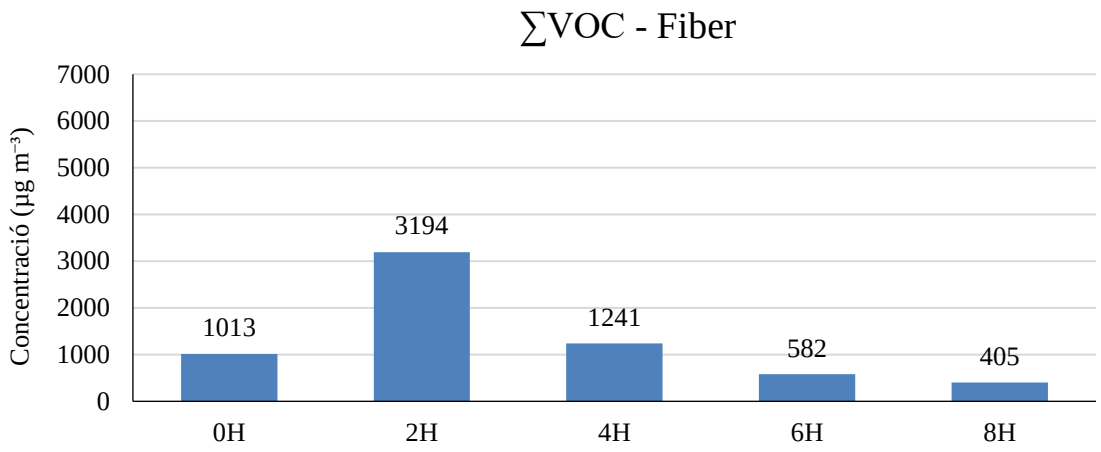


Figure 19. Graphical representation of the total volatile compounds inside the silo along time.

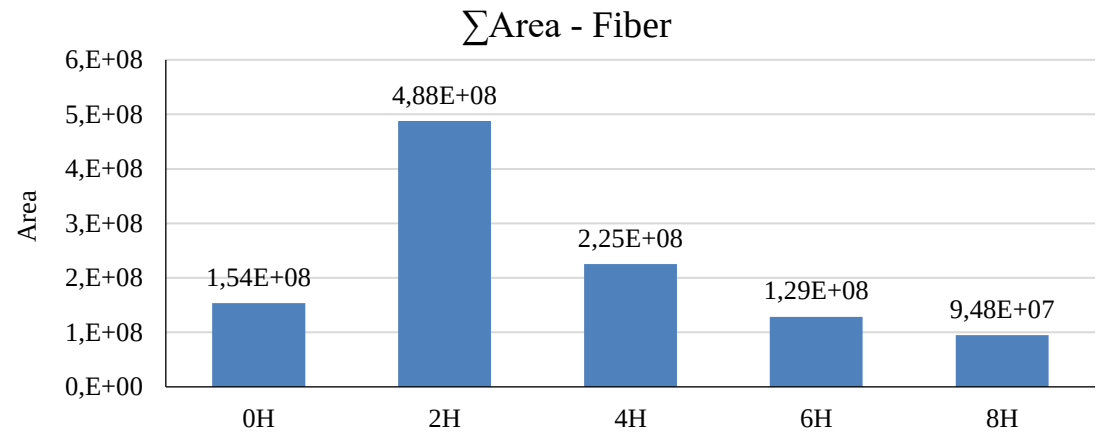


Figure 20. Graphical representation of the total areas inside the silo along time.

For the Talc2 production, the analysis was set of a longer time, in order to check whether eight ours were enough to reduce the concentration of volatile compounds or not. The sampling was taken similarly, with two or three hours between measurements and for a period of fourteen hours. It is important to consider that, in this case, Talc2 has a significantly higher concentration of VOC and FOG in the analysis, therefore the probe showed higher values.

In this case there are some significant differences with respect to the previous production: while the sum of identified volatile compounds (Figure 21) decreases until it stabilizes at around 8 hours, as it was expected, the sum of total areas (Figure 22) in the chromatogram decreases but only to a certain extent, showing high remains of other substances, located in the middle of the chromatogram, that are assumed to be of higher molecular weight, and therefore more difficult to volatilize. One of the suggested solutions for this would be to modify the incoming air in the silo to reach higher temperatures that allow for an easier volatilization.

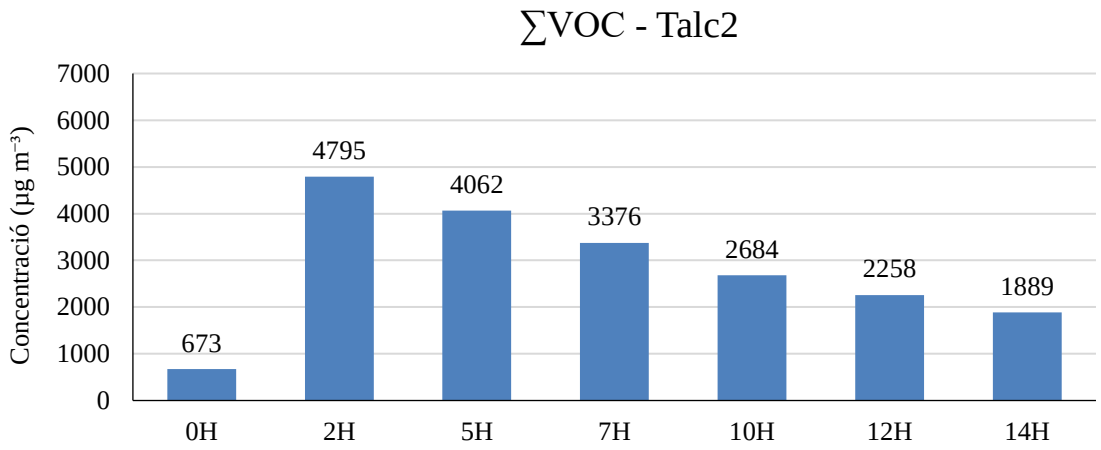


Figure 21. Graphical representation of the total volatile compounds inside the silo along time.

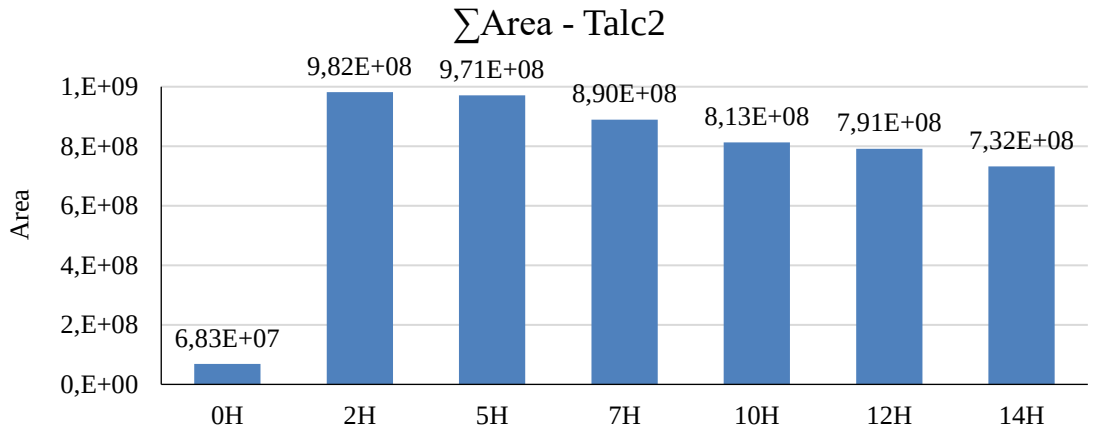


Figure 22. Graphical representation of the total areas inside the silo along time.

5. Conclusions

The most important conclusion is that the plastic analysis method was successfully set up as specified in the VDA-278 for sample analysis, following all the specifications required regarding control and calibration, and achieving verified results. From then, multiple conclusions regarding the material characteristics can be extracted.

The first important conclusion that was achieved was that the different materials showed different starting concentrations of volatile and semivolatile organic compounds, mainly depending on their composition: the partially recycled polypropylene with talc had a significantly higher initial concentration than the fully recycled polypropylene with fiber. That led to suspecting that the percentage of recycled material (and their variability) or the filler (or even both variables) have a significant effect on the material VOC and FOG concentrations.

As stated in the previous section, the silo was efficient only in four out of the two grades that were examined. From the obtained chromatograms, the hypothesis that is suggested if that the reduction is successful for those materials that present a higher initial concentration, as the least heavy compounds are volatilized. In the other hand, the materials that presented lower concentrations from the beginning had heavier compounds, and therefore the conditions required for their volatilization should be stronger, for example, applying an air flow of higher temperature. This conclusion is supported by the data obtained in the air samples, as one group of compounds remained constant along the different measurements.

Another important conclusion is the optimization of the residence time at 8 hours, as the both the variation in air samples from the silo and the t-test done for the plastic samples describe important differences in concentrations after 8 hours but none after 16 hours.

5.1. Further steps

The analytical development for the project is concluded so far, but as the global project for the emissions reduction has yet not finished, it is important to program the further steps that could be followed in order to clarify some of the unknowns that have been found by the analyses. Therefore, the following steps are recommended in order to both validate and continue with the progress done so far.

1. Compare some of the results with an external laboratory for validation of the method, even though the samples have previously shown that the reproducibility is not very high. The fundamental aspect to consider is if the tendency among the same grade is similar between both measurements. With respect to the analysis, it could be also purposeful to consider, not only the sum of volatile or semivolatile compounds, but also which are the major compounds in the samples in order to search for specific techniques for their release.

2. Analyze a higher variety of materials to test which of the polymeric differences affect both the initial concentration and their behavior after the silo treatment. The two main differences among the samples are the percentage of recycled polypropylene (30 to 70) and the type of filler (talc or fiber), therefore a factorial design varying these characteristics may be helpful to understand their behavior.

3. Regarding the conditions of the silo, it would be right to perform multiple tests for one grade at different air blower temperatures, as it is the one variable that could be modified (apart from the residence time, that has already been optimized to eight hours).

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Annexes

Annex 1. Chromatograms of plastic samples

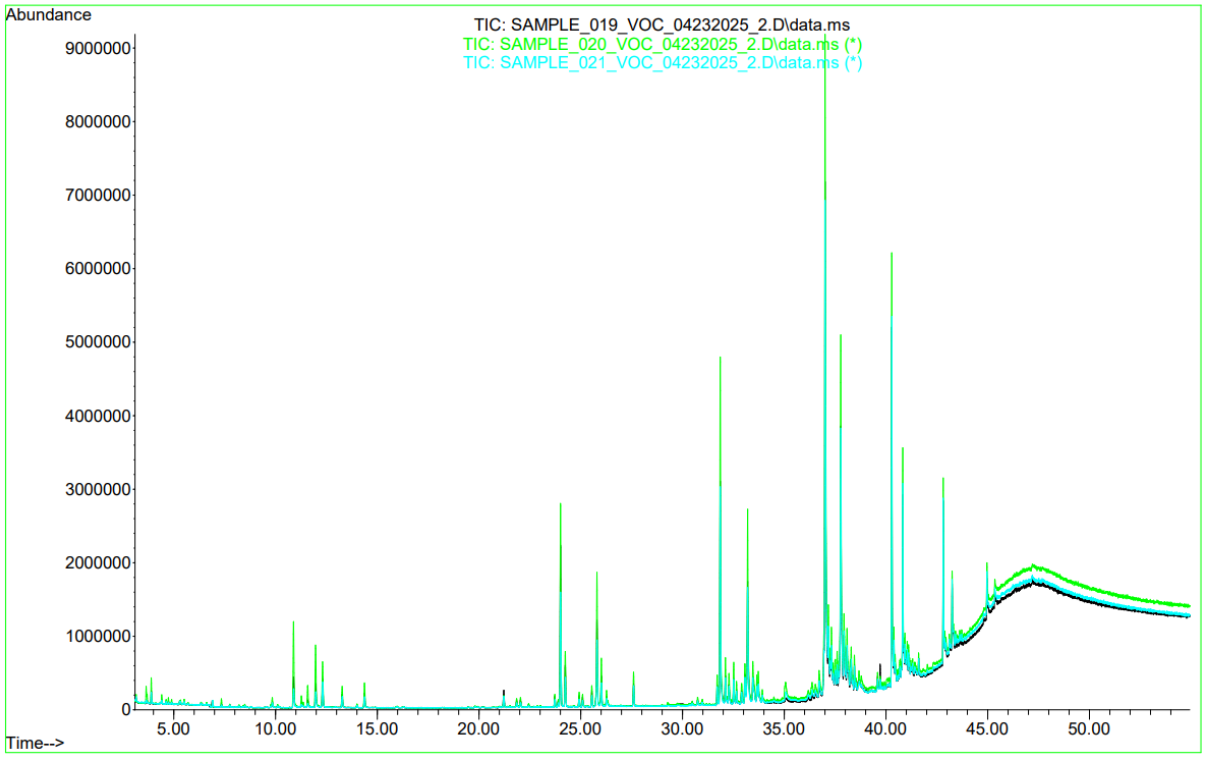

Figure A. 1. Overlapping VOC chromatograms for Talc1 samples.

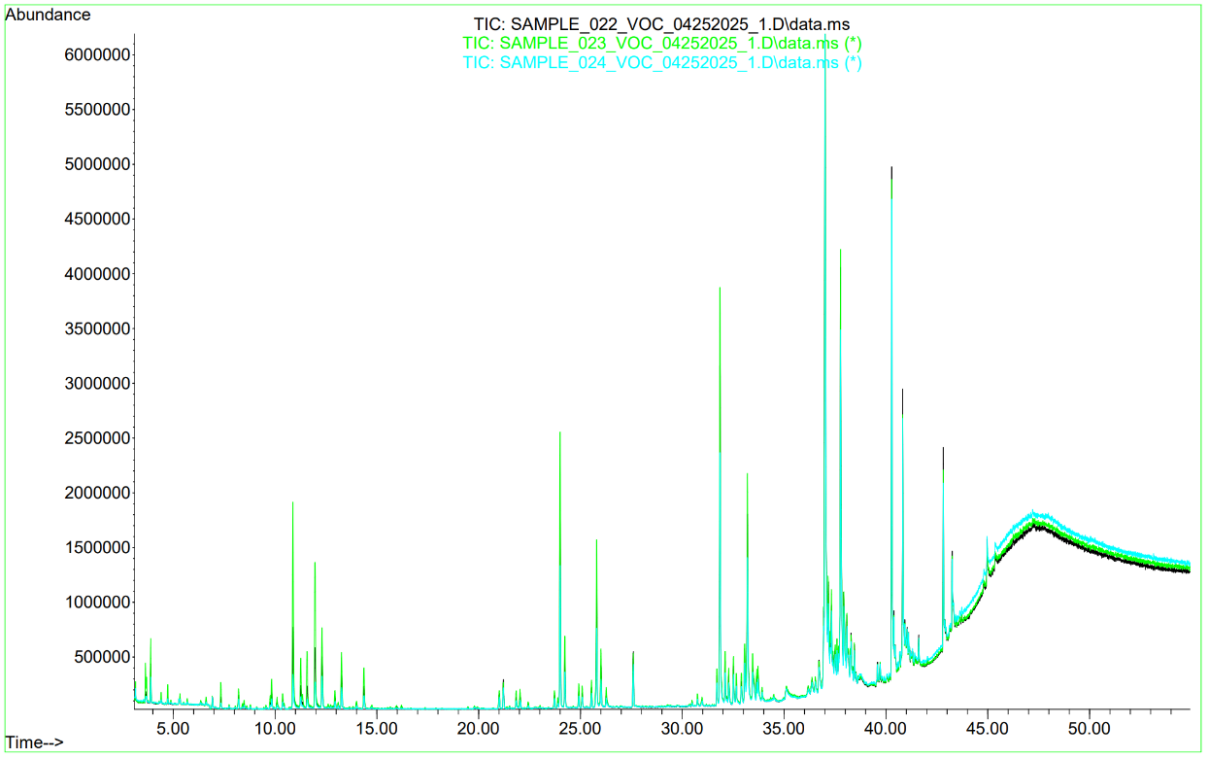

Figure A. 2. Overlapping VOC chromatograms for Talc2 samples.

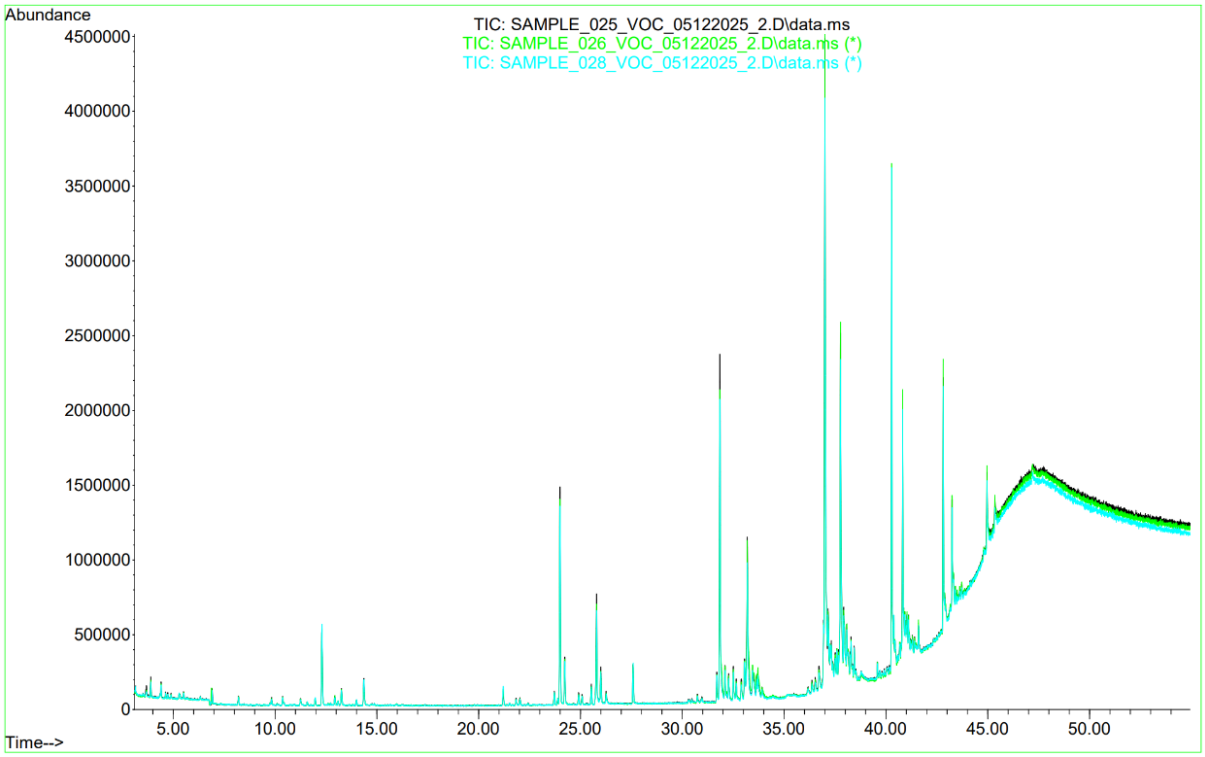

Figure A. 3. Overlapping VOC chromatograms for Talc3 samples.

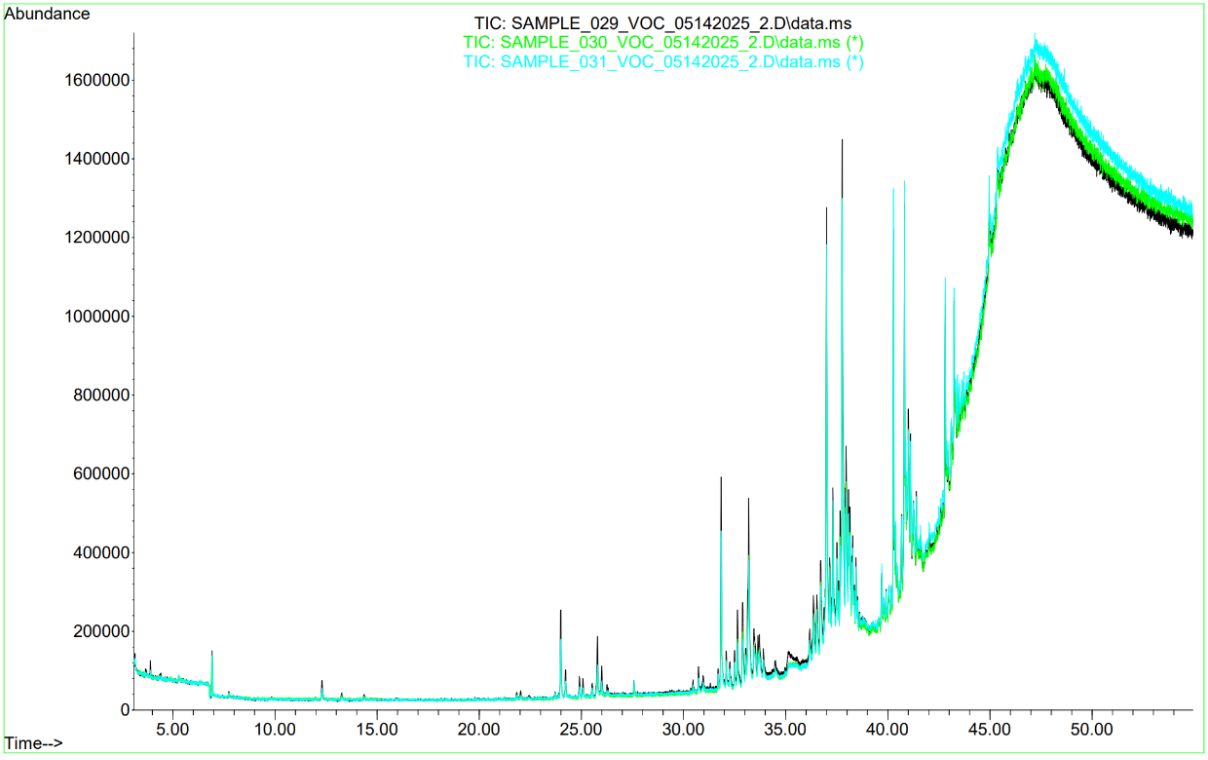

Figure A. 4. Overlapping VOC chromatograms for Fiber samples.

Table A. 1. Grubb's test data for last four productions

	Talc1			Talc2			Talc3			Fiber		
	020	**019**	**021**	**023**	**022**	**024**	**025**	**026**	**028**	**029**	**030**	**031**
Mean	258,1	176,4	182,4	234,6	207,3	184,6	132,6	126,0	116,8	66,6	56,3	56,5
Standard deviation	5,05	22,37	16,83	13,97	7,92	20,49	3,65	16,48	14,94	0,69	7,31	9,81
Alpha	0,05											
Sample size	2 (*)	3	3	3	3	3	3	3	3	3	3	3
Significance value	0,03	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02
Degrees of freedom	0,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00
t-critical	-	38,19	38,19	38,19	38,19	38,19	38,19	38,19	38,19	38,19	38,19	38,19
G-critical	-	1,15	1,15	1,15	1,15	1,15	1,15	1,15	1,15	1,15	1,15	1,15
Minimum value	254,5	157,8	163,2	218,5	198,8	162,8	130,2	107,0	99,8	66,2	48,3	46,1
G min-calculated	0,71	0,83	1,15	1,15	1,07	1,07	0,66	1,15	1,14	0,58	1,10	1,06
Hypothesis	-	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$
Maximum value	261,7	201,2	194,2	243,7	214,6	203,4	136,8	136,4	127,8	67,4	62,5	65,6
G max-calculated	0,71	1,11	0,70	0,66	0,91	0,92	1,15	0,63	0,73	1,15	0,85	0,93
Hypothesis	-	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$	$H_1\ \mu_1\neq\mu_2$	$H_0\ \mu_1=\mu_2$	$H_0\ \mu_1=\mu_2$

(*) If the sample size is smaller than three Grubb's test cannot be applied

Annex 3. F-test for variance comparison data

Table A. 2. F-test data for last four productions

	Talc1			Talc2			Talc3			Fiber		
F calculated	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo
8h silo	385,74			9,66			415,08			12935,10		
16h silo		3,12			44,70			1,48			3,25	
Blank			123,51			4,63			280,80			41980,28
F critical	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo
8h silo	39,17			15,44			15,44			15,44		
16h silo		15,44			15,44			15,44			15,44	
Blank			39,17			15,44			15,44			15,44
Hypothesis	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo
8h silo	H_1 $\sigma_1^2 \neq \sigma_2^2$			H_0 $\sigma_1^2 = \sigma_2^2$			H_1 $\sigma_1^2 \neq \sigma_2^2$			H_1 $\sigma_1^2 \neq \sigma_2^2$		
16h silo		H_0 $\sigma_1^2 = \sigma_2^2$			H_1 $\sigma_1^2 \neq \sigma_2^2$			H_0 $\sigma_1^2 = \sigma_2^2$			H_0 $\sigma_1^2 = \sigma_2^2$	
Blank			H_1 $\sigma_1^2 \neq \sigma_2^2$			H_0 $\sigma_1^2 = \sigma_2^2$			H_1 $\sigma_1^2 \neq \sigma_2^2$			H_1 $\sigma_1^2 \neq \sigma_2^2$
Same σ ?	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo
8h silo	No						No			No		
16h silo					No							
Blank			No						No			No

Annex 4. t-test for mean comparison with same variance data

Table A. 3. t-test data for last four productions of comparable variance

	Talc1			**Talc2**			**Talc3**			**Fiber**		
t calculated	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo
8h silo	4,84			2,94			0,67			2,41		
16h silo		0,37			1,79			0,72			0,02	
Blank			6,82			3,49			1,78			1,78
t critical	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo
8h silo	3,18			2,78			2,78			2,78		
16h silo		2,78			2,78			2,78			2,78	
Blank			3,18			2,78			2,78			2,78
Hypothesis	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo
8h silo	H_1 $\mu_1 \neq \mu_2$			H_1 $\mu_1 \neq \mu_2$			H_0 $\mu_1 = \mu_2$			H_0 $\mu_1 = \mu_2$		
16h silo		H_0 $\mu_1 = \mu_2$			H_0 $\mu_1 = \mu_2$			H_0 $\mu_1 = \mu_2$			H_0 $\mu_1 = \mu_2$	
Blank			H_1 $\mu_1 \neq \mu_2$			H_1 $\mu_1 \neq \mu_2$			H_0 $\mu_1 = \mu_2$			H_0 $\mu_1 = \mu_2$
Same μ ?	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo
8h silo	No			No								
16h silo												
Blank			No			No						

Table A. 4. t-test data for last four productions of non-comparable variance

	Talc1			Talc2			Talc3			Fiber		
t statistics	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo
8h silo	6,10			2,94			0,67			2,41		
16h silo		0,37			1,79			0,72			0,02	
Blank			7,31			3,49			1,78			1,78

t crit	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo
8h silo	4,30			3,18			4,30			4,30		
16h silo		2,78			3,18			2,78			2,78	
Blank			4,30			2,78			4,30			4,30

Hypothesis	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo
8h silo	H_1 $\mu_1 \neq \mu_2$			H_0 $\mu_1 = \mu_2$			H_0 $\mu_1 = \mu_2$			H_0 $\mu_1 = \mu_2$		
16h silo		H_0 $\mu_1 = \mu_2$			H_0 $\mu_1 = \mu_2$			H_0 $\mu_1 = \mu_2$			H_0 $\mu_1 = \mu_2$	
Blank			H_1 $\mu_1 \neq \mu_2$			H_1 $\mu_1 \neq \mu_2$			H_0 $\mu_1 = \mu_2$			H_0 $\mu_1 = \mu_2$

Same μ ?	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo	Blank	8h silo	16h silo
8h silo	No											
16h silo												
Blank			No			No						