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Treball Final de Grau

Determination of ethyltriphenylphosphonium bromide and butyltriphenylphosphomium chloride in saturated polyester resins by LC-MS
Determinació de bromur d'etiltrifenilfosfoni i de clorur de butiltrifenilfosfoni en resines de polièster saturat per LC-MS

Albert Altimira Esteve

June 2021

Hi ha una força motriu més poderosa que el vapor,
l'electricitat i l'energia atòmica: la voluntat.

Albert Einstein

En primer lloc, voldria agrair a la meva tutora, Anna Rigol, tota l'ajuda i coneixements que m'ha transmès, el temps dedicat i la proximitat amb el tracte.

En segon lloc, m'agradaria mencionar la meva tutora dins l'empresa, Imma Peña, que sense la seva ajuda i els seus coneixements, les hores dedicades i el tracte personal que ha tingut amb mi la realització d'aquest treball no s'hagués pogut dur a terme.

Finalment, agrair la meva família per donar-me el seu suport, en els bons i els mals moments, al llarg de tot el període universitari.

REPORT

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1. SUMMARY

Powder Coatings are a type of paintings fully applied in the form of dry powder. Thermosseting Polyester Powder Coatings, one of the most used in industry, are based in a saturated polyester resin (with –COOH or –OH functionality group) as binder and crosslinker. In certain cases small amount of catalyst is added in order to the resin to try to achieve an acceptable curing time in baking temperatures. In Arkema Química S.A.U. (Sant Celoni) two specific types of catalyst, TRAP and BTPC (phosphonium salts), are added to the polyester that they synthesizes. The R&D laboratory of the industry requires the analysis of these two catalysts in the resins. The present work aims at developing a method that allows an estimation of the proportion of TRAP and BTPC present in the resins.

Several tests have been performed to find the optimal working conditions to analyze the target catalysts by LC-MS. The chromatographic parameters have been optimized, finding the proportions of the appropriate eluents in a gradient method and the best parameters for mass detection using ES ion source. Two blank injections between every single sample analysis were determined as the best way to prevent the carry-over effect of TRAP. The extraction conditions of the catalysts in the resin have also been optimized, obtaining an approximate recovery of 90% for different sets of resin containing TRAP.

This study is the basis for future validation of the quantitative method.

Keywords: LC-MS, TRAP, BTPC, Powder Coatings, Catalyst, Saturated Polyester Resins.

2. RESUM

Els Powder Coatings són un tipus de pintura que s'aplica en forma de pols sense dissolvent. Un dels més utilitzats dins el mercat industrial són els Thermosseting Polyester Powder Coatings, els quals estan formats per una base de resina de poliester saturat (amb funcionalitat –COOH o –OH) la qual reacciona amb un crosslinker. En certs casos se li addiciona una petita quantitat de catalitzador per tal que la reacció es dugui a terme a temperatures més baixes. A Arkema Química S.A.U. (Sant Celoni) s'addicionen dos catalitzadors específics, TRAP i BTPC (salts de fosfoini), al polièster que sintetitzen. El laboratori d'I+D de la indústria requereix l'anàlisi d'aquests dos catalitzadors a la resina. L'objectiu d'aquest projecte consisteix en desenvolupar un mètode que permeti una estimació de la proporció de TRAP i BTPC presents a les resines.

Diferents estudis s'han realitzat per tal de trobar les condicions òptimes de treball per analitzar aquests dos catalitzadors per mitjà d'un LC-MS. S'ha aconseguit optimitzar els paràmetres cromatogràfics, buscant els eluents adequats i les seves proporcions en un mètode de gradient i els millors paràmetres de la detecció de masses amb font d'ionització ES. S'ha observat una tendència del TRAP a patir efecte memòria. Per tal de minimitzar-ho es defineixen dos neteges de blanc entre mostra i mostra. També s'han optimitzat les condicions d'extracció dels catalitzadors a la resina amb una solució de 5% THF en metanol, aconseguint una recuperació aproximada del 90% per diferents lots de resina que conté exclusivament TRAP.

Aquest estudi seria la base per a una futura optimització i validació del mètode quantitatiu.

Paraules clau: LC-MS, TRAP, BTPC, Powder Coatings, Catalyst, Resines de polièster saturat.

3. INTRODUCTION

The present work has been carried out at Arkema Química S.A.U., a company integrated in the Arkema group. Arkema is a worldwide company specialized in the industrial chemistry sector. It is divided into three business divisions [1]:

- Coating Solutions
- Industrial Chemicals
- Performance Products

Within the Arkema group, Arkema Química S.A.U. is focused on the production of liquid and solid coating resins. In Spain it is structured by two different industrial plants, one located in Mollet del Vallès and the other one in Sant Celoni [1].

Sant Celoni plant has several laboratories: quality control lab, synthesis lab, applications lab, wastewater treatment lab and it has also a laboratory equipped with analytical instrumentation (Gel Permeation Chromatography, Calorimetry, Infrared Spectroscopy and Gas and Liquid Chromatography) which provides support to the two industrial plants and to the R&D (research and development) labs.

The Sant Celoni industrial plant synthesizes two different types of resins [1]:

- Oil-free polyester
- Saturated polyester resins.

Saturated polyester resins are found in solid state and they are the binder of so-called thermosetting polyester powder coatings [2]. Oil free polyesters are saturated polyesters which are in solution with aromatic Naftas and acetate solvents. This type of resin is developed for use in coil coating, sheet metal decorating and general industrial applications [3]. This project is focused on the study of saturated polyester resins.

3.1. INDUSTRIAL PRODUCTION PROCESS OF SATURATED POLYESTER RESINS

Saturated polyester resins contain –COOH or –OH terminal functional groups in their branched polymer chain [3].

The synthesis process of these resins involves a direct polyesterification of polybasic acids and polyfunctional alcohols (see figure 1). Depending on which component is in molar excess, the polyester can become carboxylated or hydroxylated. [3]

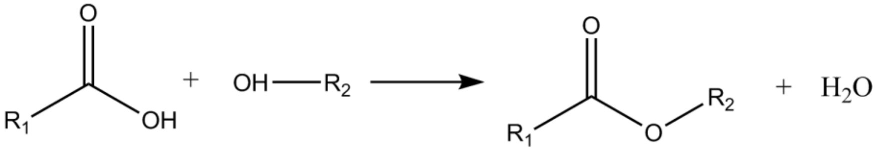
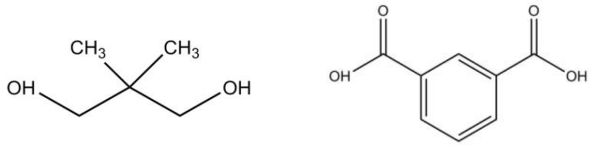


Figure 1. Polyesterification reaction.

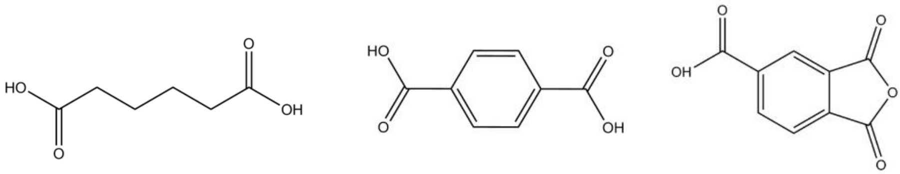
Focusing on the production of polyester resins produced by the industrial plant of Sant Celoni, the most important part consists on carboxylic final products. That means that there is a molar excess of glycol on the polyesterification reaction. The number of functional groups of this synthesized resin will depend on which crosslinker and quantity is going to react in the production of polyester powder coatings. The formulation of these resins is quite simple as it mostly follows a pattern. Depending on the acidity value, hydroxyl number and viscosity requested for the final product, the concentration of the reagents will vary [3].

Five main reagents are the basis for most resins pretended for the thermosetting polyester powder coatings sector, in some specific cases small amounts of other reagents are added to modify their properties.

As shown in Figure 2, the main reagents are: NPG (neopentylglycol), IPA (isophthalic acid), TPA (terephthalic acid), AP (adipic acid) and TMA (trimellitic anhydride) [4].



a) b)



c) d) e)

Figure 2. Chemical structures of reagents: a) NPG, b) IPA, c) AD, d) TPA, e) TMA

In order to carry out this reaction between them, the presence of some catalyst on the reaction will help the process occurs under optimal synthesis conditions [5].

The industrial synthesis of this type of polymer is classified into two stages. The first stage is when the main reaction between NPG and TPA occurs. The acidity, hydroxyl and viscosity values are constantly analysed. When the correct values are achieved, in a second stage, the minority acids (IPA, TMA and AD) are added. During the reaction acidity, hydroxyl and viscosity values are checked constantly again until the correct values are obtained [4].

These types of resins represent the most important part of resins obtained for the production of the thermosetting polyester powder coatings [3].

Carboxyl saturated polyester acts as a binder being the principal ingredient of polyester powder coatings. This type of saturated polyester is the one synthesised by Arkema.

In some selective resins, small amounts of catalysts are added during the second stage in the cooling process once the desired acidity has been reached. These catalysts are not involved in the synthesis process of the polymer, but will be extremely important to the final customer interested in this polyester in order to carry out a curing reaction on the thermosetting powder coatings process [2].

3.2. POLYESTER POWDER COATINGS

Powder coating is a type of coating that is fully applied to different surfaces in the form of dry powder that is distributed flowing freely. This kind of powder differs from conventional liquid paint, which is administered by means of a solvent, which, once applied, evaporates. [6]

Two different types of powder can be found: Thermoplastic Powder Coatings and Thermosetting Powder Coatings.

Thermosetting Powder Coatings differ from the thermoplastic in the fact that a cross-linking reaction takes place during stoving of the coating. That fact enables polymers with much lower molecular weights and, consequently, lower melting viscosities, to be used. In addition, more pigment, additives (flow agents, waxes, matting agents…) and fillers can be added in order to obtain the appropriate chemical and mechanical properties [3].

The cross-linked nature of this film makes them have a high chemical resistance due to the low permissiveness of an external attacking agent. The option of introducing a polar group into the structure of the resin or even that can be formed due the curing reaction (–OH group in curing reactions between carboxyl polyester and epoxy curing agents) improves the properties of adhesion [7]. All these wide range of properties make this type of powder coatings be present in most of the sector.

Powder Coatings are classified as: Epoxy Powder Coatings, Acrylic Powder Coatings, Unsaturated Polyester Powder Coatings, Radiation Curable Powder Coatings, Silicone-based Powder Coatings and Polyester Powder Coatings.

Arkema is responsible of synthesizing the saturated polyester resins that act as a binder being the principal ingredient for Polyester Powder Coatings. For this reason, this project focuses on the study of this type of coatings. The formulation of these coatings can be described on a simplified way as: Resin (polyester), crosslinker, pigments/fillers, flow agents, degassing agents and catalysts [8]. Excepting the catalyst that are already present in the resin (see section 3.1) the external company is the responsible making the crosslinker and the rest of ingredients react with the polyester resins made in Arkema.

The basis of this type of coating consists in the reaction between saturated polyester and a crosslinker which can vary depending on the appropriate physical and chemical properties for its application. The word crosslinker usually refers to the component of the coating which is used in minor amounts to produce a network, reacting with the functional groups of the main binder. In addition to this main reaction, some other reagents could appear on the process in order to finish conditioning its final properties [3].

Depending on what type of crosslinker is involved in this reaction it can be distinguished two types of polyester powder coatings: Interior Polyester Powder Coatings and Exterior Powder Coatings.

3.2.1. INTERIOR POLYESTER POWDER COATING

It is known as "Hybrid" those powder coatings whose base is a polyester resin as binder and epoxy resin and as a crosslinker [3].

Knowing that epoxy resins used as curing agents have two epoxy functional groups, the saturated polyester resin involved in the main process must have more than two carboxylated functional group. The carboxylic groups of the resin and the epoxy groups of the crosslinker react forming an ester. The stoichiometric relationship between the epoxy resin and the carboxylated polyester resin will determine the properties of the final film, such as impact and water resistance and the capacity of maintaining stable facing high temperatures and the attack of solvents [8].

Coating-synthesized polyester resins are characterized by a certain degree of acidity which will determine the amount of epoxy in the coating formulation.

The reaction speed between the epoxy groups and the carboxyl groups of the polyester is rather slow. Furthermore, this reaction occurs on temperatures exceeding 200°C involving more energy use. It is for this reason that these types of reactions must be catalyzed in order to try to achieve an acceptable curing time in a baking temperature between 160°C-200°C, which are the most common temperatures in practice. It is a rule that polyester resins manufacturers incorporate these catalysts in the resin during its production in order to ensure the uniformity of distribution while the resin is in the liquid state. The most commonly used catalysts to accelerate the reaction are: tertiary amines, quaternary ammonium salts and phosphonium salts. The catalyst concentration present in the resins will depend on the acidity of the polyester as the more carboxylic functional groups present, the less amount of catalyst will be needed [3].

3.2.2. EXTERIOR POLYESTER POWDER COATING

Powder coatings prepared for outdoor application have to fulfil the typical request addressed to all coatings being exposed to water, wide range of temperatures, ultraviolet sunlight and industrial atmospheres containing sulphur dioxide [3].

This resistance will be determined by the nature of the powder which contains ester groups prone to hydrolysis. The correct choice of crosslinker plays a very important role in the formulation of this powder. The crosslinker must also be resistant to UV (ultraviolet) radiation, which excludes bisphenol A as it contains ether oxygen. Unfortunately, aliphatic and cycloaliphatic epoxy compounds are liquid at room temperature. This makes it unsuitable for easy combination with polyester using fusion extrusion techniques. Therefore, those that are compatible with being solid at room temperature must be found [3]. Over the years of production, a great variety of crosslinkers has been found such as:

- Polyurethanes
- Esterified amine resins
- TCIG (Tiglycidyl isocyanurate) (see figure 3)
- B-Hidroxialquilamidas

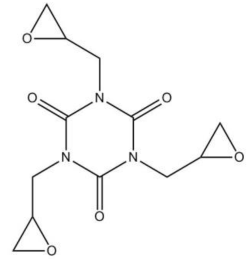


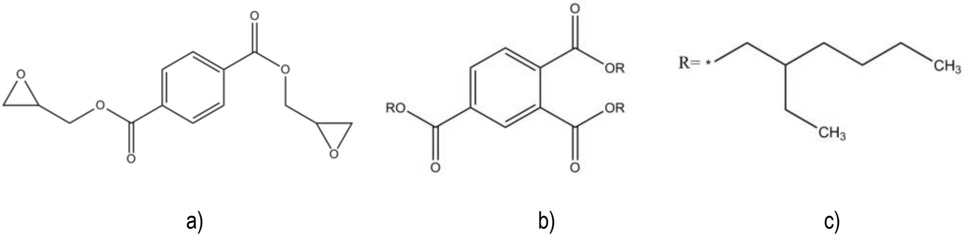
Figure 3. Chemical structure of TGIC.

Part of the production of resins synthesized in Arkema is pretended to react with TGIC. The amount of TGIC in Powders depends on the acidity index of the polyester resin. The best results are obtained when there is a stoichiometric amount of epoxy groups from the TGIC with respect to the carboxyl groups of the polyester. It is generally not necessary to catalyse the system, as the reactivity of the TGIC itself is high enough to obtain the desired curing cycle as it contains three epoxy functional groups compared to the two of epoxy resins functional groups. If faster curing programs or lower curing temperatures are required, the incorporation of a suitable catalyst is necessary, as it is the case for resins containing a 93/7 (polyester / TGIC) [4]. The type of catalyst added on the polyester intended to this type of coatings is the same as those which are applied for the interior powder coatings.

Polyester/TGIC cured resins provide a film of excellent hardness, flexibility, impact resistance, abrasion resistance and scratch resistance. The adhesion properties of TGIC systems are generally good [3].

The main problem with this type of Polyester/TGIC powder is that it was declared toxic throughout Europe in the early 90’s. This means that its market is currently outside the European continent. This leads to the emergence of another type of crosslinker which will replace TGIC in the European market [3].

The emergence of a crosslinker called ‘‘Araldite PT 910’’ is key as it will be the crosslinker that will replace the TGIC. This compound is based on a "solid solution" of one part (by weight) of liquid TML (triglyceride trimellitate) (see figure 4) in three parts of crystalline DGT (diglycidyl terephtalate) [9].



a) b) c)

Figure 4. Chemical structure of components of PT 910: a) DGT, b) & c) TML

Due to the functionality of "PT 910" is less than that of TGIC, the mechanical properties are more sensitive to the curing program and the type of resin used. The lower reactivity of "PT 910" can be compensated by adding an accelerator (or catalyst) or using more reactive polyester. In this case, the polyester resins made in Arkema intended to cure with PT-910 in some cases contain phosphonium salts as catalyst in order to increase the reaction between the carboxyl group of the polyester and the epoxy group of ‘’Araldite PT 910’’ [3].

3.3. PHOSPHONIUM SALTS AS CATALYSTS

As described in sections 3.2.1. and 3.2.2 in certain types of esterification reaction between carboxyl polyester and epoxy group to form the powder it is required the presence of catalysts. From different types of catalysts used, there are two phosphonium salts that have been the target of study of this project: TRAP (ethyltriphenylphosphonium bromide) and BTPC (butyltriphenylphosphomium chloride). Their structures are shown in figure 5.

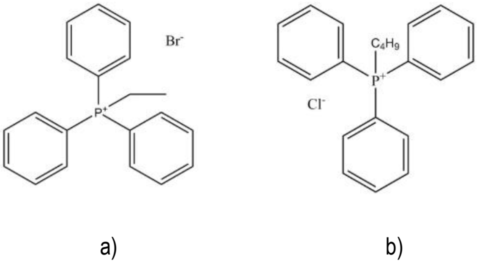


Figure 5. Chemical structure of catalyst: a) TRAP, b) BTPC

These two types of catalysts are added once the carboxylated polyester has already been formed and it is still liquid in the reactor. It is added in this step because in this way the customer ensures that the product will have been distributed evenly throughout the polyester.

These catalysts are present in polyesters intended to cure with three different types of crosslinkers: [internal Arkema information]

- Epoxy resins: 0.3%-1%.
- TGIC: 0.1%-0.3%.
- PT 910: 0.1%-0.4%.

The difference between these two types of catalysts in terms of efficiency is quite similar due to their similar chemical structure. Almost the 90% of resins manufactured in Arkema containing phosphonium salts as catalyst contain exclusively TRAP. It is the most widely used catalyst at the market level. As the BTPC is a compound whose price triplicates the one of TRAP, this type of catalyst is popularly only found in resins that cure with PT-910 and by express request from the customer. [internal Arkema information]

These two catalysts act as a PTC (phase-transfer catalyst). PTC is a phenomenon of rate enhancement of a reaction between reactants located in different phases by addition of a small quantity of an agent called phase-transfer catalyst that extracts one of the reactants. The catalyst cation is not consumed in the reaction although an anion exchange does occur [10].

3.4. DETERMINATION OF PHOSPHONIUM SALTS BY LC-MS

In order to attend a R&D demand, analytical lab wanted to study the feasability of finding a method to determine which catalysts are used in market powder resins. Simple qualitative knowledge provides a very useful information for the synthesis department. This project has been carried out using the most from the lab resources (instrumentation, reagents and material) to be able to identify and possibly quantify the phosphonium catalysts in the resins.

There was a former CG-MS (gas-chromatography mass-spectrometry) method for identifying several additives in resins but it was not able to distinguish between TRAP and BTPC. A part from the fact that they are ionic compounds, the problem was also that the ionization source in the CG-MS system was Electronic Impact, so compound fragmentation was high and it was giving the same mass spectra for the two catalysts. Furthermore they also elute at the same retention time. So, there was no way to chromatographically separate them by their mass fragmentation either. A part from the poor quality detection, it was also important to establish an estimated amount of these catalysts present in the synthesized resins in order to ensure that the actual concentration sold to the customer corresponds to the calculated one.

Another point to keep in mind is the chemical knowledge of market resins. Being able to study resins from other manufacturers would allow the company's R&D department to adjust its formulas to stay within the market requirements.

A separation technique in the first place and an identification-qualitative one in the second place were needed. The high molecular weight including the low volatility and high polarity of the compounds made it very plausible that the appropriate technique was HPLC (High pressure liquid chromatography) coupled to mass detection. LC-MS (liquid chromatography-mass spectrometry) is the combination of two selective techniques that allows the analytes of interest in highly complex mixtures to be isolated and measured [11].LC differentiates compounds by their physicochemical properties and MS (mass spectrometry) differentiates compounds by mass (specifically their mass-to-charge ratio). The mass spectrometer acts not only as the "LC detector" but, at least in principle, it provides the capability to identify the species corresponding to each chromatographic peak through its unique mass spectrum. Compared with other quantitative techniques LC-MS can have limited range where the response is linear with respect to the concentration [11].

An internal study done by Agilent Technologies [12] for Arkema Química S.A.U. showed initial LC-MS and sample treatment conditions to determine the two catalysts. This research concluded that more studies would be needed in order to carry out the determination.

This bibliographic study provided the basis for determining these two catalysts using the lab resources and setting its own internal method.

4. OBJECTIVES

The main objective of this project consists of studying the feasibility of determining the two phosphonium salts used as catalyst (TRAP and BTPC), present in polyester resins, by LC-MS using the Arkema Coatings analytical lab resources.

To achieve this objective the following specific objectives were followed:

- To evaluate the solubility of the compounds in different solvents to select those to be used in the mobile phase and the sample extraction.
- To establish for the first time the chromatographic and mass spectrometry conditions that allowed a satisfactory analysis of the target compounds.
- To assess a relationship between peak area and TRAP/BTPC concentration.
- To evaluate the extraction of both catalysts present in the resins.

5. EXPERIMENTAL SECTION

5.1. SOLUBILITY OF TRAP AND BTPC

Five different samples of TRAP (92% purity) and BTPC (92% purity) were prepared with different polar solvents available in the laboratory at a concentration of 2 g/L: water with 0.1% formic acid(v/v), acetonitrile, isopropyl alcohol, methanol, water and THF (tetrahydrofuran) (GPC grade, stabilized with 250 μg/L of BHT (butylated hydroxytoluene) all of them of a great purity grade specially for LC). On the other hand, one more test has been done checking the solubility in a 5% THF in MeOH (methanol) knowing that the resin is soluble in very few solvents, and THF is one of them. In this way, if in a first attempt using other polar solvents there is not a good extraction the resin should then be dissolved at first with THF to obtain the correct extraction of the components presents on it.

5.2. LC/MS EQUIPMENT

The chromatographic system used was an Agilent as 1260 Infinity II LC-MS. This instrument consists of the coupling of two different parts:

LC: Contains a special cabin to keep the mobile phase bottles (the solvents used as mobile phase have to be of the maximum purity), a G711B module containing a degasser (mobile phases have to enter on the system filtered and degassed to avoid the presence of bubbles which could lead to inconsistent pressure and a base line deviation), a quaternary pump that allows to work with more than one mobile phase, a G7129A module with an automatic injector incorporated, and a vial tray with a sample loop of 100μL.

The chromatographic separation of the phosphonium salts was carried out by a reverse-phase mode with Infinity Lab Poroshell 120 C18 column (3.0 mm x 150 mm and a particle size of 2.7 µm, Kinetex C18 column). Previous to the column, there is coupled an Infinity Lab Poroshell 120 C-18 precolumn (3.0 mm x 5 mm and a particle size of 2.7 µm) that prevents the column to be damaged by the particles or compounds that could be highly retained.

MS: Contains a G1978B module including an ionization source APCI/ES (10-2000amu mass ratio), a G6120BA module including a simple quadrupole LC-MS system and a detector that measures the relative abundance of compounds. The detection mass system (Ionization source + Analyzer + Detector) is calibrated by the manufacturer.

The software that controls the instrument is an Open Lab Agilent Technologies that includes an offline mode which is the one that is used to analyze the obtained results.

5.3. PRELIMINARY STUDIES

Acetonitrile was used as organic solvent in the mobile phase and water with 0.1% formic acid (v/v) as aqueous solvent. A 0.4mL/min flow rate was chosen according to the length, diameter and particle size of the column, to be in a working ratio pressure recommended for the manufacturer. It was determined that a needle wash was needed every time an injection was carried out. Before every injection every single sample was filtered in a 0.2μm filter to avoid the presence of particles in the chromatographic column.

Three different solution concentrations of each pure catalyst were prepared with MeOH (10, 20, 30 μg/mL). Isocratic conditions with different ratios of acetonitrile and water with 0.1% formic acid(v/v) as mobile phases respectively (10-90, 20-80, 30-70, 40-60, 50-50, 60-40, 70-30, 80-20, 90-10) were tested in order to evaluate the effect on the separation of the analytes. Although the system includes a quadrupole, which could identify them by their m/z ratio, a previous chromatographic separation was done for the purpose to obtain better results. In all of the preliminary studies a multimode APCI (atmospheric pressure chemical ionisation)/ES (electrospray ionisation) ion source was used in positive and negative mode. Knowing the molecular weights of the two analyst (M(TRAP)=371.26 and M(BTPC)=354.86) a scan method with a ratio 100-400 m/z was performed. The automatic injection of the samples on the chromatography system was 20 μL. In every sequence, a blank containing exclusively MeOH was injected initially. There was no injection of this blank between the samples during analysis.

In a second preliminary study lower concentrated solutions (1 μg/mL) with MeOH were injected. In this case a gradient method was used. Three different gradient conditions were performed (10/90, 20/80 and 30/70 of acetonitrile and 0.1% formic acid in water, respectively). This gradient condition consisted in a first isocratic phase with the corresponding percentage of the mobile phase for five minutes, a subsequent progressive increase of two minutes until its

100% of acetonitrile, maintaining this percentage for ten minutes and finally goes back through initial conditions for five minutes. Table 1 shows different gradient proportion of organic and aqueous solvent in different time:

	10/90		20/80		30/70	
Time [min]	Solvent A [%]	Solvent B [%]	Solvent A [%]	Solvent B [%]	Solvent A [%]	Solvent B [%]
0	10	90	20	80	30	70
5	10	90	20	80	30	70
7	100	0	100	0	100	0
17	100	0	100	0	100	0
19	10	90	20	80	30	70
24	10	90	20	80	30	70

Table 1. Different gradient conditions: Solvent A (Acetonitrile), Solvent B (water with 0.1% formic acid (v/v))

For this second preliminary study the ion sourced used is ES in positive and negative mode. The scan method used will be the same working in a range of 100-400 m/z, and then a subsequent ion extraction of m/z 291 and m/z 319 is done as a way of obtaining the representative peaks of each compound. In every sequence an initially injection of a blank containing exclusively MeOH is injected. There is no injection of this blank between the samples. The automatic injection of the samples on the chromatography system is 1 μL.

5.4. EVALUATION OF THE RELATIONSHIP BETWEEN PEAK AREA AND COMPOUND CONCENTRATION

In order to ensure the lineal relation between the different concentrations in front of the area given from the chromatogram, different amounts of the two catalysts were determined by the 20/80 chromatographic conditions established on table 1 along all of linearity tests. For this study the ion sourced used is ES in positive and negative mode. The scan method used worked in a range of 100-400 m/z, and then a subsequent ion extraction of m/z 291 and m/z 319 is done as a way of obtaining the representative peaks of each compound.

The first test consisted in analyzing different samples of TRAP and BTPC of different concentrations prepared in different days dissolved in MeOH. In every sequence an initially injection of a blank containing exclusively MeOH is injected. There is no injection of this blank between the samples. The automatic injection of the samples on the chromatography system is 1 μL.The following concentration ranges were evaluated:

- TRAP: 15 samples with different concentration (0.06 μg/mL-0.65 μg/mL of TRAP) with MeOH.
- BTPC: 7 samples with different concentration (0.02 μg/mL-0.38 μg/mL of BTPC) with MeOH.

The second test consisted in analyzing different samples of TRAP and BTPC of different concentration prepared in different days dissolved with 5% of THF in MeOH. In every sequence an initial injection of a blank containing 5% of THF in MeOH was performed. In that case, a blank was injected between samples to clean up the chromatographic column. The following concentration ranges were evaluated:

- TRAP: 11 samples with different concentration (0.01 μg/mL-1.00 μg/mL of TRAP) with 5% of THF in MeOH.
- BTPC: 11 samples with different concentration (0.02 μg/mL-0.38 μg/mL of TRAP) with 5% of THF in MeOH.

5.5. STUDY OF THE SAMPLE EXTRACTION

5.5.1 DESCRIPTION OF RESIN SAMPLES

Three samples were used to carry out the study of sample extraction. Each resin sample is produced in Arkema and has different properties being differently synthesized to react with different crosslinkers amounts. This is the reason why they all contained a different percentage by weight of the target catalyst. These three samples were from a specific batch of industrial production and must be assumed that their catalyst content was the theoretical one:

- Reafree 6660 (L-I1273156C1): 0.96% TRAP
- Reafree 2776-TS (L-J0988906C1): 0.19% BTPC
- Reafree 2872-T (L-I1265066C1): 0.03% TRAP and 0.1% BTPC

The R&D laboratory proceeded to specially manufacture resins with different well-known concentrations of TRAP added to a free-catalyst base resin (RP-3541) simulating a real process of adding catalyst in plant, so adding these additives at temperature when the resin was in liquid state. 4 different batches were obtained:

- RP-3541 (1): 0% TRAP
- RP-3541 (2): 0.1% TRAP
- RP-3541 (3): 0.2% TRAP
- RP-3541 (4): 1% TRAP

5.5.2. EXTRACION METHOD 1: METHANOL

In this study it has been chosen the resin Reafree 6660 as a sample to know which conditions are the best to extract TRAP from the polyester. It would be interesting to do this study with all polyester resins available but there was not enough time to execute it. This resin containing 0.96% of TRAP by weight is the one chosen to study the extraction of the compounds. A first test was done preparing three grinded sample replicates of Reafree 6600 diluted in MeOH (10 μg/mL) with a stirring of 40 minutes. A second trial was performed preparing three grinded sample replicates of Reafree 6660 diluted in MeOH (10 μg/mL) with a stirring of 20, 40 and 60 minutes, respectively. A final test was carried out preparing three sample replicates of Reafree 6660 with 0.2% of TRAP in weight added and homogenized with the grinded sample in a grinder diluted in MeOH (10 μg/mL) with a stirring of 20 minutes. All of these tests were done under 20/80 gradient conditions (see table 1) and with ES working as the main ion source in positive and negative mode. The scan method used works in a range of 100-400 m/z, and then a subsequent ion extraction of m/z 291 and m/z 319 is done as a way of obtaining the representative peaks of each compound. In every sequence an initially injection of a blank containing exclusively MeOH is injected. There was no injection of this blank between samples.

5.4.3. EXTRACTION METHOD 2: METHANOL WITH 5% THF

This method extraction was followed for all samples described in 5.4.1. Different samples concentration of each resin were prepared in different days and subsequently analyzed. All of these samples were prepared as it is described in the following explanation: At first, the calculated amount of the resin was diluted with THF (the amount of THF depended on the total 5% final solution of MeOH) with constant stirring. Once it was dissolved, the solution was completed to volume with MeoH stirring for 20 minutes. The final solution was filtered with a 0.2 μm filter and it was introduced on the vial to be analysed.

All of the samples were determined under the 20/80 chromatographic conditions set in table 1. The scan method used works in a range of 100-400 m/z, and then a subsequent ion extraction of m/z 291 and m/z 319 is done as a way of obtaining the representative peaks of each compound. The automatic injection was 1μL. In every sequence an initial injection of a blank containing 5% THF in MeOH was performed. A blank was injected between samples to clean up the chromatographic column and avoid carry over effect. To quantify the samples, the trend line obtained in the linearity test of the samples diluted with 5% THF in MeOH by TRAP and BTPC is used.

6. RESULTS AND DISCUSSION

6.1. SOLUBILITY OF TRAP AND BTPC

In a first stage, solubility tests of the two pure compounds were carried out to determine which solvent could be used as mobile phases and to know in which solvent the samples were going to be dissolved. Table 2 shows in which solvent TRAP and BTPC are soluble:

	TRAP	**BTPC**
0.1% Formic acid in water	+	+
Isopropanol	+	+
MeOH	+	+
Water	+	+
Acetonitrile	+	+
THF	-	-
5% THF in MeOH	+	+

Table 2. Solubility TRAP/BTPC in different solvents: += soluble/ -=insoluble.

As both catalysts are phosphonium salts, they tend to be soluble in polar solvents, but not in THF. These results are of great importance to determine which solvents are going to be used as mobile phases. Being aware that the saturated polyester is soluble in THF, a test with a solution of 0.5% THF in MeOH was carried out for a future extraction of TRAP and BTPC in resins.

By reference to a previous study done for Agilent Technologies for the determination of these two compounds [12] where 0.1% formic acid in water and 10%THF in MeOH were used as mobile face; water modified with 1% of formic acid (v/v) and acetonitrile were selected as solvents for the mobile phase. THF is a very aggressive compound so this project tried to work with another organic solvent that allows a good elution of the products and less harmful for the chromatographic system. Acetonitrile is the most common organic solvent used for a LC-MS system which is less viscous than MeOH and therefore generates less pressure on the system. In addition, it allows a faster elution of the compounds and to get shorter chromatograms. The aqueous solvent chosen, 0.1% formic acid in water (v/v) was considered appropriate to obtain a better separation of the products and it is mostly used working in a gradient system of LC-MS.

6.2. PRELIMINARY TESTS ON LC/MS CONDITIONS

Three different solution concentrations of each pure catalyst were prepared with MeOH (10, 20, 30 μg/mL) and analyzed using different ratios of acetonitrile and 0.1% formic acid in water as mobile phases in isocratic conditions. The automatic injection of the samples on the chromatography system was 20 μL. Multimode APCI/ES ion source was used in positive and negative mode using a SCAN method between 100-400 m/z. The automatic injection of the samples on the chromatography system was 20 μL. In every sequence, a blank containing exclusively MeOH was injected initially. There was no injection of this blank between the samples during analysis.

The first tests carried out determined that TRAP and BTPC could be analysed by a LC-MS system. In the different SCAN obtained, the mass spectra of the chromatographic peaks obtained showed the presence of two molecular ions with m/z 319 and m/z 291 corresponding to the BTPC and TRAP ionized forms.

Between APCI and ES it was decided that working exclusively with ES more sensitive results were obtained. Within the positive or negative ionization modes, the positive mode was the one that gave signal.

Despite observing the presence of the catalysts in the mass spectrum of the obtained chromatogram, it was not possible to achieve separated peaks. First, the 20 μL automatic injection saturated the mass detector and the signal obtained was not satisfactory. Second, the concentration of the prepared samples was too high and the peaks of the products appeared in blanks injected after the solutions of target compounds. Finally, the retention times of the analytes were very variable among the different chromatograms. Therefore, the high concentration and injection volume caused the retention of the target compounds in the chromatographic column, that is carry-over problems. Although the system was saturated, it was observed that the two analytes were eluted faster with a higher proportion of acetonitrile in the mobile phase. Different conclusions were drawn from the obtained results of these two first preliminary tests. Firstly, the amount injected has to be lower to avoid saturation on the mass detector due to the high sensitivity of the target compounds. Secondly, the concentration amount of the samples was too high leading a carry-over on the chromatographic column.

In a second preliminary study lower concentrated solutions (1 μg/mL) with MeOH were analyzed under three different gradient conditions (10/90, 20/80 and 30/70) as are shown in table 1. The automatic injection of the samples on the chromatography system was 1 μL. ES mode was used in positive and negative mode using a SCAN method between 100-400 m/z. In every sequence an initially injection of a blank containing exclusively MeOH is injected. There is no injection of this blank between the samples.

In this second set of preliminary tests, it was decided to work in gradient conditions (see table 1) in order to obtain a better separation. In the first step, the presence of a higher proportion of the aqueous phase is needed to allow the catalysts separate better. In a second step the presence of more organic solvent made elute quickly the two catalysts present in the sample to prevent the carry over effect. In a final step, the conditions must be the same as the initial ones to equilibrate the column for the next analysis. Three different gradients were tested as described in table 1. There was a good separation of TRAP and BTPC in the tests done with 10/90 and 20/80 gradient conditions. Figure 6a shows, as an example, the MS-SCAN chromatogram of TRAP. Furthermore, an ion extraction method was used with the aim of obtaining an exact area of the analyte of interest peak. Figure 6b shows, as an example, the MS-SCAN ion extraction of m/z: 291 (TRAP). Figure 6c shows, as an example, the MS-SCAN chromatogram of BTPC. Figure 6d shows, as an example, the MS-SCAN ion extraction of m/z: 319 (BTPC).

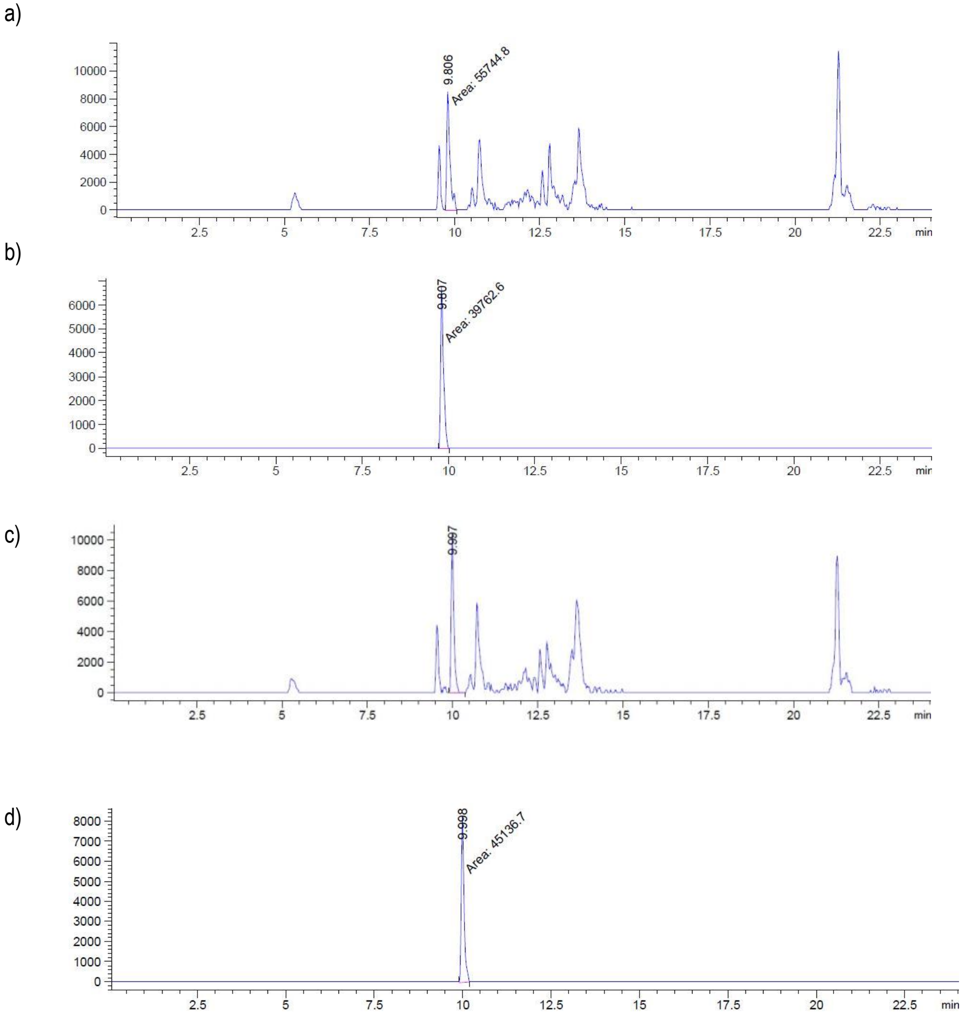


Figure 6. Example of a) MS-SCAN chromatogram of TRAP in 10/90 gradient, b) MS-SCAN chromatogram ion extraction of m/z: 291 (TRAP) in 10/90 gradient, c) MS-SCAN chromatogram of BTPC in 10/90 gradient and d) MS-SCAN chromatogram ion extraction of m/z: 319 (BTPC) in 10/90 gradient.

As shown in MS-SCAN chromatogram different peaks appear along the sequence. The presence of all these peaks were caused by the present impurities of TRAP and BTPC (92%

purity). The aim of these tests was to select the gradient that provided a better chromatographic separation in order to obtain better results with the mass detector. An additional criterium was to establish the gradient that led to the cleanest chromatographic peak. Table 3 shows the retention time obtained for the two catalyst under different acetonitrile/ 0.1% formic acid in water proportion in mobile phase, all the conditions set for these gradient conditions are shown in table 1:

Initial proportion of acetonitrile/0.1% formic acid in water in mobile phase	**Retention Time (min)**	
	TRAP	**BTPC**
10/90	9.807	9.998
20/80	9.587	9.827
30/70	6.345	9.560

Table 3. TRAP and BTPC retention time in front of different mobile phase gradient conditions.

The retention time is closely related to the proportion of acetonitrile used in the mobile phase. The presence of a higher proportion of the organic solvent as mobile phase reduces the retention time. Taking into account the results obtained with the 30/70 mobile phase gradient conditions, in spite that acetonitrile causes a faster elution of TRAP and presented a better separation between compounds, the shape of the peak is more irregular and not as satisfactory as the ones obtained in different gradient conditions. Figure 7 shows the MS-SCAN chromatogram ion extraction of m/z: 291 (TRAP) trap in 30/70 gradient conditions.

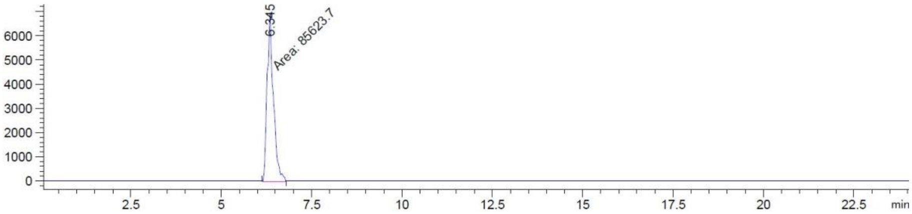


Figure 7. MS-SCAN chromatogram ion extraction of m/z: 291 (TRAP) in 30/70 gradient

With the obtained results it was observed that, with a lower amount of the sample injection, the mass detector was not saturated so the peaks were distinguishable. Besides, it is seen that with lower concentration there is less carry-over effect, although small amounts of TRAP and BTPC still appear in blanks analyses. The presence of small amounts of the analytes in the blank injection might be due to two main reasons: in the first place, the two compounds could still be present in the column after the initial injection of 20 μL of high concentrations in the preliminary tests; in the second place, with the gradient conditions applied it was not possible to totally elute the target compounds from the column and small amounts remain. In order to know what was the reason that still made a carry-over, an evaluation of the relationship between peak area and compound concentration in different mediums tests were carried out comparing two situations: with and without injection of blanks between samples.

6.3. ANALYSIS OF TRAP AND BTPC IN METHANOL MEDIUM

6.3.1. EVALUATION OF THE RELATIONSHIP BETWEEN PEAK AREA AND COMPOUND CONCENTRATION

In this study several standards of TRAP and BTPC at different concentrations were injected in the LC-MS system in different days in order to evaluate, on the on hand, if the peak area for a given concentration was constant and if there was a straight relationship between peak area and compound concentration (i.e. linearity). All tests were done under 20/80 gradient condition established in table 1. The automatic injection of the samples on the chromatography system was 1 μL. ES mode was used in positive and negative mode using a SCAN method between 100-400 m/z. MS-SCAN chromatogram ion extraction (m/z: 291 for TRAP and m/z: 319 for BTPC) was obtained for every sample analysis of each compound. In every sequence an initially injection of a blank containing exclusively MeOH was injected. There was no injection of this blank between the samples.

The results obtained in this first test gave two plots that represented the obtained area in front of the different amounts in different days of TRAP and BTPC with MeOH as solvent. Figure 8 shows the relationship between peak area and TRAP concentration in MeOH used as solvent:

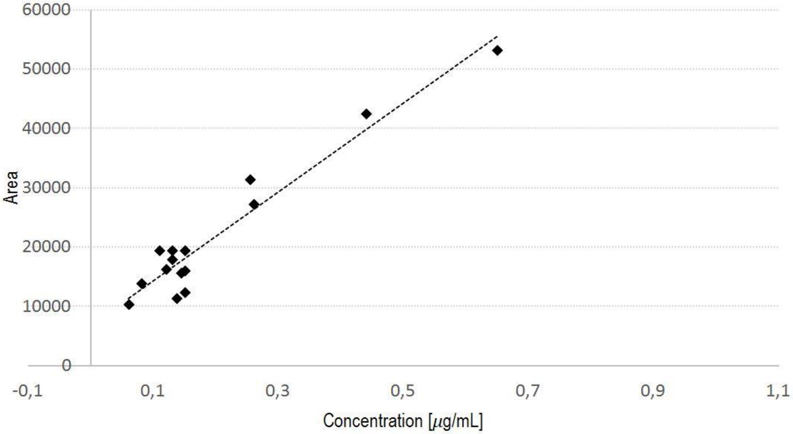


Figure 8. In this plot is represented the peak area obtained in front of the amount of 15 different concentrated TRAP samples diluted with MeOH. This plot also shows the trend line obtained.

The results obtained in figure 8 showed a good linearity of the relationship between peak area and TRAP concentration in different days. The regression line obtained (y=74981(±12648)x + 6826(±3142)) showed an intercept different from zero suggesting a carry-over effect. With the gradient conditions set, TRAP did not elute completely causing a high retention in the chromatographic column. Therefore, when blanks are injected it can be observed the presence of a certain amount of the compound. Because of that, it was determined that the best way to proceed was performing two blank injections between samples that ensure every analysis was on equal terms.

Figure 9 shows the relationship between peak area and BTPC concentration in MeOH used as solvent:

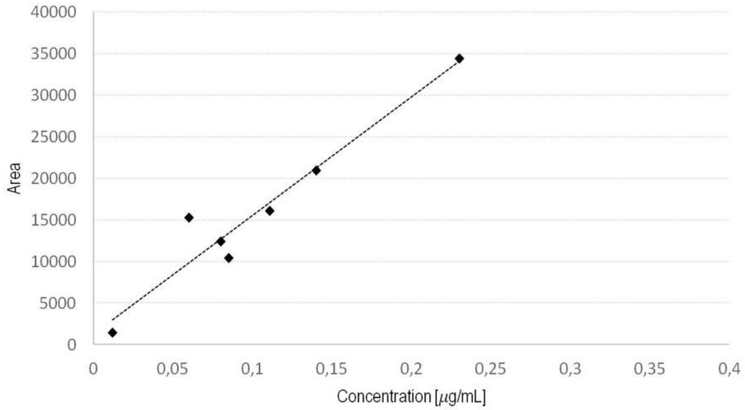


Figure 9. In this plot is represented the peak area obtained in front of the amount of 6 different concentrated BTPC samples diluted with MeoH. This plot also shows the trend line obtained.

The results obtained in figure 9 showed a good linearity of the relationship between peak area and BTPC concentration in different days. The regression line obtained (y=142413(±44343)x + 1274(±5357)) showed an intercept not significantly different from zero. It could not be confirmed that there was no carry-over effect at all but it corroborates that BTPC tends to be less retained in the chromatographic column. Although two blank injections between samples, that prevents carry-over effects, would not be required for BTPC, it was decided to work with the same conditions for both compounds.

6.3.2. EXTRACTION OF TRAP FROM REAFREE 6660

As there was no time to study the extraction behaviour of all the resins it was assumed that the Reafree 6660 extraction was valid for all of them. The study of the results in this section has been carried out by comparing the % of TRAP measured from the regression line obtained in figure 9 with the % of TRAP theoretically present in Reafree 6660 resin. Although the final results may not be totally accurate due to the bias of the y-intercept of the regression line, this study will be helpful to know if using MeOH as solvent is enough to obtain a good extraction from the catalyst.

Three different studies were performed under 20/80 gradient condition established in table 1. The first study consisted in analysing 3 replicates of Reafree 6660 resin of 10 μg/ml with 40 minutes of stirring. The second study consists in analysing 3 replicates of Reafree 6660 resin of

10 μg/ml with different stirring time for each one. No logical results were obtained from that study. Finally, there were analysed 3 replicates of 10μg/mL for Reafree 6660 resin with an extra 0.2% in weight of TRAP added. The automatic injection of the samples on the chromatography system was 1 μL. ES mode was used in positive and negative mode using a SCAN method between 100-400 m/z. MS-SCAN chromatogram ion extraction m/z: 291 (TRAP) was obtained for every sample analysis of Reafree 6660 resin. In every sequence an initially injection of a blank containing exclusively MeOH was injected. There was no injection of blanks between the samples. Table 4 shows the mean of % of TRAP measured from the 3 replicates of the first study and the recovery from the theoretical % value.

Resin		n	%Theoretical	%Measured	%Recovery
Reafre 6660	TRAP	3	0.96	Mean: 0.28 SD: 0.18	Mean: 29.2 SD:19

Table 4. Results of % of TRAP measured from the 3 replicates of the first study and the recovery from the theoretical % value.

These results showed a poor TRAP extraction from the theoretical %TRAP concentration in weight in 6660 resins. As it can be observed, the SD is too high determining that there is not a good repeatability of the replicates. The difference between three replicates results affect directly on the SD of the recovery. The fact that an injection blank is not done between samples, the results obtained are totally affected for the previous injection. Although the evidence that the sample can be extracted from the resin, the recovery is far from what it was expected.

A subsequent study of 3 replicates of Reafree 6660 with different stirring minutes was done but no useful results were obtained. The carry-over effect of TRAP did not allow getting good results.

Finally, 3 replicates of Reafree 6660 with 0.2% of TRAP in weight added were analyzed. Table 5 shows the mean of % of TRAP measured from the 3 replicates of the first study and the recovery from the theoretical % value.

Resin		n	%Theoretical	%Measured	%Recovery
Reafre 6660	TRAP	3	1.16	Mean: 0.75 SD: 0.23	Mean: 64.6 SD: 19

Table 5. Results of % of TRAP measured from the three replicates of the 3rd study and the recovery from the theoretical % value.

The results obtained from table 5 shows a high SD for %TRAP measured and the recovery so that, there was not a good repeatability for the three replicates. Carry-over effects still affect on the results making them not repeatable. Furthermore, it has been demonstrated that catalyst addition in resins by simply mixing two solids at room temperature in a grinder, does not guarantee a totally incorporation. Another fact to keep in mind is that when the resin was in a MeOH solution a viscous white solid was formed (it did not dilute) and it was believed that some part of TRAP was trapped inside it and did not allow a good extraction of the catalyst.

With these studies, two main reasons that caused a bad extraction results could be concluded. First of all, a carry-over effect was taking place because of there was not any blank injection between sample analysis. This fact did not allow a good repeatability of the results. Secondly, there was a problem with the solubilisation of the sample. The resin sample is not soluble in MeOH making more difficult to completely extract the compound. It was concluded that the best way to proceed to extract the samples was, in a first step, to dilute the saturated polyester with THF (the equivalent volume to get a 5% of THF in MeOH final solution) and complete to volume with MeOH to ensure that the two catalysts were not retained and be completely diluted in the solution. Furthermore, it is necessary to perform two blank injections to ensure no TRAP is carried in the chromatograph column. The time of stirring did not have an important role, especially when the resin sample is dissolved in the first place, so it is decided that a stirring time of 20 minutes will be enough to ensure the totally homogeneity of the final sample solution.

6.4. ANALYSIS OF TRAP AND BTPC IN METHANOL WITH 5% OF THF MEDIUM

6.4.1. EVALUATION OF THE RELATIONSHIP BETWEEN PEAK AREA AND COMPOUND CONCENTRATION

The tests done with MeOH as solvent leads to analyse several standards of TRAP and BTPC diluted with MeOH modified with 5% of THF at different concentrations by LC-MS system in different days in order to evaluate, on the one hand, if the peak area for a given concentration is constant and if there is a straight relationship between peak area and compound concentration (i.e. linearity). All tests were done under 20/80 gradient condition established in table 1. The automatic injection of the samples on the chromatography system was 1 μL. ES mode was used in positive and negative mode using a SCAN method between 100-400 m/z. MS-SCAN chromatogram ion extraction (m/z: 291 for TRAP and m/z: 319 for BTPC) was obtained for every sample analysis. In every sequence an initially injection of a blank containing exclusively 5% of THF in MeOH was injected. There were two injection of this blank between the samples.

The results obtained in the first test give two plots that depicts the obtained area in front of the different amounts in different days of TRAP and BTPC with 5% of THF in MeOH as solvent. Figure 10 shows the relation between peak area and TRAP concentration in 5% in MeOH used as solvent:

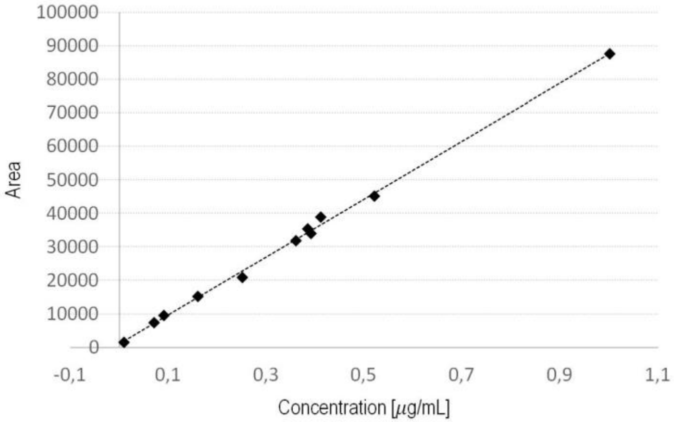


Figure 10. In this plot is represented the area obtained in front of the amount of 11 different concentrated TRAP samples diluted with 5% THF in MeoH. This plot also shows the regression line obtained.

The results obtained in figure 10 were very satisfactory as they confirm the origin of the error in the first tests already done. These results showed a good linearity of the relationship between peak area and TRAP concentration in different days. The regression line obtained (y=86541(±2964)x + 1141(±1254)) goes through the y-intercept confidence confirming there was no carry-over effect. This fact determines that making two blank injections between sample analysis minimize the carry-over effect of TRAP. Every single sample was analysed with the chromatographic column free from TRAP making every analysis under the same conditions. The fact of introducing this small percentage of THF into the solvent has not affected the relation between peak area and TRAP concentration. Furthermore, THF may minimize the carry-over effect of TRAP with a better elution in the chromatographic column.

Figure 11 shows the relation between peak area and BTPC concentration in 5% of THF in MeOH used as solvent:

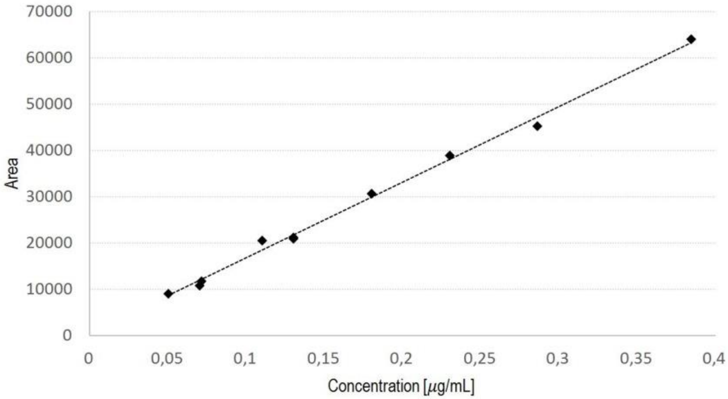


Figure 11. In this plot is represented the area obtained in front of the amount of 10 different concentrated BTPC samples diluted with 5% of THF in MeoH.. This plot also shows the trend line obtained.

The results obtained in figure 11 showed a good linearity of the relationship between peak area and BTPC concentration in different days. The regression line obtained (y=163771(±9100)x + 470(±1757)) goes through y-intercept confidence meaning that there is no carry-over effect. Although in former test using exclusively MeOH as solvent was determined that there was not a carry-over effect, this last test with 5% THF in MeOH showed better linearity and less bias in the y-intercept confidence.

This analyse showed that the best way to obtain good results was still with two blanks injections between samples. Although it has been observed that BTPC tended to be less retained than TRAP, it was decided to proceed in the same way with both compounds so that all the factors were controlled.

6.4.2. EXTRACTION OF TRAP AND BTPC FROM RESINS SAMPLES

Two different sets of resin samples have been studied. In first set, samples (Reafree 6660, Reafre 2776-TS and Reafree 2872-T) were from industrial production batches and the known catalyst value was the theoretical one. The second set consisted in a special R&D preparation adding different amount of catalyst to the free-catalyst resin simulating a real industrial process (melting the resin and adding the catalyst at high temperatures) which guarantees completely homogeneity and incorporation. The study of the results in this section has been carried out by comparing the % of TRAP and BTPC measured from the regression lines obtained in figure 11 and 12 with the % of TRAP and BTPC theoretically present in resin samples. All tests studies were performed under 20/80 gradient condition established in table 1. Different samples of each resin have been analysed obtaining the % of catalyst measured. The automatic injection of the samples on the chromatography system was 1 μL. ES mode was used in positive and negative mode using a SCAN method between 100-400 m/z. MS-SCAN chromatogram ion extraction (m/z: 291 for TRAP and m/z: 319 for BTPC) was obtained for every sample analysis of different resins. In every sequence an initially injection of a blank containing exclusively 5% of THF in MeOH was injected. There were two injections of this blank between the samples.

Table 6 shows the mean of % of TRAP and BTPC measured from the first set samples and the recovery from the theoretical % value.

Resin		**n**	**% Theoretical**	**% Measured**	**%Recovery**
Reafre 6660	TRAP	3	0.96	Mean: 0.81 SD: 0.050	Mean:84.4 SD:5
Reafre 2872-T	TRAP	10	0.030	Mean: 0.032 SD: 0.050	Mean: 115.09 SD=16
	BTPC	7	0.10	Mean: 0.091 SD: 0.010	Mean: 91.0 SD: 10
Reafree 2776-TS	BTPC	8	0.19	Mean: 0.12 SD: 0.0060	Mean: 62.5 SD: 3

Table 6. Mean of % of TRAP and BTPC measured from the first set samples and the recovery from the theoretical % value.

The results obtained in table 5 the extraction of the samples first diluted with 5% of THF in MeOH encourages a better extraction of the catalysts from the polyester resins compared with the ones already measured using MeOH as solvent. Furthermore, it has been demonstrated that making two blank injections of 5% of THF in MeOH improves the repeatability of the results for all samples avoiding the carry-over effect. Although it has been demonstrated a better extraction of catalysts in resins, these results did not show the same recovery in both catalyst. Different resins containing TRAP showed a recovery of 84.38(±5) for Reafree 6660 and 115.09(±16) for Reafree 2872-TS. Resins containing BTPC showed a similar behaviour, a first recovery of 91.02(±10) for Reafree 2872-T and 62.52(±3) for Reafree 2776-TS. The fact that the theoretical value of these resins comes from industrial production, synthesized in large-scale, does not ensure that they are the real values. That was causing big differences in the final recoveries for the same catalysts in different resins. For this reason, a study of a free catalyst resin with known amounts of added TRAP was needed.

Table 7 shows the mean of % of TRAP measured from different samples of the same resin with known distinct amounts of TRAP added:

Resin		n	%Theoretical	%Measured	%Recovery
RP-3541	TRAP	2	0	Mean: 0	No recovery
		10	0.10	Mean: 0.090 SD: 0.016	Mean: 90.4 SD: 16
		8	0.20	Mean: 0.18 SD: 0.031	Mean: 90.8 SD: 16
		5	1.0	Mean: 0.87 SD: 0.12	Mean: 86.7 SD: 12

Table 7. Mean of % of TRAP and BTPC measured from the second set samples and the recovery from the theoretical % value.

The results obtained in table 7 confirmed that there was a satisfactory TRAP extraction of the samples when a dilution of 5% of THF in MeOH was used. Making two blank injections improves the repeatability of the results avoiding the carry-over effect. Furthermore, it has been demonstrated that there is a straight relationship for all the 3 different batches of the resin obtaining a similar recovery and standard deviation. This fact confirms the uncertainty of analysing resins from industrial production where the theoretical value can differ from the real one. In order to know if the extraction of catalyst value depends on the type of resin the extraction is done, more tests should be performed with a known concentration of catalysts in the resin, following the same process as in resin RP-3541.

According to the company’s needs, the results obtained are quite satisfactory. It is important to underline that these results will help the R&D lab to know an approximate amount of theses catalysts in the target resins. These results do not require an extremely accuracy since they are for internal knowledge.

It is understood that through these conditions, it is almost impossible to get a 100% of the expected quantity but it can be the basis for future studies. In order to optimize and validate the method, it would be necessary to build a good calibration curve measuring all the standards in the same day. Based on that calibration, some other resins of known catalyst content should be analysed to establish a consistent recovery factor for each target. In that way, unknown samples could be determined.

7. CONCLUSIONS

In this work, the viability of the determination of the phosphonium salts TRAP and BTPC, used as catalysts in polyester resins, has been thoroughly studied using LC-MS. From this evaluation several conclusions can be drawn:

- The most suitable solvents used as mobile phases are acetonitrile, which allows a fast elution of the target compounds and to get shorter chromatograms, and 0.1% formic acid in water to obtain a better separation.
- The MS detector is very sensitive so the amount of sample injected must be of 1μL.
- The concentration of catalysts in samples has to be around 1 μg/mL to minimize carry-over effects.
- A satisfactory chromatographic separation of the two compounds was obtained using gradient conditions: starting with a 20/80 proportion of acetonitrile and 0.1% formic acid in water to chromatographically separate the compounds, and a subsequent increase to 100% of acetonitrile to minimize carry-over effects.
- ES ion source in positive mode gives a satisfactory peak resolution. MS-SCAN ion extraction of each compound (m/z 291 for TRAP and m/z 319 for BTPC) provides suitable peak areas.
- The injection of blanks between samples is recommended to decrease carry-over effects.
- The use of methanol with 5% of methanol is preferred since it improves the quality of the calibration curve and the extraction of the target compounds from the resin.
- Once the viability of the determination of TRAP and BTPC in polyester resin has been demonstrated, future work should be focused on the obtention of a calibration curve in the same day, the evaluation of reproducibility, and the performance of extraction analysis from a higher number of resins with an exact known amount of TRAP and BTPC added to establish the recovery factor. Finally, a validation of the method will be required.

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9. ACRONYMS

APCI Atmospheric pressure chemical ionisation

BHT Butylated hydroxytoluene

BTPC Butyltriphenylphosphomium chloride

CG-MS Gas-chromatography mass-spectrometry

DGT Diglycidyl terephtalate

ES Electrospray Ionisation

HPLC High pressure liquid chromatography

IPA Isophtalic acid

LC-MS Liquid-chromatography mass-spectrometry

MeOH Methanol

MS Mass spectrometry

NPG Neopentilglicol

PTC Phase-transfer catalyst

R&D Research and Development

SD Standard Deviation

TGIC Tiglycidyl isocyanurate

THF Tetrahydrofurane

TMA Trimellitic anhydre

TML Triglyceride trimellitate

TPA Terephtalic acid

TRAP Ethyltriphenylphosphonium bromide

UV Ultraviolet