INNOVATIVE DIGITAL WATERMARKS AND GREEN SOLVENTS FOR THE RECOVERY AND RECYCLING OF MULTI-LAYER MATERIALS

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DELIVERABLE N°2.1

Analysis on multilayer packaging

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1 Introduction

The SOL-REC² project aims to investigate the recycling of different types of multilayer packaging. The difficulty in recycling this type of packaging is due to the fact that the different layers are made up of different materials that are not compatible for recycling. In multilayer packaging we can find different types of materials in each layer, such as paper, cardboard, aluminium or different types of plastics such as polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP) or even polyvinyl chloride (PVC) or some type of polyamide (PA).
The aim of work package 2 (WP2) is to identify different samples of pouches and pharmaceutical blister packs, in order to be able to determine the materials from which multilayer packaging is made.
In this deliverable, the results achieved by two different testing techniques are presented. On the one hand, characterisation analyses have been carried out, where the different layers have been identified by means of cuts on the packaging itself, without the need for separation. On the other hand, the different layers of the packs have been identified thanks to a physical separation with solvents. In the first technique, the different layers were identified using infrared equipment (FTIR), as well as the thickness of each layer. In the second technique, different types of solvents were used to separate each of the layers and subsequently identify them by infrared (IR).

2 Collection of different samples of laminate pouches and pharma blisters.

The first step in testing the identification of multilayer packaging materials was to collect representative samples that would allow conclusions to be drawn. To do this, both partners, Plastigram and Mikrolin, carried out the search for these materials. Plastigram was in charge of sending AIMPLAS different multilayer pouch laminates. All of them were production waste from pouch manufacturing companies, which facilitated the analysis both by characterisation and by solvents, as the containers were not degraded. Mikrolin sent samples of pharmaceutical blister packs to AIMPLAS. On the one hand, they sent pre-consumer samples, i.e. production losses, and on the other hand, it sent post-consumer samples. Both types of samples were analysed, but the identification focused on pre-consumer pharmaceutical blister packs.
Once the samples of pouches and pharmaceutical blister packs were collected, the analysis of these products began in the AIMPLAS laboratories. The aim of these analyses was firstly to identify the different materials that make up both types of packaging, and secondly, using representative samples of both products, to identify the most common structures used for both products.

3 Analysis of laminate packaging

The collected samples have been both analysed by non-destructive FTIR measurements and by delamination test following the JRC guide. These two analyses in parallel are complementary, as FTIR-ATR with the optical microscope can define the type of the layer and their composition, while the delamination tests can provide the quantitative composition of the sample and confirm unclear results.

3.1. Sample 1 (22-10)

3.1.1. Characterisation analysis

During this WP, the analysis and identification of the layers are done for both types of samples pouches and pharma blisters. The proposed analysis on those samples is the identification and measurement of the number of layers and thickness. Different methods are proposed for obtaining those characteristics, they are based on the observation of the layers through the optical microscope and the identification of the layers is done through different methodologies based on the difficulty of obtaining that information from the sample, at the end.

This identification methodologies are FTIR-ATR that can be integrated or not on the microscope, that will be used in case the different number of layers. If it is possible to identify the different layers without using this equipment, this analysis task will be the preferred one. Finally, in order to identify the different adhesives between layers, if it is needed or cannot be done through FTIR

or the one coupled with the microscope, destructive techniques will be applied in order to delaminate and obtain the different layers separately.

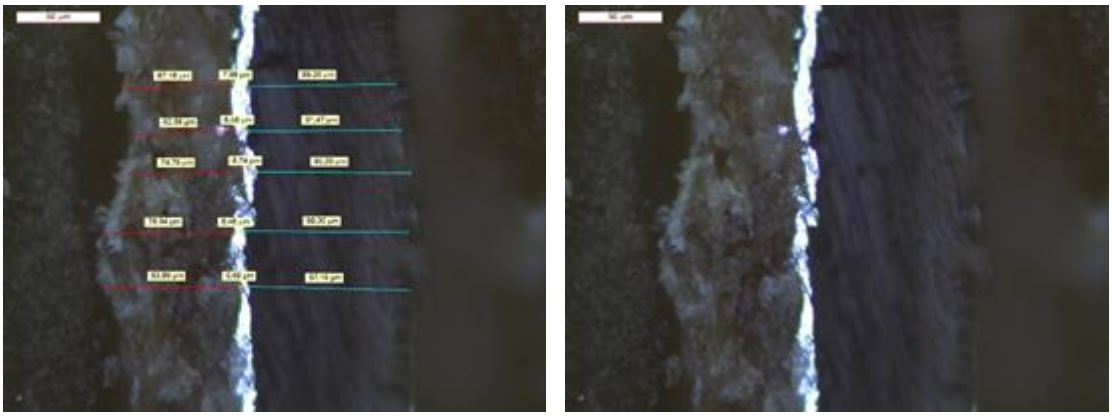
The procedure applied is, first identifying the number of layers observed and their thickness. After it, a identification methodology from the ones described on the introduction of the WP is applied.

Equipment:	Optical microscopy LEITZ DMRX + Microtome LEICA RM2255
Method:	Transmission optical microscopy
Magnifinications:	20x
Sample preparation:	Manual cutting on the support tool for the ATR Imaging
Evaluation:	Visual

This methodology applies to microscopy. The one associated with FTIR is the following one:

Method:	Internal Procedure Q15
Equipment:	Infrared spectrophotometer by Fourier Transform from Fourier Perkin Elmer Frontier
Measurement method:	ATR in GLADIATR by Diamond Crystal Transmission
Number of scans:	4
Resolution (cm-1):	4
Scan range (cm-1):	4000-400
Sample preparation method:	None
Equipment:	Infrared spectrophotometer by Fourier Transform from Fourier Perkin Elmer Frontier connected to IR SPOTLIGHT 400 microscope
Measurement method:	ATR Imaging
Number of scans:	2 per pixel
Resolution (cm-1):	16
Scan range (cm-1):	4000-680
Sample preparation method:	Location in tool for IR microscopy

A transversal cut is done over the film and 5 measurements are done through the different identified layers.



Photomicrograph nº1: Photomicrograph from PRO20-001-02-03-02. Magnification -x20.

Table 1
Thickness (µm)

Specimen	Red (External)	Yellow (Aluminum)	Blue (Interal)
1	20,66	22,40	5,07
2	20,20	21,80	4,60
3	19,30	18,08	4,30
4	18,02	19,10	4,65
5	16,81	19,62	4,59
Mean value	**19,00**	**20,20**	**4,64**
Standard deviation	1,59	1,83	0,28

The identification, as it can be seen, there are 3 layers, the one in between is aluminum. So, applying an infrared beam on each side of the sample will be enough to identify the materials that are present on this sample:

The infrared spectrum from transmission shows characteristic bands of PE (polyethylene) on the inner face.

The infrared spectrum from transmission shows characteristic bands of cellophane on the outer face.

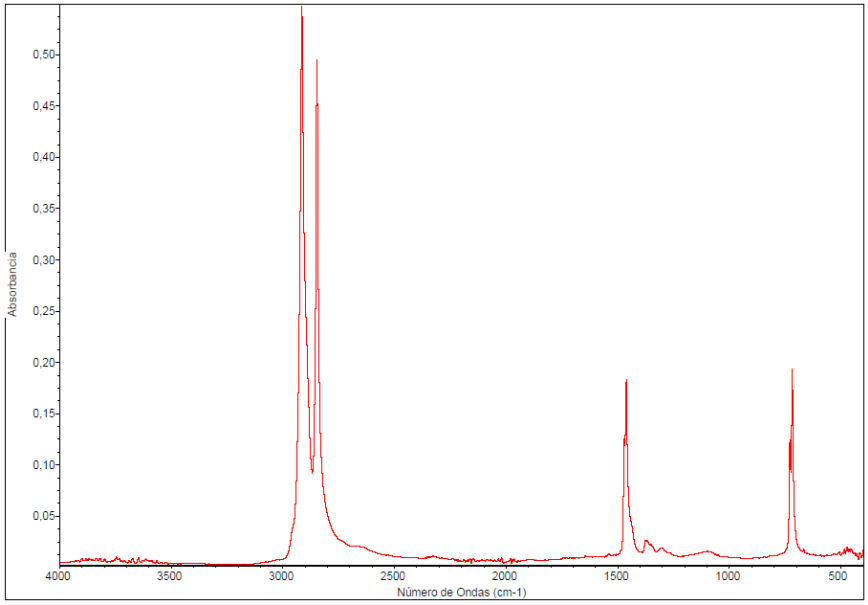


Figure 1
Infrared Spectra from the Outer Face from "PRO20-0017-02-03-02"

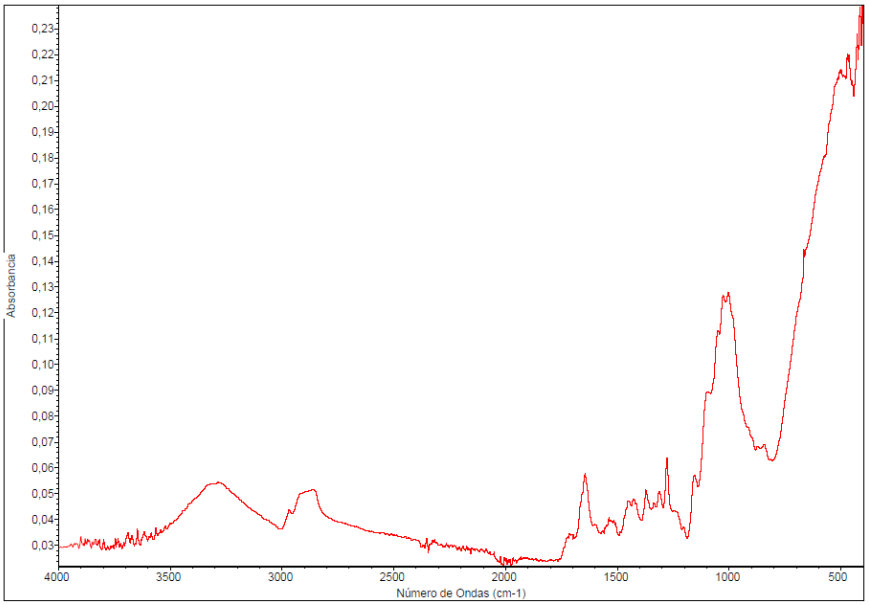
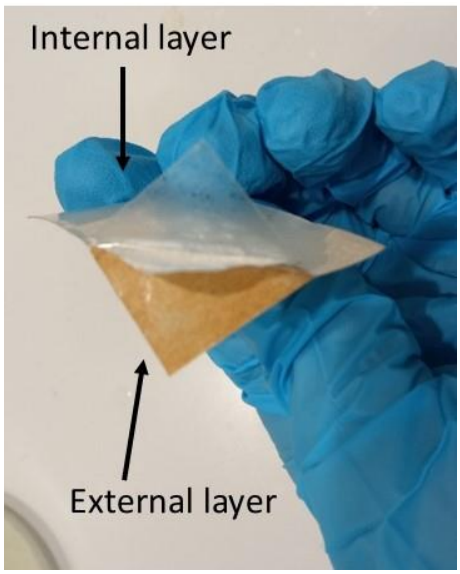
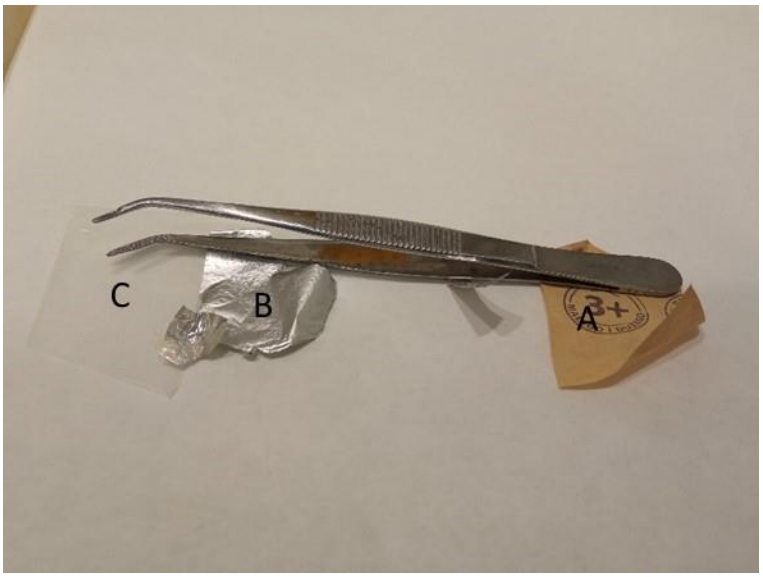


Figure 2
Infrared Spectra from the Inner Face from "PRO20-0017-02-03-02"

3.1.2. Solvent analysis

Preliminary FTIR of the sample showed that the internal layer is made of PE and the external layer is made of paper.
The sample (263.00 mg) was immersed in AcOEt for 30 minutes at room temperature. After this time, the layers started to separate and were peeled off from each other.





The obtained layers were then analysed by FTIR to determine their composition:

- Layer A (81.13 mg): paper with a bit of polyether urethane (adhesive) on the internal face
- Layer B (40.23 mg): clean aluminum foil
- Layer C (140.28 mg): PE with polyether urethane (adhesive) on the internal face

The complete removal of the adhesive was tough, as it did not disappear in boiling HCOOH, EtOAc or DMSO at 90ºC. It could be partially removed with a paper swollen in acetone and by rubbing the surface with some force.

As a result, the proposed composition of the laminate packaging is as following:

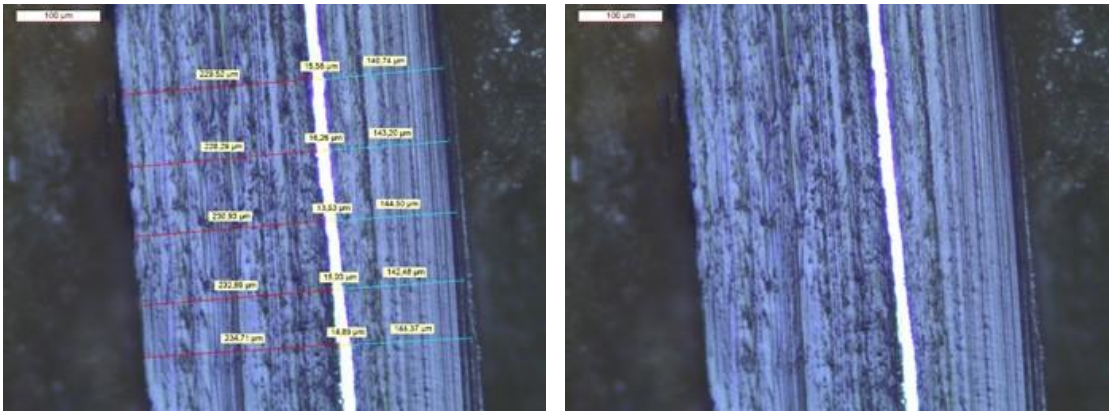
Paper (31% of total mass)
Polyurethane adhesive
Aluminum foil (16% of total mass)
Polyurethane adhesive
Polyethylene (53% of total mass)

Note: the mass of the adhesives has not been considered for calculating the percentage in mass of each component.

3.2. Sample 2 (24-3)

3.2.1. Characterisation analysis

The same procedure is applied on this sample. A transversal cut is done over the film and 5 measurements are done through the different identified layers.



Photomicrograph nº2: Photomicrograph from PRO20-001-02-01-01. Magnification -x20.

Table 2

Specimen	Thickness (µm) Red (External)	Yellow (Aluminum)	Blue (Internal)
1	229,52	15,58	140,74
2	228,29	16,26	143,2
3	230,93	13,53	144,5
4	232,89	15,03	144,37
5	234,71	14,89	142,48
Mean value	**231,27**	**15,06**	**143,06**
Standard deviation	2,58	1,01	1,55

The identification, as it can be seen, there are 3 layers, the one in between is aluminum. So, applying an infrared beam on each side of the sample will be enough to identify the materials that are present on this sample.

The infrared spectrum from transmission shows characteristic bands of PE (polyethylene) in the outer face.

The infrared spectrum from transmission shows characteristic bands of PE (polyethylene) plus PUR from the adhesive in the inner face.

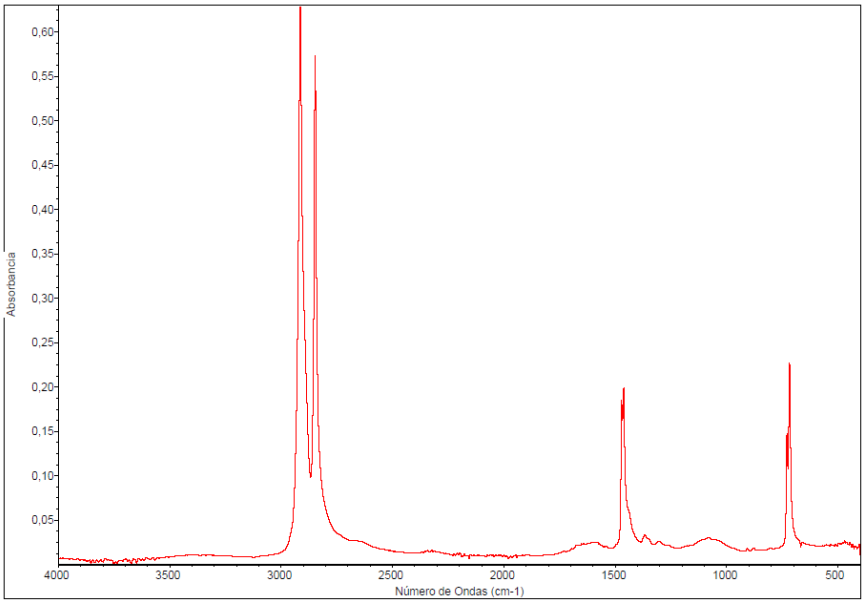


Figure 3
Infrared Spectra from the Outer Face from "PRO20-0017-02-01-01"

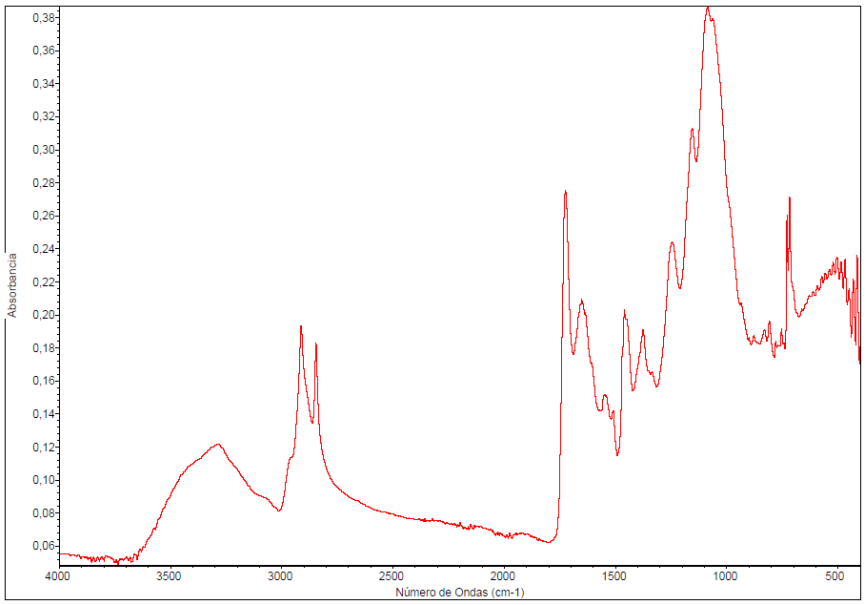
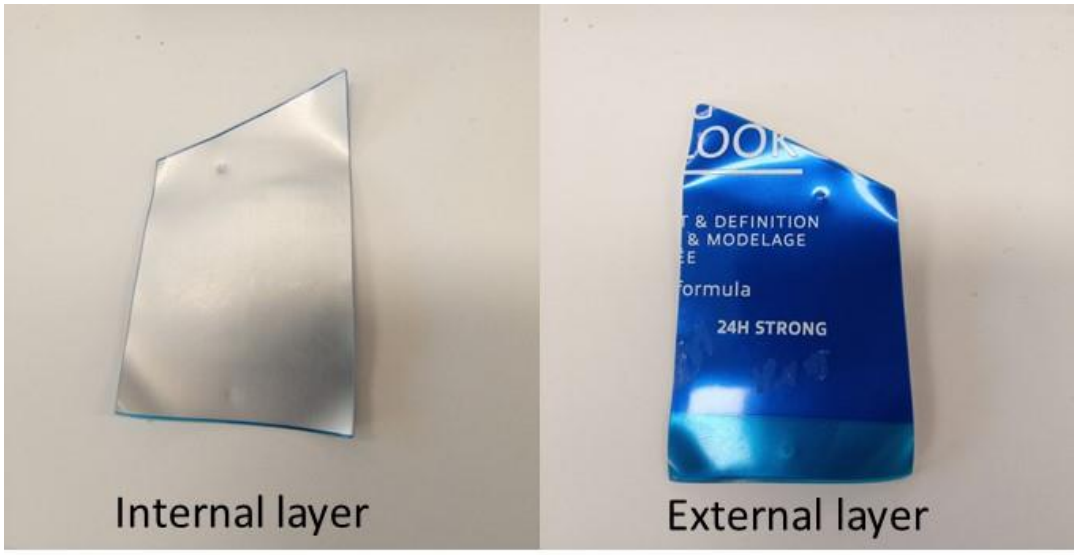


Figure 4
Infrared Spectra from the Inner Face from "PRO20-0017-02-01-01"

3.2.2. Solvent analysis

Preliminary FTIR of the sample showed that the internal layer is made of PE, while the composition of the external layer cannot be identified as a mixture of signals was observed.



The sample (287.63 mg) was immersed in AcOEt at room temperature, then heated up to 80ºC with no changes. The sample was then immersed in boiling HCOOH for 10 minutes, and delamination occurred in 3 layers.

The obtained layers were then analysed by FTIR to determine their composition:

- Layer A (112.43 mg): PE, with a bit of adhesive on the internal face
- Layer B (17.70 mg): Aluminum foil completely clean
- Layer C (158.80 mg): PE at the internal face, acrylate with other peaks at the external face.

The adhesive was present in such a low quantity on the internal faces of the layers that it could not be identified by FTIR. However, according to the JRC guide, it is reasonable to assume that it is a type of PUR, as this type of adhesives are easily dissolved in such solvent.

With the aim of removing the printed acrylate present on layer C, it was subjected to different solvents at room temperature then at 90ºC without any change. The solvents employed were formic acid, DMSO, acetone. Finally, Layer C was immersed in toluene at 90ºC with the aim of dissolving the PE and check if other polymers are also present.

The final composition of the multilayer material with the relative percentages of each layer is as follows:

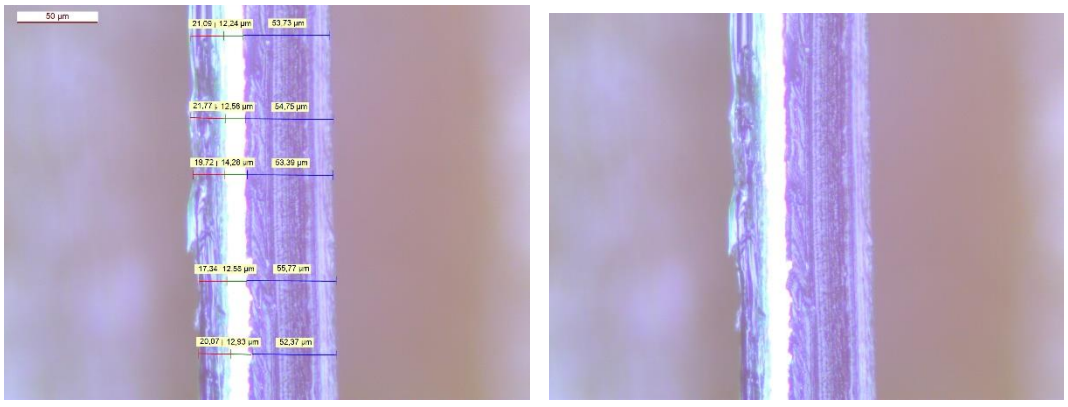
Printed acrylate
Polyethylene (55% of total mass)
Adhesive PUR
Aluminum foil (6% of total mass)
Adhesive PUR
Polyethylene (39% of total mass)

Note: the mass of the adhesives has not been considered for calculating the percentage in mass of each component.

3.3. Sample 3 (104-7)

3.3.1. Characterisation analysis

The same procedure is applied on this sample. A transversal cut is done over the film and 5 measurements are done through the different identified layers.



Photomicrograph nº2: Photomicrograph from PRO20-001-02-02-02. Magnification -x20.

Table 2

Specimen	Thickness (µm)		
	Red (External)	**Yellow (Aluminum)**	**Blue (Internal)**
1	21,09	12,24	53,73
2	21,77	12,58	54,75
3	19,72	14,28	53,39
4	17,34	12,58	55,77
5	20,07	12,93	52,37
Mean value	**20,00**	**12,92**	**54,00**
Standard deviation	1,69	0,08	1,30

The identification, as it can be seen, there are 3 layers, the one in between is aluminum. So, applying an infrared beam on each side of the sample will be enough to identify the materials that are present on this sample.

The infrared spectrum from transmission shows characteristic bands of PE (polyethylene) in the outer face.

The infrared spectrum from transmission shows characteristic bands of PET (polystyrene) plus PUR from the adhesive in the inner face.

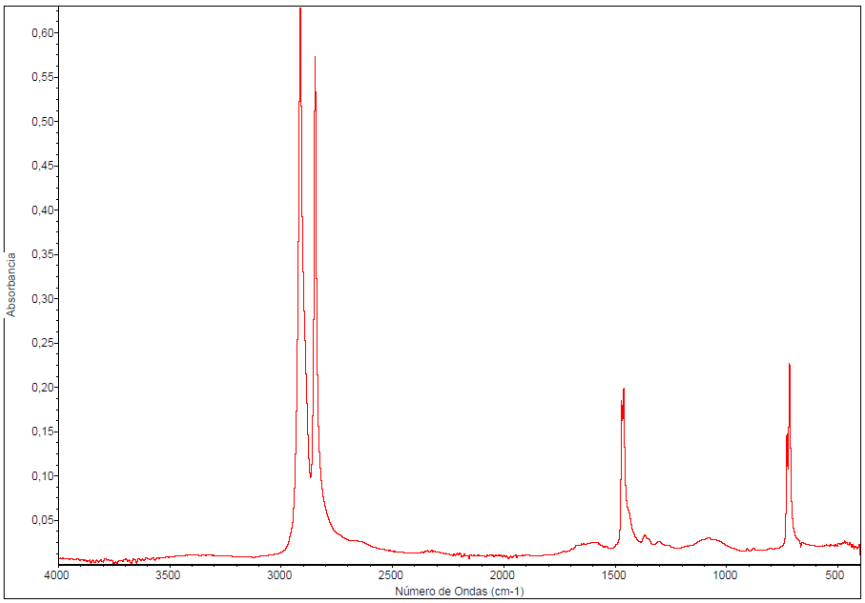


Figure 3
Infrared Spectra from the Outer Face from "PRO20-0017-02-02-02"

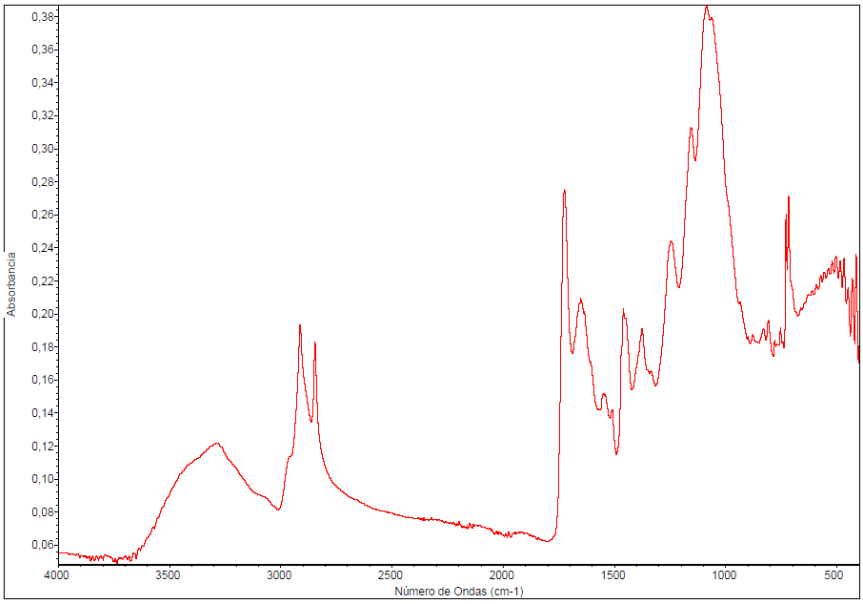
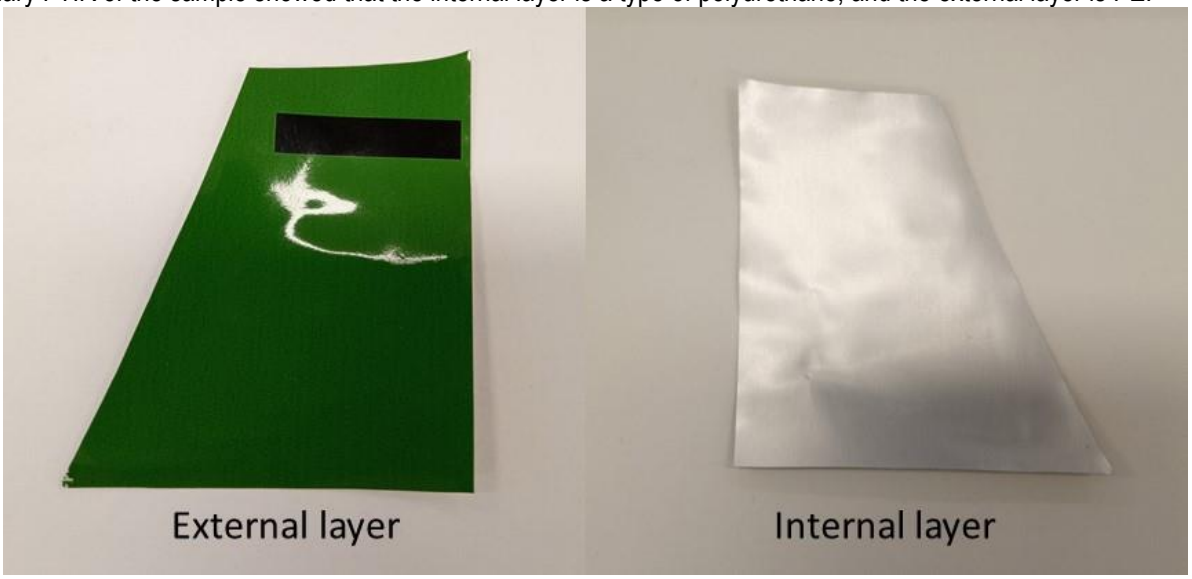


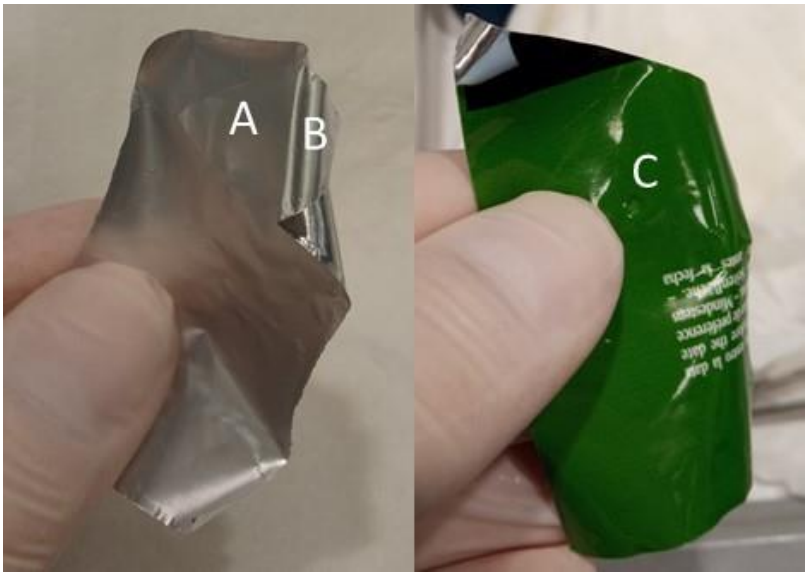
Figure 4
Infrared Spectra from the Inner Face from "PRO20-0017-02-01-01"

3.3.2. Solvent analysis

Preliminary FTIR of the sample showed that the internal layer is a type of polyurethane, and the external layer is PE.



The sample (230.65 mg) was immersed in AcOEt at room temperature, then heated up to 80ºC with no changes. The sample was then immersed in boiling HCOOH for 10 minutes, and delamination occurred in 3 layers.



The obtained layers were then analysed by FTIR to determine their composition:

- Layer A (116.63mg): PE with polyesther urethane on its internal face.
- Layer B (57.66mg): Clean aluminum foil
- Layer C (58.76mg): PET with polyesther urethane on its internal face

Layer C was immersed in HCOOH at 90ºC for 15 minutes without any changes. However, by rubbing the internal layer with a piece of paper swollen in acetone, the printed layer was removed.

The same procedure is applied to layer A but the polyurethane adhesive is still present (this can be explained because of a stronger interaction between PE and the adhesive or because the fact that the adhesives employed between layers were not exactly the same).
The final composition of the multilayer material with the relative percentages of each layer is as follows:

PET (25% of total mass)
Printed urethane

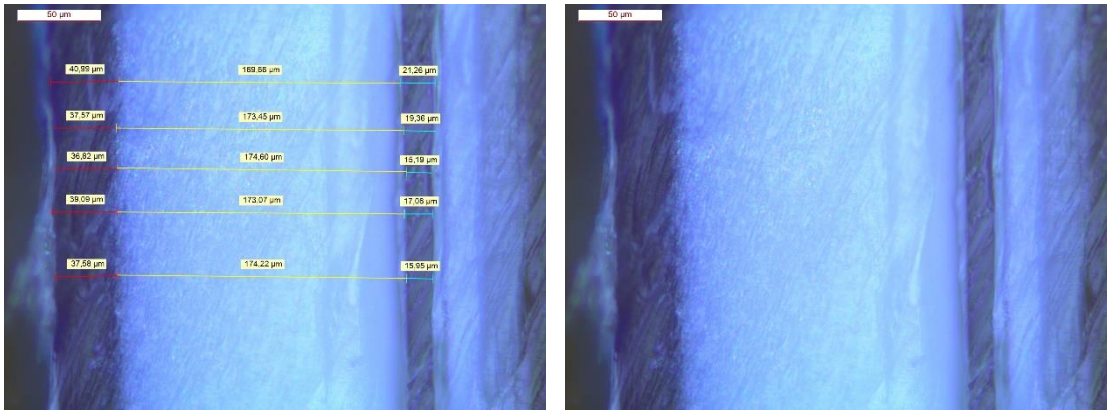
Adhesive PUR
Aluminum foil (25% of total mass)
Adhesive PUR
Polyethylene (50% of total mass)

Note: the mass of the adhesives has not been considered for calculating the percentage in mass of each component.

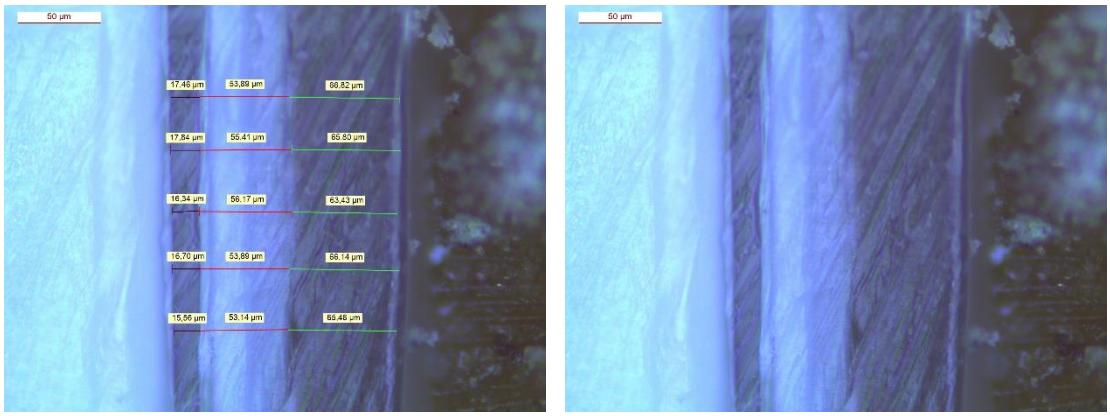
3.4. Sample 4 (24-2)

3.4.1. Characterisation analysis

The same procedure is applied on this sample. A transversal cut is done over the film and 5 measurements are done through the different identified layers.



Photomicrograph nº-: Photomicrograph from PRO20-001-02-01-02. Magnification -x20.



Photomicrograph nº-: Photomicrograph from PRO20-001-02-01-02. Magnification -x20.

Table			
	Thickness (µm)		
Specimen	Red (External)	Yellow	Blue
1	40,99	169,66	21,26
2	37,57	173,45	19,36
3	36,82	174,6	15,19
4	39,09	173,07	17,08

5	37,58	174,22	15,95
Mean value	**38,41**	**173,00**	**17,77**
Standard deviation	1,66	1,96	2,51

Table

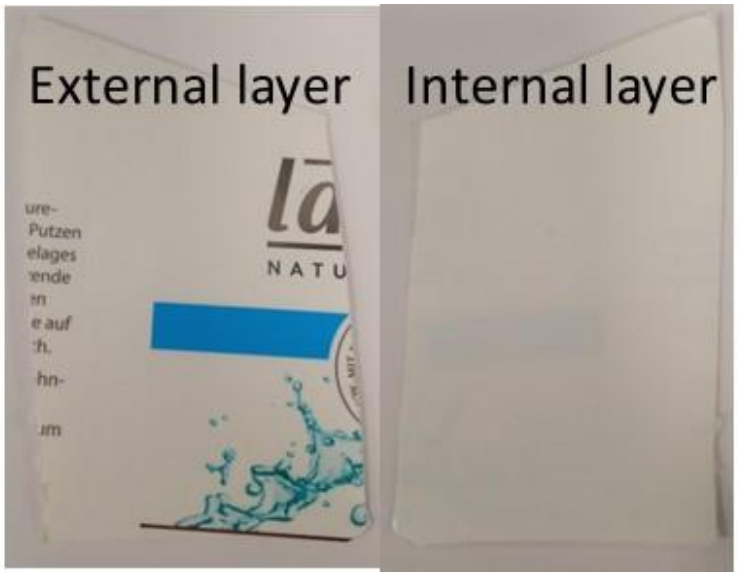
Thickness (µm)

Specimen	**Red**	**Green (External)**
1	53,89	66,82
2	55,41	65,80
3	56,17	63,43
4	53,89	66,14
5	53,14	65,46
Mean value	**54,5**	**65,53**
Standard deviation	1,25	1,28

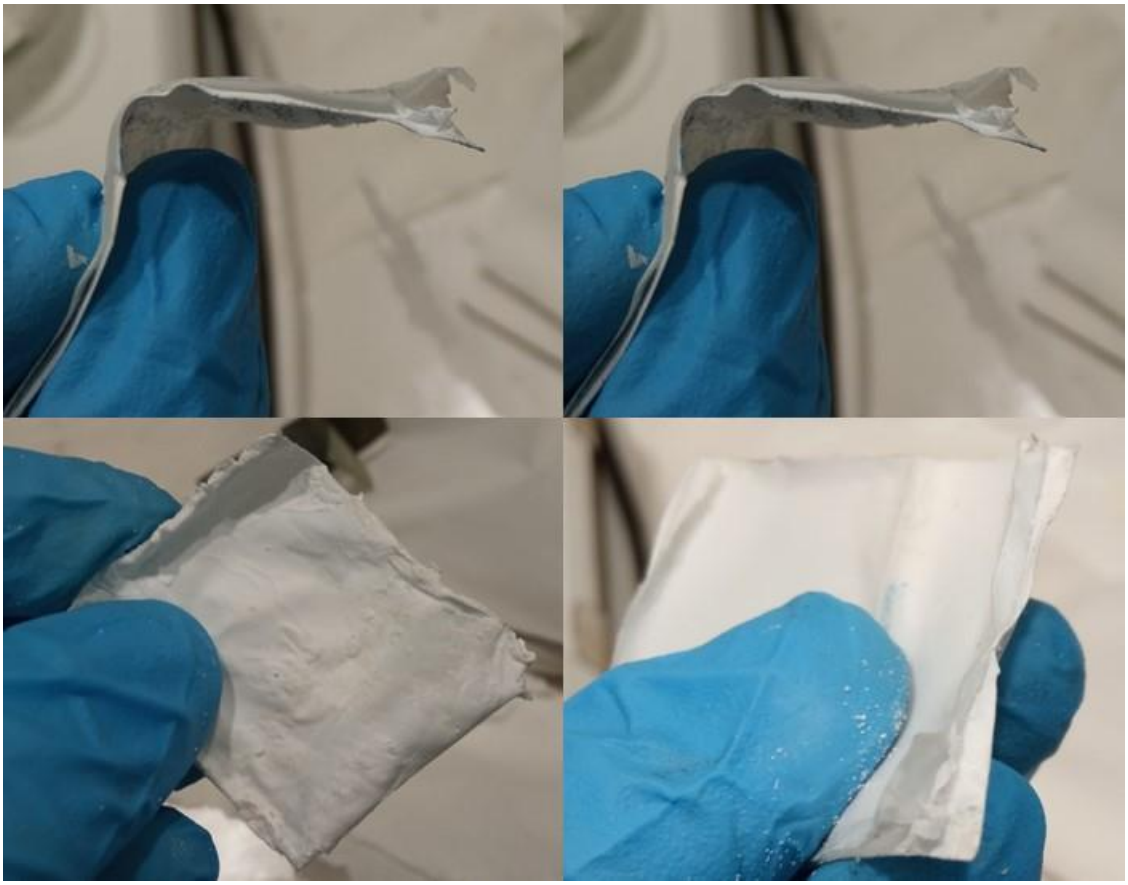
The identification, as it can be seen, there are 5 layer. So, a ATR-FTIR is not the technic that suits the identification procedure and other techniques are required (like the dissolvents in order to obtain the different layers separately and apply the IR scan or the micro-IR).

3.4.2. Solvent analysis

Preliminary FTIR of the sample showed that both the internal and the external layer are made of PE with more than 90% of accuracy.



The sample is immersed in AcOEt at room temperature, then at 70ºC but it is not affected. The same procedure is followed when employing HCOOH but the sample is neither affected.
The sample is then immersed in toluene at 70ºC and the PE layers start to separate. However, an effective separation is not achieved, as the polymer starts to dissolve in the toluene.

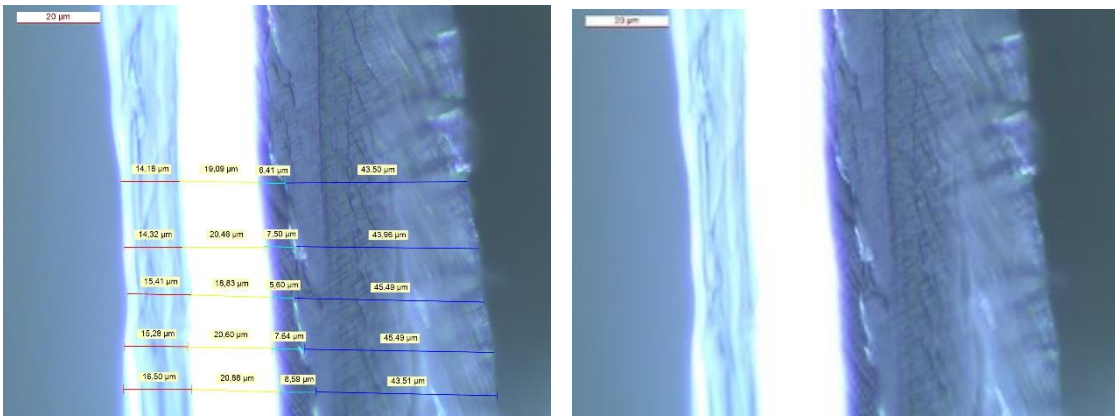


IR analysis of all the separated layers demonstrate that the multilayer material is composed by multiple layers of PE sticked together with an adhesive that could not be identified. This specific sample should be analysed by the microscope and FTIR to determine its composition. No presence of aluminum was observed.

3.5. Sample 5 (27-6)

3.5.1. Characterisation analysis

The same procedure is applied on this sample. A transversal cut is done over the film and 5 measurements are done through the different identified layers.



Photomicrograph n°4: Photomicrograph from PRO20-0017-02-02-01. Magnification -x20.

Table 4

Specimen	Thickness (µm) Red (External)	Yellow (Aluminum)	Cyan	Blue (Interal)
1	14,18	19,09	5,6	43,5
2	14,32	20,46	7,5	43,96
3	15,41	18,83	6,41	45,49
4	15,28	20,6	7,64	45,49
5	16,5	20,88	8,59	43,51
Mean value	**15,14**	**19,97**	**7,15**	**44,39**
Standard deviation	0,94	0,94	1,16	1,02

The identification, as it can be seen, there are 4 layers, the one in between is aluminum. So, applying an infrared beam on each side of the sample will be enough to identify the materials that are present on this sample.

The infrared spectrum from transmission shows characteristic bands of PET on the outer face.

The infrared spectrum from transmission shows characteristic bands of PE0 on the outer face.

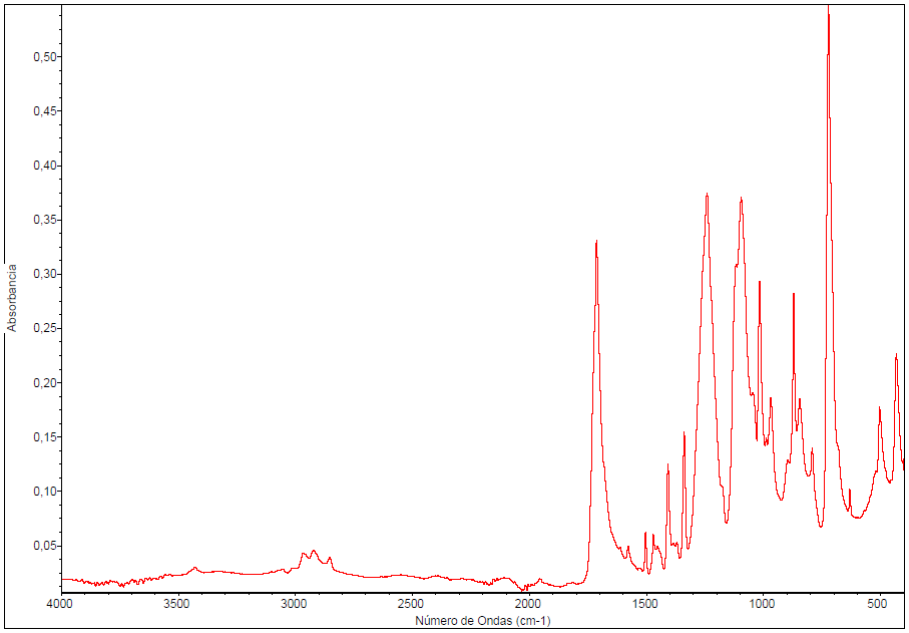


Figure 5
Infrared Spectra from the Outer Face from "PRO20-0017-02-02-01"

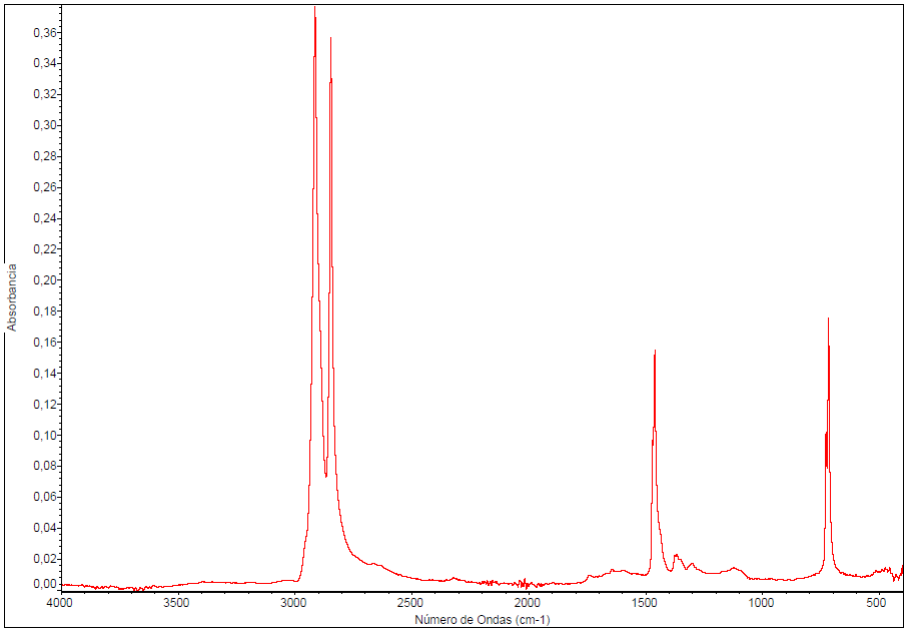


Figure 6
Infrared Spectra from the Inner Face from "PRO20-0017-02-02-01"

3.5.2. Solvent analysis

Preliminary FTIR of the sample showed that the internal layer is made of PE and the external layer is made of PET.

The sample (256.01 mg) was immersed in AcOEt at room temperature, then heated up to 80ºC with no changes. The sample was then immersed in boiling HCOOH for 10 minutes, and delamination occurred in 3 layers.

The obtained layers were then analysed by FTIR to determine their composition:

- Layer A (119.40 mg): PE film
- Layer B (71.41 mg): clean aluminum layer
- Layer C (4.03 mg): Printed layer of polyetherurethane 75%.
- Layer D (119.40 mg): PET with polyetherurethane on its internal layer.

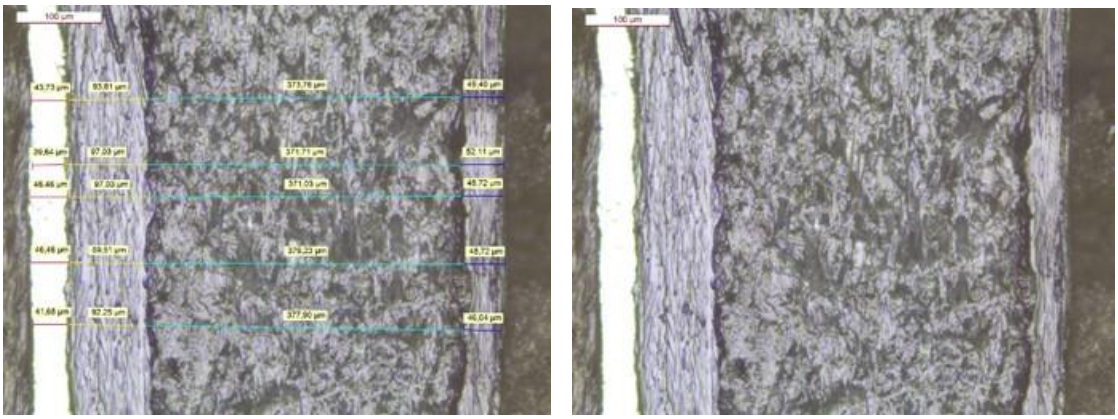
PE (47% of total mass)
Adhesive PUR
Aluminum foil (27.5% of total mass)
Printed layer PUR (1.5% of total mass)
PET (24% of total mass)

Note: the mass of the adhesives has not been considered for calculating the percentage in mass of each component.

3.6. Sample 6 (7-1)

3.6.1. Characterisation analysis

The same procedure is applied on this sample. A transversal cut is done over the film and 5 measurements are done through the different identified layers.



Photomicrograph nº5: Photomicrograph from PRO20-001-02-03-01. Magnification -x20.

Table -

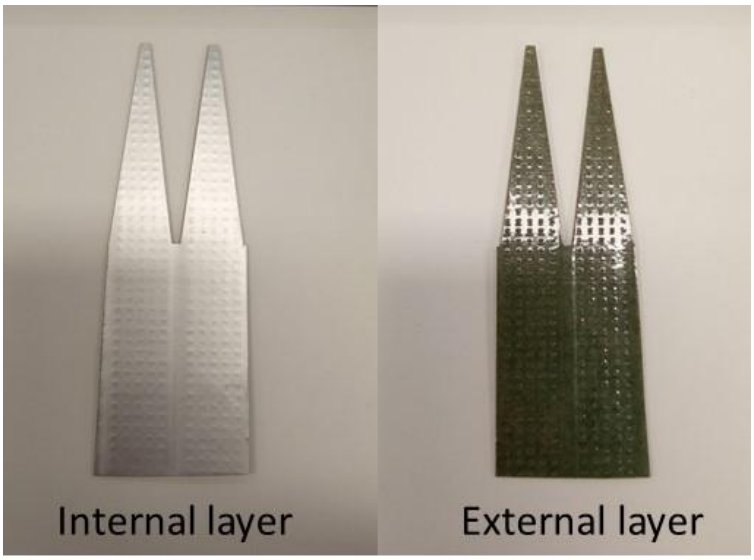
Thickness (µm)				
Specimen	**Red (External-Aluminum)**	**Yellow**	**Cyan**	**Blue (Interal)**
1	43,73	93,61	373,76	49,4
2	39,64	97,03	371,71	52,11
3	46,46	97,03	371,03	48,72
4	46,46	89,51	379,23	48,72
5	41,68	92,25	377,9	46,04
Mean value	**44,39**	**93,89**	**374,73**	**49,00**
Standard deviation	1,02	3,23	3,68	2,17

The identification, as it can be seen, there are 4 layers, the one in the outer side is aluminum. So, applying an infrared beam on each side of the sample will be enough to identify the materials that are present on this sample.

The identification, as it can be seen, there are 4 layer. So, an ATR-FTIR is not the technic that suits the identification procedure and other techniques are required (like the dissolvents to obtain the different layers separately and apply the IR scan or the micro-IR).

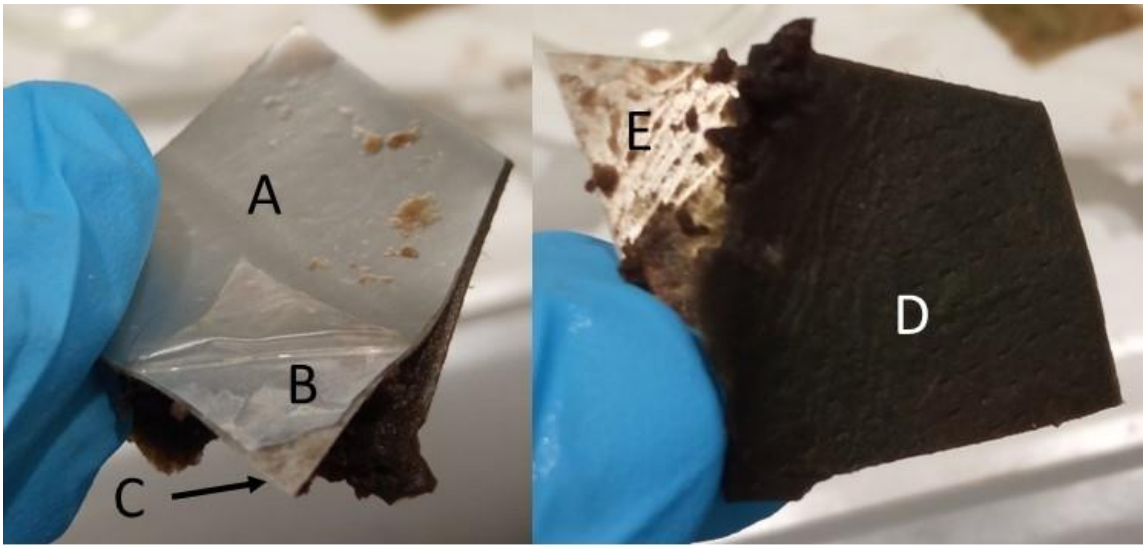
3.6.2. Solvent analysis

Preliminary FTIR of the sample showed that the internal layer is made of PE and the external layer is made of PET.



The sample was immersed in AcOEt observing the swelling of the cardboard. However, the adhesives were not dissolved and an effective delamination did not occur. The same behaviour was observed in HCOOH, even heating both solvents.

A new sample was then immersed in HCl at 80ºC, leading to the dissolution of the aluminum layer as well as the swelling of the cardboard, allowing that time the separation of different layers.



The obtained layers were then analysed by FTIR to determine their composition:

- Layer A (46.33mg): PE film, with isophtalates on the internal face.
- Layer B: aluminum layer
- Layer C (163.37 mg): plastic layer with an adhesive on its surface. This adhesive was identified as a polyisophtalate by FTIR. It could be removed by rubbing it with a paper swollen in AcOEt, leaving a clean layer of PET.
- Layer D: cardboard

- Layer E (76.42 mg): PET film, with isophtalates on the internal face.

The final composition of the multilayer material with the relative percentages of each layer is as follows:

PE (4% of total mass)
Adhesive isophtalate
Aluminum foil
Adhesive isophtalate
PET (15% of total mass)
Adhesive isophtalate
Cardboard
Adhesive isophtalate
PET (7% of total mass)

Note: the mass of the adhesives has not been considered for calculating the percentage in mass of each component. The mass of the aluminum foil could not be determined as its dissolution was the only way of delaminating the material. It was also impossible to determine the mass of the carboard as it was partially suspended in the aqueous HCl and the rest of it absorbed the solvent.

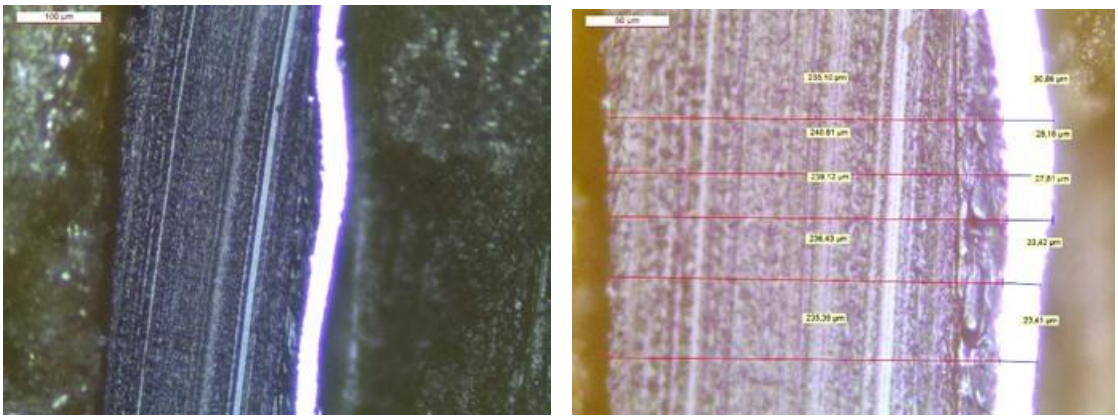
4 Analysis of pharma blister packaging

Two types of pharmaceutical blister samples were collected. On the one hand, Mikrolin sent to AIMPLAS a pre-consumer sample, and on the other hand, different post-consumer samples. The amount of pre-consumer samples was sufficient for both characterisation and solvent analysis. In contrast, in the post-consumer samples, only the quantity was not sufficient for the analysis with both methodologies. Since all structures were very similar, some samples were analysed by characterisation and others by solvent separation.

4.1. Sample 1 (Lisinopril, pre-consumer sample)

4.1.1. Characterisation analysis

A transversal cut is done over the film and 5 measurements are done through the different identified layers.



Photomicrograph nº6: Photomicrograph from PRO20-0017-01-01. Magnification -x20.

Table -

Specimen	Thickness (µm) Red (External)	Blue
1	238,10	30,86
2	240,81	28,16
3	239,12	27,81
4	236,43	23,42
5	235,39	23,41
Mean value	**237,97**	**26,73**
Standard deviation	2,15	3,25

The identification, as it can be seen, there are 2 layers, the one in the outer side is aluminum. So, applying an infrared beam on each side of the sample will be enough to identify the materials that are present on this sample.

The infrared spectrum from transmission shows characteristic bands of PVC plus an acrylic compound, probably an adhesive. Which could be verified through other technics.

The infrared spectrum from transmission shows characteristic bands of polymethacrylate.

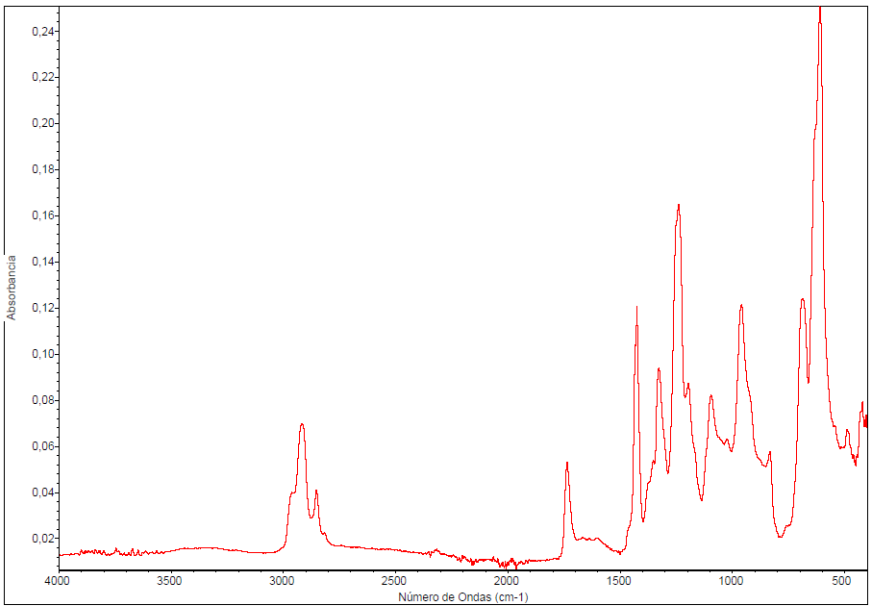


Figure 5
Infrared Spectra from the Outer Face from "PRO20-0017-01-01"

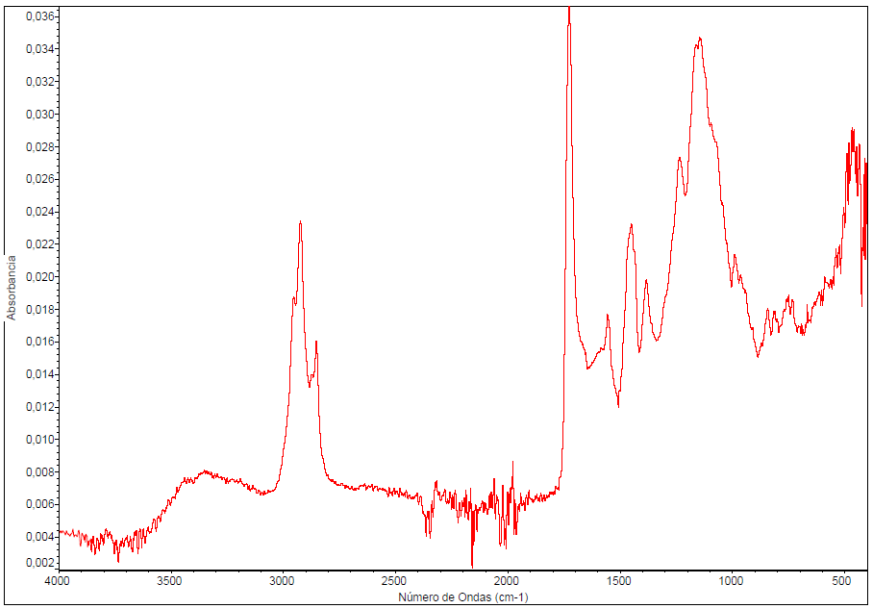
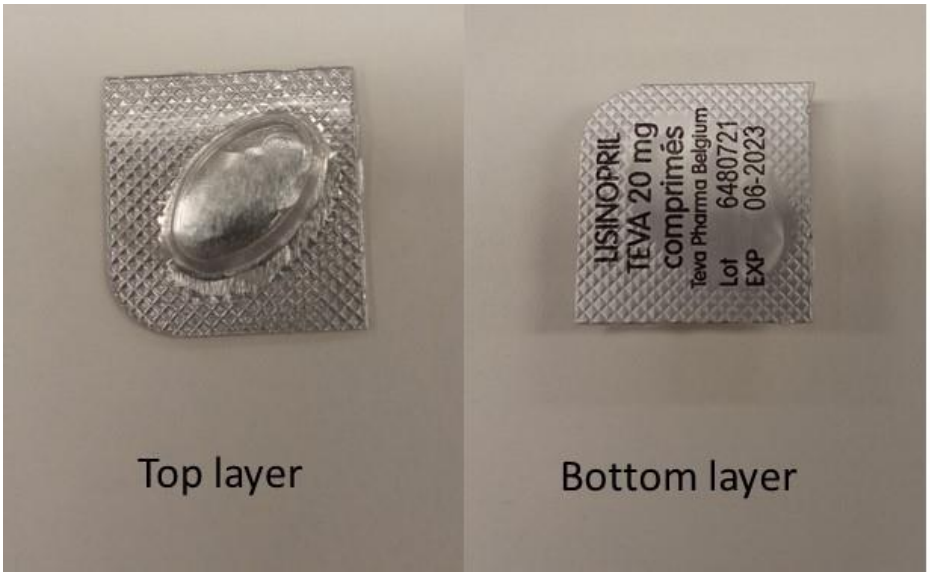


Figure 6
Infrared Spectra from the Inner Face from "PRO20-0017-01-01"

4.1.2 . Solvent analysis

Preliminary FTIR of the sample showed that the bottom layer is made of a polyacrylate polymer (the printed layer) while the top plastic layer is PVC with signals of an acrylate resin. This could mean that the PVC layer is thin and the layer under it is also detected.



For this type of samples, the use of HCl was preferred as it allowed the separation of the different plastic layers. One sample of the aluminum foil was immersed in HCl at room temperature, allowing the separation of a very fragile printed layer, and a thicker plastic layer. Both of these layers were identified as a type of acrylate by FTIR. The internal face of the PVC layer also matched a poly methacrylate, which could be removed by rubbing it with a paper swollen in AcOEt.

To determine the quantitative composition of the blister, a fresh sample (137.88 mg) was immersed in HCl to dissolve the aluminum and recover the other plastic layers. A thick layer of PVC (120.19 mg) was obtained, as well as the metacrylate layer (16.73 mg). The remaining mass (0.96 mg) was attributed to the thin printed metacrylate layer.

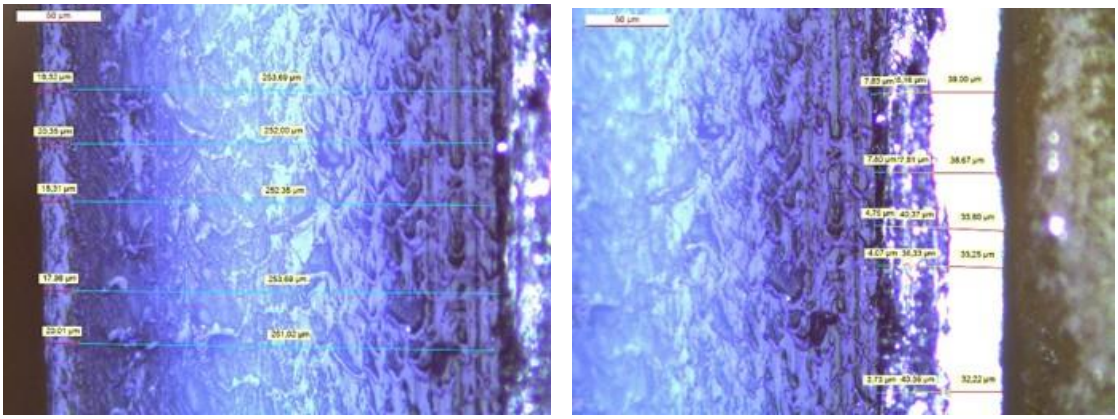
The final composition of the blister with the relative percentages of each layer is as follows:

PVC (87.2% of total mass)
Polymetacrylate (12.2% of total mass)
Aluminum foil
Printed polymetacrylate (0.6% of total mass)

4.2. Sample 2 (01-04-01: Pharma Blister Klacid (postconsumo))

4.2.1. Characterisation analysis

A transversal cut is done over the film and 5 measurements are done through the different identified layers.



Photomicrograph nº6: Photomicrograph from PRO20-001-01-04-01. Magnification -x20.

Table -

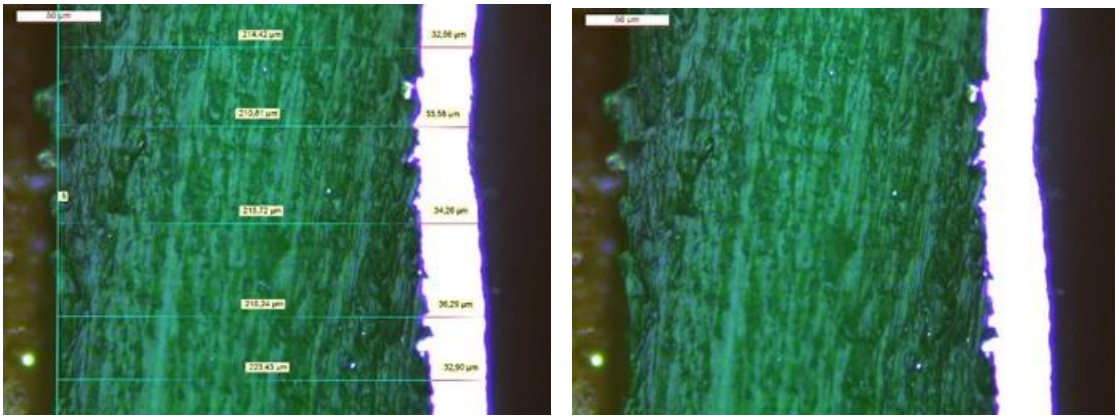
Thickness (µm)					
Specimen	**Red (External)**	**Blue**	**Green**	**Yellow**	**Red (Internal)**
1	18,32	253,69	7,83	28,16	33,6
2	20,35	252,00	7,80	27,81	39,
3	18,31	252,35	4,75	40,37	38,67
4	17,98	253,69	4,07	38,33	33,25
5	20,01	251,02	3,73	40,36	32,22
Mean value	**18,99**	**252,55**	**5,64**	**35,01**	**35,35**
Standard deviation	1,10	1,15	2,02	6,46	3,23

The identification, as it can be seen, there are 5 layer. So, an ATR-FTIR is not the technic that suits the identification procedure and other techniques are required (like the dissolvents to obtain the different layers separately and apply the IR scan or the micro-IR).

4.3. Sample 3 (01-03-01:Muestra Pharma Blister 3 Furan (postconsumo)

4.3.1. Characterisation analysis

A transversal cut is done over the film and 5 measurements are done through the different identified layers.



Photomicrograph nº6: Photomicrograph from PRO20-0017-01-03-01. Magnification -x20.

Table -

Specimen	Green (External)	Red (Internal)
1	214,42	32,56
2	210,81	33,58
3	215,72	34,26
4	218,24	36,29
5	223,43	32,90
Mean value	**216,52**	**33,92**
Standard deviation	4,70	1,48

The identification, as it can be seen, there are 2 layers, the one in the outer side is aluminum. So, applying an infrared beam on each side of the sample will be enough to identify the materials that are present on this sample.

The infrared spectrum from transmission shows characteristic bands of PVC plus an acrylic component, probably from an adhesive, on the outer layer.

The infrared spectrum from transmission shows characteristic bands of PVC plastified, probably from an adhesive, on the outer layer.

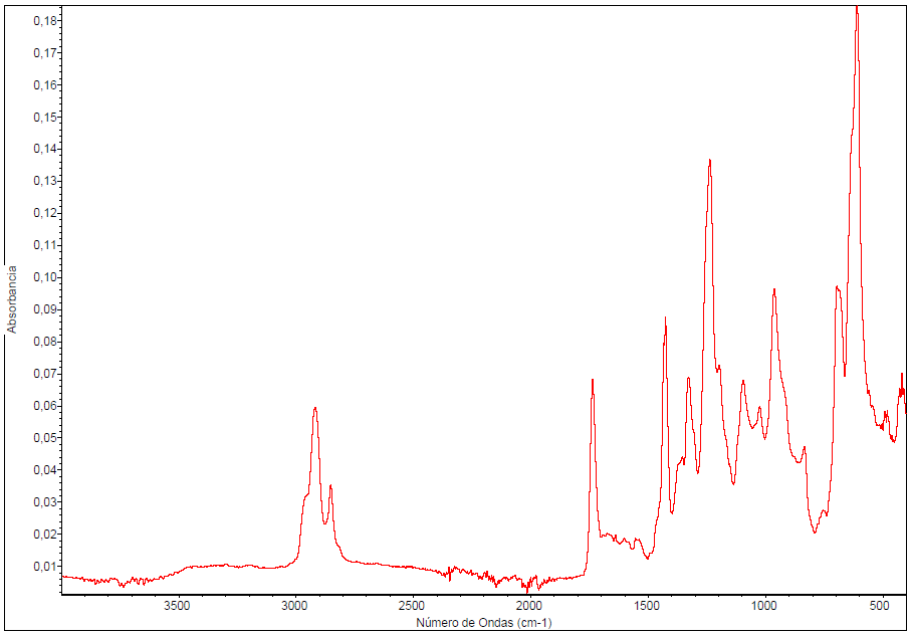


Figure 5
Infrared Spectra from the Outer Face from "PRO20-0017-01-03-01"

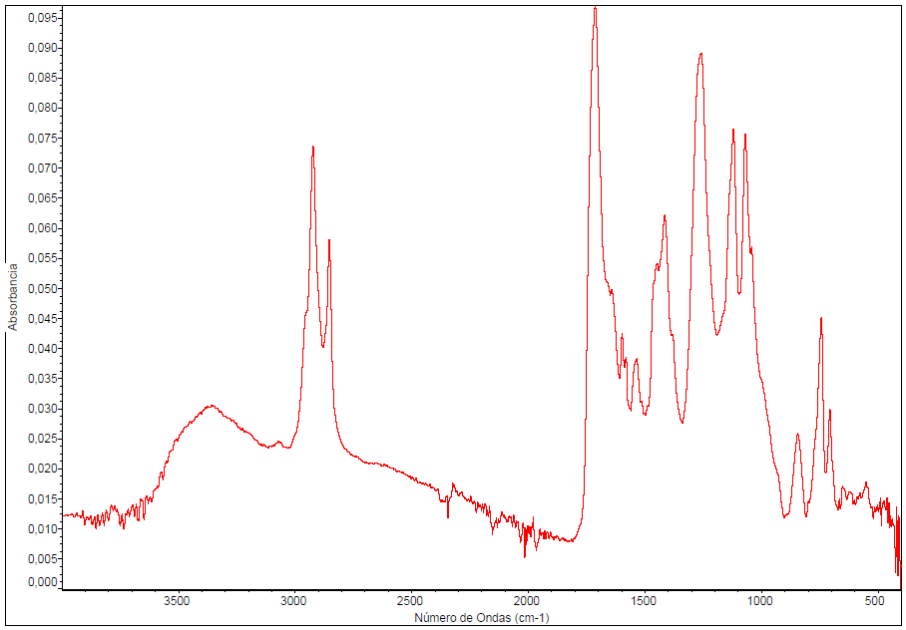
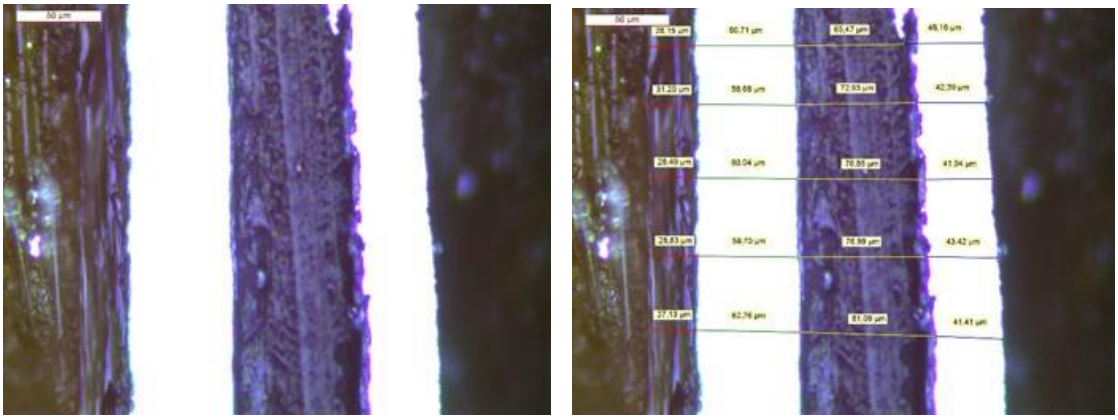


Figure 6
Infrared Spectra from the Inner Face from "PRO20-0017-01-03-01"

4.4. Sample 4: 01-02-01:Muestra Pharma Blister 5 Metfogamma (pre-consumer)

4.4.1. Characterisation analysis

A transversal cut is done over the film and 5 measurements are done through the different identified layers.



Photomicrograph nº7: Photomicrograph from PRO20-0017-01-05-01. Magnification -x20.

Table -

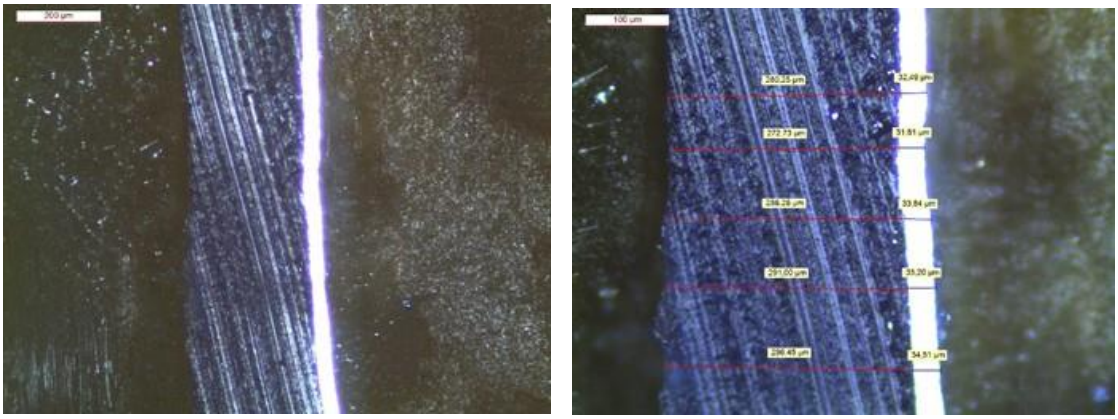
Specimen	Red (External)	Green	Yellow	Blue
1	28,15	60,71	65,47	48,16
2	31,2	58,68	72,93	42,39
3	28,49	60,04	76,65	41,04
4	28,83	59,7	76,99	43,42
5	27,13	62,76	81,09	41,41
Mean value	**28,76**	**60,38**	**74,63**	**43,28**
Standard deviation	1,51	1,52	5,88	2,88

The identification, as it can be seen, there are 5 layer. So, an ATR-FTIR is not the technic that suits the identification procedure and other techniques are required (like the dissolvents to obtain the different layers separately and apply the IR scan or the micro-IR).

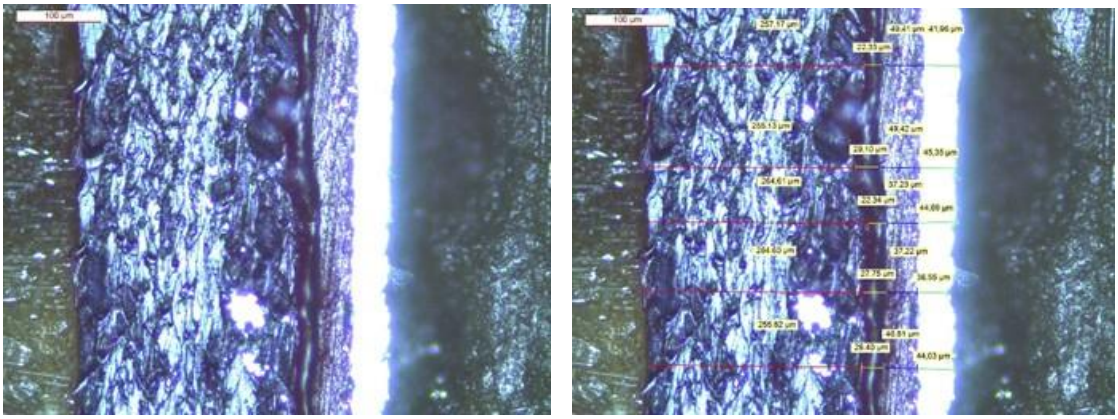
4.5. Sample 5 (01-05-01:Muestra Pharma Blister 5 Letrox (postconsumo)

4.5.1. Characterisation analysis

A transversal cut is done over the film and 5 measurements are done through the different identified layers. In this case, it is easy to differentiate on the sample that the are 2 zones to analyze.



Photomicrograph nº8: Photomicrograph from PRO20-0017-01-05-01. Magnification -x20.



Photomicrograph nº9: Photomicrograph from PRO20-0017-01-05-01. Magnification -x20.

Table -

Specimen	Green (External)	Red (Internal)
1	280,25	32,49
2	272,73	31,81
3	286,26	33,84
4	291,00	35,20
5	296,45	34,51
Mean value	**285,34**	**33,57**
Standard deviation	9,24	1,40

Table -

Specimen	Green (External)	Red	Blue	Green (Internal)
1	257,17	22,33	49,41	41,96
2	255,13	29,10	49,42	45,35
3	264,61	22,34	37,23	44,69
4	264,60	27,75	37,22	36,55
5	255,82	26,40	40,61	44,03
Mean value	**259,47**	**25,58**	**42,78**	**42,52**
Standard deviation	4,75	3,12	6,21	3,57

The identification, as it can be seen, there are 2 and 4 layers, the ones in the outer side is aluminum. So, applying an infrared beam on each side of the sample will be enough to identify the materials that are present on this sample, but to the one referred to the 2 layers sample.

The infrared spectrum from transmission shows characteristic bands of

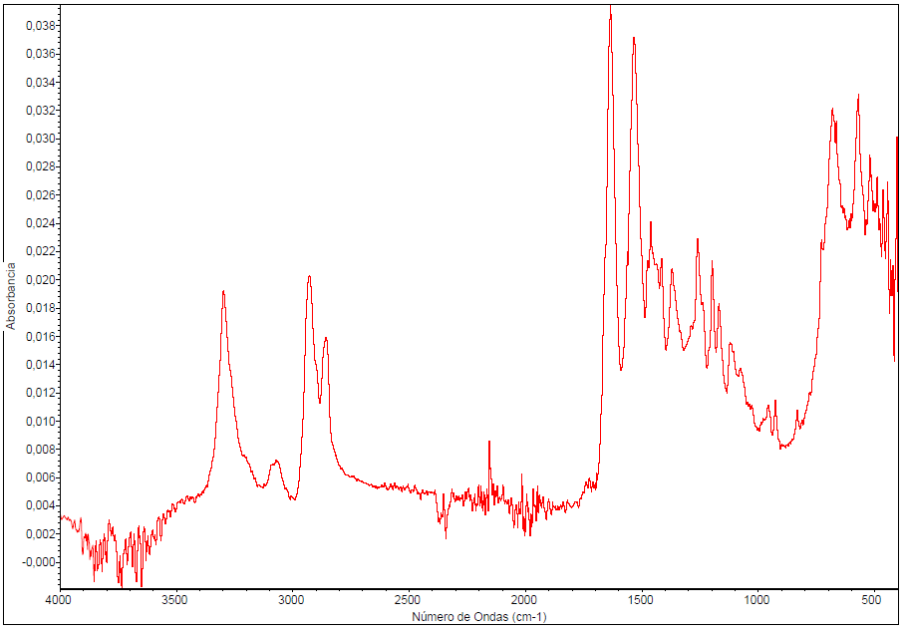


Figure 5
Infrared Spectra from the Outer Face from "PRO20-0017-01-05-01"

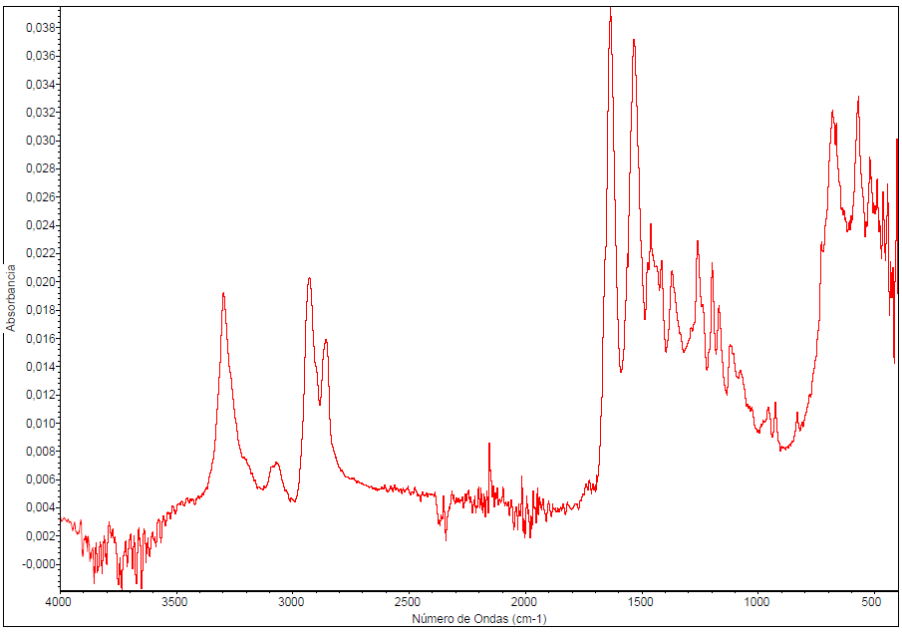
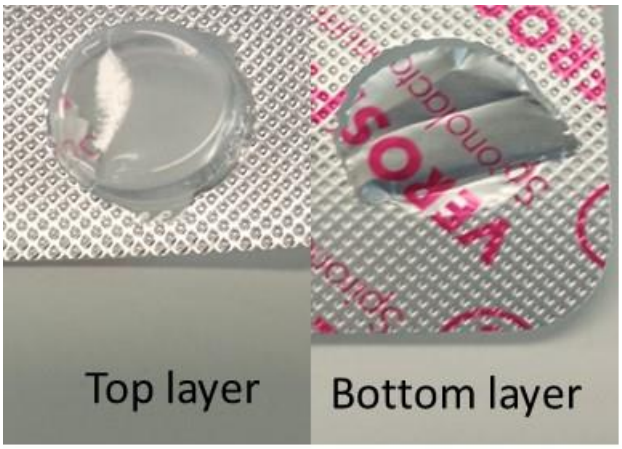


Figure 6
Infrared Spectra from the Inner Face from "PRO20-0017-01-05-01"

4.6. Sample 6 (Verospiron post-consumer)

4.6.1. Solvent analysis

Preliminary FTIR of the sample showed that the bottom layer is made of a polyacrylate polymer (the printed layer) while the top plastic layer is PVC.



In this case, the aluminum foil was detached manually from the PVC layer, and the internal face of this aluminum foil was measured by FTIR, matching with a type of polyacrylate. Then, this foil was washed with a piece of paper swollen in AcOEt achieving the full removal of the acrylates and leading to a clean layer of aluminum.

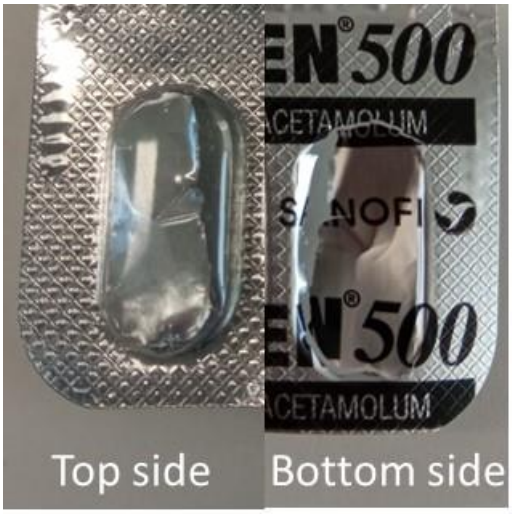
The final composition of the blister is as follows:

PVC
Polymetacrylate
Aluminum foil
Printed polymetacrylate

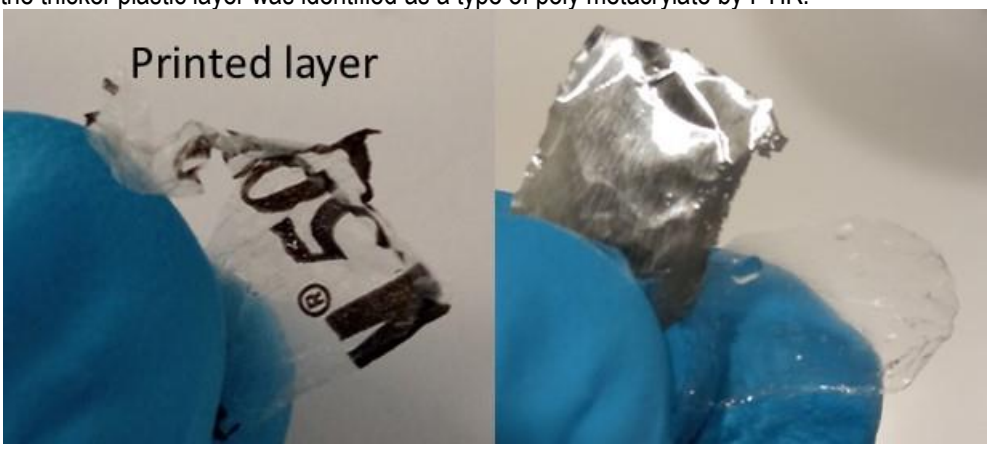
4.7. Sample 7 (Paralen post-consumer)

4.7.1. Solvent analysis

Preliminary FTIR of the sample showed that the bottom layer is made of a polyacrylate polymer (the printed layer) while the top plastic layer is PVC.



In this case, the aluminum foil was detached manually from the PVC layer and it was immersed in HCl at room temperature, allowing the separation of a very fragile printed layer, and a thicker plastic layer. The printed layer was identified as a type of isophtalate while the thicker plastic layer was identified as a type of poly metacrylate by FTIR.



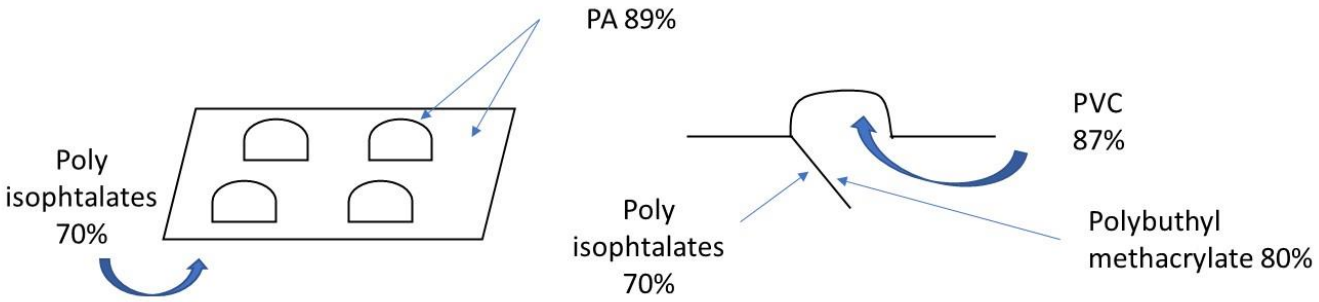
The internal face of the PVC layer also matched a poly methacrylate, which could be removed by rubbing it with a paper swollen in AcOEt.

The final composition of the blister is as follows:

PVC
Polymetacrylate
Aluminum foil
Printed isophtalate

4.8. Sample 8 (Rosucard post-consumer)

Preliminary FTIR of the sample showed that the top layer is a polyamide while the bottom layer is a type of isophtalate. The plastic under the PA is identified as PVC and the internal face of the aluminum layer us made of a type of polybutyl metacrylate.



The blister is immersed in HCOOH at 90ºC to remove the PA, obtaining a clean aluminum layer on the top side, while PVC is still present on the bottom side. Then the sample is immersed in HCl to dissolve the aluminum, obtaining only PVC.

This means a layer of aluminum is present between the layers of PA and PVC.

The final composition of the blister is as follows:

PA
Aluminum
PVC
Polybutyl methacrylate
Aluminum
Printed Polyisophtalate

5 Conclusions

For the realization of this work package, different samples were collected from pharmaceutical blister packs and pouches. Both pre-consumer and post-consumer samples were received. In the case of the pouches, to facilitate characterization, tests were performed on the pre-consumer samples. In the case of pharma blister packs, the treatment of the post-consumer pharma blister is different than a pre-consumer. This type of waste is classified in a special container to the posterior treatment. At first, the drug is separate from the pack. The drug are separate and the pack receive a decontamination and recycled treatment.

The characterization starts with a pre-screening of the samples by microscopic observation. For observation, the sample is prepared by cross-sectioning to expose all the layers of the multilayer structure. With this, the number of layers and their thickness are obtained for each sample, observing a variability in number and thickness between them. However, the vast majority of the sample have from 2 to 3 layers (pharma), which means an easier identification in the recyclability process. Finally, in means of materials that are more present in the different studied samples, it is easy to identify a PE, PET, Aluminum and cellulose based materials. This last materials are the ones related to pouches samples, for pharma blisters it is possible to talk about PVC and Aluminum, and, in some occasions, PE.

In relation with the solvents treatments, remarkable results are obtained. The most common adhesives that are found in this type of pouches and pharma blisters are polyurethanes and acrylates and in some cases are found inks.

To dissolve the different adhesives, the most common solvents that has been used are formic acid, ethil acetate, HCl and toluene.

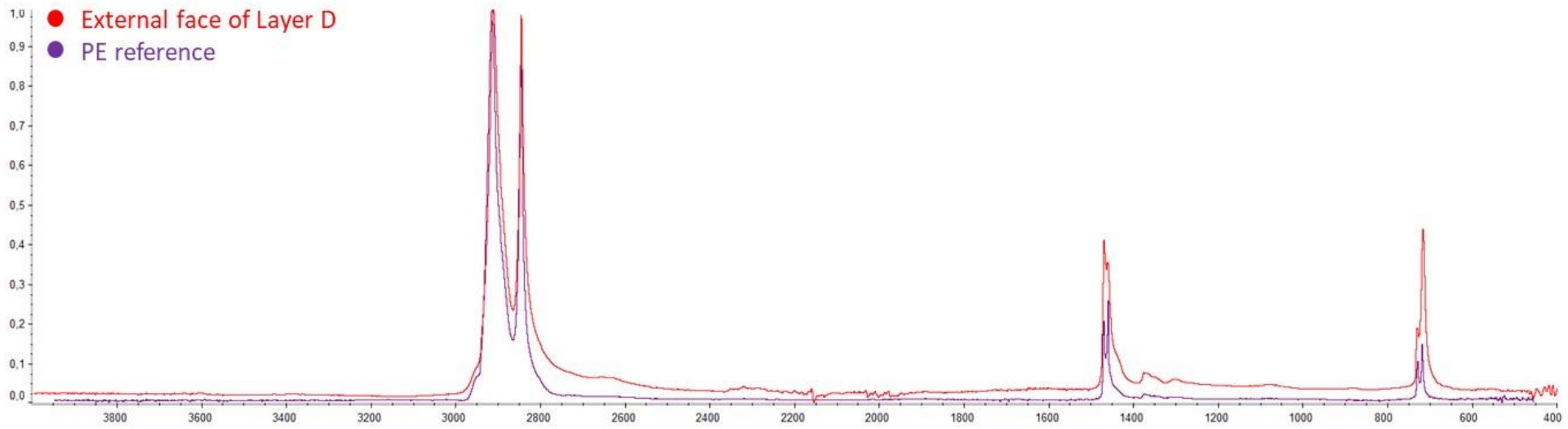
In conclusion, the laboratory analysis with the two methods has been successful. Hence, the solvent analysis are able to use in a pilot plant scale.

6 Annexes

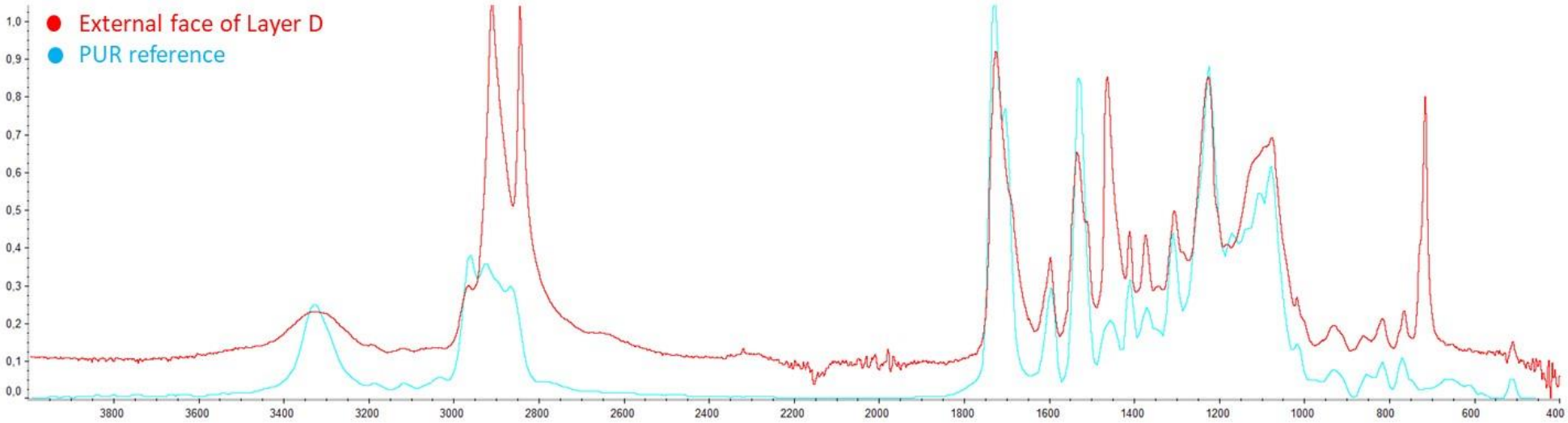
6.1. IR spectra of laminate packaging

6.1.1 Sample 1 (22-10)

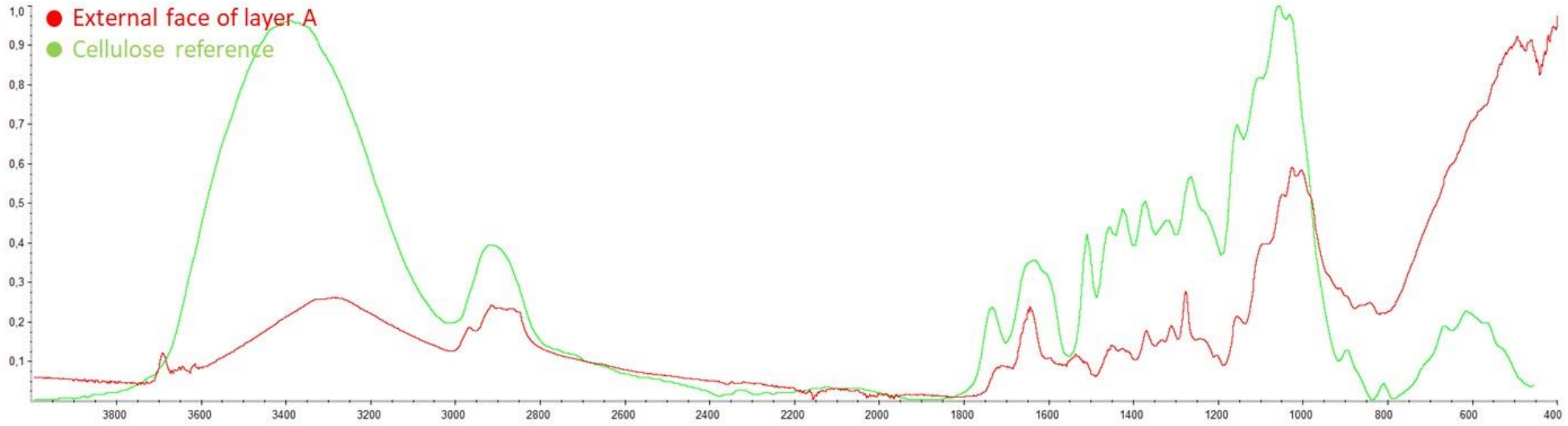
FTIR of external face of Layer D, 96% match with PE from library



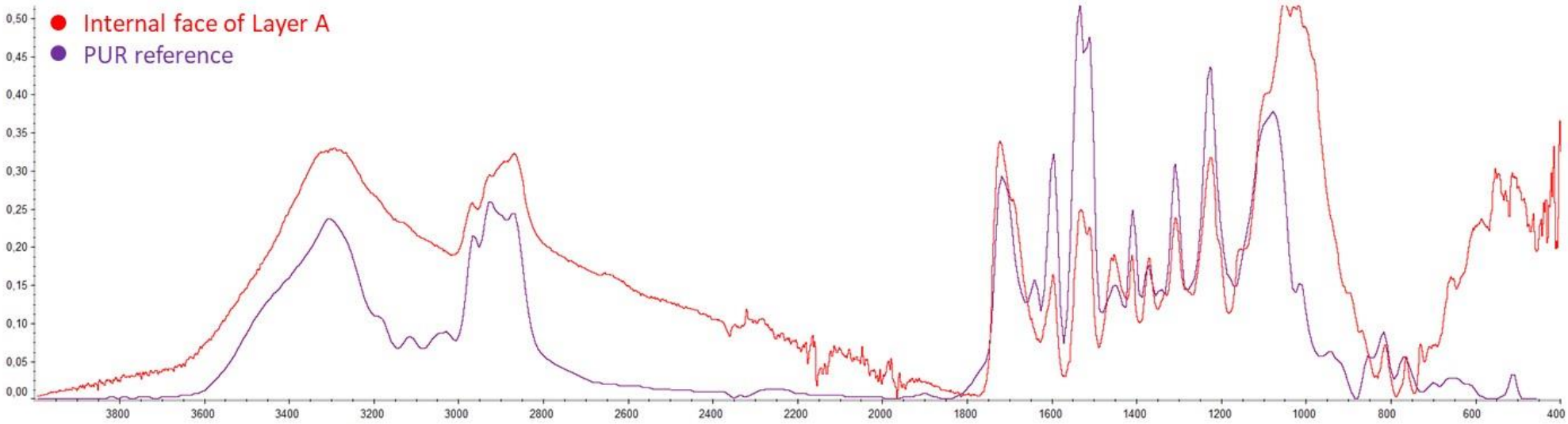
FTIR of internal face of layer D, 60% match with PUR from library



FTIR of external face of layer A, 55% match with cellulose reference from library

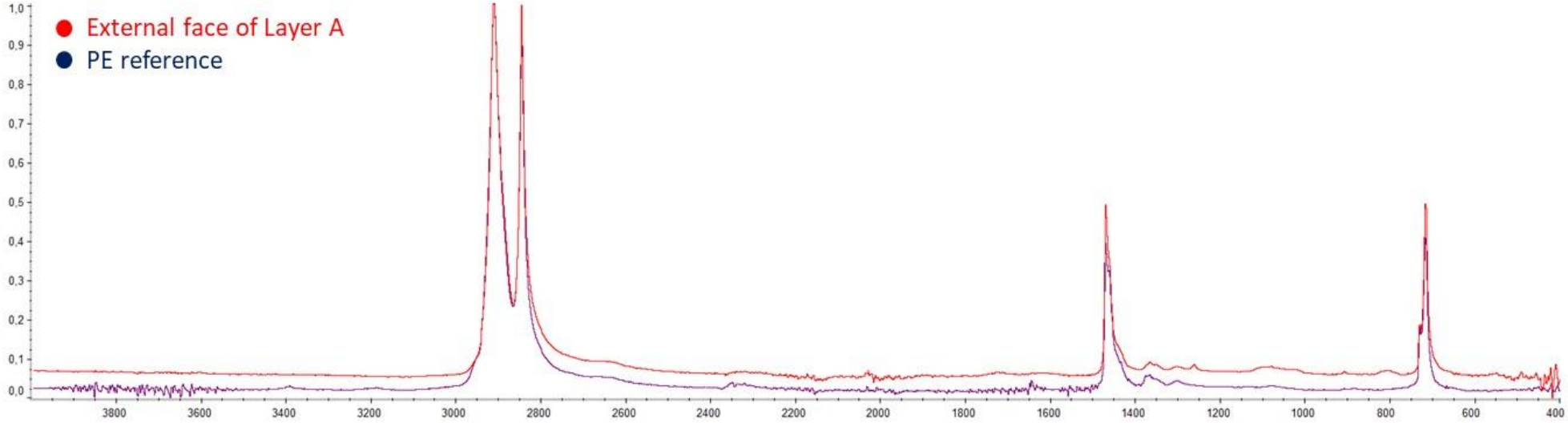


FTIR of internal face of layer A, 70% match with PUR from library

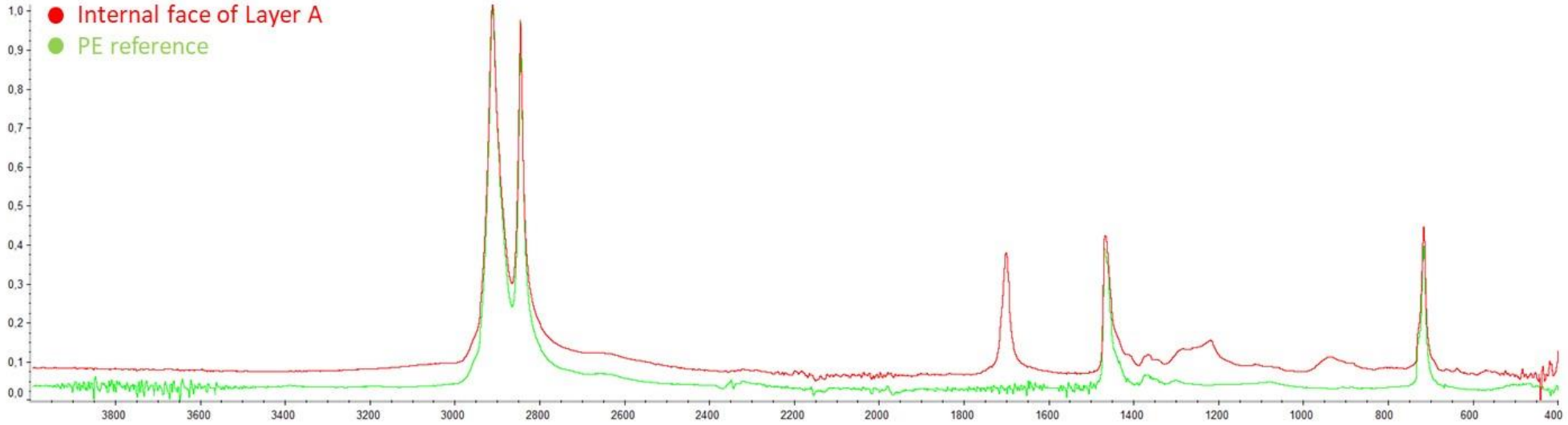


6.1.2. Sample 2 (24-3)

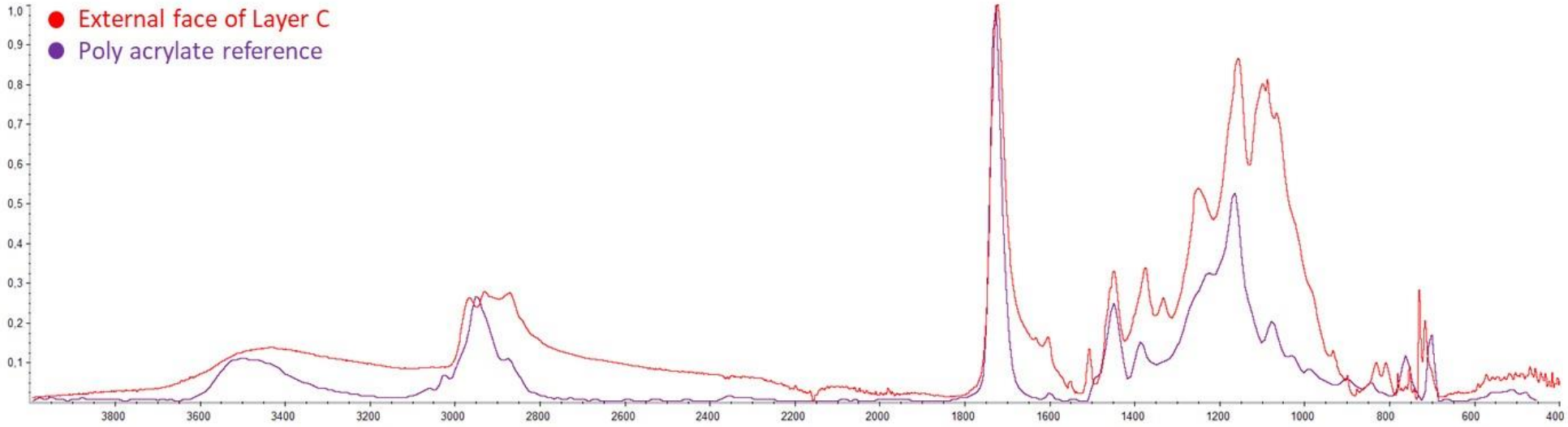
FTIR of external face of Layer A, 98% match with PE from library



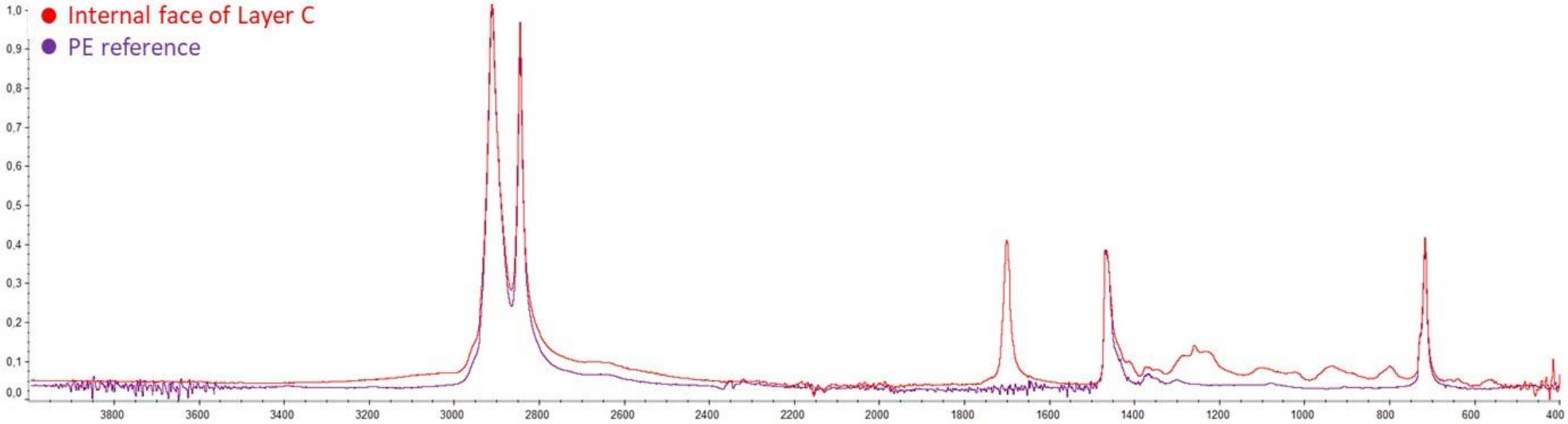
FTIR of internal face of Layer A, 95% match with PE from library



FTIR of external face of layer C, 75% match with acrylate from library

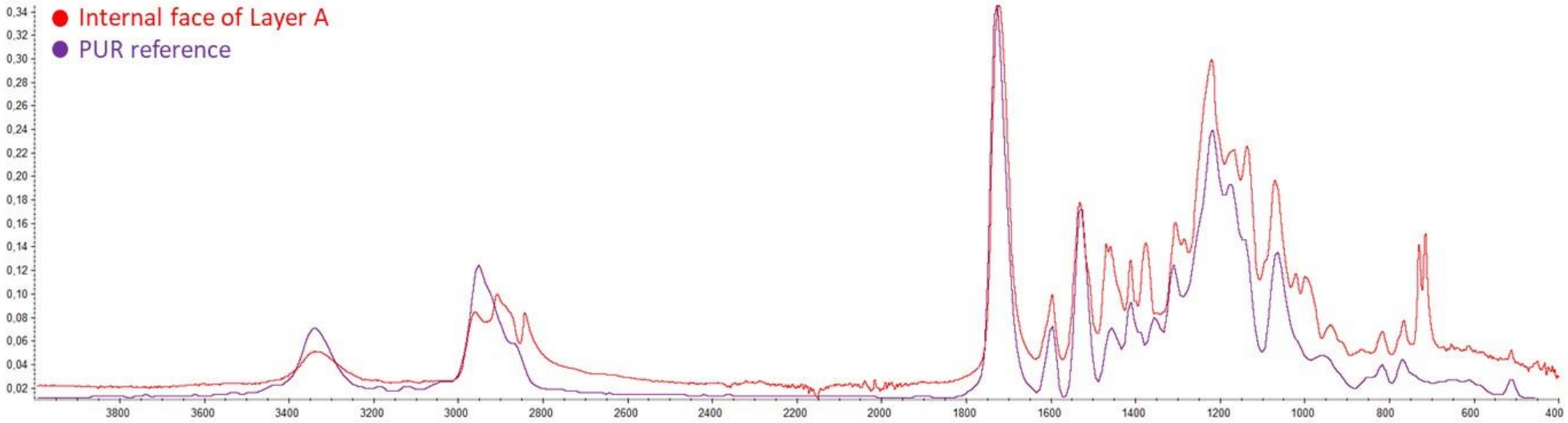


FTIR of internal face of Layer C, 95% match with PE from library

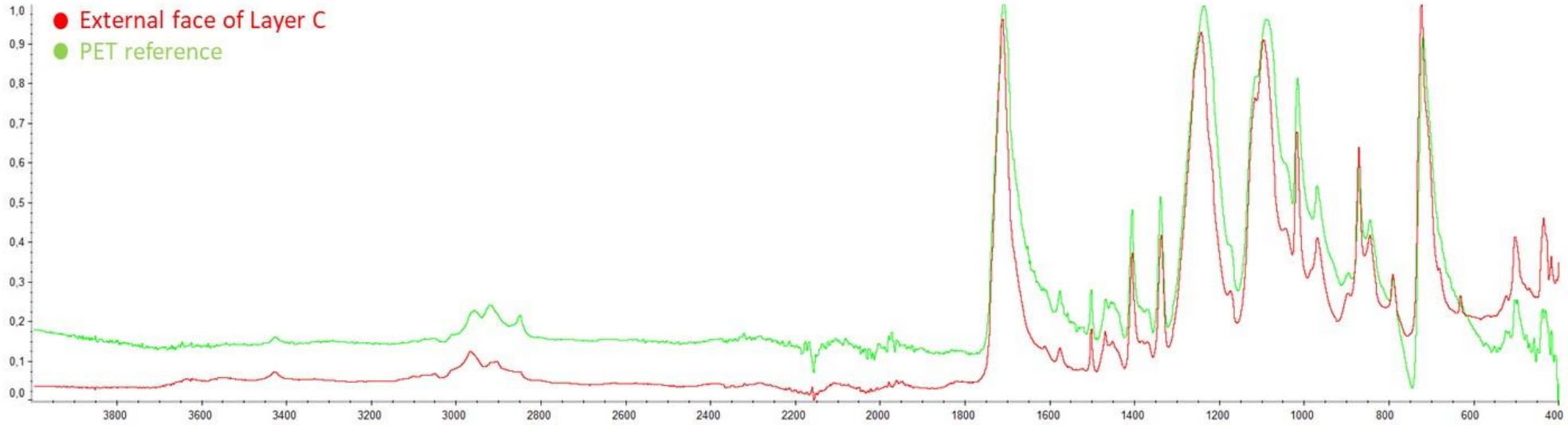


6.1.3. Sample 3 (104-7)

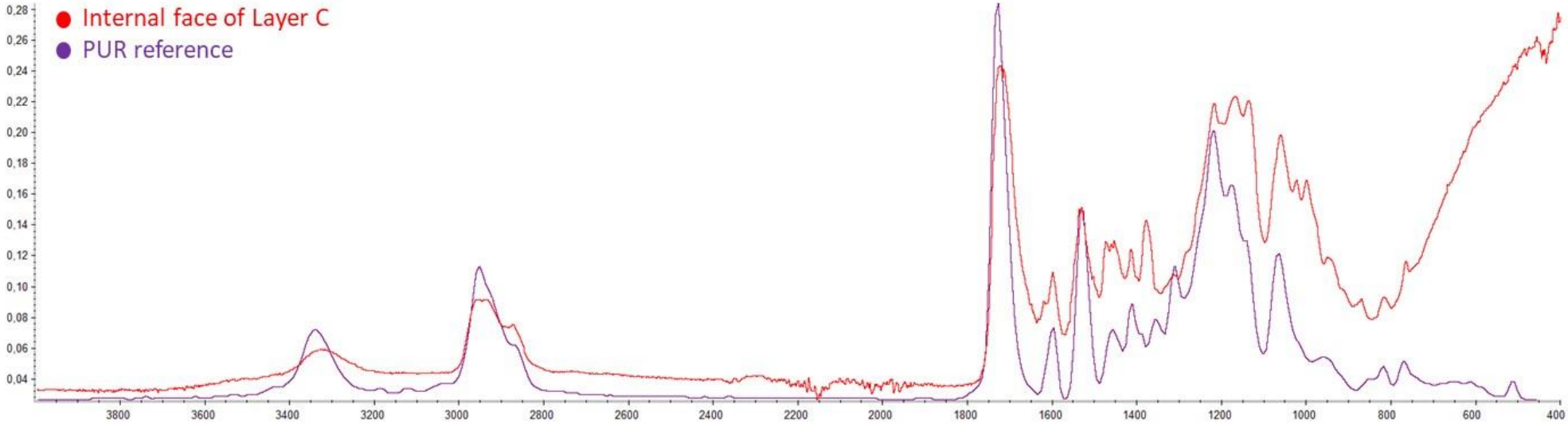
FTIR of internal face of Layer A, 85% match with polyester urethane from library



FTIR of external face of Layer C, 93% match with PET from library

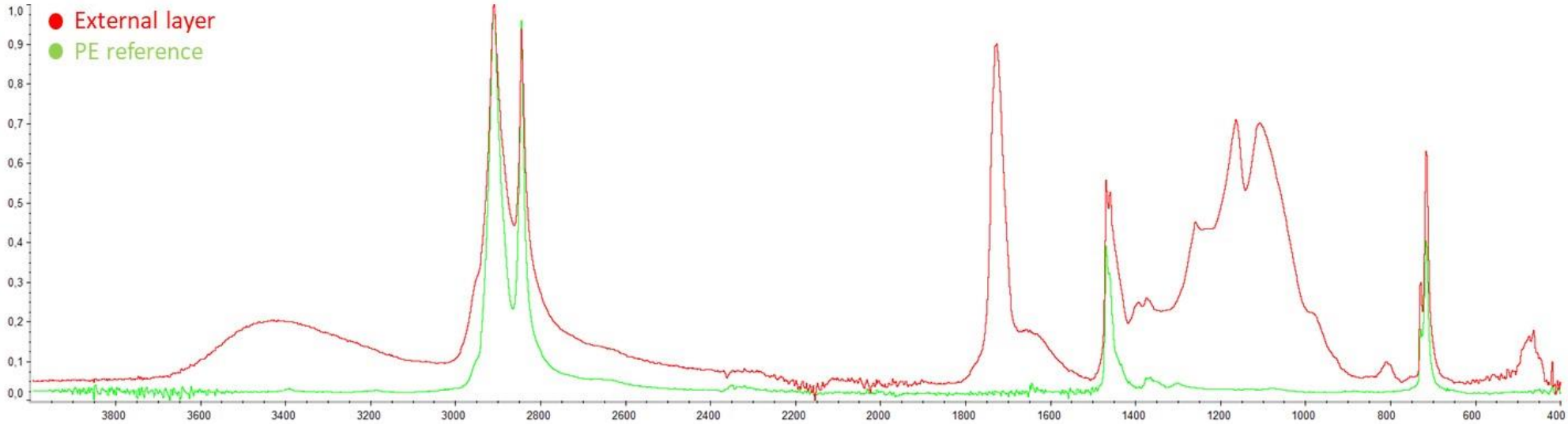


FTIR of internal face of Layer C, 80% match with polyester urethane from library

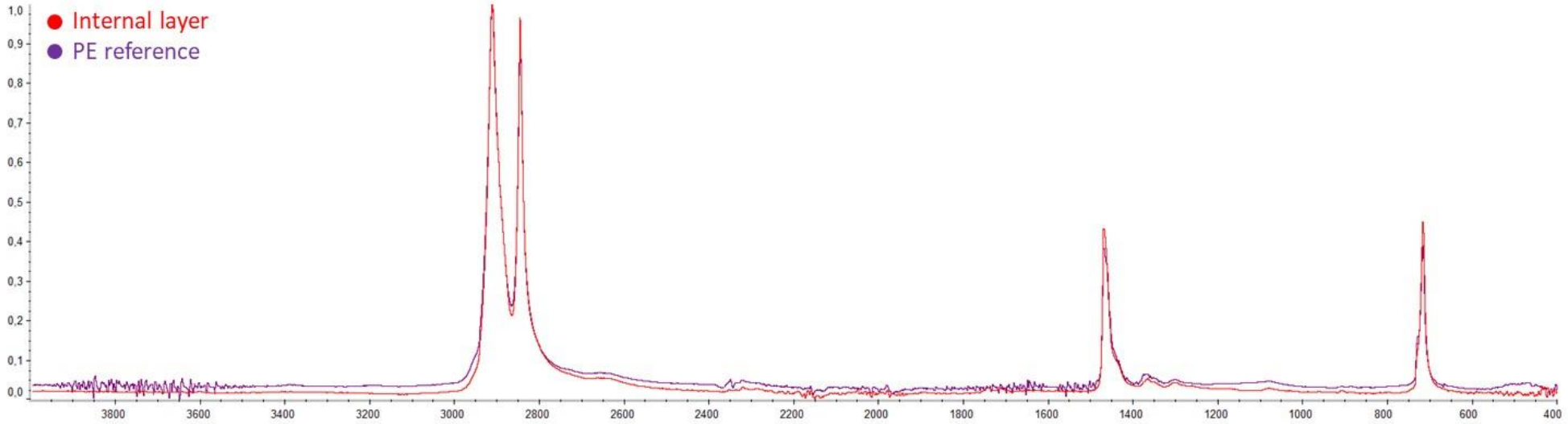


6.1.4. Sample 4 (24-2)

FTIR of printed external layer, 80% match with PE from library

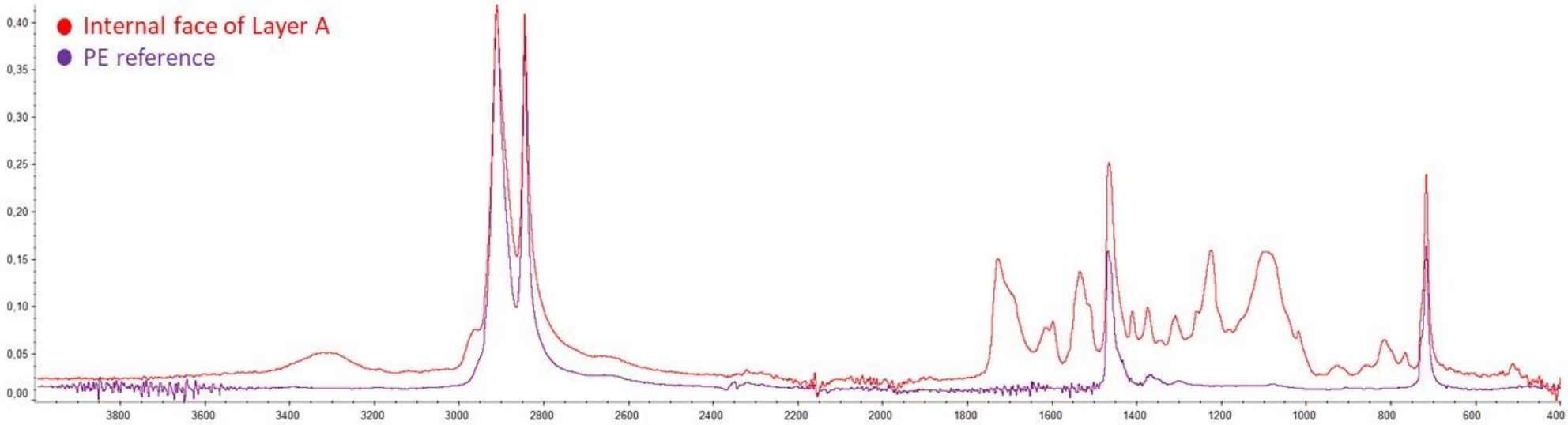


FTIR of internal layer, 95% match with PE from library

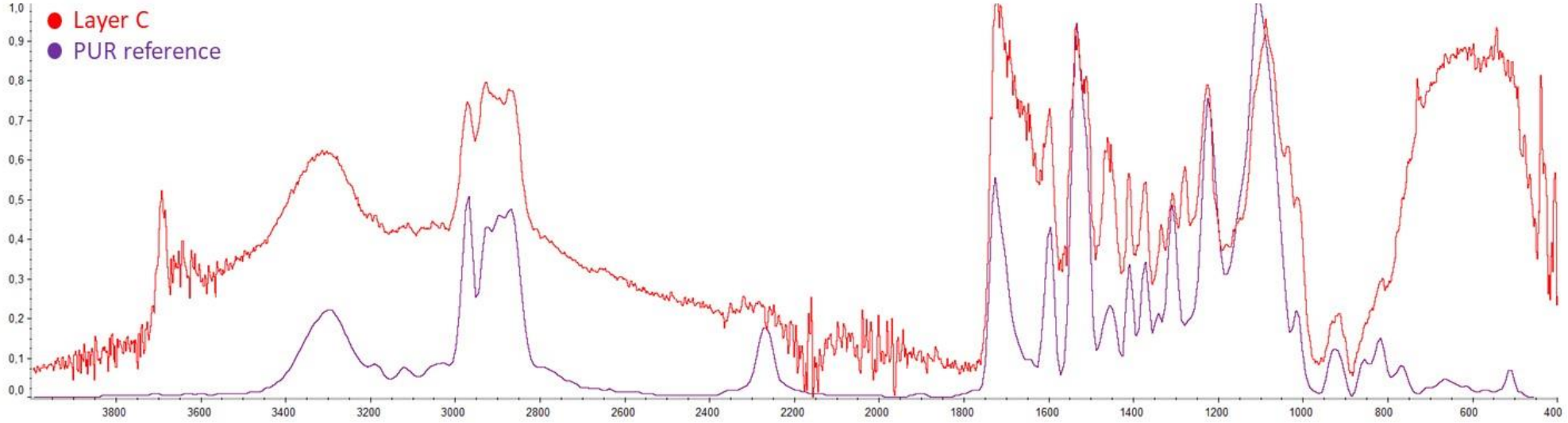


6.1.5. Sample 5 (27-6)

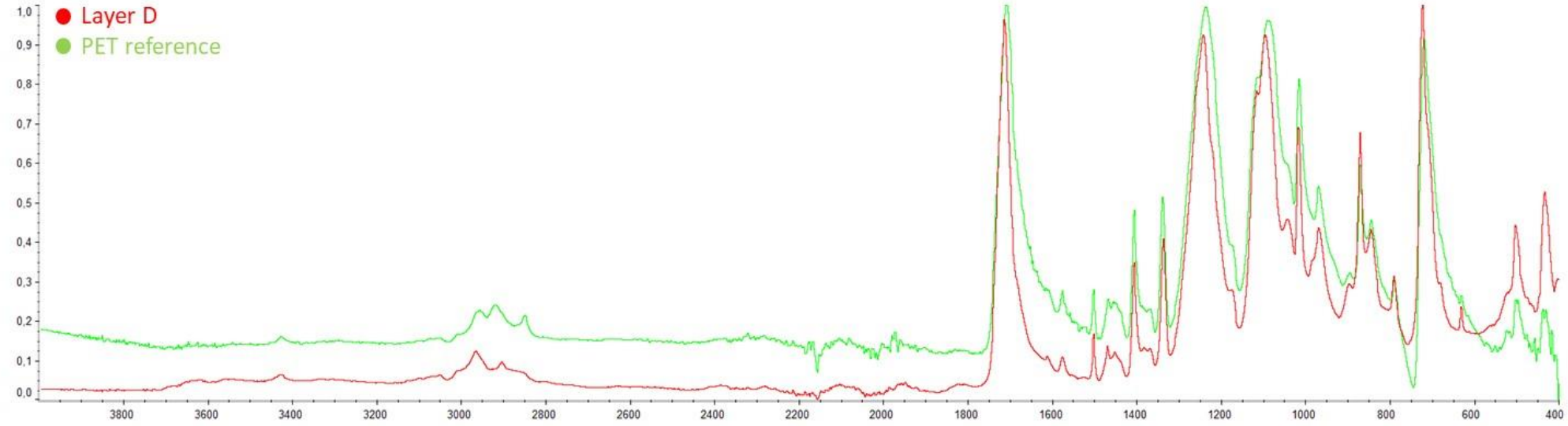
FTIR of internal face of Layer A, 90% match with PE from library



Layer C, 75% match with polyether urethane from library

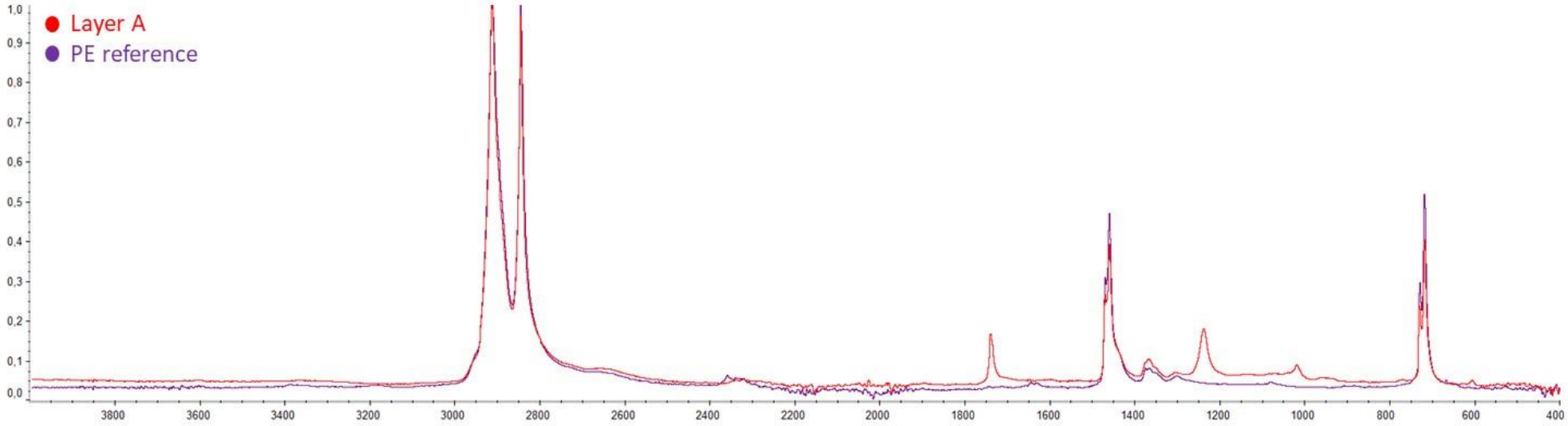


FTIR of layer D, 88% match with PET from library

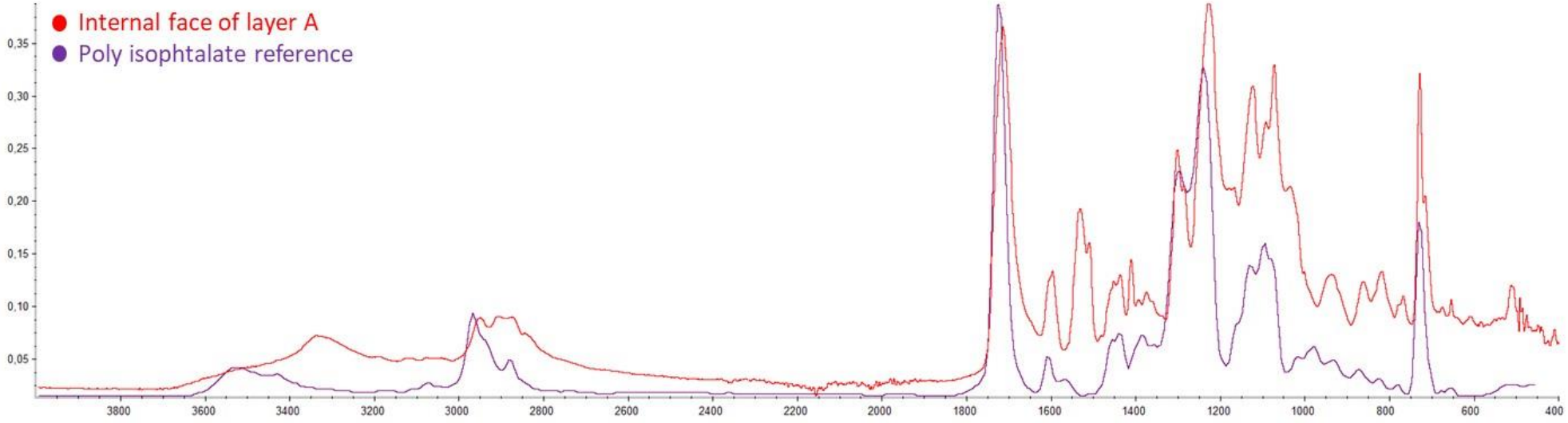


6.1.6. Sample 6 (7-1)

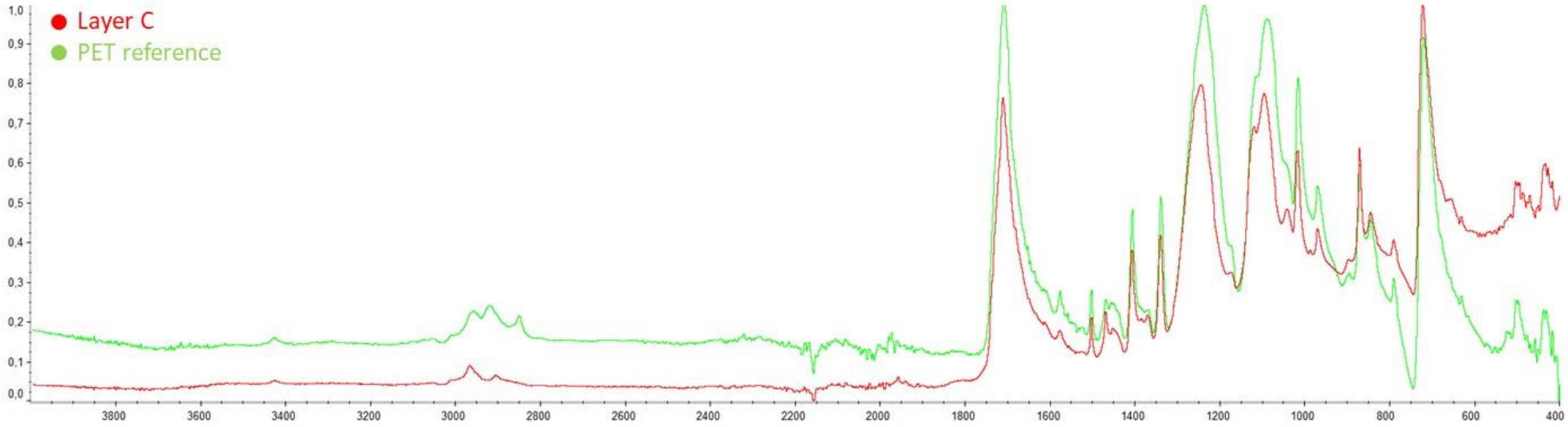
FTIR of Layer A, 90% match with PE from library



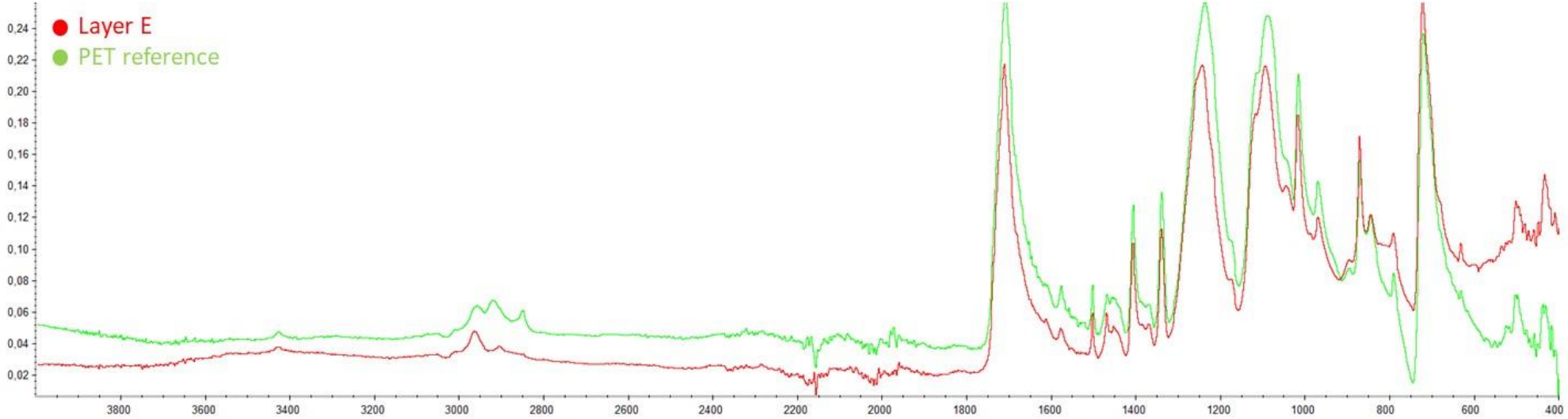
FTIR of Internal face of Layer A, 72% match with poly-isophtalate from library



FTIR of layer C, 95% match with PET from library



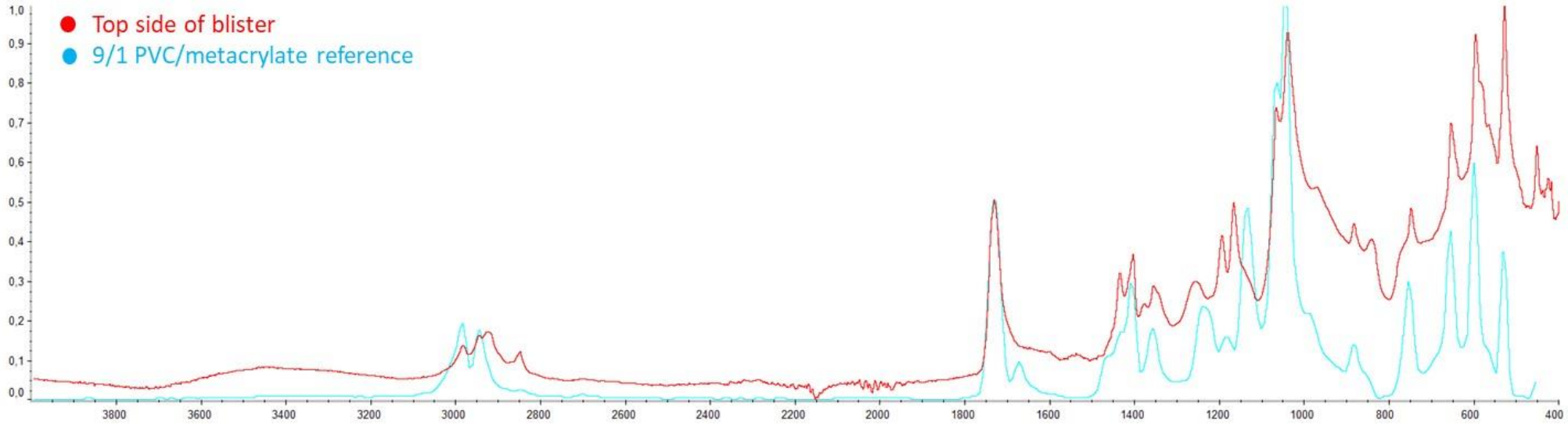
FTIR of layer E, 95% match with PET from library



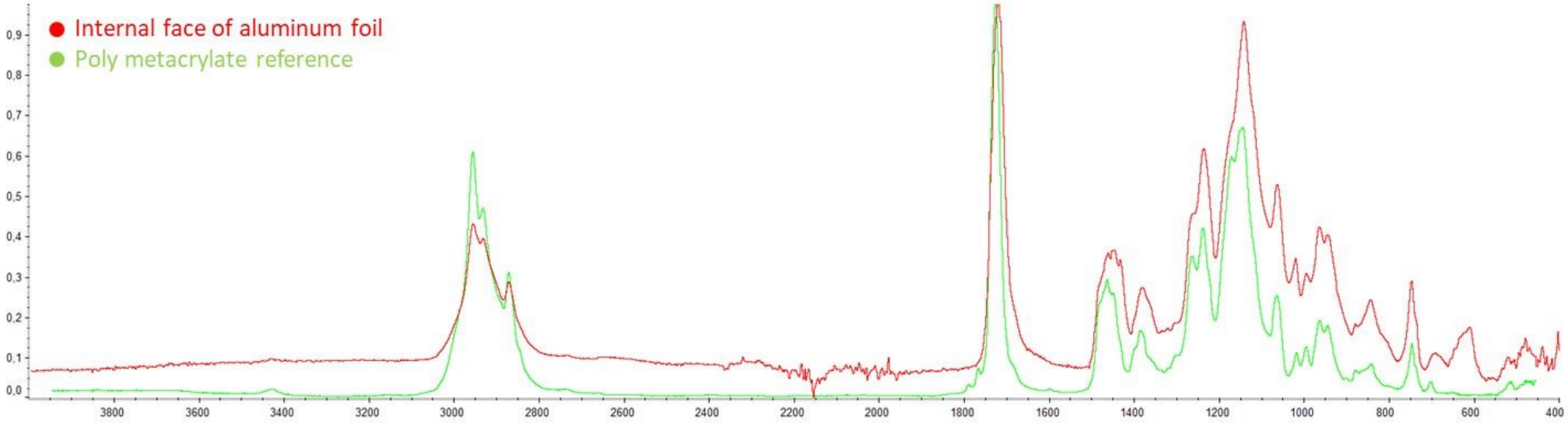
6.2. IR spectra of blister packaging

6.2.1 Sample 1 (Lisinopril)

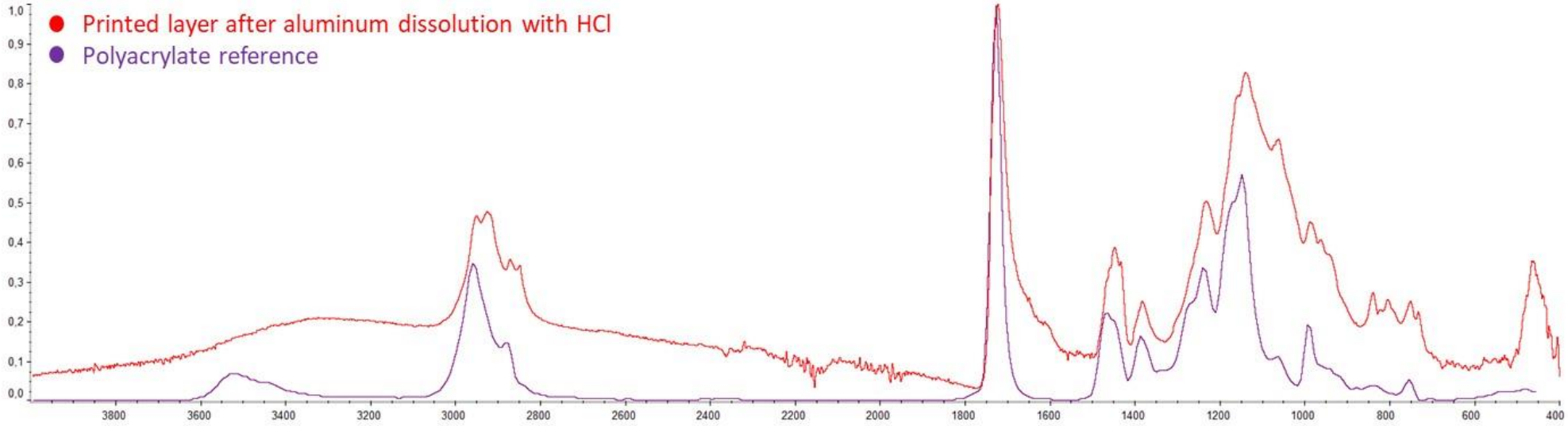
FTIR of top side of blister, 75% match with a 9/1 mixture of PVC with a polymetacrylate from library



FTIR of internal face of aluminum foil, 78% match with poly metacrylate from library

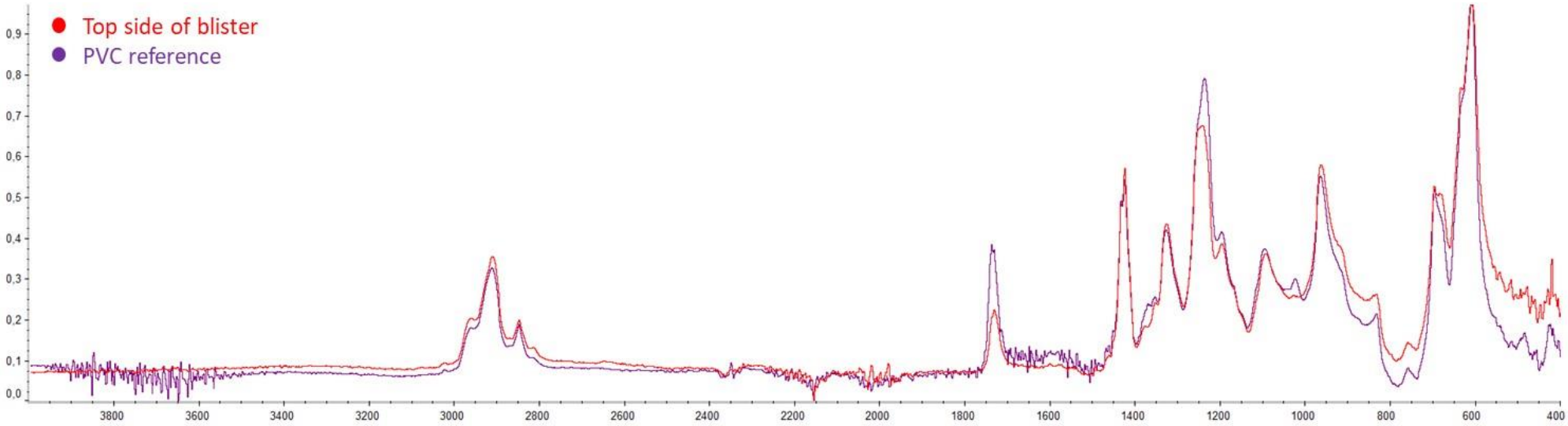


FTIR of printed layer after aluminum dissolution with HCl, 82% match with a polyacrylate from library

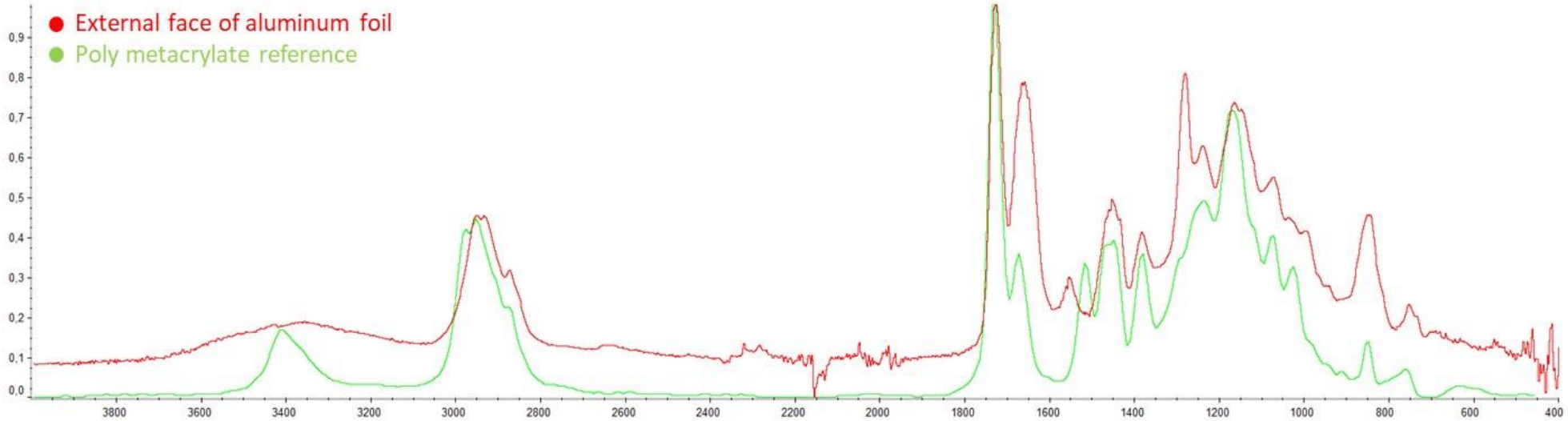


6.2.2 Sample 1 (Verospiron)

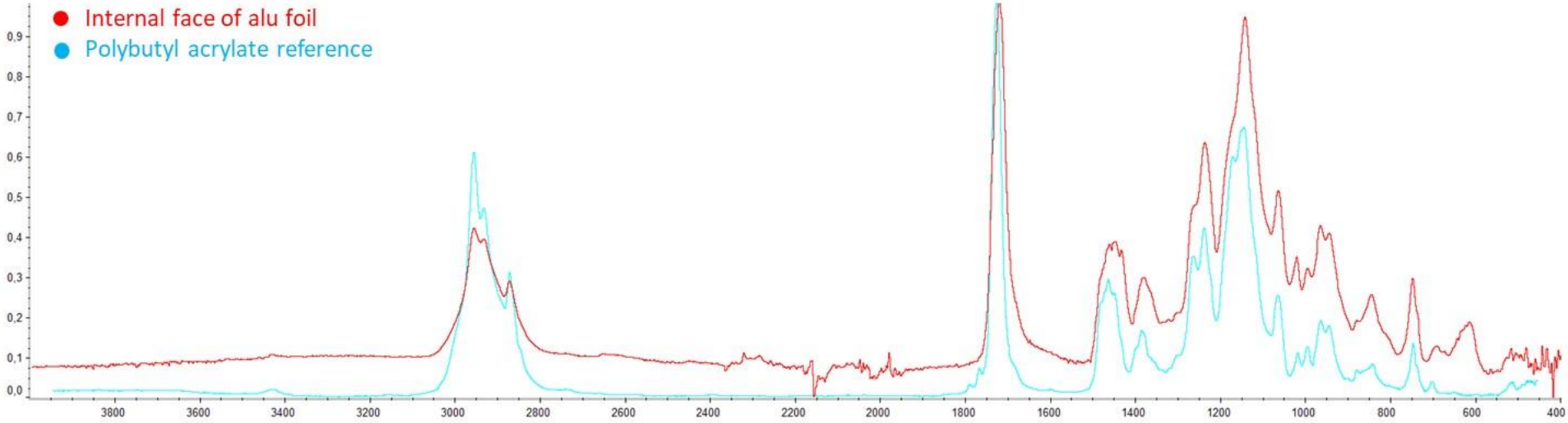
FTIR of top side of blister, 89% match with a PVC reference from library



FTIR of external face of aluminum foil, 75% match with a poly metacrylate reference from library

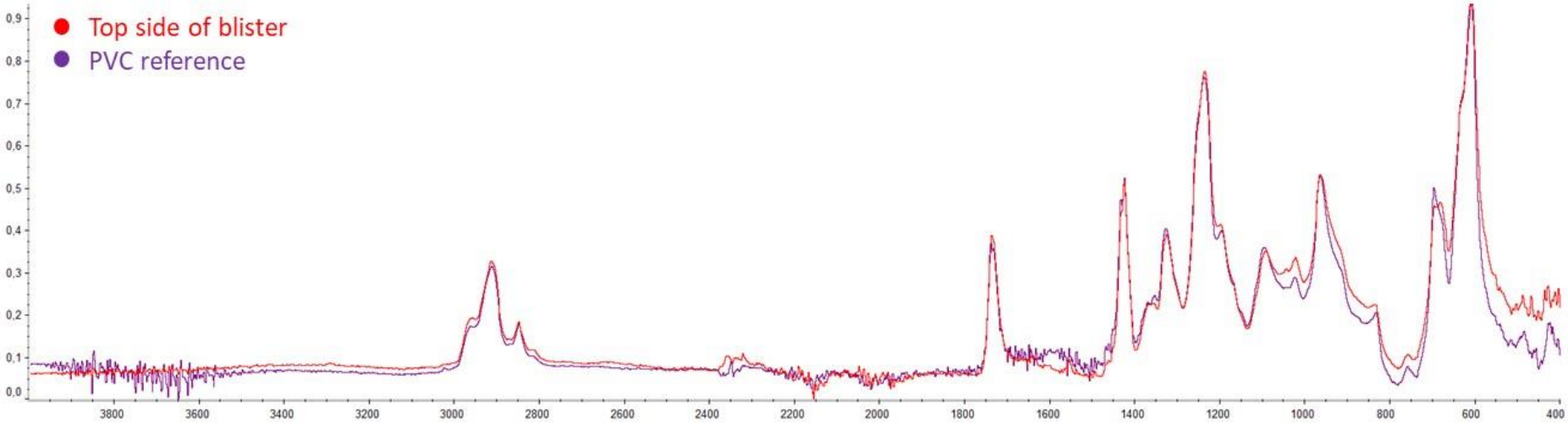


FTIR of internal face of aluminum foil, 77% match with a poly metacrylate reference from library

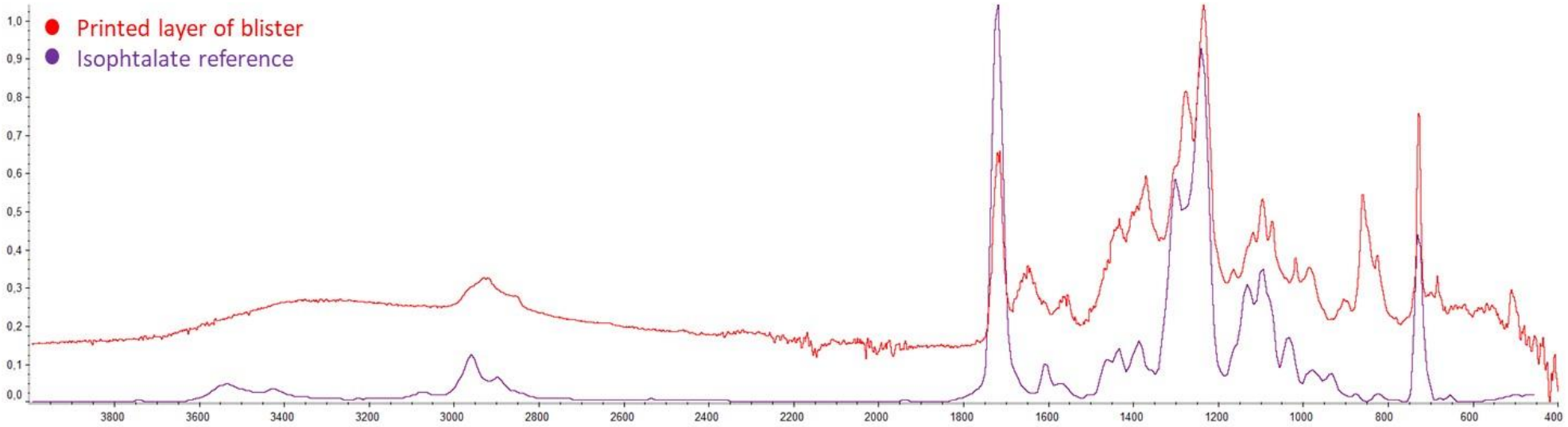


6.2.3 Sample 1 (Paralen)

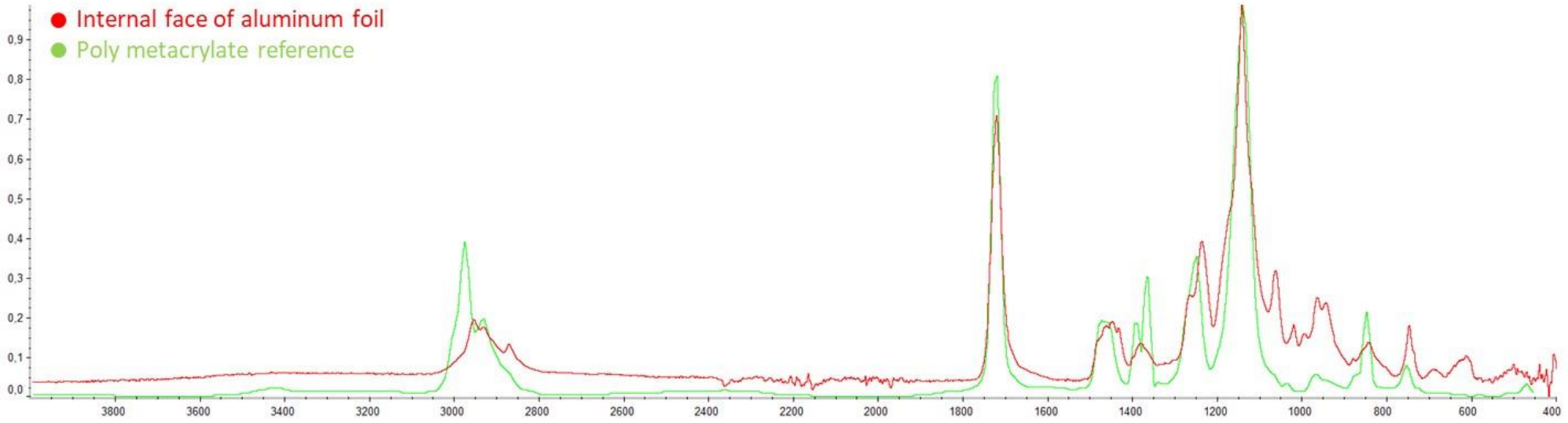
FTIR of top side of blister, 92% match with a PVC reference from library



FTIR of external face of aluminum foil, 76% match with a poly isophtalate reference from library

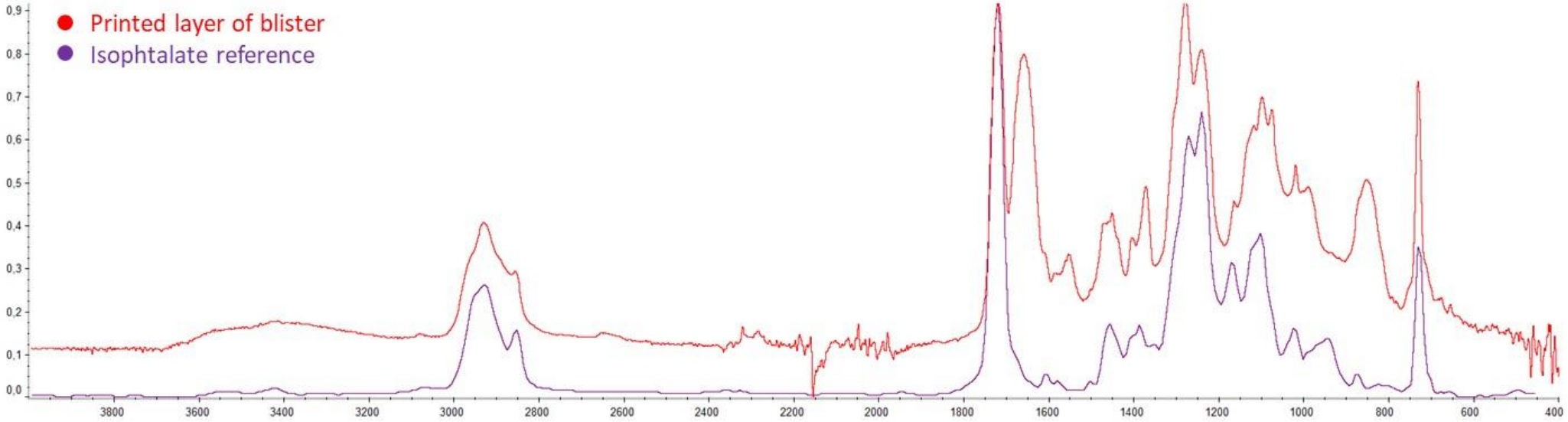


FTIR of internal face of aluminum foil, 77% match with a poly metacrylate reference from library

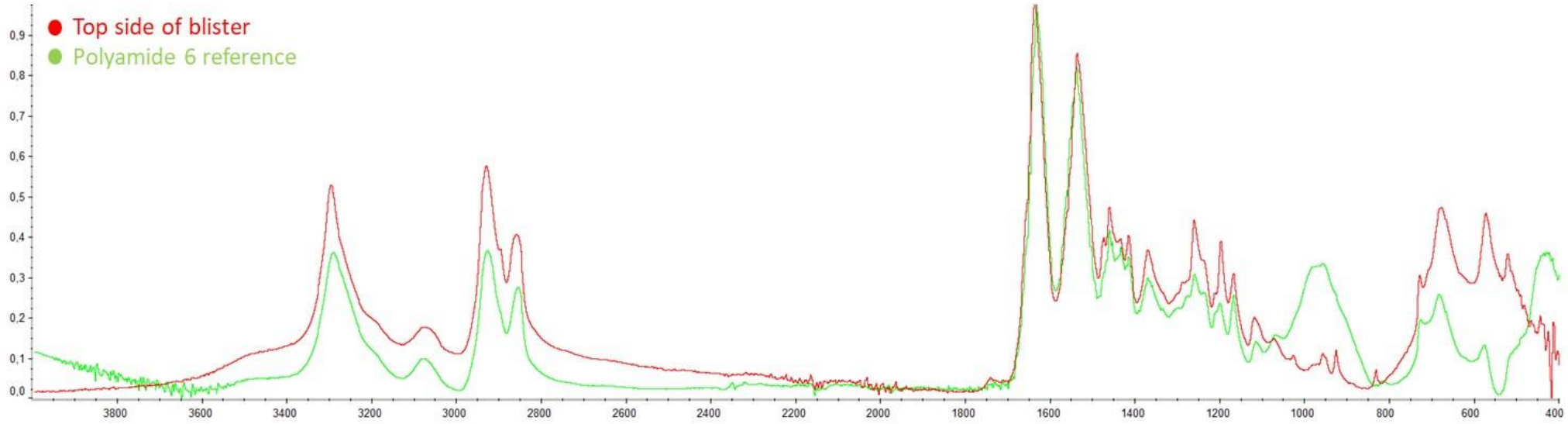


6.2.3 Sample 8 (Rosucard)

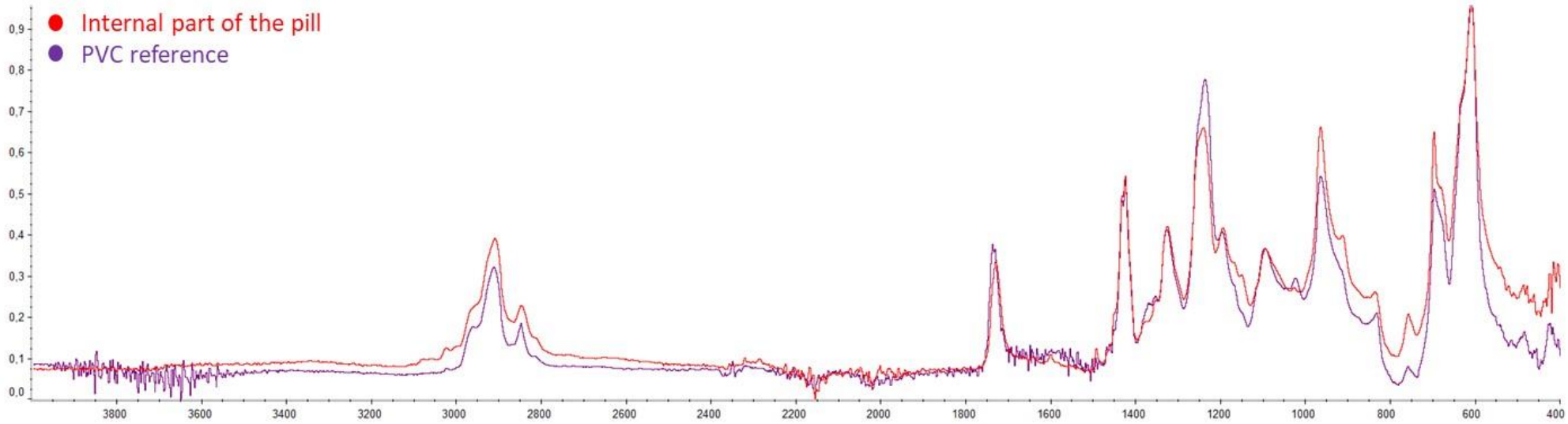
FTIR of external face of aluminum foil, 78% match with a poly isophtalate reference from library



FTIR of top side of blister, 86% match with a polyamide 6 reference from library



FTIR of internal part of the pill, 87% match with PVC from library



FTIR of internal face of aluminum foil, 80% match with a poly metacrylate