





Conference entitled

FINISHED PRODUCT AND NEW
FORMULATIONS OF VARNISHES,
INKS, ADHESIVES AND VARIOUS
TYPES OF COATINGS IN
RESPONSE TO THE EUROPEAN
DIRECTIVES ON SUSTAINABLE
FOOD PACKAGING

Tuesday, October 22nd 2024 - h 09,00 at the NH Hotel Congress Centre,
Strada 1 - Milanofiori, Assago (Milan) in conjunction with the third edition of Paint & Coatings Italy trade fair.

Analytical evaluation of the barrier effects of coatings with a focus on the release of microplastics, referring to management of environmental claims such as plastic free.

Marinella Vitulli, Owner & Director, Food Contact Center & Food Contact Services



Marinella Vitulli- m.vitulli@foodcontactcenter.com

Senior Food Contact Specialist, Founder of Food Contact Center& Food Contact Services srl

- degree in Pharmaceutical Chemistry, currently Chemist and Food Contact Expert
- more than 20 years seniority in FCM
- Laboratory Director also for multinational companies
- key point in Western Europe for enterprises wanting to enhance their Quality Systems
- member of European technical tables



PISTOIA-TUSCANY

BRESCIA-LOMBARDY

CUNEO-PIEDMONT

Food Contact Center & Food Contact Services





27 food contact experts





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SYNERGY





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Laboratory expert in the field Chemical, physical and microbiological tests.

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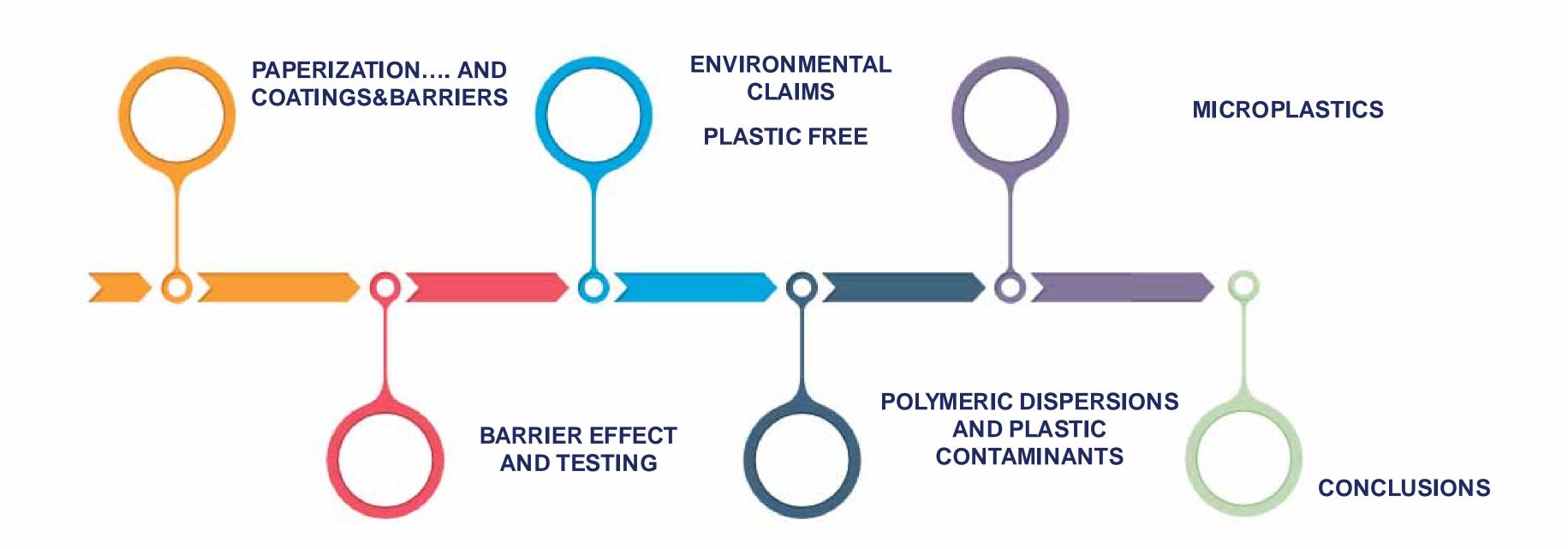
microbiology department

through research, we go beyond the standards.

Analytical evaluation of the barrier effects of coatings with a focus on the release of microplastics, referring to management of environmental claims such as plastic free.

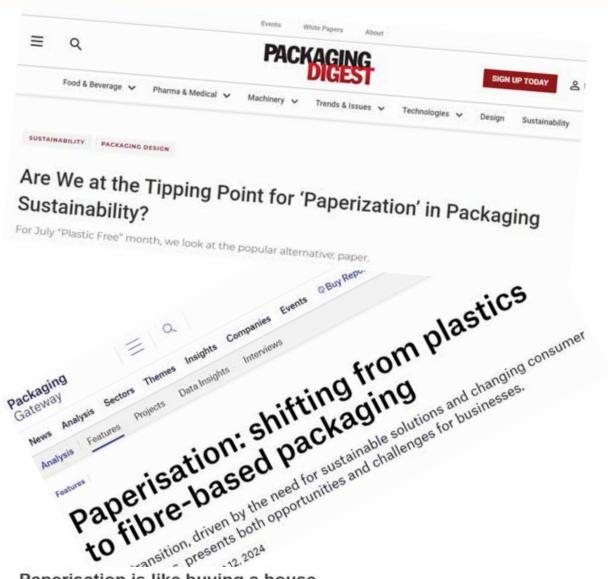


AGENDA:



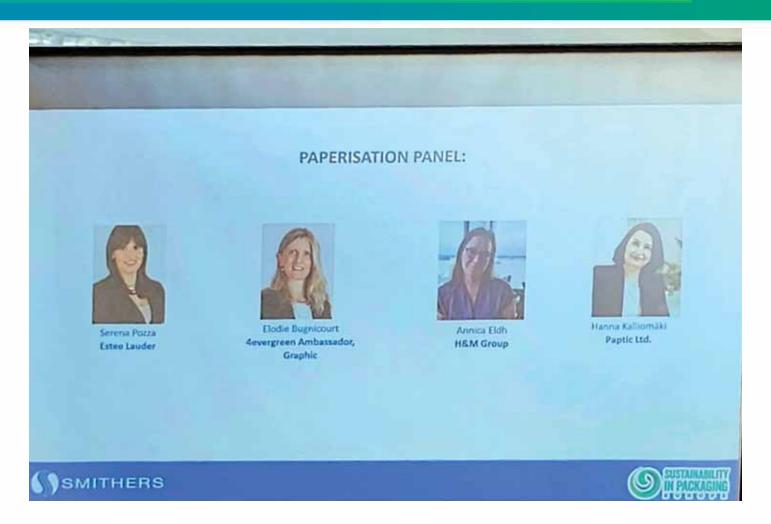
PAPERISATION/PAPERIZATION.... SLANG OR TECHNICAL TERM?





Paperisation is like buying a house...





Sustainability in Packaging Barcelona 8-10 Oct 2024

THE PROCESS IS STARTED....
THE MARKET NEEDS NEW MATERIALS,
HAVING MORE RESISTANCE, TO GAS, WET,
GREESE...

THE SOLUTION CAN BE ACHIEVED ADDING ADDITIVES IN THE PAPER... OR USING A COATING

Barrier and other functionality can be added at multiple points in the value chain, in multiple ways; where and how coatings are applied is as important as what coatings are used.

There are benefits and challenges in coating during paper production vs during printing.

BARRIER? COATINGS?







3-4 September 2024
Austria Trend Hotel Savoyen Vienna, Austria

MANY COMPANIES ARE CURRENTLY WORKING TO DEVELOP COATINGS/BARRIER



CHEMICALS? SOLUTIONS?

- -STARCH (STARCH IS A POLYSACCHARIDE MADE UP OF 1,4 LINKAGES BETWEEN GLUCOSE MONOMERS)
- -MICROFIBRILLATED CELLULOSE
 (IS DEFINED AS AN AGGREGATION OF CELLULOSE MICROFIBRILS OBTAINED BY DISINTEGRATION OF CELLULOSE FIBERS)
- -MICROCRYSTALLINE CELLULOSE
 IS GENERALLY OBTAINED FROM PARTIAL
 HYDROLYSIS OF CELLULOSE AND HAS A
 POLYMERIZATION LENGTH OF 40–200 UNITS.
- -TROPICAL RED SEAWEEDS (BIOBASED POLYMERS)

Image Source https://gmz.Itd/product/plastic-free-paper-hot-cups/

BARRIER? COATINGS?



CHEMICALS? SOLUTIONS?

-SILANES Inorganic coating, silicon based.

-PVOH, SB = Styrene Butadiene SA = Styrene Acrylate Polymer Coatings

-PHA
Bio polymer coating

- OTHER POLYMERIC DISPERSIONS
- POLYURETANE PAPER COATINGS

Source Image: Yanxiyan



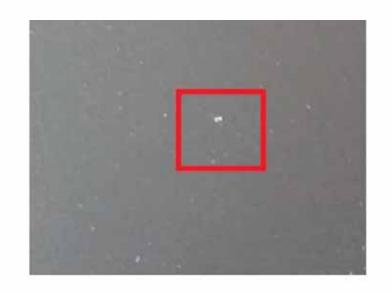


Figura 2. microforo sulla superficie

PROPERTIES? TESTING? A GOOD SCREENING METHOD



But there is a problem...

...Plastic is waterproof and paper isn't!

Paper needs to be **coated** to work.

But, the coating needs to keep the paper recyclable and be pin-hole free.

Guy Newcombe - Archipelago Technology

PINHOLE??

TECHNICAL SPECIFICATION
SPÉCIFICATION TECHNIQUE
TECHNISCHE SPEZIFIKATION

CEN/TS 14234

October 2002

ICS 67.250

English version

Materials and articles in contact with foodstuffs — Polymeric coatings on paper and board — Guide to the selection of conditions and test methods for overall migration

EUROPEAN STANDARD NORME EUROPÉENNE

EUROPÄISCHE NORM

ICS 55.040; 67.250

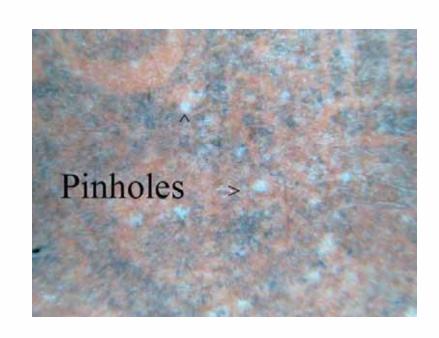
English version

EN 13676

April 2001

Polymer coated paper and board intended for food contact -Detection of pinholes





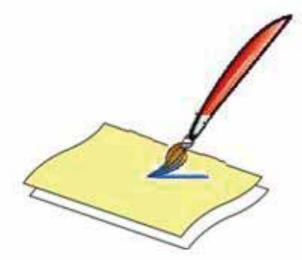




Image source: wikipedia



TESTING ON PAPER SAMPLES

Air Permeability (SCAN - P 60:87) according to Bendtsen

WVTR 23°C - 50% RH*

Heat resistance (e.g. 70°C)

Tear resistance (SCAN-P 11:96)

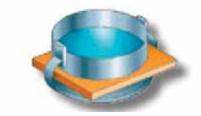
Tensile strength (SCAN-P 38:80)

Elongation (SCAN-P 11:96)

Tensile Energy Absorption (SCAN-P 11:96)

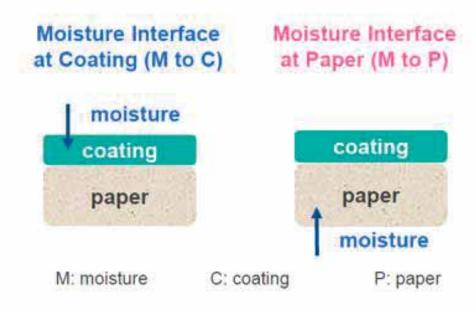
Burst (SCAN-P 25:81)

Water Absorption (Tappi T441-Cobb 1800)

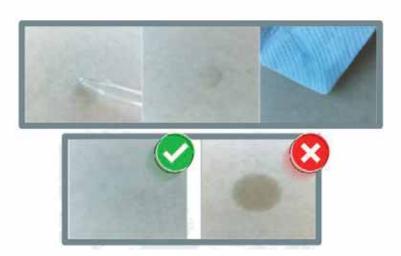


Greese resistance (Tappi T559- Oil Cobb)
(source image CMPC)

Two Testing Directions



Bernhard Kainz - DOW

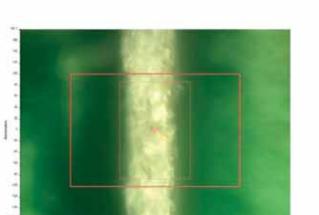


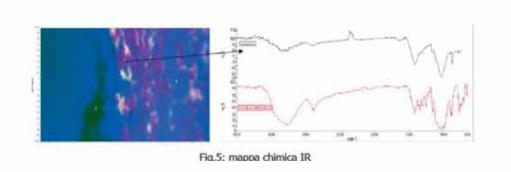


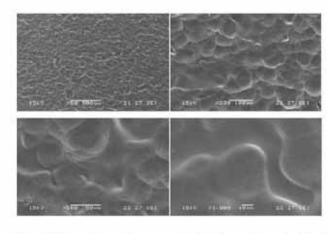
TESTING ON PAPER SAMPLES

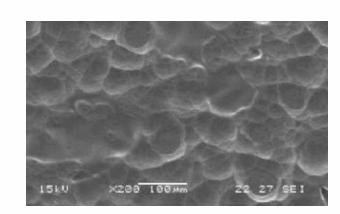
Visual test

Scanning electron microscope (SEM) surface & crosscut samples



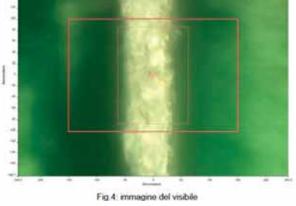


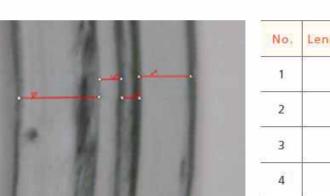




Imaging

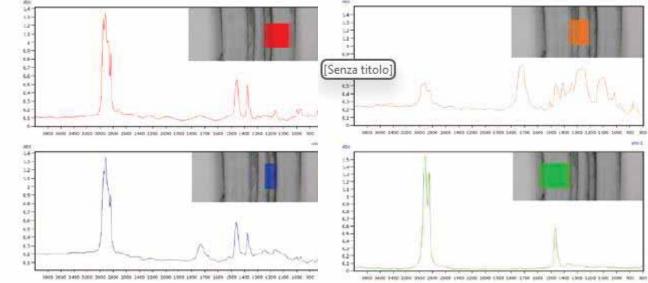
Micro FT IR





	76 11	No.	Length(µn
		1.	27
2	•	2	9
	N 14	3	11
	22 44 4	4	42

Photographs and length measurement results of multilayer film cross sections (inside on left side of screen)





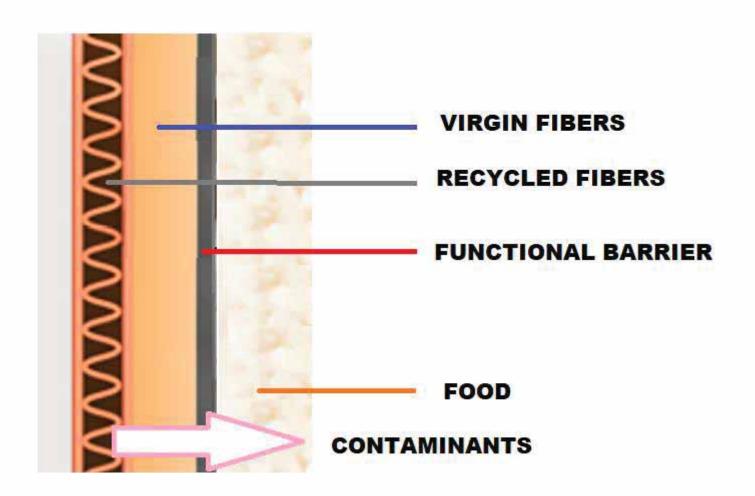


TESTING? SAFETY FIRST



When we talk about barriers, historically we are referring to the barrier against the transfer of gaseous substances and humidity. This barrier was designed for the organoleptic and microbiological protection of the food product.

Talking about safety and food contamination, the use of barrier layers has the function of containing the migration of all potentially migrating compounds



Functional barrier (Reg UE 10:2011 cons. 27)

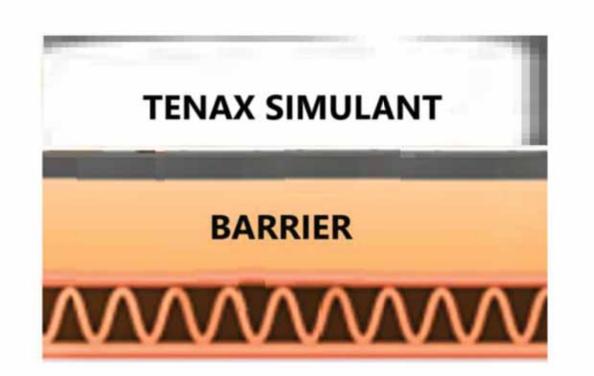
This barrier is a layer within food contact materials or articles preventing the migration of substances from behind that barrier into the food. Behind a functional barrier, non-authorised substances may be used, provided they fulfil certain criteria and their migration remains below a given detection limit. Taking into account foods for infants and other particularly susceptible persons, as well as the large analytical tolerance of the migration analysis, a maximum level of 0,01 mg/kg in food should be established for the migration of a non-authorised substance through a functional barrier





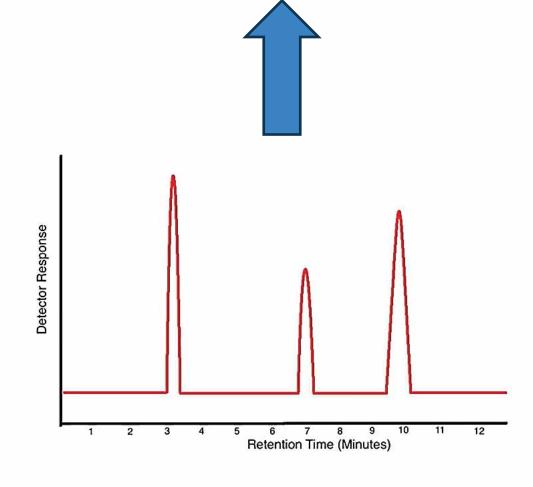
The coated sample is in a glass box and covered with the tenax simulant, after migration in different condition (at lest 40°C 10 days), tenax is tested in order to check the migration of contaminants

1)Uttam et al. Mater. Res. Express 4 (2017)



TENAX EXTRACTION TESTING

CONTAMINANT
IDENTIFICATION AND
RISK ASSESSMENT







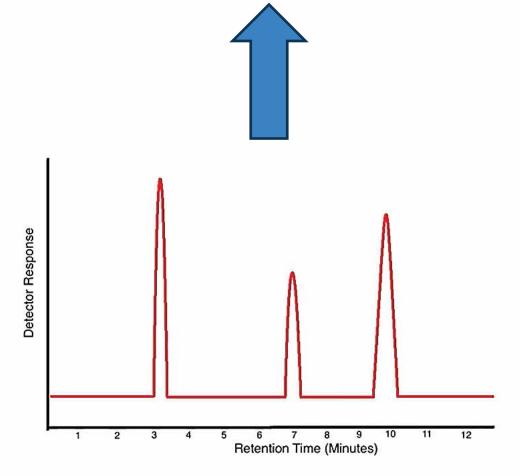
There is a Nitrogen flux; the cell is connected with a valve to a trap and then directly to the GC

2) Ewender et al (2013) migration in a permeation cell under nitrogen flux





TESTING



CONTAMINANT

IDENTIFICATION AND

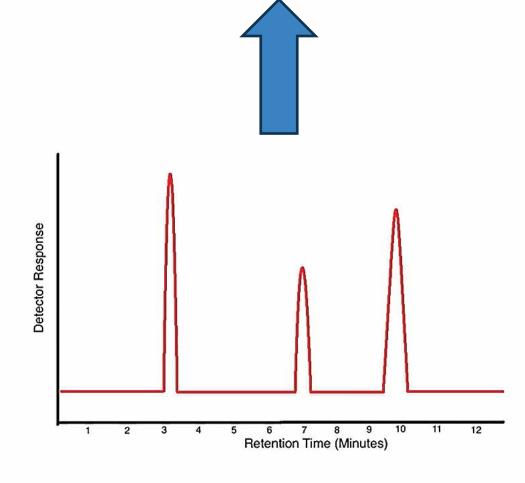
RISK ASSESSMENT





A silicone paper is used as a simulant and the experiment is made between two alluminium foils

CONTAMINANT
IDENTIFICATION AND
RISK ASSESSMENT



3) Grob et al. (2014) Packaging, technology and science

SILICONE PAPER EXTRACTION

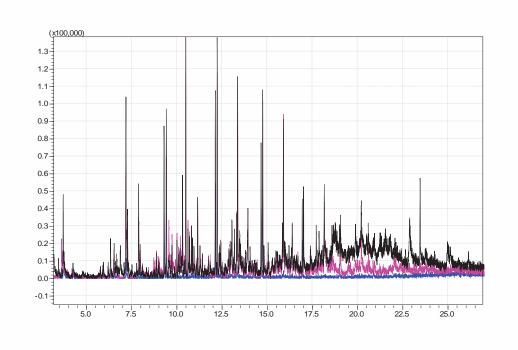
TESTING



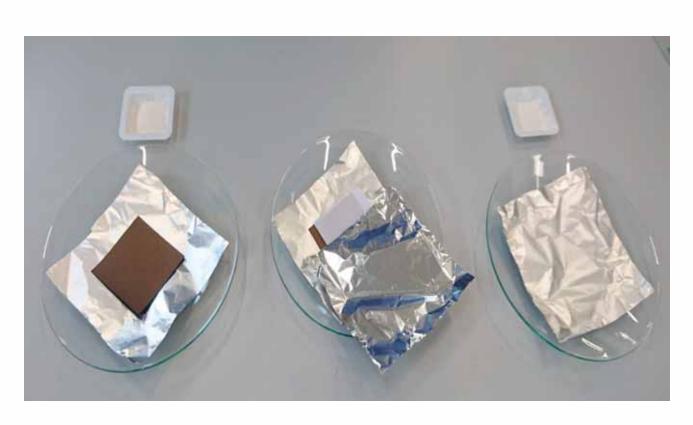
The silicon paper is used as receptor, as new food simulant

In our experience alluminium foil need to be purified before the use, we have done organic extraction of hydrocarbons from commercial alluminium foils, and we have found some aliphatic hydrocarbons (below m/z 85 extraction of chromatograms)





Tenax blank
Silicon paper blank
Solvent extraction blank

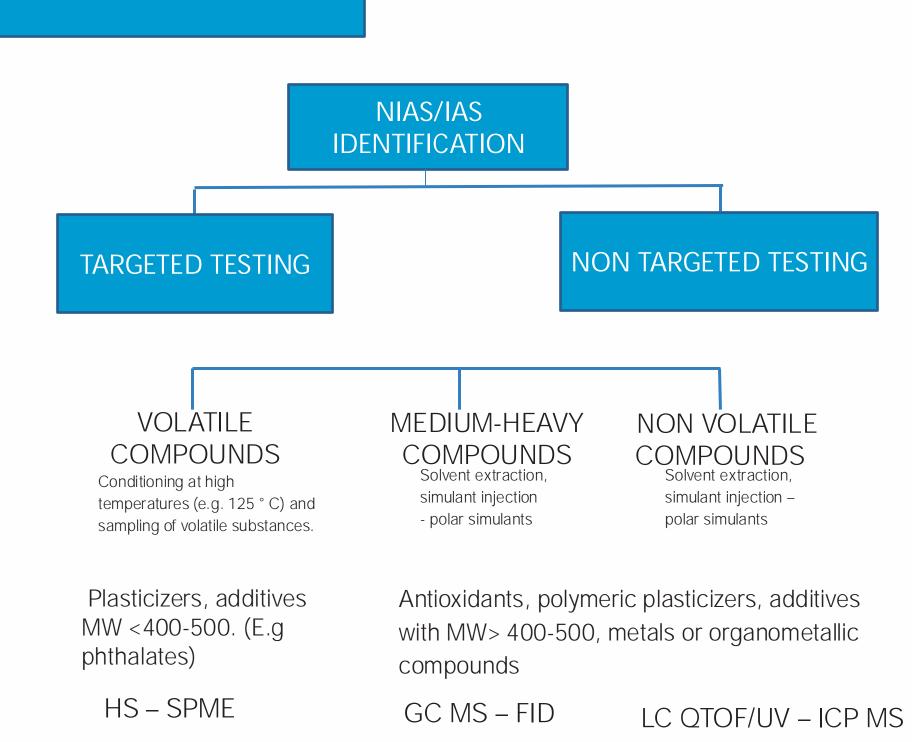


IAS... and NIAS -ANALYTICAL CHALLENGES



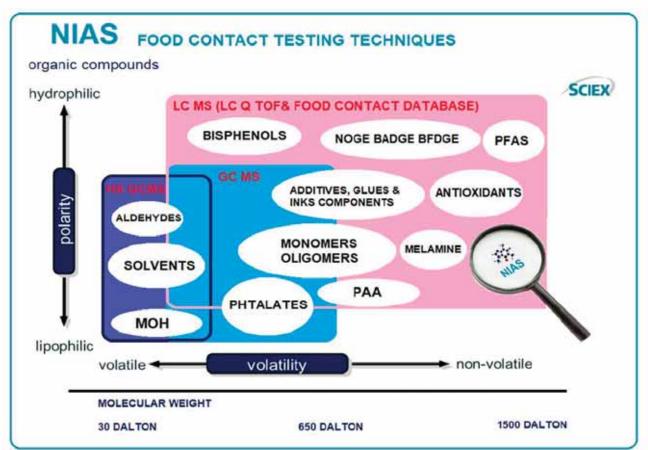
IAS & NIAS

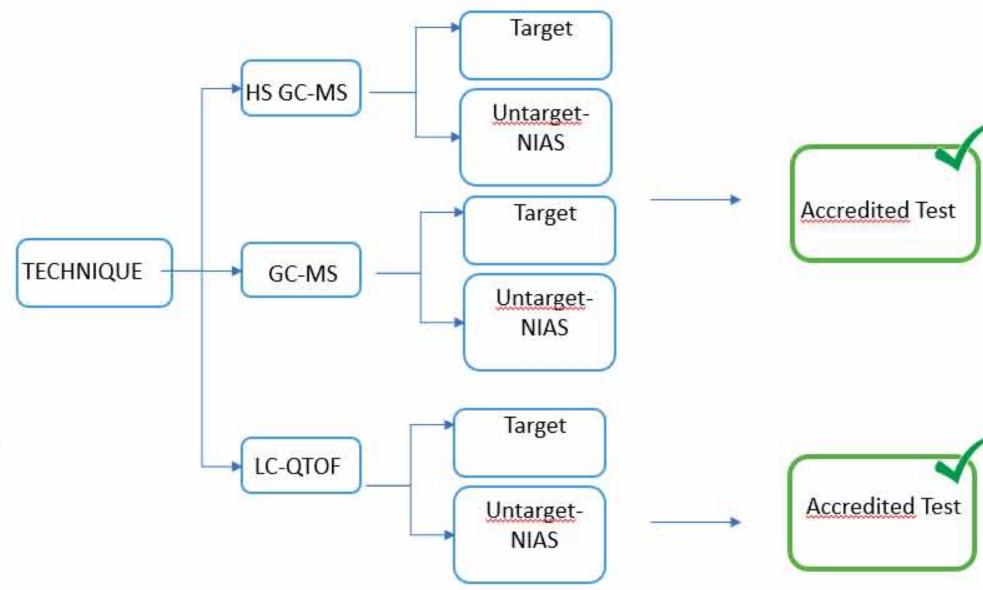
- IAS (Intentionally Added Substances): specifically added during the manufacturing process of materials, having a function in the manufacturing process or in the final product.
- Row materials starting substances
- Monomers
- Additives
- Solvents
- Colourings
- NIAS (Non intentionally added substances): impurities in the substances used, reaction intermediate formed during the production process, or products of reaction or decomposition.
- Additives degradation
- Polymer degradation
- Residues
- Neoformed products
- Impurities



ANALYTICAL CHALLENGES







More than 10 years to build a Library of 12000 compounds



Food Contact Center Srl

Via del Redolone 65 51034 Serravalle Pistoiese PT

Allegato al certificato di accreditamento n. 1786L

Materiali a base di plastica ed articoli destinati a venire in contatto con gli alimenti/Plastic materials and articles intended to come into contact with foodstuffs

Denominazione della prova / Campi di prova	Metodo di prova	Tecnica di prova	081
Composti organici semi volatili (Valutazione semi-quantitativa)/Semi volatile organic compounds (Semi-quantitative evaluation) (0,01 - 10 mg/Kg simulante)	MHTH088 rev.1 2023	GC-MS	
Composti organici non volatili (Valutazione semi-quantitativa)/Non volatile organic compounds (Semi-quantitative evaluation) (0,01 - 10 mg/kg simulante)	MHTH089 Rev.1 2023	HPLC-HRMS	







RECYCLABE...

PLASTIC FREE PRODUCT.....
OFFICIAL DEFINITIONS?



Image Source https://gmz.ltd/product/plastic-free-paper-hot-cups/

















MANY LABELS, JUST GOOGLING...



EN ISO 14024

TYPE I: Eco-Labels Voluntary THIRD PARTY CERTIFICATION program that uses multiple criteria EXAMPLES: SEAL Ecolabel www.ecolabel.eu

Single Product Line or Criteria







EN ISO 14021

TYPE II: Green Claims

Self Declarations by Manufacturers

EXAMPLES:

CFC-Free Dolphin Friendly Recycled Content

EN ISO 14025

TYPE III:

Environmental Impact

Voluntary THIRD-PARTY
VERIFICATION* program that uses
quantifiable
environmental data

EXAMPLES:

Environmental Product Declarations (EPD)

> No evaluation; only verification

*business-to-business declarations and labels require independent verification of the data only, not third-party certification, Business-toconsumer declarations require thirdparty certification.



EN ISO 14021:2016/A1:2021

Environmental labels and declarations - Self-declared environmental claims (Type II environmental labelling) - Amendment 1: Carbon footprint, carbon neutral (ISO 14021:2016/Amd 1:2021)



EN ISO 14021:2016/A1:2021

Environmental labels and declarations - Self-declared environmental claims (Type II environmental labelling) -Amendment 1: Carbon footprint, carbon neutral (ISO 14021:2016/Amd 1:2021)



3.1.17 sustainable development

development that meets the needs of the present without compromising the ability of future generations to meet their own needs

5.4 Statements like "free of..."

An environmental claim of "... free" shall only be made when the level of the specified substance is no more than that which would be found as a trace contaminant or background level.

5.5 Sustainability claims

The concepts involved in sustainability are extremely complex and still under study.

At the moment there are no definitive methods to measure sustainability or confirm its achievement. Thus, no assertion of must be made achieving sustainability.





Brussels, 22.3.2023 COM(2023) 166 final 2023/0085 (COD)

Proposal for a

DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

on substantiation and communication of explicit environmental claims (Green Claims Directive) On top of requirements on substantiation and communication applicable to all types of claims, this proposal builds on the requirements of the proposal on empowering consumers banning labels based on self-certification, and provides additional safeguards to improve the quality of ecolabelling schemes by requiring the following transparency and credibility requirements

The 'self-certified' sustainability labels, where no third-party verification and regular monitoring takes place as regards compliance with the underlying requirements of the sustainability label are prohibited.

- SUPPORT DOCUMENTATION
- THIRD-PARTY VERIFICATION



BUT WHAT IS A PLASTIC?

The following definitions are based on the following relevant standards and provisions.

- Regulation (EC) No. 1907/2006 (REACH)
- Regulation (EU) No. 10/2011 Commission Regulation on plastic materials and articles intended to come into contact with food
- Single Use Plastic Directive
- Directive 94/62/EC regarding packaging and packaging waste (PPWR proposal)
- DIN 55405
- DIN EN ISO 472 Plastics Glossary of technical terms (ISO/TC 61/SC1)
- EN 13130-1 Materials and articles in contact with foodstuffs Substances in plastics subject to limitations Part 1: Guidelines for test methods for the specific migration of substances from plastics into foodstuffs and test foods, the determination of substances in plastics and the selection of contact conditions with test foods
- EN 643 Paper, cardboard and paperboard European list of standard waste paper grades



Definition of plastic:

The term plastic is understood to mean a polymer material which may have additives or other added substances and which may act as the **main** structural component of finished end products.

Definition of polymer:

The term polymer is understood to mean a substance consisting of molecules characterized by a chain of one or more types of monomer units within a certain molecular weight range...

Substances having polymeric nature, used in specialty papers?



In Italy, paper packaging intended for food contact is regulated by law DM 21.03.73. In this decree there are interesting info relating to the composition of paper, that can be used in the evaluation of the "Plastic Free" claim. Italian legislation authorizes in the case of paper food packaging, for which migration tests are required and consisting of at least 75 percent fibrous materials, a maximum of 10 percent of filler substances and a maximum of 15 percent auxiliary substances. In fact, the following sentence is reported:

... The presence, in trace quantities, according to good industrial technique, of technological processing aids with the function of reactives, **dispersion**, flotation and drainage agents, anti-foam and anti-slime agents is permitted;

Among the auxiliary substances that can be used in paper and present in the positive lists of the Italian Ministerial Decree, there are substances soluble or non-soluble in organic solvents, which are organic substances also of a polymeric nature.

Even the German guidelines, BfR Recommendations XXXVI Paper and board for food contact, contains the same compositional informations



The risk assessment necessary to determine the food contact compliance of the items must take into account the use of any polymer dispersions, but this does not change the definition of paper ...

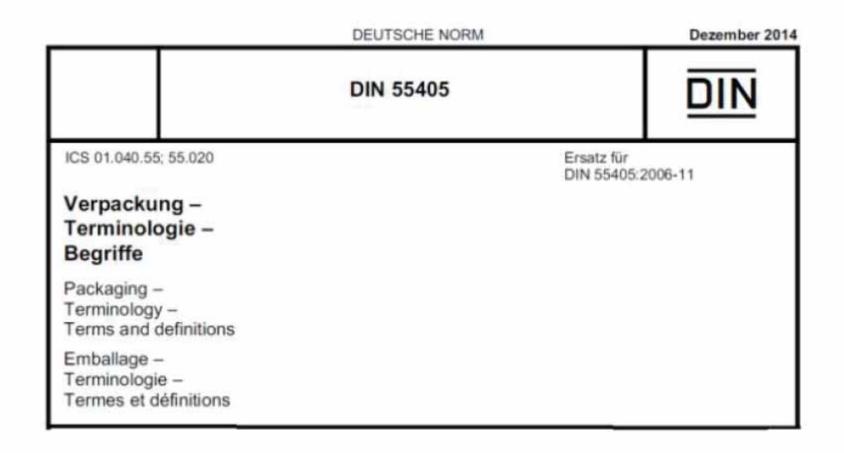
Even evaluating paper from a recycling point of view, to be included in the definition of "paper to be recycled", products made up of multiple materials must be predominantly composed (in a predominant, i.e. > 50% by weight) from paper and cardboard, as per UNI EN 643 standard.

Among other opinions, it is relevant the position paper of <u>EPDLA</u>, the European Polymer Dispersion and Latex Association:

..... When using polymer dispersions, the polymer content in the final product can be as low as 5%, so that we are convinced that such articles should not be seen as "plastic"



DIN 55405 standard



Items are plastics when the polymer constitutes the main material of the finished product.... "the main structural component of finished end products".

Plastic

Ethylene-vinyl alcohol copolymer (EVOH)

- Polyamide (PA)
- Polyethylene (PE)
- Low density polyethylene (PE-LD)
- High density polyethylene (PE-HD)
- Polypropylene (PP)
- Polystyrene (PS)
- Polyethylene terephthalate (PET)
- Polyvinyl chloride (PVC)
- Polycarbonate (PC)
- Polyvinylidene chloride (PVDC)
- Cellophane



PLASTIC FREE PAPERS





???

EN ISO 14021:2016/A1:2021

Environmental labels and declarations - Self-declared environmental claims (Type II environmental labelling) - Amendment 1: Carbon footprint, carbon neutral (ISO 14021:2016/Amd 1:2021)

5.4 Statements like "free of..."

An environmental claim of "... free" shall only be made when the level of the specified substance is no more than that which would be found as an acknowledged trace contaminant or background level.

ENVIRONMENTAL CLAIMS: PLASTIC FREE... AND MICROPLASTICS?



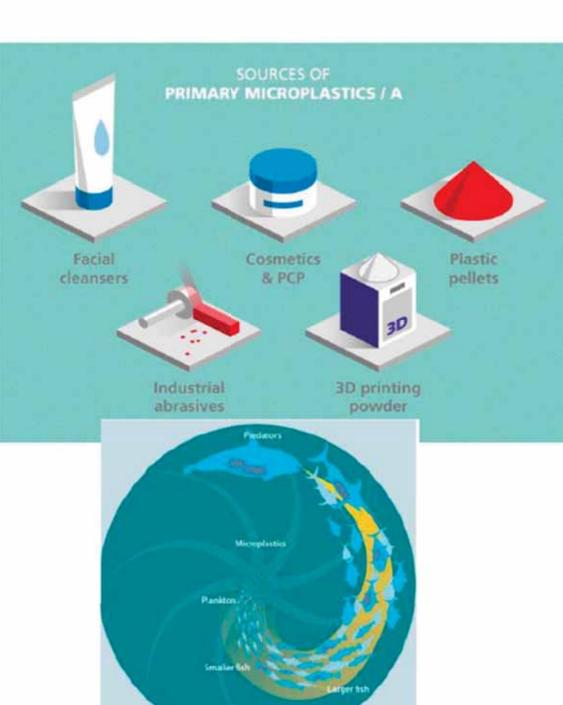
WHAT ARE THE MICROPLASTICS TO EVALUATE.... THOSE ADDED INTENTIONALLY OR EVEN THOSE RELEASED?

- Deliberately produced

One of the main sources of primary nanoplastics in the marine environment is cosmetics and personal hygiene products.

Resulting from fragmentation

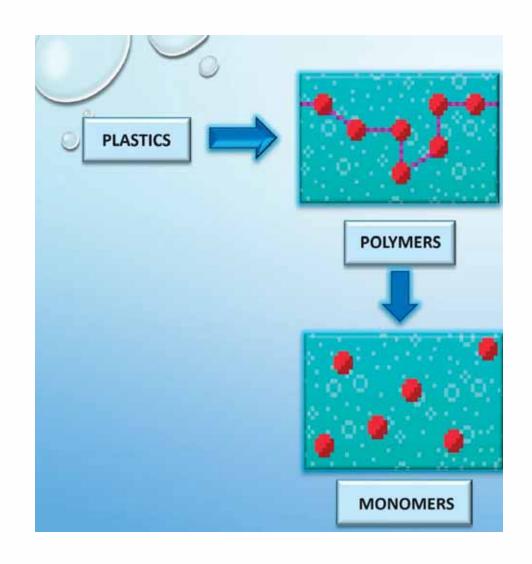
Secondary nanoplastics derived from postconsumer waste as well as from meso- or microplastics via degradation pose a specific challenge to the marine environment





THE ANALYTICAL METHODS

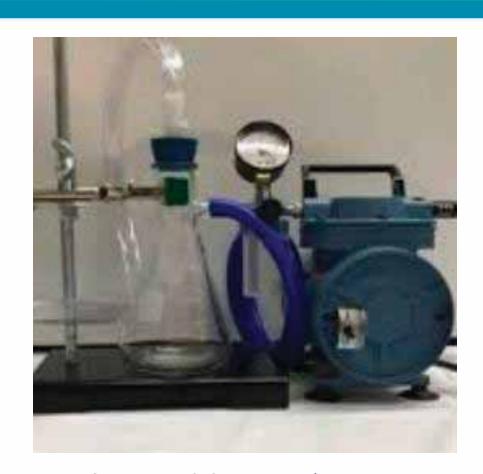
It is important to point out that many experts express a fundamental doubt:



Does the test identify microplastics?

Or maybe we detect the presence of monomers and oligomers, which are blocked by filters with particular porosity????



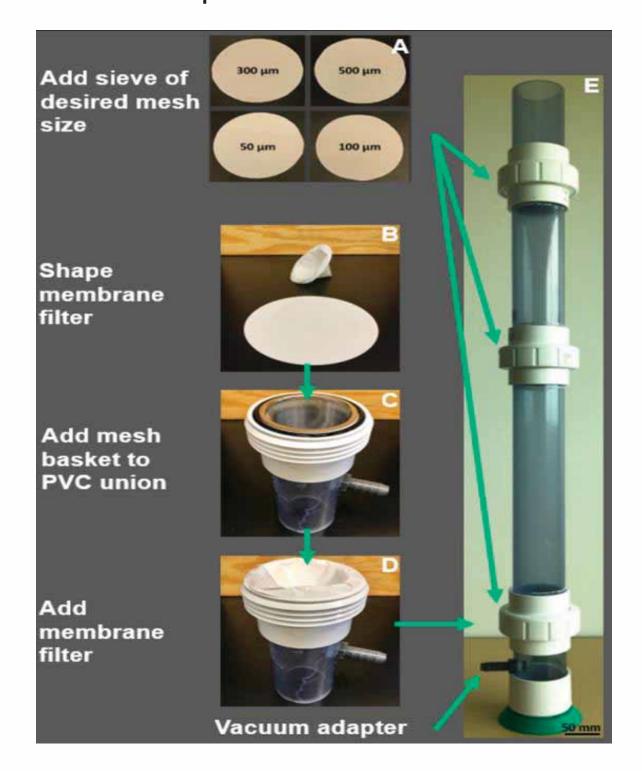


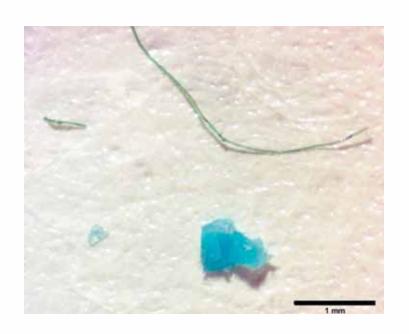
Images: doi:10.3791/57969

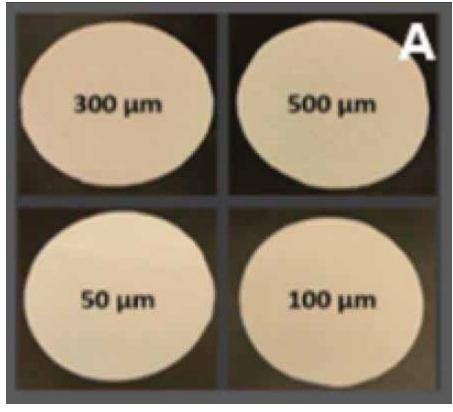
Pretreatment and filtration procedures

- Digestion
- Density flotation
- Filtration

Most labs perform filtration.





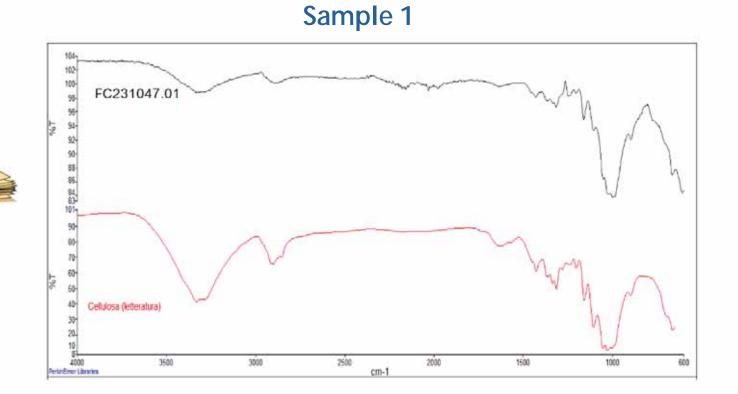




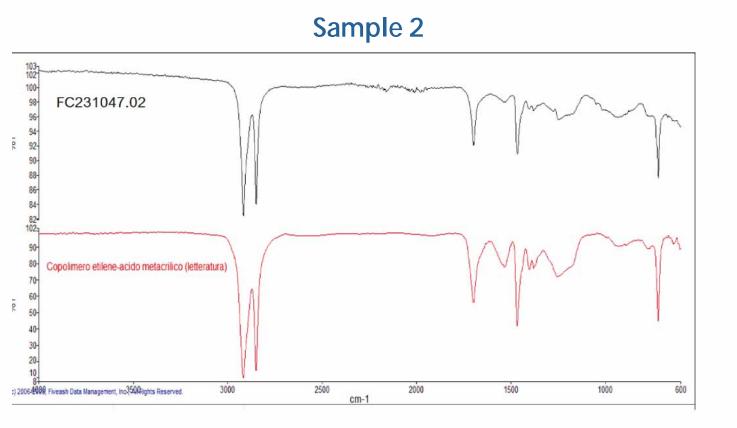
The evaluation of paper and cardboard contaminants to support environmental claims

Practical case verification of the possibility of declaring paper Plastic Free - ANALYTICAL EVALUATION

The two paper samples object of this study (glass and straw) were characterized by FT-IR analysis with ATR accessory, thermogravimetric analysis (TGA) and DSC analysis (Differential Scanning Calorimetry) to investigate the possible presence of polymeric compounds present in the matrix.



In figure 1 the sample 1 is compared with the library reference that provided the best match. The FT-IR analysis shows the **typical signals of Cellulose**.



In figure 2 the sample 2 is compared with the library reference that provided the best match. The FT-IR analysis shows the typical signals of the ethylene-methacrylic acid copolymer (the analysis was carried out on the inside of the glass). It is therefore a polymer coating.



MICROPLASTIC ANALYSIS ON AQUEOUS EXTRACT

The two samples were subjected to analysis of the cold and hot aqueous extract obtained according to the provisions of the UNI EN 645:2019 and UNI EN 647:1994 standards, to identify the release of microplastics. The results obtained are shown in the following table, where A indicates the cold extractions and B indicates the hot extractions.

	Acque destinata al consumo umano: 1047.01 A - FC231047.01 A		Acque destinata al consumo umano: 1047.01 B - FC231047.01 B Particelle su campione (N/L)		Acque destinata al consumo umano: 1047.02 A - FC231047.02 A Particelle su campione (N/L)		Acque destinata al consumo umano: 1047.02 B - FC231047.02 B Particelle su campione (N/L)					
	Particelle su campione (N/L)											
	20-50um	50-100um	100-500um	20-50um	50-100um	100-500um	20-50um	50-100um	100-500um	20-50um	50-100um	100-500um
Polyethylene	0	0	0	59	0	0	30	30	30	0	0	0
Polypropylene	71	36	0	593	296	178	502	30	0	915	30	30
Polyethylene terephthalate	0	9	0	1482	0	0	30	0	0	30	0	0
Polycarbonate	27	0	0	415	0	0	0	0	0	0	0	0
Polystyrene	0	0	0	59	0	0	0	0	0	0	0	0
Polytetrafluoroethylene	0	0	0	711	59	0	30	0	0	30	0	0
Polyvinyl chloride	0	O	0	3497	0	0	0	0	0	0	0	0
Polyamide	53	0	0	16952	771	237	0	0	30	295	0	0
Polymethyl methacrylate	124	9	0	59	0	0	0	0	0	0	0	0
Polyurethane	9	0	0	5868	296	0	30	0	30	30	0	0
Acrylonitrile butadiene styrene	9	0	0	2312	0	0	0	0	0	0	0	0
Other particles	604	80	62	5157	771	415	1358	177	118	6554	295	30

From the data reported, in the case of the SAMLPLE 1 the release of polymeric material (presumably polymer dispersions added in the production of paper) under hot extraction conditions is highlighted



Case History conclusions

Based on characterization tests carried out on the samples, it is possible to state that there are no plastic materials in the SAMPLE 1, since these materials were not present in the characterization testing carried out. But the hot extraction of the SAMPLE 1 shows the presence of polymeric components

IN CONCLUSION BOTH ITEM HAVE A POLYMERIC COMPONENT...

IS IT POSSIBLE TO DECLARE THE «PLASTIC FREE»??



COATING AND BARRIER MUST BE CHARACTERIZED

PLASTIC FREE PAPERS



???

- ☐ Plastic free claim is a self-certified sustainability label
- ☐ Plastic/Polymers can be detected only as trace contaminants
- ☐ It's important to check the presence/release of microplastics or other polymeric components

- SUPPORT DOCUMENTATION
- THIRD-PARTY VERIFICATION



Thanks for your kind attention!

. . questions?







FOOD CONTACT CENTER & FOOD CONTACT SERVICES S.r.I.

Phone: +39 0573 245244

e-mail: info@foodcontactcenter.com

website: www.foodcontactcenter.com

Offices and Materials Testing – Food Contact Services

Via Aldo Moro16, 25124 Brescia Italy

Office

Via Roma 64, 12100 Cuneo Italy

Laboratory

Via Redolone 65 51030 – Serravalle Pistoiese (PT) Italy

R&D - Pilot Plant

Via E. Pestalozzi 63 51100 – Pistoia (PT) Italy

Legal Address

Via Vecchia Provinciale Lucchese 19E

51030 – Serravalle Pistoiese (PT) Italy

