BISPHENOLS ANALYSIS IN LEATHER

Karine Lio, Nicolas Blanc

CTC, 4, rue Hermann FRENKEL 69367 LYON CEDEX 07, klio@ctcgroupe.com

ABSTRACT
In October 2020, Germany announced its intention to submit a proposal to restrict the use of Bisphenol A (BPA) in leathers in the EU along with any structurally related bisphenols of similar concern (BosC) for the environment including Bisphenol S (BPS) and Bisphenol F (BPF).
The following limits were proposed by Germany in the consultation document published in October 2021:
• 10 mg/kg for the sum of BPA and BosC in mixtures and leather articles
• 0,04 mg/l for the migration in articles exceeding the 10 mg/kg limit.
In the leather industry, Bisphenol F (CAS No. 620-92-8) can be an impurity in synthetic tanning agents. Bisphenol S (CAS No. 80-09-1) is a monomer that is used to manufacture synthetic tanning agents, which can lead to residues in the final product.
The purpose of this article is to describe the technical work produces by TC289 WG1 in order to assist the leather industries in anticipating potential bisphenol regulation.

Keywords: bisphenols– standardisation – TC289 WG1 – prEN ISO 11936 – REACh - syntan

1. Introduction

Bisphenol A is one of the most well-known substances in a bigger family of bisphenols, it is an industrial chemical that has been commonly used since the 1960s. BPA has been used in polycarbonate plastic and epoxy resin for decades. Products made of polycarbonate plastic include common consumer goods, such as re-usable plastic tableware and bottles for drinks, sports equipment, CDs and DVDs. Epoxy resins containing BPA are used to coat the inside of water pipes and the inside of cans for food and drink to increase their shelf-life and avoid getting a metallic taste on the food or drink.

BPA has been restricted as a substance on its own and in mixtures intended for consumer use in the EU since March 2018. Its use in thermal paper has been restricted since January 2020. From then on, substituting BPA with BPS became the norm across thermal paper manufacturers. BPS has the same properties as BPA for the industrial process but it is also suspected to affect human reproductive and hormonal systems.

To avoid this kind of substitutions where one hazardous bisphenol is replaced with another that may be equally hazardous, ECHA and the Member States have assessed the regulatory needs of 148 bisphenols as a group as a preparatory work for a more comprehensive regulatory strategy concerning these chemicals and to avoid possible regrettable substitution. In its report, ECHA proposes to address the uses of these substances as such, in mixtures and in articles such as thermal paper, plastics, textiles, leather and fur.

The difficulties for the leather sectors begin now. Indeed, BPA is not used in leather processing but others like BPS and BPF are involved in the tannery process. The leather sector reacted and asked to TC289 WG1 for a method in order to analyze Bisphenols in leathers and in particular BPS and BPF.

2. Regulatory context today

a. At the start: BPA regulation,

BPA is classified in the EU as a substance that causes damage fertility, may cause respiratory irritation, causes serious eye damage and may cause skin allergies. First let's focus on the EU food restriction. BPA can be used only as a monomer or primary substances but banned as an additive or auxiliary in materials that come into contact with food. Only a limited amount (0.05 mg/kg) is allowed to leach from the material into food. In addition, BPA has been banned in infant feeding bottles across the EU since June 2011 and in plastic bottles and packaging containing food for babies and children under three years since September 2018. Currently, The European Food Safety Authority (EFSA) is re-assessing the risks to public health related to BPA in foodstuffs and plans to finalise the updated assessment in 2022. In parallel, in toys, the migration limit on the amount of BPA that is allowed to leach out of toys for children up to the age of three and in any toys that are intended to be placed in a child's mouth was lowered from 0.1 mg/l to 0.04 mg/l in 2017.

b. German proposal and sensitizers

In October 2020, German authorities are preparing a proposal to restrict the use of BPA and other bisphenols with endocrine-disrupting properties for the environment. In April 2022, ECHA and the Member States have assessed a group of 148 bisphenols and recommended that 34 of them be subject to a group restriction within the meaning of Annex XVII of REACh due to their potential hormonal or reprotoxic effects. According to ECHA, many bisphenols are known endocrine disrupters both for human health and the environment. They also have reprotoxic properties. As they are widely used, a group restriction has been identified as the best way to manage the risks of 34 bisphenols. For the moment, three bisphenols (bisphenol A, bisphenol B and 2,2-bis(4'-hydroxyphenyl)-4- methylpentane) have already been identified by ECHA as substances of very high concern (SVHCs). In the coming year, the list of bisphenols deemed to have potential endocrine disrupting and reprotoxic properties will be extended based on existing data and new data obtained. Once it is clearer which bisphenols the German proposal will cover, ECHA and the European Commission will consider any further needs for regulatory action on bisphenols. After two postponements, the German proposal submission is now expected for the end of 2022. In addition, the French and Swedish authorities have proposed to restrict over 1 000 skin sensitising chemicals in clothing, footwear and other articles with a similar skin contact including BPA and other bisphenols which have been identified as skin sensitisers.

3. Bisphenols in tannery industries

In the leather industry, bisphenol F (CAS No. 620-92-8) can be an impurity in synthetic tanning agents. Bisphenol S (CAS No. 80-09-1) is a monomer that is used to manufacture synthetic tanning agents, which can lead to residues in the final product. These tanning and re-tanning agents allow the manufacture of white leathers and to give a better levelling and filling effect on the leather.

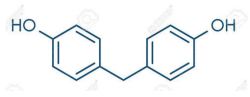
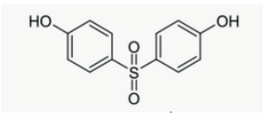
Chemical substances	CAS N°	ECS N°	Synonymes	Physical aspect
bisphenol F $C_{13}H_{12}O_2$ 	620-92-8	210-658-2	BPF ; 4,4'-methylenediphenol ; bis(4-hydroxyphenyl)methane ; 4-[(4-hydroxyphenyl)methyl] phenol ; p,p'-methylenediphenol ; p-(p-hydroxybenzyl)phenol	Solid
bisphenol S $C_{12}H_{10}O_4S$ 	80-09-1	201-250-5	BPS ; 4.4'-bisphenol S ; 4,4'-sulphonyldiphenol ; bis(4-hydroxyphenyl)sulfon ; 4-((4-hydroxybenzène)sulfonyl) phenol ; 4,4'-dihydroxydiphenyl sulfone ; bis(p-hydroxyphenyl) sulfone ; 4,4'-dihydroxydiphenol sulfone ; 1,1'-sulfonylbis[4-hydroxybenzene]	White powder

Table 1. Reference of Bisphenol S and F

4. Steps of the method

When industries understood that their process will be impacted by the regulation even if we don't know at that time which components, which limit and if the regulation will focus on the migration or total amount. One thing is sure, it is that the use of BPS and BPF will be regulated in the future.

Leather sector decided to challenge experts in the TC289 WG1 in order to develop a new method to extract the total amount of BPS and BPF from the leather and to quantify them with the best Limit of Quantification (LOQ).

BPS and BPF are new substances but we can lean on the already existing method to analyse BPA in thermal paper.

To evaluate the relevancy of this method and before starting to write a new standard, an interlaboratory trial was organised.

a. Interlaboratory trials

This interlaboratory trial was organised with 7 laboratories on 6 leathers coming from production. Laboratories carried out this trial by using the same extraction procedure but analytical technics could be different: liquid chromatography (LC) with triple quadrupole mass spectrometer (MS/MS) or with ultraviolet (UV) detector or with Diode Array Detector (DAD) or Fluorescence Detector (FLD) due to the availability of the apparatus. The main difference is the LOQ (from 10mg/kg to 100mg/kg).

	Bisphenol S		Bisphenol F	
	Mean (mg/kg)	Standard Deviation (mg/kg)	Mean (mg/kg)	Standard Deviation (mg/kg)
Leather A	3591	745	< LOQ	
Leather B	457	89	< LOQ	
Leather C	1009	181	303	74
Leather D	< LOQ		< LOQ	
Leather E	1406	244	100	11
Leather F	201	40	116	27

Table 2. Results of the interlaboratory trial

According to these satisfactory results in table 2, the standardisation of the method can begin.

b. The method description

As described above, the analysis of the bisphenols is possible with liquid chromatography (LC) with triple quadrupole mass spectrometer (MS/MS) or with ultraviolet (UV) detector or with Diode Array Detector (DAD) or Fluorescence Detector (FLD). But considering the future requirements imposed by the EU regulation, the best quantification limits we can reach, the best answer we can give to the leather industries with this objective, the following method described will use LC-MS/MS.

- **Sample preparation and extraction**

1 g of leather pieces were weighed. Leather sample is manually cut into small pieces (from 3 mm to 5 mm side length). The sample is placed in a screw-top glass container with 20 ml of methanol. After closing the container, the extraction can begin for 60 ± 5 minutes in an ultrasonic bath at 60 ± 5°C.

- **Calibration and quantification**

After cooling down to room temperature, an aliquot of the extraction solution is removed and transferred into a Liquid Chromatography sample vial, ready for the LC-MS/MS analysis.

Calibration is carried out using individual commercial solutions at 1mg/l or 10mg/l in the methanol Thus, a

mixture in methanol of all Bisphenols at 1µg/L is carried out and is prepared following the table 3.

To offset the systematic errors due to the leather matrix effects, an internal standard at 50mg/L in methanol is prepared and added in all the standard solutions, blank and sample. This internal standard must have similar chemical properties as Bisphenols and Bisphenol A-D8, CAS No. 92739-58-7 is a good compromise.

Concentration (µg/l)	**20**	**50**	**100**	**200**	**500**	**1000**
Volume methanol (µl)	980	950	900	980	950	900
Volume of mix of bisphenols,1 mg/l (µl)	20	50	100			
Volume of mix of bisphenols,10 mg/l (µl)				20	50	100
Volume of internal standard at 50 mg/l (µl)	20	20	20	20	20	20

Table 3. Example of calibration solutions for LC-MS/MS

The separation is carried out on LC with a column C18 (2.7 µm), (150 × 3,0) mm, with methanol and ultrapure water as mobile phase. The flow rate is 400µl/min and the injection volume is 2µl. The gradient program is described in table 3.

Time (min)	**Eluent 1: methanol (%)**	**Eluent 2: Ultrapure water (%)**
0	45	55
12	90	10
14	90	10
14.1	45	55
21	45	55

Table 4. Gradient Program

The detection is performed with a triple quadrupole mass spectrometer, with electrospray ion source in negative mode. The source parameters are given in the table 4.

Parameter	**Value**
Drying gas temperature	300 °C
Drying gas flow	6 L/min
Nebulization pressure	45 psi
Sheath gas temperature	320 °C
Sheath gas flow	11 L/min
Capillary voltage	2000 V

Table 5. Electrospray ion source parameters

The mode « Multiple Reaction Monitoring » (MRM) allows the quantification of the bisphenols.

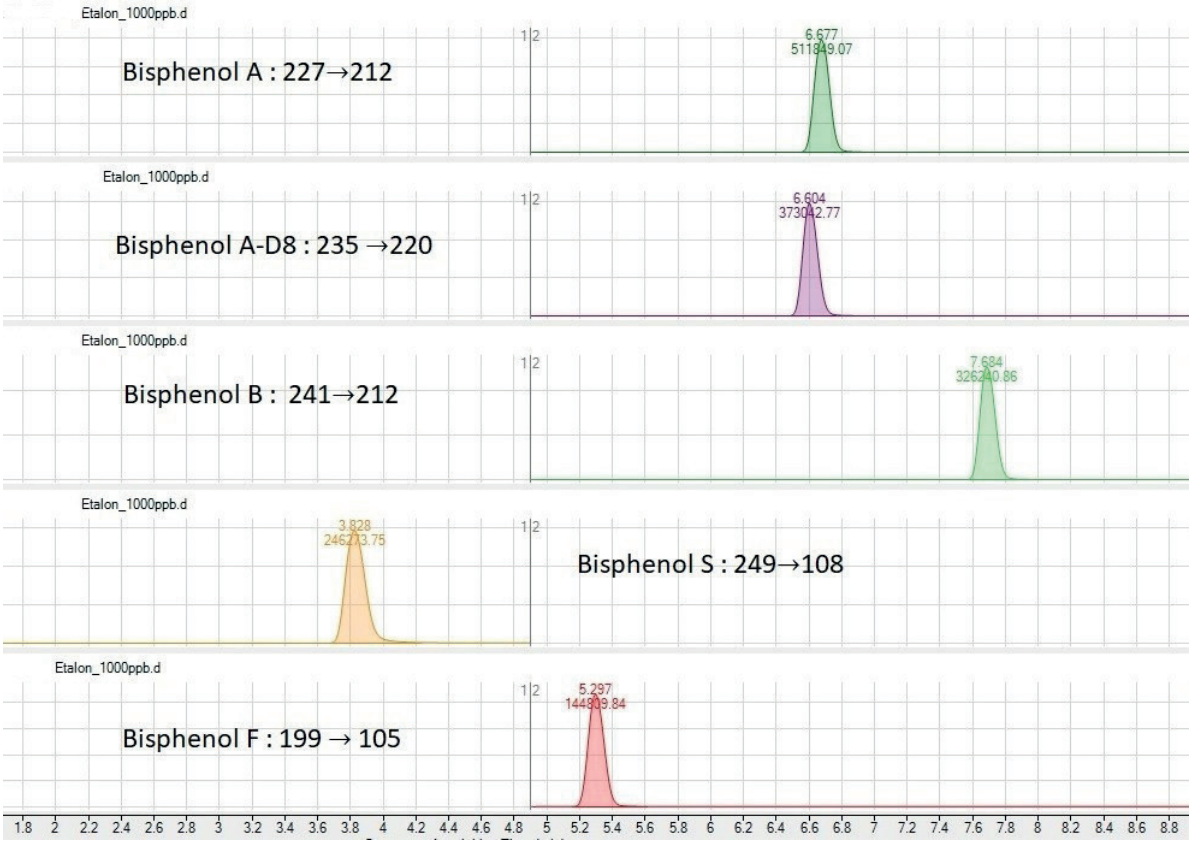


Table 6. Chromatogram and Precursor and Product ions

c. Different stages of the bisphenol standard's planning

We are Here

Stage	Description	Period
Working Draft	Elaboration of the Draft comments by IUC experts	2021.10.05 to 2022.01.27
DIS (Draft) registered	Registration of the draft ISO/DIS 11936 managed by the experts from IUC	2022.03.10
DIS (Draft) Ballot	Member bodies vote and make editorial and technical comments	2022.05.12 to 2022.08.04
	Discussion of the technical and editorial comments and improvement of the draft by IUC experts	Join meeting IUC TC289 WG1 in October 2022
FDIS (Final Draft) registered for formal vote	Member bodies vote and make editorial comments	Target date 2022.11.24
	Discussion of editorial comments and improvement of the Final Draft by IUC experts	Join meeting IUC TC289 WG1 in march 2023
International standard published	Publication of the standard ISO 11936 by ISO	Target date 2023.03.10 and limit date 2023.10.18

Table 7. Steps of standard's planning

5. Conclusion and prospect

This method's development conducted by IUC/TC289 WG1 at the request of the leather sector has provide a first standard draft economically viable and easily applicable in laboratory. This method is necessary to answer to the current regulation and will be improve thanks to standardization process. In spring 2023, the laboratories will dispose of a harmonize method and will provide comparable results referring to the ISO 11936.

Presently, we don't know what will be the regulation in the next years but we are sure that the number of substances will not decrease and the requirement regarding the acceptable limits will not increase.

The standardization and the experts will be more and more responsive and adaptable to quickly add new relevant substances to the method and to elaborate new way to extract these substances for example if regulation will consider migration and not total amount.

6. Acknowledgements

Thank you to Mr. Pierre-Marie Plouhinec for his help in for reviewing this article.

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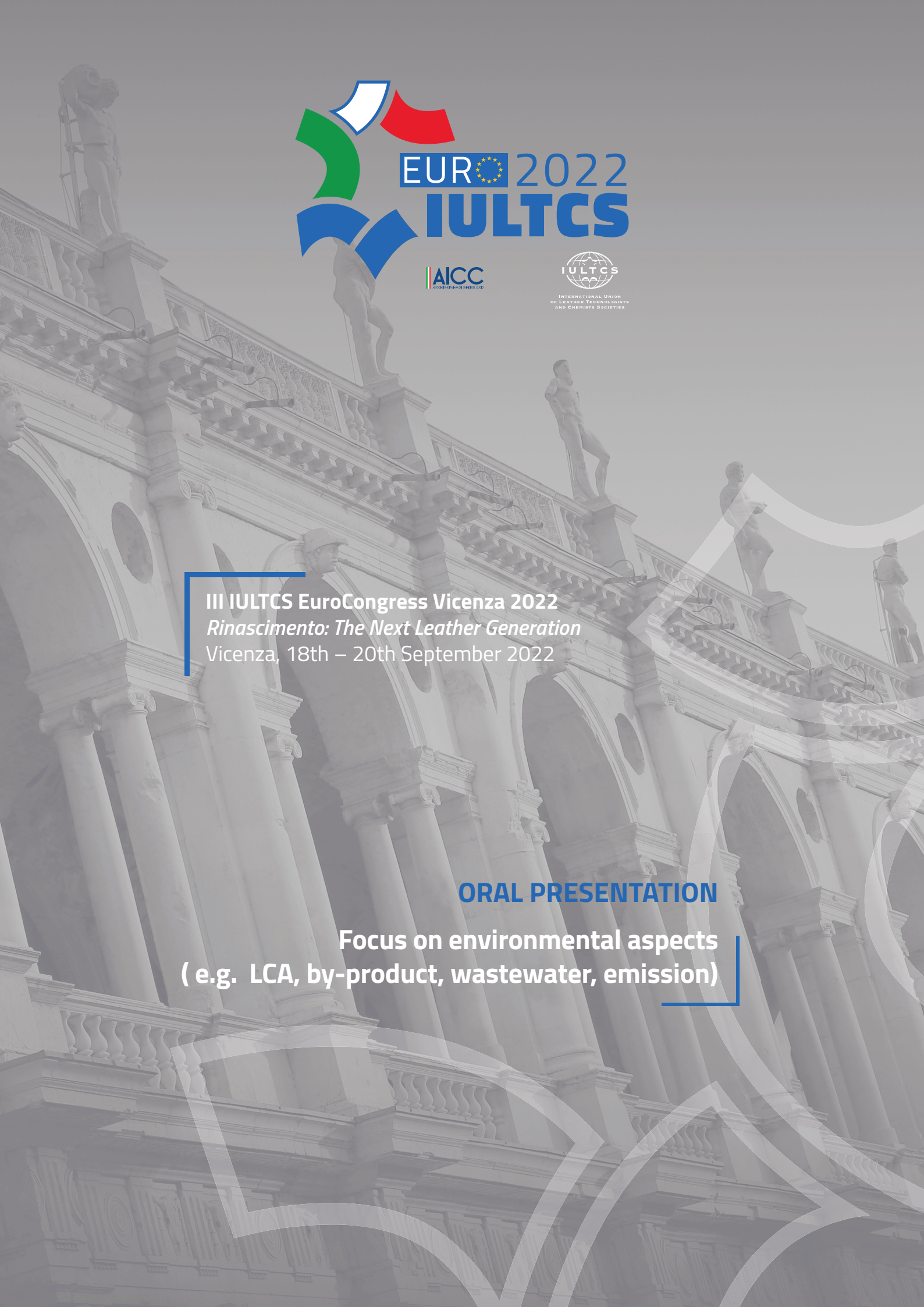
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5. ISO 13528:2015 Statistical methods for use in proficiency testing by interlaboratory comparison

Note





III IULTCS EuroCongress Vicenza 2022
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Vicenza, 18th – 20th September 2022

ORAL PRESENTATION

Focus on environmental aspects
(e.g. LCA, by-product, wastewater, emission)