



TÜRKİYE ŞİŞE VE CAM FABRİKALARI A.Ş.
Research and Technologies Development Presidency
Science, Technology and Design Center, Cumhuriyet Mahallesi Şişecam yolu Sokak,
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AB-1033-T
25838
Month-Year (07-2020)

REPORT

Requested by	: Paşabahçe Cam San. ve Tic. A.Ş. Customer Technical Services Management
Applicant Address	: İçmeler Mah. D-100 Karayolu Cad. No.44 – A 34947 Tuzla / İstanbul
Delivered on	: 01.07.2020
Sample Definition	: Antimicrobial coated glassware
Sample No	: 24527-24528-24530
Date of Analysis	: 02.07.2020-08.07.2020
Report Date	: 08.07.2020

Method No and Standard Name	: AKL.DM.020- 84/500/EEC - BS 6748 - ASTM C738 - Italian Legislation DM - EN 1388-2 - DIN 51032
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An experimental work on the antibacterial coated glass sample was required by Paşabahçe Cam San. ve Tic. A.Ş. Customer Technical Services Management to certify whether they are suitable for use with foodstuffs.

The release of related elements defined below from the surface of the glass samples and total migration are analysed using the methods;

- 84/500/EEC Directive and BS 6748, "Specification for limits of metal release from ceramic ware, glassware, glass ceramic ware and vitreous enamel ware"
- ASTM C738, "Standard test method for lead and cadmium extracted from glazed ceramic surfaces"
- EN 1388-2, "Silicate surfaces in contact with foodstuffs - Determination of the release of lead and cadmium from silicate surfaces other than ceramic ware"
- DIN 51032, "Ceramics, glass, glass ceramics - Permissible limits for the release of lead and cadmium from articles intended for use in contact with food"
- Italian Legislation DM 21.03.73 Articles In Contact With Food Total Migration Test

The results of the experiments conducted with above mentioned methods are given in the following tables.

According to the 84/500/EEC Directive and BS 6748 standard, the release of lead (Pb) and cadmium (Cd) from the surface of the glassware intended to come into contact with foodstuffs using with %4 (v/v) acetic acid at 22±2°C and during 24±0.5h were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The results are given below in Table 1 and the limit values according to the Regulations; EU-EC/84/500, China GB 4806.5-2016, Germany LFGB, Austrian-BGBl

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Form No: KG.FO.20-2

Yayın Tarihi: 01.05.2005

Revizyon No: 08

Revizyon Tarihi: 06.12.2019



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Nr. 893/1993, France-2004/64DM/4B/COM/002, South Korea&Japan and Taiwan are given in Table 2. Besides the related elements (Pb, Cd), out of scope of the standard methods, the release amounts of barium (Ba), cobalt (Co), aluminium (Al), zinc (Zn), copper (Cu), tin (Sn) were determined by ICP-OES and antimony (Sb) and arsenic (As) by inductively coupled plasma mass spectrometry (ICP-MS) using 4% (v/v) acetic acid solution at 22±2°C during 24±0.5h. The results are given in Table 1.

Table 1. Pb, Cd, Ba, Co, Al, Zn, Sb, As, Cu, Sn release values from the surface of the glassware product

Product Description	Sample	Filling Volume (mL)	Pb Release (mg/L)	Cd Release (mg/L)	Ba Release (mg/L)	Co Release (mg/L)	Al Release (mg/L)	Zn Release (mg/L)	Sb Release (mg/L)	As Release (mg/L)	Cu Release (mg/L)	Sn Release (mg/L)
V-Block Coated Glassware	Sample 1	360	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
	Sample 2	360	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
	Sample 3	360	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
	Sample 4	360	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d

n.d.: not detected

Table 2. The limit values given in the Regulations

Regulation	Type of glass holloware	Limit (mg/L)							
		Pb	Cd	Ba	Co	Al	Zn	Sb	As
EU-EC/84/500	Articles with filling volume up to 1 L (All articles which can be filled)	4.0	0.3	_*	_*	_*	_*	_*	_*
Germany-LFGB		4.0	0.3	_*	0.1	_*	_*	_*	_*
Austrian-BGBl. Nr. 893/1993		4.0	0.3	1.0	0.1	_*	3.0	1.0	_*
France-2004/64DM/4B/COM/002		4.0	0.3	_*	0.02	1.0	_*	_*	0.002
China GB 4806.5-2016	< 600 mL	1.5	0.5	_*	_*	_*	_*	_*	_*
South Korea & Japan		1.5	0.5	_*	_*	_*	_*	_*	_*
Taiwan	< 1.1 L	5.0	0.5	_*	_*	_*	_*	_*	_*

*No limit value specified

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Another standard, applied during the experimental study is ASTM C738. The standard specifies simulated method of test with acetic acid solution for the release of Pb and Cd from the surface of the glassware, respectively, intended to come into contact with foodstuffs.

The release of Pb, Cd and Ba amounts using with %4 (v/v) acetic acid solution at $22\pm 2^{\circ}\text{C}$ and during $24\pm 0.5\text{h}$ were measured by ICP-OES. The results obtained for the elements leached in parts per million for each unit tested and the limit values for the related elements according to California Prop.65 and the Norwegian Requirements are given in Table 3 and 4.

Table 3. Pb, Cd, Ba release values from the surface of the glassware product with acetic acid (ASTM C738 standard method)

Product Description	Sample	Filling Volume mL	Pb Release mg/L	Cd Release mg/L	Ba Release mg/L
V-Block Coated Glassware	Sample 1	90	n.d	n.d	n.d
	Sample 2	90	n.d	n.d	n.d
	Sample 3	90	n.d	n.d	n.d
	Sample 4	90	n.d	n.d	n.d

n.d.: not detected

Table 4. The limit values given in the regulations

Regulation	Type of Article	Pb	Cd	Ba
Norwegian Requirements	Category 1: 1-Articles which cannot be filled 2-Articles which can be filled, the internal depth of which, measured from the lowest point to the horizontal plane passing through the upper rim, does not exceed 25mm (flatware articles) 3-The mouth rim of articles meant for drinking purposes (eg. mugs and cups)	0.02 mg/dm ²	0.002 mg/dm ²	0.2 mg/dm ²
	Category 2: All other articles which can be filled, except flatware articles	0.1 mg/l	0.01 mg/l	1 mg/l
	Category 3: 1- Cooking ware 2- Storage vessels having a capacity of more than three liters	1.5 mg/l	0.1 mg/l	-*
California Prop. 65	Flatware	0.226 mg/l	1.853 mg/l	-*
	Hollowware	0.100 mg/l	0.189 mg/l (for small hollowware) 0.049 mg/l (for large hollowware)	-*

*No limit value specified

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EN 1388-2/ DIN 51032 specify a method for testing the rim of drinking vessels, which comes into the contact with lips. The release of Pb and Cd from the lip and rim area of the glassware intended to come into contact with foodstuffs at 20°C to 24°C for 24 h and are measured by atomic absorption spectrometry. The results and the limit values given in DIN 51032 are shown below in Table 5.

Table 5. Pb and Cd release values from the drinking rim of the glassware products according to EN 1388-2 and DIN 51032 standard methods

Product Description	Samples	Pb* (mg/drinking rim)	Cd* (mg/drinking rim)	Ba* (mg/drinking rim)	Cu** (mg/drinking rim)	Zn** (mg/drinking rim)	Sn** (mg/drinking rim)	The Limit Values Given in DIN 51032	
								Pb (mg/drinking rim)	Cd (mg/drinking rim)
V-Block Coated Glassware	Sample 1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2	0.2
	Sample 2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
	Sample 3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
	Sample 4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		

n.d.: not detected

*Norwegian Requirements – Pb: 0.02 mg/dm²; Cd: 0.002 mg/dm²; Ba: 0.2 mg/dm²

**No limit value specified

The measurable limits (Limit of Quantifications - LOQ) for the related methods are listed below:

Elements	LOQ mg/L
Pb (ICP-OES)	0.01
Cd (ICP-OES)	0.0005
Ba (ICP-OES)	0.0006
Co (ICP-OES)	0.0007
Al (ICP-OES)	0.004
Zn (ICP-OES)	0.0005
Cu (ICP-OES)	0.001
Sb (ICP-MS)	0.00003
As (ICP-MS)	0.0001
Sn (ICP-OES)	0.002

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Total Migration Test

Italian Legislation DM 21.03.73 standard was also applied to the glassware samples. Italian Legislation DM 21.03.73 Category B specifies a method (including extraction with distilled water at 80°C for 2 hours and determination of the total migration) for containers to be used in contact with food at temperatures lower than 80°C. The results and limit values are given below in Table 6.

Table 6. The result of migration test of the glassware product (DM 21.03.73 Cat B)*

Product Description	Total Volume (mL)	The Number of Samples Taken into The Test	Cat. B 80 °C (mg/L)	Official Limit Value acc. to DM 21.03.73 for Cat. B (mg/L)
V-Block Coated Glassware	338.6	2	1.06	50

*Out of accreditation scope

RESULTS:

- Leachable elements from the surface of the antimicrobial coated glassware samples with acetic acid solution by using the methods defined in Directive 84/500/EEC, BS 6748 and ASTM C738 did not show any detection.
- The results obtained did not show any detection for Pb and Cd migration from the lip and rim area of the glassware products within the measurable limits according to EN1388-2, DIN 51032 standard methods.
- The obtained value from the analysis did not exceed the limit values given in Italian Legislation DM 21.03.73.

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Analyst

Tester

Esra Duman
Analyst

Approval

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