TÜRKİYE ŞİŞE VE CAM FABRİKALARI A.Ş.
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Test
TS EN ISO/IEC 17025
AB-1033-T

AB-1033-T
2023-14114
Month-Year (04-2023)

REPORT

Requested by	:	Certification and Product Performance Management
Applicant Address	:	İçmeler Mah. D-100 Karayolu Cad. No.44 – A 34947 Tuzla / İstanbul
Delivered on	:	17.01.2023 (Request date)
Sample Definition	:	Glassware Products (Soda-lime- silicate glass type)
Sample No	:	2023(2839-2840-2842-2843)
Date of Analysis	:	23.01.2023-05.04.2023
Report Date	:	07.04.2023

Method No and Standard Name	:	**AKL.DM.020- *84/500/EEC - BS 6748 – ASTM C738 AKL.DM.005***

An experimental work on the glassware products (automatic soda-lime-silica type glass products, manufactured at Şişecam Cam Ev Eşyası Kırklareli Plant Branch, Şişecam Cam Ev Eşyası Eskişehir Plant Branch, Paşabahçe Bulgaria EAD, Paşabahçe Egypt Glass Manufacturing S.A.E, were required by Certification and Product Performance Management to certify whether they are suitable for use with foodstuffs.

The release of lead, cadmium from the inner surface of the glass sample and the heavy metal contents in the glass sample are analysed using the methods below;

- 84/500/EEC Directive and BS 6748," Specification for limits of metal release from ceramic ware, glassware, glass ceramic ware and vitreous enamel ware"
- ISO 7086-1: Glass hollowware in contact with food — Release of lead and cadmium — Part 1: Test method
- ISO 7086-2: Glass hollowware in contact with food — Release of lead and cadmium — Part 2: Permissible limits
- ES:2060-2/ 2007 Release of lead and cadmium from ware in contact with food and beverages Part (2) : Ceramic ware, glass-ceramic ware, and glass dinner ware.
- ISO 6486-1: Ceramic ware, glass ceramic ware and glass dinnerware in contact with food — Release of lead and cadmium — Part 1: Test method
- ASTM C738, "Standard Test Method for Lead and Cadmium Extracted from Glazed Ceramic Surfaces"

- "A recommended procedure for the determination of lead and cadmium at trace levels in glass" Glass Technol., 2000, 41 (4), 130-134, developed by Technical Committee 2 (TC2), Chemical Durability and Analysis of International Commission on Glass (ICG)
- "A collaborative study for the determination of mercury in glass packaging by cold vapour atomic absorption spectrometry" Glass Technol., 2001, 42 (1), 24-29, developed by TC2, ICG
- "Collaborative study on the determination of hexavalent chromium in container glasses" Glass Technol., 2001, 42 (6), 148-52, developed by TC2, ICG

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

The Release of Elements from the Inner Surface of the Glassware

According to the 84/500/EEC Directive, ISO 7086-1, ES:2060-2/ 2007, ISO 6486-1 and BS 6748 standard, the release of lead (Pb) and cadmium (Cd) from the inner surface of the glassware intended to come into contact with foodstuffs using with %4 (v/v) acetic acid at 22±2ºC and during 24±0.5h were determined by inductively coupled plasma optic emission spectrometry (ICP-OES) The results are given below in Table 1 and the limit values according to the Regulations; EU-EC/84/500, ISO 7086-2, China GB 4806.5-2016, Germany LFGB, Austrian-BGBI Nr. 893/1993, France-2004/64DM/4B/COM/002, South Korea & Japan Spain 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), antimony (Sb), and arsenic (As) using both 4% (v/v) acetic acid solutions at 22±2°C and during 24±0.5h, was determined by ICP-OES and inductively coupled plasma mass spectrometry (ICP-MS). The results are given below in Table 1.

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Table 1. Pb, Cd, Ba, Co, Al, Zn, Sb, As release values from the inner surface of the glassware product using acetic acid

Product Description	Samples	Filling Volume mL	Results	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
ŞCEE Kırklareli Plant Branch Automatic SLS type glass products	Sample 1	275	PASS	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
	Sample 2	275	PASS	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
	Sample 3	275	PASS	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
	Sample 4	275	PASS	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
ŞCEE Eskişehir Plant Branch Automatic SLS type glass products	Sample 1	200	PASS	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
	Sample 2	200	PASS	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
	Sample 3	200	PASS	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
	Sample 4	200	PASS	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Paşabahçe Bulgaria EAD Automatic SLS type glass products	Sample 1	280	PASS	n.d	n.d	n.d	n.d	<0.03	n.d	n.d	n.d
	Sample 2	200	PASS	n.d	n.d	n.d	n.d	<0.03	n.d	n.d	n.d
	Sample 3	200	PASS	n.d	n.d	n.d	n.d	<0.03	n.d	n.d	n.d
	Sample 4	200	PASS	n.d	n.d	n.d	n.d	<0.03	n.d	n.d	n.d
Paşabahçe Egypt Glass Manufacturing S.A.E Automatic SLS type glass products	Sample 1	215	PASS	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
	Sample 2	215	PASS	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
	Sample 3	215	PASS	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
	Sample 4	215	PASS	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 / Standard	Type of glass hollowware	Limit (mg/L)							
		Pb	Cd	Ba	Co	Al	Zn	Sb	As
EU-EC/84/500	Category 2 : All other articles which can be filled	4.0	0.3	-*	-*	-*	-*	-*	-*
Germany-LFGB	Fillable article < 1.1 Liter	4.0	0.3	-*	-*	-*	-*	-*	-*
ISO 7086-2	Small (<600 mL)	1.5	0.5	-*	-*	-*	-*	-*	-*
	Large (600 mL – 3L)	0.75	0.25	-*	-*	-*	-*	-*	-*
	Storage (≥ 3 L)	0.5	0.25	-*	-*	-*	-*	-*	-*
ISO 6486-2	Small Hollow Ware	2	0.5	-*	-*	-*	-*	-*	-*
	Large Hollow Ware	1	0.25	-*	-*	-*	-*	-*	-*
	Storage Ware	0.5	0.25	-*	-*	-*	-*	-*	-*
	Flatware	0.8 mg/dm^2	0.07 mg/dm^2	-*	-*	-*	-*	-*	-*
Austrian-BGBI. Nr. 893/1993	Fillable article < 1.1 Liter	4.0	0.3	1.0	-*	-*	3.0	1.0	-*
France-2004/64DM/ 4B/COM/002	Fillable article < 1.1 Liter	4.0	0.3	-*	0.02	1.0	-*	-*	0.002
China GB 4806.5-2016	Fillable article < 1.1 Liter	0.75	0.25	-*	-*	-*	-*	-*	-*
South Korea & Japan	Fillable article < 600 ml	1.5	0.5	-*	-*	-*	-*	-*	-*
Taiwan	Fillable article < 1.1 Liter	5.0	0.5	-*	-*	-*	-*	-*	-*
ES:2060-2/2007	Small Hollow Ware	2	0.5	-*	-*	-*	-*	-*	-*
	Large Hollow vessels	1	0.25	-*	-*	-*	-*	-*	-*
	Hollow Storage Ware	0.5	0.25	-*	-*	-*	-*	-*	-*

**No limit value specified*.

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 inner 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±2ºC and during 24±0.5h were determined by ICP-OES and ICP-MS. 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 inner surface of the glassware product with acetic acid (ASTM C738 standard method)

Product Description	Samples	Results	Filling Volume mL	Pb Release mg/L	Cd Release mg/L	Ba Release mg/L
ŞCEE Kırklareli Plant Branch Automatic SLS type glass products	Sample 1	PASS	275	n.d	n.d	n.d
	Sample 2	PASS	275	n.d	n.d	n.d
	Sample 3	PASS	275	n.d	n.d	n.d
	Sample 4	PASS	275	n.d	n.d	n.d
ŞCEE Eskişehir Plant Branch Automatic SLS type glass products	Sample 1	PASS	200	n.d	n.d	n.d
	Sample 2	PASS	200	n.d	n.d	n.d
	Sample 3	PASS	200	n.d	n.d	n.d
	Sample 4	PASS	200	n.d	n.d	n.d
Paşabahçe Bulgaria EAD Automatic SLS type glass products	Sample 1	PASS	280	n.d	n.d	n.d
	Sample 2	PASS	200	n.d	n.d	n.d
	Sample 3	PASS	200	n.d	n.d	n.d
	Sample 4	PASS	200	n.d	n.d	n.d
Paşabahçe Egypt Glass Manufacturing S.A.E Automatic SLS type glass products	Sample 1	PASS	215	n.d	n.d	n.d
	Sample 2	PASS	215	n.d	n.d	n.d
	Sample 3	PASS	215	n.d	n.d	n.d
	Sample 4	PASS	215	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 3-The mounth 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*.

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)	0.001
Ba (ICP-MS)	0.00006
Co (ICP-OES)	0.02
Al (ICP-OES)	0.03
Zn (ICP-OES)	0.02
Sb (ICP-MS)	0.00006
As (ICP-MS)	0.0001

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Heavy Metal (Pb, Cd, Cr^{+6}, Hg) Content

The amount of heavy metal contents in the glassware product are determined by using the methods listed above is given in Table 5.

Table 5. Heavy metal analysis of the glassware product

Product Description	Pb ppm	Cd ppm	Cr^{+6} ppm	Hg ppm
ŞCEE Kırklareli Plant Branch Automatic SLS type glass products	n.d.	n.d.	n.d.	n.d.
ŞCEE Eskişehir Plant Branch Automatic SLS type glass products	n.d.	n.d.	n.d.	n.d.
Paşabahçe Bulgaria EAD Automatic SLS type glass products	n.d.	n.d.	n.d.	n.d.
Paşabahçe Egypt Glass Manufacturing S.A.E Automatic SLS type glass products	n.d.	n.d.	n.d.	n.d.

n.d: not detected

The methods are sensitive down to the values (LOD) of FAAS listed below:

Cd	0.1 ppm
Hg	0.1 ppm
Cr^{+6}	0.2 ppm
Pb	0.5 ppm

Chemical Composition

The chemical composition of automatic soda-lime-silica type glass products, which are manufactured at Şişecam Cam Ev Eşyası Kırklareli Plant Branch, Şişecam Cam Ev Eşyası Eskişehir Plant Branch, Paşabahçe Bulgaria EAD, Paşabahçe Egypt Glass Manufacturing S.A.E are regularly controlled by the analyses carried out with X-ray fluorescence spectrometer.

The chemical composition ranges of the above mentioned products are given in below Tables.

Table 6. The Chemical Composition Ranges of Colourless Automatic Tableware Products Manufactured by Şişecam Cam Ev Eşyası Kırklareli Plant Branch *

Constituent Oxide	% (wt)
SiO_2	< 72.0
Al_2O_3	< 1.74
Fe_2O_3	< 0.024
TiO_2	< 0.045
CaO	< 10.4
MgO	< 2.34
Na_2O	< 13.7
K_2O	< 0.08
SO_3	< 0.30
CeO_2	< 0.03

Table 7. The Chemical Composition Ranges of Flint Automatic Tableware Products Manufactured by Şişecam Cam Ev Eşyası Eskişehir Plant Branch*

Constituent Oxide	% (wt)
SiO_2	< 72.0
Al_2O_3	< 1.60
Fe_2O_3	< 0.022
TiO_2	< 0.05
CaO	< 8.60
MgO	< 3.60
Na_2O	< 14.6
K_2O	< 0.07
SO_3	< 0.30
CeO_2	< 0.04

Table 8. The Chemical Composition Ranges of Colourless Automatic Tableware Products Manufactured by Paşabahçe Bulgaria EAD. *

Constituent Oxide	% (wt)
SiO_2	< 72.3
Al_2O_3	< 1.76
Fe_2O_3	< 0.020
TiO_2	< 0.040
CaO	< 10.3
MgO	< 1.36
Na_2O	< 14.5
K_2O	< 0.09
SO_3	< 0.24

Table 9. The Chemical Composition Ranges of Colourless Automatic Tableware Products Manufactured by Paşabahçe Egypt Glass Manufacturing S.A.E *

Constituent Oxide	% (wt)
SiO_2	< 72.5
Al_2O_3	< 1.30
Fe_2O_3	< 0.02
TiO_2	< 0.03
CaO	< 10.3
MgO	< 1.40
Na_2O	< 14.6
K_2O	< 0.03
SO_3	< 0.30
CeO_2	< 0.03

**The producer keeps the right to change the composition of the products at any time without notice.*

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RESULTS:

- Leachable elements from the inner surface of the glass samples with acetic acid solution by using the methods defined in Directive 84/500/EEC, BS 6748 and ASTM C738 did not exceed the limit values given in the related regulations.
- According to European Parliament and Council Directive 94/62/EC, Article 11 specifies that “Member States shall ensure that the sum of concentration levels of lead, cadmium, mercury and hexavalent chromium present in packaging or packaging components shall not exceed 100 ppm by weight.

  According to National Legislation of Turkey, The Control of Packaging Waste Directive, Article 16 specifies that “Packaging manufacturers must ensure that the sum of concentration levels of lead, cadmium, mercury, and hexavalent chromium present in packaging or packaging components does not exceed 100 ppm by weight. However, this requirement does not apply to packages made from lead crystal glass. In the case of recycled material used for glass packaging production, the average values of total heavy metal content that are carried out the monthly analysis of the samples from each furnace, must not exceed 200 ppm level.

  The result of the tests according to the above-mentioned method with the above sensitivity limits showed that the heavy metals (lead, cadmium, hexavalent chromium and mercury) did not exist in measurable quantities in the mentioned products.

Approval		*Tester*			
Pınar Mercan	**Şirin Ustabaşı**	**Reyhan Arda**	**Çağrı Öztü**	**Derya Karahan**	**Sevda Lepter**
Lead Sn. Researcher	**Senior Researcher**	**Analyst**	**Analyst**	**Analyst**	**Analyst**