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AB-1033- T
Report No
2022-
16223
21529
21532
21535
21536
Month-Year
(05-22)

REPORT

Requested by	Şişecam Glassware-Certification and Product Performance Management
Applicant Address	İçmeler mahallesi D-100 Karayolu Cad. No.44 – A 34947 Tuzla / İstanbul
Delivered on	: 03.03.2022
Sample Definition	: Glassware Products (Soda-lime- silicate glass type)
Sample No	: 2022- (11789-11790-11791-11793-11794)
Date of Analysis	: 16.03.2022-20.04.2022
Report Date	: 11.05.2022

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, and Posuda Ltd.) were required by Şişecam Glassware-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"
- 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)

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AB-1033-T Report No 2022-16223 21529 21532 21535 21536 Month-Year (05-22)

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REPORT

- "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.

According to the 84/500/EEC Directive, 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±2°C and during 24±0.5h were determined by Flame Atomic Absorption Spectrometry (FAAS). 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-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	Pb Release mg/L	Cd Release mg/L	Ba Release mg/L	Co Release mg/L	AI Release mg/L	Zn Release mg/L	Sb Release mg/L	As Release mg/L
ŞCEE Kırklareli	Sample 1	200	n.d	n.d	n.d	n.d	0.023	n.d	n.d	n.d
Plant Branch Automatic SLS	Sample 2	200	n.d	n.d	n.d	n.d	0.024	n.d	n.d	n.d
type glass	Sample 3	200	n.d	n.d	n.d	n.d	0.021	n.d	n.d	n.d
products	Sample 4	200	n.d	n.d	n.d	n.d	0.022	n.d	n.d	n.d
ŞCEE Eskişehir	Sample 1	200	n.d	n.d	n.d	n.d	0.019	n.d	n.d	n.d
Plant Branch	Sample 2	200	n.d	n.d	n.d	n.d	0.019	n.d	n.d	n.d
Automatic SLS type glass	Sample 3	200	n.d	n.d	n.d	n.d	0.019	n.d	n.d	n.d
products	Sample 4	200	n.d	n.d	n.d	n.d	0.019	n.d	n.d	n.d
Paşabahçe	Sample 1	200	n.d	n.d	n.d	n.d	0.021	n.d	n.d	n.d
Bulgaria EAD	Sample 2	200	n.d	n.d	n.d	n.d	0.020	n.d	n.d	n.d
Automatic SLS type glass	Sample 3	200	n.d	n.d	n.d	n.d	0.020	n.d	n.d	n.d
products	Sample 4	200	n.d	n.d	n.d	n.d	0.021	n.d	n.d	n.d
Paşabahçe Egypt Glass	Sample 1	200	n.d	n.d	n.d	n.d	0.028	n.d	n.d	n.d
Manufacturing	Sample 2	200	n.d	n.d	n.d	n.d	0.028	n.d	n.d	n.d
S.A.E Automatic SLS	Sample 3	200	n.d	n.d	n.d	n.d	0.018	n.d	n.d	n.d
type glass products	Sample 4	200	n.d	n.d	n.d	n.d	0.018	n.d	n.d	n.d
	Sample 1	300	n.d	n.d	n.d	n.d	0.020	n.d	n.d	n.d
Posuda Ltd. Automatic SLS	Sample 2	300	n.d	n.d	n.d	n.d	0.020	n.d	n.d	n.d
type glass products	Sample 3	300	n.d	n.d	n.d	n.d	0.020	n.d	n.d	n.d
products	Sample 4	300	n.d	n.d	n.d	n.d	0.020	n.d	n.d	n.d

n.d: not detected

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Table 2. The limit values given in the Regulations

Dogulation	Type of glass				Limit ((mg/L)				
Regulation	hollowware	Pb	Cd	Ва	Со	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	_*	_*	_*	_*	_*	_*	
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	-*	_*	_*	_*	_*	_*	
	Small Hollow Ware	2	0.5	-*	-*	-*	-*	-*	-*	
ES:2060-2/2007	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±2°C and during 24±0.5h were determined by FAAS and 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.

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AB-1033-T Report No 2022-16223 21529 21532 21535 21536 Month-Year (05-22)

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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	Filling Volume mL	Pb Release mg/L	Cd Release mg/L	Ba Release mg/L
	Sample 1	200	n.d	n.d	n.d
ŞCEE Kırklareli Plant Branch	Sample 2	200	n.d	n.d	n.d
Automatic SLS type glass products	Sample 3	200	n.d	n.d	n.d
·	Sample 4	200	n.d	n.d	n.d
	Sample 1	200	n.d	n.d	n.d
ŞCEE Eskişehir Plant Branch	Sample 2	200	n.d	n.d	n.d
Automatic SLS type glass products	Sample 3	200	n.d	n.d	n.d
,	Sample 4	200	n.d	n.d	n.d
	Sample 1	200	n.d	n.d	n.d
Paşabahçe Bulgaria EAD Automatic SLS type glass	Sample 2	200	n.d	n.d	n.d
products	Sample 3	200	n.d	n.d	n.d
•	Sample 4	200	n.d	n.d	n.d
	Sample 1	200	n.d	n.d	n.d
Paşabahçe Egypt Glass Manufacturing S.A.E Automatic	Sample 2	200	n.d	n.d	n.d
SLS type glass products	Sample 3	200	n.d	n.d	n.d
71 3 1	Sample 4	200	n.d	n.d	n.d
	Sample 1	300	n.d	n.d	n.d
Posuda Ltd.	Sample 2	300	n.d	n.d	n.d
Automatic SLS type glass products	Sample 3	300	n.d	n.d	n.d
,	Sample 4	300	n.d	n.d	n.d

n.d: not detected

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AB-1033-T Report No 2022-16223 21529 21532 21535 21536 Month-Year (05-22)

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Table 4. The limit values given in the regulations

Regulation	Type of Article	Pb	Cd	Ва
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/dm²	0.002 mg/dm²	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	-*
	Flatware	0.226 mg/l	1.853 mg/l	-*
California Prop. 65	Hellowwere	0.100 ms/l	0.189 mg/l (for small hollowware)	_*
	Hollowware	0.100 mg/l	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 (FAAS)	0.05
Cd (FAAS)	0.004
Ba (ICP-OES)	0.001
Co (ICP-OES)	0.001
AI (ICP-OES)	0.01
Zn (ICP-OES)	0.001
Sb (ICP-MS)	0.00003
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.
Posuda Ltd. 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

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AB-1033-T Report No 2022-16223 21529 21532 21535 21536 Month-Year (05-22)

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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, and Posuda Ltd. 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 Al ₂ O ₃ Fe ₂ O ₃ TiO ₂ CaO MgO Na ₂ O K ₂ O SO ₃	< 72.0 < 1.90 < 0.022 < 0.05 < 10.5 < 2.40 < 14.0 < 0.07 < 0.30 < 0.03

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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 Al ₂ O ₃ Fe ₂ O ₃ TiO ₂ CaO MgO Na ₂ O K ₂ O SO ₃ CeO ₂	< 72.0 < 1.60 < 0.022 < 0.05 < 8.60 < 3.60 < 14.6 < 0.09 < 0.30 < 0.04

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

Constituent Oxide	% (wt)
SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ TiO ₂ CaO MgO Na ₂ O K ₂ O SO ₃	< 72.5 < 1.75 < 0.025 < 0.045 < 10.3 < 1.40 < 14.5 < 0.05 < 0.30

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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 Al ₂ O ₃ Fe ₂ O ₃ TiO ₂ CaO MgO Na ₂ O K ₂ O SO ₃	< 72.3 < 1.40 < 0.017 < 0.03 < 10.3 < 1.40 < 14.6 < 0.02 < 0.30 < 0.03

Table 10. The Chemical Composition Ranges of Colourless Automatic Tableware Products Manufactured by Posuda Ltd. *

Constituent Oxide	% (wt)
SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ TiO ₂ CaO MgO Na ₂ O K ₂ O SO ₃	< 73.0 < 2.00 < 0.025 < 0.010 < 11.3 < 0.50 < 14.0 < 0.02 < 0.30

^{*}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
Pinar Mercan
Lead Researcher

Reyhan Arda Analyst Tester

Çağrı Öztü Analyst

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