

Measures to Ensure Compliance with the Limit Value for Phosphorus in Automatic Dishwasher Detergents

Working Group Ad hoc AG „Phosphorbestimmung in Gemischen“ in The German Cosmetic, Toiletry, Perfumery and Detergent Association*

abstract

As of 1 January 2017, the Amendment (EU) No. 259/2012 for Annex VIa of the Detergents Regulation (EU) No. 648/2004 goes into effect. It states that consumer automatic dishwasher detergents can only be placed on the market if their total content of phosphorus is less than 0.3 grams in the standard dosage (reference: 12 place settings of normally soiled tableware). Automatic dishwasher detergents, which have already been placed on the market up until 31 December 2016 within the meaning of the Detergents Regulation and still contain 0.3 grams of phosphorous or more in the standard dosage, can still be sold without any restriction, also beyond 1 January 2017. This applies to both retail supplies for final consumers as well as products which were already made available by their manufacturers to other companies and are still in stock.

The German Cosmetic, Toiletry, Perfumery and Detergent Association (IKW) recommends certain measures for manufacturers, in order to comply with the phosphorous restriction with a view to avoiding cost and work intensive methods.

From 1 January 2017 the phosphorus restriction of 0.3 g of phosphorus per standard dosage for consumer automatic dishwasher detergents applies in the European Economic Area (EEA) [1], according to Regulation (EC) No 648/2004 on detergents (Detergents Regulation).

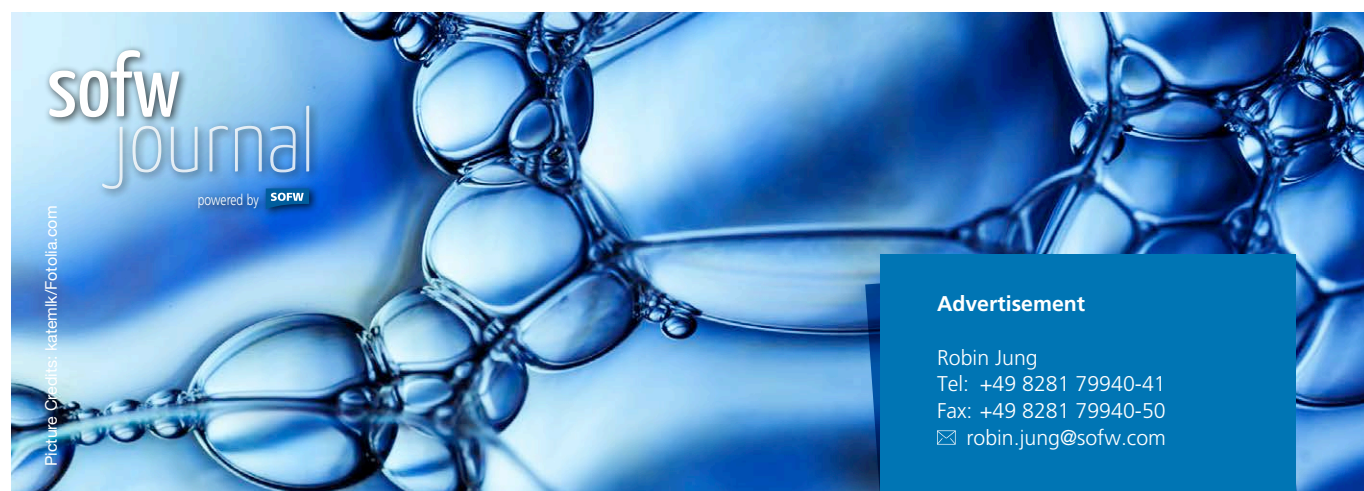
The protection goal of this provision is to lower the release of phosphates in surface waters and to reduce the ensuing costs of phosphates removal in waste water treatment plants [2].

The Detergents Regulation does not prescribe any measures for complying with the phosphorus limit value. Consequent-

ly, it is the responsibility of manufacturers of automatic dishwasher detergents to apply suitable measures.

The IKW (German Cosmetic, Toiletry, Perfumery and Detergent Association) recommends the following measures to manufacturers of automatic dishwasher detergents for complying with the phosphorus restriction:

1. Check the total phosphorus content by way of in-process control, with the help of weighing protocols within quality assurance measures (see error analysis in **Tab. 1**).



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2. Check the phosphorus content in raw materials by way of suitable analytical methods or certificates from raw material suppliers.
3. Only in special cases: Check the phosphorus content in the finished product by way of suitable analytical methods, e.g. when changing processes (see error analysis in [Tab. 2](#)).

By checking the weighed-in quantity, the limit value of 0.3 g of phosphorus/standard dosage is reliably complied with during one production campaign (see error analysis in [Tab. 1](#)). Thus, the protection goal of the Detergents Regulation is achieved (see Calculation for complying with the maximum phosphorus content, with the help of an example formulation in [Appendix I](#)).

The analysis of finished products is generally less reliable, due to complex compositions (see error analysis in [Tab. 2](#)).

[Appendix II](#) presents a choice of analytical methods for determining the total phosphorus content.

The following part of this paper compares the advantages and disadvantages of quality assurance by way of in-process control and downstream analysis of finished products, based on potential error sources and probabilities of error occurrence.

References

- [1] The European Economic Area (EEA) consists of the EU Member States and Iceland, Liechtenstein and Norway.
- [2] Recital 1 of the amending Regulation (EU) No 259/2012 as regards the use of phosphates and other phosphorus compounds in consumer laundry detergents and consumer automatic dishwasher detergents

	Aspect	Explanations	Potential error sources	Error probability
1	Phosphorus content in the raw materials	By way of suitable analytical methods or certificates from raw material suppliers	Faulty specifications by the supplier, faulty own measuring	Very low
2	Weighed-in raw materials	Weighing-in data is obtained in continuous or discontinuous dosing of the raw materials	Lacking quality assurance (e.g. non-calibrated scales), mix-ups of raw materials	Very low
3	Respective tolerance limit for weighed-in quantity	Tolerated process deviations	Constant dosing of raw materials containing phosphorus at the upper tolerance limit of weighed-in quantity	Low (can be made up for by taking into account the maximum quantities of raw materials containing phosphorus)
4	Goal and maximum phosphorus content in the finished product	The goal is the targeted amount of phosphorus in the finished product. The maximum content is the mass of phosphorus that can be expected due to process deviations.	Calculation errors	Very low

Tab. 1 Error analysis – in-process control, with the help of weighing protocols

	Aspect	Potential error sources	Error probability
1	Sample taking	Lacking representativeness (especially for solids)	Very high
2	Storage	Change of weighed-in quantity due to change in mass of non-portioned goods (hygroscopicity/ decomposition)	Low
3	Sample preparation (weighing-in, dissolving / solubilising)	Inhomogeneity, weighing errors, incomplete solubilisation, contamination	High
4	Determination method / Evaluation	Matrix effects, calibration errors, measuring and calculation errors	Medium

Tab. 2 Error analysis – checks through the analysis of finished products

Appendix I: Calculation for complying with the maximum phosphorus content, with the help of an example formulation*

		Ingredients of an example formulation		Scales & Process tolerance		Phosphorus		
[%]	[g]	Tolerance [g]		[%]	max [g]	Ratio [%]	[g/dose]	max [g/dose]
30	6	sodium citrate	± 0.3	2	6.42	0.01	0.0006	0.000642
33.5	6.7	sodium carbonate	± 0.38	2	7.169	0.01	0.00067	0.0007169
7	1.4	sodium percarbonate (if coating contains phosphorus)	± 0.07	2	1.498	0.25	0.0035	0.0037
5	1	sodium phosphonate	± 0.05	2	1.07	21	0.21	0.2247
3	0.6	possibly tab recycling#	± 0.03	2	0.642	10	0.06	0.0642
2	0.4	TAED	± 0.02	2	0.428	0.01	0.00004	0.0000428
10	2	sodium disilicate	± 0.1	2	2.14	0.01	0.0002	0.000214
2	0.4	non-ionic surfactant	± 0.02	2	0.428	0.01	0.00004	0.0000428
1.5	0.3	enzymes	± 0.02	2	0.321	0.01	0.00003	0.0000321
6	1.2	polycarboxylate	± 0.06	2	1.284	0.01	0.00012	0.0001284
100	20	theoretical maximum weight of one tab:			21.4		0.275 phosphorus (target value)	0.294 phosphorus (maximum value)

* derived from IEC D: proposal for a formulation (powder) for DIN EN 50242

if products containing 1.3 % sodium tripolyphosphate (STPP) (still) recycled (10% phosphorus = 40% phosphate)

Explanation

The ingredients listed in red can be intended to contain phosphorus. The other ingredients can contain traces of phosphorus which – assuming a “worst case” scenario – are included in the calculation at 0.01 percent by weight of phosphorus.

Appendix II: Choice of analytical methods for total phosphorus determination

	Method	Characteristic	Phosphorus determination limit (referred to the finished product – dosage 20 g)	Cost and workload	Service provider available
Wet chemical method with photometric determination	ASTM D820	Not non-destructive; partly disturbed by sample matrix effect	1000 ppm = 0.1 %, (0.02 g/20 g)	High: Analytical experience in this field is essential; costs of instruments and reagents are relatively low.	Yes, widely available
ICP-OES (Inductively coupled ion plasma with optical emission spectroscopy)	DIN EN 11885: 2009-09	Not non-destructive; Multi-element analysis possible	100 ppm = 0.01 %, (0.002g/20 g); possibly 10 ppm, (0.0002 g/20 g)	Low: Considerable validation effort in sample preparation, in order to ensure suitability for detergents; major effort for providing instrumental analytics; can be carried out at low cost.	Yes, widely available
XRF analysis (X-ray fluorescence analysis)	DIN 51418-1:2008-08 (general standard on the use of XRF analysis)	Non-destructive; Multi-element analysis possible	100 ppm = 0.01%, (0.002 g/20 g); possibly 10 ppm, (0.0002 g/20 g)	Very low: Relatively high effort for calibration; can be carried out fast; medium-range costs.	Yes, available

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