DLA
Dienstleistung
Lebensmittel
Analytik GbR

Evaluation Report
proficiency test

37/2014

Cosmetic Products IV:

Coenzyme Q10 (Ubiquinone) and Panthenol

in Skin Care Emulsion (Bodylotion)

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Content

1. Introduction

The participation in proficiency testing schemes is an essential element of the quality-management-system of every laboratory testing food and feed, cosmetics and food contact materials. The implementation of proficiency tests enables the participating laboratories to prove their own analytical competence under realistic conditions. At the same time they receive valuable data regarding the validity of the particular testing method.
The purpose of DLA is to offer proficiency tests for selected parameters in concentrations with practical relevance.
Realisation and evaluation of the present proficiency test follows the technical requirements of DIN EN ISO/IEC 17043 (2010) and DIN ISO 13528:2009 (6).

2. Realisation

2.1 Test material

The test material is a mixture of three common in commerce skin care emulsions (bodylotions) from European suppliers. The materials were mixed and homogenized from equal aliquots of weight. Afterwards the samples were packaged lightproof in portions to approximately 25 g. The portions were numbered chronologically.

The composition (list of ingredients) is given in table 1.

Table 1: Composition of DLA-Sample

Mixture of Bodylotions:
Bodylotion I List of Ingredients (INCI): Aqua, Glycerin, C15-19 Alkane, Isopropyl Palmitate, Glyceryl Glucoside, Cetearyl Alcohol, Dimethicone, Glyceryl Stearate SE, **Panthenol**, Glyceryl Stearate, Myristyl Alcohol, Cera Microcristallina, Hydrogenated Coco-Glycerides, Paraffinum Liquidum, Sodium Carbomer, Sodium Cetearyl Sulfate, Phenoxyethanol, Methylparaben, Ethylparaben, Linalool, Benzyl Alcohol, Parfum
Bodylotion II List of Ingredients (INCI): Aqua, Glycerin, Paraffinum Liquidum, Isopropyl Palmitate, Petrolatum, Stearyl Alcohol, Dimethicone, Glycerol Stearate, PEG-100 Stearate, Palmitic Acid, Stearic Acid, **Panthenol**, Allantoin, Simmondsia Chinensis Seed Oil, Ethylhexylglycerin, Ammonium Acryloyidimethyltaurate/VP Copolymer, Acrylates/C-10-30 Alkyl Acrylate Crosspolymer, Disodium EDTA, Sodium Hydroxide Phenoxyethanol, Parfum
Bodylotion III List of Ingredients (INCI): Aqua, Glycine Soja Oil, Ethylhexyl Stearate, Glycerin, Polyglyceryl-3 Diisostearate, Phenoxyethanol, Tocopheryl Acetate, Caprylyl Glycol, Allantoin, Acrylates/C10-30 Alkyl Acrylate Crosspolymer, Carbomer, Parfum, Xanthan Gum, Sodium Hydroxide, Sodium Stearoyl Glutamate, Alcohol denat., Lecithin, **Ubiquinone**, Linalool

2.1.1 Homogeneity

Homogeneity of the test material was checked by 5fold determination of ubiquinone by HPLC. With a repeatability standard deviation of < 1,0 % the homogeneity of the test material was considered acceptable. The results are given in the documentation.

The calculation of the repeatability standard deviation of the participants was also used as an indicator of homogeneity. For panthenol it was 1,8 % and in the lower range of common relative repeatability standard deviations of HPLC methods (14). The repeatability standard deviation of the participants for panthenol is given in the documentation.

2.2 Test

Two portions of test material were sent to every participating laboratory in the 48th week of 2014. The testing method was optional. The tests should be finished at 16th january 2015.

2.3 Submission of results

The participants submitted their results in standard forms, which have been sent by email or were available on our website.
The finally calculated concentration of ubiquinone and panthenol as an average of a duplicate determination of both numbered samples was used for each statistical evaluation.
Queried and documented were single results, recovery and the testing methods used.
One laboratory canceled the participation. All other participants submitted the results in time.

3. Evaluation

3.1 Assigned value

Because the analysed material was no certified reference material the robust mean of the submitted results was used as assigned value X (6). The distribution of submitted results showed no hint for bimodal distribution or other reasons for a higher variability.

3.2 Standard deviation

For comparison to the target standard deviation a robust standard deviation (S^x) was calculated (6).

3.3 Outliers

Statistical outliers were determined by Mandel´s-H-Statistic for 95% significance niveau (5). Detected outliers were stated for information only, when z-score was < -2 or > 2.

3.4 Target standard deviation

The target standard deviation of the assigned value is determined according to the following methods.

In general the Horwitz target standard deviation is suitable for the statistical evaluation of interlaboratory tests where different analytical methods are applied. The standard deviation from precision experiments are derived from proficiency tests where a specific analytical method is mandatory.

For all analytes the target standard deviation according to the general model (Horwitz) was applied.

3.4.1 General model (Horwitz)

The relative target standard deviation in % of the assigned value is derived from following equation (Horwitz)

$$\hat{\sigma}_{(\%)} = 2^{(1-0,5\log X)}$$

From the result the target standard deviation is calculated

$$\hat{\sigma} = X * \hat{\sigma}_{(\%)} / 100.$$

3.4.2 Value by precision experiment

Using the reproducibility standard deviation σ_R and the repeatability standard deviation σ_r of a precision experiment the between-laboratories standard deviation can be calculated σ_L :

$$\sigma_L = \sqrt{(\sigma_R^2 - \sigma_r^2)} \quad .$$

And then, using the number of replicate measurements n, each participant is to perform, the target standard deviation for proficiency assessment is calculated :

$$\hat{\sigma} = \sqrt{(\sigma_L^2 + (\sigma_r^2/n))} \quad .$$

There are no standard methods for the determination of ubiquinone and panthenol in cosmetic products.

3.4.3 Value by perception

The target standard deviation for proficiency assessment can be set at a value that corresponds to the level of performance that the coordinator would wish laboratories to be able to achieve (6).

For the evaluation in the present proficiency testing the model according to Horwitz was applied.

For ***ubiquinone*** the suitability of the model of Horwitz with the normal relative target standard deviation was limited (quotients $S^x/\hat{\sigma} > 2$ and $u_X/\hat{\sigma} > 0{,}3$)). **Therefore the evaluation of participants' results was done for ubiquinone using z'-values and the target standard deviation** $\hat{\sigma}$ **'** (s. 3.6 and 3.8).

3.5 z-Score

To assess the results of the participants the z-score is used. It indicates about which multiple of the target standard deviation ($\hat{\sigma}$) the result (x) of the participant is deviating from the assigned value (X) (6).
Participants' z-scores were derived as:

$$z = (x - X) / \hat{\sigma} \ ;$$

the requirements for the analytical performance are generally considered as fulfilled if

$$-2 \leq z \leq 2 \ .$$

3.6 z'-Score

The z'-score can be used for the valuation of the results of the participants, in cases the standard uncertainty has to be considered (s. 3.8). The z'-score represents the relation of the deviation of the result (x) of the participant from the respective assigned value (X) to the square root of quadrat sum of the target standard deviation ($\hat{\sigma}$) and the standard uncertainty (Ux) (6).

Participants' z'-scores are derived as:

$$z' = (x - X) / \sqrt{\hat{\sigma}^2 + u_X^2}$$

In the following we define the denominator $\sqrt{\hat{\sigma}^2 + u_X^2}$ as the target standard deviation $\hat{\sigma}'$.

The requirements for the analytical performance are generally considered as fulfilled if

$$-2 \leq z' \leq 2 \ .$$

3.7 Quotient $S^x/\hat{\sigma}$

Following the Horrat-value the results of a proficiency-test (PT) can be considered convincing, if the quotient of robust standard deviation and target standard deviation does not exceed the value of 2.
A value > 2 means an insufficient precision, i.e. the analytical method is too variable, or the variation between the test participants is higher than estimated. Thus the comparability of the results is not given (11).
In the present proficiency tests the quotients $S^x/\hat{\sigma}$ were

In the present proficiency test the quotient $S^x/\hat{\sigma}$ for ubiquinone was 6,1. Therefore the evaluation was done according to 3.6 z'-scores. For panthenol the quotient $S^x/\hat{\sigma}$ was satisfactory with 1,4.

3.8 Standard uncertainty

The assigned value X has a standard uncertainty u_X that depends on the analytical method, differences between the analytical methods used, the test material, the number of participant laboratories and perhaps on other factors. The standard uncertainty u_X for this PT is calculated as follows (6).

$$u_X = 1{,}25 * S^x/\sqrt{(p)}$$

If $u_X \leq 0{,}3 * \hat{\sigma}$ the standard uncertainty of the assigned value needs not to be included in the interpretation of the results of the PT (6).

In the present proficiency test the quotient $U_x/\hat{\sigma}$ was 3,4 for ubiquinone. Therefore for the valuation of the participants' results the z'-Score considering the standard uncertainty was used (s. 3.6).

4. Results

All following tables are anonymized. With the delivering of the evaluation-report the participants are informed about their individual evaluation-number.
In the upper table the characteristics are listed:

Statistic Data
Number of results
Number of outliers
Mean
Median
Robust mean (X)
Robust standard deviation (S^x)
Target range:
Target standard deviation for information
Target standard deviation $\hat{\sigma}$ '
lower limit of target range (X - 2 $\hat{\sigma}$) or (X - 2 $\hat{\sigma}$ ') *
upper limit of target range (X + 2 $\hat{\sigma}$) or (X + 2 $\hat{\sigma}$ ') *
Quotient S^x/ $\hat{\sigma}$ '
Standard uncertainty u_X
Quotient $u_X/\hat{\sigma}$ '
Number of results in the target range

* Target range is calculated with z-score or z'-score

In the lower table -laboratories- the individual results of the participating laboratories are listed:

evaluation number	test result	deviation from assigned value	Z-Score Horwitz	Z'-Score Horwitz	Remarks

4.1 Coenzyme Q10 (Ubiquinone) (in mg/100 g)

Statistic Data	
Number of results	*5 **
Number of outliers	*0*
Mean	*31,6*
Median	28,4
Robust mean (X)	31,6
Robust standard deviation (S^x)	13,1
Target range:	
Target standard deviation $\hat{\sigma}'$	7,63
lower limit of target range **	16,4
upper limit of target range **	46,9
Quotient $S^x/\hat{\sigma}'$	1,7
Standard uncertainty u_X	*7,32*
Quotient $u_X/\hat{\sigma}'$	*0,96*
Number of results in the target range	*4 (75%)*

** result no. 7 was excluded*
*** target range calculated from z'-score*

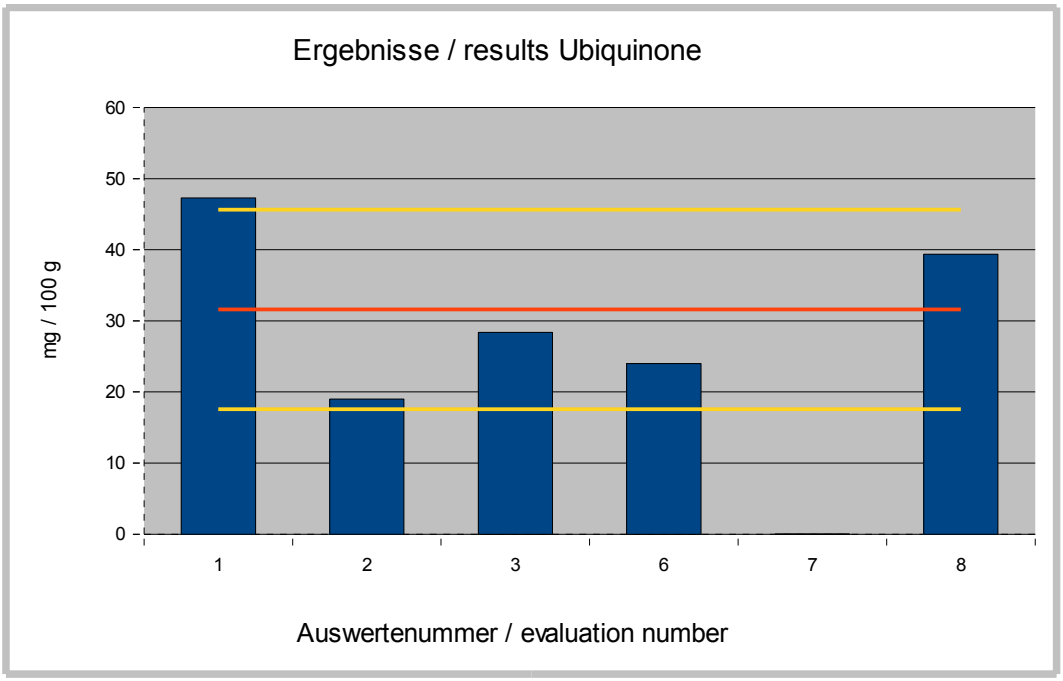

Fig. 3: Results Coenzyme Q10 (Ubiquinone)
(red line = robust mean, yellow lines = target range)

Results of participants

Evaluation number	Result	Deviation	Z-Score (zur Info)	Z'-Score	Remarks
	[mg/100g]	X rob. Mean	Horwitz	Horwitz	
1	47,3	15,7	7,4	2,2	
2	19	-12,6	-5,9	-1,8	
3	28,4	-3,2	-1,5	-0,5	
6	24	-7,6	-3,6	-1,1	
7	0,018				not included, error in units?
8	39,38	7,8	3,7	1,1	

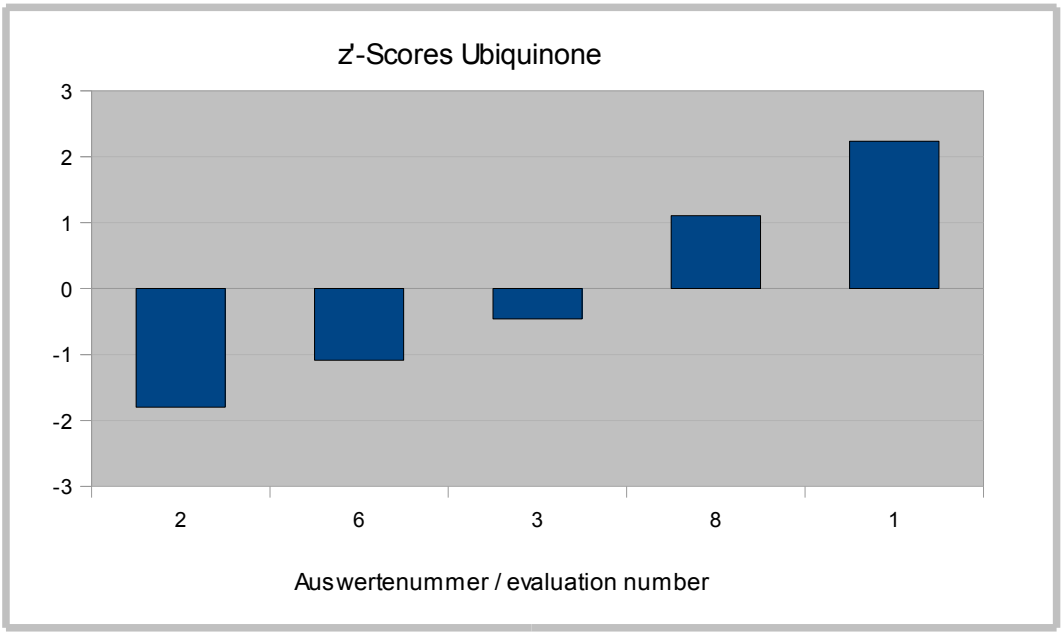

Fig. 4: Z'-Scores Coenzyme Q10 (Ubiquinone)

4.2 Panthenol (in mg/100 g)

Statistic Data	
Number of results	*8 **
Number of outliers	*1*
Mean	240
Median	239
Robust mean (X)	238
Robust standard deviation (S^x)	16,5
Target range:	
Target standard deviation $\hat{\sigma}$ (Horwitz)	11,8
lower limit of target range (X - 2 $\hat{\sigma}$)	214
upper limit of target range (X + 2 $\hat{\sigma}$)	262
Quotient $S^x/\hat{\sigma}$	*1,4*
Standard uncertainty u_X	*7,27*
Quotient $u_X/\hat{\sigma}$	*0,62*
Number of results in the target range	*7 (88%)*

** result no. 7 was excluded*

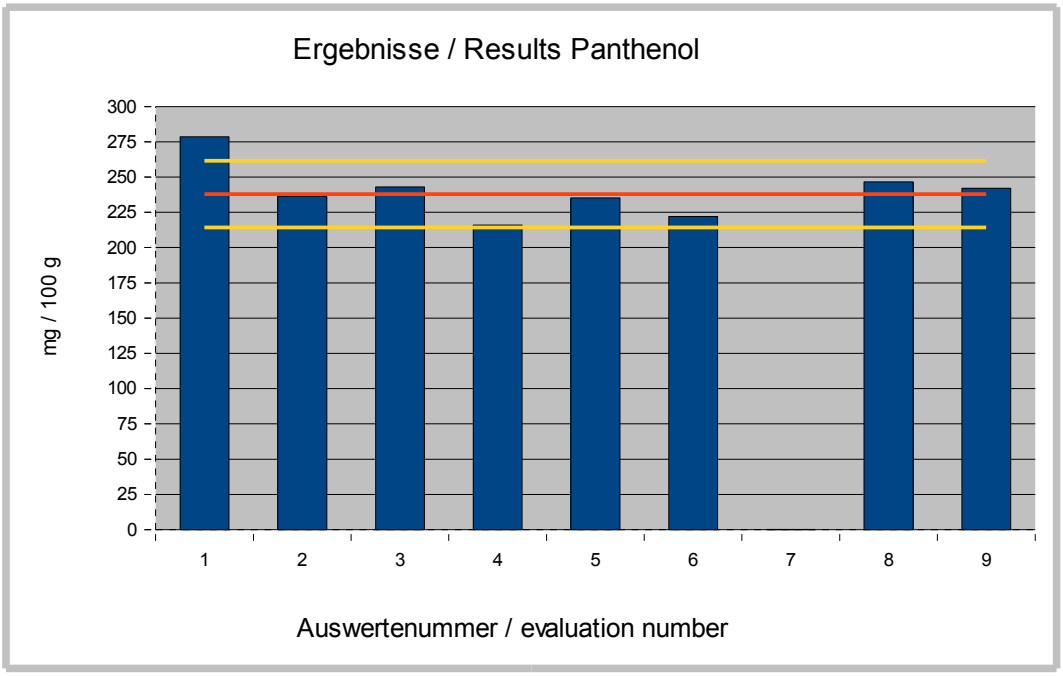

Fig. 5: Results Panthenol
(red line = robust mean, yellow lines = target range)

Results of participants

Evaluation number	Result	Deviation	Z-Score	Remarks
	[mg/100g]	X rob. MW	Horwitz	
1	278,6	40,6209	3,4	outlier
2	236,2	-1,7791	-0,2	
3	243	5,0209	0,4	
4	216	-21,9791	-1,9	
5	235,3	-2,6791	-0,2	
6	222	-15,9791	-1,4	
7	0,237			not included, error in units?
8	246,57	8,5909	0,7	
9	242,1	4,1209	0,3	

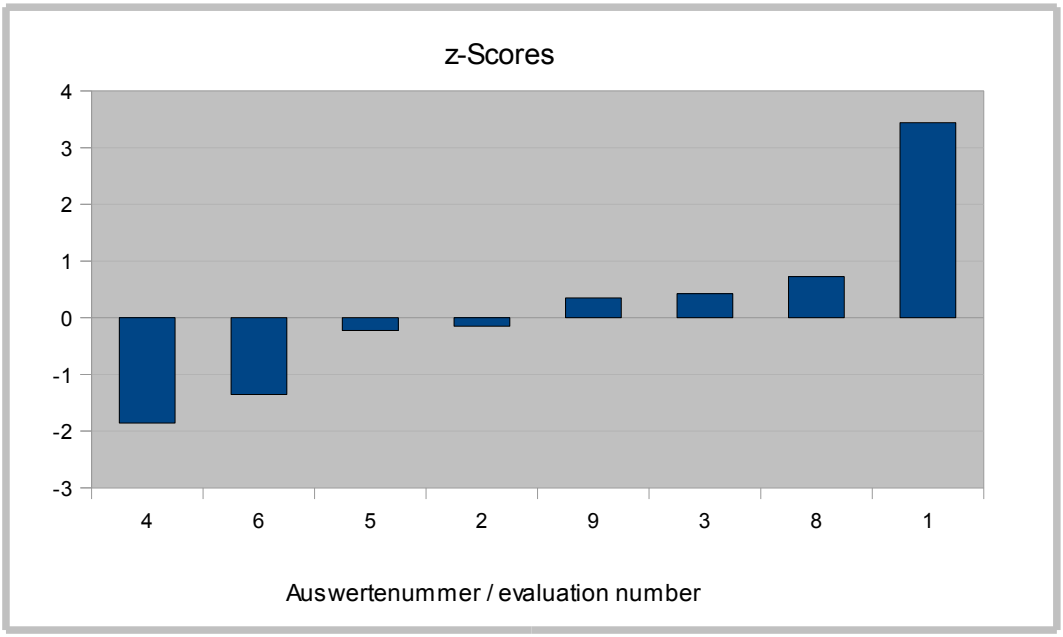

Fig. 6: Z-Scores Panthenol

5. Documentation

5.1 Primary data

5.1.1 Coenzyme Q10 (Ubiquinone)

Evaluation number	Result	Sample-No. A	Sample No. B	Result A	Result B	Recovery Rate
	[mg/100g]			[mg/100g]	[mg/100g]	%
1	47,3	33	54	37 (45,1)	39,3 (47,9)	122
2	19	25	49			
3	28,4			25,4	31,3	
4						
5		17	44			
6	24			24	23	102
7	0,018			0,018	0,018	
8	39,38			39,81 (39,33)	38,95 (37,66)	98,8 / 96,7
9	/			/	/	/

5.1.2 Panthenol

Evaluation number	Result	Sample-No. A	Sample No. B	Result A	Result B	Recovery Rate
	[mg/100g]			[mg/100g]	[mg/100g]	%
1	278,6	33	54	273,1 (374,1)	280 (383,6)	73
2	236,2	25	49			
3	243			241	244	
4	216			212	219	99
5	235,3	17	44	236,0	234,7	
6	222			223	220	100
7	0,237			0,237	0,237	
8	246,57			248,65 (243,68)	244,49 (239,6)	98
9	242,1			241,9 (240,5)	245,1 (243,7)	100,6

5.2 Homogeneity

5.2.1 Homogeneity test before the PT

Homogeneity test for ubiquinone by HPLC.

Independant samples	mg/100g
1	36,4
2	36,3
3	36,0
4	36,0
5	36,7

Mean	36,3	
Repeatability Standard Deviation	0,29	0,8%

5.2.2 Repeatability standard deviation of duplicate tests of the participants

The repeatability standard deviation was calculated with the data documented in 5.1.3 for panthenol. It is 4,2 mg/100g = 1,8 % of X.

5.2.3 Comparison of sample number / test result

A comparison of sample numbers and results was not possible, because only three participants reported the sample numbers.

5.3 Analytical Methods

Details by the participants

5.3.1 Coenzyme Q10 (Ubiquinone)

Evaluation number	Method description and further remarks	Recovery with same matrix	Accredited	Remarks
1	Sample extraction with solvent and FeCl3-solution, afterwards determination of content by HPLC-DAD with external calibration	yes	no	A=33, B=54
2	HPLC-DAD RP C18		yes	
3	in-house method	no	no	
4				
5				We don't quantify Ubiquinone in our lab.
6	RP-HPLC with UV-Detection	yes	yes	
7	M 12.4113.01, HPLC-DAD	no	yes / no	
8	in-house method HPLC	yes	yes	
9	/	/	/	currently not analyzed

5.3.2 Panthenol

Evaluation number	Method description and further remarks	Recovery with same matrix	Accredited	Remarks
1	Extraction with solvent followed by derivatisation; GC-MS	no	no	
2	HPLC-DAD RP C18		yes	
3	in-house method	no	yes / no	
4	HPLC-DAD (aqueous extract)	no	yes	
5	HPLC-UV in-house method	no	no	
6	RP-HPLC with UV-Detection	yes	yes	
7	M 12.4112.05, HPLC-DAD	no	yes / no	
8	in-house method HPLC	yes	yes	
9	in-house method, HPLC	yes	yes	/

6. Index of participant laboratories

Teilnehmer / Participant	Ort / Town	Land / Country
		GERMANY
		GERMANY
		GERMANY
		FRANCE
		GERMANY
		GERMANY
		GERMANY
		GERMANY
		GERMANY

7. Index of references

1. DIN EN ISO/IEC 17043:2010; Konformitätsbewertung – Allgemeine Anforderungen an Eignungsprüfungen / Conformity assessment – General requirements for proficiency testing
2. Verordnung / Regulation 882/2004/EU; Verordnung über amtliche Kontrollen / Regulation on official controls
3. DIN EN ISO/IEC 17025:2005; Allgemeine Anforderungen an die Kompetenz von Prüf- und Kalibrierlaboratorien / General requirements for the competence of testing and calibration laboratories
4. Richtlinie / Directive 1993/99/EU; über zusätzliche Maßnahmen im Bereich der amtlichen Lebensmittelüberwachung / on additional measures concerning the official control of foodstuffs
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13. ASU § 64 LFGB K 84.00-21 Nachweis und Bestimmung von Benzylalkohol in kosmetischen Mitteln
14. ASU § 64 LFGB K 84.00-23 Nachweis und Bestimmung von Benzoesäure, 4-Hydroxybenzoesäure, Sorbinsäure, Salicylsäure und Propionsäure in kosmetischen Mitteln
15. ASU § 64 LFGB K 84.00-24 Nachweis und Bestimmung von 2-Phenoxyethanol, 1-Phenoxypropan-2-ol, Methyl-, Ethyl-, Propyl-, Butyl- und Benzyl-4-Hydroxybenzoat in kosmetischen Mitteln

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