MINISTÉRIO DAS OBRAS PÚBLICAS, TRANSPORTES E COMUN ICAÇÕES

Laboratório Nacional de Engenharia Civil

Departamento de Materiais

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QUALANOD INTER-LABORATORY TESTS OF ANODIZED ALUMINIUM TESTING METHODS

STATISTICAL ANALYSIS - DETERMINATION OF REPEATABILITY AND REPRODUCIBILITY

REPORT 297/2006 - DM

Lisboa, Outubro 2006

Trabalho realizado para

QUALANOD (EURAS/EWAA)

QUALANOD INTER-LABORATORY TEST OF ANODIZED ALUMINIUM TESTING METHODS

STATISTICAL ANALYSIS - REPEATIBILITY AND REPRODUCIBILITY DETERMINATION

Institutions/laboratories that intended to participate in this inter-laboratory test

Country	Name	Laboratory
AUSTRIA	Aluminium Ranshofen Service GmbH	AMAG
BELGIUM	CORI - Coatings Research Institute	CoRI
FRANCE	TESTAL	-
GERMANY	IFO GmbH - Institut für Oberflächentechnik	IO GmbH
GREECE	AAG Quality – EKANAL for Aluminium Ass. Of Greece	EKANAL
HUNGARY	ÉMI KHT - Institut für Qualitätskontrolle	ÉMI KHT
ITALY	QUALITAL	QUALITAL
NETHERLANDS	Adviescentrum VOM B.H.	A VOM B. V.
POLAND	Instytut Mechaniki Precyzyjnej	IMP
PORTUGAL	LNEC - Laboratório Nacional de Engenharia Civil	LNEC
SPAIN	QUALESPAÑA - Ministerio de Vivienda Subdirección General de Innovación y Calidad de la Edificación	CEDEX
SWITZERLAND	EMPA, Abtl. Korrosion	EMPA
TURKEY	Turkish Standards Institution	-

Laboratories from Turkey and France haven't sent any results

Testing methods

• **EN ISO 2360:2003** - *Non-conductive coatings on non-magnetic electrically conductive basis materials.* ***Measurement of coating thickness****. Amplitude-sensitive eddy current method (ISO 2360:2003*)

• **EN 12373-7:2002** (2nd Ed.) - *Aluminium and aluminium alloys. Anodizing. Part 7: Assessment of* ***quality of sealed anodic oxidation coatings by measurement of the loss of mass*** *after immersion in phosphoric acid/chromic acid solution with prior acid treatment*

• **EN 12373-5:1998** - *Aluminium and aluminium alloys. Anodizing. Part 5: Assessment of* ***quality of sealed anodic oxidation coatings by measurement of admittance***

• **EN 12373-4:1998** - *Aluminium and aluminium alloys. Anodizing. Part 4: Estimation of loss absorptive power of anodic oxidation coatings after sealing by* ***dye spot test*** *with prior acid treatment*

General characteristics of the test specimens

ALUMINIUM	Alloy Type	Type of product	Dimensions of testing specimens	
	6060	Sheet with 1 mm of thickness	70mmx140 mm	
ANODIC COATING	**Type**	**Thickness class**	**Sealing**	**Colour**
Polished surface	**P**	15 µm	3 min/µm	natural
	IP	15 µm	not sealed	natural
	I	25 µm	1 min/µm	bronze
Satined surface	**A**	20 µm	3 min/µm	natural

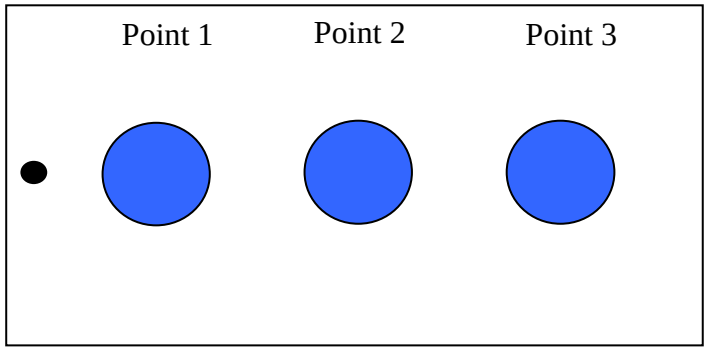
Fifty specimens of each coating type were produced

Anodizing and sealing conditions used for the production of test specimens

Coating type	Anodizing bath		Sealing bath	
P	*Free H_2SO_4 -*	184,7 g/l	*Demineralised water*	
	Al content -	12,8 g/l	*pH -*	5,70
	Temperature -	18,0 ºC	*Additive -*	Anodal SH1
	Current density -	1,6 A/dm^2	*Time -*	3 min/µm
I	*Free H_2SO_4 -*	182,1 g/l	*Demineralised water*	
	Al content -	11,4 g/l	*pH -*	5,75
	Temperature -	19,0 ºC	*Additive -*	Anodal SH1
	Current density -	1,7 A/dm^2	*Time -*	1 min/µm
IP	*Free H_2SO_4 -*	184,7 g/l	*Not sealed*	
	Al content -	12,8 g/l		
	Temperature -	19,0 ºC		
	Current density -	1,6 A/dm^2		
A	*Free H_2SO_4 -*	184,7 g/l	*Demineralised water*	
	Al content -	12,8 g/l	*pH -*	5,70
	Temperature -	19,0 ºC	*Additive -*	Anodal SH1
	Current density -	1,7 A/dm^2	*Time -*	3 min/µm

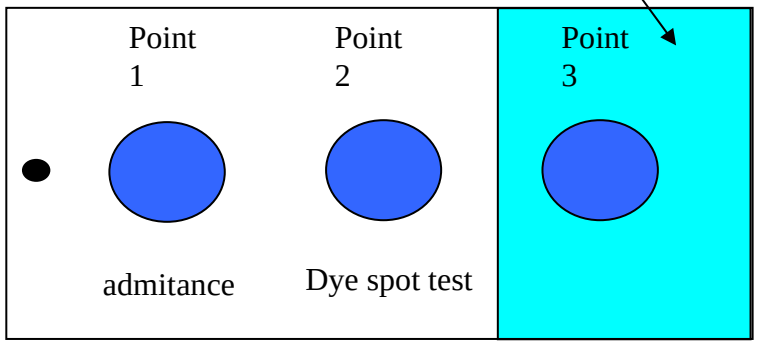
Instructions

- Laboratory code number
- Measuring points



Scheme of the testing zones for thickness measurement

Scheme of testing zones for sealing quality assessment



EXCEL Worksheets for data registration

Protocol

Test laboratory:	LNEC
Sample type:	P
Tested by:	N Garcia
Date of report:	

Test conditions

Temperature:	21	±	2	°C
Date of the test:	05-12-2005			yyyy-mm-dd
Zero base	0,0	±		µm
Calibration standard 1	23,5	±	0,5	µm
Calibration standard 2		±		µm
Calibration standard 3		±		µm

Test results

Thickness results (ISO 2360)

Sample No.	Front side (µm)			
P15	1st point	2nd point	3rd point	
measure 1	21,6			
measure 2	22,0			
measure 3	21,3			
Average thickness	21,6			21,6

Sample No.	Front side (µm)			
	1st point	2nd point	3rd point	
measure 1				
measure 2				
measure 3				
Average thickness				

Sample No.	Front side (µm)			
	1st point	2nd point	3rd point	
measure 1				
measure 2				
measure 3				
Average thickness				

Weight loss results (EN 12373-7)

Sample No.	Height H	Lenght L	Sample thickness T	Area A	Weigth loss
P15	(mm)	(mm)	(mm)	(dm^2)	(mg/dm^2)
measure 1	71,59	50,29	1,04	-	-
measure 2	71,34	50,86	1,05	-	-
measure 3	71,83	51,08	1,03	-	-
Average	71,59	50,74	1,04	0,7506	15

Sample No.	Height H	Lenght L	Sample thickness T	Area A	Weigth loss
P15	(mm)	(mm)	(mm)	(dm^2)	(mg/dm^2)
measure 1				-	-
measure 2				-	-
measure 3				-	-
Average					

Sample No.	Height H	Lenght L	Sample thickness T	Area A	Weigth loss
	(mm)	(mm)	(mm)	(dm^2)	(mg/dm^2)
measure 1				-	-
measure 2				-	-
measure 3				-	-
Average					

Admittance results (EN 12373-5)

Sample No.	Measurement	Thickness	Temperature	Admittance
P15	Ym	(µm)	(°C)	Y
	10,5	24,6	21,2	8,0

Dye spot results (EN 12373-4)

Dye spot	0-1

Sample No.	Measurement	Thickness	Temperature	Admittance
	Ym	(µm)	(°C)	Y

Dye spot	

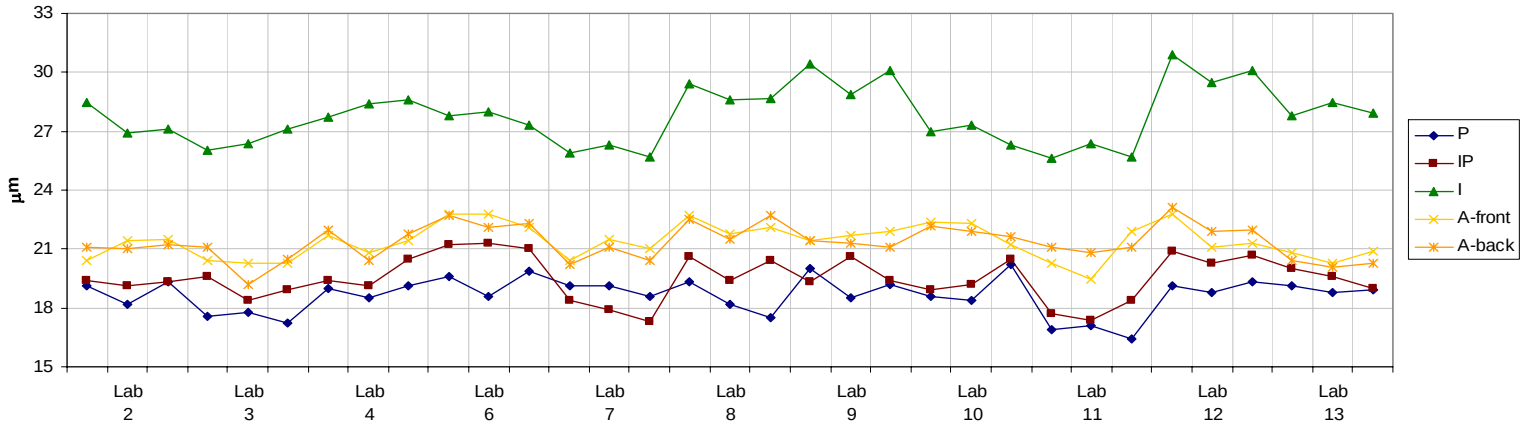
Sample No.	Measurement	Thickness	Temperature	Admittance
	Ym	(µm)	(°C)	Y

Dye spot	

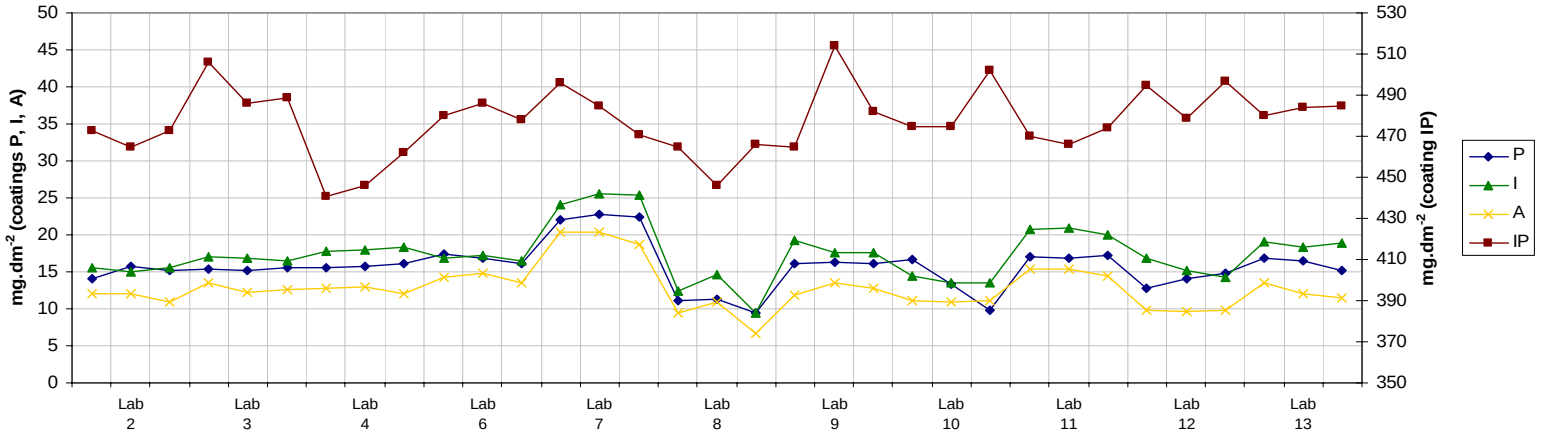
Example for the registration of tests results for specimens of coating type P

Results reported

Test results of method EN ISO 2360

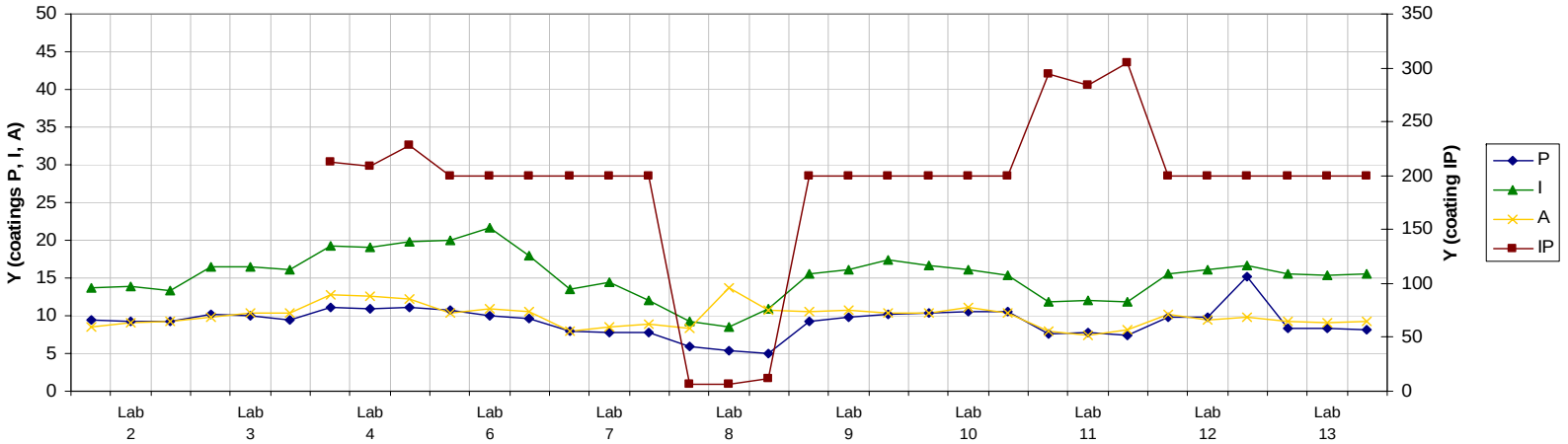


Test results of method EN 12373-7

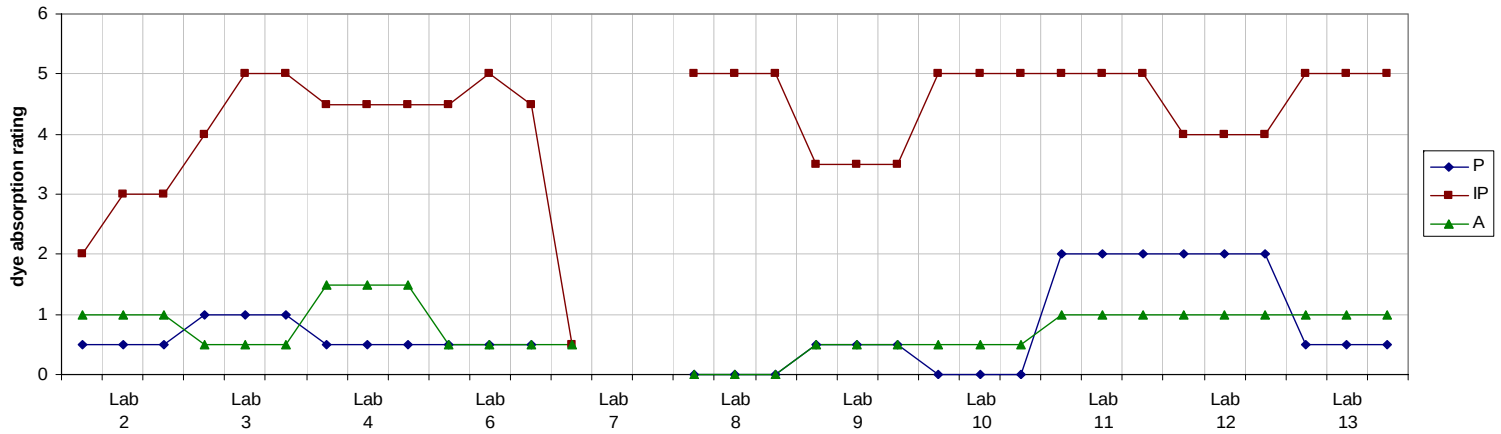


Results reported

Test results of method EN 12373-5



Test results of method EN 12373-4



Precision analysis according to ISO 5725-2

- Consistency tests
  - **Graphical consistency technique** – Mandel's *h* and *k* statistics

$$h_{ij} = \frac{\bar{y}_{ij} - \bar{\bar{y}}_j}{\sqrt{\frac{1}{(p_j - 1)}\sum(\bar{y}_{ij} - \bar{\bar{y}}_j)^2}} \qquad k_{ij} = \frac{s_{ij}\sqrt{p_j}}{\sqrt{\sum s_{ij}^2}}$$

  - **Numerical outlier technique** – Cochran's and Grubb's tests

$$C = \frac{s_{max}^2}{\sum_{i=1}^{p} s_i^2} \qquad G_p = (x_p - \bar{x})/s \qquad G_1 = (\bar{x} - x_1)/s$$

$$G = s_{p-1,p}^2 / s_0^2 \qquad G = s_{1,2}^2 / s_0^2$$

- Calculation of the **general mean** and **variances**

$$\hat{m}_j = \bar{\bar{y}}_j = \frac{\sum_{i=1}^{p} n_{ij}\bar{y}_{ij}}{\sum_{i=1}^{p} n_{ij}} \qquad s_{rj}^2 = \frac{\sum_{i=1}^{p}(n_{ij} - 1)s_{ij}^2}{\sum_{i=1}^{p}(n_{ij} - 1)}$$

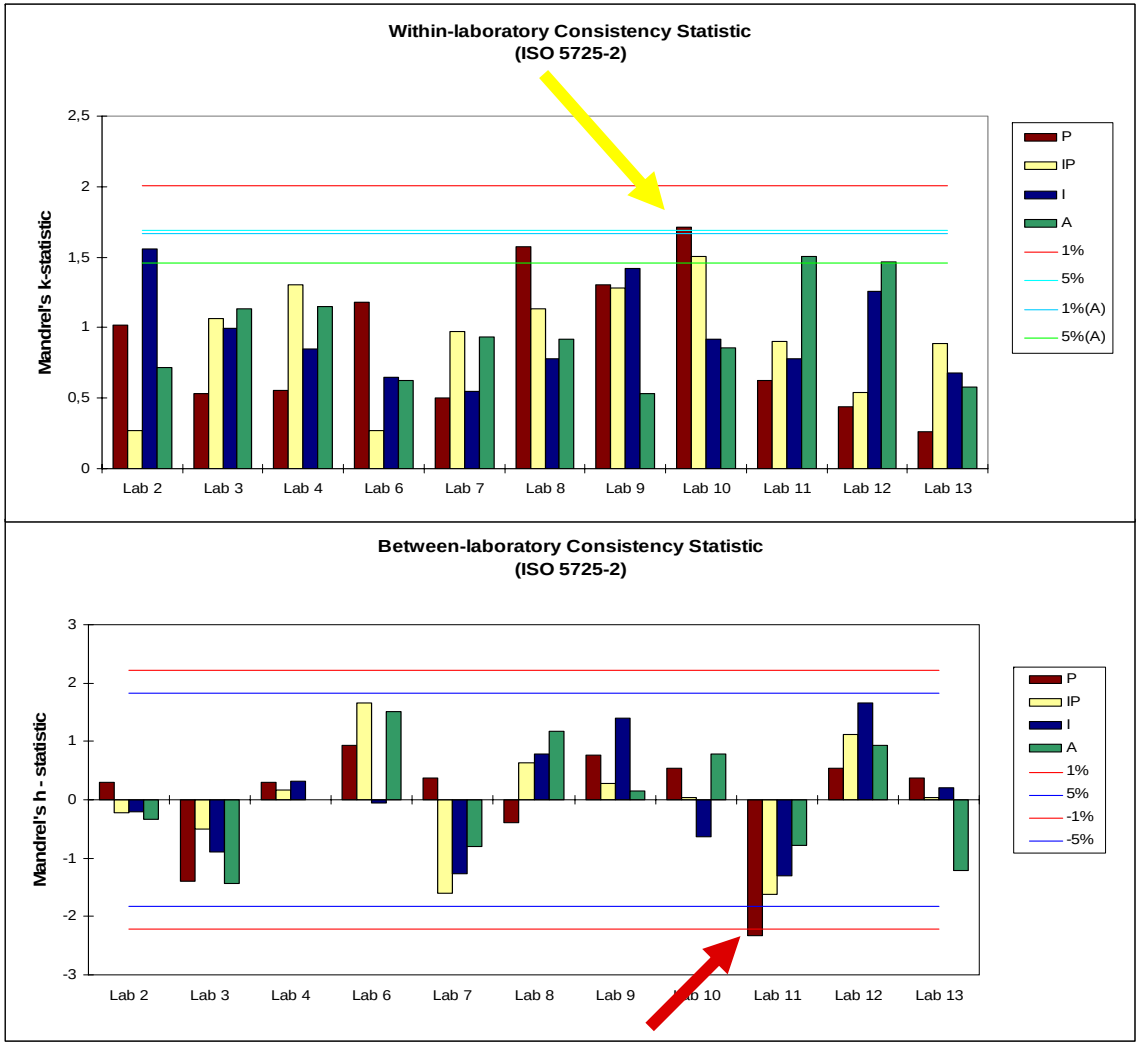
Repeatability variance

$$s_{Rj}^2 = s_{rj}^2 + s_{Lj}^2$$

Reproducibility variance

$$\left(\quad s_{dj}^2 = \frac{1}{p-1}\sum_{i=1}^{p} n_{ij}(\bar{y}_{ij} - \bar{\bar{y}}_j)^2 = \frac{1}{p-1}\left[\sum_{i=1}^{p} n_{ij}(\bar{y}_{ij})^2 - (\bar{\bar{y}}_j)^2 \sum_{i=1}^{p} n_{ij}\right] \quad \right)$$

Thickness measurement (EN ISO 2360)



Thickness measurement (EN ISO 2360)

Laboratories outside critical value lines of Mandel's statistics

Level	P	IP	I	A
Mandel's k-plot	Lab 10	-	-	Lab 11; Lab 12
Classification	*Straggler*	-	-	*Straggler*
Mandel´s h-plot	Lab 11	-	-	-
Classification	*Outlier*	-	-	-

Cochran's test results

Level	P	IP	I	A
Valid laboratories *p*	11	11	11	11
Number of replicates *n*	3	3	3	6
1% Critical value $C_{Cr\ (1\%)}$	0,504	0,504	0,504	0,332
5% Critical value $C_{Cr\ (5\%)}$	0,417	0,417	0,417	0,281
Cochran's test statistic ***C***	0,266	0,148	0,222	0,206
Classification	*correct*	*correct*	*correct*	*correct*
Outlier Lab (***C*** >$C_{Cr\ (1\%)}$)	-	-	-	-

Thickness measurement (EN ISO 2360)

Grubb's test results

Level	P	IP	I	A
Valid laboratories *p*	11	11	11	11
Single G_{Cr} (1%)	2,564	2,564	2,564	2,564
Single G_{Cr} (5%)	2,355	2,355	2,355	2,355
Single high G_p	0,926	1,650	1,658	1,512
Single low G_1	2,328	1,627	1,308	1,430
Classification (low)	*correct*	*correct*	*correct*	*correct*
Outlier Lab ($G_p > G_{Cr}$ (1%))	-	-	-	-
Classification (low)	*correct*	*correct*	*correct*	*correct*
Outlier Lab ($G_1 > G_{Cr}$ (1%))	-	-	-	-
Double G_{Cr} (1%)	0,1448	0,1448	0,1448	0,1448
Double G_{Cr} (5%)	0,2213	0,2213	0,2213	0,2213
Double high $G_{largest}$	0,826	0,5152	0,4244	0,5539
Double low $G_{smalest}$	0,1084	0,3662	0,5964	0,5738
Classification (two largest)	*correct*	*correct*	*correct*	*correct*
Outlier Lab($G_{largest} < G_{Cr}$ (1%))	-	-	-	-
Classification (two smallest)	*Outliers*	*correct*	*correct*	*correct*
Outlier Lab($G_{smalest} < G_{Cr}$ (1%))	Lab 3; Lab 11	-	-	-

Single: test for one outlying observation; Double: test for two outlying observations

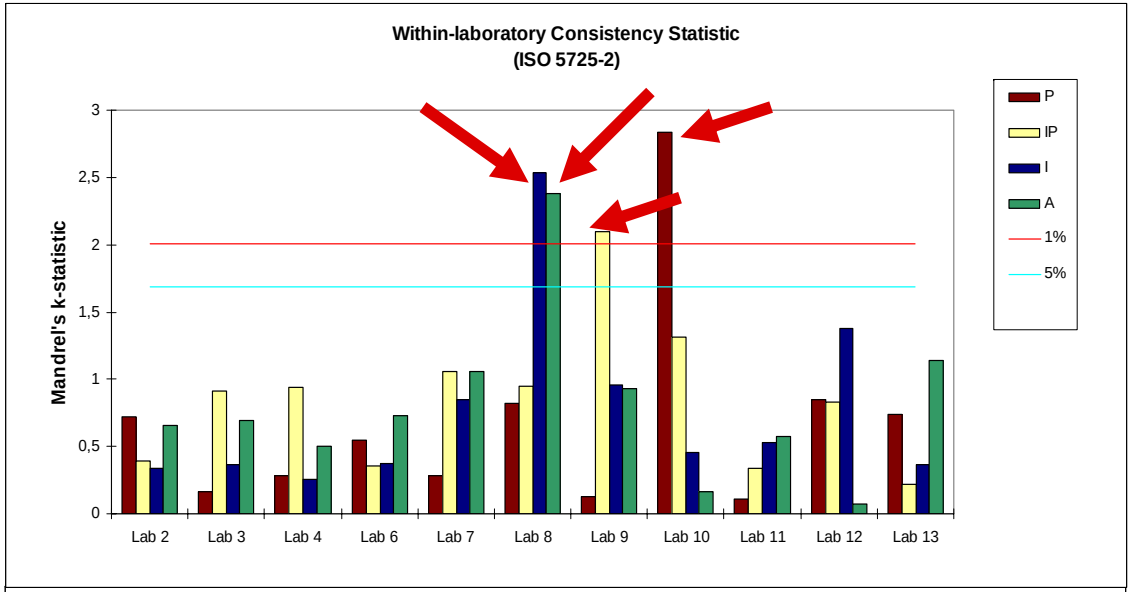
Thickness measurement (EN ISO 2360)

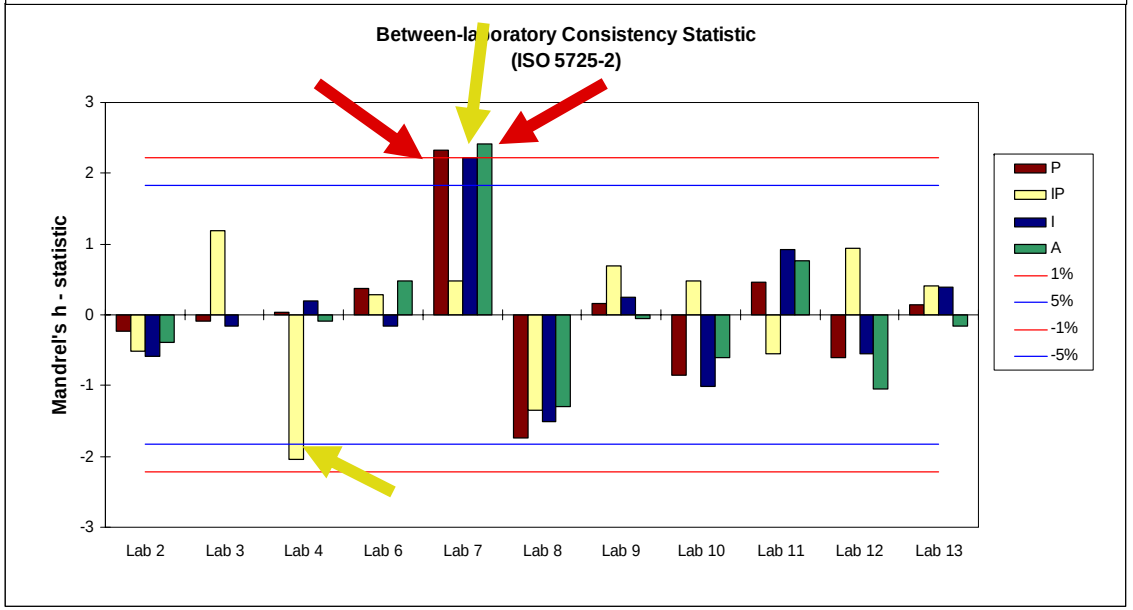
Results of precision analysis

Level	P	IP	I	A
Number of replicates *n*	3	3	3	6
Valid laboratories *p*	11	11	11	11
General mean *m* / µm	**18,64**	**19,49**	**27,78**	**21,35**
Repeatability variance s_r^2	0,333	0,321	0,312	0,294
Between-lab variance s_L^2	0,511	0,928	1,966	0,493
Reproducibility variance s_R^2	0,844	1,248	2,278	0,788
Repeatability std. dev. s_r	**0,58**	**0,57**	**0,56**	**0,54**
Reproducibility std. dev. s_R	**0,92**	**1,12**	**1,51**	**0,89**
Repeatability COV (s_r/m)	3,1%	2,9%	2,0%	2,5%
Reproducibility COV (s_R/m)	4,9%	5,7%	5,4%	4,2%
Number of outliers	2	0	0	0
Number of excluded outliers	0	0	0	0
Outlier type	[1]M*h*, [2]G(II)	-	-	-
Outlier laboratories	Lab 3 [2] Lab 11 [1,2]	-	-	-

Outlier type: M*h* – Mandel's *h* ;M*k* – Mandel's *k* ; C - Cochran's ; G(I) – Grubs (one outlying observation) ; G(II) – Grubs (two outlying observations)

Sealing quality assessment by mass loss (EN 12373-7)





Sealing quality assessment by mass loss (EN 12373-7)

Laboratories outside critical value lines of Mandel's statistics

Level	P	IP	I	A
Mandel's k-plot	Lab 10	Lab 9	Lab 8	Lab 8
Classification	*Outlier*	*Outlier*	*Outlier*	*Outlier*
Mandel´s h-plot	Lab 7	Lab 4	Lab 7	Lab 7
Classification	*Outlier*	*Straggler*	*Straggler*	*Outlier*

Cochran's test results

Level	P	IP	I	A
Valid laboratories *p*	11	11	11	11
Number of replicates *n*	3	3	3	3
1% Critical value $C_{Cr\ (1\%)}$	0,504	0,504	0,504	0,504
5% Critical value $C_{Cr\ (5\%)}$	0,417	0,417	0,417	0,417
Cochran's test statistic ***C***	0,731	0,400	0,583	0,515
Classification	*Outlier*	*correct*	*Outlier*	*Outlier*
Outlier Lab (***C*** >$C_{Cr\ (1\%)}$)	Lab 10	-	Lab 8	Lab 8

Sealing quality assessment by mass loss (EN 12373-7)

Grubb's test results

Level	P	IP	I	A
Valid laboratories *p*	11	11	11	11
Single G_{Cr} (1%)	2,564	2,564	2,564	2,564
Single G_{Cr} (5%)	2,355	2,355	2,355	2,355
Single high G_p	2,320	1,181	2,213	2,417
Single low G_1	1,746	2,040	1,512	1,299
Classification (high)	*Correct*	*correct*	*correct*	*Straggler*
Straggler Lab ($G_p > G_{Cr}$ (5%))	-	-	-	Lab 7
Classification (low)	*Correct*	*correct*	*correct*	*correct*
Outlier Lab ($G_1 > G_{Cr}$ (1%))	-	-	-	-
Double G_{Cr} (1%)	0,1448	0,1448	0,1448	0,1448
Double G_{Cr} (5%)	0,2213	0,2213	0,2213	0,2213
Double high $G_{largest}$	0,3530	0,7224	0,3164	-
Double low $G_{smalest}$	0,5480	0,2748	0,5986	0,6591
Classification (two largest)	*Correct*	*correct*	*correct*	-
Outlier Lab($G_{largest} < G_{Cr}$ (1%))	-	-	-	-
Classification (two smallest)	*Correct*	*correct*	*correct*	*correct*
Outlier Lab($G_{smalest} < G_{Cr}$ (1%))	-	-	-	-

Single: test for one outlying observation; Double: test for two outlying observations

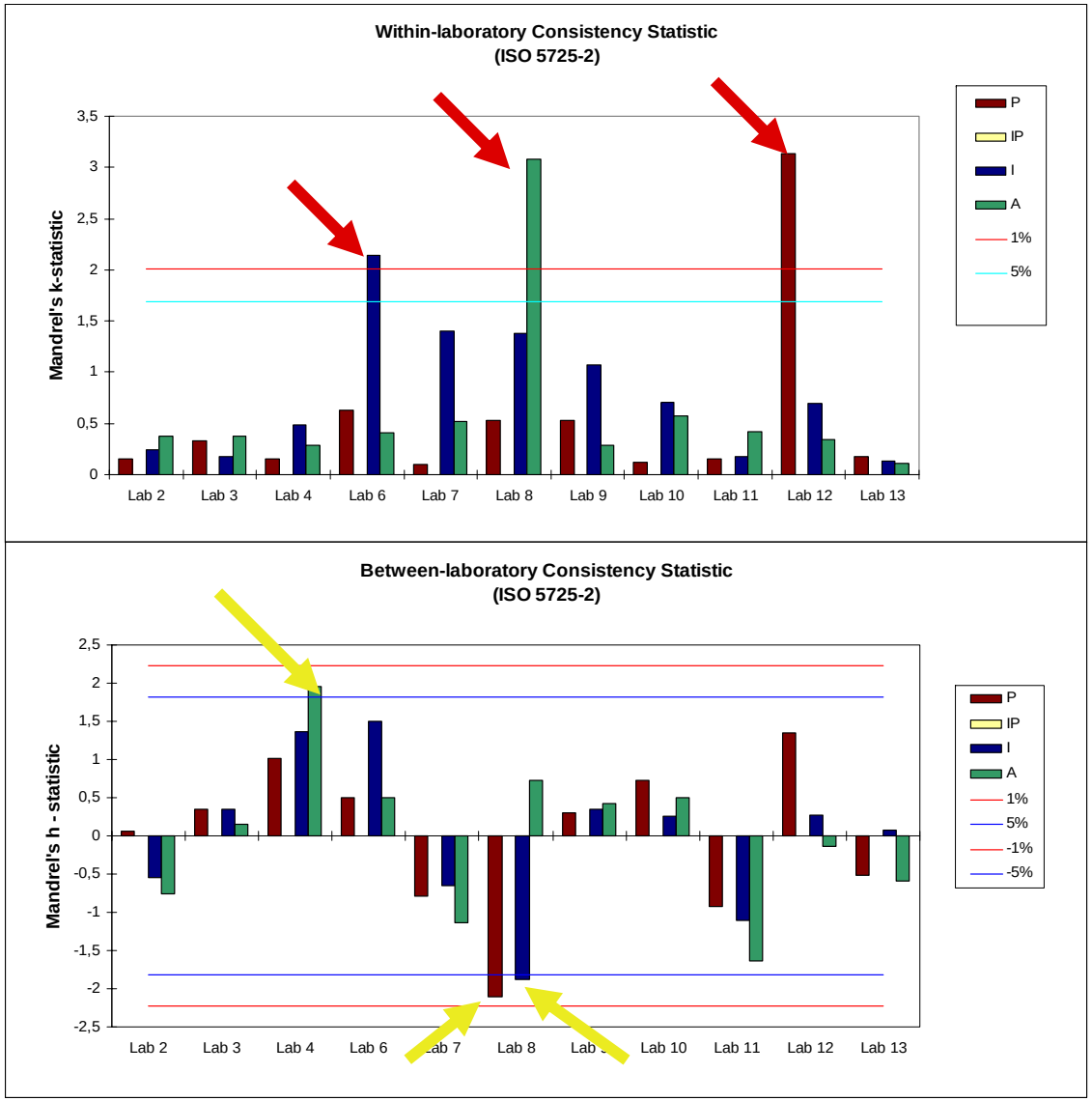
Sealing quality assessment by mass loss (EN 12373-7)

Results of precision analysis

Level	P	IP	I	A
Number of replicates *n*	3	3	3	3
Valid laboratories *p*	10	11	10	10
General mean *m* / g.dm^{-2}	**15,92**	**477,5**	**17,86**	**13,19**
Repeatability variance s_r^2	0,426	140,55	0,457	0,430
Between-lab variance s_L^2	8,359	141,11	9,708	7,442
Reproducibility variance s_R^2	8,785	281,66	10,164	7,871
Repeatability std. dev. s_r	**0,65**	**11,7**	**0,68**	**0,66**
Reproducibility std. dev. s_R	**2,96**	**16,8**	**3,19**	**2,81**
Repeatability COV (s_r/*m*)	4,1%	2,5%	3,8%	5,0%
Reproducibility COV (s_R/*m*)	18,6%	3,5%	17,9%	21,3%
Number of outliers	2	1	1	3
Number of excluded outliers	1	0	1	1
Outlier type	[1]M*h*, [2]M*k*, [3]C	M*k*	M*k*, C	[1]M*h*, [2]M*k*, [3]C
Outlier laboratories	Lab 7 [1] Lab 10 [1,2,3]	Lab 9	Lab 8	Lab7 [1] Lab 8 [2,3]

Outlier type: M*h* – Mandel's *h* ;M*k* – Mandel's *k* ; C - Cochran's ; G(I) – Grubs (one outlying observation) ; G(II) – Grubs (two outlying observations)

Sealing quality assessment by measurement of admittance (EN 12373-5)



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Qualanod

Sealing quality assessment by measurement of admittance (EN 12373-5)

Laboratories outside critical value lines of Mandel's statistics

Level	P	IP	I	A
Mandel's k-plot	Lab 12	n.a.	Lab 6	Lab 8
Classification	*Outlier*	n.a.	*Outlier*	*Outlier*
Mandel´s h-plot	Lab 8	n.a.	Lab 8	Lab 4
Classification	*Straggler*	n.a.	*Straggler*	*Straggler*

n. a. – not applied

Cochran's test results

Level	P	IP	I	A
Valid laboratories *p*	11	n.a.	11	11
Number of replicates *n*	3	n.a.	3	3
1% Critical value $C_{Cr\ (1\%)}$	0,504	n.a.	0,504	0,504
5% Critical value $C_{Cr\ (5\%)}$	0,417	n.a.	0,417	0,417
Cochran's test statistic ***C***	0,893	n.a.	0,419	0,862
Classification	*Outlier*	n.a.	*Straggler*	*Outlier*
Outlier Lab (***C*** >$C_{Cr\ (1\%)}$)	Lab 12	n.a.	Lab 6	Lab 8

n. a. – not applied

Sealing quality assessment by measurement of admittance (EN 12373-5)

Grubb's test results

Level	P	IP	I	A
Valid laboratories *p*	11	n.a.	11	11
Single G_{Cr} (1%)	2,564	n.a.	2,564	2,564
Single G_{Cr} (5%)	2,355	n.a.	2,355	2,355
Single high G_p	1,352	n.a.	1,497	1,961
Single low G_1	2,099	n.a.	1,884	1,642
Classification (high)	*correct*	n.a.	*correct*	*correct*
Outlier Lab ($G_p > G_{Cr}$ (1%))	-	n.a.	-	-
Classification (low)	*correct*	n.a.	*correct*	*correct*
Outlier Lab ($G_1 > G_{Cr}$ (1%))	-	n.a.	-	-
Double G_{Cr} (1%)	0,1448	n.a.	0,1448	0,1448
Double G_{Cr} (5%)	0,2213	n.a.	0,2213	0,2213
Double high $G_{largest}$	0,6505	n.a.	0,4987	0,4826
Double low $G_{smalest}$	0,3741	n.a.	0,4238	0,5148
Classification (two largest)	*correct*	n.a.	*correct*	*correct*
Outlier Lab($G_{largest} < G_{Cr}$ (1%))	-	n.a.	-	-
Classification (two smallest)	*correct*	n.a.	*correct*	*correct*
Outlier Lab($G_{smalest} < G_{Cr}$ (1%))	-	n.a.	-	-

Single: test for one outlying observation; Double: test for two outlying observations
n. a. – not applied

Sealing quality assessment by measurement of admittance (EN 12373-5)

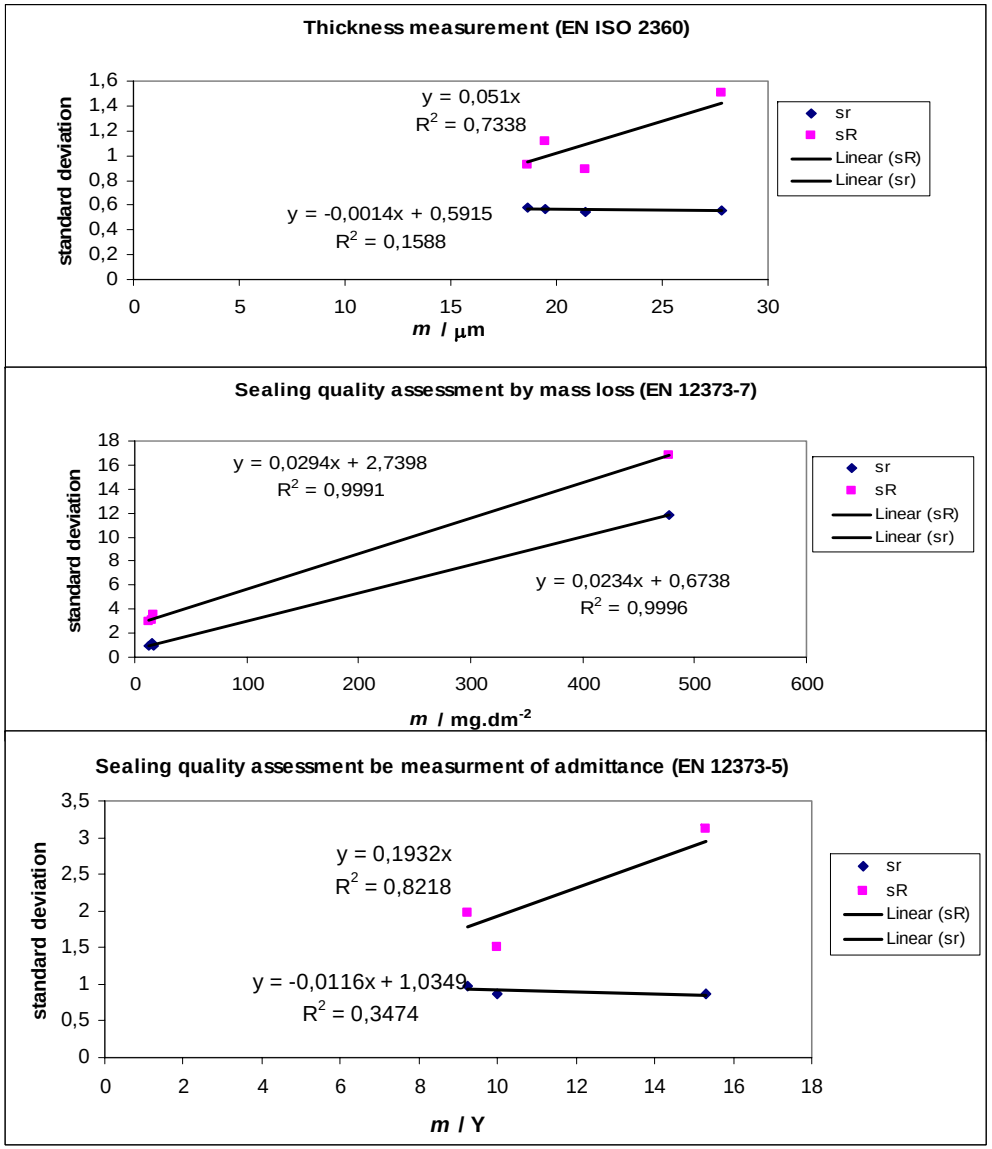
Results of precision analysis

Level	P	I	A
Number of replicates *n*	3	3	3
Valid laboratories *p*	10	11	10
General mean *m* / Y	**8,98**	**15,29**	**9,88**
Repeatability variance s_r^2	0,113	0,747	0,113
Between-lab variance s_L^2	2,858	8,974	1,794
Reproducibility variance s_R^2	2,970	9,720	1,907
Repeatability std. dev. s_r	**0,34**	**0,86**	**0,34**
Reproducibility std. dev. s_R	**1,72**	**3,12**	**1,38**
Repeatability COV (s_r/m)	3,7%	5,7%	3,4%
Reproducibility COV (s_R/m)	19,2%	20,4%	14,0%
Number of outliers	2	1	1
Number of excluded outliers	1	0	1
Outlier type	[1]M*h*, [2]M*k*, [3]C	M*k*	M*k*, C
Outlier laboratories	Lab 8 [1] Lab 12 [2,3]	Lab 6	Lab 8

Outlier type: M*h* – Mandel's *h* ;M*k* – Mandel's *k* ; C - Cochran's ; G(I) – Grubs (one outlying observation) ; G(II) – Grubs (two outlying observations)

Dependency analysis of

precision (repeatability and reproducibility) with the mean



Precision analysis results

EN ISO 2360 – Thickness measurement	Coating type				Excluded data lab:coating type
	P	IP	I	A	
General mean *m* / µm	18,6	19,5	27,8	21,4	None
Repeatability std. dev. s_r	0,58	0,57	0,56	0,54	
Reproducibility std. dev. s_R	0,92	1,12	1,51	0,89	
Global repeatability std. dev.	0,56				
Global reproducibility std. dev.	$S_R = 0{,}051\ m$ (R^2=0,7338)				

Thickness
Repeatability=0.56
Reproducibility=1.51

(standard :
1 µm (until 10 µm or 10%

EN 12373-7 - Sealing quality assessment by mass loss	Coating type				Excluded data lab:coating type
	P	IP	I	A	
General mean *m* / g.dm^{-2}	15,9	477,5	17,9	13,2	Lab 10:P Lab 8:I Lab 8:A
Repeatability std. dev. s_r	0,65	11,9	0,68	0,66	
Reproducibility std. dev. s_R	2,96	16,8	3,19	2,81	
Global repeatability std. dev.	$S_R = 0{,}0234\ m + 0{,}6738$ ($R^2 \approx 1$)				
Global reproducibility std. dev.	$S_R = 0{,}0294\ m + 2{,}7398$ ($R^2 \approx 1$)				

Sealing/mass loss
< 30
Repeatability=1
Reproducibility=3

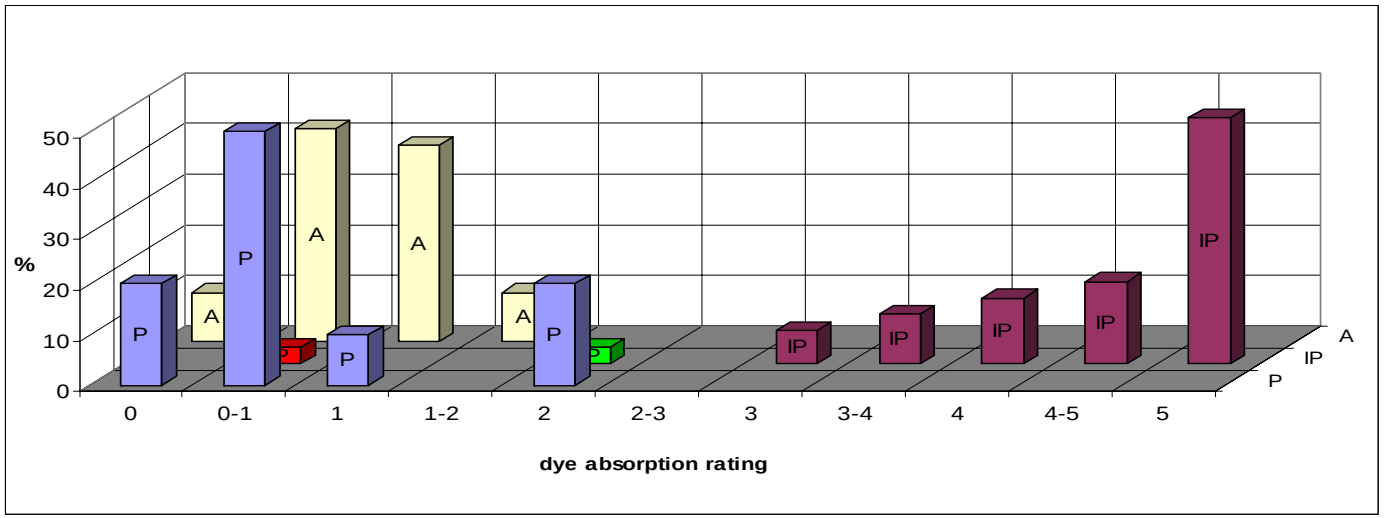
EN 12373-5 - Sealing quality assess. by admittance	Coating type				Excluded data lab:coating type
	P	IP	I	A	
General mean *m* / Y	8,98	n.a	15,29	9,88	Lab 12:P Lab 8:A
Repeatability std. dev. s_r	0,34	n.a	0,86	0,34	
Reproducibility std. dev. s_R	1,72	n.a	3,12	1,38	
Global repeatability std. dev.	0,51				
Global reproducibility std. dev.	$S_R = 0{,}1932\ m$ (R^2=0,8218)				

Sealing/admitance
Repeatability=0.51
Reproducibility=3.12

Estimation of loss of absorptive power of anodic oxidation coatings after sealing by dye spot test (EN 12373-4)

Analysis of qualitative results

Frequency distribution of the results



Coating type	*Dye absorption rating*			Laboratory with results outside the range of 95%
	Mode	Median	Range of 95% of results	
P	0-1	0-1	0 to 2	None
IP	5	Between 4-5 and 5	3 to 5	Lab 2 (1 result)
A	0-1	0-1	0 to 1-2	None