

FLUXANA®

XRF Application Solutions

RV-2017-01

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Final Proficiency Test Report

for Used Auto Catalytic Converters

FLX-CRM 132, FLX-CRM 133



Bedburg-Hau, 16 October 2017

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Statistics and Report
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FLX-CRM 132	Rh	Pt	Pd
Unit	mg/kg	mg/kg	mg/kg
No. of laboratories	9	9	9
Reference value C_{Ref}	295	1770	1673
Mean m	290,7	1779,3	1666,8
Reproducibility standard deviation S_R	14,8	88,2	31,9
Repeatability standard deviation s_r	7,0	14,3	9,7
Robust standard deviation s^*	11,9	117,1	36,7
Uncertainty U (s^*) P=95%	10,0	97,5	30,6
Uncertainty U (S_R) P=95%	12,3	73,5	26,6
$C_{Ref} - 2 \cdot S_R$	266	1594	1609
$C_{Ref} + 2 \cdot S_R$	325	1946	1737

FLX-CRM 133	Rh	Pt	Pd
Unit	mg/kg	mg/kg	mg/kg
No. of laboratories	9	9	9
Reference value C_{Ref}	242	465	1075
Mean m	239,7	463,9	1072,7
Reproducibility standard deviation S_R	22,1	33,2	48,6
Repeatability standard deviation s_r	2,8	5,7	10,3
Robust standard deviation s^*	16,0	33,6	87,2
Uncertainty U (s^*) P=95%	13,3	28,0	72,7
Uncertainty U (S_R) P=95%	18,4	27,7	40,5
$C_{Ref} - 2 \cdot S_R$	198	399	978
$C_{Ref} + 2 \cdot S_R$	286	532	1172



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Introduction

X-ray fluorescence analysis is a widely used technique for the rapid screening analysis of catalytic converter samples.

However, for the calibration of XRF instruments dedicated standard material is needed. As a worldwide supplier for XRF laboratories, FLUXANA has developed a number of services to support XRF users. One of these services is the production of new reference materials and the organization of proficiency tests (PT).

In 2011, FLUXANA introduced its own quality management.

In February 2014, FLUXANA received accreditation from German DAKKS according to DIN EN ISO/IEC 17025 for the test laboratory in Bedburg-Hau.

The production of reference materials and the performance of proficiency tests is not yet accredited. However, FLUXANA has applied for the accreditation process at DAKKS.

Nevertheless, all evaluations are performed in agreement with DIN EN ISO/IEC 17043:2010-05, ISO Guide 34:2009, ISO Guide 31:2000 and ISO Guide 35:2006.

Further information

In the following evaluation report all laboratory data are listed. Also the used methods and the working under ISO 17025. Under Comment additional information is given. The report is based on z-scores. The diagram shows the relative difference to the assigned values.

Outliers

Outliers in the statistical sense are typically not detected when using robust statistical methods, because the robust A+S algorithms were found to work better than the classical approach (which is outlier detection plus arithmetic mean and classical s.d. formula). Outliers shown in the evaluation are only based on z-scores and marked in yellow and red.



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Participants

PSA Groupe	France
FLUXANA GmbH & Co.KG	Germany
HTV Conservation GmbH	Germany
ReMetall Deutschland AG	Germany
Saxonia Edelmetalle GmbH	Germany
Spectro Analytical Instruments GmbH	Germany
Thermo Fisher Scientific Messtechnik GmbH	Germany
Oxford Instruments Industrial Analysis	Great Britain

Statistical Evaluation

Reference concentration c_{Ref}

The reference concentration was determined in an extra proficiency test study RV132.

Calculation of Mean m

The mean m for all laboratories was calculated using the Hampel estimator (ISO/TS 20612:2007 9.2.3) based on the laboratory means μ .

Calculation of reproducibility standard deviation s_R

The reproducibility standard deviation s_R was calculated using the Q-method (ISO/TS 20612:2007 9.2.3).

Calculation of repeatability standard deviation s_r

The repeatability standard deviation s_r was also calculated using the Q-method.



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Calculation of robust standard deviation s^*

The robust standard deviation s^* was calculated from the laboratory means μ using the Q-method.

Calculation of uncertainty U_{S_R} (according Nordtest TR 537 ed 3.1.)

The **uncertainty U_{S_R}** for a confidence interval of P=95% (k=2) can be calculated from the **reproducibility standard deviation S_R** (factor 1.25 for average median, robust statistics):

$$U_{S_R} = 2 * 1.25 * \frac{S_R}{\sqrt{p}}$$

Calculation of uncertainty U_{s^*} (according ISO 13528:2015)

The **uncertainty U_{s^*}** for a confidence interval of P=95% (k=2) can be calculated from the **robust standard deviation s^*** (factor 1.25 for average median, robust statistics):

$$U_{s^*} = 2 * 1.25 * \frac{s^*}{\sqrt{p}}$$

The **uncertainty U_{s^*}** takes only the between laboratories uncertainty into account while the **uncertainty U_{S_R}** also includes the within laboratories uncertainty. Therefore **U_{S_R}** is recommended for use in accredited laboratories.



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Laboratory performance

Laboratory proficiency assessment was based on z-scores.
From all laboratory means μ the **z-score** z was calculated:

$$z = \frac{\mu - C_{Ref}}{S_R}$$

C_{Ref}	Reference concentration
μ	Mean value of individual laboratory
S_R	Reproducibility standard deviation

Assessment on z-scores:

$ z \leq 2.0$	indicates, satisfactory' performance = generates no signal
$2.0 < z < 3.0$	indicates, questionable' performance = generates a warning signal
$ z \geq 3.0$	indicates, unsatisfactory' performance = generates an action signal

Z-scores with $|z| \geq 2$ were highlighted with a yellow color, z-scores with $|z| \geq 3$ were highlighted with a red color.

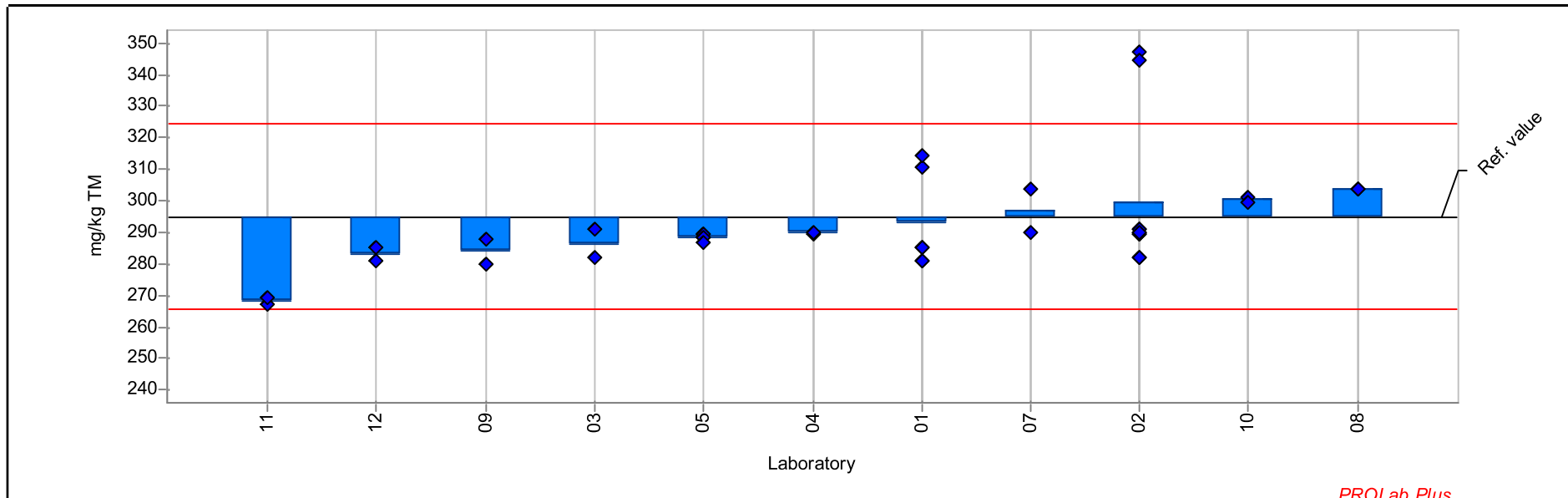
Comment

- 1) Spectro XEPOS I
- 2) Niton XL 3t
- 3) ICP AES (fusion melt with copper, digestion with aqua regia) Thermo Fisher ICAP 6300
- 4) ICAP7400rad, Y int. Std,after collection with copper
- 5) Spectro XEPOS
- 6) Method: Car Catalyst, Instrument: X-MET8000
- 7) standard-free, fundamental parameter-based measuring, stationary XRF
- 8) Sample has not been dried. Hanheld XRF Thermo Scientific Niton Analyzer XL3t 980
- 9) S8 Tiger Bruker

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Summary results

Sample:	FLX-CRM 132	Reprod. s.d.	14,8 mg/kg TM
Measurand:	Rh	Repeat. s.d	7,0 mg/kg TM
Mean ± U(Mean):	290,7 ± 10,0 mg/kg TM	Range of tolerance:	265,5 - 324,5 mg/kg TM (z-score ≤ 2,000)
No. of laboratories:	9	Statistical method	Q/Hampel
Ref. value	295,0 mg/kg TM	Target s.d.	14,8 mg/kg TM (Empirical value)



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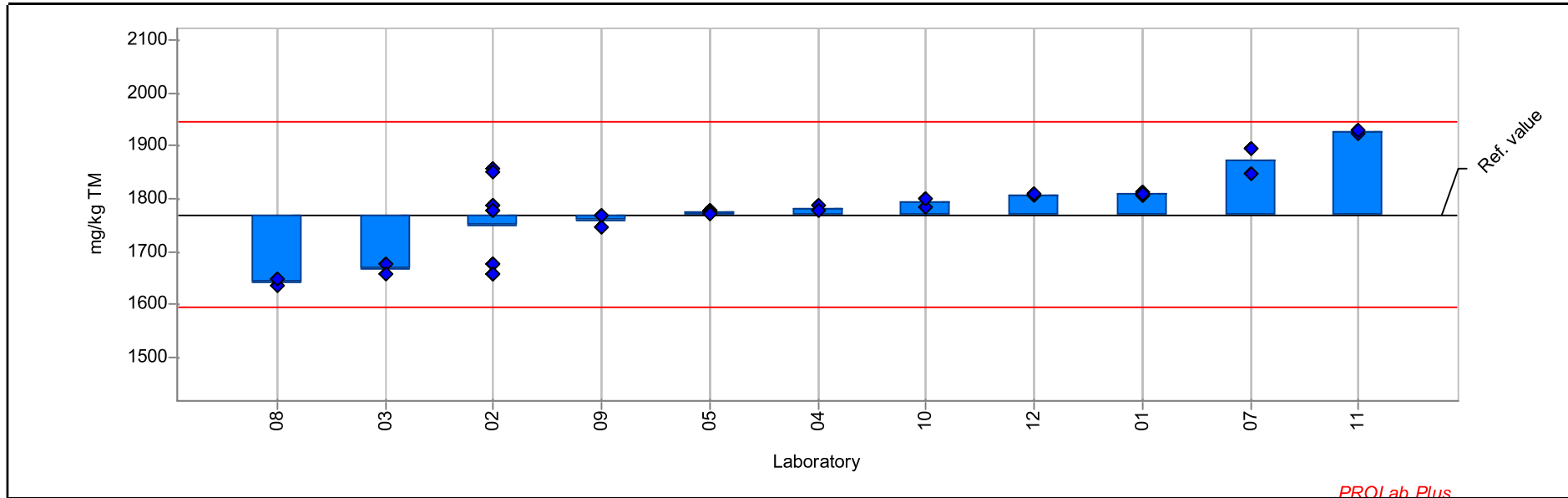
Lab code	Lab mean	s.d.	z-score	Conc. 1	Conc. 2	Conc. 3	Conc. 4	Conc. 5	Conc. 6	Comment
01	293,0	15,3	-0,137	310,5	314,6	285,3	281,1	285,3	281,1	
02	299,7	24,5	0,320	347,0	344,4	291,0	282,0	289,7	290,2	1)
03	286,5	6,4	-0,575	291,0	282,0					2)
04	289,9	0,4	-0,342	289,7	290,2					info only 3)

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Lab code	Lab mean	s.d.	z-score	Conc. 1	Conc. 2	Conc. 3	Conc. 4	Conc. 5	Conc. 6	Comment
05	288,5	1,0	-0,439	288,3	289,6	289,2	288,5	287,0		info only 4)
07	296,8	9,5	0,118	303,5	290,0					7)
08	304,0	0,0	0,609	304,0	304,0					9)
09	284,0	5,7	-0,745	280,0	288,0					8)
10	300,3	0,8	0,359	300,9	299,7					6)
11	268,3	1,8	-1,811	267,0	269,5					5)
12	283,2	3,0	-0,799	285,3	281,1					

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Sample: FLX-CRM 132 **Reprod. s.d.:** 88,2 mg/kg TM
Measurand: Pt **Repeat. s.d.:** 14,3 mg/kg TM
Mean ± U(Mean): 1779,3 ± 97,5 mg/kg TM **Range of tolerance:** 1593,6 - 1946,4 mg/kg TM (|z-score| ≤ 2,000)
No. of laboratories: 9 **Statistical method:** Q/Hampel
Ref. value: 1770,0 mg/kg TM **Target s.d.:** 88,2 mg/kg TM (Empirical value)



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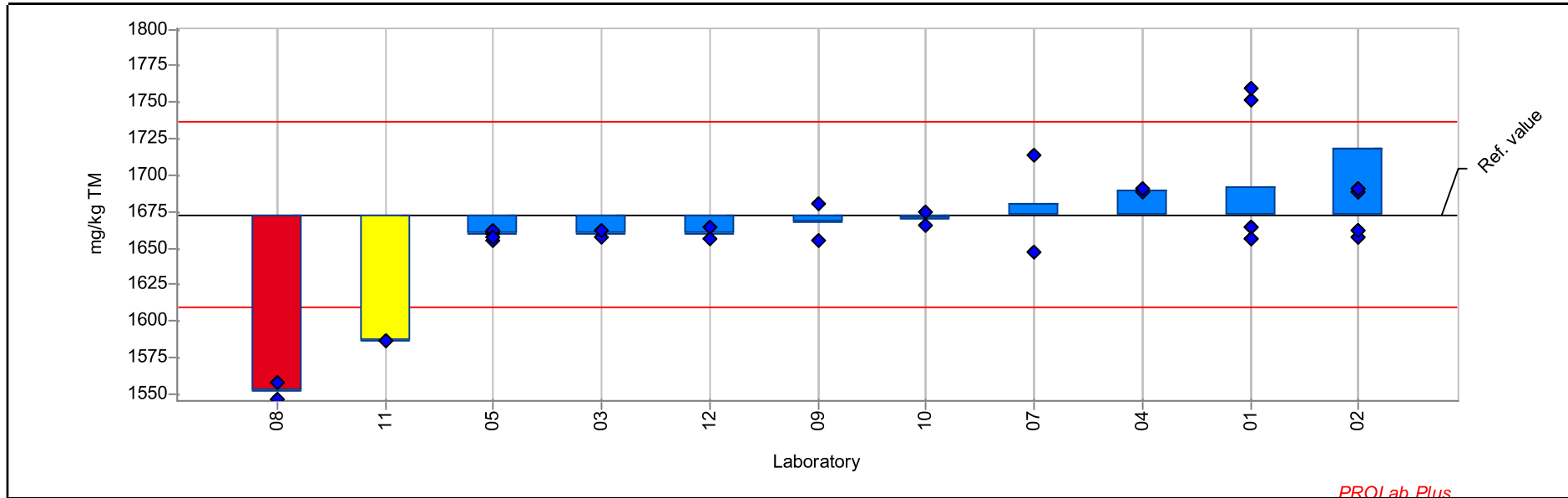
Lab code	Lab mean	s.d.	z-score	Conc. 1	Conc. 2	Conc. 3	Conc. 4	Conc. 5	Conc. 6	Comment
01	1808,0	2,7	0,431	1812,0	1808,0	1805,0	1809,0	1805,0	1809,0	
02	1750,6	77,1	-0,220	1857,3	1849,7	1676,8	1657,8	1787,7	1777,3	1)
03	1667,3	13,4	-1,164	1676,8	1657,8					2)
04	1782,5	7,4	0,142	1787,7	1777,3					info only 3)
05	1775,7	2,1	0,065	1776,9	1777,3	1776,3	1776,2	1772,0		info only 4)

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Lab code	Lab mean	s.d.	z-score	Conc. 1	Conc. 2	Conc. 3	Conc. 4	Conc. 5	Conc. 6	Comment
07	1871,5	31,8	1,151	1849,0	1894,0					7)
08	1643,0	8,5	-1,440	1637,0	1649,0					9)
09	1758,0	15,6	-0,136	1747,0	1769,0					8)
10	1792,8	10,0	0,258	1785,7	1799,9					6)
11	1927,0	5,7	1,780	1923,0	1931,0					5)
12	1807,0	2,8	0,419	1805,0	1809,0					

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Sample: FLX-CRM 132 **Reprod. s.d.:** 31,9 mg/kg TM
Measurand: Pd **Repeat. s.d.:** 9,7 mg/kg TM
Mean ± U(Mean): 1666,8 ± 30,6 mg/kg TM **Range of tolerance:** 1609,1 - 1736,9 mg/kg TM (|z-score| <= 2,000)
No. of laboratories: 9 **Statistical method:** Q/Hampel
Ref. value: 1673,0 mg/kg TM **Target s.d.:** 31,9 mg/kg TM (Empirical value)



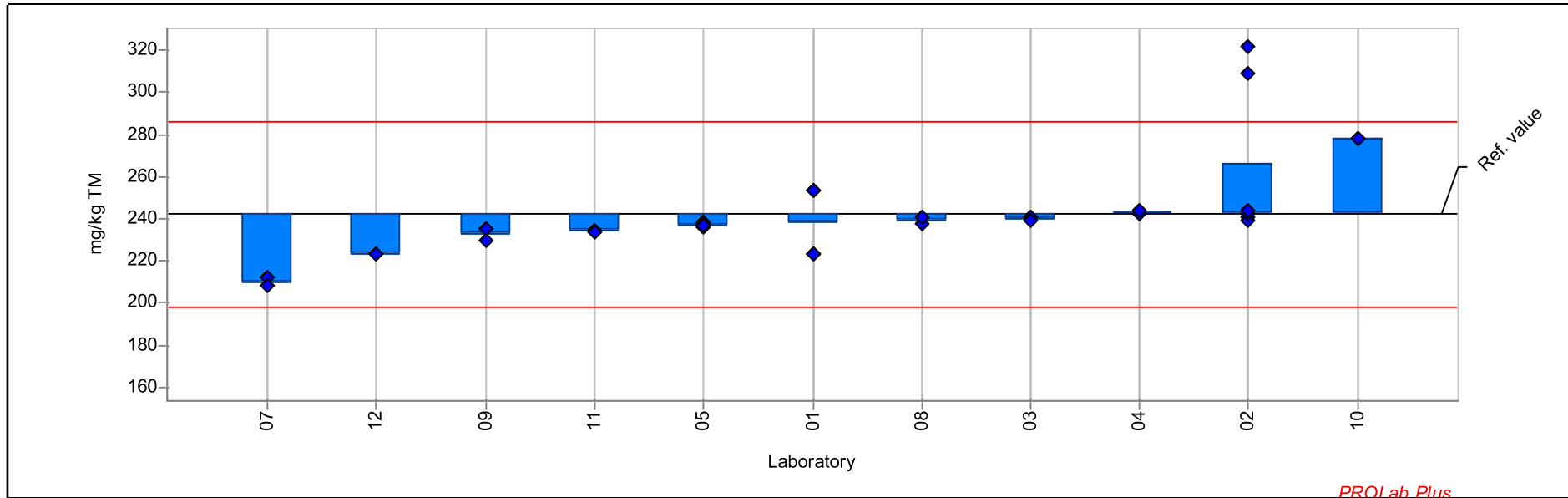
Lab code	Lab mean	s.d.	z-score	Conc. 1	Conc. 2	Conc. 3	Conc. 4	Conc. 5	Conc. 6	Comment
01	1691,7	49,3	0,585	1751,0	1759,0	1664,0	1656,0	1664,0	1656,0	
02	1717,9	92,8	1,405	1891,3	1892,3	1657,0	1662,0	1688,0	1690,5	1)
03	1659,5	3,5	-0,423	1657,0	1662,0					2)
04	1689,3	1,8	0,509	1688,0	1690,5					info only 3)
05	1659,4	2,8	-0,427	1660,3	1661,3	1662,3	1655,5	1657,4		info only 4)

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Lab code	Lab mean	s.d.	z-score	Conc. 1	Conc. 2	Conc. 3	Conc. 4	Conc. 5	Conc. 6	Comment
07	1680,6	47,6	0,236	1714,2	1646,9					7)
08	1552,0	8,5	-3,790	1546,0	1558,0					9)
09	1668,0	18,4	-0,157	1681,0	1655,0					8)
10	1670,2	5,8	-0,088	1666,1	1674,3					6)
11	1586,5	0,7	-2,709	1586,0	1587,0					5)
12	1660,0	5,7	-0,407	1664,0	1656,0					

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Sample: FLX-CRM 133 **Reprod. s.d.:** 22,1 mg/kg TM
Measurand: Rh **Repeat. s.d.:** 2,8 mg/kg TM
Mean ± U(Mean): 239,7 ± 13,3 mg/kg TM **Range of tolerance:** 197,8 - 286,2 mg/kg TM (|z-score| ≤ 2,000)
No. of laboratories: 9 **Statistical method:** Q/Hampel
Ref. value: 242,0 mg/kg TM **Target s.d.:** 22,1 mg/kg TM (Empirical value)



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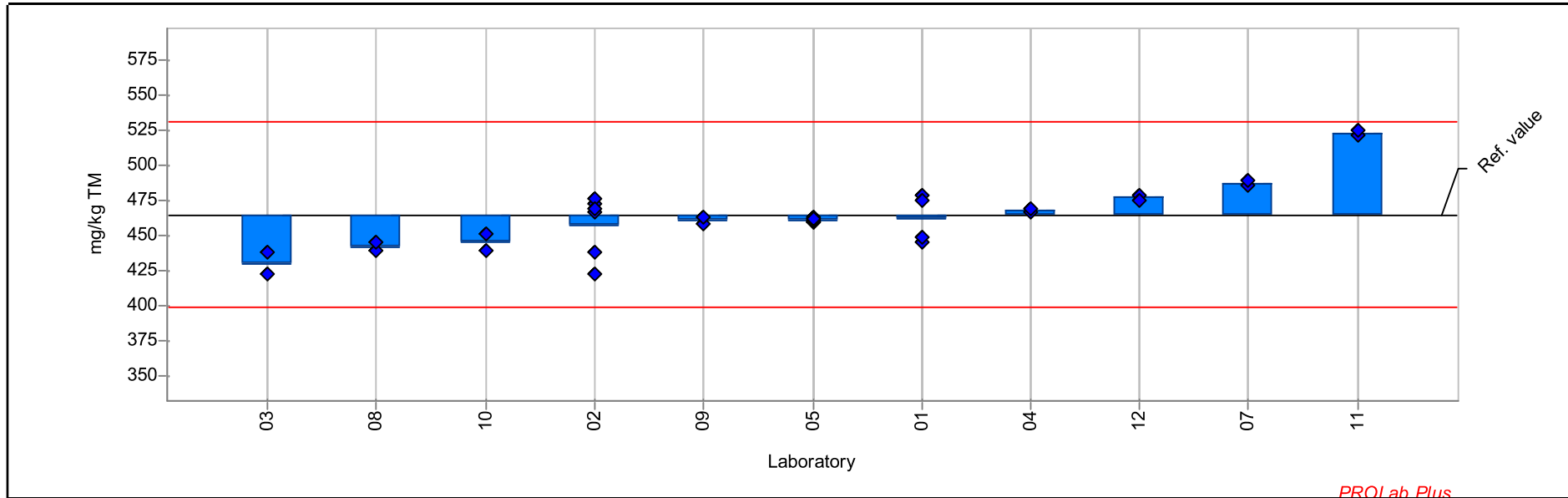
Lab code	Lab mean	s.d.	z-score	Conc. 1	Conc. 2	Conc. 3	Conc. 4	Conc. 5	Conc. 6	Comment
01	238,4	17,4	-0,164	253,4	253,5	223,3	223,3			
02	266,2	38,4	1,095	308,9	322,0	240,9	238,9	242,3	244,3	1)
03	239,9	1,4	-0,095	240,9	238,9					2)
04	243,3	1,4	0,059	242,3	244,3					info only 3)
05	237,2	0,8	-0,219	237,2	238,2	237,3	236,0	237,1		info only 4)

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Lab code	Lab mean	s.d.	z-score	Conc. 1	Conc. 2	Conc. 3	Conc. 4	Conc. 5	Conc. 6	Comment
07	210,3	3,2	-1,436	212,5	208,0					7)
08	239,5	2,1	-0,113	238,0	241,0					9)
09	232,5	3,5	-0,430	230,0	235,0					8)
10	278,1	0,1	1,635	278,2	278,1					6)
11	234,3	0,5	-0,350	234,6	233,9					5)
12	223,3	0,0	-0,846	223,3	223,3					

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Sample: FLX-CRM 133 **Reprod. s.d.:** 33,2 mg/kg TM
Measurand: Pt **Repeat. s.d.:** 5,7 mg/kg TM
Mean ± U(Mean): 463,9 ± 28,0 mg/kg TM **Range of tolerance:** 398,5 - 531,5 mg/kg TM (|z-score| ≤ 2,000)
No. of laboratories: 9 **Statistical method:** Q/Hampel
Ref. value: 465,0 mg/kg TM **Target s.d.:** 33,2 mg/kg TM (Empirical value)



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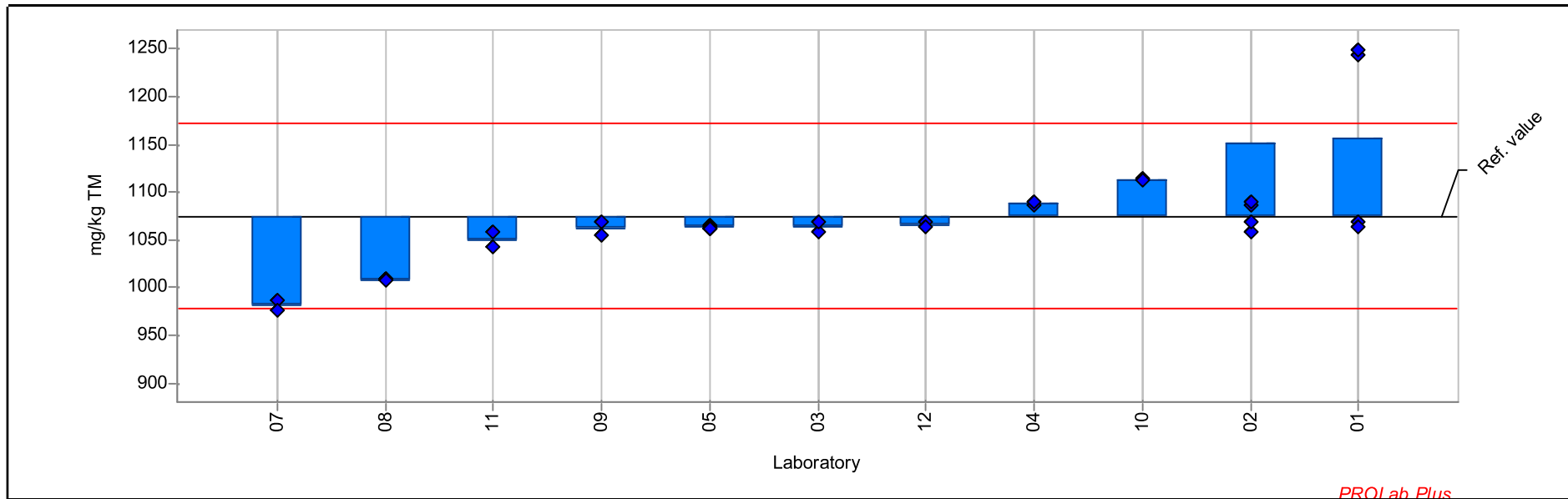
Lab code	Lab mean	s.d.	z-score	Conc. 1	Conc. 2	Conc. 3	Conc. 4	Conc. 5	Conc. 6	Comment
01	462,1	17,3	-0,086	445,6	448,8	478,6	475,5			
02	457,4	22,1	-0,229	473,2	476,0	422,2	437,7	466,5	468,8	1)
03	429,9	11,0	-1,054	422,2	437,7					2)
04	467,6	1,6	0,080	466,5	468,8					info only 3)
05	461,1	1,4	-0,116	459,8	459,7	461,4	462,7	462,1		info only 4)

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Lab code	Lab mean	s.d.	z-score	Conc. 1	Conc. 2	Conc. 3	Conc. 4	Conc. 5	Conc. 6	Comment
07	487,5	2,0	0,677	486,1	488,9					7)
08	442,0	4,2	-0,692	439,0	445,0					9)
09	460,5	3,5	-0,135	458,0	463,0					8)
10	444,9	8,6	-0,606	450,9	438,8					6)
11	523,3	2,8	1,752	521,3	525,2					5)
12	477,1	2,2	0,362	478,6	475,5					

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Sample:	FLX-CRM 133	Reprod. s.d.	48,6 mg/kg TM
Measurand:	Pd	Repeat. s.d	10,3 mg/kg TM
Mean ± U(Mean):	1072,7 ± 72,7 mg/kg TM	Range of tolerance:	977,7 - 1172,3 mg/kg TM (z-score ≤ 2,000)
No. of laboratories:	9	Statistical method	Q/Hampel
Ref. value	1075,0 mg/kg TM	Target s.d.	48,6 mg/kg TM (Empirical value)



Lab code	Lab mean	s.d.	z-score	Conc. 1	Conc. 2	Conc. 3	Conc. 4	Conc. 5	Conc. 6	Comment
01	1156,0	104,0	1,665	1243,0	1249,0	1069,0	1063,0			
02	1150,4	116,2	1,550	1295,3	1303,8	1058,3	1068,2	1086,8	1090,0	1)
03	1063,3	7,0	-0,242	1058,3	1068,2					2)
04	1088,4	2,3	0,275	1086,8	1090,0					info only 3)
05	1063,1	2,1	-0,244	1066,0	1064,4	1062,6	1061,4	1061,2		info only 4)

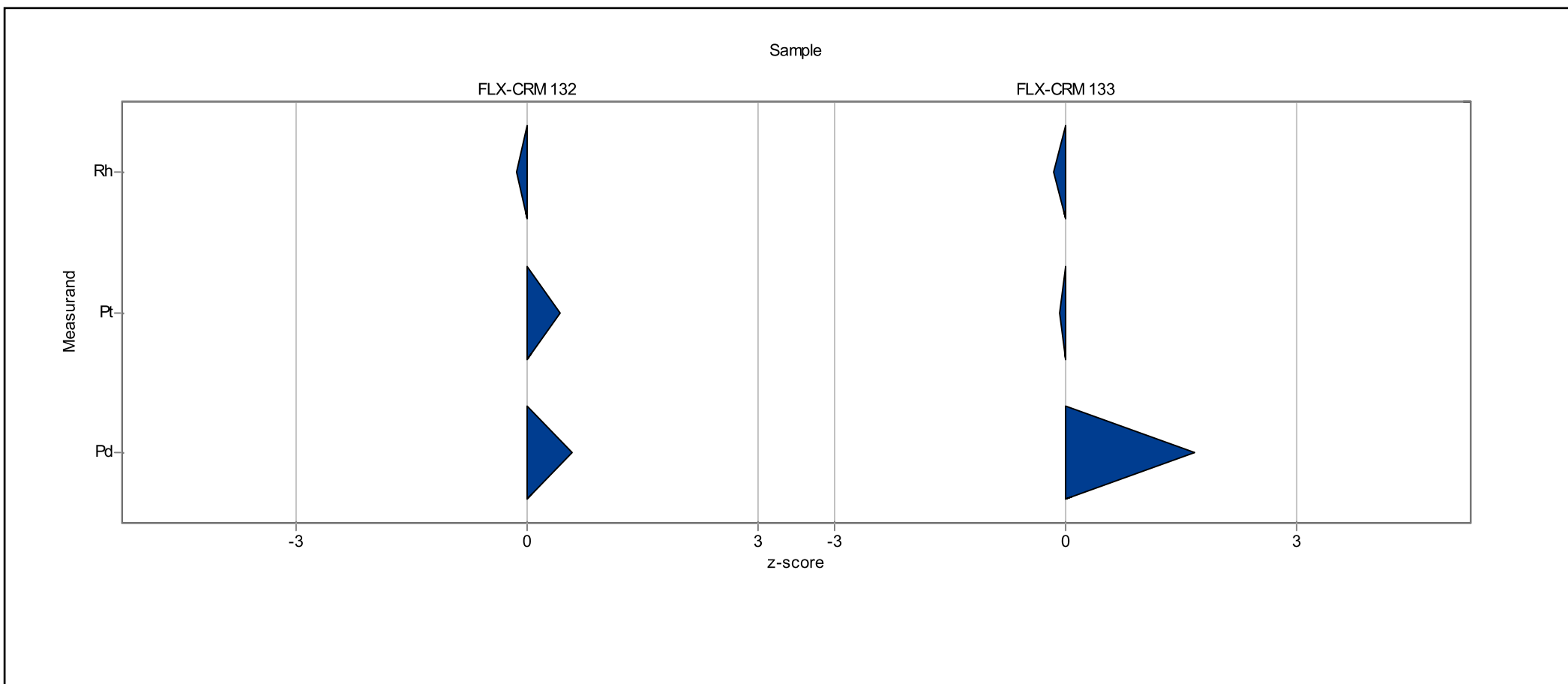
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Lab code	Lab mean	s.d.	z-score	Conc. 1	Conc. 2	Conc. 3	Conc. 4	Conc. 5	Conc. 6	Comment
07	981,7	6,9	-1,918	986,6	976,8					7)
08	1008,5	2,1	-1,367	1010,0	1007,0					9)
09	1062,0	9,9	-0,267	1069,0	1055,0					8)
10	1113,3	1,8	0,787	1114,6	1112,0					6)
11	1050,0	11,3	-0,514	1058,0	1042,0					5)
12	1066,0	4,2	-0,185	1069,0	1063,0					

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Laboratory chart of z-scores

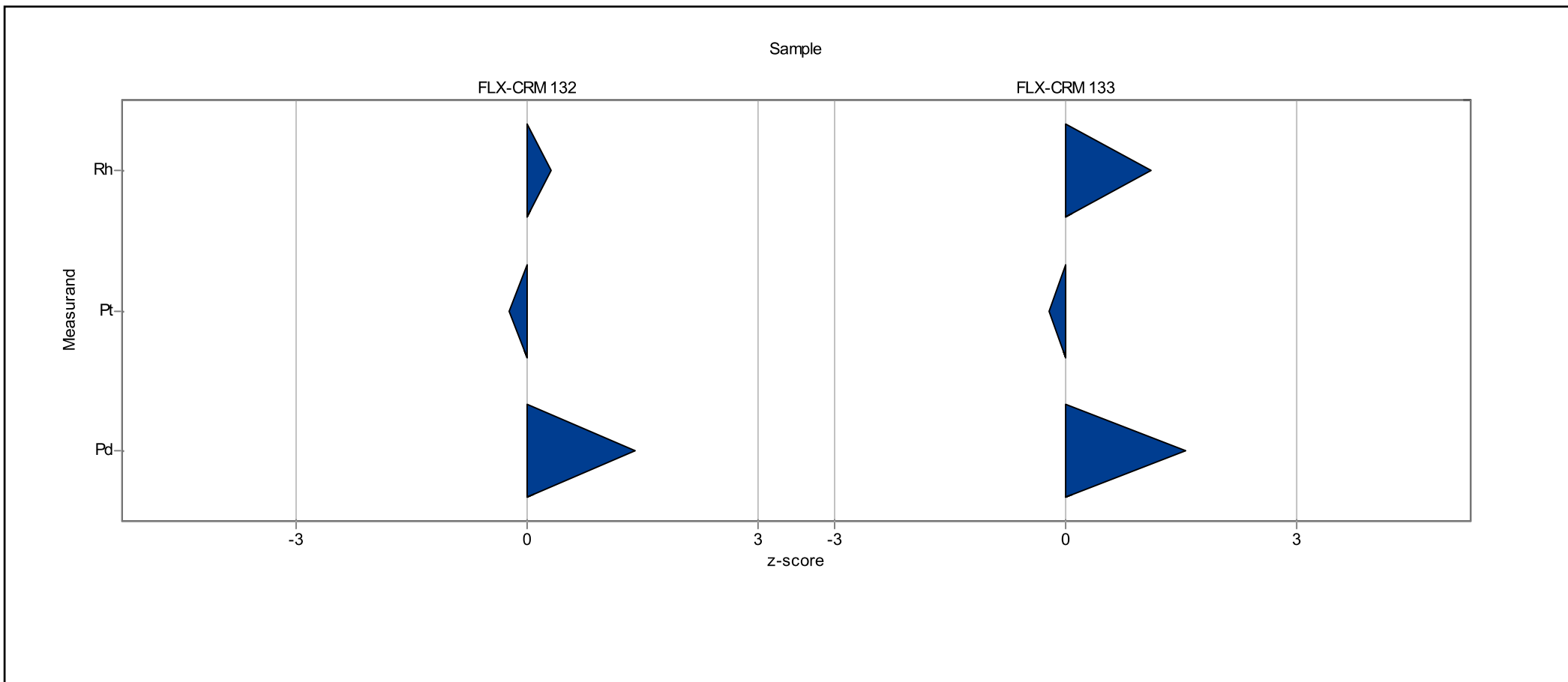
Laboratory: 01



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Laboratory chart of z-scores

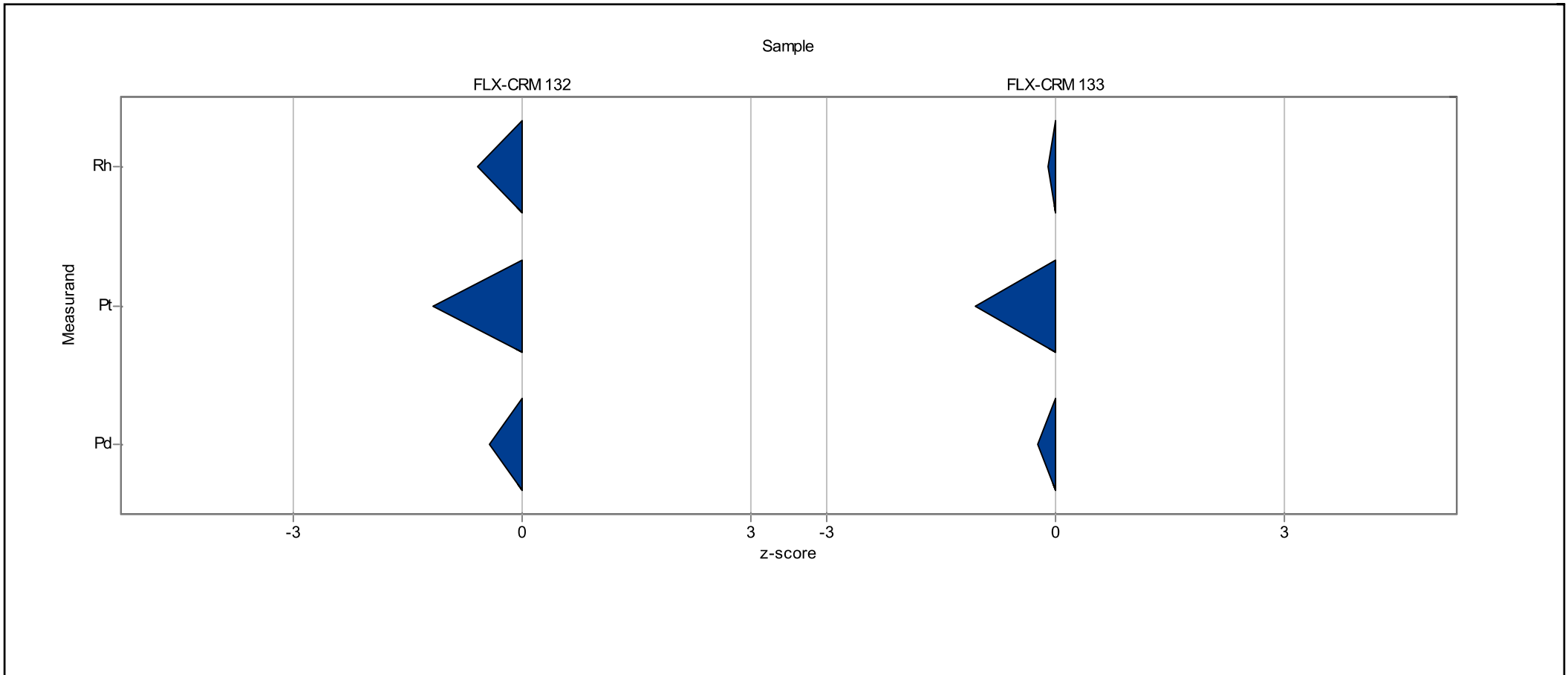
Laboratory: 02



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Laboratory chart of z-scores

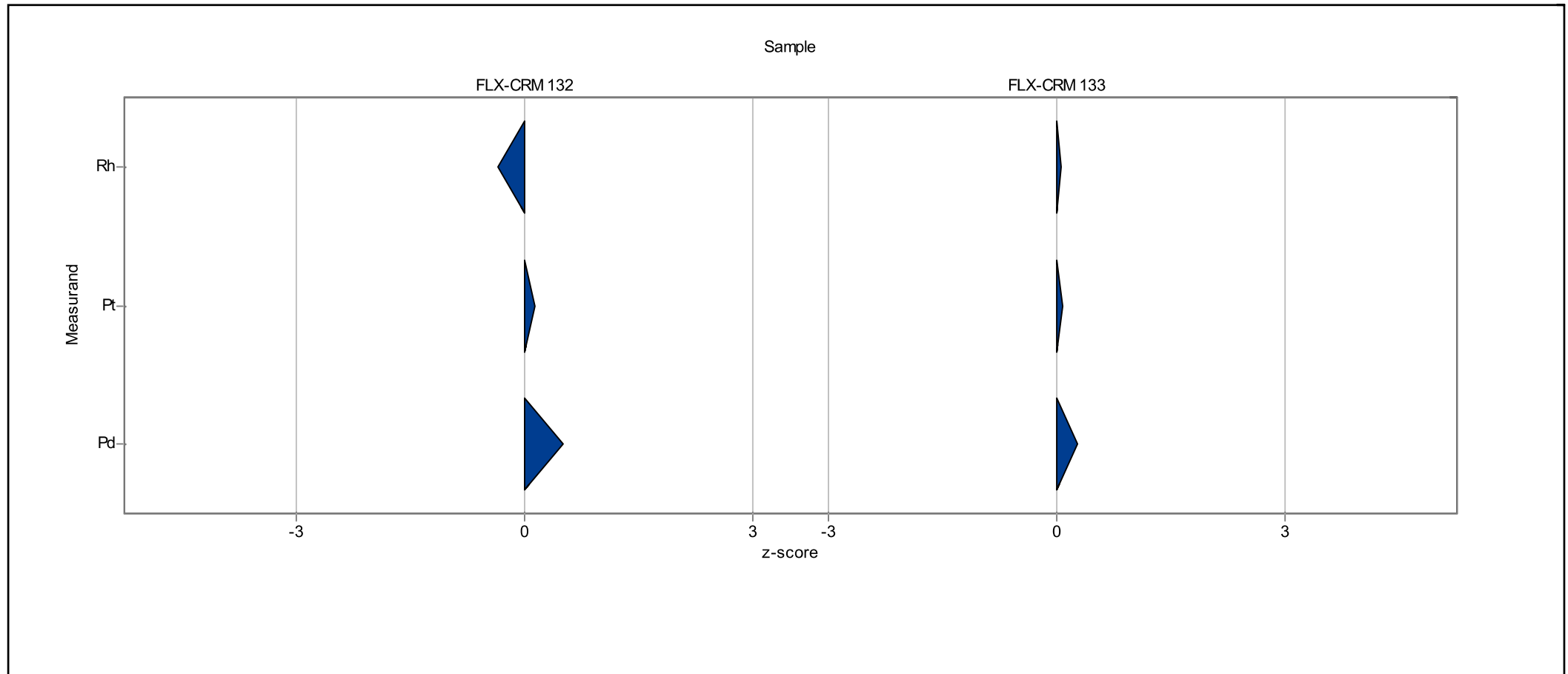
Laboratory: 03



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Laboratory chart of z-scores

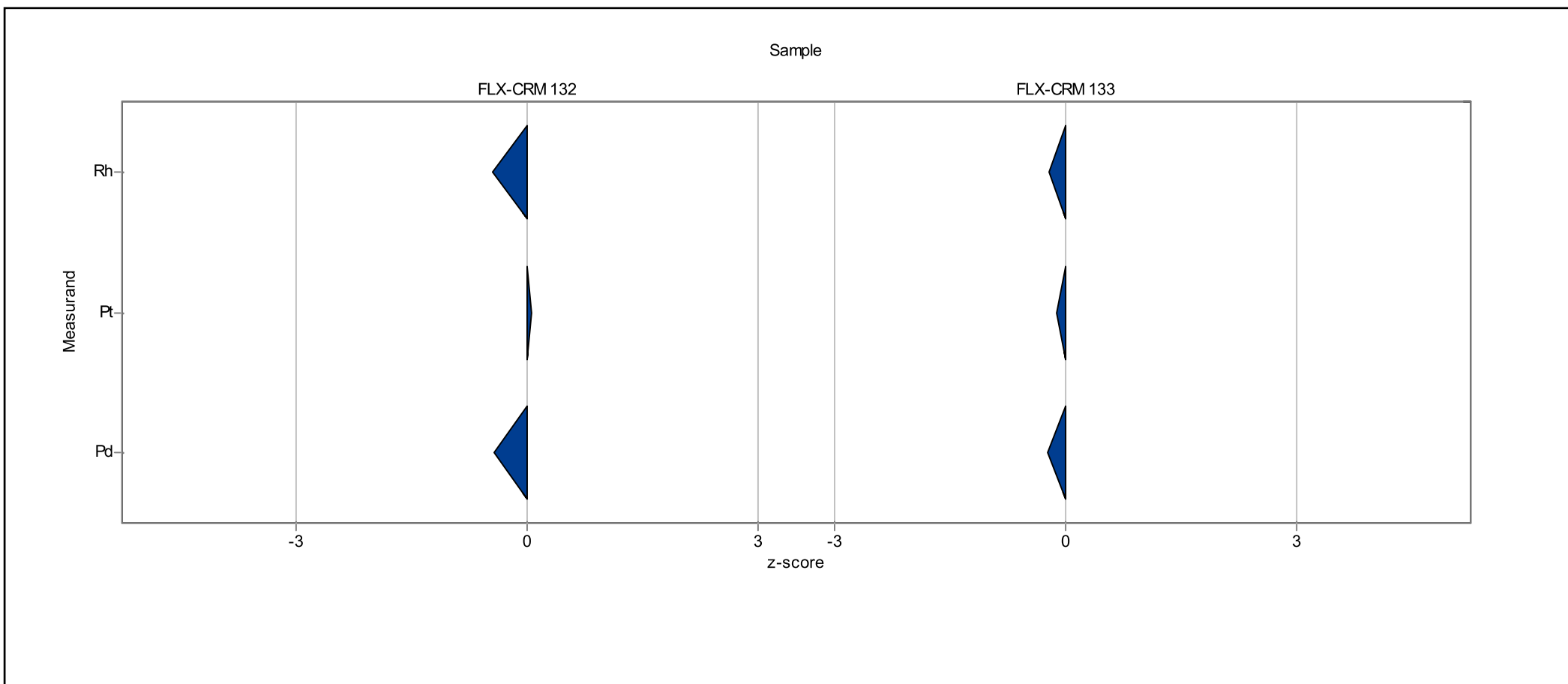
Laboratory: 04



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Laboratory chart of z-scores

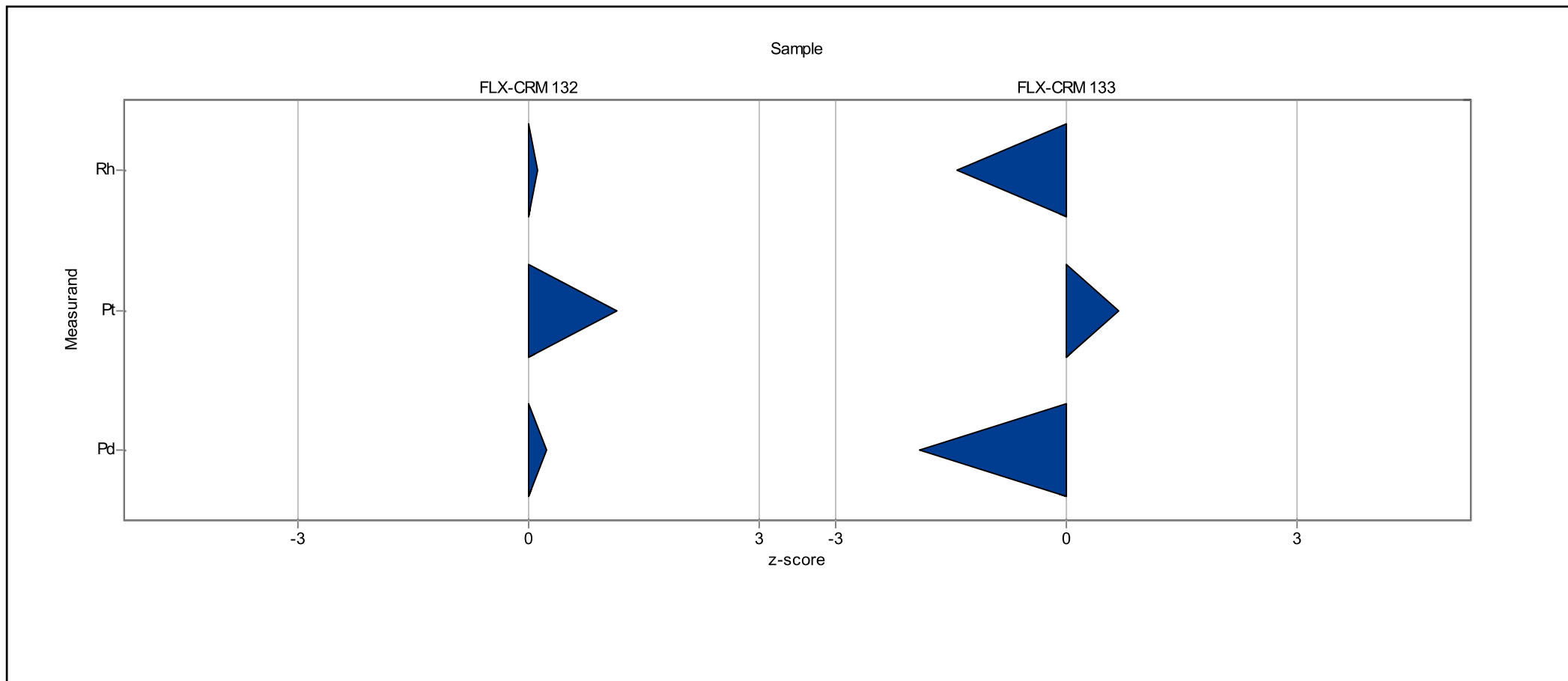
Laboratory: 05



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Laboratory chart of z-scores

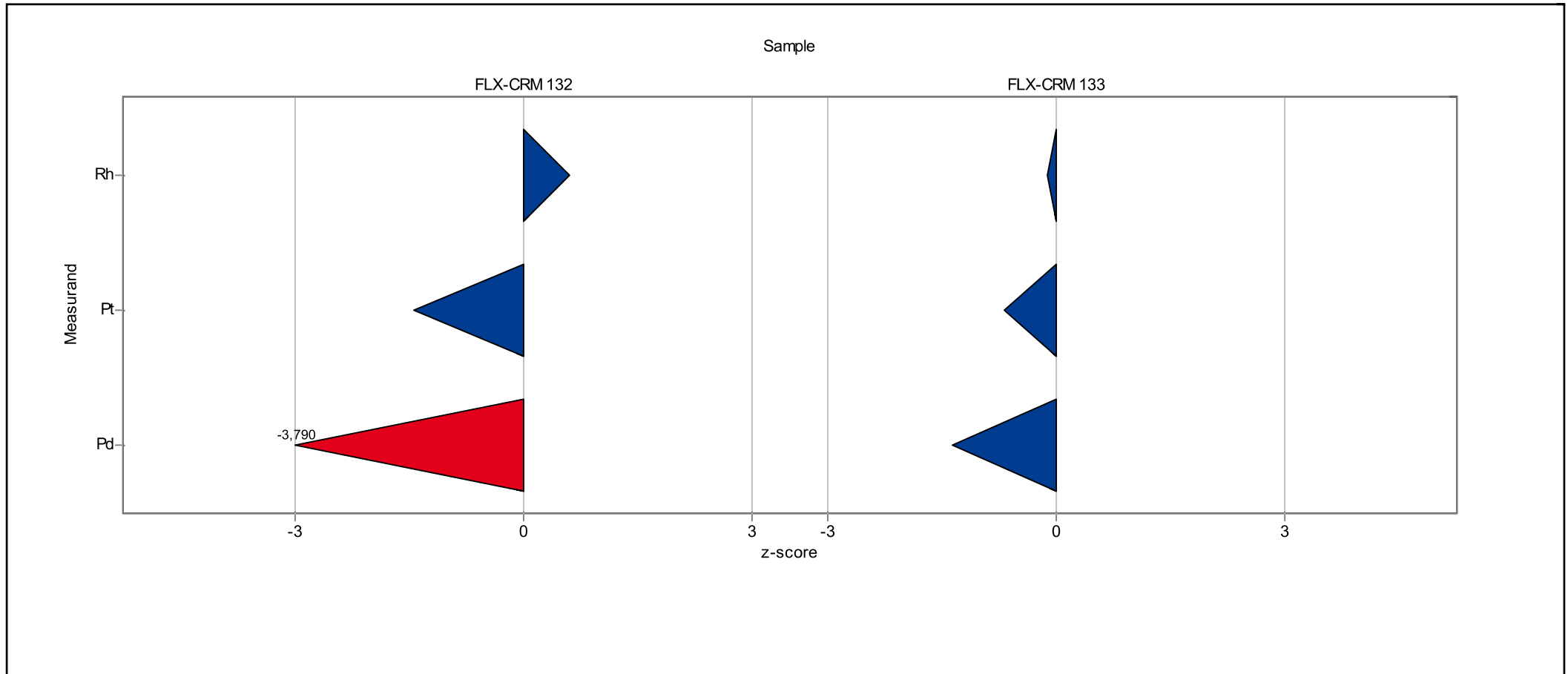
Laboratory: 07



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Laboratory chart of z-scores

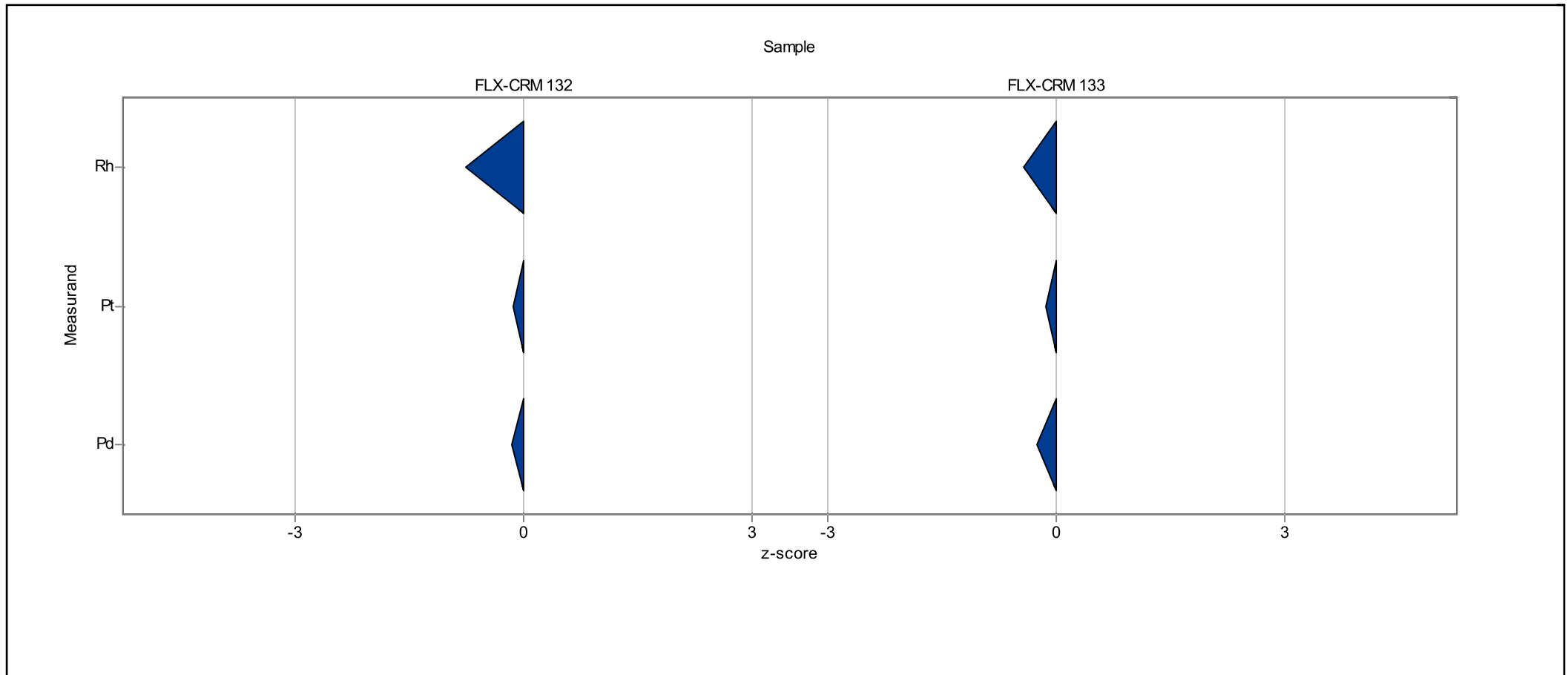
Laboratory: 08



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Laboratory chart of z-scores

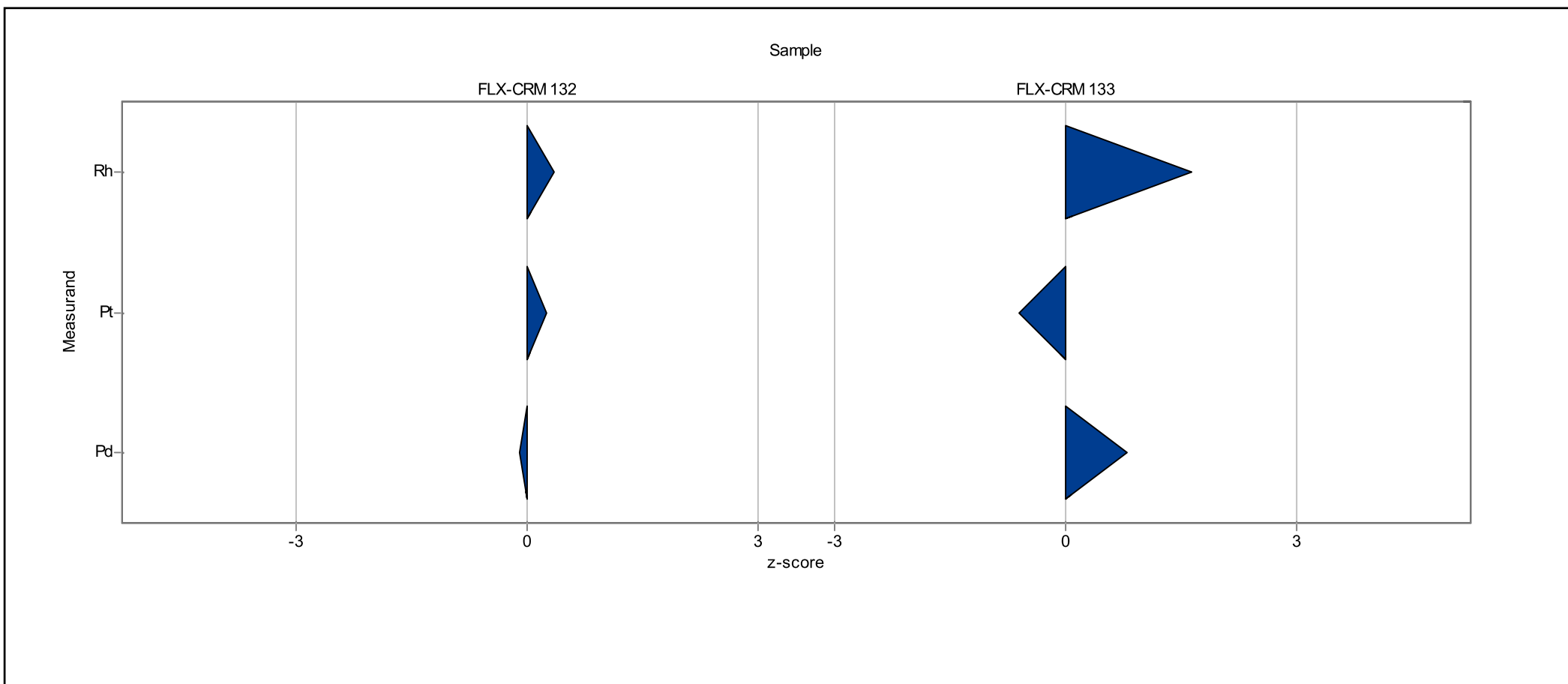
Laboratory: 09



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Laboratory chart of z-scores

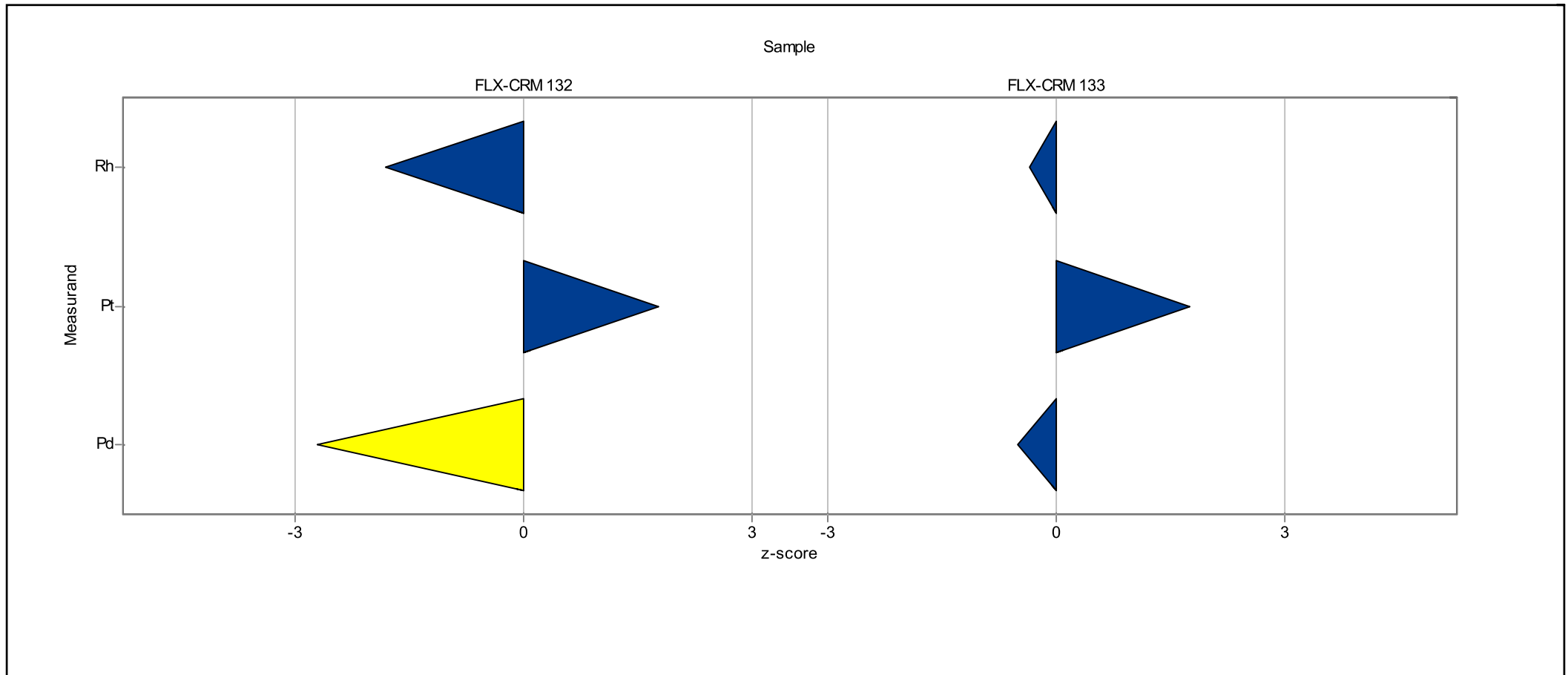
Laboratory: 10



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Laboratory chart of z-scores

Laboratory: 11



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Laboratory chart of z-scores

Laboratory: 12

