

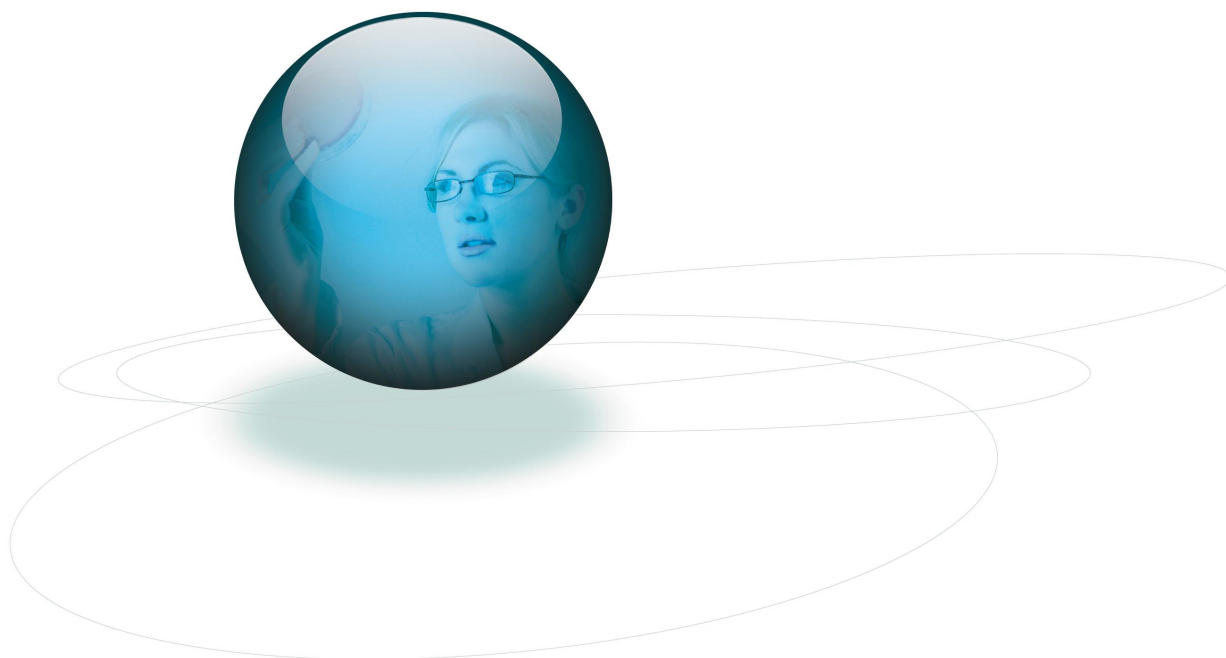


# **FIRMS - Forensic Isotope Ratio Mass Spectrometry PT Scheme**

## **Round: 216**

Issue Number 1

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### **LGC Standards Proficiency Testing**

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## Scheme Information

### Aims of Scheme

The primary aim of the Forensic Isotope Ratio Mass Spectrometry Proficiency Testing Scheme (FIRMS) is to enable laboratories performing isotope ratio analysis of a range of test materials to monitor their performance and compare it with that of their peers. The FIRMS scheme also aims to provide information to participants on technical issues and methodologies relating to isotope ratio analysis.

Further information on the scheme organisation, the test materials, and the statistical analysis of data are available in the FIRMS Scheme Description and the LGC PT General Protocol.

### Performance Assessment

Once a PT round has closed, the results will be analysed and the assigned value determined for each analyte, according to the criteria provided in the Scheme Description. Information regarding the traceability of each calculated assigned value is also provided in the Scheme Description.

For quantitative data, the participant's result,  $x$ , (or  $\log_{10} x$  for microbiological data) is converted into a  $z$  score using the following formula;

$$z = \frac{(x - X)}{\text{SDPA}}$$

$X$  = Assigned value

SDPA = Standard deviation for proficiency assessment

For quantitative data, the uncertainty of the assigned value is calculated to ensure that it would have a negligible effect on participants' performance scores. If the uncertainty of the assigned value is greater than  $0.3 \times \text{SDPA}$ , then this is not considered negligible. In this situation, a  $z'$  ( $z$  prime) performance score is automatically calculated rather than a  $z$  score, in order to take account of the measurement uncertainty of the assigned value. The  $z'$  score is calculated using the following formula;

$$z' = \frac{(x - X)}{\sqrt{(\text{SDPA}^2 + Ux^2)}}$$

$X$  = Assigned value

SDPA = Standard deviation for proficiency assessment

$Ux$  = Uncertainty of the assigned value

Trend graphs will use a mixture of  $z$  and  $z'$  scores, i.e. the 'performance score' for the round.

For quantitative data, gross errors or blunders are removed from the data by removal of any results that are greater than the assigned value  $\pm 5 \times \text{SDPA}$ . These results are not used in the final calculation of the assigned value and other summary statistics and will be included in the number of 'Excluded Results'. All results, including excluded results, will be given a performance score.

For the purposes of performance assessment for a single round,  $z$  and  $z'$  scores are interpreted as follows:

<b><math>z/z'</math> score</b>	<b>Interpretation</b>	<b>Colour coding</b>
$ z  \leq 2.00$	Satisfactory result	Green
$2.00 <  z $ and $< 3.00$	Questionable result	Amber
$ z  \geq 3.00$	Unsatisfactory result	Red
No score given	See below	No colour coding

Performance scores will not be given for the following:

- For qualitative results, where satisfactory performance is based on the participants reporting the

same result as the assigned result. e.g. detected, not detected. For these results, colour coding of green (satisfactory) or red (unsatisfactory) will apply.

- For results of zero; such a result is not normally appropriate and should not be reported, the result should be reported as less than the detection limit rather than zero.  
Note: for a very small number of analytes it may be appropriate to report a result of zero, depending on the type of measurement scale being used.
- For quantitative results where the analyte under test is present in the test material but participants report non-numerical results e.g. 0, <1, >300. In these cases, it is not possible to allocate a performance score and participants should assess their performance based on the assigned value and satisfactory range given.
- For quantitative results, for microbiological test materials, where the analyte under test is not present in the test material, the assigned value will be classified as 'Absent'. Results reported as 'less than' at or below the detection level for our method of confirmation will be assessed as satisfactory (green colour code). Results reported at a higher detection level will not be assessed and participants will need to use their own judgement to determine whether their result is fit for its intended use. Results reporting a positive count will be assessed as unsatisfactory (red colour code).

In some cases, performance scores may not be provided or may be provided but with colour coding suspended (indicating that scores need to be interpreted with caution). For example:

- For small data sets where less than 8 results have been submitted and the assigned value is derived using a consensus value from the participants' results. In these circumstances, there may be increased uncertainty of the assigned value, given the low number of participants, and performance scores will be given for information only.
- In cases where the distribution of the results gives cause for concern e.g. bi-modal data sets. These circumstances will be dependent on the statistical design that is in place.
- If the assigned value falls below a concentration threshold (only applies to some schemes).

In these or similar circumstances, further explanation as to the reasons for suspension of performance scoring or colour coding, and on the interpretation of results, will be given in the report.

Note: Data displayed in the report will have been rounded to the required number of decimal places. However statistical calculations will have been performed on unrounded data. For this reason, there may appear to be differences between displayed data and calculated data, but this does not affect results in any way.

### **Confidentiality**

A unique laboratory reference code is used to report results in order to ensure confidentiality.

### **Contact details**

The Technical Scheme Coordinator is Matthew Whetton

Please contact [customerservice@lqcpt.com](mailto:customerservice@lqcpt.com) if you have any questions or comments regarding the scheme.

### **Authorisation**

This report was authorised by Matthew Whetton, Head of Chemistry on the 13 June 2014



## Sample Details

Samples were despatched on 28 April 2014.  
The reporting deadline was 06 June 2014.

The following samples were distributed in FIRMS Round 214:

- 1: 1 x 0.5g synthetic vanillin for the determination of delta 2H, 13C, and 18O
- 2: 1 x 0.5g magnesium stearate for the determination of delta 2H, 13C and 18O

Further information regarding assigned values, performance assessment and technical comments can be found under the individual sample and analyte results.

Calculated within and between participant standard deviations

### Sample 1 (synthetic vanillin)

Analyte	Within participant SD	Between participant SD
Delta 2H	1.5307	33.3052
Delta 13C	0.1129	0.1755
Delta 18O	0.3115	0.3636

### Sample 2 (magnesium stearate)

Analyte	Within participant SD	Between participant SD
Delta 2H	2.0188	30.9948
Delta 13C	6.0639	0.0891
Delta 18O	0.5552	0.2145

## Quality Control

All homogeneity assessments have been conducted in accordance with the principles stipulated in ISO 13528<sup>[1]</sup> and/or the IUPAC<sup>[2]</sup> Harmonized PT Protocol. Further details regarding the assessment of homogeneity can be found in the LGC Standards Proficiency Testing General Protocol.

Sample	Analyte/Test	Result (SD)	Assessment
1 (synthetic vanillin)	delta 13C	-30.35 (0.04)*	Pass
2 (magnesium stearate)	delta 13C	-29.95 (0.02)*	Pass

\*Results were scaled to the NBS19-LSVEC scale.

Analysis carried out for the purposes of homogeneity testing was sub-contracted by LGC to an external laboratory.

For quantitative testing in this round, a comparison of the standard deviation of the homogeneity results returned and the SDPA expected for the participant assessment was carried out. The samples were considered to be sufficiently homogeneous for use in the PT scheme, based on the values returned.

For qualitative testing, the target analyte must be detected in 100% of test materials analysed.

For any analyte which has not been proven to be sufficiently homogeneous, and any closely related analytes, the value set for the SDPA may be suspended in order to take account of any potential inhomogeneity. The actual value used for the standard deviation for proficiency assessment is shown at the foot of the results and z-score tables in this report.

Often a particular test material does not require homogeneity assessment prior to distribution. Such sample types include standard solutions and aqueous solutions.

[1] ISO 13528 (2005), 'Statistical methods for use in proficiency testing by inter-laboratory comparisons'.

[2] M Thompson, S L R Ellison, R Wood, 'International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories', *Pure Appl. Chem.*, 2006, 78, 145-196.

## Sample: 01 - FIRMS sample 1

## Analyte: delta 2H (VSMOW)

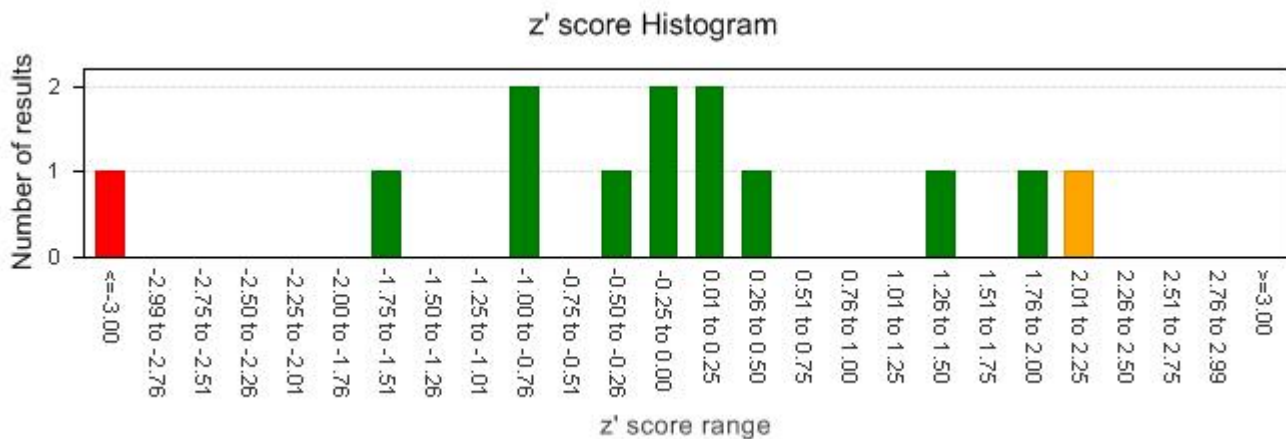
Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	51.90	0.21
FM0009	Isotope Ratio Mass Spectrometry	71.33	2.01
FM0010	Isotope Ratio Mass Spectrometry	51.32	0.15
FM0011	Isotope Ratio Mass Spectrometry	47.90	-0.16
FM0012	Isotope Ratio Mass Spectrometry	40.81	-0.82
FM0014	Isotope Ratio Mass Spectrometry	-227.78	-25.79
FM0016	Isotope Ratio Mass Spectrometry	52.99	0.31
FM0018	Isotope Ratio Mass Spectrometry	44.86	-0.45
FM0022	Isotope Ratio Mass Spectrometry	39.91	-0.91
FM0025	Isotope Ratio Mass Spectrometry	33.00	-1.55
FM0026	Isotope Ratio Mass Spectrometry	70.29	1.92
FM0027	Isotope Ratio Mass Spectrometry	65.17	1.44
FM0028	Isotope Ratio Mass Spectrometry	48.00	-0.15

## Data Statistics

	Value
Number of Results	13
Number of Excluded Results	1
Mean	51.46
Median	49.66
Standard Deviation	12.044
Robust Standard Deviation	10.121
Result Range	33.00 to 71.33

## Performance Statistics

	Value
Assigned Value	49.66
Uncertainty of Assigned Value	3.65
SDPA	10.121
Satisfactory Range	28.14 to 71.18
Satisfactory z' scores	84.6%
Questionable z' scores	7.7%
Unsatisfactory z' scores	7.7%



## Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat. %
Isotope Ratio Mass Spectrometry	13	1	100	49.66	10.121	33.00 to 71.33	84.6
All	13	1	100	49.66	10.121	33.00 to 71.33	84.6

## Comments

The participants in the FIRMS scheme were allowed to report up to 10 results, for the purposes of calculating individual and group summary statistics, plus a mean result, which was used to calculate the summary statistics subsequently applied in the assessment of performance.

As has been seen in previous rounds the inclusion of test materials and compounds with exchangeable hydrogen for 2H analysis has many pitfalls unless a strict protocol is provided, to which participants must adhere. In this round participants were requested to apply their routine method of analysis and as a result the values reported ranged from 33.0 to 71.33. The spread of data, as defined by the robust standard deviation was also comparatively large 10.121.

**Sample: 01 - FIRMS sample 1**

**Analyte: delta 2H (VSMOW)**

In comparison the range of results returned for  $^{13}\text{C}$  in synthetic vanillin was from -30.69 to -30.27 with a robust standard deviation of just 0.059.

Currently the SDPA used in the calculation of performance scores for participants is the calculated using the robust standard deviation. In cases where the results returned are varied, the robust standard deviation will also be large and by definition a wide range of results will be assessed as satisfactory. Participants are advised to consider the magnitude of this statistic and the absolute difference for their result from the median value (bias), when interpreting the assessment of their performance.

A fixed SDPA, which can also be a percentage of the assigned value, is being considered by LGC and the FIRMS advisory group.

It is apparent from the data reported that one participant has inadvertently transcribed their 2H results for the two test materials provided. This participant is advised to recalculate their performance score using the appropriate statistics provided within this report.

\*Please note, participant performance for this analyte has been assessed using a z' score, rather than a z score, in order to account for the measurement uncertainty of the assigned value which is not negligible when compared to the SDPA.

## Sample: 01 - FIRMS sample 1

## Analyte: delta 13C (VPDB)

Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	-30.48	-0.96
FM0003	Isotope Ratio Mass Spectrometry	-30.46	-0.64
FM0009	Isotope Ratio Mass Spectrometry	-30.41	0.16
FM0010	Isotope Ratio Mass Spectrometry	-30.46	-0.64
FM0011	Isotope Ratio Mass Spectrometry	-30.39	0.48
FM0012	Isotope Ratio Mass Spectrometry	-30.42	0.00
FM0014	Isotope Ratio Mass Spectrometry	-30.58	-2.57
FM0016	Isotope Ratio Mass Spectrometry	-30.45	-0.48
FM0018	Isotope Ratio Mass Spectrometry	-30.42	0.00
FM0021	Isotope Ratio Mass Spectrometry	-30.27	2.41
FM0022	Isotope Ratio Mass Spectrometry	-30.37	0.80
FM0025	Isotope Ratio Mass Spectrometry	-30.30	1.93
FM0026	Isotope Ratio Mass Spectrometry	-30.69	-4.33
FM0027	Isotope Ratio Mass Spectrometry	-30.42	0.00
FM0028	Isotope Ratio Mass Spectrometry	-30.40	0.32

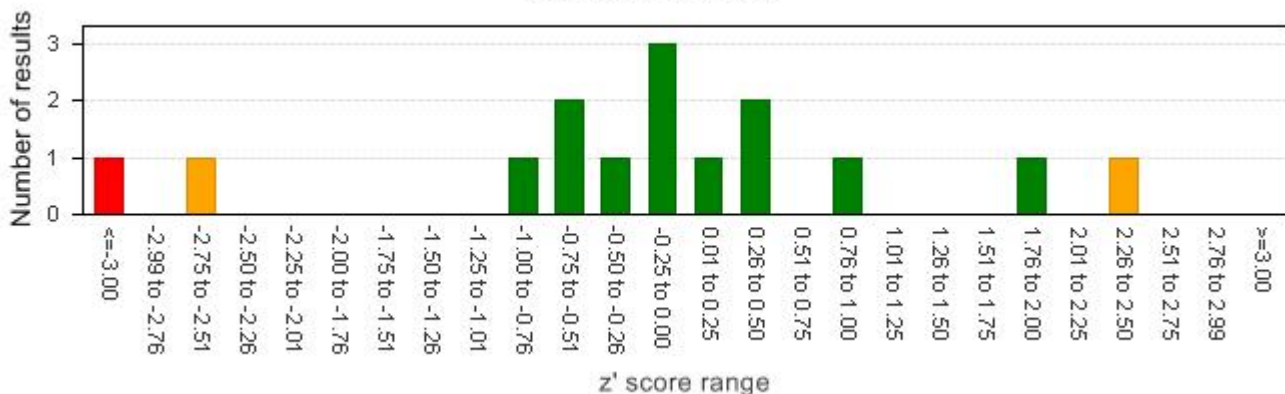
## Data Statistics

	Value
Number of Results	15
Number of Excluded Results	0
Mean	-30.43
Median	-30.42
Standard Deviation	0.101
Robust Standard Deviation	0.059
Result Range	-30.69 to -30.27

## Performance Statistics

	Value
Assigned Value	-30.42
Uncertainty of Assigned Value	0.02
SDPA	0.059
Satisfactory Range	-30.54 to -30.30
Satisfactory z' scores	80.0%
Questionable z' scores	13.3%
Unsatisfactory z' scores	6.7%

z' score Histogram



## Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	15	0	100	-30.42	0.059	-30.69 to -30.27	80.0
All	15	0	100	-30.42	0.059	-30.69 to -30.27	80.0

## Comments

\*Please note, participant performance for this analyte has been assessed using a z' score, rather than a z score, in order to account for the measurement uncertainty of the assigned value which is not negligible when compared to the SDPA.





## Sample: 02 - FIRMS sample 2

## Analyte: delta 2H (VSMOW)

Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	-231.60	-0.64
FM0003	Isotope Ratio Mass Spectrometry	-227.40	0.03
FM0009	Isotope Ratio Mass Spectrometry	-212.46	2.39
FM0010	Isotope Ratio Mass Spectrometry	-233.88	-1.00
FM0011	Isotope Ratio Mass Spectrometry	-223.90	0.58
FM0012	Isotope Ratio Mass Spectrometry	-227.57	0.00
FM0014	Isotope Ratio Mass Spectrometry	45.54	43.18
FM0016	Isotope Ratio Mass Spectrometry	-238.52	-1.73
FM0018	Isotope Ratio Mass Spectrometry	-228.52	-0.15
FM0022	Isotope Ratio Mass Spectrometry	-226.36	0.19
FM0025	Isotope Ratio Mass Spectrometry	-227.00	0.09
FM0026	Isotope Ratio Mass Spectrometry	-247.02	-3.08
FM0027	Isotope Ratio Mass Spectrometry	-233.46	-0.93
FM0028	Isotope Ratio Mass Spectrometry	-212.00	2.46

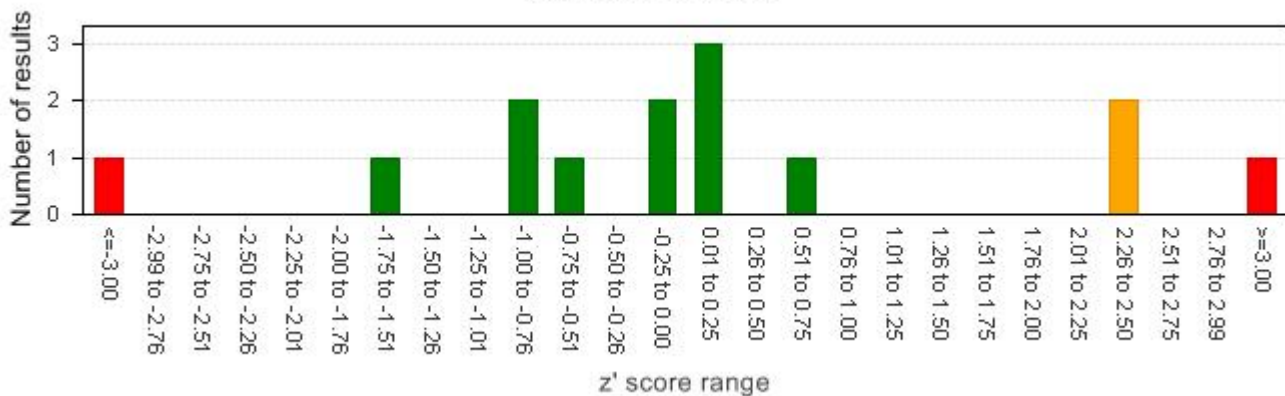
## Data Statistics

	Value
Number of Results	14
Number of Excluded Results	1
Mean	-228.44
Median	-227.57
Standard Deviation	9.426
Robust Standard Deviation	5.976
Result Range	-247.02 to -212.00

## Performance Statistics

	Value
Assigned Value	-227.57
Uncertainty of Assigned Value	2.07
SDPA	5.976
Satisfactory Range	-240.22 to -214.92
Satisfactory z' scores	71.4%
Questionable z' scores	14.3%
Unsatisfactory z' scores	14.3%

z' score Histogram



## Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	14	1	100	-227.57	5.976	-247.02 to -212.00	71.4
All	14	1	100	-227.57	5.976	-247.02 to -212.00	71.4

## Comments

Please refer to synthetic vanillin, delta 2H for report comments.

\*Please note, participant performance for this analyte has been assessed using a z' score, rather than a z score, in order to account for the measurement uncertainty of the assigned value which is not negligible when compared to the SDPA.

## Sample: 02 - FIRMS sample 2

## Analyte: delta 13C (VPDB)

Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	-30.37	-0.64
FM0003	Isotope Ratio Mass Spectrometry	-30.41	-1.06
FM0009	Isotope Ratio Mass Spectrometry	-30.26	0.53
FM0010	Isotope Ratio Mass Spectrometry	-30.33	-0.21
FM0011	Isotope Ratio Mass Spectrometry	-30.29	0.21
FM0012	Isotope Ratio Mass Spectrometry	-30.33	-0.21
FM0014	Isotope Ratio Mass Spectrometry	-30.46	-1.60
FM0016	Isotope Ratio Mass Spectrometry	-30.37	-0.64
FM0018	Isotope Ratio Mass Spectrometry	-30.31	0.00
FM0021	Isotope Ratio Mass Spectrometry	-30.12	2.02
FM0022	Isotope Ratio Mass Spectrometry	-30.25	0.64
FM0025	Isotope Ratio Mass Spectrometry	-30.15	1.70
FM0026	Isotope Ratio Mass Spectrometry	-30.59	-2.98
FM0027	Isotope Ratio Mass Spectrometry	-30.27	0.43
FM0028	Isotope Ratio Mass Spectrometry	-30.30	0.11

## Data Statistics

	Value
Number of Results	15
Number of Excluded Results	0
Mean	-30.32
Median	-30.31
Standard Deviation	0.116
Robust Standard Deviation	0.089
Result Range	-30.59 to -30.12

## Performance Statistics

	Value
Assigned Value	-30.31
Uncertainty of Assigned Value	0.03
SDPA	0.089
Satisfactory Range	-30.50 to -30.12
Satisfactory z' scores	86.7%
Questionable z' scores	13.3%
Unsatisfactory z' scores	0.0%

z' score Histogram



## Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	15	0	100	-30.31	0.089	-30.59 to -30.12	86.7
All	15	0	100	-30.31	0.089	-30.59 to -30.12	86.7

## Comments

\*Please note, participant performance for this analyte has been assessed using a z' score, rather than a z score, in order to account for the measurement uncertainty of the assigned value which is not negligible when compared to the SDPA.

## Sample: 02 - FIRMS sample 2

## Analyte: delta 18O (VSMOW)

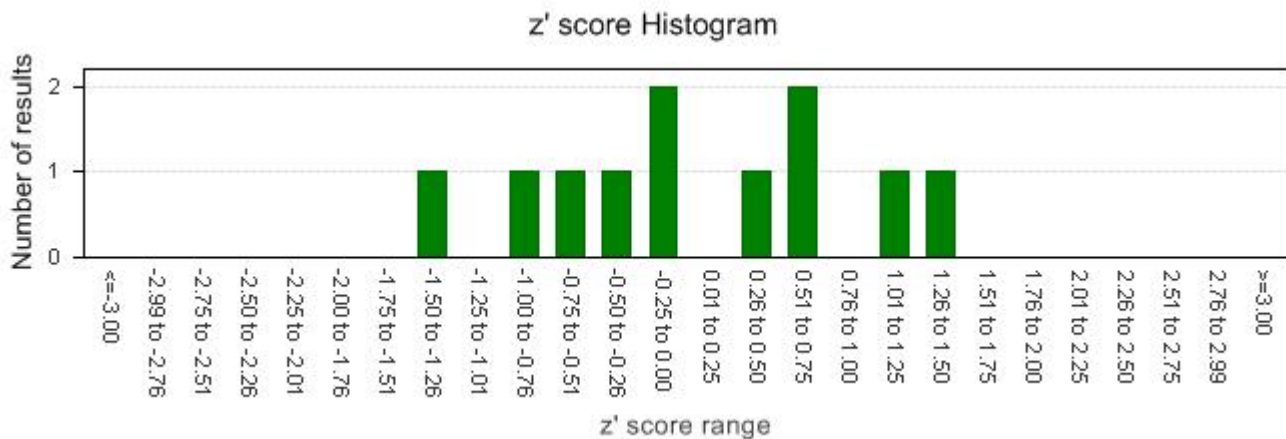
Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	3.55	-0.89
FM0003	Isotope Ratio Mass Spectrometry	5.17	0.26
FM0009	Isotope Ratio Mass Spectrometry	2.86	-1.37
FM0011	Isotope Ratio Mass Spectrometry	5.80	0.71
FM0012	Isotope Ratio Mass Spectrometry	6.82	1.43
FM0016	Isotope Ratio Mass Spectrometry	5.56	0.54
FM0018	Isotope Ratio Mass Spectrometry	6.22	1.01
FM0022	Isotope Ratio Mass Spectrometry	4.29	-0.36
FM0025	Isotope Ratio Mass Spectrometry	4.80	0.00
FM0026	Isotope Ratio Mass Spectrometry	4.68	-0.09
FM0027	Isotope Ratio Mass Spectrometry	3.91	-0.63

## Data Statistics

	Value
Number of Results	11
Number of Excluded Results	0
Mean	4.88
Median	4.80
Standard Deviation	1.189
Robust Standard Deviation	1.320
Result Range	2.86 to 6.82

## Performance Statistics

	Value
Assigned Value	4.80
Uncertainty of Assigned Value	0.50
SDPA	1.32
Satisfactory Range	1.98 to 7.62
Satisfactory z' scores	100.0%
Questionable z' scores	0.0%
Unsatisfactory z' scores	0.0%



## Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat. %
Isotope Ratio Mass Spectrometry	11	0	100	4.80	1.320	2.86 to 6.82	100.0
All	11	0	100	4.80	1.320	2.86 to 6.82	100.0

## Comments

\*Please note, participant performance for this analyte has been assessed using a z' score, rather than a z score, in order to account for the measurement uncertainty of the assigned value which is not negligible when compared to the SDPA.