



Hydrogen Sulfide Proficiency Testing Programme - June 2024

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Round:	4

Introduction

This report summarises the results from the Hydrogen Sulfide Proficiency Testing Programme (PTP) which was conducted in June 2024.

Description

The PTP is open to users to aid with compliance to test methods IP 570 and ASTM D7621. Participation in the PTP will assist with verifying correct calibration and analyser performance, as well as the performance of the operator. Each round a new batch of samples containing hydrogen sulfide is made and an individual sample is delivered to each participant. The volume supplied, 15 to 20 mL, provides enough sample for a maximum of three measurements. Instructions and suitable means to aliquot the sample are provided with the sample. The participant measures the sample within the allotted time frame (while the round is "open") and enters the data into a website (<https://www.seta-pt.co.uk/>). Up to 3 data points may be entered, and 2 are encouraged so that repeatability can be confirmed. All measurements must be undertaken within 4 hours of the sample being opened to prevent sample degradation. Immediate feedback, if the result is outside the expected target range, is provided to enable laboratories to perform further checks for this important safety parameter. Participants are allocated a unique Laboratory ID. Participants take part in a blind fashion, that is to say that each Laboratory's identity is confidential and only known by the PT Scheme administrator and the individual laboratory.

Sample Homogeneity and Stability - Assigned Value

The sample was calculated to have 2.30 mg/kg Hydrogen Sulfide in the liquid phase when it was manufactured. This has an expanded uncertainty of 0.10 mg/kg (The reported expanded uncertainty is based on a combined standard uncertainty multiplied by a coverage factor of $k=2.00$, providing a level of confidence of approximately 95%). To further check this value Stanhope Seta measured 6 individual bottles during a 43 day period. The results had a mean value of 2.32 mg/kg with standard deviation of 0.10 with no outliers.

Manufacturing/Meteorological Traceability

Samples are manufactured according to Stanhope-Seta method RL-LAB-PR-012. Mass balances used in the preparation of the sample hold a current BS EN ISO/IEC 17025 calibration certificate with the calibration of the balance having been conducted at the place and location of use, by an organisation accredited to BS EN ISO/IEC 17025, for the calibration of balances.



Results

37 laboratories subscribed to the scheme. 29 laboratories submitted data. 8 laboratories did not submit data. The mean for all results was 2.00 mg/kg and the standard deviation 0.27 mg/kg.

Table 1: Results						
Lab ID	Result 1	Result 2	Result 3	Repeatability	Mean	z-score
3	1.91	1.91	1.91	0.00	1.91	-0.41
4	1.64	1.36	-	0.28	1.50	-2.15
7	-	-	-	-	-	-
8	2.26	2.28	-	0.02	2.27	1.11
11	2.39	2.35	-	0.04	2.37	1.53
22	-	-	-	-	-	-
24	2.30	2.44	-	0.14	2.37	1.53
30	2.17	2.21	-	0.04	2.19	0.77
35	1.96	2.00	-	0.04	1.98	-0.12
39	1.85	1.84	1.76	0.01	1.82	-0.81
48	1.85	1.92	-	0.07	1.89	-0.52
63	2.45	2.35	-	0.10	2.40	1.66
67	-	-	-	-	-	-
68	2.00	2.47	-	0.47	2.24	0.96
82	1.85	1.96	1.90	0.11	1.90	-0.44
87	1.80	1.69	-	0.11	1.75	-1.11
88	-	-	-	-	-	-
89	2.30	2.51	-	0.21	2.40	1.68
91	2.02	1.96	-	0.06	1.99	-0.08
94	1.76	1.90	-	0.14	1.83	-0.75
96	-	-	-	-	-	-
103	1.84	1.78	-	0.06	1.81	-0.84
109	1.79	1.38	-	0.41	1.58	-1.79
110	0.74	0.81	-	-	-	-
111	1.73	1.73	1.74	0.00	1.73	-1.16
127	1.69	1.75	1.85	0.06	1.76	-1.04
143	2.17	2.29	2.28	0.12	2.25	1.01
148	1.90	1.88	-	0.02	1.89	-0.50
160	2.13	2.16	2.17	0.03	2.15	0.62

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168	-	-	-	-	-	-
173	1.85	1.68	-	0.17	1.77	-1.03
175	2.20	2.21	-	0.01	2.21	0.83
178	2.13	-	-	-	2.13	0.52
179	2.34	2.35	2.36	0.01	2.35	1.45
180	-	-	-	-	-	-
181	1.87	1.71	-	0.16	1.79	-0.92
182	-	-	-	-	-	-

Repeatability exceeds expected IP 570 Procedure A precision

Results removed by GESD

z-score > 2 or < -2

< 50% of expected value



Analysis

Statistical Approach

The reported data has been processed in conformance with the statistical requirements of BS EN ISO 4259-3. Pre-screening is applied to the reported data: Results that do not conform to IP 570 repeatability and results whose magnitude does not meet 50% of the calculated value are excluded*. GESD is applied to the remaining results according to ISO 4259-1 and ISO 4259-3. The distribution of the data is assessed for normality and an Anderson-Darling statistic (AD) is reported. The z-scores are calculated as defined in ISO 13528 (9.4), using the following calculated values: the average result for each laboratory, the PTP average and the standard deviation for proficiency assessment (σ_{pt})**. The Z-score for each laboratory is calculated as follows:

$$Z = \frac{\text{Laboratory Average} - \text{PTP Average}}{\sigma_{pt}}$$

*Due to the unique nature of this PTP, whereby Hydrogen Sulfide is a highly reactive substrate which is sensitive to handling, results lower than 50% of the calculated value or repeated results that fail IP 570 repeatability are deemed unacceptable. (Results which are 50% lower than the calculated value have the effect of significantly reducing the overall mean, which in turn causes Z-scores for labs who are close to the calculated value to have Z-scores which exceed 2.0). Results which are lower than 50% could indicate an issue during sample handling.

**A general model for σ_{pt} has been used based on the reproducibility of the measurement method as per ISO 13528 (8.4). σ_{pt} is calculated using the published reproducibility at the property level of the PT divided by $k\sqrt{2}$. For this PTP round, $\sigma_{pt} = 0.236$.

Repeatability and GESD

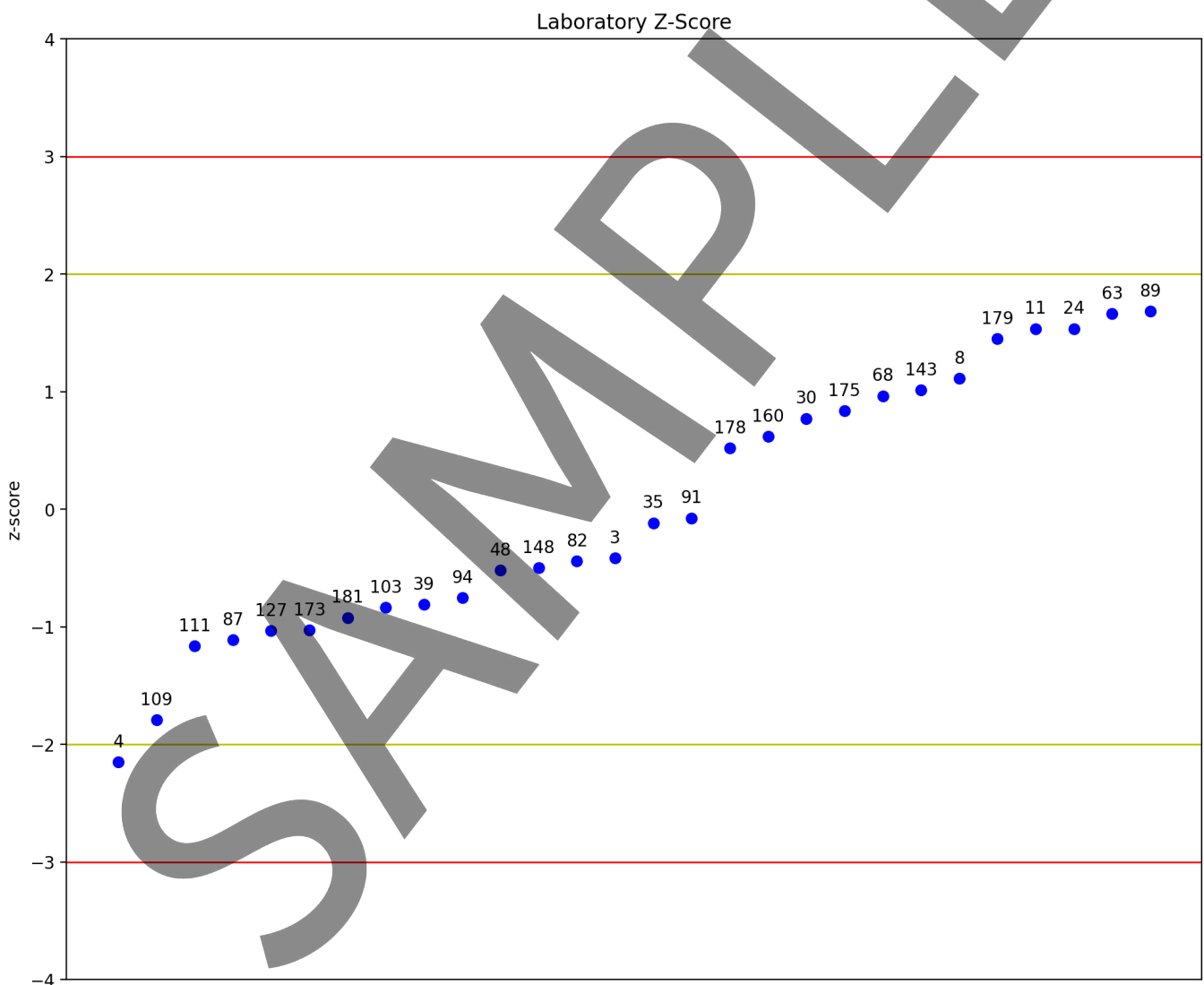
Repeatability was calculated using the test method precision at the level of the PTP mean. GESD was calculated at a 1% confidence level. Laboratories which exceed the repeatability of the method, did not meet 50% of the calculated value or were statistically removed by GESD should take action to remedy these issues ahead of future PT rounds. These laboratories are encouraged to review their procedures, equipment, calibration and operator training.

Z-scores

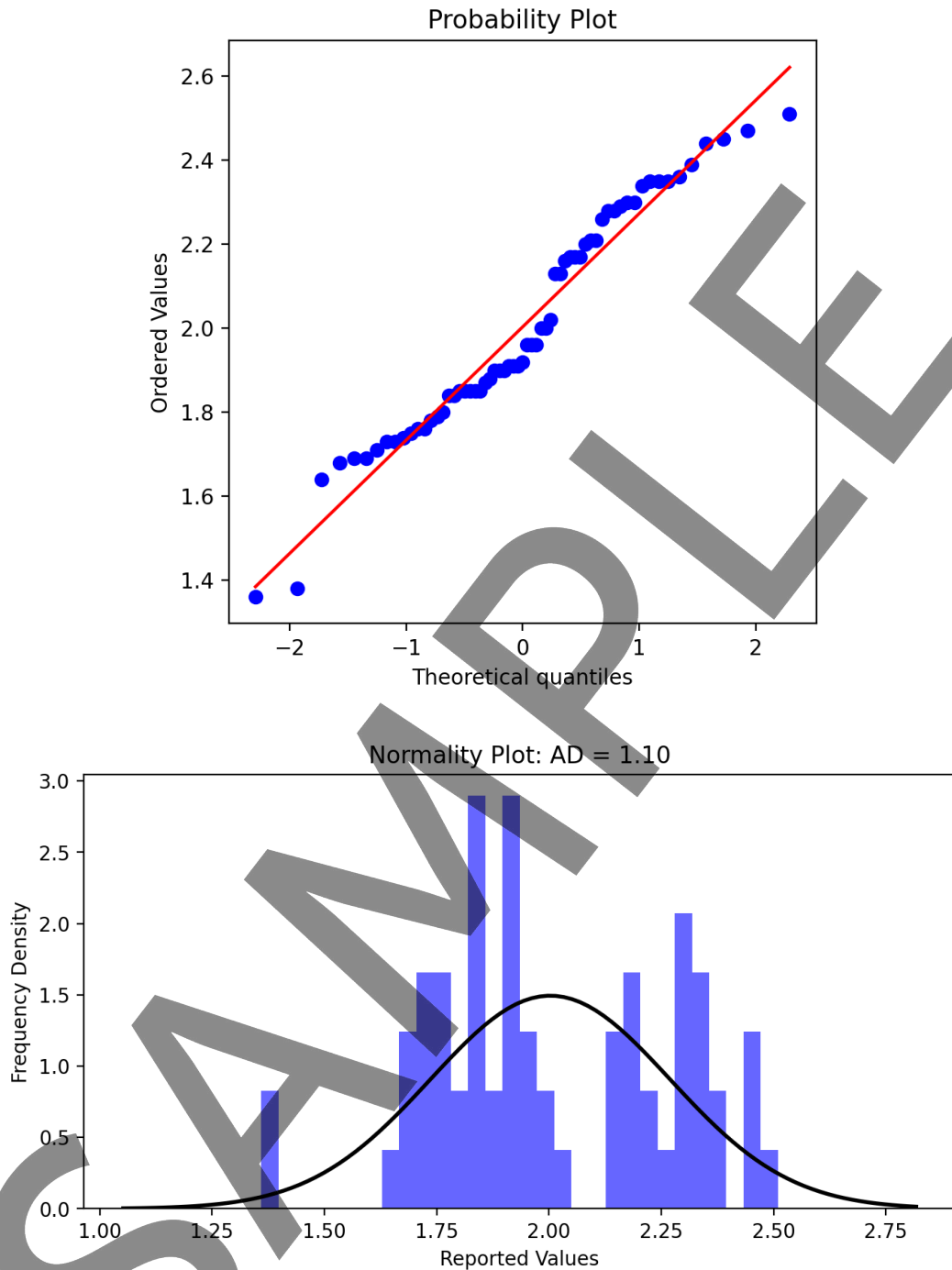
Z-scores were calculated by taking the ratio of the difference between the collective mean and mean test result, and the test method reproducibility standard deviation. The Z-score is an indication of performance against the published test method precision. Laboratories with a Z-score higher than 2.00 or lower than -2.00 are encouraged to review their procedures, equipment, calibration and operator training. Laboratories with a Z-score higher than 3.00 or lower than -3.00 should seek immediate remediation. If issue persist, contact the Stanhope-Seta service department at service@stanhope-seta.co.uk.

Summary of Performance

No laboratories were removed by GESD. 1 laboratory had results which did not meet 50% of the calculated value. No laboratories had a repeatability that exceeded the expected IP 570 Procedure A precision. 27 laboratories met the Z-score requirement, indicating good performance. 1 laboratory exceeded the Z-score indicating performance outside expectations. The TPI for this PT round is equal to 0.85. An F-test was performed on the variance ratio according to ISO 4259-3 (5.2). The calculated variance ratio (1.39) did not exceed the critical value (2.10), hence there is insufficient statistical evidence to suggest the performance of the PTP is inconsistent with the published reproducibility for this PT round.



Normality Assessment



END OF REPORT