Australian Government
Department of Industry, Innovation and Science
National Measurement Institute

Proficiency Test Report
AQA 18-17
Cocaine

March 2019

ACKNOWLEDGMENTS

This study was conducted by the National Measurement Institute (NMI). Support funding was provided by the Australian Government Department of Industry, Innovation and Science.

I would like to thank the management and staff of the participating laboratories for supporting the study. It is only through widespread participation that we can provide an effective service to laboratories.

The assistance of the following NMI staff members in the planning, conduct and reporting of the study is acknowledged.

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SUMMARY

AQA 18-17 was conducted in December 2018. Three test samples of cocaine hydrochloride were sent to thirty-one laboratories. Three laboratories submitted extra sets of results analysed independently by different analysts.

The assigned values were the robust average of participants' results.
Traceability: The consensus of participants' results is not traceable to any external reference, so although expressed in SI units, metrological traceability has not been established.

The outcomes of the study were assessed against the aims as follows:

- *assess the proficiency of laboratories measuring cocaine in samples typical of a routine seizure;*

Laboratory performance was assessed by z-score and E_n-score.

Laboratories **1**, **3**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **13**, **14**, **15**, **16**, **17**, **18**, **19**, **20**, **22**, **23**, **24**, **26**, **27**, **28**, **29**, **31**, **32**, **33** and **34** returned satisfactory z and E_n-scores for all results.

Laboratory **25** returned questionable or unsatisfactory z-scores for all samples. Laboratory **2** returned unsatisfactory E_n -scores for all samples.

Of the 102 results for which z-scores were calculated, 91 (89%) returned $|z| \leq 2$ indicating a satisfactory performance.

Of the 102 results for which $|E_n|$-scores were calculated, 95 (93%) returned $|E_n| \leq 1$ indicating agreement of the participants' results with the assigned value within their respective expanded uncertainties.

- *develop a practical application of traceability and measurement uncertainty and provide participants with information that will assist uncertainty estimates; and*

Ninety-nine results (97%) were reported with an associated expanded uncertainty. Laboratory **2** did not report uncertainty. This laboratory was not accredited.

Laboratories **12**, **15**, **20**, **24**, **30** and **33** reported an identical uncertainty for samples which were of significantly different concentrations.

The magnitude of reported uncertainties was within the range 1.5% to 52% relative.

- *test the ability of participants to identify a cutting agent commonly found in controlled drug preparation*

Samples were prepared using an illicit seizure of cocaine hydrochloride, approximately 84% base (m/m) supplied by the Australian Federal Police. The study coordinator added, phenacetin in Sample S2 and procaine in Sample S3.

Thirty-three participants (96%) reported on the identity of the cutting agents and correctly identified all of them.

1 INTRODUCTION

1.1 NMI Proficiency Testing Program

The National Measurement Institute (NMI) is responsible for Australia's national measurement infrastructure, providing a range of services including a chemical proficiency testing program.

Proficiency testing (PT) is: 'evaluation of participant performance against pre-established criteria by means of interlaboratory comparison.'[1] NMI PT studies target chemical testing in areas of high public significance such as trade, environment, law enforcement and food safety. NMI offers studies in:

- pesticide residues in fruit and vegetables, soil and water;
- petroleum hydrocarbons in soil and water;
- PFAS in water, soil and biota;
- metals in soil, water, food and pharmaceuticals;
- controlled drug assay and clandestine laboratory;
- allergens in food; and
- Folic acid in flour.

1.2 Study Aims

The aims of the study were to:

- assess the proficiency of laboratories measuring cocaine in samples typical of a routine seizure;
- develop a practical application of traceability and measurement uncertainty and provide participants with information that will assist uncertainty estimates; and
- Test the ability of participants to identify a cutting agent commonly found in controlled drug preparation.

The choice of the test method was left to the participating laboratories.

1.3 Study Conduct

NMI is accredited by the National Association of Testing Authorities, Australia (NATA) to ISO 17043[1] as a provider of proficiency testing schemes. This controlled drug proficiency test is within the scope of NMI's accreditation.

The conduct of NMI proficiency tests is described in the NMI Chemical Proficiency Testing Study Protocol.[2] The statistical methods used are described in the NMI Chemical Proficiency Testing Statistical Manual.[3] These documents have been prepared with reference to ISO 17043 and The International Harmonized Protocol for Proficiency Testing of (Chemical) Analytical Laboratories.[4]

2 STUDY INFORMATION

2.1 Study Timetable

The timetable of the study was:

Invitation issued:	24 September 2018
Samples dispatched:	06 December 2018
Results due:	22 February 2019
Interim report issued:	01 March 2019

2.2 Participation

A total of ninety-nine international, national, state government and private laboratories were invited to participate.

Thirty-one laboratories agreed to participate and submitted results. Three laboratories requested two sets of test samples in order to be analysed by different analysts and reported two sets of results.

2.3 Test Material Specification

Three test samples were prepared in September 2018. The starting material was cocaine hydrochloride approximately 84% base (m/m) supplied by the Australian Federal Police. Phenacetine and procaine purchased from Sigma Aldrich were used as cutting agents. Sample S1 was uncut, phenacetin was used for Sample S2 and procaine for Sample S3.

The cocaine was ground and sieved through a 180 μm sieve. The cutting agents were processed similarly to the cocaine powder.

Test samples were then prepared by mixing a known mass of sieved drug material with a known mass of sieved cutting agent in a tumbler overnight.

Portions of 150 mg of each of the test samples were weighed into labelled glass vials.

Sample S1 was prepared to contain ~84% cocaine base (m/m).

Sample S2 was prepared to contain ~40% cocaine base (m/m).

Sample S3 was prepared to contain ~26% cocaine base (m/m).

2.4 Laboratory Code

Each participant was randomly assigned a confidential laboratory code.

2.5 Test Sample Homogeneity

The preparation of homogeneous test samples is an important part of a proficiency testing study. Given the small (<150 mg) test portions normally used for controlled substances analysis the particle size must be sufficiently small and uniformly distributed to ensure minimal influence on analytical precision.

The procedure for the preparation of the study samples has been validated in previous studies. No homogeneity testing was conducted in this proficiency study. Results returned by the participants gave no reason to question the homogeneity of test samples.

2.6 Sample Dispatch and Receipt

A set of three test samples, each containing approximately 150 mg of test material, were dispatched on 06 December 2019.

The following items were packaged with the samples:

- a covering letter with instructions for participants; and
- a form for participants to confirm the receipt of the test samples.

An Excel spreadsheet for the electronic reporting of results was e-mailed to participants.

2.7 Instructions to Participants

Participants were asked to analyse the samples using their routine quantitative method and return the following information:

- one result for each sample as % m/m cocaine base;
- an estimate of the expanded uncertainty associated with the result as % m/m cocaine base at the 95% confidence level;
- brief detail on how the uncertainty was calculated e.g. uncertainty budget method;
- the identity of the cutting agents in all three samples, if part of routine analysis;
- origin and stated purity of the analytical reference standard used;
- brief summary of the quantitative method used;
- the completed results sheet by 22 February 2019, as late results cannot be included in the report; and
- Any other comment.

2.8 Interim Report

An interim report was emailed to all participants on 01 March 2019.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Method Summaries

Reported participant method summary is presented for information in Table 1.

Table 1 Participant Summary of Test Methods

Lab. Code	Extraction solvent	Internal standard	Calib. points	Technique	Detector	Column
1	ACN/MEOH/ H2O	Analog of cocaine	7	UPLC	MSMS	C-18 coloumn
2	Ethanol	Propylparaben	7	UPLC	DAD	BEH Shield RP18
3	Methanol		4	HPLC	DAD	Zorbax Eclipse XDB-C18
4	water/acetonitrile/n10 sulphuric acid 90:10:1		3	HPLC	Diode Array	Shimpack XR-ODS
5				HPLC	DAD	ZORBAX ECLIPSE XDB-C18 (5mm pore size,4,6mmx150mm)
6	Methanol	Tetracosane	4	GC	FID	SGE 12 x 0,22 mm
7	Methanol	Vanillin	1	LC	DAD	Lichrospher 60 RP-select B, 25cm x 4 mm id, 5um
8	Acetonitrile/water 20:80 acidified		5	HPLC	UV	C18
9	Ethanol	2,2,2-triphenylacetophenone (TPAP)	3	GC	FID, MSD	HP-1MS
10	Sodiumphosphate (pH4,5)		4	HPLC	UV-DAD	Hypersil GOLD C8
11	Mobile Phase (S1 and S3); Chloroform (S2)	None (S1 and S3); 2,2,2-triphenylacetophenone (S2)	4	HPLC (S1,S3) GC (S2)	PDA (S1, S3) FID (S2)	C18 ubondapack (S1 and S3); HP-5 (S2)
12	Acetonitrile:water 25:75		3	HPLC	UV	ODS2-interpak 25.0cm x 4.6mm
13	Dichloromethane	Tetracosane	7	GC	MS	DB5
14	Acetonitril/water		1	HPLC	DAD	Kromasil
15	Water/Acetonitrile (80:20)		3	HPLC	UV/VIS	C18
16	ethanol	tribenzylamine	6	GC	FID	HP5

Lab. Code	Extraction solvent	Internal standard	Calib. points	Technique	Detector	Column
17	CDCl3	1,4-bis(trimethylsilyl)benzene		QNMR		
18	Methanol		6	UPLC	PDA	Acquity UPLC BEH 1.7um 2.1 x 100mm
19	Ethanol	Tetracosane	6	GC	FID	HP5
20	Methanol	Diazepam	6	GC	FID	J&W 128-5512
21	acétonitrile/water 80/20	External Standard	2	HPLC	DAD	09-D-29
22	Acetonitrile	Strychnine	6	GC	FID	HP-1
23	Ethanol	Tetracosane	3	GC	FID	BPX5
24	72% water ultra pure + 28% acétronitrile		5	HPLC	UV	Kromasil C8
25	Methanol		6	UPLC	PDA	Acquity UPLC BEH 1.7um 2.1 x 100mm
26	Acetonitrile/Methanol (95:5)	Pholcodine 1mg/ml	3	UPLC	PDA	ACQUITY C-18
27	Acetonitrile:Water 75:25	Diethylphthalate	3	UPLC	DAD	BEH C18 1.7mm (2.1x100mm)
28	ethanol	tribenzylamine	4-	GC	FID	HP-1
29	acétonitrile/water (80/20)		3	HPLC	DAD	C8
30	Ethanol	Eicosane	1	GC	MS	ZB -5ms
31	Methanol		5	HPLC	DAD	Kinetex 2.6 µ XB-C18
32	Methanol	External Standard	6	HPLC	UV 235 nm	Phenomenex C18 5um Luna
33	Acetonitrile:Water (40:60)		5	HPLC	UV	KROMASIL
34	Methanol	Vanillin	1	LC	DAD	Lichrospher 60 RP-select B, 25cm x 4 mm id, 5um

3.2 Reported Basis of Participants' Measurement Uncertainty Estimates

Participant returns as received are listed in Table 2.

Table 2 Reported Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation		Guide Document for Estimating MU
		Precision	Method Bias	
1	Top Down - precision and estimates of the method and laboratory bias	Control samples		
2				
3		Control samples, Duplicate analysis	Standard purity	Eurolab Technical Report No1/2007
4	Profesional judgment	Control samples, Duplicate analysis	Standard purity, Instrument calibration	ISO/GUM
5	Top Down - precision and estimates of the method and laboratory bias	Control samples, Duplicate analysis	Laboratory bias from PT studies, Standard purity Instrument calibration, Masses and volumes, Homogeneity of sample	Nordtest Report TR537
6	Top Down - precision and estimates of the method and laboratory bias	Control samples	Laboratory bias from PT studies, Recoveries of spiked samples, Standard purity, Matrix effects, Instrument calibration, Masses and volumes, Homogeneity of sample	EA-4/16: 2003 and ILAG G-17:2002
7	Top Down - precision and estimates of the method and laboratory bias	Control samples, Duplicate analysis	Laboratory bias from PT studies, Recoveries of spiked samples	Eurachem/CITAC Guide
8	Top Down - precision and estimates of the method and laboratory bias	Control samples, Duplicate analysis	Recoveries of spiked samples	Eurachem/CITAC Guide
9	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control samples, Duplicate analysis	Recoveries of spiked samples, Standard purity, Matrix effects, Instrument calibration, Masses and volumes, Homogeneity of sample	Eurachem/CITAC Guide
10	Top Down - precision and estimates of the method and laboratory bias	Control samples, Duplicate analysis	Laboratory bias from PT studies	Nordtest Report TR537
11				
12	Professional judgment		Instrument calibration	ISO/GUM

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation		Guide Document for Estimating MU
		Precision	Method Bias	
13	Top Down - precision and estimates of the method and laboratory bias	Control samples, Duplicate analysis	Laboratory bias from PT studies, Recoveries of spiked samples, Standard purity, Instrument calibration	
14	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples		
15	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples, Duplicate analysis	Standard purity, Masses and volumes, Homogeneity of sample	Eurachem/CITAC Guide
16	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples	Standard purity	
17	Top Down - precision and estimates of the method and laboratory bias	Control samples, Duplicate analysis	Matrix effects, Instrument calibration	Eurachem/CITAC Guide
18	Top Down - precision and estimates of the method and laboratory bias	Control samples, Duplicate analysis	Standard purity, Instrument calibration, Masses and volumes, Homogeneity of sample	Nata Technical Note 33
19	Top Down - precision and estimates of the method and laboratory bias	Control samples, Duplicate analysis	Standard purity, Matrix effects	ISO/GUM
20	Estimating Measurement Uncertainty by black box by pairs of values	Standard deviation from PT studies only		ISO/GUM
21		Duplicate analysis	Standard purity, Instrument calibration	ISO/GUM
22	Top Down - reproducibility (standard deviation) from PT studies used directly	Control samples, Duplicate analysis	Laboratory bias from PT studies, Standard purity, Instrument calibration, Masses and volumes, Homogeneity of sample	Nata Technical Note 33
23	Uncertainty budget	Control samples, Duplicate analysis	Standard purity, Instrument calibration, Masses and volumes	Internal SOP
24	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control samples, Duplicate analysis	Laboratory bias from PT studies, Standard purity, Instrument calibration, Masses and volumes	ISO/GUM
25	Top Down - precision and estimates of the method and laboratory bias	Control samples, Duplicate analysis	Standard purity, Instrument calibration, Masses and volumes, Homogeneity of sample	Nata Technical Note 33
26	Top Down - precision and estimates of the method and laboratory bias	Control samples, Duplicate analysis	Standard purity, Instrument calibration, Masses and volumes, Homogeneity of sample	Nata Technical Note 33

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation		Guide Document for Estimating MU
		Precision	Method Bias	
27	Top Down - precision and estimates of the method and laboratory bias	Control samples, Duplicate analysis	Standard purity, Homogeneity of sample	Eurachem/CITAC Guide
28	Top Down - precision and estimates of the method and laboratory bias	Control samples, Duplicate analysis	Laboratory bias from PT studies	Internal quality online document based on Eurachem/CITAC, ISO/GUM
29	Top Down - precision and estimates of the method and laboratory bias	Control samples	Laboratory bias from PT studies , Standard purity	
30	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples, Duplicate analysis	Masses and volumes, Homogeneity of sample	Eurachem/CITAC Guide
31	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control samples	Standard purity, Instrument calibration	Eurachem/CITAC Guide
32	Top Down - precision and estimates of the method and laboratory bias	Control samples	Laboratory bias from PT studies	Eurachem/CITAC Guide
33	Top Down - precision and estimates of the method and laboratory bias	Control samples, Duplicate analysis	Instrument calibration, Masses and volumes	
34	Top Down - precision and estimates of the method and laboratory bias	Control samples, Duplicate analysis	Laboratory bias from PT studies, Recoveries of spiked samples	Eurachem/CITAC Guide

3.3 Details of Participant Calibration Standard

Participant returns as received are listed in Table 3.

Table 3 Participant Calibration Standard

Lab. Code	Reference Standard*	Purity (%)
1	Unikem	100
2	NMI	96.1
3	LGC	1 ±0,003 mg/mL
4	LGC	99.7
5	LIPOMED	99.35
6	Merck	100
7	Lipomed	99.706 ± 0.007
8	Johnson Matthey	99.7
9	NMI	96.1 +/- 2.6
10	Sigma Aldrich	100
11	Macfarlan Smith Limited	100.4
12	MacFarlane Smith	99.1
13	Lipomed	86.7
14	Sigma-Aldrich	98.7
15	Sigma-Aldrich	99.2
16	NMI	99.8
17		
18	NMI	96.1
19	Alcaliber	100.1
20	LIPOMED	99.7
21	NMI	96.1
22	NMI	96.1
23	NMI	96.1
24		
25	NMI	96.1
26	NMI	96.1
27	NMI	99.8 ± 2.0
28	Fagron	99.5
29	Lipomed	99.706
30	Sigma-aldrich	99
31	Lipomed	>98.5
32		100
33	SIGMA	
34	Lipomed	99.706 ± 0.007

3.4 Participants' Comments

The study manager welcomes comments or suggestions from participants as it provides information which will improve future studies. All returns are listed as received in Table 4 along with the study manager's response, where appropriate.

Table 4 Participant Comments

Lab. Code	Participant comments	Study Manager's response
5	Qualitative analysis was carried out by GC-MS	
11	Insufficient sample to repeat analysis if needed.	Most participants use less than 50 mg for each analysis. For reasons of security and accountability, NMI conducts these PT's using the minimum practical amount of drug.
24	Solutions 1 and 2 were analyzed in HPLC-UV. Solution 3 was analyzed in GCMS	

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 7 with resultant summary statistics: mean, median, maximum, minimum, robust average, robust standard deviation (Robust SD) and robust coefficient of variation (Robust CV).

Bar charts of results and performance scores are presented in Figures 2 to 4.

An example chart with interpretation guide is shown in Figure 1.

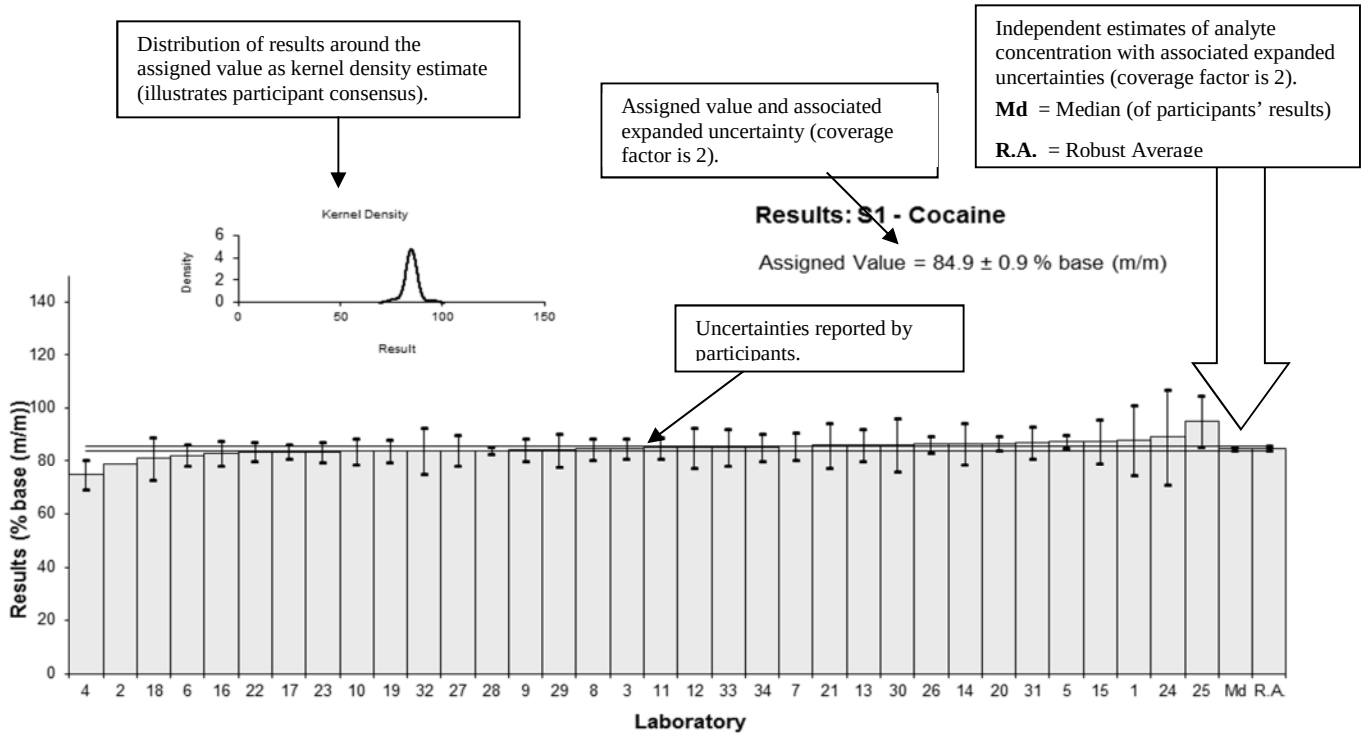


Figure 1 Guide to Presentation of Results

4.2 Assigned Value

The assigned value is defined as: 'value attributed to a particular property of a proficiency tet item.' [1]

For a proficiency test, the assigned value is the best available measurement of the true concentration of an analyte in the test sample.

4.3 Performance Coefficient of Variation (PCV)

The performance coefficient of variation (PCV) is a measure of the between laboratory variation that in the judgement of the study organiser would be expected from participants given the sample concentration. It is important to note that this is a performance measure set by the study coordinator; it is not the coefficient of variation of participant results.

4.4 Target Standard Deviation

The target standard deviation (σ) is the product of the assigned value (*X)* and the performance laboratory coefficient of variation (PCV) as presented in Equation 1. This value is used for calculation of participant z-score.

$$\sigma = X * PCV \qquad \textit{Equation 1}$$

4.5 z-Score

For each participant result a z-score is calculated according to Equation 2 below:

$$z = \frac{(\chi - X)}{\sigma} \qquad \textit{Equation 2}$$

where:

z is z-score

χ is participants' result

X is the study assigned value

σ is the target standard deviation from equation 1

A z-score with absolute value (|z|):

- $|z| \leq 2$ is satisfactory;
- $2 < |z| < 3$ is questionable;
- $|z| \geq 3$ is unsatisfactory.

4.6 E_n-Score

The E_n-score is complementary to the z-score in assessment of laboratory performance. E_n-score includes measurement uncertainty and is calculated according to Equation 3 below:

$$E_n = \frac{(\chi - X)}{\sqrt{U_\chi^2 + U_X^2}} \qquad \textit{Equation 3}$$

where:

E_n is E_n-score

χ is a participants' result

X is the assigned value

U_χ is the expanded uncertainty of the participant's result

U_X is the expanded uncertainty of the assigned value

An E_n-score with absolute value ($|E_n|$):

- $|E_n| \leq 1$ is satisfactory;
- $|E_n| > 1$ is unsatisfactory.

4.7 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2017[5] must establish and demonstrate the traceability and measurement uncertainty associated with their test results. Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem /CITAC Guide. [6]

5 TABLES AND FIGURES

Table 5

Sample Details

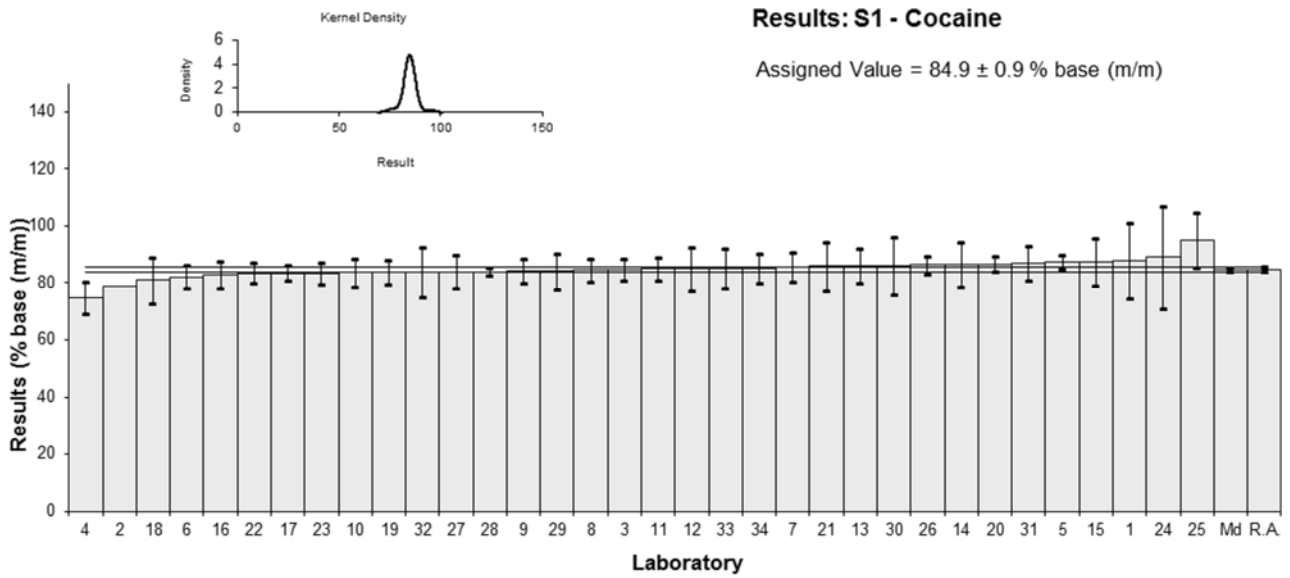
Sample No.	S1
Matrix.	Powder
Analyte.	Cocaine
Units	% base (m/m)

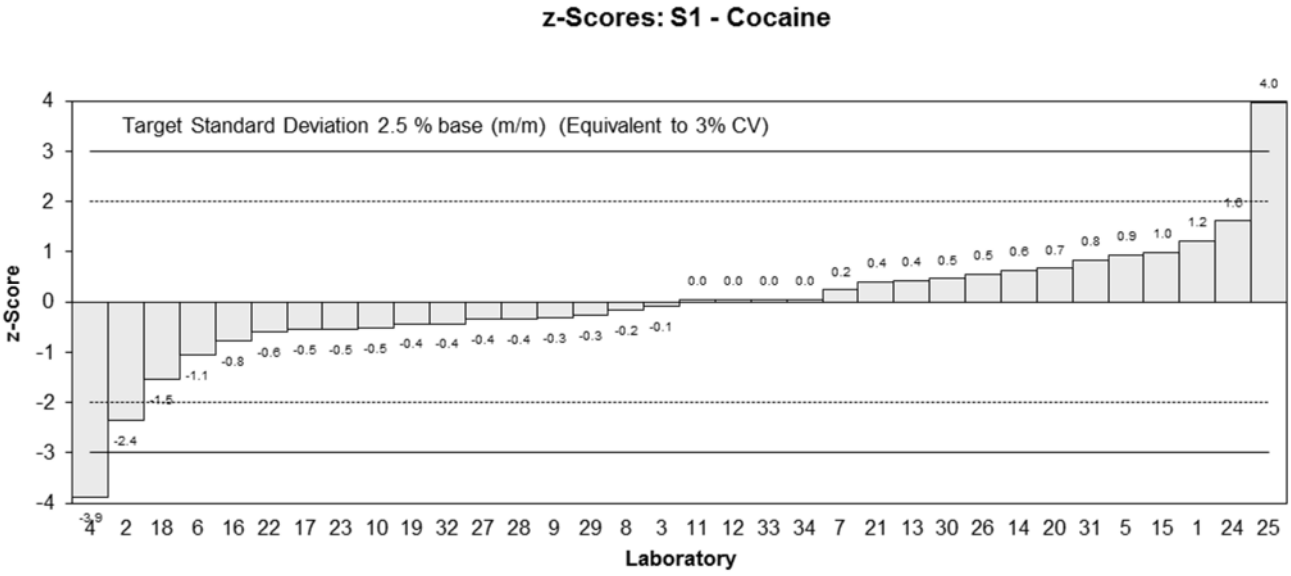
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	88	13.2	1.22	0.23
2	78.9	NR	-2.36	-6.67
3	84.7	4.0	-0.08	-0.05
4	75	5.6	-3.89	-1.75
5	87.3	2.4	0.94	0.94
6	82.2	4.2	-1.06	-0.63
7	85.5	5.2	0.24	0.11
8	84.5	4.2	-0.16	-0.09
9	84.1	4.3	-0.31	-0.18
10	83.6	5.0	-0.51	-0.26
11	85	4.1	0.04	0.02
12	85	7.5	0.04	0.01
13	86	6	0.43	0.18
14	86.5	7.8	0.63	0.20
15	87.4	8.166	0.98	0.30
16	82.9	4.7	-0.79	-0.42
17	83.5	2.8	-0.55	-0.48
18	81	8.1	-1.53	-0.48
19	83.8	4.4	-0.43	-0.24
20	86.6	2.6	0.67	0.62
21	85.9	8.6	0.39	0.12
22	83.4	3.6	-0.59	-0.40
23	83.5	3.8	-0.55	-0.36
24	89	18	1.61	0.23
25	95	9.5	3.97	1.06
26	86.3	3	0.55	0.45
27	84.0	6.0	-0.35	-0.15
28	84.0	1.3	-0.35	-0.57
29	84.20	6.32	-0.27	-0.11
30	86.08	10	0.46	0.12
31	87	6.1	0.82	0.34
32	83.8	8.6	-0.43	-0.13
33	85	7	0.04	0.01
34	85.0	5.1	0.04	0.02

Statistics

Assigned Value	84.9	0.9
Robust Average	84.9	0.9
Median	84.9	0.7
Mean	84.8	
N	34	
Max.	95	
Min.	75	
Robust SD	2.0	
Robust CV	2.4%	


Kernel Density
Density
Result
Results: S1 - Cocaine
Assigned Value = 84.9 ± 0.9 % base (m/m)
Results (% base (m/m))
Laboratory
4 2 18 6 16 22 17 23 10 19 32 27 28 9 29 8 3 11 12 33 34 7 21 13 30 26 14 20 31 5 15 1 24 25 Md R.A.


z-Scores: S1 - Cocaine
Target Standard Deviation 2.5 % base (m/m) (Equivalent to 3% CV)
z-Score
Laboratory
4 2 18 6 16 22 17 23 10 19 32 27 28 9 29 8 3 11 12 33 34 7 21 13 30 26 14 20 31 5 15 1 24 25

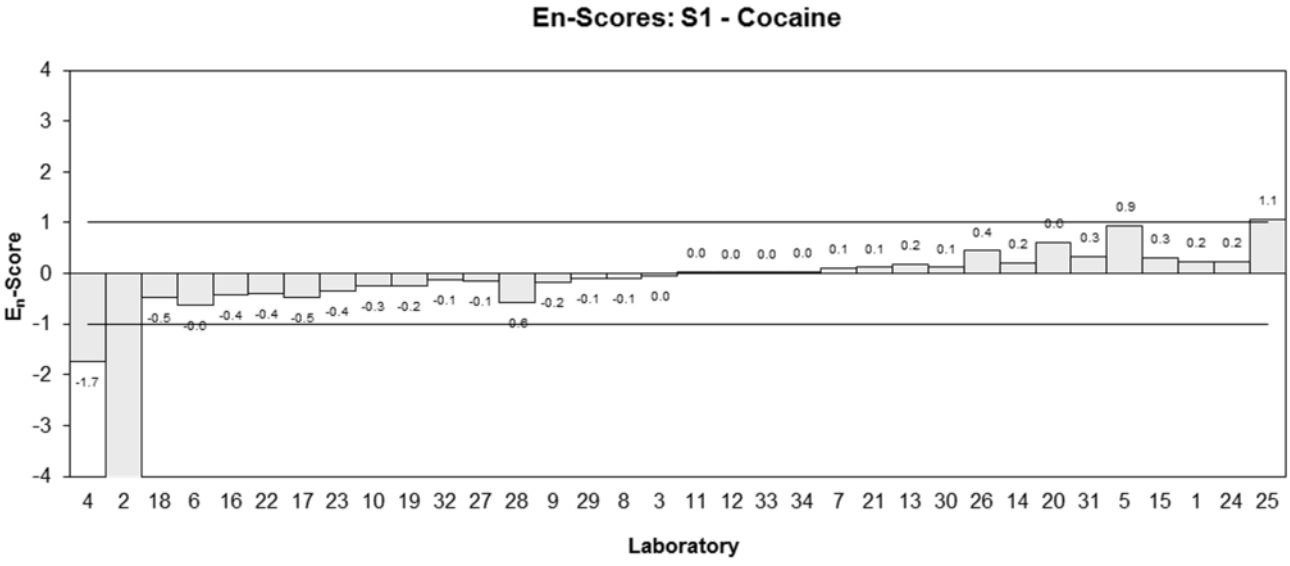

En-Scores: S1 - Cocaine
En-Score
Laboratory
4 2 18 6 16 22 17 23 10 19 32 27 28 9 29 8 3 11 12 33 34 7 21 13 30 26 14 20 31 5 15 1 24 25

Figure 2

Table 6

Sample Details

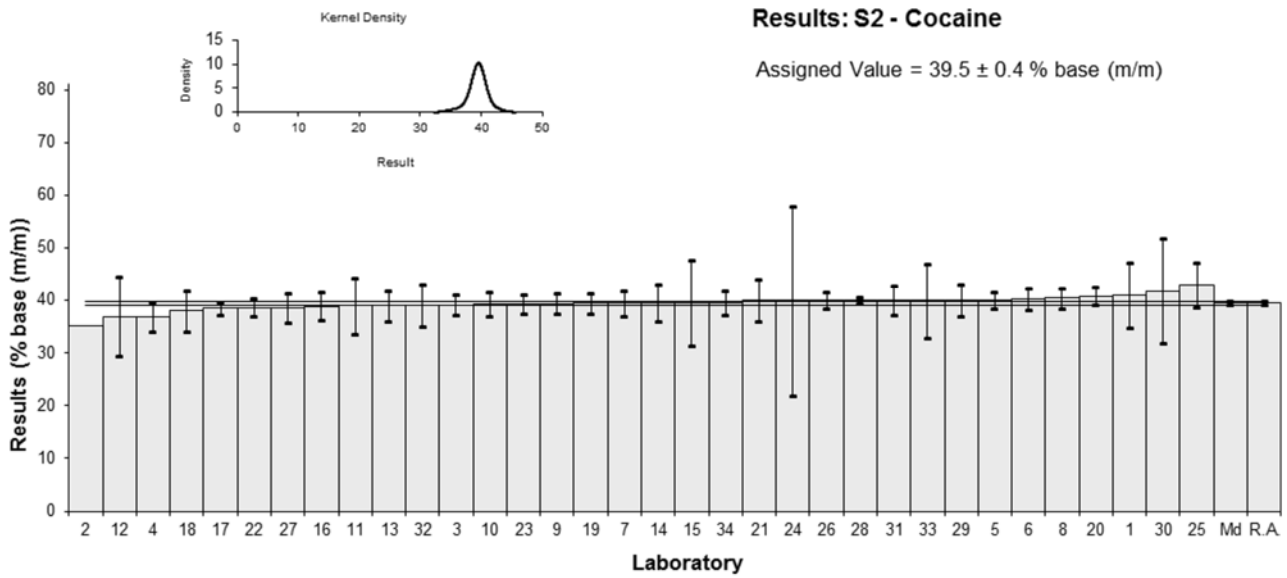
Sample No.	S2
Matrix.	Powder
Analyte.	Cocaine
Units	% base (m/m)

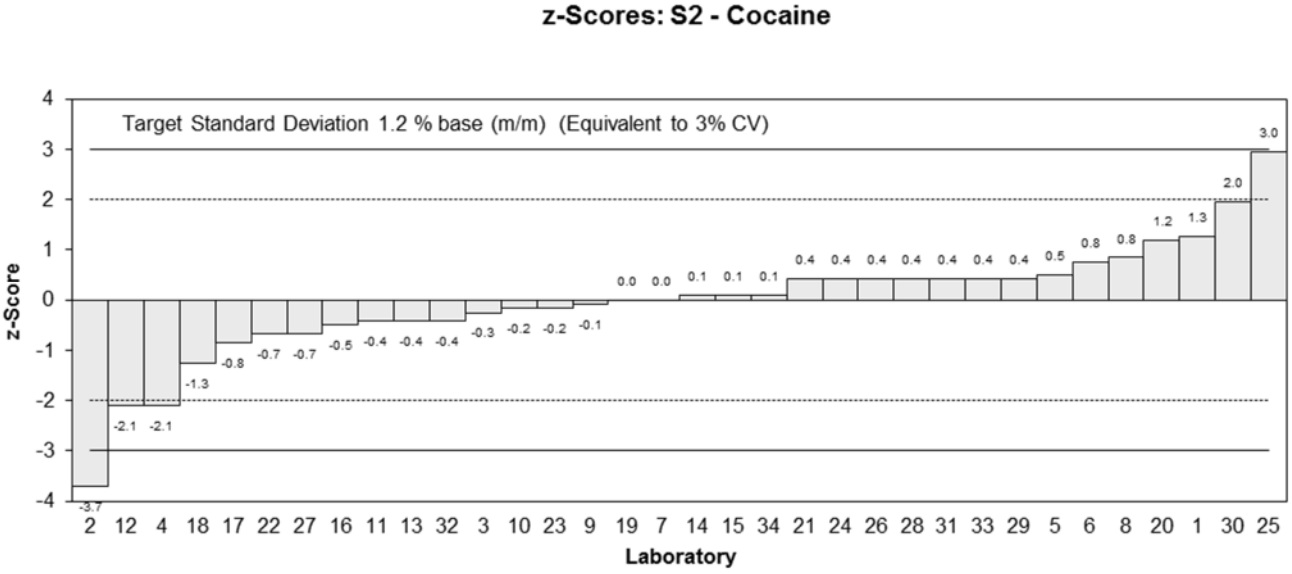
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	41	6.2	1.27	0.24
2	35.1	NR	-3.71	-11.00
3	39.2	2.0	-0.25	-0.15
4	37	2.8	-2.11	-0.88
5	40.1	1.5	0.51	0.39
6	40.4	2.1	0.76	0.42
7	39.5	2.4	0.00	0.00
8	40.5	2.0	0.84	0.49
9	39.4	2.0	-0.08	-0.05
10	39.3	2.3	-0.17	-0.09
11	39	5.4	-0.42	-0.09
12	37	7.5	-2.11	-0.33
13	39	3	-0.42	-0.17
14	39.6	3.6	0.08	0.03
15	39.6	8.166	0.08	0.01
16	38.9	2.7	-0.51	-0.22
17	38.5	1.3	-0.84	-0.74
18	38	3.8	-1.27	-0.39
19	39.5	2.0	0.00	0.00
20	40.9	1.7	1.18	0.80
21	40.0	4.0	0.42	0.12
22	38.7	1.7	-0.68	-0.46
23	39.3	1.8	-0.17	-0.11
24	40	18	0.42	0.03
25	43	4.3	2.95	0.81
26	40.0	1.6	0.42	0.30
27	38.7	2.8	-0.68	-0.28
28	40.0	0.6	0.42	0.69
29	40.01	3.00	0.43	0.17
30	41.82	10	1.96	0.23
31	40	2.8	0.42	0.18
32	39.0	4.0	-0.42	-0.12
33	40	7	0.42	0.07
34	39.6	2.4	0.08	0.04

Statistics

Assigned Value	39.5	0.4
Robust Average	39.5	0.4
Median	39.6	0.3
Mean	39.5	
N	34	
Max.	43	
Min.	35.1	
Robust SD	1.0	
Robust CV	2.5%	


Kernel Density
Density
Result
Results: S2 - Cocaine
Assigned Value = 39.5 ± 0.4 % base (m/m)
Results (% base (m/m))
Laboratory
2 12 4 18 17 22 27 16 11 13 32 3 10 23 9 19 7 14 15 34 21 24 26 28 31 33 29 5 6 8 20 1 30 25 Md R.A.


z-Scores: S2 - Cocaine
Target Standard Deviation 1.2 % base (m/m) (Equivalent to 3% CV)
z-Score
Laboratory
2 12 4 18 17 22 27 16 11 13 32 3 10 23 9 19 7 14 15 34 21 24 26 28 31 33 29 5 6 8 20 1 30 25

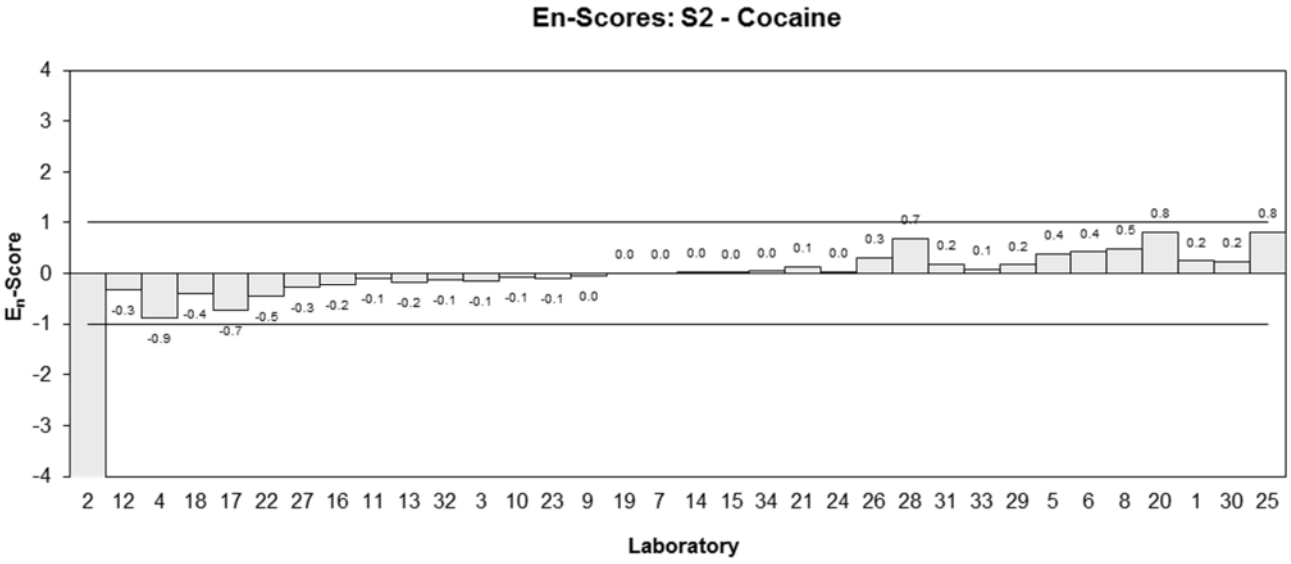

En-Scores: S2 - Cocaine
En-Score
Laboratory
2 12 4 18 17 22 27 16 11 13 32 3 10 23 9 19 7 14 15 34 21 24 26 28 31 33 29 5 6 8 20 1 30 25

Figure 3

Table 7

Sample Details

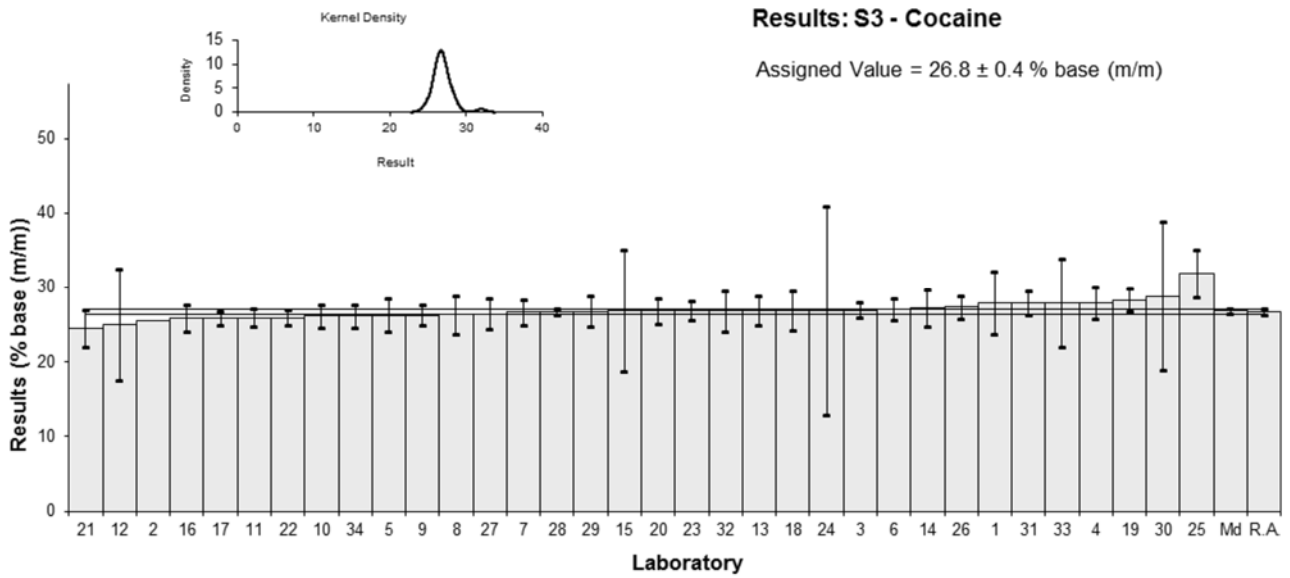
Sample No.	S3
Matrix.	Powder
Analyte.	Cocaine
Units	% base (m/m)

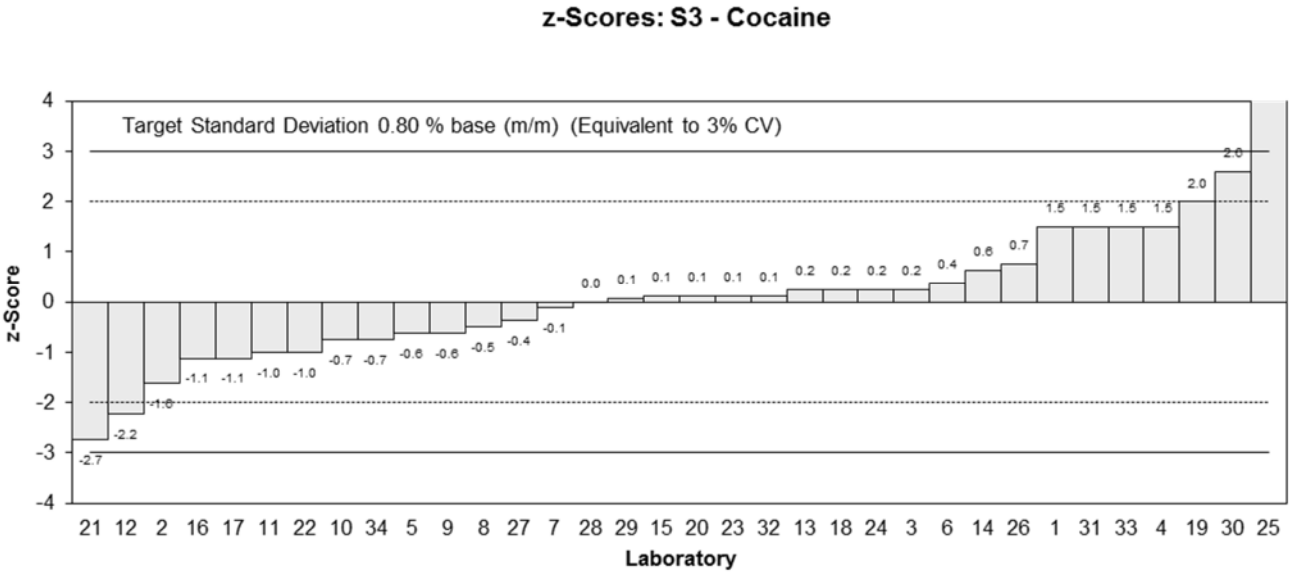
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	28	4.2	1.49	0.28
2	25.5	NR	-1.62	-3.25
3	27.0	1.0	0.25	0.19
4	28	2.1	1.49	0.56
5	26.3	2.2	-0.62	-0.22
6	27.1	1.4	0.37	0.21
7	26.7	1.7	-0.12	-0.06
8	26.4	2.6	-0.50	-0.15
9	26.3	1.4	-0.62	-0.34
10	26.2	1.6	-0.75	-0.36
11	26	1.2	-1.00	-0.63
12	25	7.5	-2.24	-0.24
13	27	2	0.25	0.10
14	27.3	2.5	0.62	0.20
15	26.9	8.166	0.12	0.01
16	25.9	1.8	-1.12	-0.49
17	25.9	0.9	-1.12	-0.91
18	27	2.7	0.25	0.07
19	28.4	1.5	1.99	1.03
20	26.9	1.7	0.12	0.06
21	24.6	2.5	-2.74	-0.87
22	26.0	1.1	-1.00	-0.68
23	26.9	1.3	0.12	0.07
24	27	14	0.25	0.01
25	32	3.2	6.47	1.61
26	27.4	1.5	0.75	0.39
27	26.5	2.0	-0.37	-0.15
28	26.8	0.4	0.00	0.00
29	26.86	2.01	0.07	0.03
30	28.88	10	2.59	0.21
31	28	1.7	1.49	0.69
32	26.9	2.8	0.12	0.04
33	28	6	1.49	0.20
34	26.2	1.6	-0.75	-0.36

Statistics

Assigned Value	26.8	0.4
Robust Average	26.8	0.4
Median	26.9	0.3
Mean	26.9	
N	34	
Max.	32	
Min.	24.6	
Robust SD	0.90	
Robust CV	3.4%	


Kernel Density
Density
Result
Results: S3 - Cocaine
Assigned Value = 26.8 ± 0.4 % base (m/m)
Results (% base (m/m))
Laboratory
21 12 2 16 17 11 22 10 34 5 9 8 27 7 28 29 15 20 23 32 13 18 24 3 6 14 26 1 31 33 4 19 30 25 Md R.A.


z-Scores: S3 - Cocaine
Target Standard Deviation 0.80 % base (m/m) (Equivalent to 3% CV)
z-Score
Laboratory
21 12 2 16 17 11 22 10 34 5 9 8 27 7 28 29 15 20 23 32 13 18 24 3 6 14 26 1 31 33 4 19 30 25

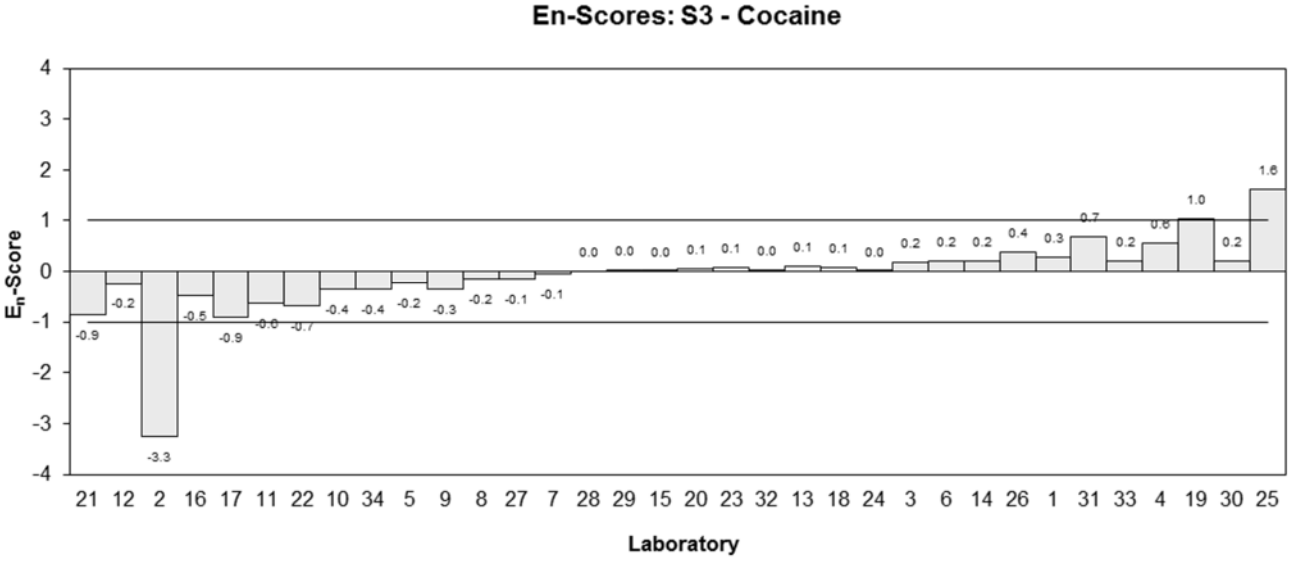

En-Scores: S3 - Cocaine
En-Score
Laboratory
21 12 2 16 17 11 22 10 34 5 9 8 27 7 28 29 15 20 23 32 13 18 24 3 6 14 26 1 31 33 4 19 30 25

Figure 4

Table 8 Participants' identification of cutting agents

Lab Code	Cutting agents	
	S2	S3
1	Phenacetin	Procaine
2	Phenacetin :56,1 %	Procaïne : 52,7 %
3	Phenacetin	Procaine
4	Phenacetin	Procaine
5	Phenacetine	Procaine
6	Phenacetine	Procaine
7	Phenacetin	Procaine
8	Phenacetin	Procaine
9	Phenacetin	Procaine
10	Phenacetin	Procaine
11	Phenacetin	procaine
12	Phenacetin	Procaine
13	Phenacetin	Procaine
14	Phenacetin	Procaine
15	Phenacetin	Procaine Hydrochloride
16	52.7% phenacetin	Procaine
17	Phenacetin	Procaine
18	Phenacetin	Procaine
19	Phenacetin	Procaine
20	Phenacetin	Procaine
21	Phenacetin	Procaine
22	Phenacetin	Procaine
23	Phenacetin	Procaine
24	Phenacetin	Procaine
25	Phenacetin	Procaine
26	Phenacetin	procaine
27	Phenacetin	Procaine
28	Phenacetin	Procaine
29	Phenacetin	Procaine
30	Phenacetin	Procaine Hydrochloride
31	Phenacetin	Procaine
32	-	-
33	Phenacetin	-
34	Phenacetin	Procaine

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The assigned value is the robust average of the results reported by the participants. The robust average and associated expanded uncertainties were calculated using the procedure described in 'ISO13528:2015, Statistical methods for use in proficiency testing by interlaboratory comparisons'.[7] The calculation procedure for the expanded uncertainty in Sample S1 is presented in Appendix 1.

Traceability: The consensus of participants' results is not traceable to any external reference, so although expressed in SI units, metrological traceability has not been established.

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results and the basis of this uncertainty estimate (Table 2).

It is a requirement of the ISO Standard 17025[5] that laboratories have procedures to estimate the uncertainty of chemical measurements and to report this uncertainty in specific circumstances, including 'when the client's instruction so requires.' From 1 July 2012 this is also a requirement of ASCLD/Lab-International accreditation program.

Ninety-nine results (97%) were reported with an associated expanded uncertainty. Laboratory **2** did not report uncertainty. This laboratory was not accredited.

Laboratories **12**, **15**, **20**, **24**, **30** and **33** reported an identical uncertainty for samples which were of significantly different concentrations.

The magnitude of reported uncertainties was within the range 1.5% to 52% relative.

Sixty-seven of ninety-nine (68%) expanded uncertainties were between 3% and 10% relative to the result. Laboratories reporting uncertainties smaller than 3% or larger than 10% relative may wish to consider whether these estimates are realistic or fit for purpose.

Laboratories having a satisfactory z-score and an unsatisfactory E_n-score are likely to have underestimated the expanded uncertainty associated with the result.

In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write the uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places (for example instead of 87.4 ± 8.166% the recommended format is 87.4 ± 8.2%).[6]

6.3 z-Score

A target standard deviation equivalent to 3% performance coefficient of variation (PCV) was used to calculate z-scores. Target SDs, the between-laboratory coefficient of variation predicted by Thomson - Horwitz equation[8] and between-laboratories coefficient of variation obtained in this study are presented in Table 9.

Table 9 Target standard deviations, coefficient of variations from predictive model and between laboratories

Sample	Analyte	Assigned value (% base m/m)	Target SD (as PCV)	Thompson Horwitz CV	Between laboratories CV
S1	Cocaine	84.9	3%	2.0%	2.4%
S2	Cocaine	39.5	3%	2.3%	2.5%
S3	Cocaine	26.8	3%	2.4%	3.4%

A summary of z-scores by laboratory is presented in Figure 5.

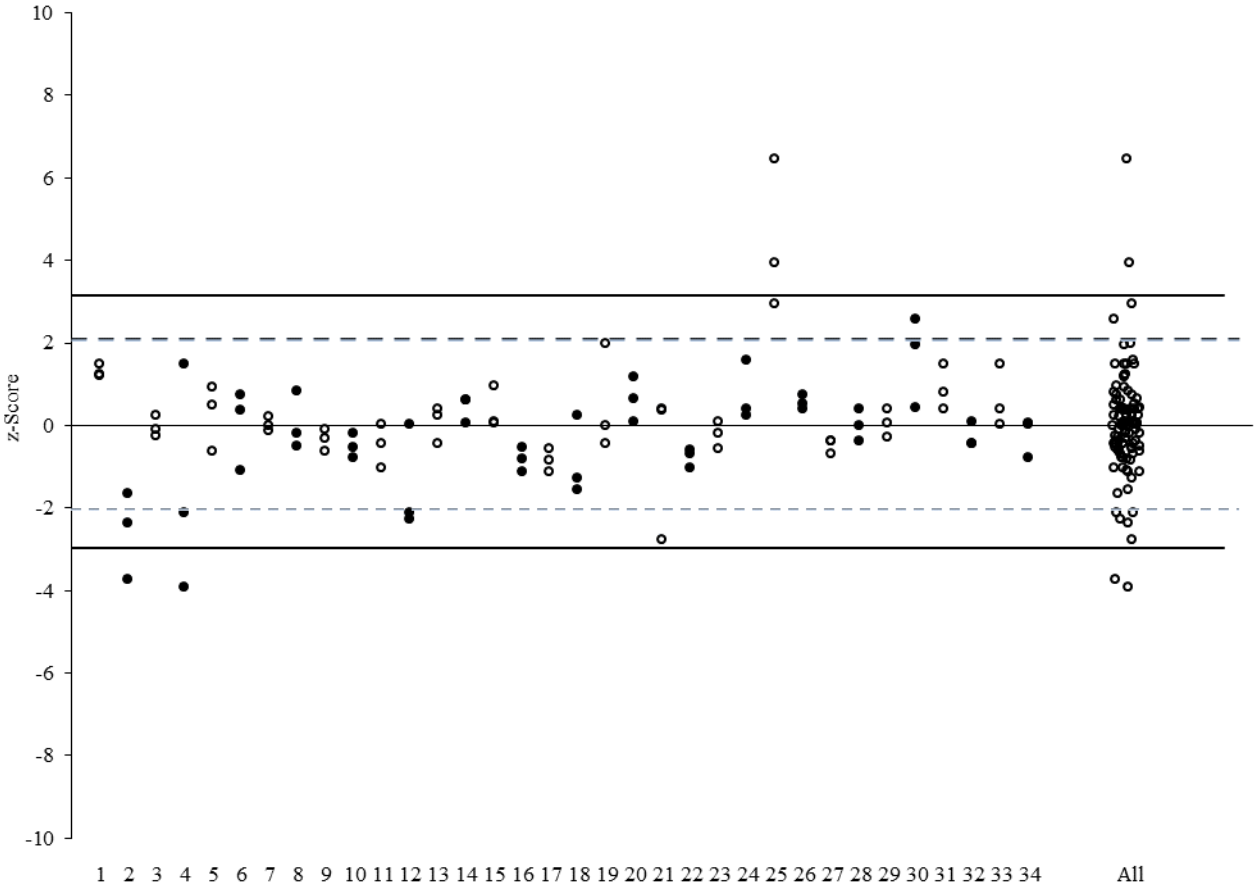


Figure 5 Summary of participants' z-score.

Ninety-one of 102 numeric results (89%) returned a satisfactory z-score with $|z| \leq 2$**.**

- Twenty-eight participants (82%) - **1**, **3**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **13**, **14**, **15**, **16**, **17**, **18**, **19**, **20**, **22**, **23**, **24**, **26**, **27**, **28**, **29**, **31**, **32**, **33** and **34** returned satisfactory scores for all three samples;
- Five participants returned at least one questionable or unsatisfactory z-score;
- Laboratory **25** returned questionable or unsatisfactory z-scores for all test samples demonstrating an unsatisfactory performance. This laboratory reported all results higher than the assigned value (positive bias) and may need to investigate the source of bias.

6.4 E_n-Score

The dispersal of participants' E_n-scores is graphically presented in Figure 6. Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score.

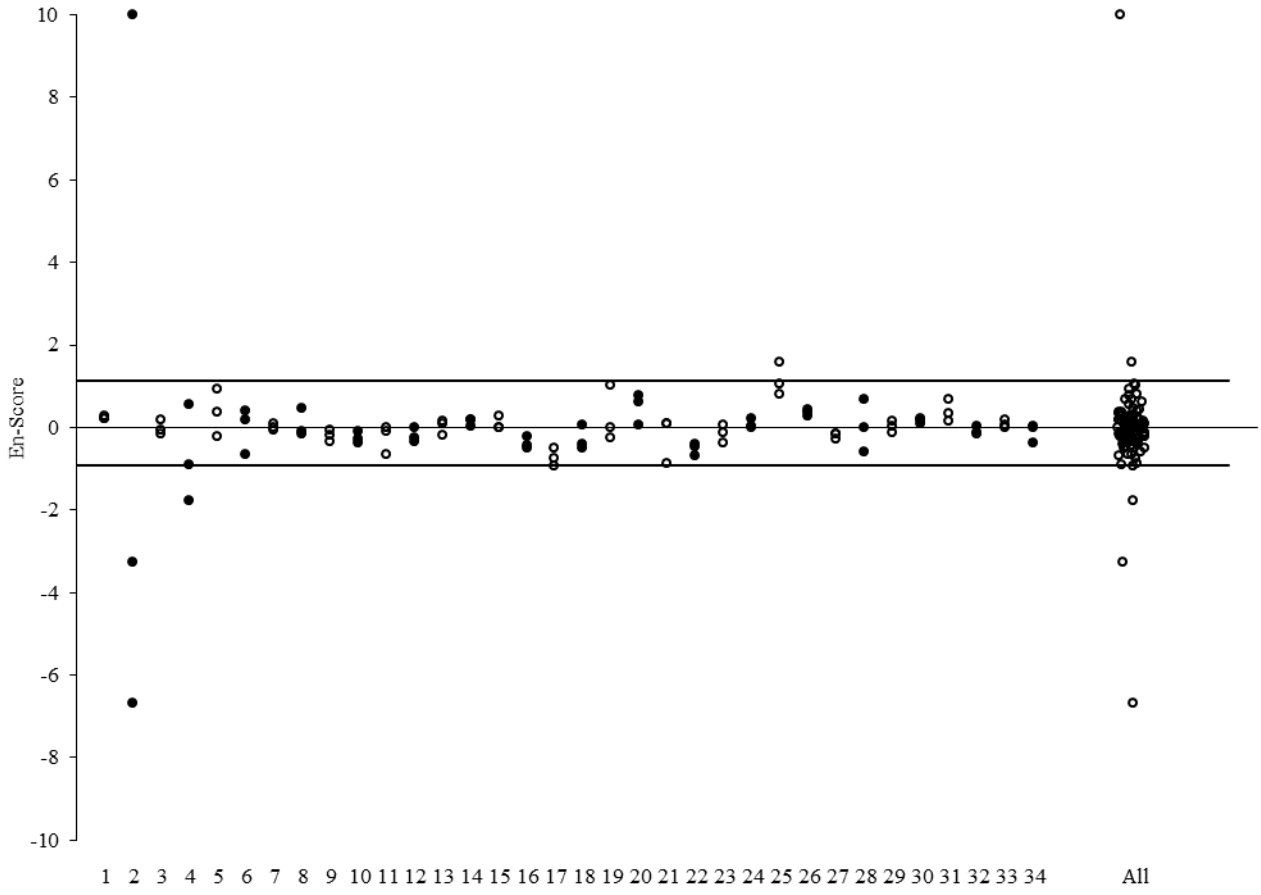


Figure 6 Summary of participants' E_n-Score

Ninety-five of 102 numeric results (93%) returned a satisfactory E_n-score with $|E_n| \leq 1$.

- Thirty-one (91%) – **1**, **3**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **12,** **13**, **14**, **15**, **16**, **17**, **18**, **19**, **20**, **21,** **22**, **23**, **24**, **26**, **27**, **28**, **29**, **30**, **31**, **32**, **33** and **34** returned satisfactory scores for all three samples;
- Two laboratories returned at least one questionable E_n-score; and
- Laboratory **2** returned $|E_n| > 1$ for all samples.

6.5 Identification of Cutting Agent

Samples were prepared using an illicit seizure of cocaine hydrochloride, approximately 84% base (m/m) supplied by the Australian Federal Police. The study coordinator added, phenacetin in Sample S2 and procaine in Sample S3.

Thirty-three participants (96%) reported on the identity of the cutting agents and correctly identified all of them. (Table 8).

6.6 Theoretical Concentration (% base cocaine)

The maximum concentration of cocaine as base (MW = 303.3) in anhydrous cocaine Hydrochloride (MW = 339.8) is 89.3%. Laboratory **25** reported the result for sample S1 as 95% base m/m.

6.7 Participants' Analytical Methods

Participants were requested to analyse the samples using their normal test methods and to report a single result for each sample as they would normally report to a client. Results reported in this way reflect the true variability of results reported to laboratory clients. The method descriptions provided by participants are presented in Table 1.

A summary of accreditation status, participants' methods and reference standards is presented below.

Accredited	Laboratory Code
Yes to ISO 17025	1 3 4 5 6 7 8 9 10 11 13 14 15 16 17 18 19 20 22 23 24 25 26 27 28 30 31 32 34
Yes to other	7 23 34
No	2 12 21 29 33

Sample Mass Used (mg)	Laboratory Code
4-10	3 14 19 33
11-30	4 8 9 10 12 13 15 16 17 18 20 21 24 25 26 29 30 31 32
31-50	1 2 5 6 7 22 23 27 28 34
51-100	
101-150	11

Instrument Used for quantification	Laboratory Code
GC-FID	6 9 13 16 19 20 22 23 28 30
UPLC-MS(MS)	1 2 18 25 26 27
HPLC (UPLC)-DAD	3 4 5 7 8 10 11 12 14 15 21 24 29 31 32 33 34
QNMR	17

Sources of Calibration Standard	Laboratory Code
NMI Australia	2 9 16 18 22 23 25 26 27 32
Lipomed	5 7 13 20 29 31 34
Sigma Aldrich	14 15 30 33
Other	1 3 4 6 8 10 11 12 17 19 21 24 28

Plots of measurement extraction solvent vs z-score, measurement instrument used vs z-score and calibration standard vs z-score are presented in Figures 7, 8 and 9. No trends were observed.

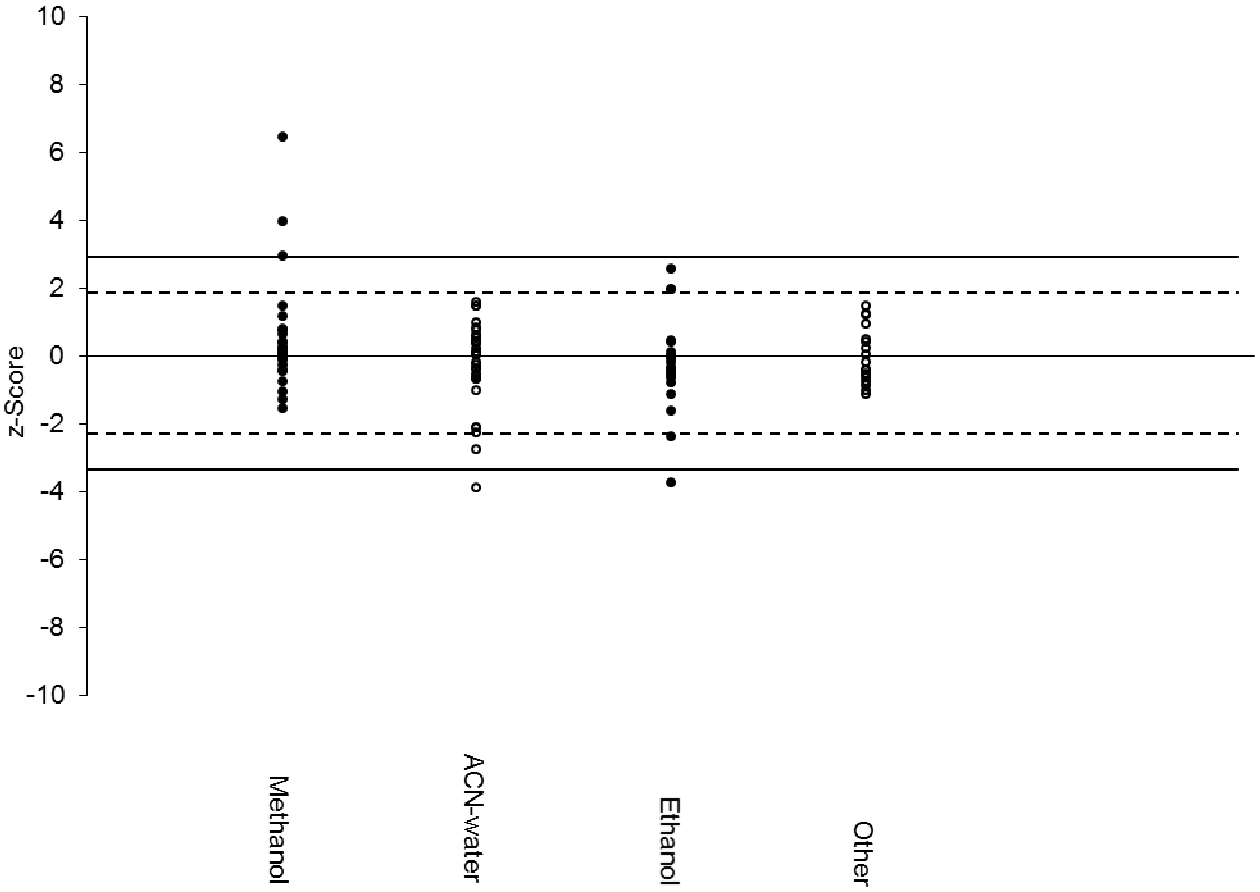


Figure 7 Extraction solvent vs z-score

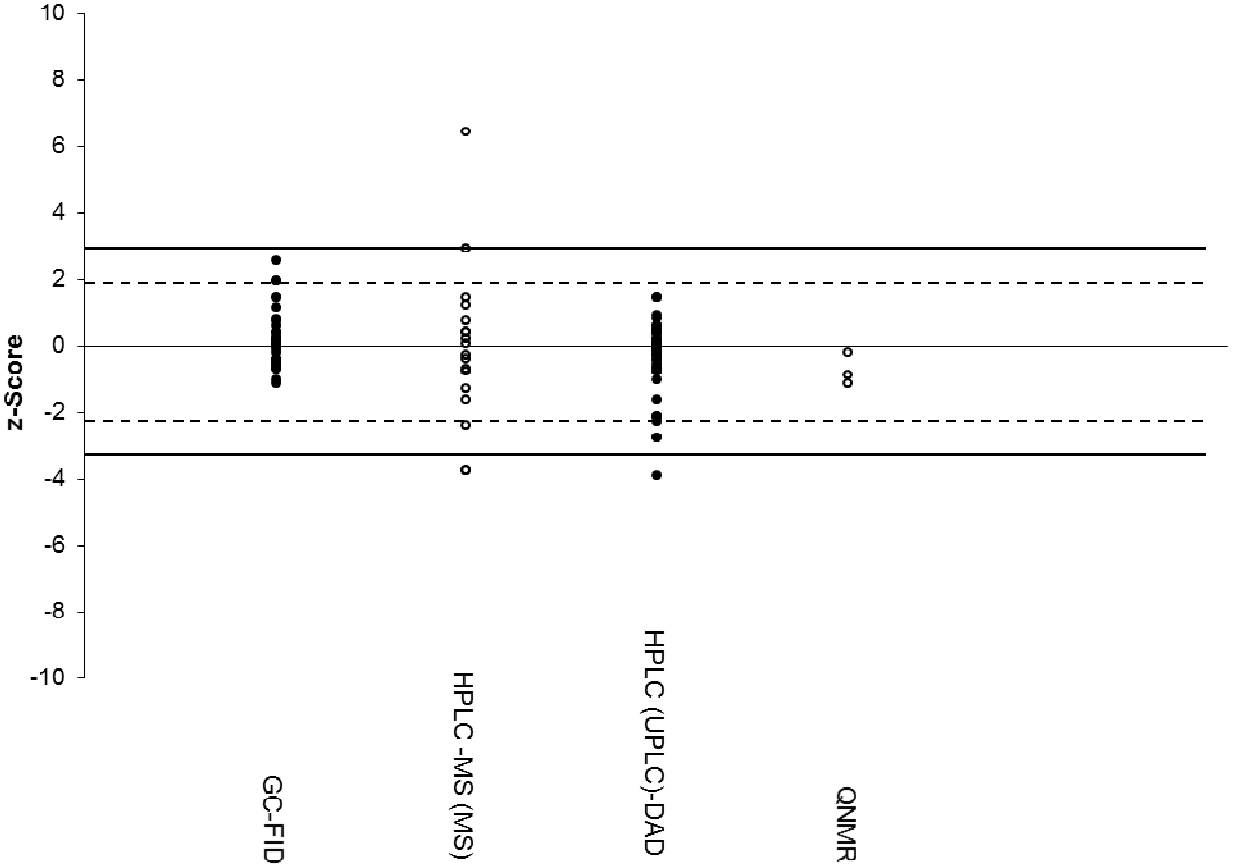


Figure 8 Measurement instrument vs z-score

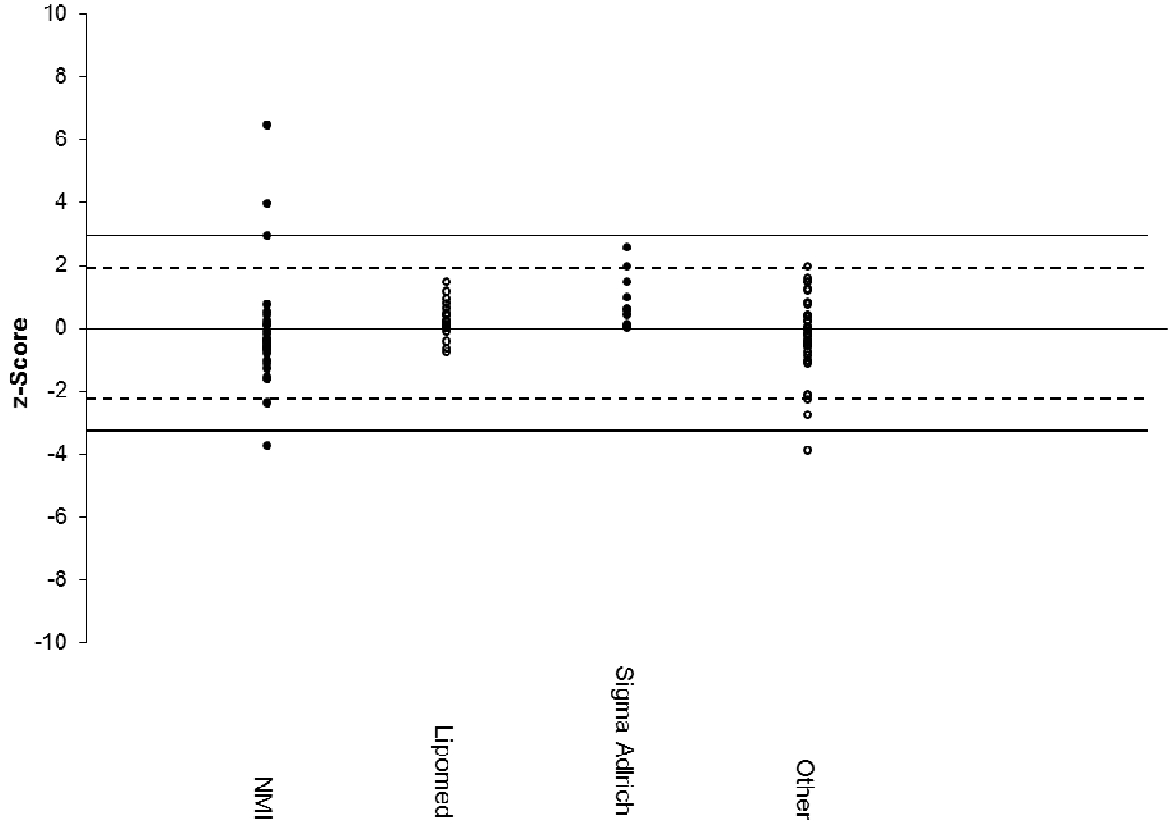


Figure 9 Calibration standard vs z-score

6.8 Summary of participation and performance in Cocaine Studies

Overall percentages of satisfactory z-scores and E_n-scores obtained by laboratories since 2009 are presented in Figure 10. The proportion of satisfactory z-scores and E_n-scores over 9 years on average is 79% and 80% respectively.

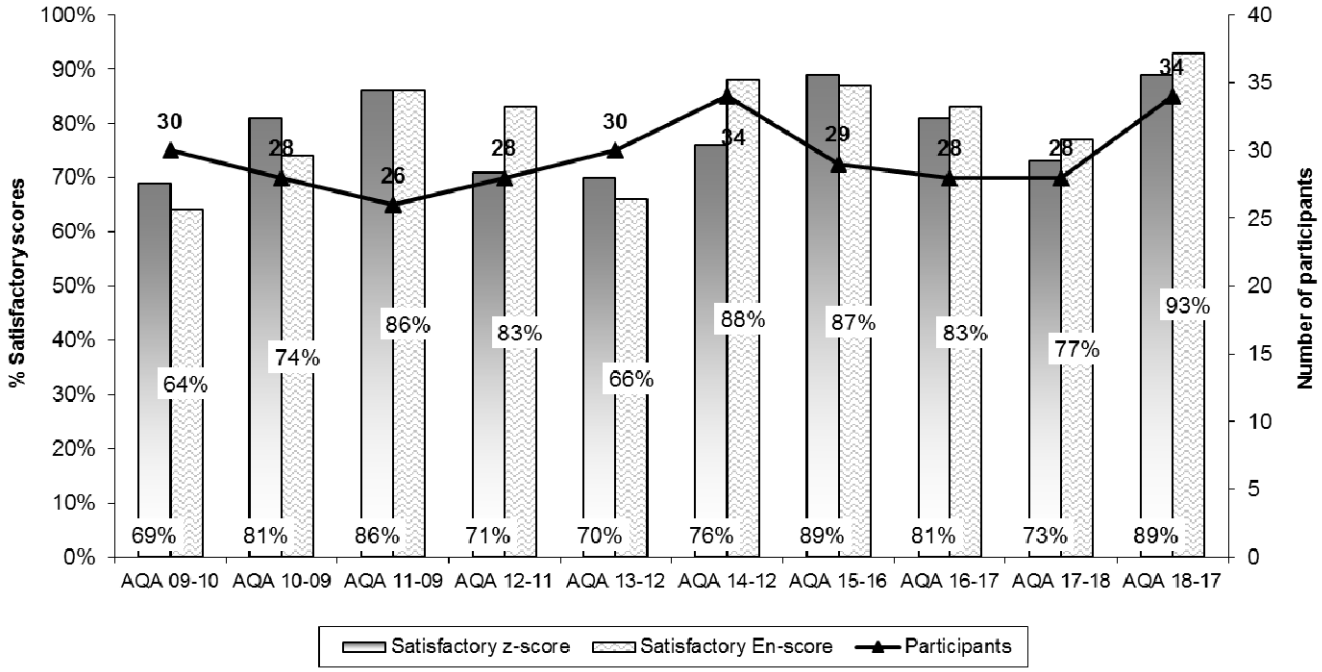


Figure 10 Summary of participants' performance since 2009

7 REFERENCES

[1] ISO/IEC 17043:2010, Conformity assessment – General requirements for proficiency testing, ISO Geneva

[2] NMI Chemical Proficiency Testing Study Protocol
http://www.measurement.gov.au → Products and Services → Chemical Proficiency Testing→ Details of Our Program

[3] NMI Chemical Proficiency Testing Statistical Manual
http://www.measurement.gov.au → Products and Services → Chemical Proficiency Testing→ Details of Our Program

[4] Thompson, M. E, S. L. R. and Wood, R., The international harmonized protocol for proficiency testing of (chemical) analytical laboratories, Pure Appl. Chem. 78, 145-196, 2005.

[5] ISO/IEC 17025:2017 General requirements for the competence of testing and calibration laboratories, ISO Geneva

[6] Eurachem/CITAC Guide Quantifying uncertainty in analytical measurement third edition, (2012), http:// http://eurachem.org/images/stories/guides/pdf/quam2012_P1.pdf

[7] ISO 13528:2015, Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO Geneva

[8] Thompson, M. and Lowthian, P.J., A Horwitz-like function describes precision in a proficiency test, Analyst, 120, 271-272, 1995.

APPENDIX 1 - MEASUREMENT UNCERTAINTY OF THE ASSIGNED VALUE

When the assigned value is calculated as the robust average using the procedure described in 'ISO13528:2015, Statistical methods for use in proficiency testing by interlaboratory comparisons – Annex C'[7], the uncertainty is estimated as:

$$u_{rob\ average} = 1.25 * S_{rob\ average} / \sqrt{p} \qquad \text{Equation 4}$$

where:

$u_{rob\ average}$	robust average standard uncertainty
$S_{rob\ average}$	robust average standard deviation
p	number of results

The expanded uncertainty ($U_{rob\ average}$) is the standard uncertainty multiplied by a coverage factor of 2 at approximately 95% confidence level.

A worked example is set out below in Table 10.

Table 10 Uncertainty of assigned value for Sample S1 as % base (m/m)

No. results (p)	34
Robust average	84.89
$S_{rob\ average}$	2.07
$u_{rob\ average}$	0.44
k	2
$U_{rob\ average}$	0.88

The assigned value for Sample S1 is 84.9 ± 0.9% cocaine base (m/m).

APPENDIX 2 - ACRONYMS AND ABBREVIATIONS

ASCLD	American Society of Crime Laboratory Directors
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DAD	Diode Array Detector
$\|E_n\|$	Absolute value of an E_n-score
FID	Flame Ionization Detector
GC	Gas Chromatography
GC-MS	Gas Chromatography Mass Spectrometry
GUM	Guide to the expression of uncertainty in measurement
HPLC	High Performance Liquid Chromatography
ISO	International Standards Organisation
LC	Liquid Chromatography
Max	Maximum value in a set of results
Md	Median
Min	Minimum value in a set of results
NATA	National Association of Testing Authorities
NMI	National Measurement Institute Australia
NR	Not Reported
NT	Not Tested
PDA	Photodiode array
PT	Proficiency Test
QNMR	Quantitative Nuclear Magnetic Resonance
Robust CV	Robust Coefficient of Variation
Robust SD	Robust Standard Deviation
SI	International System of Units
Target SD (σ)	Target standard deviation
UPLC	Ultra Performance Liquid Chromatography
UV	Ultraviolet
$\|z\|$	Absolute value of a z-score

END OF REPORT