Solid Matrix EQA Scheme (SOM@S)

Annual Report: 2013-14

4th July 2014

EQA@S

External Quality Assessment at Surrey

Introduction

Introduced in 2012-13 after a successful pilot scheme coordinated by the Scottish Trace Element and Micronutrient Reference Laboratory, Royal Infirmary Glasgow, the solid matrix EQA scheme (SOM@S) provides EQA specimens for laboratories that undertake the analysis of solid samples for Cu and Fe. The scheme is coordinated by External Quality Assessment at Surrey (EQ@S), which runs the TEQAS scheme and is part of UKNEQAS and based at the Surrey Research Park.

Clinically, in patients suspected of having Wilson's Disease or haemochromatosis, a liver biopsy sample may be taken for the determination of Cu or Fe to aid diagnosis (Wilson's and haemochromatosis respectively). To ensure accurate testing methods and facilitate suitable QA/QC in these complex determinations this scheme sends out small mass (10 - 20 mg) powdered samples of animal organs or other suitable organic solid materials, which are analysed by the participants for their Cu and Fe content. The analytical procedure used requires the organic materials sent to be converted to a liquid prior to analysis. This step can be carried out in a number of ways using various combinations of reagents and heating methods. Ultimately this complex step can lead to significant errors being introduced due to contamination or under-recovery of the analyte from the matrix. The scheme is designed to assess this step of the process with the aim of improving the participant's performance.

Distribution Process

Seventeen participants were registered in 2013-14. A single distribution contains 3 tissue samples of different origin (Table 1), a covering letter and an answer sheet. Packages are sent out quarterly and labs are given 4 to 6 weeks to return the results and also the methodology they used (Table 2) in preparing the samples. Reports are then compiled and returned to the participant.

Materials Distributed in 2013-14

Table 1: Materials and distribution:

		µg/g concentrations			2013			
Reference	**Tissue**	Cu	Fe	Hg	1st dist.	2nd dist.	3rd dist.	4th dist.
A13	Blood	4.3	2400	-			**C3**	
1577b	Bovine Liver	160	184	0.003			**C2**	
ERM-278	Mussel Tissue	5.98	161	0.071	**A1**			**D2**
ERM-422	Fish Muscle	1.67	9.4	0.601	**A2**			
ERM-184	Bovine Muscle	2.31	75	-	**A3**	**B2**		**D3**
ERM186	Pig Kidney	36.5	255	-		**B1**	**C1**	**D1**
H4	Animal Muscle	4	49	-		**B3**		
		Date distributed:			29/05/2013	29/08/2013	30/10/2013	08/01/2014
		Date to be returned:			31/07/2013	30/09/2013	31/12/2013	29/03/2014

Table 1: Overview of distributed materials and dispatched dates.

N.B. Each specimen was individually weighed into a 1ml ThermoFisher™ cryogenic microcentrifuge tube. On average, each tube contained 15 - 18mg of dried tissue sample.

MethodologyOverview

Method of Digestion	Method of Analysis	Number of labs
Microwave Digester	ICP-MS	5
Microwave Digester	Flame and Flameless AAS	1
Oven	ICP-MS	1
Oven	PE ICP-MS DRC II	1
Oven	GFAS	1
Teflon Digestion bomb	ICP-MS DRC	1
Heating block	ICP-MS	2
Hot plate	ICP-MS	1
Incomplete data*		4

Table 2: Overview of methods used by participants:

*Four participants (23% of the laboratories taking part) failed to return information on digestion or analysis methods, or both.

Table 3: Overview of results:

		Copper				Iron			
		Certified value (µg/g)	Mean (µg/g)	Standard deviation	CV (%)	Certified value (µg/g)	Mean (µg/g)	Standard deviation	CV (%)
1st distribution	A1	5.98	6.11	0.74	12.0	161	114	46.3	40.5
	A2	1.67	1.91	0.68	35.7	9.40	11.9	7.09	59.51
	A3	2.31	2.19	0.78	35.5	75.0	67.6	20.7	30.7
2nd distribution	B1	36.5	32.8	3.76	11.47	255	223	59.9	26.8
	B2	2.31	2.59	0.88	34.11	75.0	83.8	54.6	65.2
	B3	4.00	4.17	1.82	43.7	49.0	59.4	49.2	82.9
3rd distribution	C1	36.5	38.2	10.4	27.1	255	238	42.8	18.0
	C2	160	304	568	187	184	197	41.3	20.9
	C3	4.30	7.85	13.6	173	2400	2297	337.5	14.7
4th distribution	D1	36.50	33.23	8.74	26.3	255	230	55.4	24.1
	D2	5.98	7.09	2.57	36.25	161	118	46.5	39.4
	D3	2.31	3.46	2.74	79.2	75.0	72.5	13.9	19.2

	Material	Target		Av. Bias 1st Dist.	Av. Bias 2nd Dist.	% of labs which improved
OVER RECOVERY	ERM-278 Mussel Tissue	Cu	5.98	9.90	-11.61	44
	A1/ D2	Fe	161	11.87	17.81	0
	ERM-184 Bovine Muscle	Cu	2.31	34.20	41.46	33
	A3/ B2	Fe	75	24.74	-7.73	50
	ERM-184 Bovine Muscle	Cu	2.31	39.29	-10.89	83
	B2/ D3	Fe	75	82.24	36.37	50
	ERM186 Pig Kidney	Cu	36.5	16.71	-1.84	100
	B1/ C1	Fe	255	18.05	-4.29	100
	ERM186 Pig Kidney	Cu	36.5	12.01	2.54	29
	C1/ D1	Fe	255	36.82	6.04	80
UNDER RECOVERY	**Material**	**Target**		**Av. Bias 1st Dist.**	**Av. Bias 2nd Dist.**	**% of labs which improved**
	ERM-278 Mussel Tissue	Cu	5.98	-11.82	-16.48	40
	A1/ D2	Fe	161	-36.46	-16.16	82
	ERM-184 Bovine Muscle	Cu	2.31	-26.06	-8.76	22
	A3/ B2	Fe	75	-22.04	4.97	57
	NCS ZC 81001 Pork Muscle	Cu	2.31	-21.56	0.06	71
	B2/ D3	Fe	75	-23.47	21.12	100
	ERM186 Pig Kidney	Cu	36.5	-12.48	-6.72	50
	B1/ C1	Fe	255	-22.67	-7.16	56
	ERM186 Pig Kidney	Cu	36.5	-16.46	-17.59	60
	C1/ D1	Fe	255	-12.19	-13.94	55

Table 4: Percentage of labs with improved result bias for materials that were distributed more than once. Participants are divided into those that under or over recovered. One result (1112.1ug/g) removed as outlier.

RSCH TEQ@S UKNEQAS

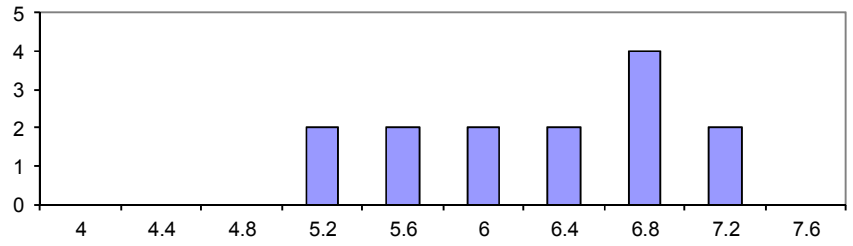
Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Distribution : Jun 2013 | Report date: Sep 2013

Specimen	Description	COPPER µg/g
A1	Mussel Tissue	5.98
A2	Fish Muscle	1.67
A3	Bovine Muscle	2.31

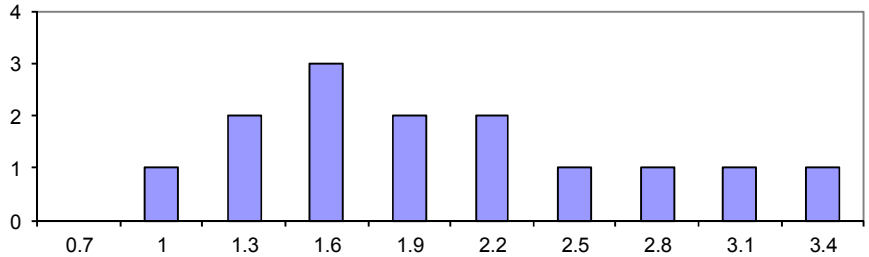
Specimen A1

n	ALTM	SD	CV(%)
14	6.1	0.74	12.0



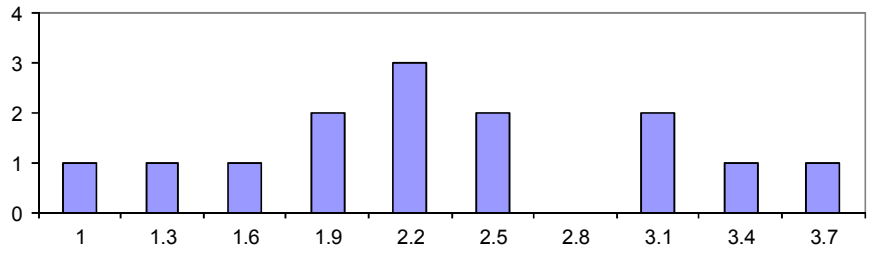
Specimen A2

n	ALTM	SD	CV(%)
14	1.9	0.7	35.7



Specimen A3

n	ALTM	SD	CV(%)
13	2.2	0.78	35.5



Comments

RSCH TEQ@S UKNEQAS

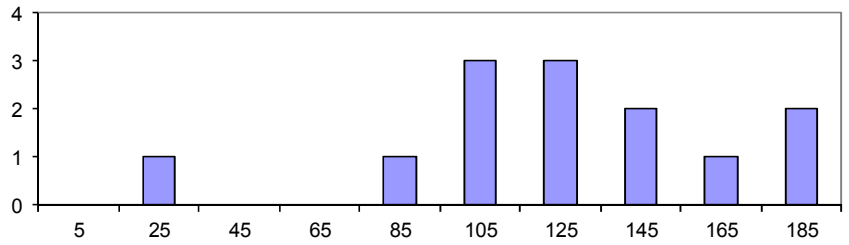
Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Distribution : Jun 2013 | Report date: Sep 2013

Specimen	Description	IRON µg/g
A1	Mussel Tissue	161.00
A2	Fish Muscle	9.40
A3	Bovine Muscle	75.00

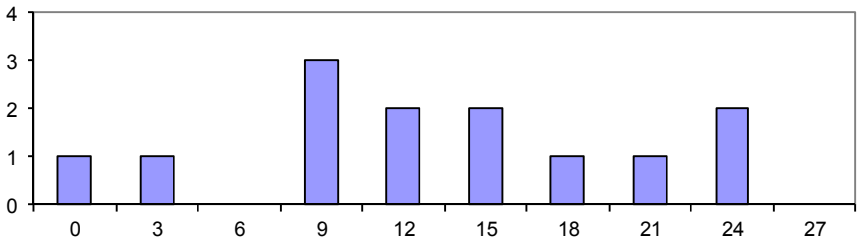
Specimen A1

n	ALTM	SD	CV(%)
13	114.3	46.32	40.5



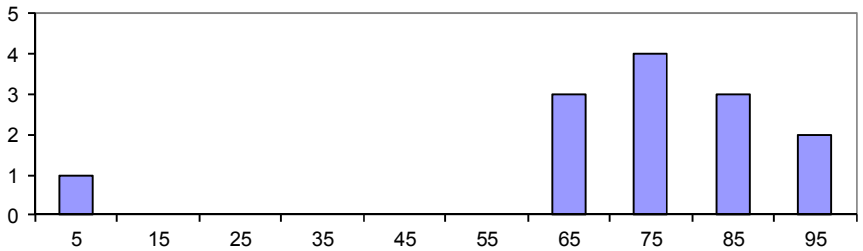
Specimen A2

n	ALTM	SD	CV(%)
13	11.9	7.1	59.5



Specimen A3

n	ALTM	SD	CV(%)
13	67.6	20.73	30.7



Comments

RSCH TEQ@S UKNEQAS

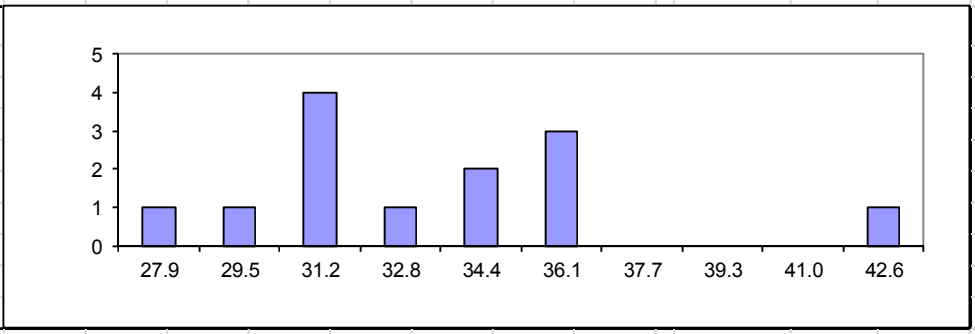
Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Distribution : Sep 2013 | Report date Oct 2013

Specimen	Description	COPPER µg/g
B1	Pig Kidney	36.50
B2	Bovine Muscle	2.31
B3	Animal Muscle	4.00

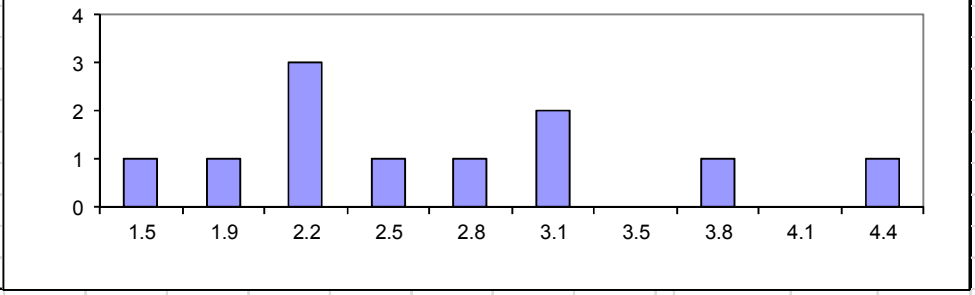
Specimen B1

n	ALTM	SD	CV(%)
13	32.8	3.76	11.5



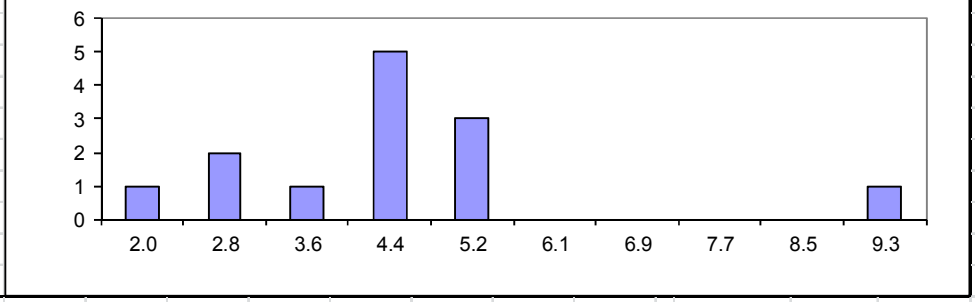
Specimen B2

n	ALTM	SD	CV(%)
12	2.6	0.9	34.1



Specimen B3

n	ALTM	SD	CV(%)
13	4.2	1.82	43.7



Comments

The following result was omitted:
28.00 µg/g removed from sample B2

RSCH TEQ@S UKNEQAS

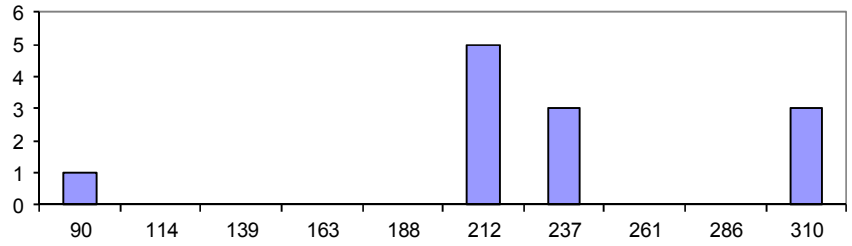
Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Distribution : Sep 2013 | Report date Oct 2013

Specimen	Description	IRON µg/g
B1	Pig Kidney	255.00
B2	Bovine Muscle	75.00
B3	Animal Muscle	49.00

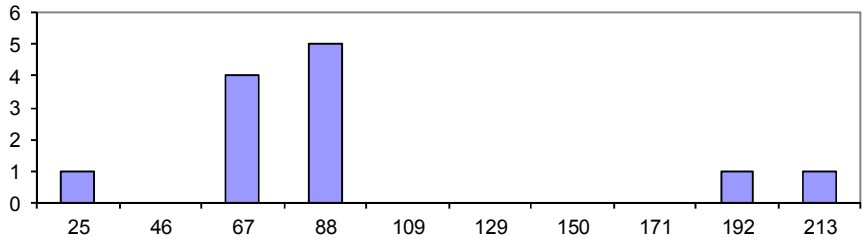
Specimen B1

n	ALTM	SD	CV(%)
12	223.2	59.85	26.8



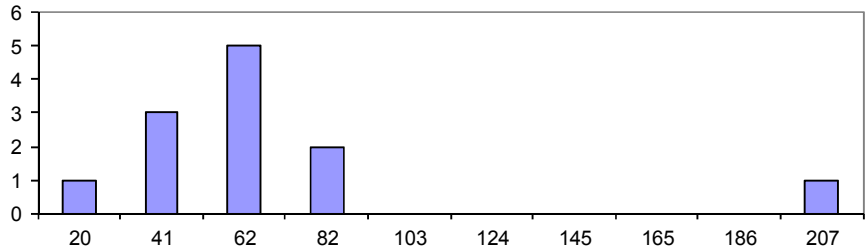
Specimen B2

n	ALTM	SD	CV(%)
12	83.8	54.6	65.2



Specimen B3

n	ALTM	SD	CV(%)
12	59.4	49.21	82.9



Comments

RSCH TEQ@S UKNEQAS

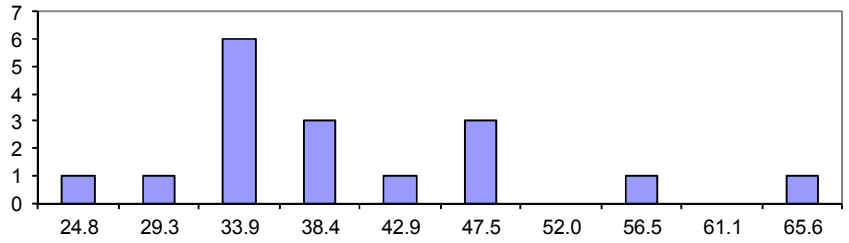
Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Distribution: Nov 2013 | Report date: Dec 2013

Specimen	Description	COPPER
C1	Pig Kidney	36.50 µg/g
C2	Bovine Liver	160.00 µg/g
C3	Animal Blood	4.30 µg/g

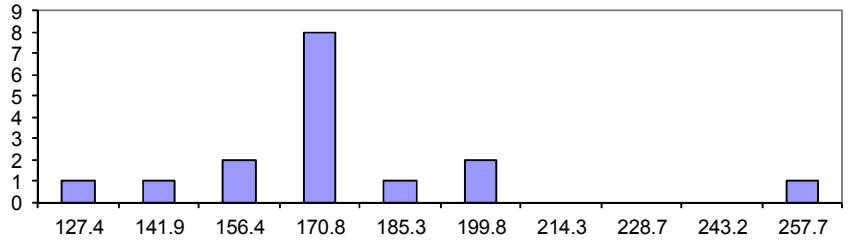
Specimen C1

n	ALTM	SD	CV(%)
17	38.2	10.35	27.1



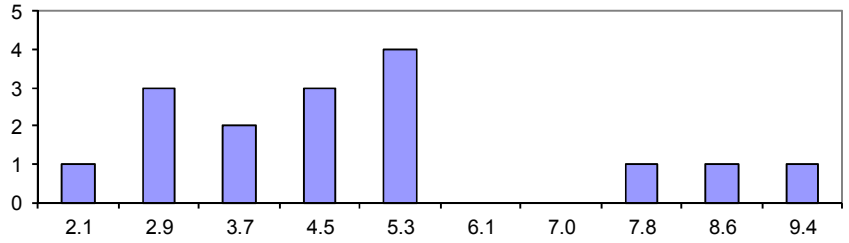
Specimen C2

n	ALTM	SD	CV(%)
16	166.1	29.0	17.4



Specimen C3

n	ALTM	SD	CV(%)
16	4.6	2.21	48.1



Comments

The following results were omitted:

2507µg/g removed from sample C2

60µg/g removed from sample C3

RSCH TEQ@S UKNEQAS

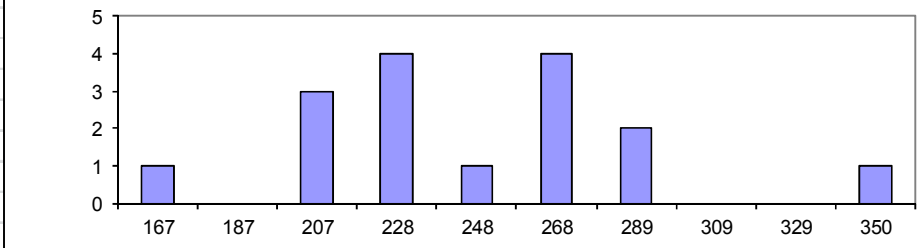
Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Distribution: Nov 2013 | Report date: Dec 2013

Specimen	Description	IRON
C1	Pig Kidney	255.00 µg/g
C2	Bovine Liver	184.00 µg/g
C3	Animal Blood	2400.00 µg/g

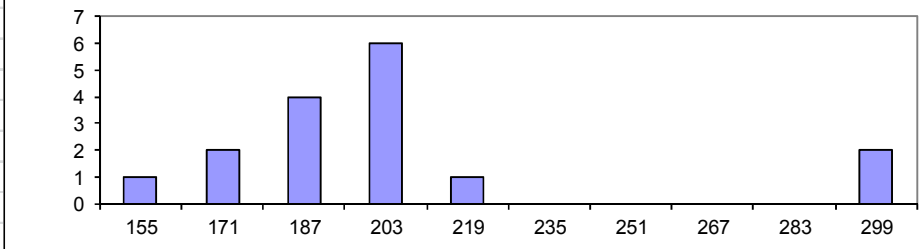
Specimen C1

n	ALTM	SD	CV(%)
16	237.7	42.83	18.0



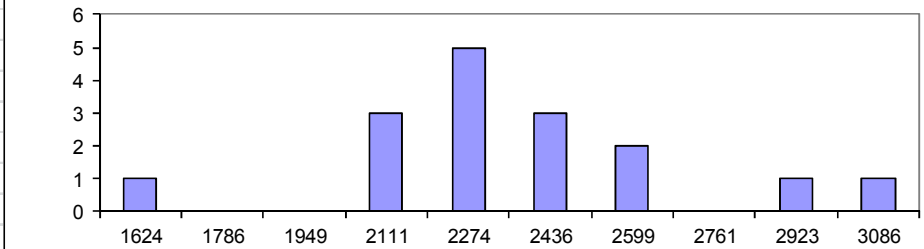
Specimen C2

n	ALTM	SD	CV(%)
16.00	197.3	41.3	20.9



Specimen C3

n	ALTM	SD	CV(%)
16	2296.5	337.45	14.7



Comments

RSCH TEQ@S UKNEQAS

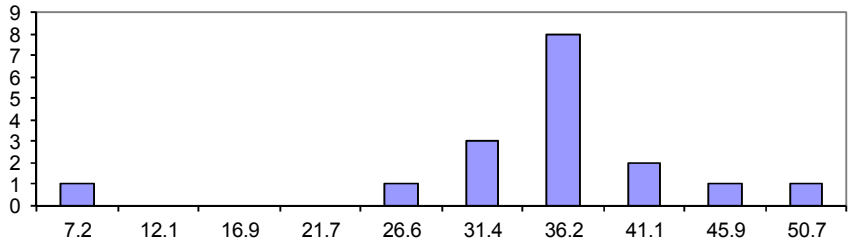
Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Distribution:	Jan	2014	Report date:	Mar	2014

	Specimen	Description	COPPER	
	D1	Pig Kidney	36.50	µg/g
	D2	Mussel Tissue	5.98	µg/g
	D3	Bovine Muscle	2.31	µg/g

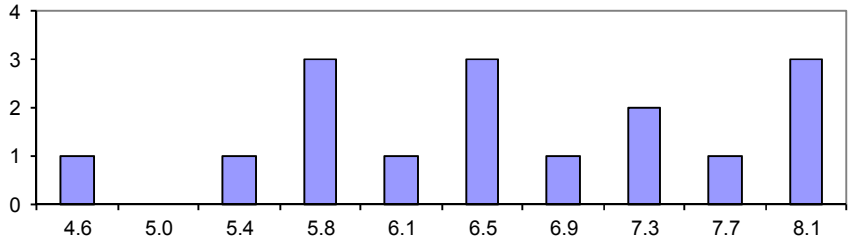
Specimen D1

n	ALTM	SD	CV(%)
17	33.2	8.74	26.3



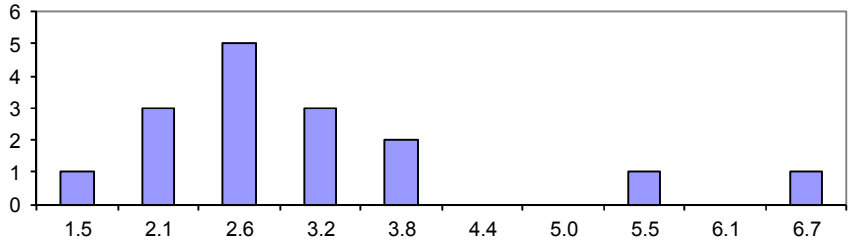
Specimen D2

n	ALTM	SD	CV(%)
16	6.5	1.1	16.5



Specimen D3

n	ALTM	SD	CV(%)
16	2.9	1.31	45.7



Comments

The following results were omitted:

16.20µg/g removed from sample D2

12.90µg/g removed from sample D3

RSCH TEQ@S UKNEQAS

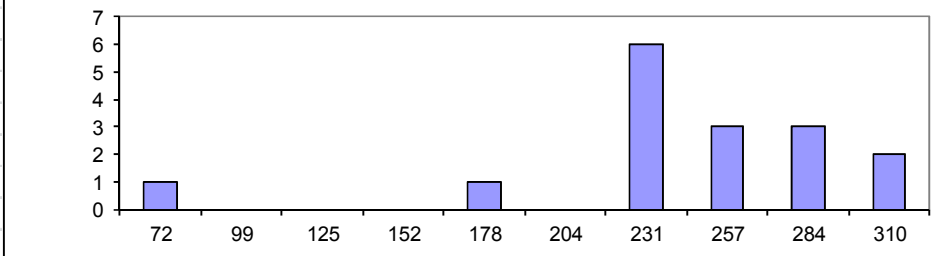
Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Distribution: Jan 2014 | Report date: Mar 2014

Specimen	Description	IRON
D1	Pig Kidney	255.00 µg/g
D2	Mussel Tissue	161.00 µg/g
D3	Bovine Muscle	75.00 µg/g

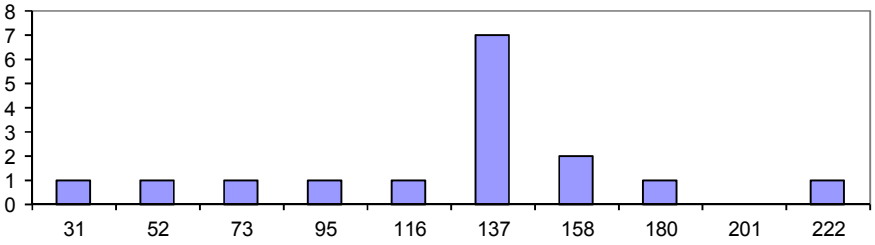
Specimen D1

n	ALTM	SD	CV(%)
16	229.7	55.43	24.1



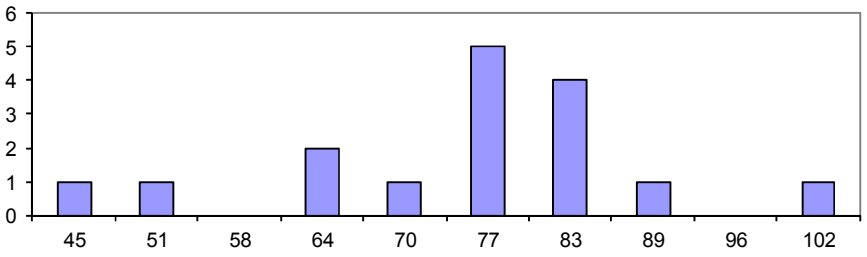
Specimen D2

n	ALTM	SD	CV(%)
16	118.0	46.5	39.4



Specimen D3

n	ALTM	SD	CV(%)
16	72.5	13.90	19.2



Comments

Discussion

The participant results for the scheme this year showed that 58 of the 306 results returned were within acceptable limits as set by the certified values from suppliers of the materials used. In percentage terms this means 19% of the results were within the CRM limits compared to 22% last year. The acceptable results were not evenly spread across the 4 distributions however, but most participants showed a gradual improvement, once again peaking at the third distribution where 27 of the acceptable returns were found, in a similar trend to the previous year. Results were split into those that had returned results with a positive bias (over-recovery/contamination?) and those with a negative bias (under-recovery/loss of materials?). Table 4 details how labs improved their performance in cases where the same material has been distributed twice in a scheme year. Overall, those that under-recovered in their first distribution improved more than those that over-recovered, suggesting that contamination may be a problem in those participant's analytical methods.

Deviations from the certified value occurred both above and below the target. This year, the most common problem was an underestimation of the result for both analytes, but iron in particular. Under estimates are likely due to incomplete recovery at these stages. In general, those that underestimated in the first distribution became more accurate in the second; and most underestimating labs showing an overall improvement in accuracy. However, participants which provided an over estimated concentration, struggled to get a more accurate result, suggesting that there may be some contamination in the process that is not being accounted for by the blank, or which could be mitigated against by improvements in the procedure.

As with last year, participants who returned the best results demonstrated that the use of a microwave digester and extensive drying (80 - 100°C for 24 hours) was most effective. Slower digestion methods (24 hours at room temperature) also demonstrated a good overall return. Use of hot plates and ovens in digestion appears to be less efficient than the alternatives, with a tendency to under-recovery. Returns for copper were generally more accurate than iron, despite on average being present in much lower concentrations. There was little variation between under and over recovery when comparing the two elements, with most labs seeing the same positive and negative bias for copper as they do for iron.

We had a much better return than last year from participants returning additional information about their methods, with only 23% of labs missing complete information. This information is invaluable to us as it helps to give advice and guide people towards the best method for analysis.

Of the materials distributed, some gave a better return than others. Samples A3/B2/D3 (Bovine Muscle) gave generally accurate results across all laboratories when analysed for copper content. Results from the iron returns for sample D3 however, show a large bias. Sample B1/C1/D1 (Pig Kidney) gave very accurate results in most distributions, with biases all under 10%, with only one exception, again with measurement of iron.

Conclusions

Compared with last year, there has been a slight drop in the accuracy of the returned results, with only 58 being within acceptable bounds compared with 78 results from 2012. Additionally, 2013 showed more labs failing to improve on the accuracy of previous returns, compared with the same period last year.

The scheme has helped to highlight areas of the analytical procedure used for the preparation of liver biopsy samples that require improvement to achieve the best possible accuracy. In general the best accuracy was achieved by digesting the materials in a microwave digester or Teflon bomb. Comparable results could also be achieved with leaving the sample to digest at room temperature for at least 24 hours with concentrated acid. In analysis, ICP-MS in reaction cell mode appears to give the most accurate results.

In future participants are requested to provide full details of the method used as this will help to identify the most appropriate methods of sample preparation.

The organizers would like to thank the participants for their involvement in the scheme and request that they draw its existence to the attention of other laboratories who may wish to take part.

If participants have any comments on this report or the scheme in general then these should be directed to Dr Chris Harrington (Scheme Manager) at the TEQAS office (rsc-tr.guildford-eqa@nhs.net).
