TEQAS
Tel. +44 (0)1483 689022
Fax. +44 (0)1483 689979
e-mail. teqas@surrey.ac.uk

Solid Matrix EQA Scheme (SOM@S)

Annual Report: 2012-13

August 21st 2013

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 University of Surrey.

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

Sixteen participants were registered in 2012-13. 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 use (Table 2) in preparing the samples. Reports are then compiled and returned to the participant.

Materials Distributed in 2012-13

Table 1: Materials and distribution:

		µg/g concentrations			2012			
Reference	**Tissue**	Cu	Fe	Hg	1st dist.	2nd dist.	3rd dist.	4th dist.
H4	Animal Muscle	4	49	-	**A1**			
H8	Horse Kidney	32	259	-	**A2**			
A13	Blood	4.3	2400	-				**D1**
1566a	Oyster Tissue	66.3	539	0.0642		**B1**	**C1**	
BCR 186	Pig Kidney	31.9	299	1.97		**B2**		
BCR 185	Bovine Liver	189	214	0.044			**C2**	**D3**
NCS ZC 81001	Pork Muscle	3.9	43.6	-	**A3**	**B3**		
1577b	Bovine Liver	160	184	0.003			**C3**	**D2**
		Date distributed:			08/10/2012	19/11/2012	02/01/2013	11/02/2013
		Date to be returned:			16/11/2012	28/12/2012	08/02/2013	25/03/2013

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

Methodology Overview

Table 2: Overview of methods used by participants:

Method of Digestion	Method of Analysis	Number of labs
Microwave Digester	ICP-MS	4
Microwave Digester	Flame and Flameless AAS	1
Oven	ICP-MS	1
Oven	PE ICP-MS DRC II	1
Teflon Digestion bomb	ICP-MS DRC	1
Heating block	ICP-MS	1
Hot plate	ICP-MS	1
Incomplete data*		6

*Six participants (40% of the laboratories taking part) failed to return information on digestion or analysis methods, or both.

Results

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	4.00	4.74	2.36	49.9	49.0	46.8	15.9	34.0
	A2	32.0	29.9	4.47	14.9	259	268	24.9	9.28
	A3	3.9	5.13	3.31	64.4	35.5	47.3	13.9	29.3
2nd distribution	B1	66.3	62.9	6.13	9.75	539	427	109	25.4
	B2	31.9	29.3	4.09	14.00	299	276	33.4	12.1
	B3	3.90	4.22	1.64	38.8	35.5	42.4	11.1	26.1
3rd distribution	C1	66.3	65.4	4.73	7.23	539	419	115	27.4
	C2	189	180	9.38	5.20	214	202	47.2	23.4
	C3	160	163	9.84	6.04	184	187	34.9	18.7
4th distribution	D1	4.30	4.09	2.21	54.0	2400	2260	231	10.2
	D2	160	162	15.3	9.41	184	214	48.7	22.8
	D3	189	179	22.7	12.6	214	221	52.6	23.9

Table 4: Percentage improvement in result bias for materials that were distributed more than once. Participants are divided into those who under and over recovered:

	Material		Target	Av. Bias 1st Dist.	Av. Bias 2nd Dist.	% of labs which improved
OVER	1566a Oyster Tissue B1/ C1	Cu	66.3	4.89	8.56	40
		Fe	539	3.90	8.53	33
	BCR 185 Bovine Liver C2/ D3	Cu	189	2.41	5.35	33
		Fe	214	12.67	18.99	20
	NCS ZC 81001 Pork Muscle A3/ B3	Cu	3.9	68.52	75.64	50
		Fe	43.6	74.70	35.49	44
	1577b Bovine Liver C3/ D2	Cu	160	6.63	7.16	50
		Fe	184	12.05	24.67	22
UNDER	**Material**		**Target**	**Av. Bias 1st Dist.**	**Av. Bias 2nd Dist.**	**% of labs which improved**
	1566a Oyster Tissue B1/ C1	Cu	66.3	-10.61	-4.97	77
		Fe	539	-28.95	-27.47	70
	BCR 185 Bovine Liver C2/ D3	Cu	189	-6.81	-13.14	50
		Fe	214	-16.12	-19.29	57
	NCS ZC 81001 Pork Muscle A3/ B3	Cu	3.9	-19.29	-20.85	29
		Fe	43.6	-35.67	-8.95	100
	1577b Bovine Liver C3/ D2	Cu	160	-9.30	-7.59	29
		Fe	184	-16.87	-9.05	67

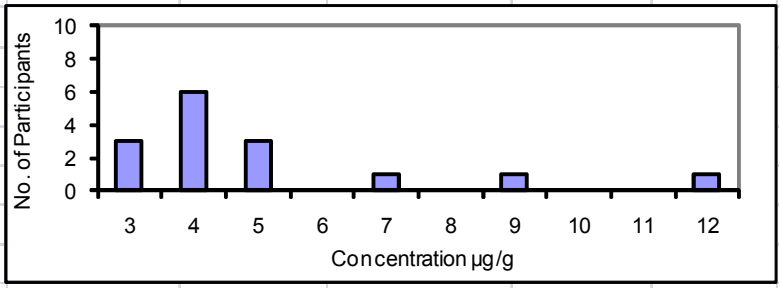
RSCH TEQ@S UKNEQAS

Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Specimen	Description	COPPER ug/g
A1	Animal muscle	4.00
A2	Horse kidney	32.00
A3	Pork muscle	3.90

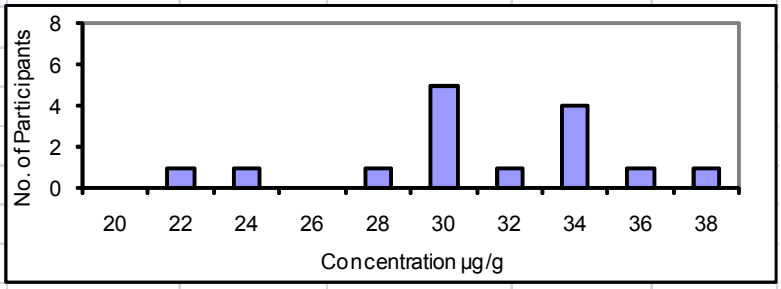
Specimen A1

n	ALTM	SD	CV(%)
16	4.7	2.36	49.9



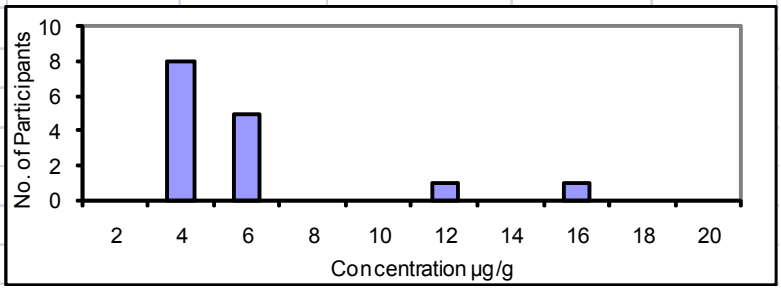
Specimen A2

n	ALTM	SD	CV(%)
16	29.9	4.5	14.9



Specimen A3

n	ALTM	SD	CV(%)
16	5.1	3.31	64.4



Comments

3 results were omitted:

Sample A1	<0.73 ug/g
Sample A2	2.44 ug/g
Sample A3	<0.78 ug/g

RSCH

TEQ@S

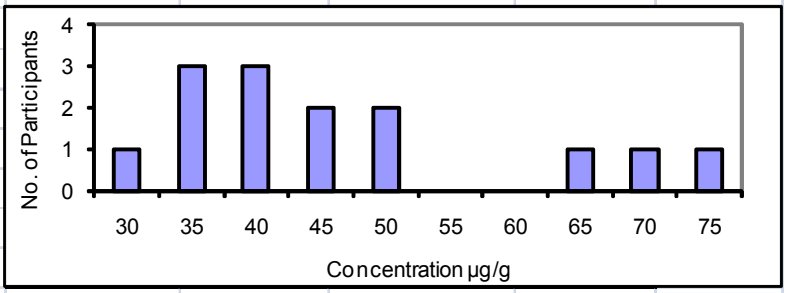
UKNEQAS

Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Specimen	Description	IRON ug/g
A1	Animal muscle	49.00
A2	Horse kidney	259.00
A3	Pork muscle	35.45

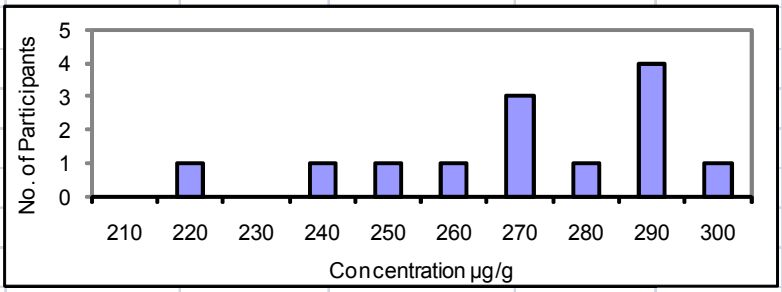
Specimen A1

n	ALTM	SD	CV(%)
15	46.8	15.90	34.0



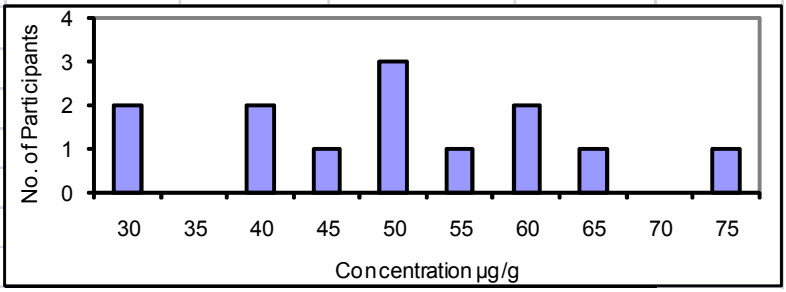
Specimen A2

n	ALTM	SD	CV(%)
15	268.1	24.9	9.3



Specimen A3

n	ALTM	SD	CV(%)
15	47.3	13.87	29.3



Comments

3 results were omitted:

Sample A2	67.2 ug/g
Sample A3	274 ug/g
Sample A3	12.8ug/g

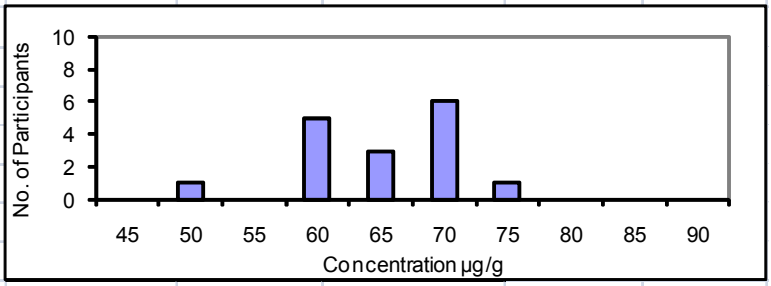
RSCH TEQ@S UKNEQAS

Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Specimen	Description	COPPER ug/g
B1	Oyster Tissue 1566a	66.30
B2	Pig Kidney BCR186	31.90
B3	Pork muscle NCSZC81001	3.90

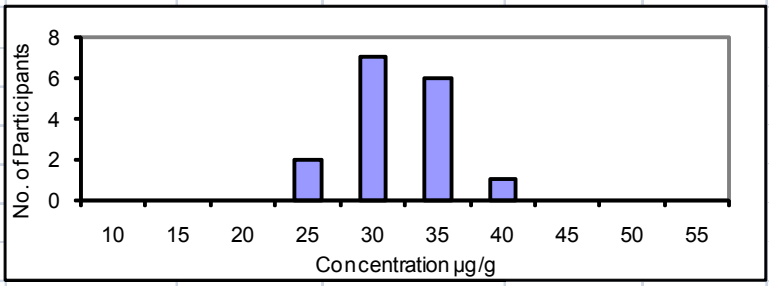
Specimen B1

n	ALTM	SD	CV(%)
16	62.9	6.13	9.75



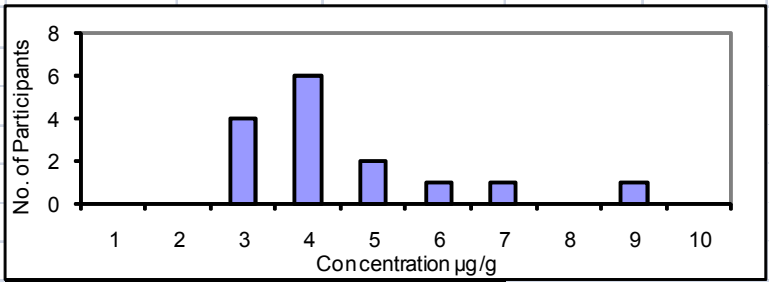
Specimen B2

n	ALTM	SD	CV(%)
16	29.3	4.1	14.0



Specimen B3

n	ALTM	SD	CV(%)
15	4.2	1.64	38.8



Comments

1 result was omitted:

Sample B3 19.6 ug/g

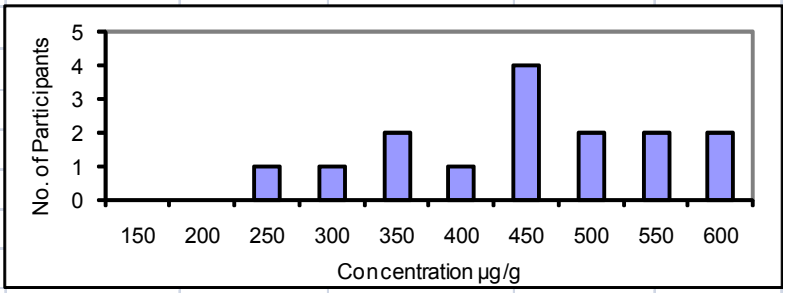
RSCH TEQ@S UKNEQAS

Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Specimen	Description	IRON ug/g
B1	Oyster Tissue 1566a	539.00
B2	Pig Kidney BCR186	299.00
B3	Pork muscle NCSZC81001	35.45

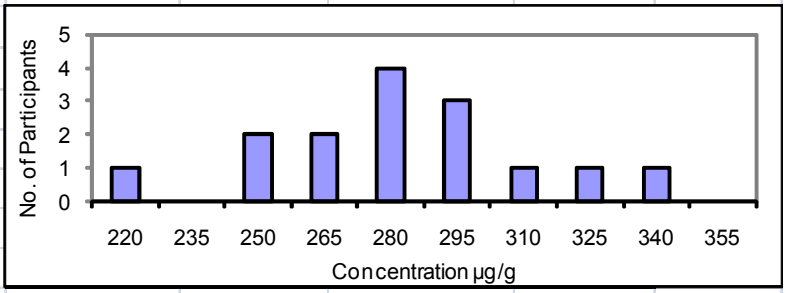
Specimen B1

n	ALTM	SD	CV(%)
15	426.9	108.5	25.4



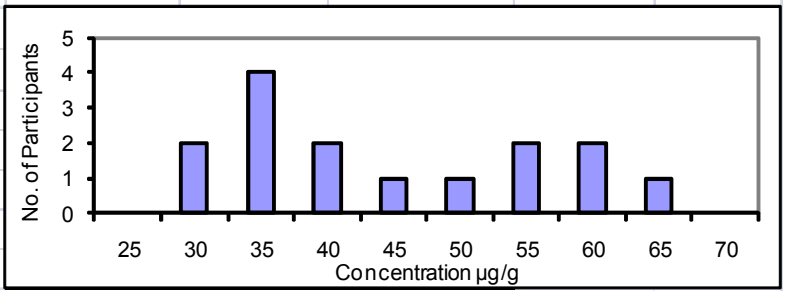
Specimen B2

n	ALTM	SD	CV(%)
15	275.6	33.4	12.1



Specimen B3

n	ALTM	SD	CV(%)
15	42.4	11.07	26.1



Comments

(None)

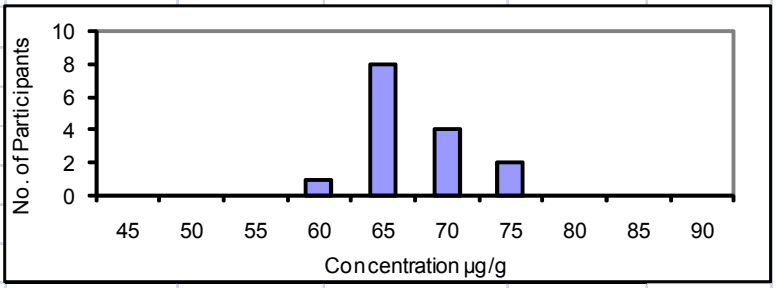
RSCH TEQ@S UKNEQAS

Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Specimen	Description	COPPER ug/g
C1	Oyster Tissue 1566a	66.30
C2	Bovine Liver BCR 185	189.00
C3	Bovine Liver 1577b	160.00

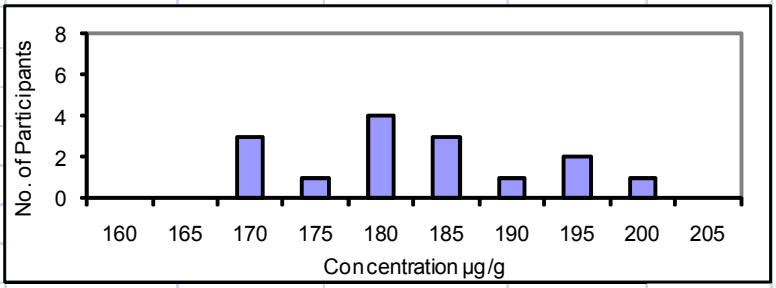
Specimen C1

n	ALTM	SD	CV(%)
16	65.4	4.73	7.2



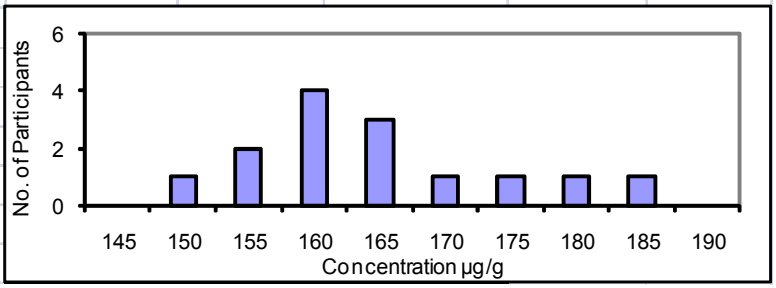
Specimen C2

n	ALTM	SD	CV(%)
16	180.4	9.4	5.2



Specimen C3

n	ALTM	SD	CV(%)
15	162.9	9.84	6.0



Comments

1 result was omitted:

Sample C3: 74.12 ug/g

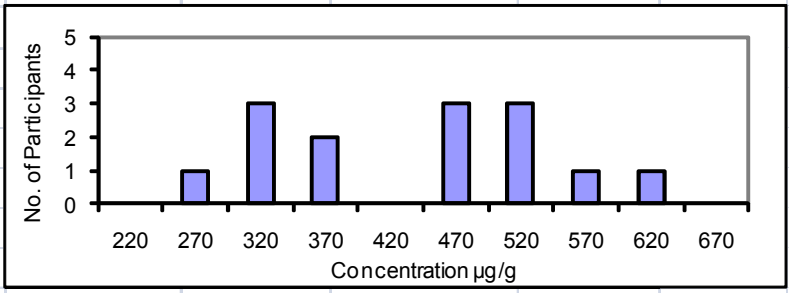
C1 was distributed previously as sample B1

RSCH TEQ@S UKNEQAS

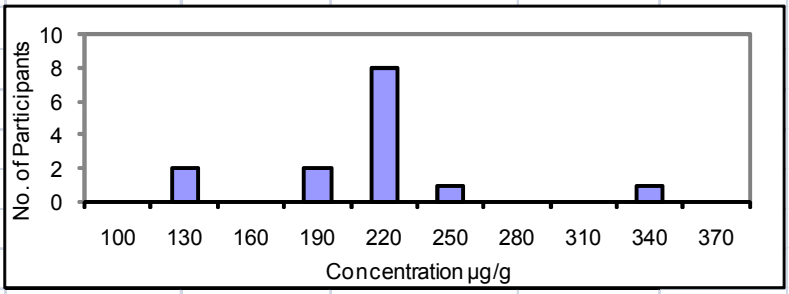
Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Specimen	Description	IRON ug/g
C1	Oyster Tissue NIST 1566a	539.00
C2	Pig Kidney BCR 185	214.00
C3	Bovine liver BCR 1577b	184.00

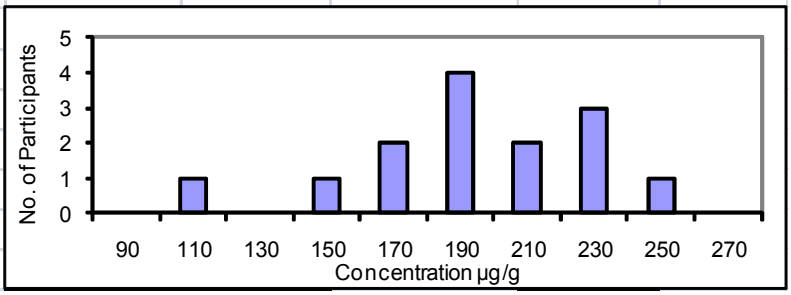
Specimen	C1		
n	ALTM	SD	CV(%)
14	418.6	114.8	27.4



Specimen	C2		
n	ALTM	SD	CV(%)
14	201.5	47.2	23.4



Specimen	C3		
n	ALTM	SD	CV(%)
14	187.2	34.92	18.7



Comments

C1 was distributed previously as sample B1

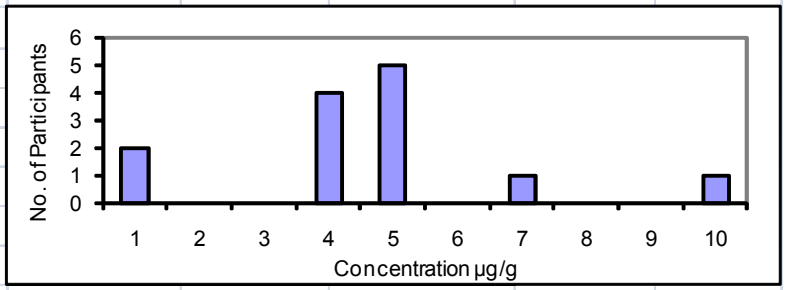
RSCH TEQ@S UKNEQAS

Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Specimen	Description	COPPER ug/g
D1	(Animal Blood A13)	4.30
D2	(Bovine Liver 1577b)	160.00
D3	(Bovine Liver BCR 185)	189.00

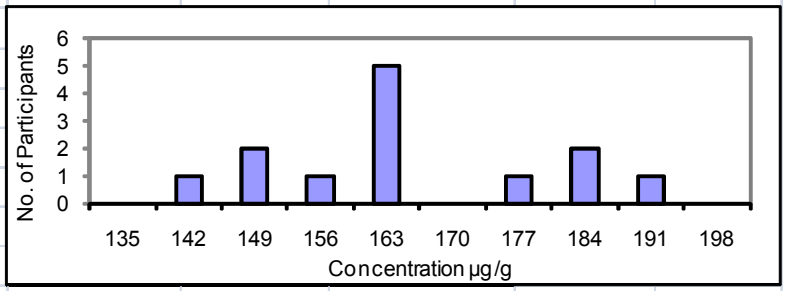
Specimen D1

n	ALTM	SD	CV(%)
13	4.09	2.21	54.01



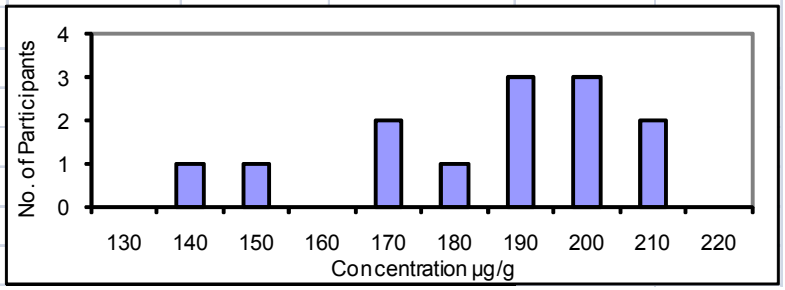
Specimen D2

n	ALTM	SD	CV(%)
13	162.26	15.26	9.41



Specimen D3

n	ALTM	SD	CV(%)
13	179.20	22.65	12.64



Comments

D2 was distributed previously as sample C3

D3 was distributed previously as sample C2

RSCH

TEQ@S

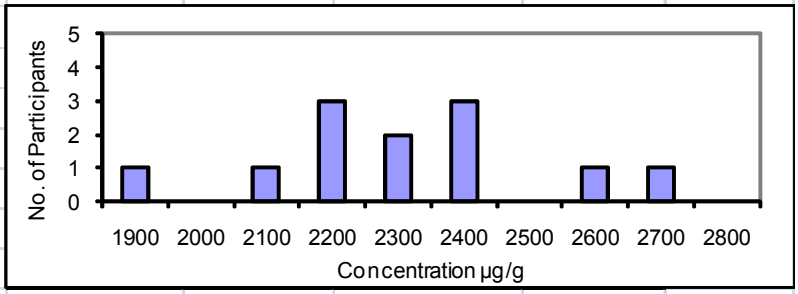
UKNEQAS

Trace Elements External Quality Assessment Scheme
UK NEQAS for Trace Elements

Specimen	Description	IRON ug/g
D1	(Animal Blood A13)	2400.00
D2	(Bovine Liver 1577b)	184.00
D3	(Bovine Liver BCR 185)	214.00

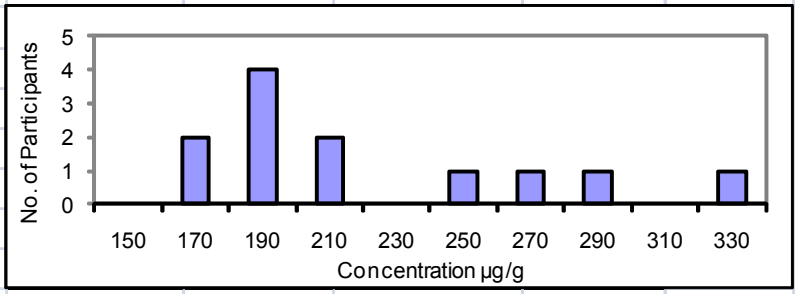
Specimen D1

n	ALTM	SD	CV(%)
12	2259.8	230.9	10.2



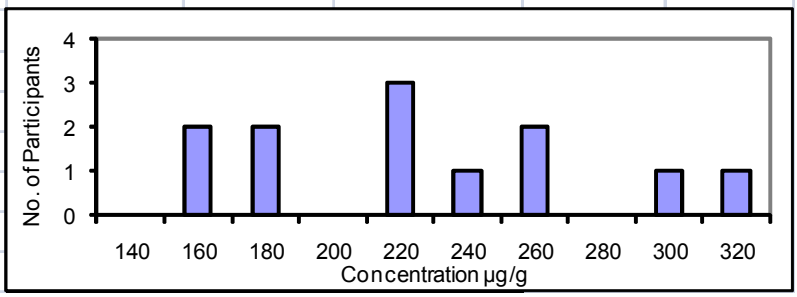
Specimen D2

n	ALTM	SD	CV(%)
12	213.9	48.7	22.8



Specimen D3

n	ALTM	SD	CV(%)
12	220.5	52.59	23.9



Comments

D2 was distributed previously as sample C3

D3 was distributed previously as sample C2

Discussion

The participant results for the scheme this year showed that 78 of the 342 results returned were within acceptable limits as set by the certified values from suppliers of the materials used. The acceptable results were not evenly spread across the 4 distributions however, but most participants showed a gradual improvement, peaking at the third distribution where 34 of the acceptable returns were found. Table 4 details the difference in average bias, for both an over and under recovery for distributions where the sample used is the same as a previous distribution. This allows us to gauge whether a participant has improved their technique or not.

Deviations from the certified value occurred both above and below the target, with the worst over- and under- estimations being up to 75% and -35% respectively. The majority of deviations were over estimations however, suggesting a problem with contamination, either from transfer or during the digestion stages of the assay. 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, achieving a better overall recovery. 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.

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. Unfortunately a number of participants (40%) did not complete the form to show what method they employed for the determination.

Of the materials distributed, some gave a better return than others. Samples C1 (blood) and D1 (oyster tissue) both gave very accurate results across all laboratories when analyzed for copper content, but conversely returned poor iron content accuracy. Sample B3 (Pork muscle) also

gave interesting results, in that participants returned both over and under estimates which were greatly deviant from the true value (up to 402% in one assay). It's possible that the sample may have been susceptible to contamination, or resistant to digestion as compared to other materials leading to these more scattered results. Similarly B2 (pig kidney) returned almost universally inaccurate results, but without as much variation.

Conclusions

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 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 (teqas@surrey.ac.uk).