REPORT NO. 500

Food Proficiency Testing Program

Round 23 – Fish Paste

March 2006

ACKNOWLEDGMENTS

PTA wishes to gratefully acknowledge the technical assistance provided for this program by Dr Richard Myors, National Measurement Institute, and Mr Mervyn Withers, AgriQuality Limited, who arranged for the supply of the samples.

PO Box 7507 Silverwater NSW 2128 AUSTRALIA

CONTENTS

1. FOREWORD

This report summarises the results of a proficiency testing program involving the analysis of fish paste samples. It constitutes the twenty third round of an ongoing series of programs involving chemical analysis of foodstuffs.

NATA's Proficiency Testing Group conducted the exercise in November 2005 as part of its laboratory accreditation activities. Note that from 1 January 2006 the delivery of proficiency testing services was transferred from NATA to a new, wholly owned subsidiary called Proficiency Testing Australia (PTA). The aim of the program was to assess laboratories' ability to competently perform the nominated tests.

2. FEATURES OF THE PROGRAM

(a) A total of 21 laboratories participated in the program, comprising of 15 Australian laboratories and 6 overseas laboratories: Hong Kong (1); Singapore (2); Taiwan (1); Thailand (1); and Vietnam (1). One laboratory did not return results for this program.

To ensure confidential treatment of results, each laboratory was allocated a unique code number. All reference to participants is by allocated code numbers.

(b) The results reported by participants are presented in Appendix A.

(c) Laboratories were provided with two samples labelled *NATA 1* and *NATA 2*. Each sample consisted of approximately 100g of fish paste.

(d) Participants were requested to determine the levels of:

- arsenic
- cadmium
- lead
- mercury
- zinc.

Laboratories were required to perform all tests for which they hold NATA accreditation and were invited to report results for any of the other tests.

(e) Laboratories were requested to perform the tests according to the *Instructions to Participants* provided and to record the results, along with an estimate of their uncertainty of measurement for each result, on the accompanying *Results Sheet*, which was distributed with the samples. An additional sheet was included with the *Results Sheet* for participants to describe the method they used to determine the measurement uncertainty for each reported measurement result, as well as the analytical techniques used for obtaining their results. Copies of these documents appear in Appendix C.

(f) Prior to sample distribution, ten randomly selected samples were analysed for homogeneity by AgriQuality New Zealand Limited. Based on the results of this testing, the homogeneity of the samples was established.

3. FORMAT OF THE APPENDICES

(a) Appendix A is divided into 5 sections (A1-A5). These sections contain the analysis of results reported by laboratories for arsenic, cadmium, lead, mercury and zinc.

Each section contains:

i) a table of results reported by laboratories, along with an estimate of their uncertainty of measurement, for each test;
ii) a table of calculated z-scores;
iii) a listing of the summary statistics;
iv) ordered z-score charts (between-laboratories and within-laboratory);
v) a Youden diagram of laboratories' results for the sample pair.

(b) Appendix B contains details of the sample preparation and homogeneity testing.

(c) Appendix C contains copies of the *Instructions to Participants* and *Results Sheet*s.

4. STATISTICAL DESIGN OF THE PROGRAM

A uniform pair statistical design was chosen for this program. Samples *NATA 1* and *NATA 2* were identical for arsenic, cadmium, lead, mercury and zinc.

5. EXTREME RESULTS

Robust z-scores have been used to assess each laboratory's testing performance. When calculated from pairs of results, z-scores are used to detect excessively large between-laboratories or within-laboratory variations.

Each pair of results reported by a laboratory has a between-laboratories z-score and a within-laboratory z-score calculated. Any pair of results which has an absolute z-score greater than three (ie <-3 or >3) is classified as an outlier.

For further details on the calculation and interpretation of robust z-scores, please see the *Guide to NATA Proficiency Testing (2004).*

Table A: Summary Statistics for All Tests

The following summary statistics were sent to participants shortly after the return of results to provide them with “early information” about the results for the program.

Test	Summary Statistics	NATA 1	NATA 2
Arsenic (mg/kg)	No. of Results	18	18
	Median	4.0395	4.0185
	Normalised IQR	0.5992	0.3451
Cadmium (mg/kg)	No. of Results	16	16
	Median	0.490	0.495
	Normalised IQR	0.055	0.047
Lead (mg/kg)	No. of Results	15	15
	Median	0.420	0.430
	Normalised IQR	0.066	0.046
Mercury (mg/kg)	No. of Results	18	18
	Median	0.410	0.435
	Normalised IQR	0.116	0.107
Zinc (mg/kg)	No. of Results	17	17
	Median	6.340	6.200
	Normalised IQR	0.586	0.415

Table B: Summary of Statistical Outliers

Test	**Sample Pair NATA 1 & NATA 2**	
	Between Laboratories	Within Laboratory
Arsenic	17	-
Cadmium	17	14
Lead	4, 17, 19	10, 11, 17
Mercury	17	-
Zinc	4	-

6. PTA AND TECHNICAL ADVISER'S COMMENTS

The summary statistics and outliers identified for each of the tests are reported in Tables A and B above. Complete details of the statistical analyses appear in Appendix A.

6.1 Return rate

Twenty of the 21 laboratories (95%) that participated in the program returned results. Fourteen of these 20 laboratories (70%) provided results for all five of the tests.

Of the laboratories that returned results for this program, the return rate for all tests is as follows:

• Arsenic	18 out of 20	90%
• Cadmium	16 out of 20	80%
• Lead	15 out of 20	75%
• Mercury	18 out of 20	90%
• Zinc	17 out of 20	85%

6.2 Performance summary

Overall, the performance of participants in this program was better than the performance of participants in a similar APLAC program conducted in July 1998 (see APLAC Report T009).

One or more statistical outliers were reported by 6 of the 20 laboratories (30%) that returned results in this program. For comparison, 51% of the participants in the 1998 APLAC Fish program reported statistical outliers.

A total of 168 results were submitted for analysis in this round of the program. Of these results, 11 (7%) were outlier results. In the 1998 APLAC Fish program 13% of the total results reported were outlier results.

6.3 Arsenic

The most common techniques used for arsenic were ICP-MS and AAS (hydride generation), with 9 laboratories using ICP-MS and 3 laboratories using AAS (hydride generation). There was one laboratory that used a technique other than those listed on the *Instructions to Participants*, while one laboratory did not report the technique used.

Microwave digestion with nitric acid was most commonly used by laboratories for arsenic. Two laboratories did not report a digestion code. There were no noticeable differences in the results between the different techniques and digestions used.

The robust CVs of 14.8% and 8.6% for the two samples are much lower than the robust CVs from the 1998 APLAC Fish program for arsenic, where values of 41.2% and 39.6% were obtained for the two samples tested (see APLAC Report T009).

Laboratory 17 reported a between-laboratories outlier result. Four other laboratories (2, 4, 14 and 18) obtained an $|z|$ score > 2 for between-laboratories precision. There were no within-laboratory outlier results for arsenic, but one laboratory (14) reported an $|z|$ score > 2 for within-laboratory precision.

Four of the laboratories that reported results for arsenic did not provide an estimate of the measurement uncertainty for their results.

6.4 Cadmium

The most common technique used for cadmium was again ICP-MS, with 9 laboratories using this technique. Four laboratories used the AAS (flame) technique. One laboratory did not report the technique used.

Microwave digestion with nitric acid was most commonly used by laboratories for cadmium. One laboratory did not report a digestion code. There were no noticeable differences in the results between the different techniques and digestions used.

The robust CVs of 11.2% and 9.5% for the two samples compare well with the robust CVs from the 1998 APLAC Fish program for cadmium, where values of 11.8% were obtained for both samples (see APLAC Report T009).

Laboratory 17 reported a between-laboratories outlier result. Laboratory 14 reported a within-laboratory outlier result.

Two of the laboratories that reported results for cadmium did not provide an estimate of the measurement uncertainty for their results.

6.5 Lead

Eight laboratories used the ICP-MS technique for lead. The next most commonly used technique was AAS (flame), with 4 laboratories using this technique. One laboratory did not report the technique used.

Microwave digestion with nitric acid was most commonly used by laboratories for lead. One laboratory did not report a digestion code. Noticeable differences in the results between the different techniques and digestions used were not apparent.

The robust CVs for the two samples were 15.6% and 10.6%. These CVs are much lower than the values of 30.1% and 24.9%, obtained in the 1998 APLAC Fish program for lead (see APLAC Report T009).

Three laboratories (4, 17 and 19) reported between-laboratories outlier results. One other laboratory (10) obtained an |z| score > 2 for between-laboratories precision. Three laboratories (10, 11 and 17) reported within-laboratory outlier results. One other laboratory (18) obtained an |z| score > 2 for within-laboratory precision.

Two of the laboratories that reported results for lead did not provide an estimate of the measurement uncertainty for their results.

6.6 Mercury

The most common techniques used for mercury were ICP-MS and AAS (cold vapour), with 8 laboratories using ICP-MS and 7 laboratories using AAS (cold vapour). One laboratory did not report the technique used.

Microwave digestion with nitric acid was most commonly used by laboratories for mercury. Two laboratories did not report a digestion code. There were no noticeable differences in the results between the different techniques and digestions used.

The mercury results were the most variable, with robust CV values of 28.3% and 24.7%. These CV values are slightly higher than those obtained in the 1998 APLAC Fish program for mercury, where values of 26.2% and 21.4% were obtained for the two samples tested (see APLAC Report T009).

Laboratory 17 reported a between-laboratories outlier result. There were no within-laboratory outlier results, but 4 laboratories (2, 6, 19 and 20) obtained an |z| score > 2 for within-laboratory precision.

Four of the laboratories that reported results for mercury did not provide an estimate of the measurement uncertainty for their results.

6.7 Zinc

Seven laboratories used the ICP-MS technique for zinc, while 7 laboratories used the AAS (flame) technique. One laboratory did not report the technique used. Noticeable differences in the results between the different techniques and digestions used were not apparent.

The zinc results were the least variable, with robust CV values of 9.2% and 6.7%. These CV values are lower than those obtained in the 1998 APLAC Fish program for zinc, where values of 12.0% and 13.7% were obtained for the two samples tested (see APLAC Report T009).

Laboratory 4 reported a between-laboratories outlier result. One other laboratory (12) obtained an |z| score > 2 for between-laboratories precision. There were no within-laboratory outlier results.

Two of the laboratories that reported results for zinc did not provide an estimate of the measurement uncertainty for their results.

6.8 Measurement Uncertainty

For this program, laboratories were requested to report an estimate of measurement uncertainty (MU) for each test result and to describe the method used for this estimation. Seventeen of the 20 laboratories (85%) that submitted results for this program provided estimates of their MU for some or all of their results. Of these 17 laboratories, 13 supplied a description of the method(s) used to estimate their MU.

The proportion of laboratories that returned MU estimates for each individual test is as follows:

• Arsenic	14 out of 18	78%
• Cadmium	14 out of 16	88%
• Lead	13 out of 15	87%
• Mercury	14 out of 18	78%
• Zinc	15 out of 17	88%

The number of laboratories that quoted measurement uncertainties for their analytical data in this program is encouraging. Although many different techniques were used (most using a top-down approach using pre-determined validation data), the quoted uncertainties all seem to be very small for such measurements (expected uncertainties were in the range of 15-20% for such measurements). It is important to note that some measurements of *NATA 1* and *NATA 2* (the same sample, with excellent homogeneity results - Appendix B) from some of the laboratories differed by more than the measurement uncertainty for each of the individual measurements. Laboratories in this situation should take the opportunity to review their uncertainty budgets.

Based upon the presented data, it seems the most likely sources of uncertainty in the measurements are an under-estimation of the precision of their analytical method. Some laboratories showed a significant bias in their results for some analytes, with very low results for arsenic and mercury, and very high results for cadmium and lead. Their situation was not helped by not submitting an uncertainty budget for the analysis (which may have indicated that they knew their methods suffered significant bias).

Uncertainty estimates varied considerably amongst the laboratories. Generally, laboratories that quoted very small uncertainties resulted in their two measurements of the same material not overlapping, which indicates a problem with either their measurement technique or their uncertainty estimate. Some laboratories estimated a different uncertainty for each measurement, and they were sometimes remarkably different despite the measured quantity and matrix being nominally the same. This indicates that their measurement uncertainty model is largely influenced by the precision of a single measurement, and may be underestimating the effects of bias (for example in the calibration material and recoveries of their method).

7. REFERENCES

Guide to NATA Proficiency Testing (2004).

This document can be found on the NATA website at http://www.nata.asn.au

APPENDIX A

Summary of Results

Section A1

Arsenic

Fish Paste – Arsenic (mg/kg) – Results and Measurement Uncertainty

Lab Code	NATA 1		NATA 2		Technique Code	Digestion Code
	Average	MU (±)	Average	MU (±)		
1	3.488		3.783			
2	4.736	0.50	5.057	0.55	6	1
4	2.788	0.269	2.914	0.281	3	5
5	4.335	10.94%	4.397	10.94%	6	5
6	4.357	0.75	4.132	0.74	6	6
8	4.104	0.2	4.118	0.2	6	5
9	4.016	0.10	3.772	0.10	3	6
10	4.400		4.400		6	
11	4.063	0.236	3.940	0.229	6	5
12	4.398	0.119	4.097	0.108	2	5
13	3.756	0.638 (17%)	3.711	0.631 (17%)	5 / 6	1
14	5.228	0.473	4.745	0.123	6	5
15	4.197	0.504	4.204	0.504	6	5
17	0.094		0.112		2	4
18	3.115	0.320	2.983	0.508	3	2
19	3.7	0.1	3.8	0.1	5	6
20	3.491		3.674		7	6
22	3.831	0.4	4.155	0.4	5	1

Laboratories that reported “Other” technique / digestion

Lab Code	Technique	Digestion
6	-	USEPA 3051A
19	-	HNO_3 / $HClO_4$
20	ICP-MS-VGA	Nitric / Perchloric acid

Fish Paste – Arsenic (mg/kg) – Z-Scores

Lab Code	NATA 1	NATA 2	Between Labs Z-Score	Within Lab Z-Score
1	3.488	3.783	-0.83	-1.54
2	4.736	5.057	2.07	-1.68
4	2.788	2.914	-2.64	-0.63
5	4.335	4.397	0.85	-0.28
6	4.357	4.132	0.57	1.27
8	4.104	4.118	0.26	-0.02
9	4.016	3.772	-0.24	1.38
10	4.400	4.400	0.93	0.06
11	4.063	3.940	0.01	0.72
12	4.398	4.097	0.58	1.69
13	3.756	3.711	-0.61	0.30
14	5.228	4.745	2.27	2.67
15	4.197	4.204	0.47	0.02
17	0.094	0.112	-8.95 §	-0.04
18	3.115	2.983	-2.18	0.77
19	3.7	3.8	-0.57	-0.48
20	3.491	3.674	-0.95	-0.93
22	3.831	4.155	-0.01	-1.70

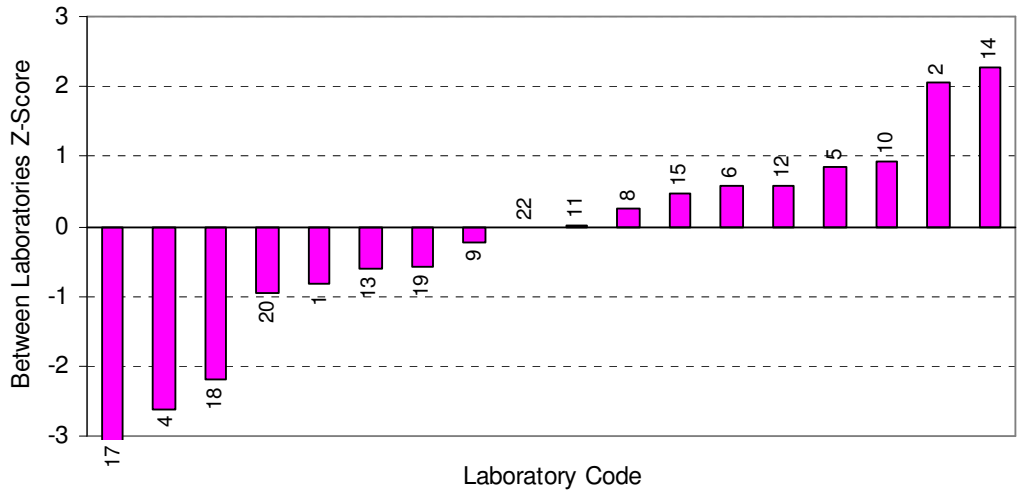
Statistic	NATA 1	NATA 2
No of Results	18	18
Median	4.0395	4.0185
Norm IQR	0.5992	0.3451
Robust CV	14.83%	8.59%
Minimum	0.094	0.112
Maximum	5.228	5.057
Range	5.134	4.945

Note:

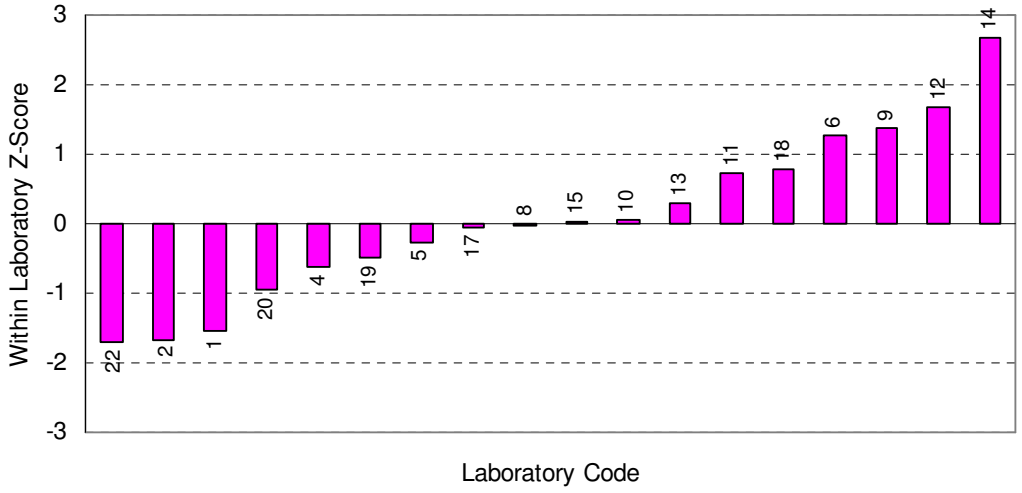
§ denotes an outlier (i.e. |z-score| > 3).

A1.3

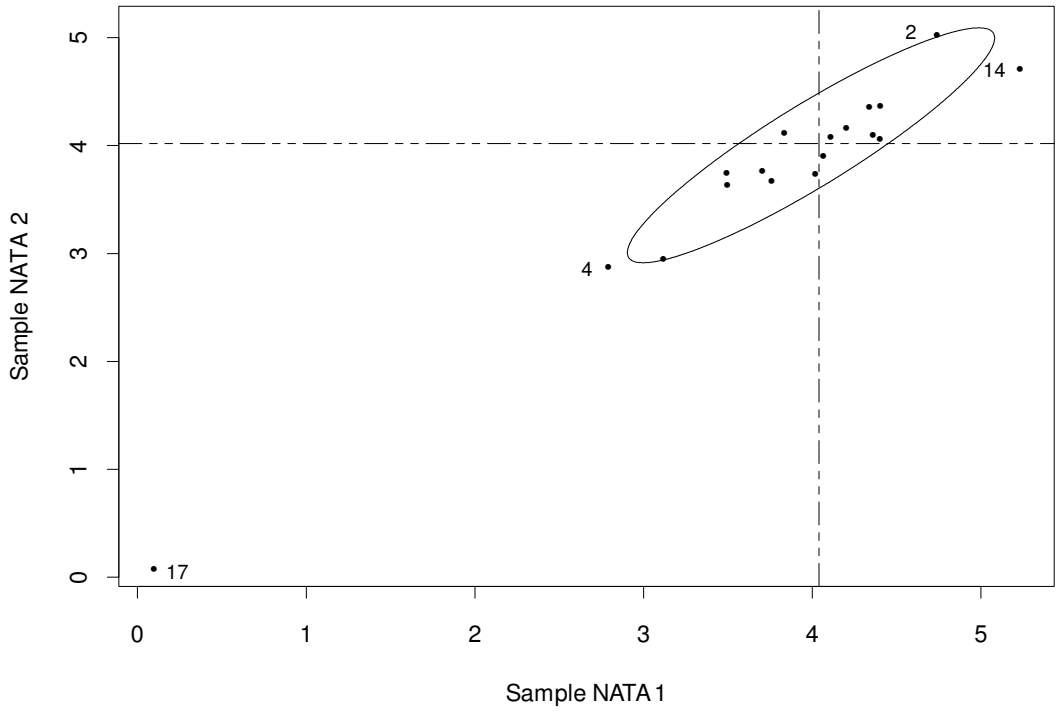
Arsenic (mg/kg)



Arsenic (mg/kg)



Arsenic (mg/kg)



Section A2

Cadmium

Fish Paste – Cadmium (mg/kg) – Results and Measurement Uncertainty

Lab Code	NATA 1		NATA 2		Technique Code	Digestion Code
	Average	MU (±)	Average	MU (±)		
1	0.39		0.44			
2	0.47	0.05	0.48	0.05	6	1
4	0.40	0.20	0.42	0.20	1	6
5	0.54	8.77%	0.53	8.77%	6	5
6	0.461	0.082	0.438	0.078	6	6
8	0.54	0.05	0.52	0.05	6	5
9	0.49	0.05	0.52	0.05	2	1
10	0.49	0.07	0.46	0.07	1	6
11	0.51	0.08	0.50	0.07	6	5
13	0.438	0.057 (13%)	0.457	0.059 (13%)	5 / 6	1
14	0.66	0.05	0.53	0.03	6	5
15	0.53	0.07	0.52	0.07	6	5
17	1.14		1.12		1	4
18	0.48	0.04	0.49	0.04	1	6
19	0.45	0.02	0.46	0.02	6	6
22	0.51	0.05	0.56	0.05	5	1

Laboratories that reported "Other" technique / digestion

Lab Code	Technique	Digestion
4	-	Dry ashing
6	-	USEPA 3051A
19	-	HNO_3 / $HClO_4$

Fish Paste – Cadmium (mg/kg) – Z-Scores

Lab Code	NATA 1	NATA 2	Between Labs Z-Score	Within Lab Z-Score
1	0.39	0.44	-1.39	1.72
2	0.47	0.48	-0.35	0.34
4	0.40	0.42	-1.48	0.69
5	0.54	0.53	0.70	-0.34
6	0.461	0.438	-0.79	-0.79
8	0.54	0.52	0.61	-0.69
9	0.49	0.52	0.17	1.03
10	0.49	0.46	-0.35	-1.03
11	0.51	0.50	0.17	-0.34
13	0.438	0.457	-0.83	0.65
14	0.66	0.53	1.74	-4.47 §
15	0.53	0.52	0.52	-0.34
17	1.14	1.12	11.04 §	-0.69
18	0.48	0.49	-0.17	0.34
19	0.45	0.46	-0.70	0.34
22	0.51	0.56	0.70	1.72

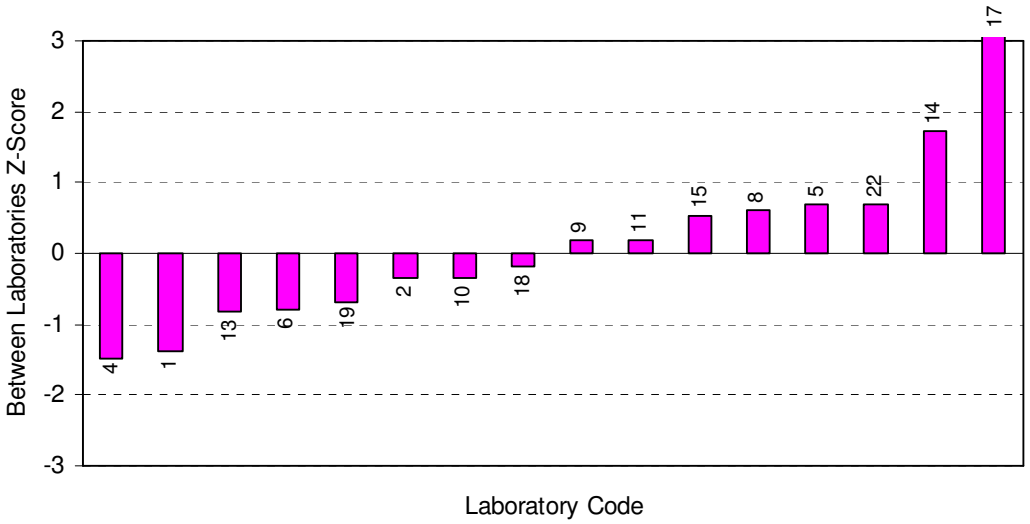
Statistic	NATA 1	NATA 2
No of Results	16	16
Median	0.490	0.495
Norm IQR	0.055	0.047
Robust CV	11.23%	9.47%
Minimum	0.39	0.42
Maximum	1.14	1.12
Range	0.75	0.70

Note:

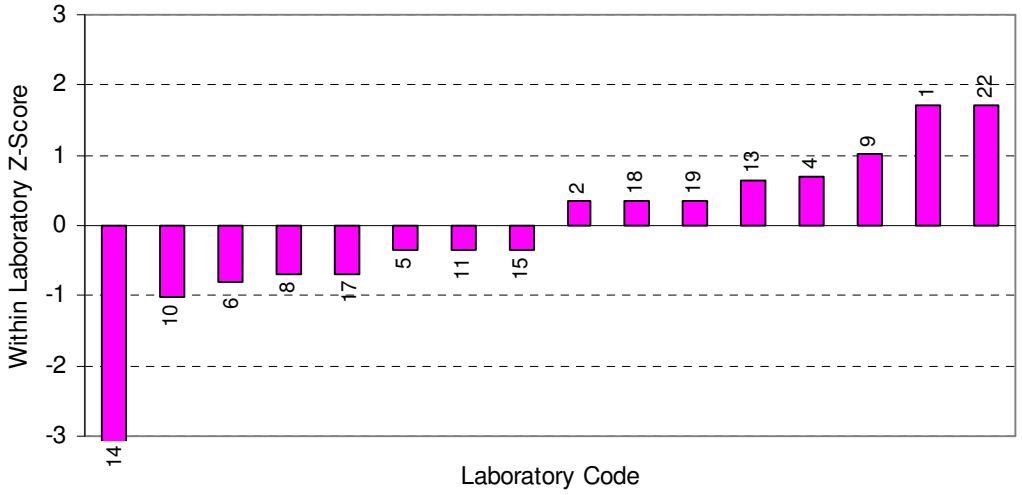
§ denotes an outlier (i.e. |z-score| > 3).

A2.3

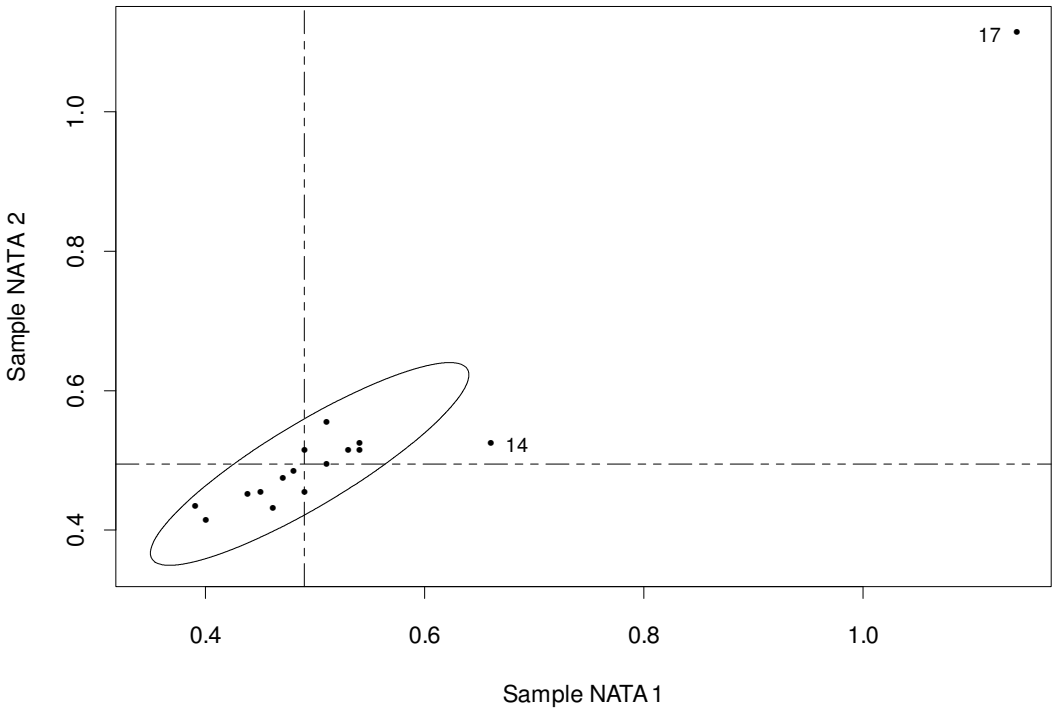
Cadmium (mg/kg)



Cadmium (mg/kg)



Cadmium (mg/kg)



Section A3

Lead

Fish Paste – Lead (mg/kg) – Results and Measurement Uncertainty

Lab Code	NATA 1		NATA 2		Technique Code	Digestion Code
	Average	MU (±)	Average	MU (±)		
1	0.38		0.42			
2	0.45	0.05	0.45	0.05	6	1
4	0.53	0.20	0.54	0.20	1	6
5	0.47	10.45%	0.43	10.45%	6	5
6	0.403	0.072	0.387	0.068	6	6
8	0.41	0.04	0.41	0.04	6	5
9	0.42	0.04	0.40	0.04	2	1
10	0.53	0.19	0.09	0.04	1	6
11	0.37	0.03	0.46	0.04	6	5
13	0.379	0.049 (13%)	0.377	0.049 (13%)	6	1
14	0.49	0.02	0.43	0.01	6	5
15	0.45	0.06	0.44	0.06	6	5
17	1.23		1.13		1	4
18	0.41	0.06	0.46	0.04	1	6
19	0.30	0.02	0.29	0.02	5	6

Laboratories that reported “Other” technique / digestion

Lab Code	Technique	Digestion
4	-	Dry ashing
6	-	USEPA 3051A
19	-	HNO_3 / $HClO_4$

Fish Paste – Lead (mg/kg) – Z-Scores

Lab Code	NATA 1	NATA 2	Between Labs Z-Score	Within Lab Z-Score
1	0.38	0.42	-0.39	1.93
2	0.45	0.45	0.90	0.39
4	0.53	0.54	3.08 §	0.77
5	0.47	0.43	0.90	-1.16
6	0.403	0.387	-0.51	-0.23
8	0.41	0.41	-0.13	0.39
9	0.42	0.40	-0.13	-0.39
10	0.53	0.09	-2.70	-16.57 §
11	0.37	0.46	0.00	3.85 §
13	0.379	0.377	-0.95	0.31
14	0.49	0.43	1.16	-1.93
15	0.45	0.44	0.77	0.00
17	1.23	1.13	19.66 §	-3.47 §
18	0.41	0.46	0.51	2.31
19	0.30	0.29	-3.08 §	0.00

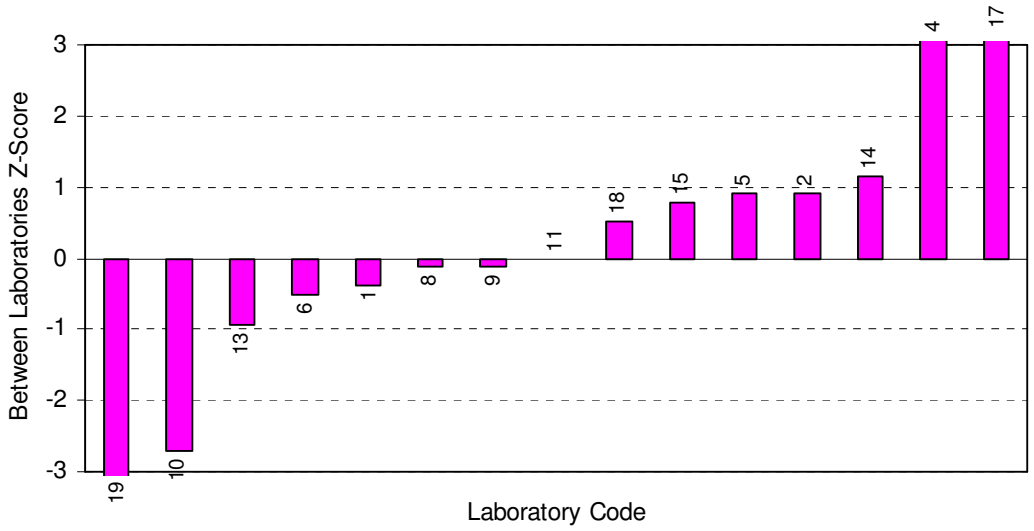
Statistic	NATA 1	NATA 2
No of Results	15	15
Median	0.420	0.430
Norm IQR	0.066	0.046
Robust CV	15.62%	10.60%
Minimum	0.30	0.09
Maximum	1.23	1.13
Range	0.93	1.04

Note:

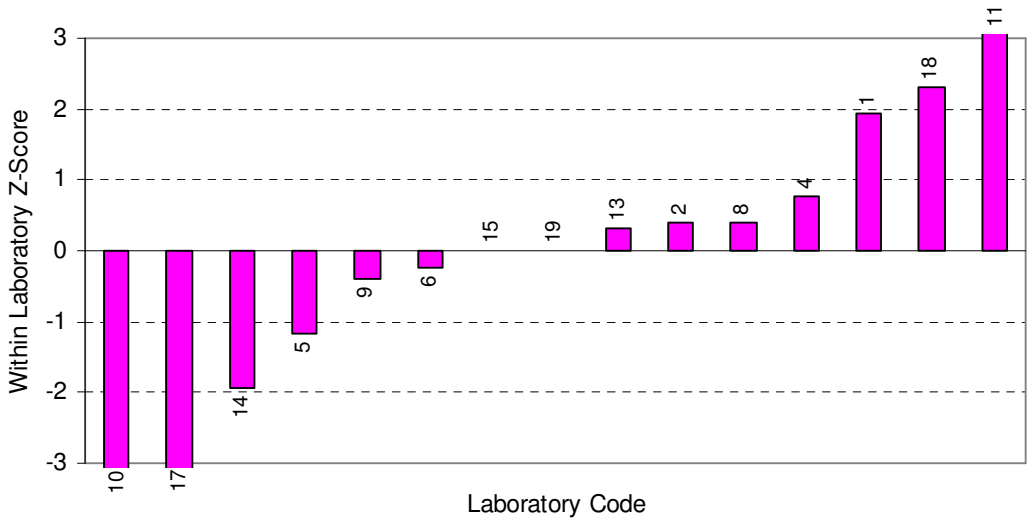
§ denotes an outlier (i.e. |z-score| > 3).

A3.3

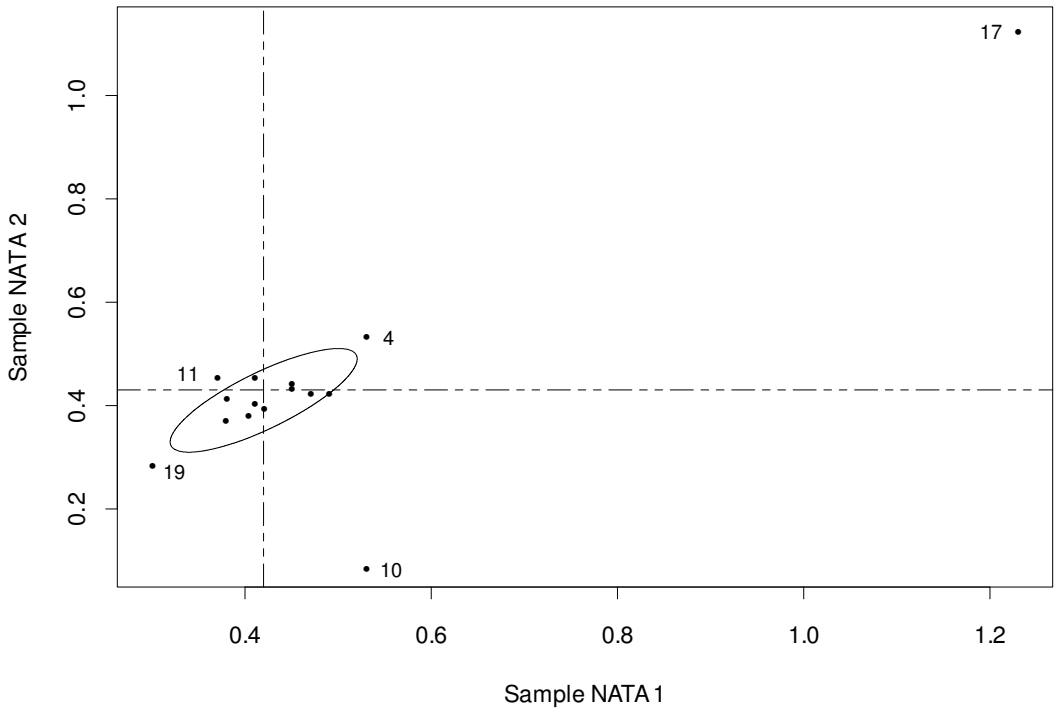
Lead (mg/kg)



Lead (mg/kg)



Lead (mg/kg)



Section A4

Mercury

Fish Paste – Mercury (mg/kg) – Results and Measurement Uncertainty

Lab Code	NATA 1		NATA 2		Technique Code	Digestion Code
	Average	MU (±)	Average	MU (±)		
1	0.39		0.42			
2	0.52	0.05	0.58	0.05	4	6
4	0.55	0.08	0.50	0.08	4	5
5	0.46	11.36%	0.45	11.36%	6	5
6	0.515	0.092	0.448	0.08	6	6
7	0.37	0.11	0.40	0.12	4	2
8	0.47	0.05	0.47	0.05	6	5
9	0.43	0.05	0.43	0.05	4	2
10	0.49		0.49		6	
11	0.52	0.03	0.49	0.03	6	5
13	0.379	0.049 (13%)	0.401	0.052 (13%)	6	1
14	0.34	0.01	0.32	0.01	6	5
15	0.54	0.12	0.52	0.12	6	5
17	0.01		0.01		2	3
18	0.30	0.06	0.31	0.03	3	2
19	0.35	0.02	0.28	0.02	4	6
20	0.36		0.44		4	5
22	0.24	0.02	0.23	0.02	4	1

Laboratories that reported "Other" technique / digestion

Lab Code	Technique	Digestion
2	-	HNO_3 / HCl
6	-	USEPA 3051A
19	-	HNO_3 / H_2SO_4 / $KMnO_4$

Fish Paste – Mercury (mg/kg) – Z-Scores

Lab Code	NATA 1	NATA 2	Between Labs Z-Score	Within Lab Z-Score
1	0.39	0.42	-0.12	1.04
2	0.52	0.58	1.24	2.08
4	0.55	0.50	1.01	-1.73
5	0.46	0.45	0.35	-0.35
6	0.515	0.448	0.60	-2.32
7	0.37	0.40	-0.30	1.04
8	0.47	0.47	0.49	0.00
9	0.43	0.43	0.12	0.00
10	0.49	0.49	0.68	0.00
11	0.52	0.49	0.82	-1.04
13	0.379	0.401	-0.26	0.76
14	0.34	0.32	-0.82	-0.69
15	0.54	0.52	1.05	-0.69
17	0.01	0.01	-3.81 §	0.00
18	0.30	0.31	-1.05	0.35
19	0.35	0.28	-0.96	-2.42
20	0.36	0.44	-0.16	2.77
22	0.24	0.23	-1.71	-0.35

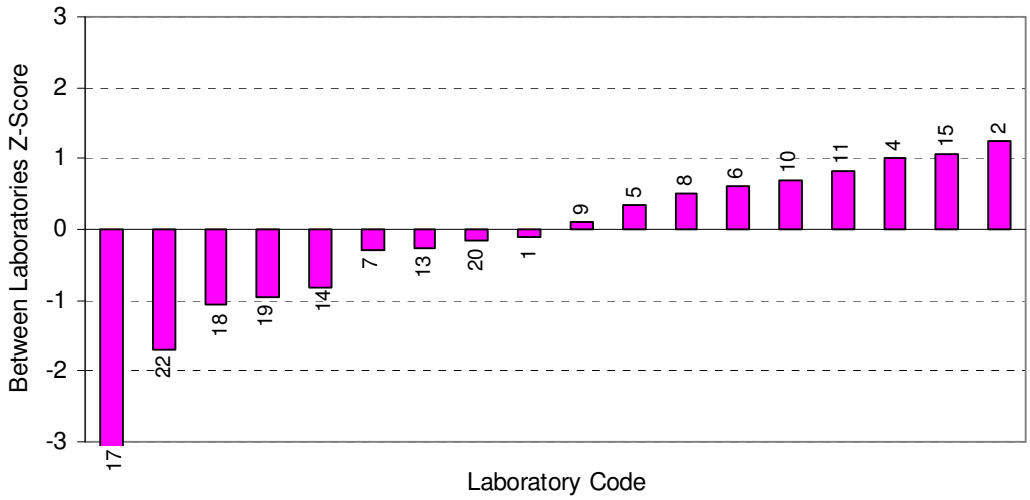
Statistic	NATA 1	NATA 2
No of Results	18	18
Median	0.410	0.435
Norm IQR	0.116	0.107
Robust CV	28.25%	24.71%
Minimum	0.01	0.01
Maximum	0.55	0.58
Range	0.54	0.57

Note:

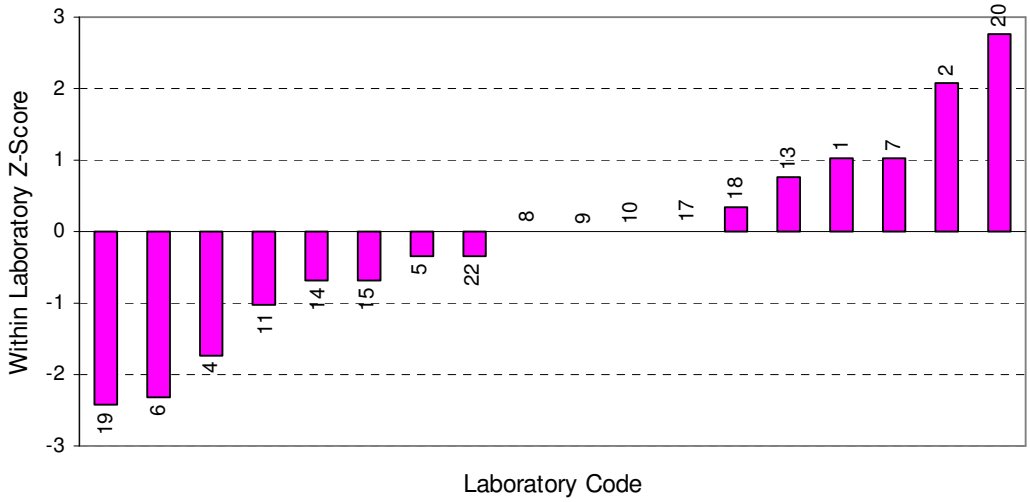
§ denotes an outlier (i.e. |z-score| > 3).

A4.3

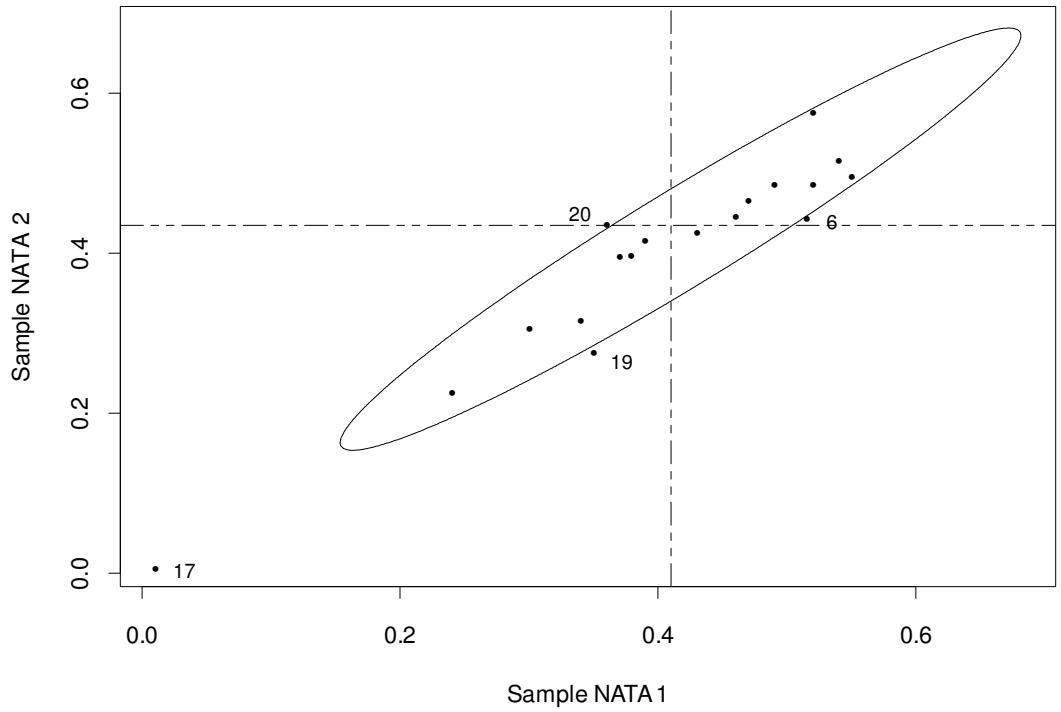
Mercury (mg/kg)



Mercury (mg/kg)



Mercury (mg/kg)



Section A5

Zinc

Fish Paste – Zinc (mg/kg) – Results and Measurement Uncertainty

Lab Code	NATA 1		NATA 2		Technique Code	Digestion Code
	Average	MU (±)	Average	MU (±)		
1	5.39		5.91			
2	6.00	0.62	6.11	0.63	6	1
4	4.48	0.50	4.49	0.50	1	6
6	5.865	1.055	5.482	0.986	6	6
8	6.76	0.4	6.47	0.4	6	5
9	6.34	0.05	6.33	0.05	1	1
10	6.75	1.6	6.30	1.6	1	6
11	6.43	0.57	6.29	0.56	6	5
12	7.78	0.21	7.48	0.26	1	5
13	5.66	0.79 (14%)	5.49	0.77 (14%)	5 / 6	1
14	6.47	0.01	6.12	0.10	6	5
15	6.91	1.24	6.49	1.17	6	5
17	6.20		5.61		1	4
18	5.96	0.07	6.18	0.38	1	6
19	6.10	0.02	6.20	0.02	5	6
21	7.12	0.4	6.59	0.3	1	1
22	6.40	0.6	6.77	0.6	5	1

Laboratories that reported "Other" technique / digestion

Lab Code	Technique	Digestion
4	-	Dry ashing
6	-	USEPA 3051A
19	-	HNO_3 / $HClO_4$

Fish Paste – Zinc (mg/kg) – Z-Scores

Lab Code	NATA 1	NATA 2	Between Labs Z-Score	Within Lab Z-Score
1	5.39	5.91	-1.28	-1.93
2	6.00	6.11	-0.48	-0.78
4	4.48	4.49	-3.59 §	-0.50
6	5.865	5.482	-1.23	0.59
8	6.76	6.47	0.63	0.34
9	6.34	6.33	0.08	-0.45
10	6.75	6.30	0.46	0.78
11	6.43	6.29	0.13	-0.08
12	7.78	7.48	2.65	0.36
13	5.66	5.49	-1.43	0.00
14	6.47	6.12	0.00	0.50
15	6.91	6.49	0.80	0.70
17	6.20	5.61	-0.77	1.17
18	5.96	6.18	-0.45	-1.09
19	6.10	6.20	-0.29	-0.75
21	7.12	6.59	1.11	1.01
22	6.40	6.77	0.58	-1.51

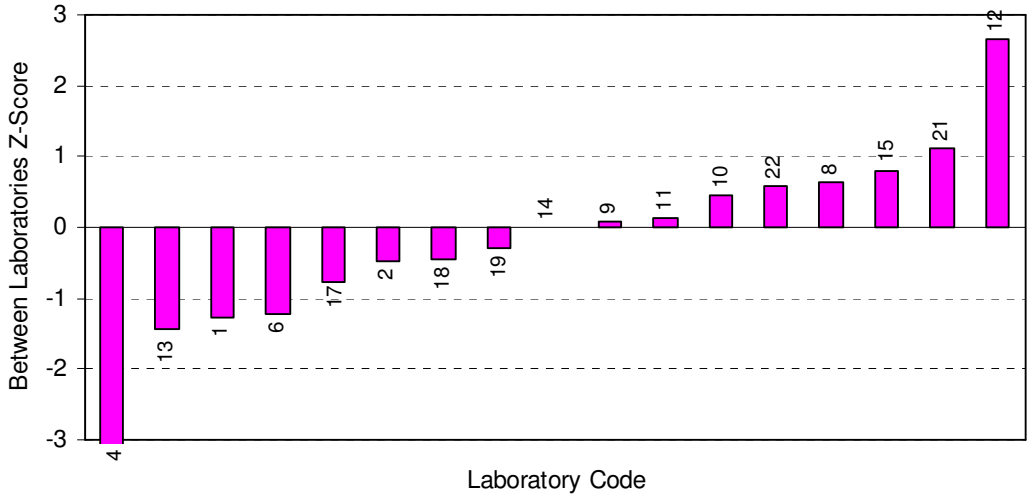
Statistic	NATA 1	NATA 2
No of Results	17	17
Median	6.340	6.200
Norm IQR	0.586	0.415
Robust CV	9.24%	6.70%
Minimum	4.48	4.49
Maximum	7.78	7.48
Range	3.30	2.99

Note:

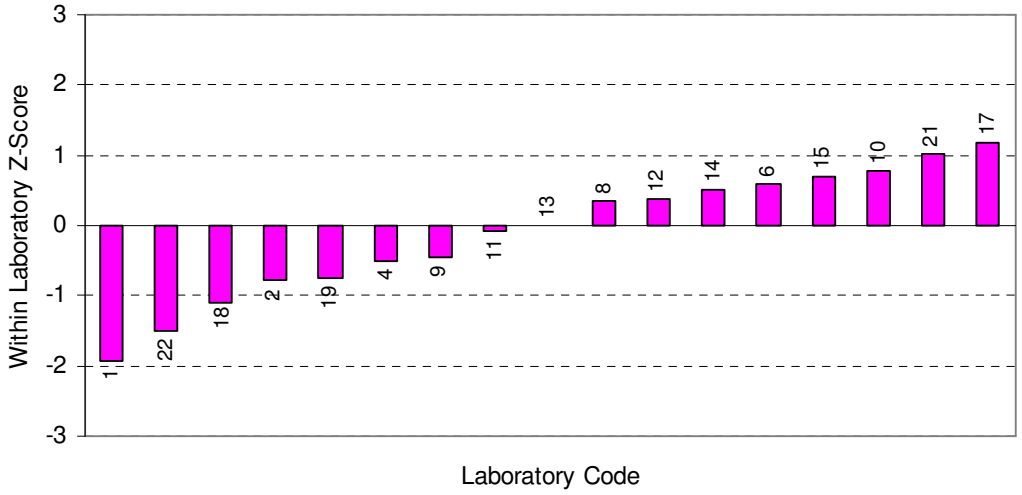
§ denotes an outlier (i.e. |z-score| > 3).

A5.3

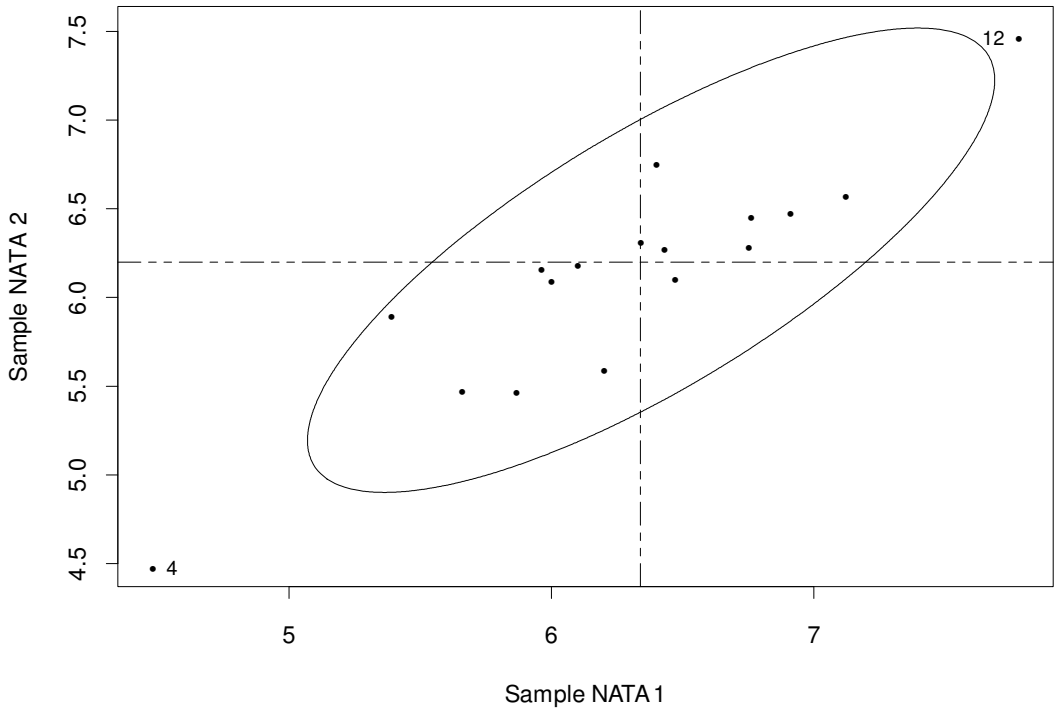
Zinc (mg/kg)



Zinc (mg/kg)



Zinc (mg/kg)



APPENDIX B

Sample Preparation
and
Homogeneity Testing

SAMPLE PREPARATION

The fish paste samples for this program were prepared by AgriQuality New Zealand Limited.

Raw Materials

Hoki fish (Macruronus Novaezelandiae) fillets, a product of New Zealand, were obtained from a licensed pack house. The mineral ingredients (AR grade) were weighed out accurately and dispensed into vials. The products were chilled to 4°C. Preservatives and paste agents were added according to procedures in SOPAC Chemistry Procedures (7th Oct 2004). The ingredients and quantities added are proprietary information to AgriQuality and AgResearch.

Processing

The fish was minced using a Bendix scientific mixer. Water, the minced fish and the ingredients were added together to create a stabilised fish mix. The temperature was monitored while mixing. More water was added and mixed until a homogenous slurry was obtained. The fish was then filled into plastic pouches and cooked, as per specifications. The pouches were removed from the heated water batch and placed in a cold-water bath. The pouches were then removed and sealed with a heat machine. A quality control check on the seals was undertaken. The product was chilled. The pouches were double gamma irradiated for long term stability.

HOMOGENEITY TESTING

Prior to distribution, ten samples of fish paste were selected at random and set aside for homogeneity testing by AgriQuality New Zealand Limited. Each sample was tested in duplicate for arsenic, cadmium, lead, mercury and zinc.

The methods used for homogeneity testing were:

- Arsenic: wet oxidation by ICP MS;
- Cadmium: wet oxidation by ICP MS;
- Lead: wet oxidation by ICP MS;
- Mercury: acid digest by ICP MS; and
- Zinc: wet oxidation ICP OES.

The results of the homogeneity testing appear in the following tables.

FISH PASTE – ARSENIC (mg/kg)		
Sample No.	**Result A**	**Result B**
2429/1	4.8	5.0
2429/2	4.7	4.9
2429/3	5.0	5.0
2429/4	5.1	4.8
2429/5	5.3	5.0
2429/6	5.4	5.3
2429/7	5.0	4.7
2429/8	5.1	4.7
2429/9	5.1	4.7
2429/10	5.1	4.9

FISH PASTE – CADMIUM (mg/kg)		
Sample No.	**Result A**	**Result B**
2429/1	0.51	0.51
2429/2	0.49	0.49
2429/3	0.49	0.49
2429/4	0.52	0.49
2429/5	0.52	0.49
2429/6	0.53	0.52
2429/7	0.52	0.48
2429/8	0.52	0.47
2429/9	0.52	0.47
2429/10	0.51	0.49

FISH PASTE – LEAD (mg/kg)		
Sample No.	**Result A**	**Result B**
2429/1	0.36	0.36
2429/2	0.34	0.35
2429/3	0.36	0.35
2429/4	0.38	0.36
2429/5	0.37	0.35
2429/6	0.38	0.37
2429/7	0.37	0.34
2429/8	0.37	0.33
2429/9	0.37	0.33
2429/10	0.37	0.35

FISH PASTE – MERCURY (mg/kg)		
Sample No.	**Result A**	**Result B**
2429/1	0.42	0.42
2429/2	0.40	0.43
2429/3	0.43	0.42
2429/4	0.44	0.42
2429/5	0.45	0.42
2429/6	0.46	0.44
2429/7	0.43	0.40
2429/8	0.44	0.39
2429/9	0.43	0.40
2429/10	0.43	0.41

FISH PASTE – ZINC (mg/kg)		
Sample No.	**Result A**	**Result B**
2429/1	6.3	6.2
2429/2	6.2	6.5
2429/3	6.1	6.3
2429/4	6.6	6.5
2429/5	6.6	6.1
2429/6	6.8	6.3
2429/7	6.2	5.8
2429/8	6.9	6.3
2429/9	5.7	6.2
2429/10	6.6	6.5

Analysis of this data indicated that the samples were sufficiently homogeneous and, therefore, any participant results identified as extreme cannot be attributed to sample variability.

APPENDIX C

Instructions to Participants

and

Results Sheets

NATIONAL ASSOCIATION OF TESTING AUTHORITIES, AUSTRALIA

FOOD PROFICIENCY TESTING PROGRAM (ROUND 23) – FISH PASTE

INSTRUCTIONS TO PARTICIPANTS

To ensure that results obtained in this program can be analysed properly, participants are asked to adhere carefully to the following instructions.

1. Each participant has been supplied with two plastic pouches of approximately 100g of fish paste labelled NATA 1 and NATA 2.
2. Testing may commence as soon as samples are received. Keep the samples refrigerated at approximately 4°C prior to and following analysis. Homogenise and sub-sample each sample for analysis.
3. The following tests are to be performed on each sample in **duplicate** and the **average result reported**:

   - Arsenic
   - Cadmium
   - Lead
   - Mercury
   - Zinc

4. Analysts should be aware of analyte stability and perform tests in an appropriate order.
5. Participants are requested to perform all tests listed above for which NATA accreditation is held. Laboratories should use the routine test methods which would normally be used to test customer supplied samples. Participants are welcome to report results for any other tests for which NATA accreditation is not held, however, please note this on the Results Sheet.
6. Please identify the methods on the Results Sheet, using the method codes listed on Page 2 of these instructions.
7. Results are to be reported in mg/kg. Tests for arsenic are to be reported to three decimal places. Tests for cadmium, lead, mercury and zinc are to be reported to two decimal places. Do not report any values as "<".
8. Laboratories are also requested to calculate and report an estimate of uncertainty of measurement for each reported measurement result. All estimates of uncertainty of measurement must be given as a 95% confidence interval (coverage factor $k \approx 2$).
9. All laboratories must return results no later than **Friday 2 December 2005** to:

Mark Bunt
National Association of Testing Authorities, Australia
7 Leeds Street
RHODES NSW 2138

Telephone: +61 2 9736 8222
Fax: +61 2 9743 6664 OR +61 2 9743 5311

FOOD PROFICIENCY TESTING PROGRAM (ROUND 23) – FISH PASTE

INSTRUCTIONS TO PARTICIPANTS

TECHNIQUE CODES

Technique	Code
AAS (flame)	1
AAS (graphite furnace)	2
AAS (hydride generation)	3
AAS (cold vapour)	4
ICP – AES	5
ICP – MS	6
Other (please specify)	7

DIGESTION CODES

Digestion	Code
Nitric Acid	1
Sulphuric/Nitric/Hydrochloric Acid	2
Sulphuric Acid/Permanganate	3
Hydrochloric Acid	4
Microwave digestion with Nitric Acid	5
Other (please specify)	6

C2.1

FOOD (ROUND 23) PROFICIENCY TESTING PROGRAM – FISH PASTE

RESULTS SHEET

Laboratory Code: ☐

Test	NATA 1		NATA 2		Technique Code	Digestion Code
	Average Result	Measurement Uncertainty (±)	Average Result	Measurement Uncertainty (±)		
Arsenic (0.001 mg/kg)						
Cadmium (0.01 mg/kg)						
Lead (0.01 mg/kg)						
Mercury (0.01 mg/kg)						
Zinc (0.01 mg/kg)						

NOTES:

1. Report results as mg/kg, to the specified number of decimal places, in the table above. All estimates of measurement uncertainty (MU) must be given as a 95% confidence interval (coverage factor $k \approx 2$).

2. NATA recognises that the precision requested (required for statistical purposes) may exceed the usual number of decimal places reported by laboratories.

Date:_____ **Signature:**_____

FOOD (ROUND 23) PROFICIENCY TESTING PROGRAM – FISH PASTE

MEASUREMENT UNCERTAINTY AND ANALYTICAL METHOD COMMENTS

Laboratory Code:

Please use the space below to briefly describe the method used to determine the measurement uncertainty for each reported measurement result. If possible, also briefly describe the analytical method(s) used to obtain your results.

Please return results no later than **Friday 2 December 2005** to:

Mark Bunt
National Association of Testing Authorities, Australia
7 Leeds Street
RHODES NSW 2138

Telephone: +61 2 9736 8222
Fax: +61 2 9743 6664 OR +61 2 9743 5311