Electronic Supplementary Material (ESI) for Analytical Methods.

Is measurement uncertainty from sampling related to analyte concentration?

Electronic Supplementary Information

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Tables S1 and S2 follow. References to sources for data in Table S2 are included after the two Tables.

Table S1: Literature study - Foodstuffs and methodology

Product	Analyte	Sampling Env/form	Sampling Target	Sampling Protocol	UfS Method - How dups taken	Sample amount	Source
Pistachio nuts	Total aflatoxin	Retail (single) loose in shells	Batch of nuts in 1 retailer over 4 days	Trading Stds Officer's	Duplicate: S1s on day 1, S2s on day 4	250 g	1
Wheat	N	Wholesale	1 x 800 tons in heap	own	CTS (n=5) using within-sampler variance	3000 g	2
	Molybdenum (Mo)						
	Lead (Pb)						
Coffee(Green)	Moisture	Wholesale	1 x 11 tons in 185 sacks	own	CTS (n=8) using within-sampler variance	500 g	
	Nickel (Ni)						
	Yttrium (Y)						
Milk	(Added) Water	Retail (multiple)	Batches in 9 retailers over 4 days	Trading Stds Officer's	Duplicate (n=9), 2 visits	568 or 500 ml	3
Spreadable fats	Fat	Retail (multiple)	Batches in 9 retailers over 4 days	Trading Stds Officer's	Duplicate (n=8), 2 visits	250-500g	3
Sausages	Meat	Retail (multiple)	Batches in 9 retailers over 4 days	Trading Stds Officer's	Duplicate (n=9), 2 visits	500 g	3
	Fat						4 p260-1
	Moisture						4 p260-1
	Ash						4 p260-1
	N						4 p260-1
Apples	Propargite (pesticide)	Wholesale	230kg in 14 boxes from 14 wholesalers	Modified Dpt. of Health	Duplicate (n=9 boxes)	2 kg	4 p102
Strawberries	Pyrimethanil	Retail (multiple)	Fruit avaiable for retail from shops and street market stalls	Modified CSL (pesticide R&D team)	Duplicate (n=9 boxes)	2 kg	5
	Chlorothalonil						
	Tolyfluanid						
	Myclobutanil						
	Bupirimate						
	Kresoxim-methyl						
	Fenhexamid						

Table S1 (Continued)

Product	Analyte	Sampling Env/form	Sampling Target	Sampling Protocol	UfS Method - How dups taken	Sample amount	Source
Infant milk	Zinc (Zn)	Retail (multiple)	Those avaiable for retail from shops inYork area	Modified MAFF(later DEFRA) survey	Duplicate (n=10 containers)	Single pots (mass unknown)	6
	Lead (Pb)						
	Copper (Cu)						
	Cadmium (Cd)						
	Arsenic(As)						4 p265
	Tin(Sn)						
Infant wet meals	Zinc (Zn)	Retail (multiple)	Those avaiable for retail from shops inYork area	Modified MAFF(later DEFRA) survey	Duplicate (n=10 containers)	Single pots (mass unknown)	6
	Lead (Pb)						
	Copper (Cu)						
	Cadmium (Cd)						
Butter(frozen)	Fat	Wholesale	20 tons (800x25kg blocks)	Modified EC 2571/97 + 2771/1999 Annex IV	Duplicate (n=8) balanced design	112 g _3 cores	7, 8
	Fat					1575 g	
	Solids-not-fat (SNF)					112g_3 cores g	
	Solids-not-fat (SNF)					1575 g	
	Free fatty acids (FFA)					~112 g - 3 cores	
	Free fatty acids (FFA)					~672 g - 3 cores	
	Moisture					~112 g - 3 cores	
	Moisture					~1575 g - 3 cores	
	Peroxide value (PV » rancidity).					~112 g _3 cores	
	Peroxide value (PV » rancidity).					~672 g _3 cores	

Table S1 (Continued)

Product	Analyte	Sampling Env/form	Sampling Target	Sampling Protocol	UfS Method - How dups taken	Sample amount	Source
Lettuce (glasshouse, ex. Iceberg)	Nitrate	Grower (glasshouse)	8 batches of 2000 - 12,000 growing plants	EC/2002/63	Duplicate (n=8) balanced design	10 heads (Nov)	9, 10 p86
						10 heads (Feb/Mar)	
						40 head	
Tuna (fresh)	Mercury (Hg)	Retail (multiple)	Available in retail outlets in one area	EC/2001/22	Duplicate (n=8) balanced design	~350 g	10
Tuna (tinned)	Mercury (Hg)	Retail (multiple)				~350 g (2 tins)	10 p134
	Mercury (Hg)	Retail (multiple)				1200 g (8 tins)	10 p134
Tomatoes (tinned)	Tin (Sn)	Retail (multiple)	Available in retail outlets in one area	EC/2004/16	Duplicate (n=8) balanced design	500 g (R1)	10 p124
	Tin (Sn)	Retail (multiple)				500 g (R2)	10 p137
	Tin (Sn)	Retail (multiple?)				4000 g	10 P137
Layer meal feed	Calcium (Ca)	Factory	1 lot of ~100 tons, made up of n loads	Manufacturer's	Duplicate (n=8) balanced design	~200 g	10 P149, p156, p170, p182
	Sodium (Na)						
	Salt (NaCl)						
	Copper (Cu)						
Chicken feed	Enzyme	Wholesale	25 kg bag	own	Modelling using Gy eqn.	500g (2g sub-sample)	11 p71
Apple Juice (cloudy)	Patulin	Factory	1 x 6,500 litres	Manufacturers	SPT (n=9)	220 ml	12
Butter (fresh)	Moisture	Factory	1 x 20.1 tons	RPA	SPT (n=9)	6 x100g	12
Corn (shelled)	Aflatoxin	Wholesale	18 lots	own	Empirical	1.13 kg (50g sub-sample)	13
	Aflatoxin	Wholesale	?	own	Empirical	0.91 kg	14
	Aflatoxin	Wholesale	?	own	Empirical	0.91 kg	15
Peanut	Aflatoxin	Wholesale	?	own	Empirical	5 kg	16
		Wholesale	40 lots of 900 kg	own	Empirical	2.27kg (sub-sample 100g)	17

Table S1 (Continued)

Product	Analyte	Sampling Env/form	Sampling Target	Sampling Protocol	UfS Method - How dups taken	Sample amount	Source
Coffee (green)	Ochratoxin A	Wholesale	25 lots of unkown mass	own	Empirical unbalanced (25 x 16 x 1or2 x 1or2)	16kg	18
Wheat	Deoxynivalenol(DON)	Wholesale		own	Empirical	0.454 kg (25g sub-sample)	19
Hazelnuts	Aflatoxin (total)	Wholesale	20 lots (of unkown mass)	own	Empirical	10kg (x 16)	20

Note 1: CTS rather than duplicate method used. If significant between-sampler contribution added, s_{samp} increase to 0.0418 (for N) and 0.0613 (for Mo), increasing U_{meas}% to 3.95 (for N) and 26.3 for (Mo) (calc by Ramsey, 2009)

Table S2: Literature study - sampling uncertainties

Product	Analyte	Units	Sample amount	s product	s samp	s samp prep*	s anal	s meas	mean conc	$\frac{s_{samp}^2 + s_{prep}^2}{s_{meas}^2}$	U_{meas}%	U_{samp}%	U_{anal}%	Source
Pistachio nuts	Total aflatoxin	ug kg^{-1}	250 g	0.228	0.194	included in s_{samp}	0.233	0.303	0.86	0.41	70.45	45.02	54.19	1
Wheat	N	% m/m	3000 g		0.022	"	0.005	0.02	2.13	0.95	2.08	2.03	0.47	2
	Molybdenum (Mo)	mg kg^{-1}			0.029	"	0.015	0.03	0.48	0.79	13.60	12.08	6.25	
	Lead (Pb)	mg kg^{-1}			0.007	"	0.005	0.01	0.017	0.67	93.68	76.47	54.12	
Coffee(Green)	Moisture	% m/m	500 g		0.099	"	0.109	0.15	11.98	0.45	2.46	1.65	1.82	
	Nickel (Ni)	mg kg^{-1}			0.540	"	0.530	0.76	4.83	0.51	31.33	22.36	21.95	
	Yttrium (Y)	mg kg^{-1}			0.006	"	0.000	0.01	0.0124	0.99	90.61	90.32	7.26	
Milk	(Added) Water	(m^oC)	568 or 500 ml		2.290	"	0.690	2.392	543.79	0.92	0.88	0.84	0.25	3
Spreadable fats	Fat	% m/m	250-500g		0.490	"	0.400	0.633	57.78	0.60	1.09	1.70	1.38	3
Sausages	Meat	% m/m	500 g		3.470	"	1.150	3.656	69.17	0.90	11.28	10.03	3.33	3
	Fat	% m/m		5.027	1.382	"	0.434	1.45	21.36	0.91	13.56	12.94	4.06	4 p260-1
	Moisture	% m/m		5.347	1.419	"	0.377	1.47	55.89	0.93	5.25	5.08	1.35	4 p260-1
	Ash	% m/m		0.3205	0.032	"	0.000	0.03	2.5	1.00	2.59			4 p260-1
	N	% m/m		0.2956	0.039	"	0.034	0.05	1.862	0.57	5.58			4 p260-1
Apples	Propargite (pesticide)	mg kg^{-1}	2 kg	0.2857	0.091	"	0.126	0.155	0.6746	0.34	46	26.98	37.36	4 p102
Strawberries	Pyrimethanil	mg kg^{-1}	2 kg		0.0481	0.0316	0.028	0.064	0.2243	0.81	57.07	42.89	24.97	5
	Chlorothalonil	mg kg^{-1}			0.0005	0	0.0005	0.001	0.001	0.25	200.00	100.00	100.00	
	Tolyfluanid	mg kg^{-1}			0.0025	0.0026	0.0021	0.004	0.0124	0.81	64.52	40.32	33.87	
	Myclobutanil	mg kg^{-1}			0.0063	0.0077	0.0045	0.011	0.0305	0.82	72.13	41.31	29.51	
	Bupirimate	mg kg^{-1}			0.0134	0.0237	0.00896	0.029	0.07138	0.88	81.26	37.55	25.11	
	Kresoxim-methyl	mg kg^{-1}			0.0008	0.0003	0.0012	0.0014	0.0017	0.37	164.71	94.12	141.18	
	Fenhexamid	mg kg^{-1}			0.0486	0.0084	0.0326	0.059	0.2257	0.70	52.28	43.07	28.89	

Table S2 (Continued)

Product	Analyte	Units	Sample amount	s product	s samp	s samp prep*	s anal	s meas	mean conc	$\frac{s_{samp}^2 + s_{prep}^2}{s_{meas}^2}$	U_{meas}%	U_{samp}%	U_{anal}%	Source
Infant milk	Zinc (Zn)	ug kg^{-1}	Single pots (mass unkown)	12810	0	included in s samp	4346	4346	49931	0.00	17.4	0.00	17.41	6
	Lead (Pb)	ug kg^{-1}		0.5815	0	"	1.271	1.271	4.815	0.00	52.8	0.00	52.79	
	Copper (Cu)	ug kg^{-1}		581.6	63.38	"	184.8	195.4	2806	0.11	13.9	4.52	13.17	
	Cadmium (Cd)	ug kg^{-1}		5.241	0.244	"	1.006	1.035	4.654	0.06	44.5	10.49	43.23	
	Arsenic(As)	ug kg^{-1}		5.936	2.341	"	2.28	3.27	10.29	0.51	63.51	45.50	44.31	4 p265
	Tin(Sn)	ug kg^{-1}		408.43	189.22	"	43.57	194.17	358.8	0.95	108.23	105.47	24.29	
Infant wet meals	Zinc (Zn)	ug kg^{-1}	Single pots (mass unkown)		431.5	"	506.1	665.1	4019.5	0.42	33.1	21.47	25.18	6
	Lead (Pb)	ug kg^{-1}			1.322	"	2.275	2.631	4.884	0.25	107.7	54.14	93.16	
	Copper (Cu)	ug kg^{-1}			77.92	"	30.19	83.57	493	0.87	33.9	31.61	12.25	
	Cadmium (Cd)	ug kg^{-1}			1.235	"	1.1	1.654	7.575	0.56	43.7	32.61	29.04	
Butter (frozen)	Fat	% m/m	112 g _3 cores	0.252	0.2165	"	0.0568	0.2238	82.92	0.94	0.54	0.52	0.14	7, 8
	Fat	% m/m	1575 g	0.374	0.151	"	0.046	0.158	83.19	0.91	0.54	0.36	0.11	
	Solids-not-fat (SNF)	% m/m	112g_3 cores g	0.035	0.0495	"	0.0399	0.0636	1.34	0.61	9.48	7.39	5.96	
	Solids-not-fat (SNF)	% m/m	1575 g	0.138	0.08	"	0.041	0.09	1.28	0.79	9.48	12.50	6.41	
	Free fatty acids (FFA)	% m/m	~112 g - 3 cores	0.031	0.0035	"	0.0057	0.0067	0.295	0.27	4.51	2.37	3.86	
	Free fatty acids (FFA)	% m/m	~672 g - 3 cores	0.009	0.001	"	0.001	0.01	0.28	0.01	4.51	0.71	0.71	
	Moisture	% m/m	~112 g - 3 cores	0.25	0.1947	"	0.0421	0.1992	15.755	0.96	2.53	2.47	0.53	
	Moisture	% m/m	~1575 g - 3 cores	0.379	0.1550	"	0.0360	0.0159	15.556	95.03	2.53	1.99	0.46	
	Peroxide value (PV » rancidity).	meq. kg^{-1}	~112 g _3 cores	0	0.024	"	0.0108	0.0263	0.083	0.83	63.3	57.83	26.02	
	Peroxide value (PV » rancidity).	meq. kg^{-1}	~672 g _3 cores	0	0.044	"	0.007	0.044	0.084	1.00	63.3	104.76	16.67	

Table S2 (Continued)

Product	Analyte	Units	Sample amount	s product	s samp	s samp prep*	s anal	s meas	mean conc	$\frac{s_{samp}^2 + s_{prep}^2}{s_{meas}^2}$	U_{meas}%	U_{samp}%	U_{anal}%	Source
Lettuce glasshouse ex. Iceberg	Nitrate	mg kg^{-1}	10 heads (Nov)	565.4	319.05	"	167.9	360.551	4408	0.78	16.4	14.48	7.62	9, 10 p86
			10 heads (Feb/Mar)	580.2	553.51	"	53.85	556.13	3148.3	0.99	35.3	35.16	3.42	
			40 head	694.3	306.16	"	42.2	309.06	3117.5	0.98	19.8	19.64	2.71	
Tuna (fresh)	Mercury (Hg)	mg kg^{-1}	~350 g	0.07	0.027	"	0.008	0.028	0.257	0.93	21.79	21.01	6.23	10
Tuna (tinned)	Mercury (Hg)	mg kg^{-1}	~350 g (2 tins)	0.142	0.015	"	0.006	0.017	0.203	0.78	16.75	14.78	5.91	10 p134
	Mercury (Hg)	mg kg^{-1}	1200 g (8 tins)	0.203	0.015	"	0.003	0.016	0.233	0.88	13.73	12.88	2.58	10 p134
Tomatoes (tinned)	Tin (Sn)	mg kg^{-1}	500 g (R1)	1.987	2.426	"	0.829	2.564	6.455	0.90	79.44	75.17	25.69	10 p124
	Tin (Sn)	mg kg^{-1}	500 g (R2)	21.19	7.3	"	2.23	7.63	74.26	0.92	20.55	19.66	6.01	10 p137
	Tin (Sn)	mg kg^{-1}	4000 g	23.95	15.61	"	2.34	15.78	78.09	0.98	40.41	39.98	5.99	10 P137
Layer meal feed	Calcium (Ca)	mg kg^{-1}	~200 g	8072	5807	"	528.4	5831	42169	0.99	27.66	27.54	2.51	10 P149, 156, 170, 182
	Sodium (Na)	mg kg^{-1}		179.8	226.5	"	30.43	228.55	1676	0.98	27.27	27.03	3.63	
	Salt (NaCl)	% m/m		0	0.081	"	0.021	0.084	0.353	0.93	47.59	45.89	11.90	
	Copper (Cu)	mg kg^{-1}		2.27	0.96	"	1.31	1.63	14.93	0.35	21.84	12.86	17.55	
Chicken feed	Enzyme	% m/m	500g (2g sub-sample)		0.00165	0.0065	0.0025	0.01	0.05	0.88	28.63	6.60	10.00	11 p71
Apple Juice (cloudy)	Patulin	ug l^{-1}	220 ml	n.a.	0 (n.d.)	"	5.1	5.1	52.6	0.00	19.4	0(n.d.)	19.39	12
Butter (fresh)	Moisture	% m/m	6 x100g	n.a.	0.052	"	0.03	0.06	15.41	0.75	0.78	0.67	0.39	12
					0.08	"	0.03	0.086	15.41	0.87	1.12	1.04	0.39	

Table S2 (Continued)

Product	Analyte	Units	Sample amount	s product	s samp	s samp prep*	s anal	s meas	mean conc	$\frac{s_{samp}^2 + s_{prep}^2}{s_{meas}^2}$	U_{meas} %	U_{samp} %	U_{anal} %	Source
Corn (shelled)	Aflatoxin	ug kg^{-1}	1.13 kg (50g sub-sample)		14.63	7.5	2.14	16.58	20	0.98	165.79	146.30	21.40	13
	Aflatoxin	ug kg^{-1}	0.91 kg		16.4	7.5	5.5	18.85	20	0.91	188.54	164.00	55.00	14
	Aflatoxin	ug kg^{-1}	0.91 kg		11.1	4.83	1.45	12.19	10	0.99	243.84	222.00	29.00	15
					328.2	388.3	79	514.52	10000	0.98	10.29	6.56	1.58	
Peanut	Aflatoxin	ug kg^{-1}	5 kg		22.8	7.69	7.08	25.08	20	0.92	250.82	228.00	70.80	16
					11.4	5.08	4.48	13.26	20	0.89	132.60	114.00	44.80	
			2.27kg (sub-sample 100g)		153.4	42.8	3.87	159.31	100	1.00	318.61	306.80	7.74	17
Coffee (green)	Ochratoxin A	ug kg^{-1}	16kg		2.79	1.685	0.332	3.28	5	0.99	131.05	111.60	13.28	18
Wheat	Deoxynivalenol (DON)	ppm (?)	0.454 kg (25g sub-sample)		0.315	0.5	0.265	0.65	5	0.83	25.906	12.60	10.60	19
Hazelnuts	Aflatoxin (total)	ug kg^{-1}	10kg (x 16)		13.19	0.86	0.52	13.23	10	1.00	264.565	263.80	10.40	20

References for Table S1 and Table S2

1. Ramsey, Lyn & Wood, *Analyst*, 2001, **126**, 1777-1783.
2. Thompson M., Willetts, P., Anderson S., Brereton P. and Wood R. (2002) Analyst, 127, 689-691.
3. Lyn, Ramsey & Wood, 2002, *Analyst*, **127**, 1252-1260
4. Lyn J. A. (2003) PhD Thesis, "Optimising uncertainty from sampling and analysis of foods and environmental samples", University of Sussex. ISNI: 0000 0001 3614 3415. EThOD ID: uk.bl.ethos.270732. URL: http://ethos.bl.uk/OrderDetails.do?uin=uk.bl.ethos.270732
5. Lyn, Ramsey, Fussell, & Wood, 2003, *Analyst*, **128**, 1391–1398,
6. Lyn, Ramsey, & Wood, 2003, *Analyst*, **128**, 379-388
7. Lyn J.A., Ramsey M.H., Damant A., and Wood R. (2005b), Analyst, 130, 1271-1279
8. Food Standards Agency Report 01055
9. Lyn, J.A., Palestra, I.M., Ramsey, M.H., Damant, A.P. and Wood, R. (2007b) Accreditation and Quality Assurance, 12, 67-74
10. Palestra (2008) PhD Thesis. "Estimation and achievement of optimal measurement uncertainty form the sampling of food and feed", University of Sussex. ISNI: 0000 0001 3464 7193. EThOS ID: uk.bl.ethos.488580 . URL: http://ethos.bl.uk/OrderDetails.do?uin=uk.bl.ethos.488580
11. Ramsey M.H., and Ellison S. L. R.,(eds.) (2007) Eurachem/EUROLAB/ CITAC/Nordtest/ AMC Guide: Measurement uncertainty arising from sampling: a guide to methods and approaches Eurachem ISBN 978 0 948926 26 6. (http://www.eurachem.org/). Example A5 p 71-73
12. Food Standards Agency Report 01070
13. Johansson, AS; Whitaker, TB; Hagler, WM; Giesbrecht, FG; Young, JH; Bowman, DT (2000) J. OF AOAC INTERNATIONAL, 83 (5): 1264-1269
14. Whitaker, T.B., 2006. *Food Additives and Contaminants*, 23 (1), 50-61.
15. Whitaker, T.B., Anders S.J. 2005. J. *Food Protection*, 68 (6), 1306-1313.
16. Whitaker, T.B., 2003. Food Control, 14, 233-237
17. Whitaker, TB; Dowell, FE, Hagler WM; Giesbrecht FG, Wu J; 1994. J. AOAC International, 77(1), 107-116
18. Vargas, E.A., Whitaker, T.B., Dos Santos, E.A., Slate, A.B., Lima, F.B., and Franca, R.C.A., 2006. Food Additives and Contaminants, 23 (1), 62-72
19. Whitaker, TB; Hagler, WM; Giesbrecht, FG; Johansson, AS, J. 2000, AOAC INTERNATIONAL, 83 (5): 1285-1292
20. Ozay, G ; Seyhan, F ; Yilmaz, A; Whitaker, TB; Slate, AB; Giesbrecht, F. 2006. J. AOAC INTERNATIONAL, 89 (4): 1004-1011.