

ESI Table 1

The dataset for n replicate measurements of each set of m sub-samples for the six sample collection strategies (S1 – S6). These values were used as the input data for the ANOVA calculations that are summarised in Table 2.

S1							S4						
Replicate measurements (n)	ACRO S1955-1	ACRO S1955-2	ACRO S1955-3	ACRO S1955-4	ACRO S1955-5	All sub-samples (m)	Replicate measurements (n)	2022-1	2022-2	2022-3	2022-4	2022-5	Sub-samples 1-4 (m)
1	0.995	0.821	0.796	0.780	0.905		1	0.129	0.137	0.118	0.115	0.320	
2	0.888	0.729	0.803	0.751	0.870		2	0.136	0.135	0.124	0.122	0.297	
3	0.959	0.848	0.891	0.853	0.923		3	0.112	0.109	0.136	0.112	0.297	
4	0.967	0.793	0.754	0.856	0.917		4	0.125	0.114	0.120	0.123	0.313	
5	0.890	0.752	0.823	0.843	0.849		5	0.129	0.117	0.126	0.124	0.310	
6	0.967	0.842	0.838	0.841	0.921		6	0.118	0.118	0.133	0.117	0.306	
Mean	0.944	0.797	0.818	0.821	0.897	0.856	Mean	0.125	0.122	0.126	0.119	0.307	0.123
sd	0.045	0.049	0.046	0.044	0.031	0.063	sd	0.009	0.011	0.007	0.005	0.009	0.003
rsd%	4.727	6.085	5.615	5.362	3.437	7.319	rsd%	7.022	9.446	5.695	4.119	3.032	2.714
S2							S5						
Replicate measurements (n)	PES S1955-1	PES S1955-2	PES S1955-3	PES S1955-4	PES S1955-5	Sub-samples 1-4 (m)	Replicate measurements (n)	2376-1	2376-2	2376-3	2376-4	2376-5	Sub-samples 1-3, 5 (m)
1	0.923	0.924	0.781	0.868	1.263		1	0.577	0.552	0.628	0.794	0.614	
2	0.857	0.891	0.901	0.782	1.158		2	0.608	0.551	0.589	0.804	0.569	
3	0.881	0.841	0.885	0.781	1.253		3	0.576	0.554	0.581	0.789	0.526	
4	0.876	0.903	0.778	0.802	1.341		4	0.559	0.564	0.601	0.806	0.595	
5	0.876	0.942	0.782	0.755	1.262		5	0.588	0.541	0.649	0.798	0.615	
6	0.733	0.905	0.816	0.797	1.173		6	0.587	0.548	0.588	0.790	0.548	
Mean	0.858	0.901	0.824	0.798	1.242	0.845	Mean	0.582	0.552	0.606	0.797	0.578	0.579
sd	0.065	0.034	0.056	0.039	0.067	0.045	sd	0.016	0.008	0.027	0.007	0.036	0.022
rsd%	7.579	3.823	6.762	4.828	5.410	5.288	rsd%	2.794	1.379	4.458	0.884	6.295	3.847
S3							S6						
Replicate measurements (n)	ACRO1956	ACRO1957	ACRO1958	ACRO1959		All sub-samples (m)	Replicate measurements (n)	ACRO2361-1	ACRO2361-2	ACRO2361-3	ACRO2361-4	ACRO2361-5	All sub-samples (m)
1	0.794	0.837	0.856	1.048			1	2.254	2.445	2.435	2.389	2.666	
2	0.814	0.817	0.914	1.099			2	2.180	2.460	2.338	2.373	2.490	
3	0.864	0.798	0.934	0.909			3	2.371	2.200	2.355	2.493	2.367	
4	0.844	0.799	0.882	0.855			4	2.436	2.225	2.400	2.686	2.439	
5	0.839	0.878	0.835	0.856			5	2.396	2.329	2.210	2.494	2.488	
6	0.863	0.884	0.878	0.828			6	2.214	2.374	2.227	2.406	2.399	
Mean	0.836	0.836	0.883	0.933		0.872	Mean	2.339	2.328	2.473	2.475	2.475	2.418
sd	0.028	0.038	0.036	0.114		0.046	sd	0.109	0.091	0.116	0.105	0.105	0.077
rsd%	3.314	4.561	4.111	12.173		5.296	rsd%	4.665	3.926	4.703	4.256	4.256	3.202

ESI Table 2

Calculations for the data shown in Table 4 using input data from Table 2. The data for the means of m replicate measurements are derived from ESI Table 1. All uncertainties are expressed as relative standard uncertainties ($k = 1$).

Calculation	Equation	control material	S1	S2	S3	S4	S5	S6
MS_{between}		0.02536	0.02352	0.01198	0.01279	6.66E-05	0.002982	0.04079
MS_{within}		0.006755	0.001868	0.0025	0.004106	7.11E-05	0.0005939	0.01122
mean of m measurements ($\text{mean}_{\text{between}}$)		1.406	0.855	0.845	0.872	0.122	0.579	2.38
n (number of replicates)		6	6	6	6	6	6	6
m (number of measurements)		3	5	4	4	4	4	5
$\sqrt{MS_{\text{within}}}$		0.08	0.04	0.05	0.06	0.01	0.02	0.11
$\sqrt{MS_{\text{within}}} * 100 / \text{mean}_{\text{between}}$		5.85	5.06	5.92	7.35	6.91	4.21	4.45
$(\sqrt{MS_{\text{within}}} * 100 / \text{mean}_{\text{between}}) / \sqrt{n}$	Equation 2 ($u_{\text{rel_repeatability}}$)	2.39	2.06	2.42	3.00	2.82	1.72	1.82
$\sqrt{((MS_{\text{between}} - MS_{\text{within}}) / n)}$		0.06	0.06	0.04	0.04		0.02	0.07
$(\sqrt{((MS_{\text{between}} - MS_{\text{within}}) / n)}) * 100 / \text{mean}_{\text{between}}$		3.96	7.03	4.70	4.36		3.45	2.95
$((\sqrt{((MS_{\text{between}} - MS_{\text{within}}) / n)}) * 100 / \text{mean}_{\text{between}}) / \sqrt{m}$	Equation 3 ($u_{\text{rel_between measurement}}$)	2.29	3.14	2.35	2.18		1.72	1.32
$\sqrt{((u_{\text{rel_repeatability}})^2 + (u_{\text{rel_between measurement}})^2)}$	Equation 4 ($u_{\text{rel_combined}}$)	3.31	3.76	3.37	3.71		2.43	2.25

$$MS_{\text{between}} = \sum_n (T_i^2 / n) - (T^2 / N)$$

$$\text{Total} = \sum_n \sum_m x_{ij}^2 - (T^2 / N)$$

$$MS_{\text{within}} = \text{Total} - MS_{\text{between}}$$

Where there are m sub-samples, each with n replicate measurements

$$N = m * n$$

T_i = sum of the n replicate measurement results for each sub-sample

T = sum of all the n replicate measurement results for all m sub-samples