Electronic Supplementary Material (ESI) for Analytical Methods. This journal is © The Royal Society of Chemistry 2017

Medium	Target Synthetic?	Analytes	No. of Particip ants	No. of rounds	Central Analysis?	Ref.	Date	Comment
Soil	No	Pb & Cu	9	1	No	1	1995	First reported SPT realisation
Air-Workplace	Yes	Hydrocarbons Aromatic & Chlorinated	38	3	No	2	1997	Not called an 'SPT', no z-scores. 3 sampling exercise each with sets of 4-8 runs. Has evidence for improved performance between rounds.
Soil	No	Pb & Cu	9	2	No	3	1998	Improved performance in second round (s down from 36% to 20%)
Soil	Yes	Ba	9	1	Yes	4	2000	Spatial resolved analyte, Synthetic Target
Gas-landfill	No	CH4, CO2, O2	9	1	No	5	2001	In situ measurements. Temporal variability monitored by reference borehole
Wheat-bulk	No	N, Mo, Pb	5	1	Yes	6	2002	All participants used same protocol
Coffee-Bulk	No	H ₂ O	8	1	Yes	6	2002	All participants used same protocol
Lettuce in field (Virtual)	Yes	NO3 ⁻	16	1	Yes	7	2008	First example of virtual SPT. Undertaken by 16 different countries
Butter - bulk	No	H ₂ O	9	1	Yes	8	2011	Results also used to make improved estimate of measurement uncertainty including between-sampler bias
Apple Juice -bulk	No	Patulin	9	1	Yes	9	2011	Limited access to the sampling target, ownership of the target, and this being the same as sampler's employer, limited independence of the samplers.
Gas - stack	Yes	Gases & particulates	4 [§]	Many – not reported	No	10	2015	[§] 4 sampler at a time, use in-house-constructed emission simulation apparatus. <i>In situ</i> measurements. Adapted homogeneity test for ISO 13528 compliance
Water-waste	No	COD, TOC, pH, Temp	16-20	3	Yes*	11	2015	In situ measurement of pH &Temp. *Own labs used as well as central analysis.
Gas – stack	Yes	Gases	15	16	No	12	2016	Run annually. 3 participants at a time, repeat over 4 to 8 days of testing. In-house constructed emission simulation rig allowing the testing of hot and wet test atmospheres. Homogeneity to EN15259.

Electronic supplementary information. A selection of the sampling 'proficiency tests' (SPT) that have been reported since the first in 1995, showing a variety of analytes in a wide range of media that include gases, liquids and solids. Eight of the exercises were only a single round to show the feasibility of the concept, but three have apparently become routine with multiple rounds.

References

- ¹ A. Argyraki, M.H. Ramsey, and M Thompson. Proficiency testing in sampling: pilot study on contaminated land.
- Analyst, 1995, 120, 2799-2804

³ A. Argyraki and M.H. Ramsey. *Evaluation of inter-organisational sampling trials on contaminated land: comparison of two contrasting sites*. In D.N. Lerner and N.R.G. Walton (eds) 1998. *Contaminated Land and Groundwater - Future Directions*. Engineering Geology Special Publication 14. Geological Society, London, 1998, pp 119-125.

⁴ S. Squire, M.H. Ramsey, M.J. Gardner and D Lister. Sampling proficiency test for the estimation of uncertainty in the spatial delineation of contamination. *Analyst*, 2000, **125**, 2026-2031.

⁵ S. Squire and M.H. Ramsey. Inter-organisational sampling trials for the uncertainty estimation of landfill gas measurements.

J.Environ. Monitoring, 2001, 3, 288 - 294.

⁶ M. Thompson, P. Willetts, S. Anderson, P. Brereton and R. Wood. Collaborative trials of the sampling of two foodstuffs, wheat and green coffee. *Analyst*, 2002, **127**, 689-691.

⁷ P. Robouch, M. H. Ramsey, J. Paepen, B. de la Calle and B.V. Robouch . *The first e-Sampling Proficiency Test in the area of food quality and safety*. JRC Technical Notes 47846. Joint Research Centre – Institute for Reference Materials and Measurements, European Communities, Geel, Belgium, 2008.

⁸ M.H. Ramsey, B. Geelhoed, A.P. Damant, and R. Wood. Improved evaluation of measurement uncertainty from sampling by inclusion of between-sampler bias using sampling proficiency testing.

Analyst, 2011, 136, 1313-1321. DOI:10.1039/C0AN00705F.

⁹ M. H. Ramsey and B. Geelhoed. *Feasibility, Practicality and Usefulness of Sampling Proficiency Tests in the Food Sector (E01070)*. Final report to FSA, 2011.

Available from https://www.food.gov.uk/science/research/supportingresearch/e01070.

¹⁰ J. Cordes, B. Stoffels and D. Wildanger. The question of homogeneity inside a chimney: application of ISO 13528 to stack emission proficiency tests. *Accred. Qual. Assur.*, 2015, **20**,287-295. DOI 10.1007/s00769-015-1139-y.

¹¹ M. Cotman and A. Pintar. Proficiency testing of wastewater sampling: What did we learn?

Accred. Qual. Assur. 2015, 20: 387. doi:10.1007/s00769-015-1170-z

¹² MD. Coleman et al, State of UK emissions monitoring of stacks and flues: an evaluation of proficiency testing data for SO2, NO and particulates, Accred Qual Assur (2013) 18:517–524, DOI 10.1007/s00769-013-1011-x

² E. Goelen, M. Lambrechts and F. Geyskens. European sampling intercomparison for aromatic and chlorinated hydrocarbons in workplace air. *Ann. Occup. Hyg.*, 1997, **41**, 527-554.