2025 IMEKO Joint Conference
TC8 - TC11 - TC25
Torino, Italy, September 14-17, 2025

Setting target uncertainty in the Validation of Measurement Proedures that Include Sampling (VaMPIS), using the Optimised Uncertainty approach.

Peter D. Rostron[1]

[1] *Secretary of Eurachem Joint Working Group on VaMPIS, Visiting Fellow at School of Life Sciences, University of Sussex, UK*

Abstract **– Approaches to the validation of measurement procedures that include sampling have recently been published. They form a joint Eurachem / EUROLAB supplement to previous publications that focussed on validation of the analytical procedure only. These approaches require the use of a target measurement uncertainty that can be compared with the measurement uncertainty obtained by experiment. In situations where this target uncertainty is not known or specified in advance, the Optimised Uncertainty approach can provide a systematic method for calculating this value. A new program called OptiMU has been created to assist in these calculations. This is described using worked examples.**

I. NEED FOR TARGET UNCERTAINTY

The recently published joint Eurachem/EUROLAB guidance on Validation of Measurement Procedures that Include Sampling (VaMPIS) [1] was produced in order to extend the already well established method validation guidance [2] to the majority of cases where primary sampling is the first stage of a measurement procedure. In this context, 'sampling' pertains to the activities of acquiring physical samples that will then be transported (possibly following storage) to an analytical laboratory, where they will be subsequently analysed and the results of these analsyes used to characterise the sampling target[a]. Alternatively, in cases where *in situ* measurement devices, such as portable X-ray fluorescence (pXRF), are used directly on the sampling target, the process of sampling is an implicit part of the experimental design, because it happens simultaneously with the analyses.

TheVaMPIS approach, represented by the flowchart in Fig. 1, is dependent on the estimation of the overall measurement uncertainty (MU), where this includes the contributions of both the uncertainty of sampling and the uncertainty of analysis. It is argued [1] that this overall measurement uncertainty is the one key metric that enables

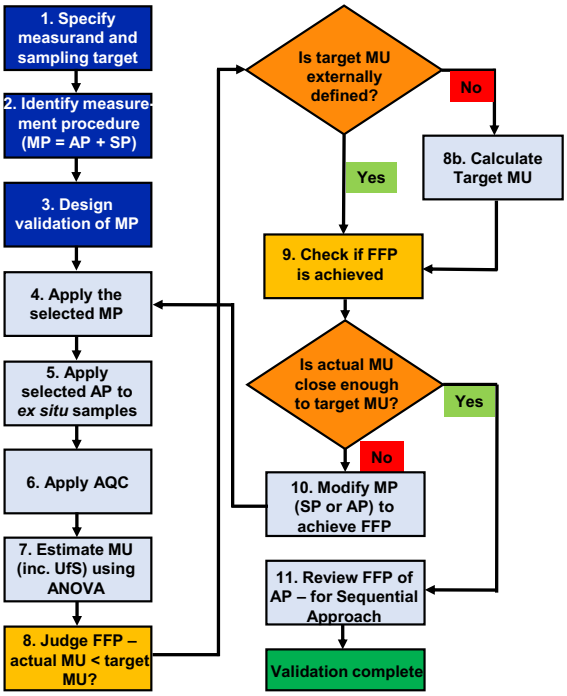

Fig. 1. Flow chart for application of VaMPIS. Taken from [1].

the establishment of fitness for purpose of a whole measurement procedure (in other words, a procedure that begins with sampling and ends with the reporting of a measured quantity value and its associated uncertainty). The actual question of whether a particular measurement procedure is fit for purpose, and hence 'validated', requires knowledge of a 'target uncertainty' (Target MU in Fig. 1), against which the measurement uncertainty that

[a] portion of material, at a particular time, that the sample is intended to represent [6]

was obtained by experiment during the validation process can be compared.

II. THE OPTIMISED UNCERTAINTY APPROACH TO SETTING TARGET UNCERTAINTY

When validation is carried out by an organisation such as an analytical laboratory, the ideal is that one person will have the overall responsibility for the quality of the reported measurement results, and hence for the quality of both the sampling and the chemical analysis. In this case, again ideally, a target uncertainty (including sampling uncertainty) will already have been mandated by an external organization such as a regulatory body. The purpose of the Optimised Uncertainty (OU) approach is one way to provide a systematic and scientifically defensible method of setting a target uncertainty when this is not the case (Step 8b in Fig. 1).

The OU approach is based on a definition of fitness for purpose first proposed by Thompson and Fearn (1996) [3]. That definition itself is based on the calculation of a minimum expectation of loss (in this case financial loss), which balances the costs of measurement with the potential losses that would be incurred by making incorrect decisions, e.g. compliance decisions. In the case of compliance, there are two encompassing possible losses: a) losses due to accepting a batch of material that is in fact non-compliant (e.g. legal costs, litigation, loss of reputation); b) losses that arise from rejecting a batch of material that is in fact compliant (e.g. disposal, re-assignment, remediation). An additional facet of the OU approach is that if a measurement procedure is found to be not fit for purpose, the approach can also assist the user to develop strategies to optimally apportion the necessary adjustment to expenditure (which may go either up or down) in order to achieve fitness for purpose at the minimum overall financial loss (i.e. cost).

Details of the calculations involved in the OU approach can be found in Appendix B of the VaMPIS guide [1]. The remainder of this paper will focus on examples of its application, specifically using newly developed software called OptiMU that is freely available on the website of the Royal Society of Chemistry, Analytical Methods Committee [4].

III. EXAMPLES OF OU APPROACH

The examples are based on Example A2 in the VaMPIS guidance [1] – *In situ measurement of total lead in top soil.*

In situ measurements were made on an area of land with a 30 m spacing, using pXRF on bare earth after turf removal. A total of 24 sampling targets were investigated, and duplicate samples were taken at each. These were acquired by repeating the process approximately 2 m away from the primary sample. The sampling component of uncertainty was then calculated using analysis of variance (ANOVA). Analytical uncertainty was similarly calculated using pXRF on extracted soil samples in a laboratory (assumed to be similar to that generated in the field). Further details are given in the VaMPIS guide [1].

Because the distribution of lead concentration between the sampling targets had a small proportion of positive outliers on an underlying normal distribution, the sampling uncertainty was calculated using robust ANOVA. This was further adjusted by subtracting the variance of analysis obtained in the laboratory. The two uncertainty values (expressed as standard deviations) were calculated as sampling uncertainty = 784 mg kg^{-1}, analytical uncertainty = 43 mg kg^{-1}, giving an overall measurement uncertainty (by the sum of variances) of 785 mg kg^{-1}.

Systematic effects

In order to measure systematic effects (measurement bias), *ex situ* samples were also taken at the same 24 locations and analysed using ICP-AES in the laboratory. Modelling of the two sets of measurements revealed a large significant bias between the *in situ* and *ex situ* measurements (*in situ* measurements were generally much lower). Potential reasons for this large bias include moisture content and particle size in the *in situ* samples, whereas *ex situ* samples were ground, sieved and dried prior to analysis. The applied threshold value of 2000 mg kg^{-1} was specified to apply to dried samples [5]. One option for dealing with systematic effects is, therefore, to correct the *in situ* measurements for this bias back to a 'dry mass basis', by applying the bias model. Another option is to add the bias and its uncertainty into the overall uncertainty value. In this particular case the overall uncertainty would become very large indeed (expended relative uncertainty of 98 %) which would not be realistic for the interpretation of these results. For this reason, and because the measurand was defined on a dry mass basis, the bias was not included.

The question of whether the high level of measurement uncertainty in this investigation was fit for purpose has been evaluated using the OU approach, for both false positive and false negative scenarios. The program OptiMU [4] was used to calculate an optimal level of uncertainty for each scenario. An additional potential purpose for the measurement results of geochemical mapping has also been included.

The generic inputs to OptiMU are as follows:

1. Threshold value: The threshold value for the maximum concentration of Pb in soil in green open spaces at the time of the experiment was 2000 mg kg^{-1}
2. Meaurement uncertainty: The analytical standard deviation was estimated by the duplicate method as 43 mg kg^{-1}. The sampling uncertainty was estimated from duplicates in the field as 784 mg kg^{-1}.
3. Costs: Measurement costs were based on total costs

of labour and equipment. Cost of sampling was estimated at €29 per sample, and analytical cost as €12 per analysis.

*Scenario 1 – False **positive**, comparison against threshold value*

In this scenario we investigate the possibility that a sampling target is identified as requiring further action, when in fact the true value of the measurand (total lead concentration on dry mass basis) is below the threshold value of 2000 mg kg^{-1}. Two further inputs are required:

1. Cost arising from missclassification: The location of each *in situ* measurement was at the centre of a square of side 30 m, so represented a sampling target of area 900 m^2. An approximate estimate of €10,000 was used to represent the cost of unnecessary remediation.
2. Concentration at which to optimise: The question of how to set this value requires consideration. Standard options (e.g. 1.1 × threshold value) can be selected within the OptiMU program, and this method was chosen in this case to represent a value that has a reasonable potential for missclassification, giving a value of 2,200 mg kg^{-1}.

The output from the OptiMU program is shown in Fig. 2. The actual measurement uncertainty (785 mg kg^{-1}) is approximately 6 times larger than the optimum (target) measurement uncertainty of 138 mg kg^{-1}, demonstrating that **this measurement procedure is not fit for this purpose**.

In the second part of the OU approach, an apportionment can be made between the sampling and analytical costs that would best achieve the optimum uncertainty, shown in Table 1. Although it is unlikely to be practical to reduce the measurement uncertainty to the target value, this shows that the most cost effective way to reduce the overall measurement uncertainty is to reduce the large sampling uncertainty. This could be acheived for example by taking composite measurements at each sampling target.

Table 1. Optimal apportioning of sampling and analytical uncertainties to achieve fitness for purpose for false positive scenario

Optimum Measurement Uncertainty:	mg kg^{-1}	138
Expectation of loss E(L):	€	1739
Optimum Sampling Uncertainty:	mg kg^{-1}	135
Estimated Optimum Sampling Cost:	€	974
Cost change factor:		33.6
Optimum Analytical Uncertainty:	mg kg^{-1}	25
Estimated Optimum Analytical Cost:	€	34
Cost change factor:		2.9

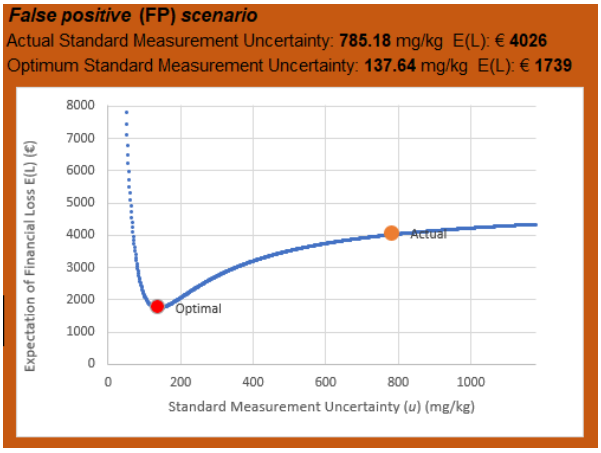

*Fig. 2. Optimisation curve and data for lead in top soil, false **positive** scenario*

*Scenario 2 – False **negative**, comparison against threshold value*

This time we consider the possibility that a sampling target is classified as below the regulatory threshold, when in fact the true value of the measurand is above the theshold. This could incur costs of litigation and/or subsequent unplanned remediation work, including delays to planned use etc. The two parameters specific to this optimisation are:

1. Cost arising from missclassification: There is no data available for the site in question, however previous studies have made an approximation of €1000,000 to represent the potentially high cost of litigation.
2. Concentration at which to optimise: Setting this parameter requires careful consideration particularly in the case of false negative scenarios, when the consequence cost may be very high. One approach is to set this parameter to 10 % below the threshold value. In this case there are three pXRF measurements that are in the range 1800 – 2000 mg kg^{-1} (see [6], table A2.4, target ID: A4, D1 and F3). Given the high level of measurement uncertainty at this site, it is considered unlikely that these three values would be accepted as compliant without further investigation. The value chosen for this optimisation in this case is 1568 mg kg^{-1} (target ID: B6). This might be seen as being representative of a value that has a realistic potential for missclassification in this particular investigation.

Results of the optimisation are shown in Fig. 3.
It can be seen that the optimum measurement uncertainty of 122 mg kg^{-1} is similar to the optimum value in the false positive scenario, and again **not fit for this purpose**.

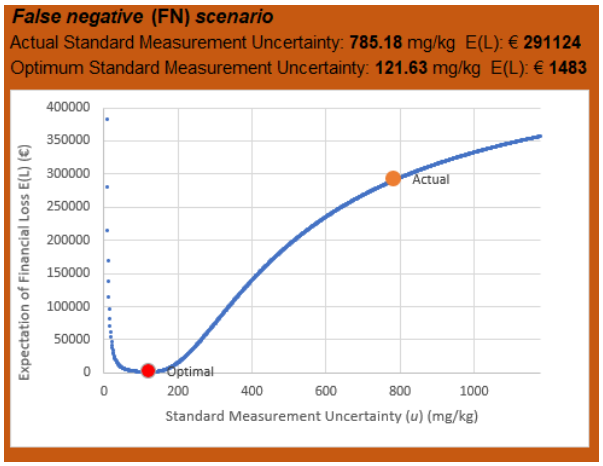

*Fig. 3. Optimisation curve and data for lead in top soil, false **negative** scenario*

Consequently the apportionment between sampling and analysis is also broadly similar to the figures in Table 1. However the total expection of loss (EL) is much higher at €291,124 because of the much larger consequence cost.

Second potential purpose – Geochemical mapping

The fitness for purpose criteria for geochemical mapping is that the measurement uncertainty should not exceed 20 % of the total variance of analyte concentration across the area to be mapped, including the variance between sampling targets[6]. In this case the standard deviation corresponding to 20 % of the total variance (total robust standard deviation = 2050 mg kg^{-1}) can be calculated as 917 mg kg^{-1}, suggesting that the acual measurement uncertainty of 785 mg kg^{-1} **is fit for the purpose of geochemical mapping**. This is in part due to the large variance of lead concentration between the sampling targets at this site. The OptiMU program can also be used to calculate optimum values of sampling and analytical uncertainty, given a value for target uncertainy. In this case fitness for purpose could still be acheived if the analytical uncertainty were to increase by as much as a factor of 3, or a smaller increase in sampling uncertainty to 900 mg kg^{-1}.

IV. CONCLUSION

The optimised uncertainty approach balances the costs of measurement with the potential costs of missclassification of a sampling target. It uses a financial loss function to estimate an optimum measurement uncertainty value that minimises the potential cost of an investigation. While in practice the exact optimum uncertainty may not be practically fully acheivable, it provides the investigator and site owner with an estimate of the financial risk associated with different cost-options for a measurement procedure with different levels of measurement uncertainty. It also provides a potentially useful tool to calculate a value for target uncertainty, when one has not been set externally. This can be particularly helpful in the validation of measurement procedures that include sampling (VaMPIS) [1].

REFERENCES

[1] M.H.Ramsey, P.Rostron, F.C.Raposo (eds.) "Eurachem/EUROLAB/CITAC/Nordtest/AMC Guide: Validation of Measurement Procedures that Include Sampling", Eurachem (2024). http://www.eurachem.org.

[2] H.Cantwell (ed.) Eurachem Guide: "The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics", Eurachem (3rd ed. 2025). http://www.eurachem.org.

[3] M.Thompson, T.Fearn, "What Exactly is Fitness for Purpose in Analytical Measurement?", Analyst, 121, 1996, pp. 275-278

[4] AMC Software https://www.rsc.org/membership-and-community/connect-with-others/join-scientific-networks/subject-communities/analytical-science-community/amc/software/

[5] UK Department of the Environment. "Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL)", London, 1987

[6] M.H.Ramsey, S.L.R.Ellison, P.Rostron, (eds.) Eurachem/EUROLAB/CITAC/Nordtest/AMC Guide "Measurement Uncertainty Arising from Sampling: a Guide to Methods and Approaches", Eurachem (2nd ed. 2019) http://www.eurachem.org.