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Ensuring quality of the analytical process in a research laboratory

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Abstract: Validation and verification of analytical methods for testing of new materials or new specific methods often pose a line of problems and require alternative approaches. The necessary analytical instrumentation, the available CRM or standard procedures are among the problems encountered. Firstly, in the research laboratory usually the equipment is tailored to the quantity and size of the samples tested. Often we need to scale down the procedure to lower weight or volume, which could alter the analytical behavior of the standard procedure used for CRM testing. Secondly, although we chose the CRM with characteristics as close as possible to the studied material, often an appropriate CRM is not commercially available. For example, analysing CRM of soils is usually a procedure for estimating the analytical behaviour of the applied method for testing mine tailings, however the discrepancy of the matrix composition or analytes content, as well as their state and speciation in the sample, doesn't allow the method to be fully studied. In some cases, standard addition approach could help for at least approximate estimation of the uncertainty of measurement, but it is difficult to attend chemical equilibrium of added analyte with matrix to the level that reflects its state in the CRM sample or testing samples, especially in solid samples. Thirdly, when studying the behaviour of newly developed procedure for estimation of specific characteristics of the sample (for example, study of alkaline reactivity of mine tailing or fly ashes as precursors for geopolymer obtaining) the problems are even more pronounced. Applying the procedure to available CRM of soils or mine tailing doesn't provide the informative data as the reference or consensus values are not available for this specific procedure. An alternative approach was to study the behaviour of pure components and phases of the sample in the tested media. However, we found that we are scaling up the method and the obtained data could only roughly present the behaviour of the method in the tested materials. Fourthly, to ensure the quality control, CRM and in-lab control samples were used in our laboratory. However, we found that the differences in particle size in standard and testing samples highly influenced the obtained results and sometimes they appeared non-informative to be applied for quality control. In the research laboratory typically one analyses limited number different samples in different conditions applying modified procedures which limits the obtaining of reasonable quantity of data for constriction of useful control charts. Nevertheless the mentioned problems we are still applying the standard procedures to available CRM for initial estimation of the uncertainty of measurement and the method behaviour in the research laboratory. More thorough estimation needs development of specific protocols.

Case 1: Scaling down the SOP - sequential extraction of mine tailing and fly ash

In the research laboratory usually the equipment is tailored to the quantity and size of the samples tested. Often we need to scale down the procedure to lower weight or volume, which could alter the analytical behavior of the standard procedure used for CRM testing.

Heavy metals distribution in geochemical phases BCR procedure

- Fraction 1: • Mobile exchangeable fraction (exchangeable ions + carbonates) • 0,11 M CH_3COOH, 16 h
- Fraction 2: • Reducible fraction • 0,1 M NH_2OHHCl, pH 1,5 (HNO_3), 16 h
- Fraction 3: • Oxidisable fraction • (a) 30 % H_2O_2, pH 2-3 (HNO_3) 2 h, t=85 °C • (b) 1 M CH_3COONH_4, pH 2 (HNO_3), 16 h
- Fraction 4: • Residual fraction • Aqua regia digestion

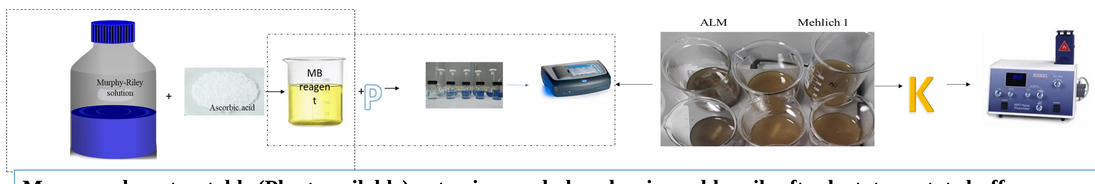
Heavy metals distribution in geochemical fraction of copper mine tailing

fraction	component, mg/kg						
	Fe	Cu	Zn	Mn	Cd	Ni	Pb
F1	447	107	5.5	20.5	< 0.25	< 0.5	3.8
F2	740	41.4	6.5	10.3	< 0.25	< 0.5	9.2
F3	8142	188	10.3	40.6	< 0.25	< 0.5	13.7
F1+F2+F3	9329	337	22.2	71.4	< 0.25	< 0.5	26.7
F4	10387	100	40.2	102	< 0.25	< 0.5	17.5
total	197116	437	62.4	173	< 0.25	< 0.5	44.2

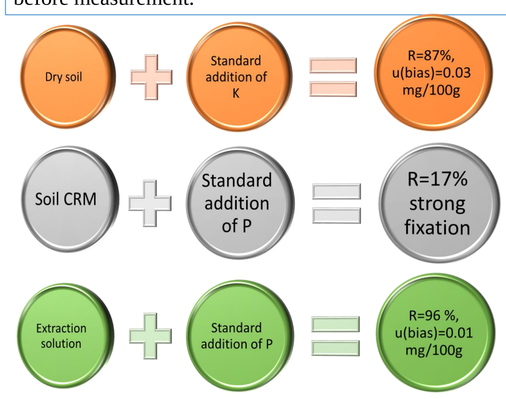
Problems:
Quality control
BCR reference material - lake sediments
Standard BCR procedure - needs to be scaled down

Case 2: Sample and CRM - standard addition

Although we chose the CRM with characteristics as close as possible to the studied material, often an appropriate CRM is not commercially available. For example, analysing CRM of soils is usually a procedure for estimating the analytical behaviour of the applied method for testing mine tailings, however the discrepancy of the matrix composition or analytes content, as well as their state and speciation in the sample, doesn't allow the method to be fully studied. In some cases, standard addition approach could help for at least approximate estimation of the uncertainty of measurement, but it is difficult to attend chemical equilibrium of added analyte with matrix to the level that reflects its state in the CRM sample or testing samples, especially in solid samples.



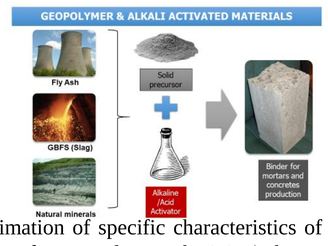
Measurands: extractable (Plant available) potassium and phosphor in arable soils after lactate-acetate buffers extraction. Two variants of the standard addition approach: (1) to assess method bias – the standard addition of potassium CRM solution before extraction and (2) to assess measurement bias – standard addition potassium CRM after extraction and before measurement.



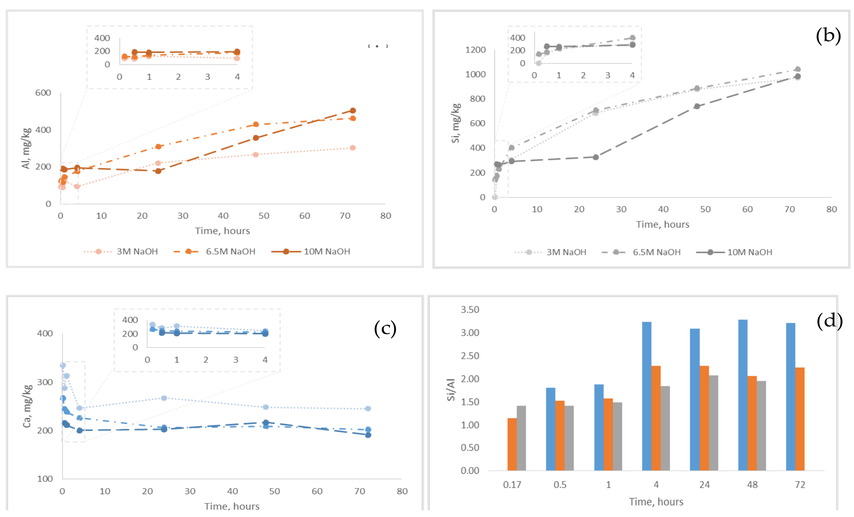
Advantage: addition before extraction - estimate bias of the whole procedure. The trueness to be evaluated in sample types usually encountered in the laboratory.
The efficiency of extracting solution depends not only on its composition and procedure used, but on the soil type and its physical and chemical properties.

Drawback: the spiked analyte could not completely reach equilibrium with the soil sample, the obtained bias appeared approximate estimate of bias of available potassium in soil
Solution: standard addition after the extraction - estimate partially the method bias.

Case 3: New specific procedure - alkaline reactivity of mine tailings and fly ash



Thirdly, when studying the behaviour of newly developed procedure for estimation of specific characteristics of the sample (for example, study of alkaline reactivity of mine tailing or fly ashes as precursors for geopolymer obtaining) the problems are even more pronounced. Applying the procedure to available CRM of soils or mine tailing doesn't provide the informative data as the reference or consensus values are not available for this specific procedure. An alternative approach was to study the behaviour of pure components and phases of the sample in the tested media. However, we found that we are scaling up the method and the obtained data could only roughly present the behaviour of the method in the tested materials.



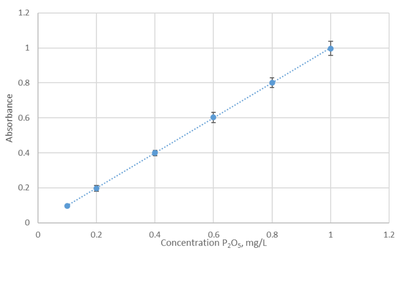
Alkaline reactivity

Problems:
ICP-OES measurement
High salt content
High concentration of target elements
Quality control
Lack of reference material
Lack of standard procedure

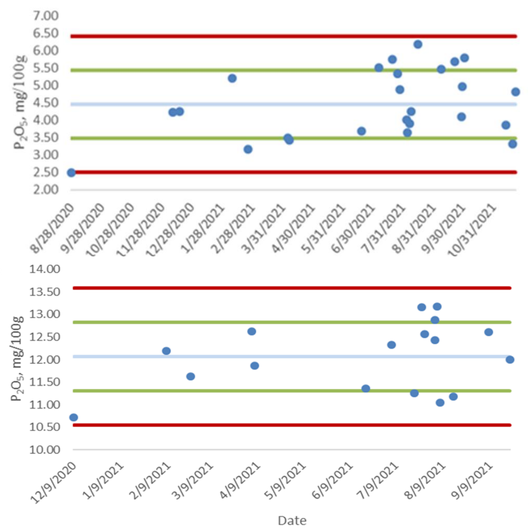
Solutions:
ICP-OES measurement
Dilution → Increased uncertainty
Observation mode
Quality control
Interlaboratory comparison

Case 4: Quality control - in-lab control sample

To ensure the quality control, CRM and in-lab control samples were used in our laboratory. However, we found that the differences in particle size in standard and testing samples highly influenced the obtained results and sometimes they appeared non-informative to be applied for quality control. In the research laboratory typically one analyses limited number different samples in different conditions applying modified procedures which limits the obtaining of reasonable quantity of data for constriction of useful control charts.



Mean calibration curve - molybdenum blue method, n=169, one year



Control charts of arable soil sample containing (a) 4.6 and (b) 12.1 mg/100 g P_2O_5. The precision was estimated in within lab reproducibility conditions by standard deviation of concentration values obtained during one-year period by different analysts with different reagents, but the same instruments. The warning limits (green lines) were set at 1*s and the action limits (red line) at 2*s, blue line presented the mean value

References:

1. Magnusson B.; Örnemark, U. (eds.) EURACHEM Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics 2nd ed. 2014, www. eurachem.org
2. Bettencourt Da Silva, R.; Bulska, E.; Godlewska-Zylkiewicz, B.; Hedrich, M.; Majcen, N.; Magnusson, B. Analytical measurement: Measurement uncertainty and statistics. Joint Research Center, European Commission 2013, 58-146, https://doi. org/10.2787/5825
3. Kruve, A.; Rebane, R.; Kipper, K.; Oldekop, M.-L.; Evard, H.; Herodes, K., Ravio, P.; Leito, I. Tutorial review on validation of liquid chromatography–mass spectrometry methods: Part I. Anal. Chim. Acta 2015, 870, 29-44.
4. Kruve, A.; Rebane, R.; Kipper, K.; Oldekop, M.-L.; Evard, H.; Herodes, K.; Ravio, P.; Leito I. Tutorial review on validation of liquid chromatography–mass spectrometry methods: Part II. Anal. Chim. Acta, 2015, 870, 8-28;
5. E. Ciciri, B. Giussani, A. Pozzi, C. Dossi, S. Recchia, problems in the application of the three-step BCR sequential extraction to low amounts of sediments: An alternative validate route, Talanta, 2008, 76, 621-626
6. R. A. Sutherland, BCR®-701: A review of 10-years of sequential extraction analyses, Analytica Chimica Acta 680 (2010) 10–20
7. D. Ilieva, M. Argirova, L. Angelova, R. V. Gradinaru, G. Drochioiu, A. Surleva, Application of chemical and biological tests for estimation of current state of a tailing dump and surrounding soil from the region of Tarnița, Suceava, Romania, Environmental Science and Pollution Research (2020) 27:1386–1396
8. Lyudmila Angelova, Nezabravka Genova, Stiliyana Stoyanova, Olya Surleva, Ioan-Hristian Nekov, Darya Ilieva, Andriana Surleva, Comparative study of soil test methods for determination of plant available potassium in Bulgarian arable soils, Analytics and Control, 2021, 25 (3) pp. 182-192
9. L. Angelova, N. Genova, G. Pencheva, Y. Statkova, V. Yotova, A. Surleva, Contribution to the Molybdenum Blue Reaction and its Application in Soil Analysis, Methods and objects of chemical analysis, 2022, Vol. 17, No. 2, 59–69

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