Certificates of Analysis in the Magruder Program

February 2019
Frank J. Sikora

Magruder samples have a certificate of analysis (COA) available on the website by clicking on "COA" for each sample in the Reports section. An example of a COA is in the Appendix. The COA presents standard uncertainties for concentration of analytes in a sample. An explanation of standard uncertainty and the value of that information are presented here.

Standard uncertainty is different from robust standard deviation on the Magruder Analyte Reports. The robust standard deviation is a measure of the variability of all results submitted by laboratories. Approximately 67% of the results are within the robust mean ± robust standard deviation. Approximately 95% of the results are within the robust mean ± 2 × robust standard deviation. The standard uncertainty on COA reports is a measure of where the true analyte concentration is expected to be and is calculated using the robust standard deviation (robust stdev) and number of laboratory results (n) as shown below (ISO 13528:2015).

$$\text{Standard Uncertainty} = 1.25 \times \text{robust stdev} / \sqrt{n}$$

Since the number of laboratory results is in the denominator, the uncertainty becomes smaller as the number of laboratory results increase. In other words, there is greater certainty on the location of the true analyte concentration with an increased number of laboratory results. The COA reports only contain analyte uncertainties with 17 or more laboratory results.[1]

The standard uncertainty can be used to predict where the true concentration lies at different confidence intervals. A 67% confidence interval ranges from the robust mean – standard uncertainty and robust mean + standard uncertainty. An approximate 95% confidence interval ranges from the robust mean – (2 × standard uncertainty) and robust mean + (2 × standard uncertainty).

[1] Uncertainties for less than 17 laboratory results can be found on the Magruder Analyte Reports.

Some examples of robust standard deviation, standard uncertainty, and 95% confidence interval for true analyte concentration are shown for Magruder sample 180411 below.

Analyte	Robust Mean	Robust stdev	Standard Uncertainty	95% confidence interval
Total N (%)	11.81	0.23	0.03	11.74 to 11.89
Direct Available P as P2O5 (%)	25.16	0.72	0.12	24.86 to 25.46
Soluble K as K2O (%)	12.89	0.56	0.07	12.72 to 13.07
Total S (%)	1.161	0.11	0.022	1.106 to 1.216
Acid Soluble B (%)	0.05867	0.01380	0.00252	0.05237 to 0.06497

A laboratory can evaluate their laboratory bias using uncertainty in the Certificates of Analysis. Laboratory bias is one component of measurement uncertainty for an analytical method. Other components of measurement uncertainty include variability in preparing an analytical sample from the laboratory sample and reproducibility of results from the analytical sample. ISO 11532 and NORDTEST (2017) provide detailed information on how to use uncertainties from a proficiency test program to determine bias. If uncertainties of the proficiency test samples are too large, samples with smaller analyte uncertainties may be required such as Reference Materials obtained from an organization such as the National Institute of Standards and Technology (NIST, Standard Reference Materials).

REFERENCES

Eurachem/CITAC Guide: Quantifying Uncertainty in Analytical Measurement, 3rd, S.L.R. Ellison and A. Williams, eds. (2012). Available at www.eurachem.org.

ISO 11352. Water quality – Estimation of measurement uncertainty based on validation and quality control data. ISO 11352:2012(E).

ISO 13528. Statistical methods for use in proficiency testing by interlaboratory comparison. ISO 13528:2015(E).

NIST. Standard Reference Materials. www.nist.gov/srm

NORDTEST: Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories, Edition 4 (2017). Available at www.nordtest.info

APPENDIX

Association of American Plant Food Control Officials

MAGRUDER

Magruder Certificate of Analysis

Magruder Sample #180411
Grade 12-24-12

Analyte	Value	± Standard Uncertainty	# Labs
Ammoniacal Nitrogen (%)	8.335	0.054	37
Nitrate Nitrogen (%)	3.373	0.054	23
Total Nitrogen (12%)	11.81	0.03	86
Total Phosphorus as P2O5 (%)	25.76	0.13	56
Direct Available Phosphorus as P2O5 (24%)	25.16	0.12	57
Soluble Potassium as K2O (12%)	12.89	0.07	97
Acid Soluble Calcium (%)	4.334	0.091	19
Acid Soluble Magnesium (1.2%)	1.451	0.020	67
Total Sulfur (1%)	1.161	0.022	39
Acid Soluble Arsenic (ppm)	8.859	0.587	21
Acid Soluble Boron (0.04%)	0.05870	0.00250	47
Acid Soluble Cadmium (ppm)	3.058	0.217	24
Acid Soluble Chromium (ppm)	64.53	2.81	24
Acid Soluble Cobalt (ppm)	3.697	0.364	23
Acid Soluble Copper (%)	0.00080	0.00020	20
Acid Soluble Iron (%)	0.6252	0.0075	25
Acid Soluble Lead (ppm)	4.099	0.402	23
Acid Soluble Manganese (%)	0.01850	0.00040	23
Acid Soluble Molybdenum (ppm)	7.586	0.485	25
Acid Soluble Nickel (ppm)	15.23	0.88	25
Acid Soluble Zinc (0.02%)	0.02660	0.00070	58

1. Data obtained from participant results in the Magruder Check Sample Program.
2. Guaranteed concentrations noted by the value preceding the unit in Analyte name.
3. Values are robust means. Standard uncertainty determined as 1.25 x robust standard deviation / sqrt(#Labs). Results only shown for analytes tested by 16 or more labs. Values and uncertainties for analytes tested by less than 16 labs are available in Analyte Reports.
4. Technical information on Certificat of Analysis available at www.magrudercheckssample.org/prod/Articles.html