BRUKER

S1 TITAN

TRACER 5

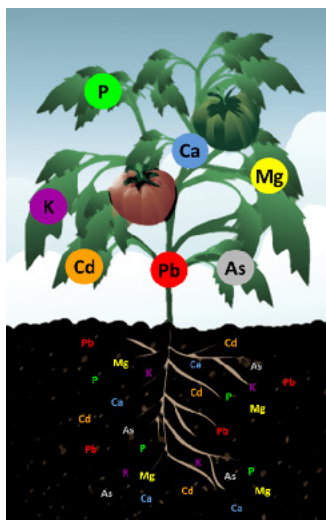Plant Calibration

CTX PXRF

Plant Cal Results

Application Note #1802a

Determination of Heavy Metals in Plants with Portable XRF

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Recent growth in the use of some plants for medical and recreational products, along with the confusion of state vs. U.S. federal legalization policies, has increased the need for the development of regulations to ensure safety and quality. Some of these plants, like hemp, are phytoremediators which can take up significant amounts of heavy metals like Pb, Cd, and As from the soil during growth. As the plant material can be concentrated during processing, levels of these toxins as a function of total mass grow and could reach dangerous levels, especially in oils and other highly concentrated final products.

Monitoring heavy metals in phytoremediating plants is an important step in ensuring the safety of the final products. Methods for detection of these elements in the plants require significant sample preparation and expensive equipment. ICP-MS (Inductively-Coupled Plasma Mass Spectrometry) is currently the standard method for measurement of heavy metals, and requires digestion of the sample in acid. Very low levels of metals can be measured with this method, usually below 1 ppm.

Some plants are phytoremediators which can take up significant amounts of heavy metals, like Pb, Cd and As, as well as nutrients from the soil.

Portable X-Ray Fluorescence (PXRF) can also be used to measure heavy metals, and can be used in the field, not just in the laboratory. Although this method can only measure concentrations above 1 ppm, it can be a useful screening tool to cut down on the amount of samples that need to be sent out for ICP-MS.

Portable XRF for Measuring Heavy Metals

A "Plants" calibration was developed for Bruker "TRACER 5" and "S1 TITAN" handheld XRF models, and "CTX" portable XRF model. This calibration can be used on plant material that has been crushed and dried with no further preparation. The material is packed into a sample cup and measured directly. The measurement time is generally 60-120 seconds.

Figure 1 shows the elements that can be measured with the calibration and their approximate limit of detection (LOD) in a TRACER 5i. LOD values for S1 TITAN and CTX will be similar. It should be noted that the LOD is an estimate of the lowest level that can be measured in the absence of "reality": if counting statistics were the only contributing factor to the error.

Element	LOD	Element	LOD
Mg	993	Ni	2
Al	119	Cu	1
Si	59	Zn	1
P	15	As	2
S	12	Se	2
Cl	24	Br	2
K	35	Rb	3
Ca	45	Sr	3
Ti	3	Mo	3
V	1	Cd	18
Cr	3	Ba	147
Mn	3	Hg	3
Fe	2	Pb	6

Figure 1. Measured elements and approximate LOD in a TRACER 5i

Overlapping elements and matrix effects are not taken into account when determining the LOD. Fortunately, in plants the cellulose matrix is non-interfering and the concentrations of interfering elements are so low that the LOD is a more reasonable estimate of measurable levels than in other applications.

Testing the Calibration on Plant Samples

Bruker partnered with Colorado State University at Pueblo (CSUP) to test the performance of the Plants calibration on real samples and to develop standards that can be used for testing and verification. CSUP created hemp-like samples with varying amounts of As, Pb, Cd, Cr, and Hg and compared ICP-MS results to the results from a Tracer 5i. The data are shown in Figure 2, including the ICP-MS values and their estimated uncertainty, the reported PXRF result, and the reported 2-sigma uncertainty on the PXRF measurement. Samples were shot for 60 seconds. Because statistical error is the major contributor to the uncertainty, longer measurement times could reduce the reported uncertainty.

This data can be viewed graphically as well. The correlation in graphical form for Pb and As is shown in Figure 3. These elements displayed good agreement between ICP-MS and XRF values. The standard deviation of three repeated shots at each level indicates the uncertainty in the precision of the XRF values. Cd showed a slightly larger spread in the XRF data, which corresponds with the reported statistical error. This suggests that longer measurement times may produce better precision.
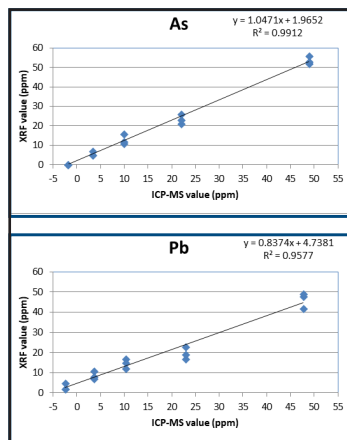
Element	ICP-MS Value (ppm)	Estimated Error (ppm)	PXRF Value (ppm)	Reported Error (ppm)
Hg	-3.0	0.12	0	2
Hg	3.3	0.04	4	2
Hg	12.0	0.11	8	2
Hg	20.7	0.20	14	2
Hg	48.9	0.51	31	2
As	-1.9	0.25	0	1
As	3.3	0.07	6	2
As	9.8	0.10	13	2
As	21.9	0.14	23	2
As	48.9	0.38	54	2
Cr	-2.9	0.07	1	2
Cr	3.1	0.06	4	2
Cr	10.5	0.20	5	2
Cr	24.2	0.13	6	2
Cr	47.1	0.54	17	2
Cd	-2.6	0.25	3	19
Cd	3.3	0.02	11	20
Cd	10.6	0.14	10	20
Cd	22.3	0.37	20	20
Cd	48.4	0.58	73	20
Pb	-2.5	0.09	3	5
Pb	3.6	0.07	9	5
Pb	10.3	0.31	15	5
Pb	22.9	0.35	20	5
Pb	47.6	1.1	46	5

Figure 2. CSUP reference samples data for PXRF correlation to ICP-MS values.

Conclusion

Portable XRF provides reasonable quantitative agreement with ICP-MS values for As and Pb. Good qualitative agreement was seen for Hg as well, but with a bias that can be corrected with type standardization. Figure 4 shows the type standardization calculation and corrected results, which show very good agreement with the ICP-MS results. For Cd, the reported error was so large that only qualitative conclusions could be made. Longer measurement times might reduce the error enough to enable a meaningful comparison. Cr showed a non-linear correlation, so further work will need to be done to allow Cr to be accurately measured.[1]

Note 1: Better detection limits for Cd have been demonstrated in spinach using very long measurement times and a customized setup on the TRACER 5i.

Figure 3. Regression curves of ICP-MS vs PXRF for arsenic (As) and lead (Pb) in plants.

As — $y = 1.0471x + 1.9652$, $R^2 = 0.9912$

Pb — $y = 0.8374x + 4.7381$, $R^2 = 0.9577$

Line Fit	Hg
Slope	1.6700
Offset	-2.6406
Correlation	99.9%

Reference Values	S1 Meas. Results	Adjusted S1 Result
-3.0	0	-2.641
3.3	4	4.039
12.0	8	10.720
20.7	14	20.740
48.9	31	49.130

Figure 4. PXRF mercury (Hg) type standardization calculation for plants calibration to ICP-MS.

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