

ICP - Mass Spectrometry

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The Elemental Analysis of Grains with the NexION 300/350 ICP-MS

Introduction

Trace elemental analysis of grains can provide associations between air pollution sources and soil variables. The

elements themselves are distributed unevenly throughout the cereal grain, with the germ and the outer layers having the highest concentrations. Therefore, the elemental analysis requires the ability to measure both trace and high levels.

The elemental capabilities and dynamic range of inductively coupled plasma mass spectrometry (ICP-MS) make it ideally suited for the analysis of food materials. The ultratrace detection limits of ICP-MS permit the determination of low-level contaminants, such as Pb, As, Se, and Hg, while the macro-level nutritional elements, such as Ca, Mg, K, and Na, can be quantified using the extended dynamic range capability of ICP-MS which provides the ability to measure concentrations over nine orders of magnitude. However, there are still a number of challenges to overcome, including complex sample matrices, high levels of dissolved solids, and interferences. With the proper ICP-MS instrumental conditions and design, all of these issues can be overcome, allowing for the successful analysis of food samples, as described elsewhere¹. This work will focus on the analysis of grains.

Experimental

Sample Preparation

NIST® 8433 Corn Bran and NIST® 8436 Wheat Flour were used in this work. Approximately 0.5-0.6 g were digested in duplicate with 5 mL of nitric acid (Fisher Scientific™, Optima grade) and 2 mL of hydrogen peroxide (Fisher Scientific™, Optima grade) in pre-cleaned PTFE microwave sample vessels. The digestion program consisted of 30 min of heating and 15 min of cooling, as shown in Table 1. All samples were completely dissolved, resulting in clear solutions that were diluted to a final volume of 50 mL with deionized water. No further sample dilutions were necessary. Gold was added to all solutions at a final concentration of 200 µg/L to stabilize mercury. Preparation blanks, consisting of the acid mixture, were taken through the same microwave digestion program as the samples.

Table 1. Microwave Digestion Program.

Step	Power (W)	Ramp (min)	Hold (min)
1	500	1	4
2	1000	5	5
3	1400	5	10
4 (cooling)	0	—	15

Instrumental Conditions

All data in this study were generated under normal operating conditions on a PerkinElmer NexION® 300/350X ICP-MS using an autosampler. The instrumental operating conditions are shown in Table 2.

Table 2. ICP-MS Instrumental Operating Conditions for this Application.

Parameter	Value
Nebulizer	Glass concentric
Spray chamber	Glass cyclonic
Cones	Nickel
Plasma gas flow	18.0 L/min
Auxiliary gas flow	1.2 L/min
Nebulizer gas flow	0.98 L/min
Sample uptake rate	300 µL/min
RF power	1600 W
Total integration time	0.5 (1.5 seconds for As, Se, Hg)
Replicates per sample	3
Universal Cell Technology™*	Collision mode

*PerkinElmer, Inc.

Calibration

Multielement calibration standards, representing all the analytes in the SRM, were made up from PerkinElmer Pure single and multielement standards and diluted into 10% HNO₃. Gold was added to all solutions at a final concentration of 200 µg/L to stabilize mercury. Calibration standard ranges were based on whether the analyte was expected to be a high-level nutritional element like potassium (K) or sodium (Na), low/medium-level essential element like manganese (Mn) or iron (Fe), or trace/ultratrace contaminant such as lead (Pb) or mercury (Hg).

Depending on the certified value of the analytes, five different calibration ranges were made up to cover the complete range of elements being determined:

- High-level nutritional analytes: 0-300 ppm
- Medium-level essential analytes: 0-20 ppm
- Low-level essential analytes: 0-2 ppm
- Trace-level contaminants: 0-200 ppb
- Ultratrace-level contaminants: 0-20 ppb

Figures 1 to 5 show representative calibration curves for each range.

In addition to the analyte elements used for the multielement calibration, the standards, blanks, and samples were also spiked on-line using a mixing tee with a solution of ⁶Li, Sc, Ge, In, and Tb for internal standardization across the full mass range. Acetic acid was added to the internal standard solution to compensate for residual carbon left over from the sample digestion.

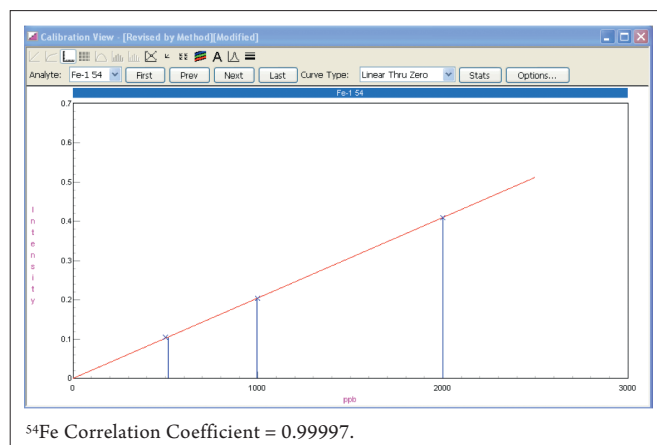


Figure 1. Calibration curves for ⁵⁴Fe (0-2 ppm).

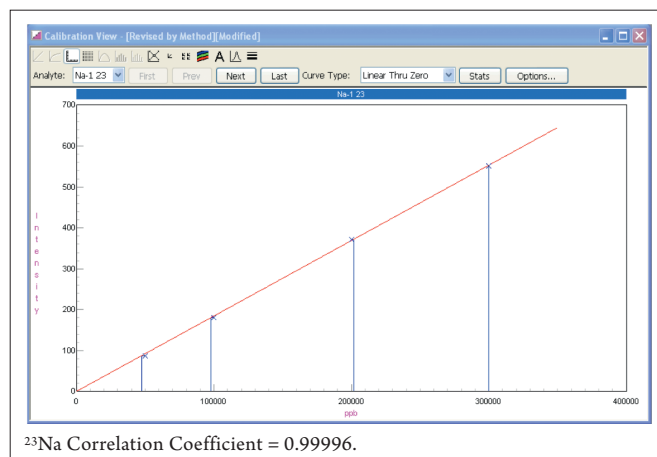


Figure 2. Calibration curve for ²³Na (0-300 ppm).

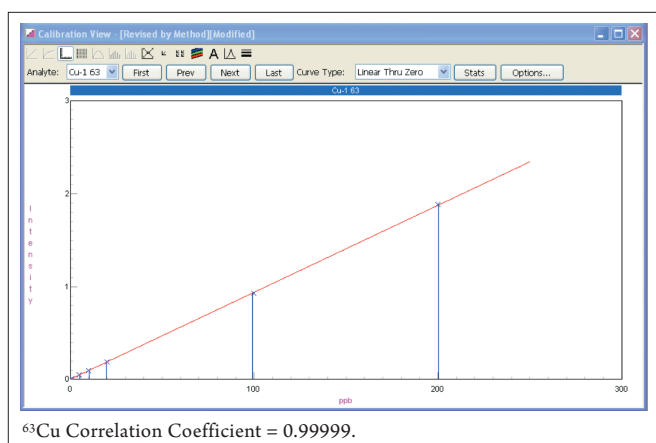


Figure 3. Calibration curve for ^{63}Cu (0-200 ppb).

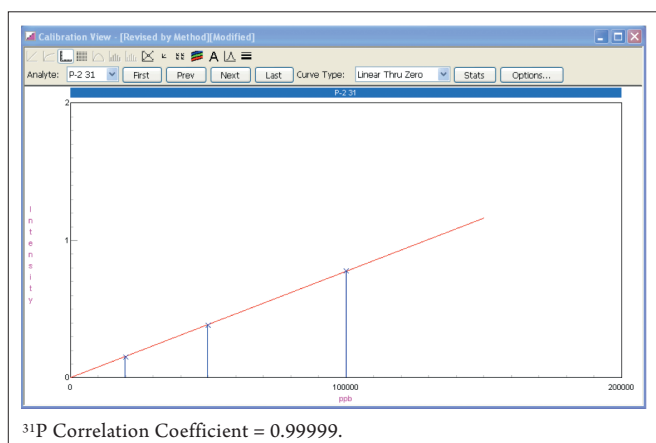


Figure 4. Calibration curve for ^{31}P (0-100 ppm).

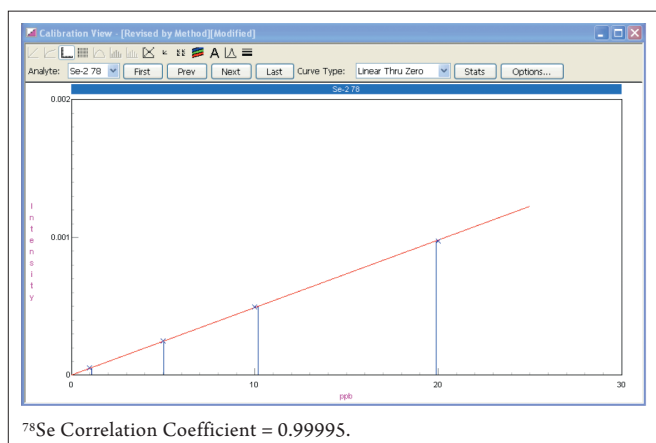


Figure 5. Calibration curve for ^{78}Se (0-20 ppb).

Results

Quantitative results for two sample preparations of the NIST® 8436 Wheat Flour and NIST® 8433 Corn Bran reference materials are shown in Tables 3 and 4. All elements in every sample were determined with Universal Cell operating in Collision mode using helium as the cell gas. Figures in parentheses () in the Reference Value column are not certified values but are included for information purposes only. The data show very good agreement with the certified values, especially for the elements that suffer from known spectral interferences. The elements that are outside the specified limits are mostly the ones that are well recognized as environmental contaminants, which have most likely been impacted by the sample preparation procedure.

Table 3. Analysis of NIST® 8436 Wheat Flour using the NexION 300/350 ICP-MS.

Element	Mass (amu)	Reference Value (mg/kg)	Experimental Value (mg/kg)
B	11	—	0.62
Na	23	16.0±6.1	17.0
Mg	26	1070±80	1030
Al	27	11.7±4.7	11.8
P	31	2900±220	2330
S	34	1930±280	1460
K	39	3180±140	2950
Ca	44	278±26	262
V	51	0.021±0.006	0.026
Cr	52	0.023±0.009	0.053
Fe	54	41.5 ±4.0	41.4
Mn	55	16.0±1.0	15.1
Co	59	0.008±0.004	0.007
Ni	60	0.17±0.08	0.17
Cu	63	4.30±0.69	4.18
Zn	66	22.2±1.7	20.6
As	75	(0.03)	0.01
Se	78	1.23±0.09	1.22
Sr	88	1.19±0.09	1.19
Mo	98	0.70±0.12	0.72
Cd	111	0.11±0.05	0.11
Sn	118	—	0.032
Sb	121	—	0.002
Ba	137	2.11±0.47	2.04
Hg	202	0.0004±0.0002	<0.0007
Pb	208	0.023±0.006	0.35
Tl	205	—	<0.0001
Th	232	—	0.001
U	238	—	0.001

Table 4. Analysis of NIST® 8433 Corn Bran using the NexION 300/350 ICP-MS.

Element	Mass (amu)	Reference Value (mg/kg)	Experimental Value (mg/kg)
B	11	2.8±1.2	3.2
Na	23	430±31	399
Mg	26	818±59	787
Al	27	1.01±0.55	1.15
P	31	171±11	158
S	34	860±150	738
K	39	566±75	548
Ca	44	420±38	434
V	51	0.005±0.002	0.005
Cr	52	(0.11)	0.08
Fe	54	14.8±1.8	13.7
Mn	55	2.55±0.29	2.53
Co	59	(0.006)	0.005
Ni	60	0.158±0.054	0.143
Cu	63	2.47±0.40	2.54
Zn	66	18.6±2.2	17.0
As	75	(0.002)	<0.006
Se	78	0.045±0.008	0.056
Sr	88	4.62±0.56	4.56
Mo	98	0.252±0.039	0.255
Cd	111	0.012±0.005	0.013
Sn	118	—	0.015
Sb	121	(0.004)	0.003
Ba	137	2.40±0.52	2.26
Hg	202	0.003±0.001	0.005
Pb	208	0.140±0.034	0.122
Tl	205	—	<0.0001
Th	232	—	<0.00008
U	238	—	<0.00002

Conclusion

This work has demonstrated the ability of PerkinElmer's NexION 300/350X ICP-MS to effectively measure macro-level nutritional elements in the same analysis run as lower-level elements, without having to dilute the samples. The agreement between experimental and certified results for NIST® 8436 Wheat Flour and NIST® 8433 Corn Bran demonstrates the accuracy of the analysis. Instrument design characteristics eliminate deposition on the ion optics, leading to long-term stability in high-matrix samples, while permitting trace levels to be accurately measured.

References

1. "The Determination of Toxic, Essential, and Nutritional Elements in Food Matrices Using the NexION 300/350 ICP-MS", PerkinElmer Application Note.