APPLICATION NOTE

ICP – Mass Spectrometry

Authors:

Cynthia Bosnak
Senior Product Specialist

Ewa Pruszkowski
Senior Product Specialist

PerkinElmer, Inc.
Shelton, CT USA

The Determination of Toxic, Essential, and Nutritional Elements in Food Matrices Using the NexION 300/350 ICP-MS

Introduction

The elemental and dynamic range of inductively coupled plasma-mass spectrometry (ICP-MS) makes 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 9-orders of magnitude. However, there are still a number of challenges to overcome, which makes the routine analysis of foods difficult unless the sample dissolution procedure is well thought out and instrumental conditions are optimized for complex sample matrices.

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For example, the wide variety of edible products available means that a highly diverse range of matrices must be brought into solution for ICP-MS analysis. These complex acid-digested matrices, which are a combination of dissolved carbohydrates, fats, and proteins, can pose major problems for any ICP-MS because of the potential for blocking of the interface cones and/or deposition on the quadrupole ion deflector (QID). For this reason, if instrument design does not account for high-matrix samples, long-term stability can be severely compromised.

In addition to signal drift, digested food matrices can also cause major spectral complications. The sample's organic components, together with macro minerals, can combine with elements present in the digestion acid and/or the plasma argon to form polyatomic interferences. For example, chloride ions (at mass 35) combine with the major argon isotope (mass 40) to produce the argon chloride interference $^{40}Ar^{35}Cl^+$, which interferes with arsenic at mass 75. Another example is the argon dimer ($ArAr^+$), which forms from the plasma gas and exists at the same masses as the major selenium isotopes. In addition, the major isotope of chromium at mass 52 is overlapped by $^{40}Ar^{12}C^+$, $^{35}Cl^{17}O^+$, and $^{35}Cl^{16}OH^+$ interferences generated by the sample matrix and the plasma gas. As a result, these kinds of spectral interferences have made the determination of both trace and macro elements in food samples extremely challenging.

To overcome these issues, a NexION® 300X ICP-MS (PerkinElmer, Inc., Shelton, CT) was used for the analysis of various food substances, focusing on toxic and typical essential and macro elements in a group of NIST® (Gaithersburg, MD) standard reference materials (SRMs).

Experimental

Six different NIST® SRM food samples that represent a typical cross-section of the types of foods for human consumption were chosen for the evaluation. The foods included spinach leaves (leafy vegetable), corn bran (grain), wheat flour (grain), bovine muscle (meat), mussel tissue (shellfish), and milk powder (dairy product). The samples were brought into solution with a Multiwave™ 3000 microwave digestion system. Details of the sample digestion procedure are shown in Table 1.

Sample Preparation

Approximately 0.5-0.6 g of each SRM was digested in duplicate with 5 mL of nitric acid (Fisher Optima HNO_3) and 2 mL of hydrogen peroxide (Fisher Optima H_2O_2) in precleaned PTFE HF-100 microwave sample vessels. The filled vessels were placed on a 16-position rotor with an internal p/T sensor positioned in one of the samples to monitor the pressure and temperature inside the sample container. In addition, an external IR sensor provided the temperatures for each individual sample in the tray. The digestion program consisted of 30 min of heating and 15 min of cooling, as shown in Table 1. All the SRM 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 Heating Program for All Six NIST® Food SRMs.**

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 NexION 300X ICP-MS using an autosampler. The instrumental operating conditions are shown in Table 2.

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

Component/Parameter	Type/Value/Mode
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)
No. of replicates per sample	3
Universal Cell Technology™*	KED mode

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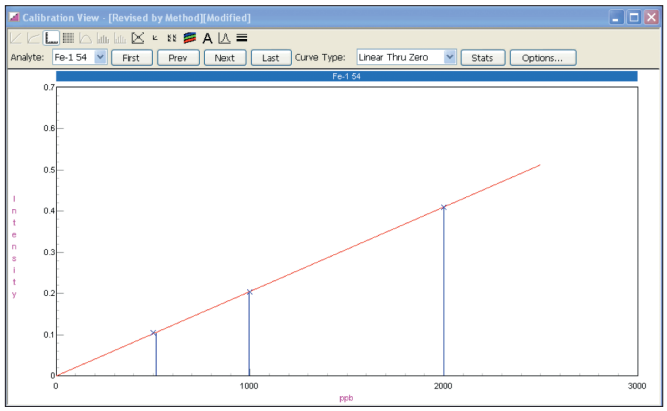
Calibration

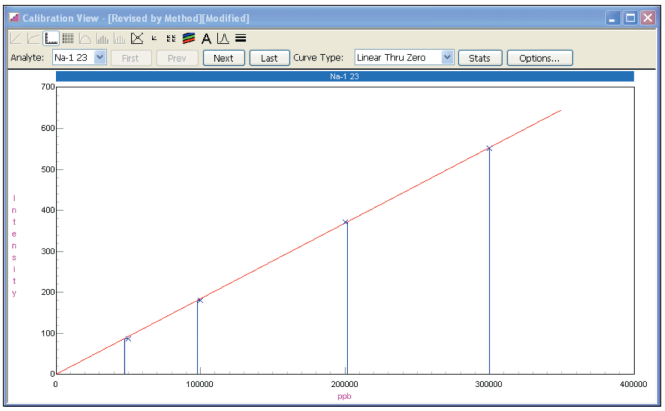
Multielement calibration standards, representing all the analytes covered by the six NIST® SRMs, were made up from PerkinElmer® Pure single and multielement standards and diluted into 10% HNO_3. Gold was added to all solutions at a final concentration of 200 µg/L to stabilize mercury. However, it is important to mention that each food SRM was certified for a slightly different group of elements. For that reason, quantitation was only carried out on the analytes that had reference values. Calibration standard ranges were based on whether the analyte was expected to be a high-level, nutritional element like potassium (K) or sodium (Na), a low/medium-level essential element like manganese (Mn) or iron (Fe), or a trace/ultratrace contaminant such as lead (Pb) or mercury (Hg). Depending on the certificate value of the analytes, five different calibration ranges were made up to cover the complete range of elements being determined. They were:

- 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

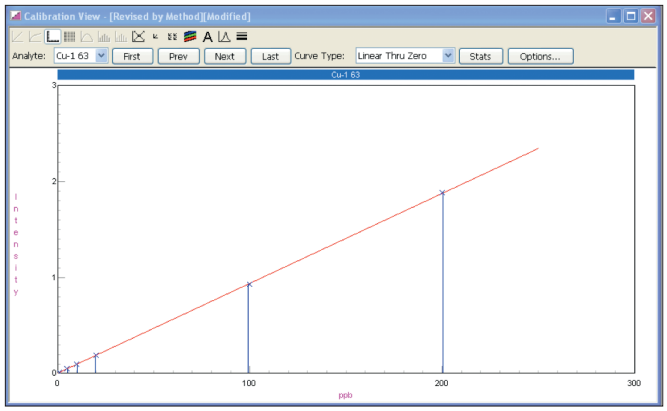
Figure 1 shows representative calibration curves for each range.



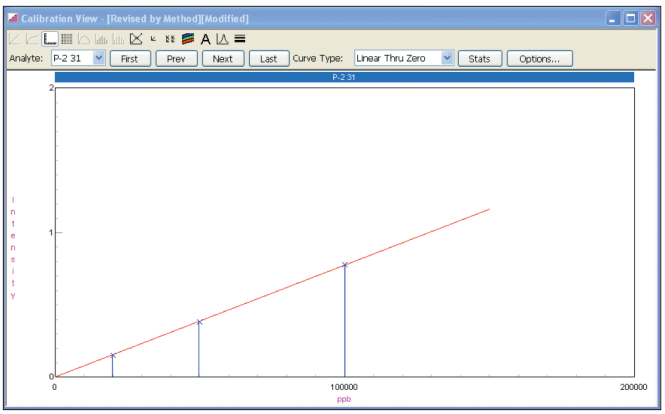
^{54}Fe Correlation Coefficient = 0.99997.



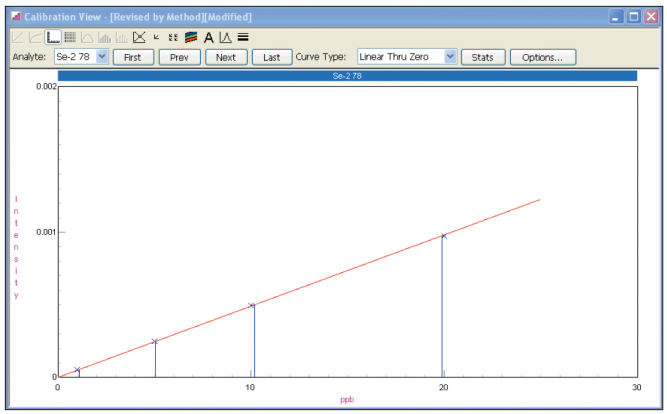
^{23}Na Correlation Coefficient = 0.99996.



^{63}Cu Correlation Coefficient = 0.99999.



^{31}P Correlation Coefficient = 0.99999.



^{78}Se Correlation Coefficient = 0.99995.

Figure 1. Calibration curves for ^{23}Na (0-300 ppm), ^{31}P (0-20 ppm), ^{54}Fe (0-2 ppm), ^{63}Cu (0-200 ppb) and ^{78}Se (0-20 ppb).

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 ^{6}Li, 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 leftover from the sample digestion.

Results

Quantitative results for two sample preparations of six NIST® SRMs (Corn Bran, Bovine Muscle, Mussel Tissue, Milk Powder, Wheat Flour, and Spinach Leaves) are shown in Tables 3-8, respectively. All elements in every sample were determined with kinetic energy discrimination (KED) mode using helium as the collision 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 probably been impacted by the sample preparation procedure.

Food samples are complex acid-digested matrices and can create major problems for some ICP-MS systems because of deposits on the interface cones and on the ion optics caused from high concentrations of dissolved solids. For this reason, long-term stability can be poor. However, the triple cone interface and the quadrupole ion deflector design of the NexION guarantee exceptional long-term stability. For six hours, food samples with high concentrations of dissolved solids were analyzed and a quality control (QC) sample was read every 5 samples. Figure 2 shows the long-term stability over 6 hours.

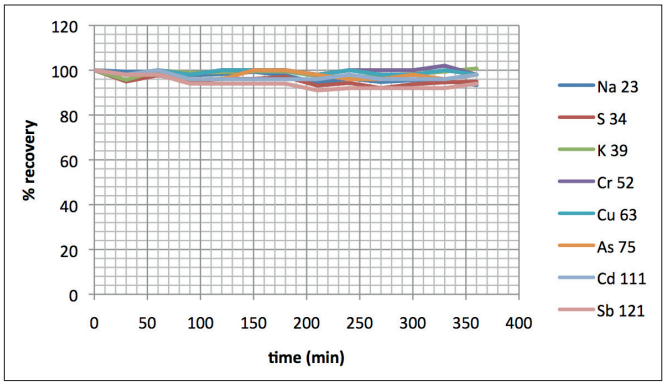


Figure 2. % Recovery of several analytes in the QC standard during 6-hour analysis.

Conclusion

The ICP-MS system used in this study is well suited for the analysis of complex digested food materials. The agreement between experimental and certified results for six NIST® food SRMs demonstrates that the NexION 300X ICP-MS can effectively measure various food samples. In addition to removing interferences, the NexION 300X allows the determination of macro-level nutritional elements in the same analysis run as lower-level elements, without having to dilute the samples. 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.

Table 3. **Analysis of NIST® 8433 Corn Bran using the NexION 300 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

Table 4. **Analysis of NIST® 8414 Bovine Muscle using the NexION 300 ICP-MS.**

Element	Mass (amu)	Reference Value (mg/kg)	Experimental Value (mg/kg)
B	11	0.6 ±0.4	0.4
Na	23	2100 ±80	2000
Mg	26	960 ±95	960
Al	27	1.7 ±1.4	1.6
P	31	8360 ±450	7250
S	34	7950 ±410	6820
K	39	15170 ±370	14180
Ca	44	145 ±20	143
V	51	(0.005)	0.006
Cr	52	0.071 ±0.038	0.092
Fe	54	71.2 ±9.2	71.2
Mn	55	0.37 ±0.09	0.44
Co	59	0.007 ±0.003	0.014
Ni	60	0.05 ±0.04	0.05
Cu	63	2.84 ±0.45	2.81
Zn	66	142 ±14	140
As	75	0.009 ±0.003	0.011
Se	78	0.076 ±0.010	0.11
Sr	88	0.052 ±0.015	0.081
Mo	98	0.08 ±0.06	0.08
Cd	111	0.013 ±0.011	0.013
Sn	118	–	0.14
Sb	121	(0.01)	0.01
Ba	137	(0.05)	0.04
Hg	202	0.005 ±0.003	0.003
Pb	208	0.38 ±0.24	0.34
Tl	205	–	0.002
Th	232	–	<0.00008
U	238	–	<0.00002

Table 5. **Analysis of NIST® 2976 Mussel Tissue using the NexION 300 ICP-MS.**

Element	Mass (amu)	Reference Value (mg/kg)	Experimental Value (mg/kg)
B	11	–	27.5
Na	23	(35000 ±1000)	35000
Mg	26	(5300 ±500)	4800
Al	27	(134 ±34)	149
P	31	(8300)	6900
S	34	(19000)	16000
K	39	(9700 ±500)	9700
Ca	44	(7600 ±300)	7400
V	51	–	0.87
Cr	52	(0.50 ±0.16)	0.50
Fe	54	171.0 ±4.9	190
Mn	55	(33 ±2)	40
Co	59	(0.61 ±0.02)	0.67
Ni	60	(0.93 ±0.12)	0.87
Cu	63	4.02 ±0.33	3.91
Zn	66	137 ±13	145
As	75	13.3 ±1.8	16.4
Se	78	1.80 ±0.15	2.52
Sr	88	(93 ±2)	79
Mo	98	–	0.56
Cd	111	0.82 ±0.16	0.88
Sn	118	(0.096 ±0.039)	0.103
Sb	121	–	0.011
Ba	137	–	0.61
Hg	202	0.061 ±0.0036	0.058
Pb	208	1.19 ±0.18	1.06
Tl	205	(0.0013)	0.003
Th	232	(0.011 ±0.002)	0.012
U	238	–	0.22

Table 6. **Analysis of NIST® 1549 Milk Powder using the NexION 300 ICP-MS.**

Element	Mass (amu)	Reference Value (mg/kg)	Experimental Value (mg/kg)
B	11	–	2.1
Na	23	4970 ±100	4700
Mg	26	1200 ±30	1170
Al	27	(2)	0.7
P	31	10600 ±200	10500
S	34	3510 ±50	3290
K	39	16900 ±300	16500
Ca	44	13000 ±500	12800
V	51	–	0.003
Cr	52	0.0026 ±0.0007	<0.003
Fe	54	1.78 ±0.10	1.98
Mn	55	0.26 ±0.06	0.26
Co	59	(0.0041)	0.005
Ni	60	–	0.013
Cu	63	0.7 ±0.1	0.6
Zn	66	46.1 ±2.2	46.7
As	75	(0.0019)	<0.006
Se	78	0.11 ±0.01	0.17
Sr	88	–	3.7
Mo	98	(0.34)	0.37
Cd	111	0.0005 ±0.0002	<0.002
Sn	118	–	<0.002
Sb	121	(0.00027)	<0.001
Ba	137	–	0.83
Hg	202	0.0003 ±0.0002	<0.0007
Pb	208	0.019 ±0.003	0.019
Tl	205	–	<0.0001
Th	232	–	<0.00008
U	238	–	<0.00002

Table 7. **Analysis of NIST® 8436 Wheat Flour using the NexION 300 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 8. **Analysis of NIST® 1570a Spinach using the NexION 300 ICP-MS.**

Element	Mass (amu)	Reference Value (mg/kg)	Experimental Value (mg/kg)
B	11	37.6 ±1.0	37.3
Na	23	18180 ±430	17350
Mg	26	(8900)	8600
Al	27	310 ±11	200
P	31	5180 ±110	4810
S	34	(4600)	4400
K	39	29030 ±520	26600
Ca	44	15270 ±410	15040
V	51	0.57 ±0.03	0.58
Cr	52	–	1.63
Fe	54	–	265
Mn	55	75.9 ±1.9	77.9
Co	59	0.39 ±0.05	0.37
Ni	60	2.14 ±0.10	1.97
Cu	63	12.2 ±0.6	11.6
Zn	66	82 ±3	80
As	75	0.068 ±0.012	0.081
Se	78	0.117 ±0.009	0.21
Sr	88	55.6 ±0.8	58.1
Mo	98	–	0.39
Cd	111	2.89 ±0.07	2.83
Sn	118	–	0.027
Sb	121	–	0.007
Ba	137	–	5.8
Hg	202	0.030 ±0.003	0.028
Pb	208	(0.20)	0.16
Tl	205	–	0.018
Th	232	0.048 ±0.003	0.045
U	238	(0.155 ±0.023)	0.154

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

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