# Enhancing the productivity of food sample analysis with ICP-MS

## Application note

Foods testing

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Verified for Agilent
**7800 ICP-MS**

## Introduction

To ensure food safety and safeguard human health, the characterization of the elemental composition of a wide range of food types is required. Since the concentration ranges for different elements vary significantly across different foods, various techniques have been used for sample characterization. In this work, we investigated the possibility of measuring all the required elements with a single configuration using an Agilent ICP-MS. The determination of trace and major elements simultaneously is possible, in part, due to the detector providing 9 orders of magnitude for the Agilent 7700 ICP-MS and 10 orders for the Agilent 7800 ICP-MS.

Interferences generated by the plasma and the sample matrix present another challenge in food analysis. In this study, we investigated the use of a single cell gas, helium, to eliminate those interferences.

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We also evaluated the use of a discrete sampling system to increase sample throughput. The Agilent ISIS-DS discrete sampling system was evaluated for its ability to reduce analysis times by minimizing uptake and washout time during the analytical run.

## Experimental

### Standard and sample preparation
Four certified reference materials (CRMs) were analyzed as part of this work. These included NIST SRM 1548a (Typical Diet, US), NIST SRM 2976 (Mussel Tissue), NRC DORM3 (Fish Tissue, Canada) and NIST SRM 8415 (Whole Egg). 250 mg of each CRM sample was digested with 3 mL of nitric acid and 1 mL of hydrogen peroxide using a microwave device (program details are listed in Table 1). The digested samples were made up to 50 mL with DI water. The resulting samples contained up to 5 g/L of matrix. Standards for calibration were prepared from 1 to 50 µg/L (100x more concentrated for the major elements) and from 0.5 to 5 µg/L for mercury by diluting multi-element solutions with 6% $HNO_3$/0.5% HCl. No matrix matching of the standards to the samples was necessary.

Table 1. Detailed program for the microwave digestion of the food CRM samples

| Step | Time (min) | Power (W) |
|---|---|---|
| 1 | 10 | 280 |
| 2 | 5 | 0 |
| 3 | 10 | 550 |
| 4 | 5 | 0 |
| 5 | 6 | 720 |
| 6 | 7 | 0 |
| 7 | 10 | 280 |

### Instrumentation
An Agilent 7700x ICP-MS featuring the 3rd generation Octopole Reaction System (ORS[3]) and fitted with a standard sample introduction system (MicroMist glass concentric nebulizer, a quartz Peltier-cooled spray chamber, and quartz torch with 2.5 mm internal diameter injector) was used for all measurements. The oxide ratio was set at 0.8% ($CeO^+/Ce^+$) resulting in excellent sample decomposition in the plasma and

minimum matrix effects. For interference suppression, the ORS[3] was operated in helium collision mode (He mode) only, which is effective at removing a wide range of plasma and matrix-based polyatomic species using kinetic energy discrimination (KED). Instrument operating conditions are summarized in Table 2.

Table 2. Agilent 7700x ICP-MS operating parameters

| Parameter | Value |
|---|---|
| Plasma power | 1550 W |
| Plasma gas flow rate | 15.0 L/min |
| Auxiliary gas flow rate | 1.0 L/min |
| Carrier gas flow rate | 0.89 L/min |
| Dilution gas flow rate | 0.15 L/min |
| Sample depth | 8.0 mm |
| Spray chamber temperature | 2 °C |
| KED | 3 V |
| Helium gas flow rate | 4.5 mL/min |

Helium mode provides several critical advantages for food analysis when compared to reactive cell gases.

- He mode effectively removes all polyatomic interferences, not just reactive polyatomics.

- Since He is inert, no new interferences are produced, regardless of the matrix.

- Unlike a reactive cell gas, He does not react with any analytes, so consistent and predictable sensitivity is maintained.

Elements that do not suffer from polyatomic interferences can be analyzed with He mode as well. But to achieve better limits of detection, they were analyzed with no gas in the cell (no gas mode). During analysis of a sample, the system automatically switches between no gas and He mode as needed, thereby permitting the measurement all elements under optimum conditions without the need for multiple analyses for a given sample. The transition time needed for switching modes is very rapid (~5 seconds), so high throughput is not significantly impacted.

## ISIS-DS discrete sampling system

Figure 1 shows the basic operation of the Agilent ISIS-DS system, which was employed to improve the throughput after the initial method was developed. The sample is rapidly drawn into the sample loop using the high speed ISIS pump (P1), while blank carrier with online internal standards is constantly pumped to the nebulizer (P2). Rotation of the 6-port valve then diverts the carrier through the loop, pushing the sample ahead of it to the nebulizer. At the same time, the autosampler probe goes to rinse position and begins rinsing before the next sample. ISIS-DS provides several benefits for this analysis:

- Sample uptake and rinse-out times are significantly reduced, resulting in very fast analysis times.

- The total exposure of the ICP-MS cones and lenses to the sample matrix is minimized, resulting in extended longterm stability.

- Carryover is reduced due to the elimination of peristaltic pump tubing from the sample path.

- Sample introduction system maintenance and cleaning are reduced.
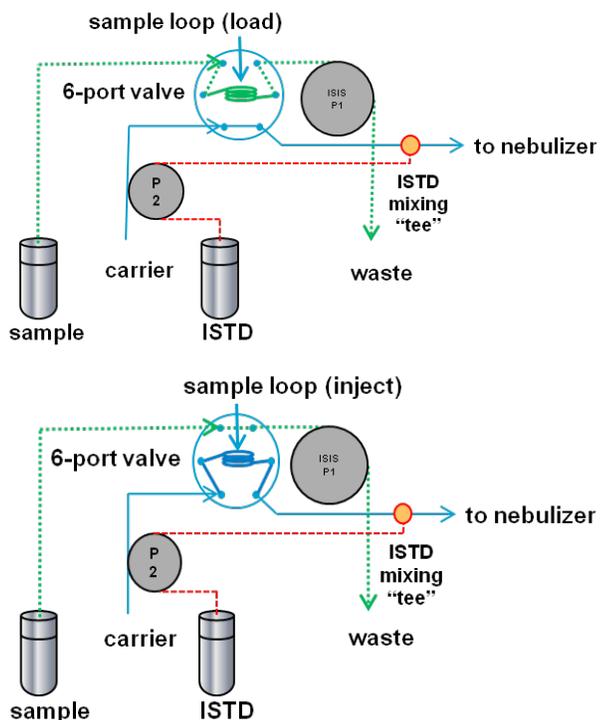


**Figure 1.** Details of the function of the Agilent ISIS-DS discrete sampling device

## Results and discussion

### Calibration

Table 3 shows the details obtained from the calibration curves, and Figure 2 shows the calibration curves obtained for a typical selection of elements. The major elements (Ca, K, Mg, Na) were calibrated up to 5 mg/L, while the trace elements were measured up to 50 µg/L. This figure underlines the sensitivity of the system, with detection limits at the ng/L level (ppt).

**Table 3.** Details of the calibration curves. R represents the coefficient of linearity. DL is the detection limit calculated as 3 sigma of the blank.

| Mass | Element | Tune step | R | DL (ppb) |
|------|---------|-----------|---------|----------|
| 23 | Na | He | 0.99998 | 0.16 |
| 24 | Mg | He | 0.99991 | 0.031 |
| 27 | Al | He | 0.99987 | 0.23 |
| 39 | K | He | 0.99989 | 1.8 |
| 44 | Ca | He | 0.99999 | 5.7 |
| 47 | Ti | He | 0.99975 | 0.041 |
| 51 | V | He | 0.99985 | 0.013 |
| 52 | Cr | He | 0.99992 | 0.0038 |
| 55 | Mn | He | 0.99991 | 0.0018 |
| 56 | Fe | He | 0.99996 | 0.021 |
| 59 | Co | He | 0.99997 | 0.0014 |
| 60 | Ni | He | 0.99996 | 0.0039 |
| 63 | Cu | He | 0.99997 | 0.103 |
| 66 | Zn | He | 0.99989 | 0.017 |
| 75 | As | He | 0.99983 | 0.0084 |
| 78 | Se | He | 0.99979 | 0.038 |
| 95 | Mo | No gas | 0.99998 | 0.0022 |
| 107 | Ag | No gas | 1.00000 | 0.016 |
| 111 | Cd | No gas | 1.00000 | 0.0007 |
| 118 | Sn | No gas | 1.00000 | 0.0028 |
| 121 | Sb | No gas | 0.99999 | 0.0005 |
| 137 | Ba | No gas | 1.00000 | 0.0020 |
| 201 | Hg | No gas | 0.99960 | 0.0030 |
| 208 | Pb | No gas | 1.00000 | 0.0013 |
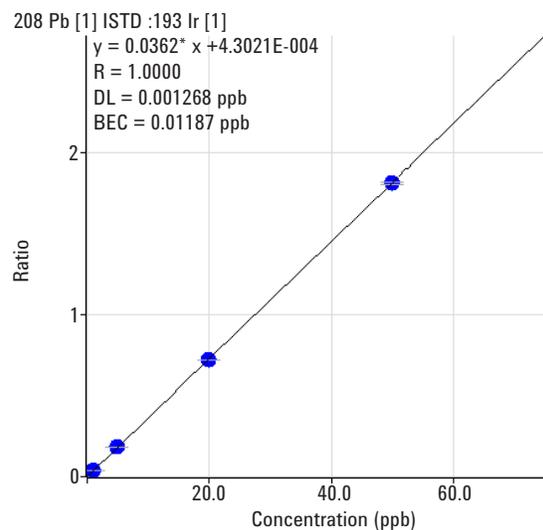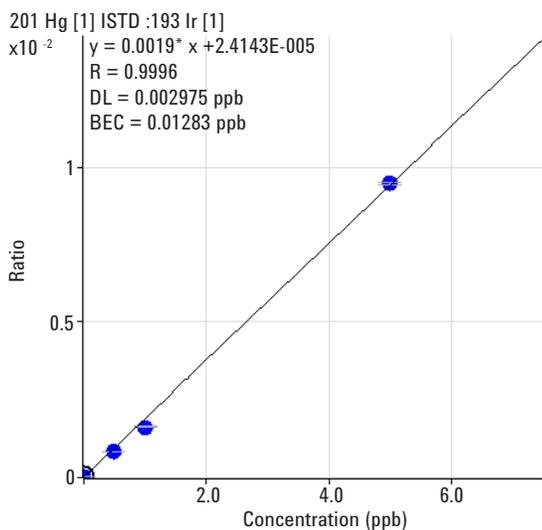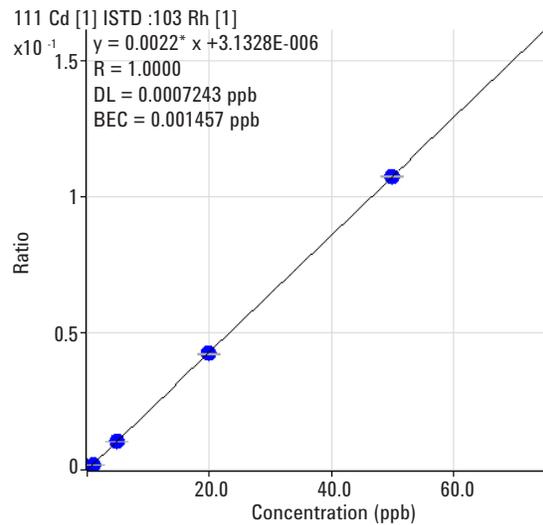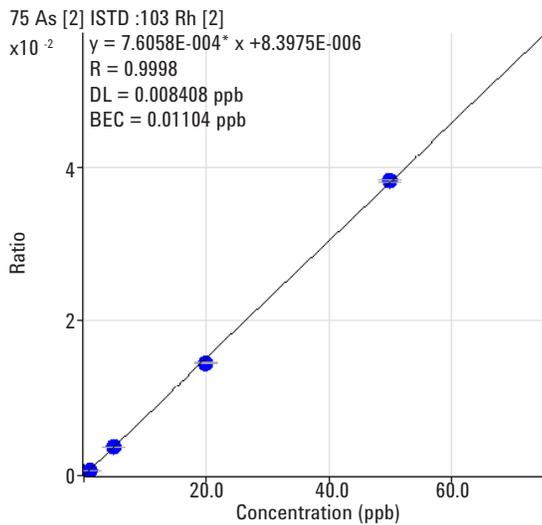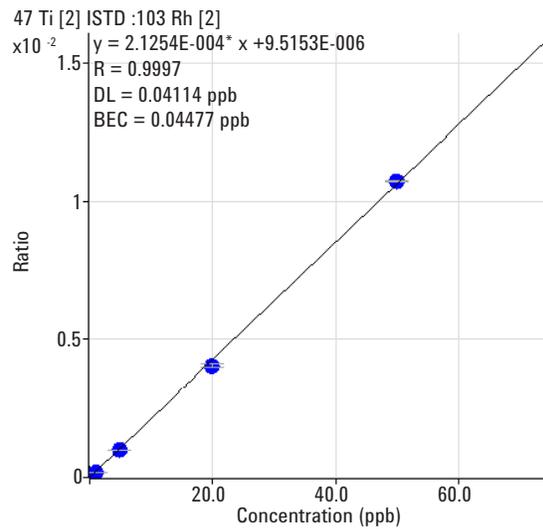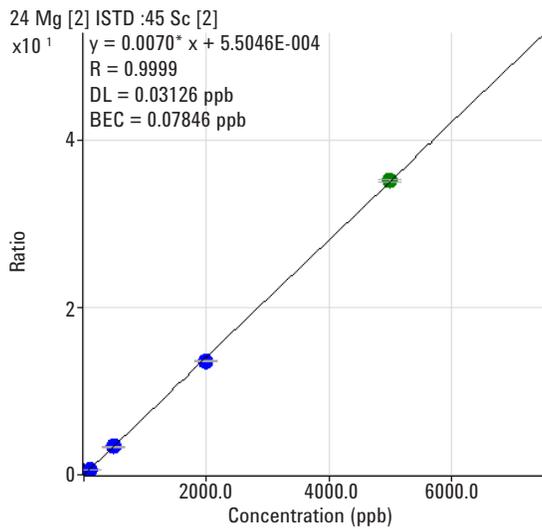
**Figure 2.** Typical calibration curves obtained during the analysis of the food CRM samples

**Interference suppression**

Initial measurements were made in order to evaluate the effectiveness of using He mode alone to manage interferences. Multiple isotopes, where available, were monitored and compared for each element in the reference materials. The results are given in Table 4.

**Table 4.** Comparison of measured concentrations between isotopes of the same element (µg/L)

|  | DORM3 | SRM2976 | SRM8415 | SRM1548a |
|---|---|---|---|---|
| 24  Mg | 2781.99 | 22407.90 | 1501.30 | 2717.79 |
| 26  Mg | 2749.48 | 23311.89 | 1531.20 | 2660.32 |
| Difference (%) | 1 | -4 | -2 | 2 |
| 43  Ca | 6249.01 | 35189.24 | 10744.70 | 7489.41 |
| 44  Ca | 6511.34 | 34589.19 | 11192.78 | 7532.89 |
| Difference (%) | -4 | 2 | -4 | -1 |
| 47  Ti | 142.90 | 21.38 | 43.91 | 10.91 |
| 49  Ti | 152.40 | 22.49 | 42.85 | 11.40 |
| Difference (%) | -7 | -5 | 2 | -5 |
| 52  Cr | 6.72 | 2.65 | 2.16 | 0.57 |
| 53  Cr | 6.74 | 2.58 | 1.99 | 0.42 |
| Difference (%) | 0 | 3 | 8 | 27 |
| 56  Fe | 1150.83 | 990.14 | 576.99 | 182.53 |
| 57  Fe | 1109.94 | 966.56 | 564.96 | 180.04 |
| Difference (%) | 4 | 2 | 2 | 1 |
| 60  Ni | 4.46 | 4.39 | 1.11 | 5.48 |
| 62  Ni | 4.45 | 4.45 | 1.10 | 5.44 |
| Difference (%) | 0 | -1 | 1 | 1 |
| 63  Cu | 49.67 | 19.86 | 15.23 | 11.61 |
| 65  Cu | 49.50 | 19.83 | 15.16 | 11.60 |
| Difference (%) | 0 | 0 | 0 | 0 |

As can be seen from Table 4, excellent agreement between isotopes was demonstrated, confirming the effective suppression of multiple interferences in varying matrices using He mode. In contrast, the use of a reactive gas such as $H_2$ or $NH_3$ cannot be applied to multiple, unknown interferences on multiple isotopes simultaneously in a single quadrupole ICP-MS. By quantifying an element using multiple isotopes, the results can be compared; good agreement validates the data, indicating that the reported concentration was not affected by any interference. The 7700/7800 ICP-MS is unique in its ability to allow the efficient suppression of multiple interferences on multiple isotopes using only helium gas.

**Method validation**

Table 5 summarizes the final results, comparing the measured values for each CRM with the certified values.

All elements in all of the CRMs showed excellent agreement with the certified values, including the major elements (Ca, K, Mg or Na), the interfered elements (As, Se, Fe...) and the non-interfered elements (Hg, Pb...). This clearly demonstrates that it is practical to measure a wide range of elements in a variety of food types over a very wide range of concentrations in a single analytical run using the Agilent 7700x ICP-MS.

**Application of discrete sampling to food analysis**

Prior to the addition of ISIS-DS, the method described above required an analysis time of 5 minutes per sample. With the addition of discrete sampling using ISIS-DS, the total analysis time per sample was reduced to 1.2 minutes. While the ISIS-DS system significantly reduces the analysis time per sample, there was no compromise in the other performance attributes of the system, that is, the capacity to measure trace, majors or interfered elements simultaneously in a range of food matrices with the use of He mode to remove interferences. Table 6 summarizes the parameters used for the ISIS-DS method.

**Table 5.** Comparison of measured versus certified values for all analyte elements in the certified reference materials (units: mg/kg except * in %)

|  | SRM 1548a Typical Diet | | SRM 2976 Mussel Tissue | | DORM3 Fish Tissue | | SRM 8415 Whole Egg | |
|  | Result | Certified | Result | Certified | Result | Certified | Result | Certified |
|---|---|---|---|---|---|---|---|---|
| Na | 8459 | 8132 +- 942 | 3.4 | 3.5 +- 0.1* | - | - | 0.317 | 0.377* |
| Ca | 1869 | 1967 +- 113 | 0.73 | 0.76 +- 0.03* | - | - | 0.235 | 0.248* |
| Mg | 603 | 580 +- 26.7 | 0.48 | 0.53 +- 0.05* | - | - | 297 | 305 |
| K | 6684 | 6970 +- 125 | 0.99 | 0.97 +- 0.05* | - | - | 0.319 | 0.319* |
| Al | 73.5 | 72.4 +- 1.52 | 140 | 134 +- 34 | - | - | 563 | 540 |
| As | 0.21 | 0.20 +- 0.01 | 14.9 | 13.3 +- 1.8 | 6.61 | 6.88 +- 0.30 | 0.015 | (0.01) |
| Cd | 0.035 | 0.035 +- 0.0 15 | 0.79 | 0.82 +- 0.16 | 0.284 | 0.290 +- 0.020 | 0.001 | (0.005) |
| Cu | 2.57 | 2.32 +- 0.16 | 4.09 | 4.02 +- 0.33 | 15.9 | 15.5 +- 0.63 | 3 | 2.7 |
| Cr | - | - | 0.54 | 0.50 +- 0.16 | 2.15 | 1.89 +- 0.17 | 0.42 | 0.37 |
| Fe | 40.4 | 35.3 +- 3.77 | 204 | 171 +- 4.9 | 368 | 347 +- 20 | 114 | 112 |
| Ni | 1.21 | 0.369 +- 0.023 | 0.90 | 0.93 +- 0.12 | 1.42 | 1.28 +- 0.24 | - | - |
| Pb | 0.12 | 0.044 +- 0.009 | 1.14 | 1.19 +- 0.18 | 0.39 | 0.395 +- 0.050 | 0.059 | 0.061 |
| Se | 0.259 | 0.245 +- 0.028 | 1.76 | 1.80 +- 0.15 | - | - | 1.45 | 1.39 |
| Sn | 14.3 | 17.2 +- 2.57 | 0.12 | 0.096 +- 0.039 | 0.10 | 0.066 +- 0.012 | - | - |
| Zn | 23.3 | 24.6 +- 1.79 | 144 | 137 +- 13 | 47.5 | 51.3 +- 3.1 | 65.8 | 67.5 |
| Hg | - | - | 0.104 | 0.061 +- 0.0036 | 0.412 | 0.409 +- 0.027 | - | - |

**Table 6.** Parameters for the ISIS-DS method

| Parameter | Value |
|---|---|
| Load time | 12 s |
| Load speed | 1.0 rps |
| Probe rinse time | 6 s |
| Probe rinse speed | 0.2 rps |
| Post rinse time | 10 s |
| Post rinse speed | 0.5 s |

## Conclusions

Food matrices present complex and challenging samples for elemental analysis, particularly using a single analytical technique, due to the varying matrix composition, very wide range of element concentrations, and potential for matrix based interferences. The Agilent 7700x ICP-MS, operated in standard configuration and using only no gas mode and He mode was demonstrated to easily and accurately measure all certified elements in a range of food certified reference materials. Excellent sensitivity was demonstrated with detection limits in the ppt (ng/L) range while at the same time maintaining sufficient dynamic range to measure elements in the high ppm range. The use of discrete sampling via ISIS-DS did not compromise the performance of the method in any way, while reducing the run time from 5 minutes to 1.2 minute per sample.

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**7800 ICP-MS**

Results presented in this document were obtained using the 7700x, but performance is also verified for the 7800 ICP-MS and faster with ISIS3.

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