Measurement of Macro and Trace Elements in Plant Digests Using the 7500c ICP-MS System

Application

Food

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Abstract

Inductively coupled plasma mass spectrometry is a powerful tool for the investigation of many materials. The Agilent 7500c with Octopole Reaction System was used to analyze major, minor and trace elements in two standard reference plant materials. The data obtained using the 7500c is compared to the certificate reference values and to results that were generated using inductively coupled plasma optical emission spectroscopy. Results for all elements obtained using the 7500c agree with the certified values.

Introduction

The reliable measurement of trace elements in food is becoming more important as information is revealing that over-dependence on processed grains such as wheat and rice is resulting in a nutritionally poor diet. Micronutrient [1] malnutrition is an identified problem that has coincided with the rapid adoption of modern cereal cropping systems. Profitable and sustainable agriculture depends on the understanding of the nutrients required and available for plant growth, as well as the nutrients for a balanced human diet.

"World food production will need to double over the next 30 years to keep pace with increasing demands from both industrialized and rapidly developing countries. As well as the need to increase production, there will be an increase in demand for higher quality and healthier food products as developing countries become more affluent."

Taken from the Commonwealth Scientific and Industrial Research Organisation (CSIRO) website: http://www.csiro.gov.au (select: Agribusiness/Field Crops/Field Crops & Australia)

Human dietary micronutrients are required by humans in very small amounts. They include at least 14 trace elements (As, B, Cr, Cu, F, I, Fe, Mn, Mo, Ni, Se, Si, V, Zn) as well as 13 vitamins (thiamin, riboflavin, niacin, pantothenic acid, biotin, folic acid, vitamins B6, B12, C, A, D, E, K)

The recommended daily intake of the micronutrient trace elements is of the order of:

- mg per day for B, Cu, F, Fe, Mn, Zn
- µg per day for As, Cr, I, Mo, Ni, Se, Si, V

Accurate determination of these trace elements in food materials is useful in ensuring that dietary intake is providing adequate levels of micronutrient elements. Due to the very low concentrations that must be measured and, in many cases, the high and variable sample matrix in which the measurements must be made, this analysis has proved challenging for elemental analysis instrumentation. Traditionally, a combination of techniques was required for a complete analysis of the plant digest—typically Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), Hydride-Atomic Absorption Spectroscopy (HG-AAS) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

Such is the performance and elemental coverage of modern inductively coupled plasma mass spectrometry (ICP-MS) instrumentation, in many cases (metals analysis in drinking water, for example) a single ICP-MS has replaced all of the above mentioned techniques, enabling all analytes to be determined in a single measurement. The analysis of plant and food digests for nutritional studies is more challenging. In ICP-MS, isobaric interferences arise from the argon used to sustain the plasma and from the reagents used for sample preparation. Table 1 summarizes some well-known interfering species. In biological sample analysis, there are well-documented interferences for ICP-MS that can bias the measurement of Fe, Cr, V, As and Se at trace levels, with the result that ICP-MS has not yet been widely adopted by the foods industry.

Table 1. Examples of Potential Interferences in Biological/Clinical Matrices

Element	Mass	Molecular interference
Cr	52; 53	$^{40}Ar^{12}C$, $^{36}Ar^{16}O$, $^{35}Cl^{16}O^{1}H$; $^{37}Cl^{16}O$
V	51	$^{35}Cl^{16}O$
Fe	56	$^{40}Ar^{16}O$
Cu	63	$^{40}Ar^{23}Na$
As	75	$^{40}Ar^{35}Cl$
Se	77; 78; 80	$^{40}Ar^{37}Cl$; $^{40}Ar^{38}Ar$; $^{40}Ar^{40}Ar$;

One obvious way to remove interferences is to eliminate the source of the interfering species. Traditionally plant materials are digested on a hot plate using a mixture of nitric and perchloric acids. Chloride-based mass spectral interferences are introduced by this method. An alternative sample preparation method is available using microwave digestion with hydrogen peroxide and nitric acid. This digestion media does not generate additional interferences for ICP-MS and is a complete digest. However, for high sample numbers, the traditional hot plate digest offers higher sample throughput than closed vessel microwave digestion [2].

Recently, the advent of collision/reaction cells has improved the detection capability of quadrupole ICP-MS (ICP-QMS) by removing spectral interferences on analytes such as Fe, Cr, V, As and Se. The Agilent 7500c ICP-MS features an Octopole Reaction System (ORS) for highly efficient removal of multiple interferences arising from complex sample matrices. The ORS removes interferences by either reacting a gas with the interference or by preventing the interfering species from entering the analyzer stage using a process called energy discrimination. The 7500c exhibits highly efficient interference removal. The Ar_2 overlap on Se at mass 80 is virtually eliminated, reducing the background equivalent concentration from 100's of ppb to <10 ppt. Moreover, the 7500c was designed specifically to handle complex matrices such as plant and food digests.

The key to the successful multi-element determination of trace elements in complex samples is a combination of matrix tolerance and efficient interference removal. Matrix tolerance is mainly determined by the "plasma efficiency", which must be optimized to ensure efficient sample decomposition, and is monitored by the CeO/Ce ratio. An efficient plasma minimizes the formation of plasma- and matrix-based interferences, while maximizing the conversion of analyte atoms into ions.

The importance of matrix tolerance of any ICP-MS system should not be underestimated, as this leads to improved analytical accuracy, better tolerance to matrix changes and reduced requirements to carry out routine maintenance of the vacuum, ion lens and pump components.

All of these aspects contribute to the usability of the analytical instrument, as routine maintenance contributes far more to the down-time of a modern, reliable ICP-MS instrument than hardware breakdowns. The unique capability of the Agilent 7500 Series lies in the mode of operation of the plasma source, which decomposes sample matrices five to 10 times more efficiently than is typical for other ICP-MS instruments.

The 7500c was designed specifically to handle complex, high matrix samples. A robust 27.12-MHz plasma, low sample uptake rate, cooled spray chamber and proven small orifice interface protect the ORS from contamination by undissociated sample matrix. A novel ion optic, mounted outside the high vacuum region for easy access, further protects the reaction cell, which features an octopole for optimum ion transmission. The octopole is mounted off-axis to minimize random background levels. A schematic of the 7500c is shown in Figure 1.

Some of the important instrument parameters that contribute to good matrix decomposition are:

- The standard low sample flow rate (100 to 400 µL/min) and Peltier-cooled spray chamber reduce the sample and water vapor loading on the plasma, which leads to a hotter plasma central channel.
- The 7500 Series uses a high efficiency, solid state 27.12-MHz plasma RF generator, ensuring good energy transfer into the plasma central channel.
- The unique wide internal diameter plasma torch design ensures that the sample aerosol is resident in the plasma for sufficient time to ensure complete matrix decomposition, leading to exceptionally good matrix decomposition (low CeO/Ce ratio).

The optimized interface design, which uses the smallest skimmer cone orifice of any commercial ICP-MS instrument, ensures that minimal sample matrix is passed into the high-vacuum part of the instrument, dramatically reducing the requirement for routine maintenance of the interface cones, the ion lenses and the collision cell.

In summary, as the complexity of the sample matrix increases, the benefit of minimized interference levels becomes more significant. Because modern analytical laboratories rarely have the luxury of pre-analyzing samples to identify the matrix, it is impractical to rely on matrix matching of the samples or data correction using complicated interference equations.

Sample Preparation and Analysis

About 800 mg of sample was accurately weighed and carefully heated with 10 mL nitric acid (70%), followed by gentle heating with the addition of 8 mL perchloric acid (70%) until colorless. After cooling, 30 mL water was added and heating resumed for 10 min. Finally, the solutions were cooled, then made to 100 mL volume with water.

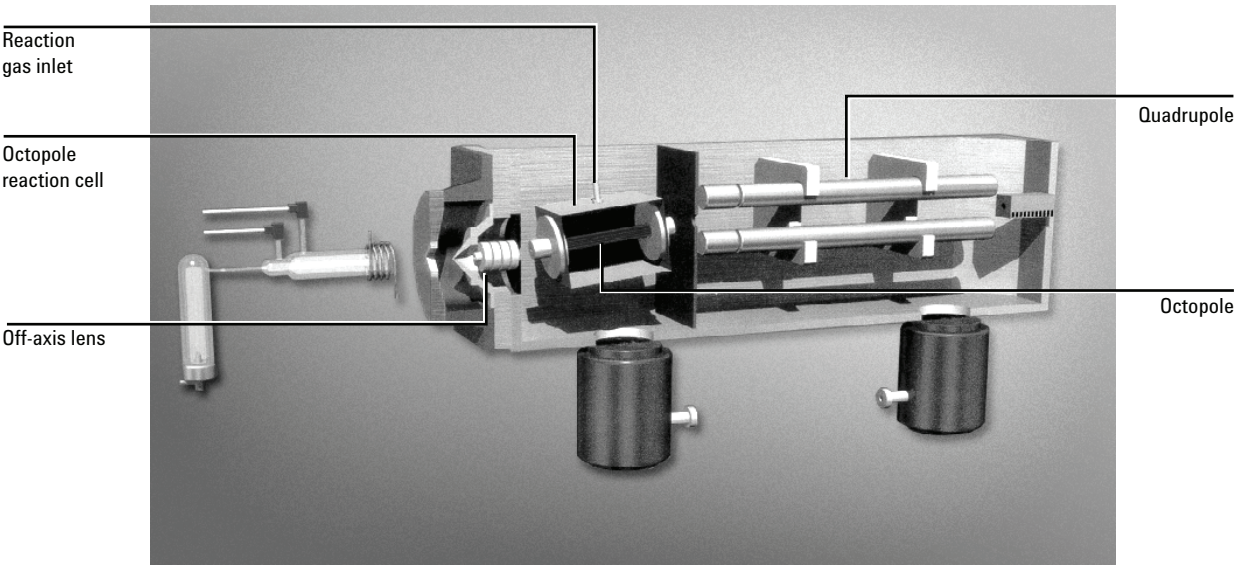

Figure 1: Schematic diagram of the Agilent 7500c Octopole Reaction System.

The instrument was tuned and optimized as detailed in Table 2. Calibrations were performed using external standards prepared from 1000 ppm single element stock, made up as appropriate with 2% nitric acid.

Table 2. Agilent 7500c Operating Conditions

Plasma RF power	1500 W
Sample depth	9.5 mm from load coil
Carrier gas flow	1.1 L/min
Spray chamber temperature	2 °C
Sample flow rate	240 µL/min
Nebulizer	Agilent microflow (PFA)
Interface	Nickel sample and skimmer cones

The external calibrations were run in the same analytical sequence as the samples. Sample concentration was calculated using the internal standard method. Table 3 summarizes the element and relevant internal standard information.

Table 3. Reaction Gases and Internal Standards Used

Measured element	Reaction gas	Internal standard
Potassium	Helium	Scandium
Calcium	Helium	Scandium
Chromium	Helium	Gallium
Iron	Helium	Gallium
Copper	Helium	Cobalt
Zinc	Helium	Cobalt
Arsenic	Helium	Yttrium
Selenium	Hydrogen	Indium (115)
Cadmium	Hydrogen	Indium (115)

Results and Discussion

The practical effect of the 7500c's unique combination of matrix tolerance and interference removal is that complex and variable samples can be measured with a simple quantification procedure using external standard calibration and internal standard correction for all masses. As and Se were accurately quantified at sub-ppb levels, even in a matrix containing 8% perchloric acid. Tables 4 and 5 summarize the results obtained in a blind analysis of plant digests using the 7500c, comparing the results with both the certified values and data obtained from analysis by ICP-OES.

Table 4. NIST 1573a (Tomato Leaves, Blank Corrected)

Name	Certified (mg/kg)	ICPOES (mg/kg)	7500c (mg/kg)
43 Ca	5.05%	5.00%	5.08%
39 K	2.70%	2.72%	2.62%
52 Cr	1.99	1.7, 1.8	1.60
53 Cr	1.99	1.7, 1.8	1.63
54 Fe	368	342, 347	368
56 Fe	368	342, 347	368
63 Cu	4.7	2.49, 2.40	4.43
65 Cu	4.7	2.49, 2.40	4.47
75 As	0.112	5.7, 6.6	0.175
78 Se	0.054	0.1, 0.8	0.061
111 Cd	1.52	5.5, 5.9	1.32

Table 5. NIST 1570a (Spinach, Blank Corrected)

Name	Certified (mg/kg)	Reference 2: (mg/kg)	7500c (mg/kg)
39 K	2.90%	2.63%	2.56%
43 Ca	1.53%	1.32%	1.39%
52 Cr	-	-	1.24
53 Cr		-	1.29
54 Fe	-	252	248
56 Fe		252	250
63 Cu	12.20	11.6	10.48
65 Cu	12.20	11.6	10.51
75 As	0.07	-	0.062
78 Se	0.12	-	0.09
111 Cd	2.89	-	2.33
54 Fe	-	252	248
56 Fe		252	250
63 Cu	12.20	11.6	10.48
65 Cu	12.20	11.6	10.51
75 As	0.07	-	0.062
78 Se	0.12	-	0.09
111 Cd	2.89	-	2.33

Measurements of Cr, Fe and Cu were made on two separate isotopes for each element. Because molecular interferences will, in many cases, only affect one of the analyte isotopes, the presence of an interference can cause a large discrepancy between results for different isotopes of the same element. An example of this is the measurement of Cu in a high Na matrix, where $^{40}Ar^{23}$ Na gives an overlap on ^{63}Cu, but no interference on ^{65}Cu. As the results indicate, the 7500c obtained excellent agreement for all the pairs of isotopes, highlighting the capabilities of the ORS in reducing interfering molecular species that, until now, have prevented the accurate trace analysis of transition metals in complex matrices by ICP-QMS.

Values for major and trace element concentrations agreed both with the expected value and the results obtained from ICP-OES. In the cases where the trace values for some elements were below the detection limit of the ICP-OES, the 7500c returned results in excellent agreement with the certified value. This data illustrates the wide dynamic range of the system and demonstrates its advantages as a replacement for traditional techniques such as ICP-OES.

The quantitative analysis of the NIST SRM samples also demonstrates that both the 7500c and the operating conditions are robust and tolerant of the changing matrix composition found in plant digests.

Conclusions

The trace analysis of plant digests is an application that can be suitably addressed by the 7500c. Advances in technology now allow the determination of multiple elements in complex sample matrices, with efficient interference removal and, in the case of the 7500c, with the excellent matrix tolerance for which the 7500 Series is renowned. Accurate quantification of As and Se at low and even sub-ppb levels in plant digests is possible, even where high concentrations of perchloric acid have been added during the sample preparation stage.

Acknowledgement

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References

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