
## Challenge

Determination of nutritional and toxic elements in foodstuffs and agricultural products

## Solution

Direct determination of all elements within a single, routine analysis using ICP-MS with all-digital detection technology

# Analysis of Food and Agricultural Samples Using PlasmaQuant® MS

## Introduction

Agricultural products play a significant role in the daily uptake of nutrients and fibers to maintain good health. The agricultural products and resulting foods contain nutritional elements in various concentrations but also elements deemed to be toxic to humans and/or animals.

Besides the organically bound elements: hydrogen, carbon, nitrogen and oxygen, there are more than 30 dietary elements necessary for the correct functioning of living organisms. According to their concentration, these elements are classified into macroelements (Ca, Mg, Na, K, P, S, Fe, Cu, Zn) with concentration levels above 0.01% and microelements (Ge, B, Cr, Sn, Zn, F, I, Co, Si, Li, Mn, Cu, Mo, Ni, Se, V, Fe) with less than 0.001% in bodily fluids and tissues. The importance of dietary elements is difficult to overestimate. The elements play a significant role in the constitution of bodies and in metabolic and other processes. For example, calcium is the main component of human bones and teeth. It also helps in clotting blood and is necessary for sending and receiving of nerve signals. Calcium deficiency can cause osteoporosis, metabolic disorder and other problems in human and animal body. Magnesium is important for ruminants to prevent grass tetany, selenium is known to be a major factor in the fertility of cows, and deficiency of manganese causes skeletal deformation in animals and inhibits the production of collagen in wound healing.

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However, there are not only nutritional elements necessary for life, but also toxic elements with adverse effects on organisms. Examples of such harmful elements include Be, Sb, Bi, Ba, U, Al, Tl, Hg, Cd and Pb. Toxic elements tend to accumulate in the liver, kidneys and pancreas. For instance, cadmium causes kidney damage and cardiovascular disease.

Lead, as a highly poisonous metal, affects almost every organ and system in the body, can even cause damage to the brain and nervous system in children. Mercury is considered by World Health Organization (WHO) to be one of the top ten toxic chemicals. Mercury has toxic effects on the nervous, digestive and immune systems as well as on lungs, kidneys, skin and eyes. Exposure mainly occurs through consumption of fish and shellfish contaminated with methylmercury.
Looking upstream in our food supply chains and in particular to the agricultural industry, it is becoming increasingly clear that providing the correct balance of macrominerals and trace metals in their feed helps livestock to thrive and remain disease free.

Accurate measurement of elemental composition in food and agricultural products is essential to ensure in ensuring product safety and to maintaining adequate levels of nutritional content. With concentrations typically ranging from sub parts-per-billion to high parts-per-million in solution, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a vital tool for, providing fast, reliable, and routine analysis of samples over a large concentration range. As such, this application note investigates the measurement of key elements in food and agricultural reference materials by ICP-MS, from trace to major levels within a single analysis.

## Experimental

A PlasmaQuant® MS was used for the analysis that includes the patented ReflexION ion optics providing unsurpassed transmission of ions from the interface to the mass analyzer. The PlasmaQuant® MS is able to achieve a sensitivity of more than 500 million c/s per mg/L of analyte ($^{115}In$), while maintaining oxide ratios ($CeO^+/Ce^+$) below 2%. The PlasmaQuant® MS is also equipped with the patented Integrated Collision Reaction Cell (iCRC) for interference-free analysis. The iCRC attenuates polyatomic ions formed in the plasma, which can interfere with the determination of elements, such as, As, Se, Cr, V, and Fe, thus improving their detection limits. Another innovative feature of the PlasmaQuant® MS is the All-Digital Detection System ($ADD^{10}$). This system provides 10-orders linear dynamic range in 'pulse-counting' mode only, allowing routine measurement of elements from ultra trace to percentage levels within a single analysis. By using the latest ICP-MS detector technology, the $ADD^{10}$ detector system eliminates the need for analog measurements, while maintaining maximum dynamic range.

### Conditions

The method parameters were optimized using the ICP-MS software's Auto-Optimization routine, which automates setting of all iCRC and plasma gas flow rates as well as ion optic voltages.

### Sample Preparation

All samples were prepared by accurately weighing 0.5 g into a microwave vessel. After carefully adding 10mL of $HNO_3$ and 1mL of HCL, the vessel was heated for 25 min. and kept at 200 °C for a further 30 minutes. Samples were left to cool to ambient temperature and filled up to 20 mL using ultra-pure water (>18 MΩ▪cm).

### Sample Analysis

Prior to analysis, samples were diluted ten-fold with ultra-pure water (>18 MΩ▪cm). An internal standard solution was prepared containing 20 µg/L of Sc, Y, Rh, Tb, and Lu, which was added online to the sample line via a 'Y piece'. Isotopes were run in normal sensitivity and iCRC mode in one continuous method. When operating in iCRC mode, hydrogen or helium gas was added to the iCRC skimmer cone to attenuate all polyatomic interferences. Hydrogen was used for the elements Ca, Fe, and Se, and helium for V, Cr, Cu, Ni, and As. Non iCRC mode was used for the remaining elements.

### Calibration

Calibration standards were created from high-purity, multi-element solutions and the acid matrix matched to the samples.

## Results and Discussion

A variety of food and agricultural reference materials, including tea leaves [1], coffee, milk powder [2], bread, kidney, and loam [3], and 'intra-laboratory' samples of lime, hay, and animal feed were analyzed. The results of some of them are summarized in the table 1. Measured concentrations for each of the samples were typically within the certified range or ±10% of the certified value, demonstrating the validity of the method. In fact, the majority of results easily fell within ± 5% of the certified value. "Interpolated" internal standard correction was the selected mode of correction to automatically adjust calibration and sample solution measurements for matrix and long term drift effects.

Table 1: Results for tea leaf reference material INCT-TL-1, brown bread reference material BCR-191, Silty Clay Loam reference material CRI7003 (aqua regia soluble) and Hay intra-laboratory reference material

| Element | Tea leaf | | Brown Bread | | Silty Clay Loam | | Hay | |
|---|---|---|---|---|---|---|---|---|
| | Measured | Certified | Measured | Certified† | Measured | Certified | Measured | Certified† |
| | mg/kg | | | | | | | |
| $^{23}Na$ | 24.0 | 24.7 | | | | | 0.33% | (0.34%) |
| $^{24}Mg$ | | | 513 | 500 | | | 0.19% | (0.21%) |
| $^{27}Al$ | 2145 | 2290 | | | | | | |
| $^{31}P$ | | | | | | | 0.37% | (0.39%) |
| $^{39}K$ | | | 3128 | 3100 | | | 0.34% | (0.35%) |
| $^{44}Ca$ | | | 422 | 410 | | | 0.54% | (0.57%) |
| $^{51}V$ | 1.84 | 1.97 | | | | | | |
| $^{52}Cr$ | 1.84 | 1.91 | 0.077 | (0.068–0.360)‡ | 41.4 | 42.4 | 1.8 | (1.9) |
| $^{55}Mn$ | 1540 | 1570 | 19.9 | 20.3 ± 0.7 | 517 | 529 | 79.1 | (81.9) |
| $^{56}Fe$ | 423 | 432 | 39.0 | 40.7 ± 2.3 | | | 498 | (531) |
| $^{59}Co$ | 0.350 | 0.387 | | | 10.1 | 10.3 | 0.18 | (0.19) |
| $^{60}Ni$ | 6.04 | 6.12 | 0.46 | (0.44) | 28.4 | 28.8 | 1.53 | (1.61) |
| $^{65}Cu$ | 20.4 | 20.4 | 2.6 | 2.6 ± 0.1 | 24.8 | 25.4 | 7.5 | (7.8) |
| $^{66}Zn$ | 34.6 | 34.7 | 19.0 | 19.5 ± 0.5 | 68.8 | 69.4 | 33.0 | (34.9) |
| $^{75}As$ | 0.104 | 0.106 | 0.024 | (0.023) | 11.3 | 11.6 | 0.27 | (0.28) |
| $^{78}Se$ | 0.062 | 0.076 | 0.026 | (0.025) | | | 0.047 | (0.049) |
| $^{114}Cd$ | 0.027 | 0.03 | 0.0270 | 0.0284 ± 0.0014 | 0.31 | 0.32 | 0.079 | (0.083) |
| $^{121}Sb$ | 0.046 | 0.050 | | | | | | |
| $^{202}Hg$ | | | 0.003 | (0.002) | 0.091 | 0.093 | 0.014 | (0.015) |
| $^{205}Tl$ | 0.064 | 0.063 | | | | | | |
| $^{206-208}Pb$ | 1.56 | 1.78 | 0.182 | 0.187 ± 0.014 | 24.6 | 25.2 | 1.14 | (1.19) |
| $^{238}U$ | 0.100 | 0.099 | | | | | | |

† Values in brackets are not certified

‡ Range of results observed

## Conclusion

This work has successfully demonstrated that the PlasmaQuant® MS with iCRC technology and All-Digital Detection System (ADD10) provides a simple and effective solution for the direct determination of elements from trace to percentage levels in food and agricultural samples within a single, routine and reliable analysis. The high-throughput capability of the method was shown for various sample types in a routine operation. This has been achieved by fast switching between the iCRC and non-iCRC modes and the innovative detection system allowing fast, accurate and precise measurement from sub parts-per-trillion to high parts-per-million element concentrations.

## References

[1] Dybczynski R., Danko B., Kulisa K., Maleszewska E., Polkowska-Motrenko H., Samczynski Z. and Szopa Z. 2004. Preparation and preliminary certification of two new Polish CRMs for inorganic trace analysis. *Journal of Radioanalytical and Nuclear Chemistry, 259 (3): 409*
[2] Certified Reference Materials 2004, Institute for Reference Materials and Measurements
[3] LGC Standards, *Analytical Reference Materials Catalog 2008/2009.*

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