



Challenge

Separation and quantification of toxic As species in rice

Solution

Combination of LC and highly sensitive ICP-MS to determine As species down to sub microgram per kilogram concentrations

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.

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

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.

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 (ADD¹⁰). 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 ADD¹⁰ 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

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						
$^{206-208}\text{Pb}$	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

All samples were prepared by accurately weighing 0.5 g into a microwave vessel. After carefully adding 10mL of HNO₃ 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

This document is true and correct at the time of publication; the information within is subject to change. Other documents may supersede this document, including technical modifications and corrections.

Headquarters

Analytik Jena GmbH
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 36 41 77 70
Fax +49 36 41 77 9279

info@analytik-jena.com
www.analytik-jena.com

Version 1.0
en · 12/2020

© Analytik Jena GmbH | Pictures ©: Istock/piotr_malczyk