Challenge

Quality control of milk and milk products includes the determination of major and trace elements but also the quantification of toxic elements.

Solution

A universal method for the determination of elements in powdered milk at different concentration ranges in a single analysis run using ICP-MS.

Characterization of Powdered Milk by ICP-MS

Introduction

Milk and dairy products play an important role in the human diet. From infants to adults, various types of dairy products accompany us in our everyday lives and provide us with important major and trace elements, vitamins, and other essential substances. Since many dairy products are perishable and have a limited shelf life, powdered milk is the alternative for preparing milk for direct consumption or for processing into other products. Its longer shelf life and ability to be easily transported make powdered milk a widely used product.

The growing use of powdered milk in infant nutrition requires a strict quality control to ensure the quality of the product on a permanent basis. Here, the samples are not only examined for toxic elements such as Cd, As, Hg, and Pb but also monitored for the levels of major and trace elements. Since the elements are present in very different concentration levels ranging from g/kg to µg/kg, different analytical techniques are usually used to cover all concentration ranges.

Inductively coupled plasma mass spectrometry (ICP-MS) is a highly flexible technique that covers a wide concentration range within a single analysis run. The PlasmaQuant MS, ICP-MS, is a sensitive and robust system that combines the highest performance, ease of use, and low running costs (economic operation). Coupling to an ASPQ 3300, autosampler allows the automated characterization of large numbers of samples.

The PlasmaQuant MS features patented solutions to drastically reduce analysis time and costs per sample while providing an easy-to-use analytical tool. The powerful Eco Plasma offers the full performance of an ICP at half of the argon plasma gas consumption. The combination of the patented ion optic system with the integrated Collision Reaction Cell allows short analysis times and removes interferences in an easy-to-use but effective way. The ADD^{10} detection system offers ten orders of linear dynamic range for the simultaneous quantification of major, trace, and ultratrace element concentrations in a single run.

Combined with a powerful method, the PlasmaQuant MS makes it possible to quantify all relevant elements at different concentration levels and in the shortest analysis time.

Materials and Methods

Certified reference materials were used for the method development and validation. The analytical process contained a sample preparation step including a microwave digestion procedure followed by the sample analysis with ICP-MS.

Samples and Reagents

Different samples of powdered milk were prepared for the analysis. A certified reference material, ERM®-BD151 Skimmed Milk Powder, was used for method development and evaluation. A sample of commercially available powdered milk was analyzed according to the developed method.

All samples were prepared in two different ways: careful dilution in water using 0.2 g of powdered milk in 20 mL de-ionized water and a microwave digestion procedure with 0.2–0.5 g made up to 50 mL.

With the microwave digestion method the powdered milk samples were digested completely using the microwave digestion system TOPwave. Each sample was prepared twice and the mean value of both measured values was formed for each element. Approximately 0.5 g of each sample was weighted and digested (vessel type PM60) with a mixture of HNO_3 and H_2O_2. Subsequently the solution was transferred into a graduated flask and filled to a volume of 50 mL with deionized water. Calibration solutions were prepared in 1% HNO_3 (ultrapure, Rothipuran) in a concentration range from 0.1 to 50 µg/L for the trace elements and 1 to 50 mg/L for matrix elements.

Instrumentation

The analyses were performed using a PlasmaQuant MS equipped with an autosampler ASPQ 3300 and standard sample introduction. Table 1 summarizes the optimized parameter and data acquisition settings. Internal standards were used to monitor the stability of the sample introduction system, the ionization, and the detection. The elements Sc, Y, Rh, and Ir were prepared in a 20 ppb solution from single-element stock solutions and added on-line via a T-piece before the sample reached the nebulizer. This ensured a constant addition and mixing of internal standard solution and sample solution during the whole analytical run.

Table 1: Instrument settings – PlasmaQuant MS

Parameter	Specification
Plasma Gas Flow	9.0 L/min
Auxiliary Gas Flow	1.25 L/min
Nebulizer Gas Flow	1.0 L/min
iCRC Gas Setting	no iCRC, H_2, He
Plasma RF Power	1.40 kW
Dwell Time	20 ms
Scans per Replicate	15 (peak hopping, 1 pt/peak)
No. of replicates	5
Pump Rate	12 rpm – black/black PVC pump tubing

Parameter	Specification
Sample uptake time	30 s
Stabilization delay	15 s
Sampling depth	6.0 mm
Nebulizer type	MicroMist (quartz concentric)
Ion Optics	Auto-optimized
Spray chamber type	Glass Scott
Spray chamber temperature	3 °C

The PlasmaQuant MS is equipped with an integrated Collision Reaction Cell to remove interferences from polyatomic ions. Table 2 lists potential polyatomic interferences for the respective analyte elements. By using different cell gas, modes the interferences were minimized. This ensured the best performance for each analyte in the milk matrix.

Table 2: Potential interferences on analyte isotopes

Isotope	Abundance [%]	Double charged interferences	Polyatomic interferences	iCRC mode
$^{39}\mathrm{K}$	93.258	$^{77}\mathrm{Se}^{++}$,$^{78}\mathrm{Se}^{++}$, $^{78}\mathrm{Kr}^{++}$, $^{79}\mathrm{Br}^{++}$	$^{23}\mathrm{Na}^{16}\mathrm{O}^{+}$, $^{38}\mathrm{Ar}^{1}\mathrm{H}^{+}$	no gas
$^{44}\mathrm{Ca}$	2.086	$^{88}\mathrm{Sr}^{++}$	$^{26}\mathrm{Mg}^{18}\mathrm{O}^{+}$, $^{28}\mathrm{Si}^{16}\mathrm{O}^{+}$, $^{12}\mathrm{C}^{16}\mathrm{O}_2^{+}$, $^{+32}\mathrm{S}^{12}\mathrm{C}^{+}$	no gas
$^{23}\mathrm{Na}$	100	$^{45}\mathrm{Sc}^{++}$, $^{46}\mathrm{Ti}^{++}$, $^{46}\mathrm{Ca}^{++}$	$^{7}\mathrm{Li}^{16}\mathrm{O}^{+}$, $^{9}\mathrm{Be}^{14}\mathrm{N}^{+}$	no gas
$^{24}\mathrm{Mg}$	78.99	$^{48}\mathrm{Ti}^{++}$, $^{48}\mathrm{Ca}^{++}$	$^{23}\mathrm{Na}^{1}\mathrm{H}^{+}$, $^{7}\mathrm{Li}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$, $^{10}\mathrm{B}^{14}\mathrm{N}^{+}$	no gas
$^{31}\mathrm{P}$	100	$^{62}\mathrm{Ni}^{++}$	$^{14}\mathrm{N}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$	Hydrogen
$^{110}\mathrm{Cd}$	12.49	$^{220}\mathrm{Rn}^{++}$	$^{94}\mathrm{Zr}^{16}\mathrm{O}^{+}$, $^{94}\mathrm{Mo}^{16}\mathrm{O}^{+}$	No gas
$^{65}\mathrm{Cu}$	30.83	$^{130}\mathrm{Te}^{++}$, $^{130}\mathrm{Ba}^{++}$	$^{49}\mathrm{Ti}^{16}\mathrm{O}^{+}$, $^{25}\mathrm{Mg}^{40}\mathrm{Ar}^{+}$, $^{27}\mathrm{Al}^{38}\mathrm{Ar}^{+}$, $^{28}\mathrm{Si}^{37}\mathrm{Cl}^{+}$	Helium
$^{56}\mathrm{Fe}$	91.72	$^{112}\mathrm{Cd}^{++}$, $^{112}\mathrm{Sn}^{++}$	$^{55}\mathrm{Mn}^{1}\mathrm{H}^{+}$, $^{40}\mathrm{Ar}^{16}\mathrm{O}^{+}$, $^{40}\mathrm{Ca}^{16}\mathrm{O}^{+}$	Hydrogen
$^{55}\mathrm{Mn}$	100	$^{110}\mathrm{Cd}^{++}$, $^{110}\mathrm{Pd}^{++}$	$^{39}\mathrm{K}^{16}\mathrm{O}^{+}$, $^{15}\mathrm{N}^{40}\mathrm{Ar}^{+}$	Helium
$^{78}\mathrm{Se}$	23.78	$^{156}\mathrm{Gd}^{++}$, $^{156}\mathrm{Dy}^{++}$	$^{38}\mathrm{Ar}^{40}\mathrm{Ar}^{+}$, $^{38}\mathrm{Ar}^{40}\mathrm{Ca}^{+}$, $^{43}\mathrm{Ca}^{35}\mathrm{Cl}^{+}$	Hydrogen
$^{66}\mathrm{Zn}$	27.90	$^{132}\mathrm{Ba}^{++}$	$^{49}\mathrm{Ti}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$, $^{26}\mathrm{Mg}^{40}\mathrm{Ar}^{+}$, $^{31}\mathrm{P}^{35}\mathrm{Cl}^{+}$, $^{32}\mathrm{S}^{34}\mathrm{S}^{+}$	Hydrogen

Results and Discussion

The analysis of the reference material for powdered milk verified the method for sample preparation and sample analysis (Table 3). With the sensitive, accurate, and robust ICP-MS method, a very good match of results with the certified numbers was obtained. The reference material was analyzed following the initial calibration. As a quality control sample, the CRM was analyzed again after two hours continuous sample analysis. The deviations, shown in Table 3 underline the stability of the method.

Table 3: Results and performance for the certified reference material BD-151 and a powdered milk sample

Element	Result [g/kg]	Certified [g/kg]	Recovery [%]	Commercial powdered milk [g/kg]	Long term stability (2h) Deviation in %
^{44}Ca	14.1	13.9 ± 0.7	101	7.05	0.97
^{39}K	16.7	17.0 ± 0.8	98	7.24	0.6
^{24}Mg	1.23	1.26 ± 0.07	98	0.61	0.98
^{23}Na	4.30	4.19 ± 0.23	103	1.98	0.98
^{31}P	10.7	11.0 ± 0.6	97	3.88	0.2

Element	Result [mg/kg]	Certified [mg/kg]	Recovery [%]	Commercial powdered milk [mg/kg]	Long term stability (2h) Deviation in %
^{110}Cd	0.104	0.106 ± 0.013	98	<0.001	0.96
^{65}Cu	4.87	5.00 ± 0.23	97	4.27	0.83
^{56}Fe	52	53 ± 4	98	92.1	0.1
^{55}Mn	0.27	0.29 ± 0.03	93	0.36	0.1
^{206,7,8}Pb	0.197	0.207 ± 0.014	95	0.008	0.1
^{78}Se	0.19	0.19 ± 0.04	100	0.14	0.1
^{66}Zn	44.5	44.9 ± 2.3	99	74	1

The two different sample preparation approaches lead to comparable results for the analyzed sample matrices. However, the dilution approach requires a careful sample introduction and handling. A deposition of powdered milk material was observed when the samples were left in the autosampler for a longer period of time. A careful shaking and sonication before analysis is required to ensure a stable sample introduction with no loss of sample material. This ultimately leads to false negative results, especially for matrix elements such as calcium.

The results for the commercially available powdered milk are in a similar range with the certified concentrations in the CRM and are in good agreement with the numbers mentioned on the label.

Conclusion

The application described demonstrates the potential of ICP-MS for the analysis of powdered milk and milk products when using a PlasmaQuant MS instrument. An accurate and robust method with very good stability is key for the routine analysis of these matrices.

Headquarters
Analytik Jena AG
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

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

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