Application Note
Food testing and Agriculture

High-Throughput, Multi-Element Analysis of Milk and Milk Powder Using ICP-MS

Fast, accurate determination of major and trace elements in the same run.

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Introduction

Milk and milk-based products are an important source of nutrients in the human diet, especially for infants and children. Milk products are widely consumed in many parts of the world. As tastes change and incomes rise, the popularity of dairy products in many Asian and developing countries is rising. With increased production to meet the growing demand, it is important to ensure product quality is maintained. The levels of major elements such as Na, K, Mg, Ca, and essential elements such as Se, P, Mn, Zn, are measured to provide valuable nutritional information. Potentially toxic elements such as As, Cd, Hg, and Pb are also measured in animal-derived milk, to monitor potential contamination from soil, fertilizer, animal feed, or processing equipment.

Agilent ICP-MS instruments are widely used in environmental and food testing laboratories due to their exceptional sensitivity, fast multi-element analysis and wide elemental coverage. Recent developments have extended the analytical dynamic range of the Agilent 7900 ICP-MS to eleven orders of magnitude, allowing routine measurement of major elements (such as Na, K and Ca) in milk, in the same analytical run as the trace elements. Advances have also been made in collision/reaction cell (CRC) technology to ensure accurate results for elements that suffer from polyatomic interferences derived from the sample matrix. Agilent ICP-MS instruments offer market leading plasma robustness, which is further extended to tolerate samples up to 25% total dissolved solids (TDS) through the use of Ultra High Matrix Introduction (UMHI) technology. When combined with increased sample throughput offered by discrete sampling (DS) with the Integrated Sample Introduction System (ISIS 3), Agilent ICP-MS systems are ideally suited to routine, high throughput determinations of a wide range of elements in food samples.

This study describes the use of the Agilent 7900 ICP-MS with UHMI and ISIS 3 for the rapid analysis of major and trace elements in milk and milk products. The analysis could also be performed on the Agilent 7850 ICP-MS. Data quality was assessed through the measurement of a Whole Milk Powder Standard Reference Material (SRM).

Experimental

Samples and reagents

Seven types of commercially available milk and milk products were purchased at a local store in Berkeley, CA USA. The samples were:

- instant, non-fat, dry powdered milk
- buttermilk powder
- whole powdered goat's milk
- cream buttermilk powder
- non-fat, dry milk powder
- whole milk
- fat free milk

National Institute of Standards and Technology (NIST, Gaithersburg, MD) 1549a Whole Milk Powder Standard Reference Material (SRM) was used to validate the method.

Sample preparation

The milk samples (0.5 g of powdered milk, 1 g of liquid milk) and the NIST 1549a SRM (0.5 g) were each digested in 6 mL nitric acid (67-69%, BASELINE®, SeaStar Chemicals, Sidney, BC, Canada) and 1 mL hydrochloric acid (32-35%, ARISTAR® ULTRA, BDH, Westchester, PA) using an UltraWAVE Single Reaction Chamber Microwave Digester (Milestone Inc., Shelton CT). The blanks consisted of 6 mL HNO_3 and 1 mL HCl. The temperature and pressure were ramped to 240 °C and 150 bar, respectively, over a 20 minute period. The final conditions were maintained for 15 min to ensure complete digestion. Each sample digest was diluted to a final volume of 10 mL with Millipore water (Milli-Q™ Water System, Darmstadt, Germany). Before analysis, the samples were further diluted by a factor of 10 using a solution of 2% HNO_3 and 0.5% HCl, and this acid mix was also used to prepare the calibration standards. Each commercial sample was prepared in triplicate and seven digests of the NIST 1549a SRM were prepared.

Instrumentation

An Agilent 7900 ICP-MS fitted with standard nickel cones, glass concentric nebulizer and UHMI was used for the analysis. UHMI maximizes the plasma robustness of the 7900 ICP-MS through a combination of aerosol dilution and automated optimization of plasma temperature.

The 7900 ICP-MS includes a 4th generation Collision/Reaction Cell (CRC), the Octopole Reaction System (ORS^4), which provides optimized operating conditions for the removal of polyatomic interferences using helium (He) collision mode. Uninterfered low-mass elements are often measured in no gas mode, but the high sensitivity of the 7900 ICP-MS allows even these analytes to be measured in He mode if a single mode analysis is required to maximize sample throughput—as was the case in this study. The optional ISIS 3 discrete sampling accessory was used to reduce sample run times to 150 sec per sample.

Analytical procedure

The Agilent ICP-MS MassHunter software has several preset plasma modes, which include the UHMI aerosol dilution factor. This simplifies instrument use, as consistent, predefined operating conditions can be selected quickly and efficiently with minimal operator input. For the analysis of the milk digests, pre-set plasma setting HMI-4 (~4x aerosol dilution) was selected, to provide the robustness and tolerance appropriate for the moderately high and variable matrix levels present in the digested samples. The instrument settings used are shown in Table 1. All lens voltages were optimized using the autotune function of the instrument.

Table 1. Agilent 7900 ICP-MS and ISIS 3 operating conditions

Parameter	Value
Plasma mode	HMI-4
RF power (W)	1600
Carrier gas flow (L/min)	0.8
Dilution gas flow (L/min)	0.15
Lens tune	Autotune
Helium cell gas flow (mL/min)	4.3
Energy discrimination (V)	5.0
Number of elements	24 analytes, 6 ISTDs
Total acquisition time (3 reps) (seconds)	150

**Shaded parameters are predefined by selecting preset plasma option HMI-4.*

ISIS-DS Parameters		
Loop volume (mL)	1.5	
	Time (sec)	Pump Speed (%)
Sample load	6	50
Stabilize	15	5
Probe rinse	30	5
Probe rinse 1	5	5
Probe rinse 2	5	5
Optional loop probe wash	15	50
Optional loop wash	15	50

Calibration

Twenty four elements were analyzed in the method plus 6 internal standards: Sc, Ge, Rh, In, Tb, and Lu. Calibration standards for the majority of the trace and mineral elements were prepared from Agilent standards containing 1,000 mg/L of Fe, K, Ca, Na, Mg and 10 mg/L of As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Pb, Sb, Se, Tl, V, Zn in a matrix of 10% HNO_3 (P/N 5183-4688). Spex single element standards (SPEX CertiPrep, Metuchen, NJ) were used for the addition of Hg and Sn (each at 1,000 mg/L), and P, Na, and Ca (each at 10,000 mg/L). Single element standards for Ti and B (1,000 mg/L) were purchased from Fisher Scientific.

A 5-point calibration between 0 and 100 µg/L was carried out for the elements Ti, V, Cr, Mn, Co, Cu, Zn, As, Se, Mo, Cd, Sn, Sb, Ba, Tl, Pb; between 0 and 500 µg/L for B; between 0 and 10,000 µg/L for Mg, P, K, Fe; and between 0 and 2 µg/L for Hg. A 6-point calibration between 0 and 200,000 µg/L was carried out for Na, and between 0 and 100,000 µg/L for Ca.

Results and discussion

Table 2. Calibration coefficients, method detection limits and background equivalent concentration data. All elements were measured in He mode.

Mass	Element	R	DL (ppb)	BEC (ppb)
9	Be	0.999957	0.140	0.051
11	B	0.999716	0.283	1.981
23	Na	1.00000	18.50	240.9
24	Mg	0.99979	0.180	0.532
27	Al	0.999916	0.036	0.362
28	Si	0.999966	62.57	651.3
31	P	0.999943	11.50	5.487
39	K	0.999901	17.39	372.7
44	Ca	0.999999	24.39	85.92
47	Ti	0.999959	0.255	0.261
51	V	0.999871	0.028	0.081
52	Cr	0.999796	0.088	0.294
55	Mn	0.999905	0.008	0.055
56	Fe	0.99989	0.254	1.026
59	Co	0.999971	0.008	0.005
60	Ni	0.999941	0.022	0.093
63	Cu	0.999956	0.033	0.109
66	Zn	0.99984	0.085	0.313
75	As	0.999974	0.010	0.017
78	Se	0.999892	0.223	0.415
95	Mo	0.999879	0.009	0.004
107	Ag	0.999943	0.001	0.002
111	Cd	0.999873	0.001	0.004
118	Sn	0.999930	0.004	0.013
121	Sb	0.999847	0.005	0.004
137	Ba	0.999884	0.008	0.003
201	Hg	0.998411	0.028	0.029
205	Tl	0.999834	0.001	0.004
208	Pb	0.999904	0.002	0.018
232	Th	0.999946	0.002	0.011
238	U	0.999995	0.001	0.004

Representative calibration curves for several elements are shown in Figure 1 and Figure 2.

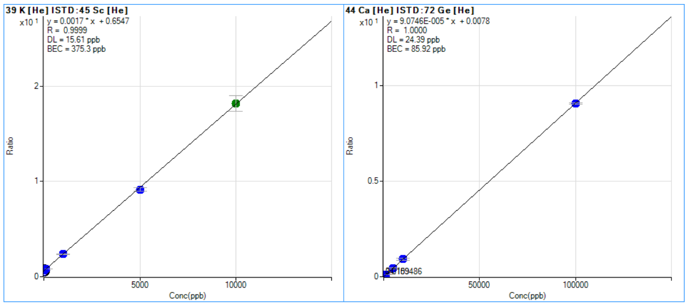

Figure 1. Calibration curves for K and Ca showing excellent linearity up to 10 mg/L and 100 mg/L respectively for the major elements

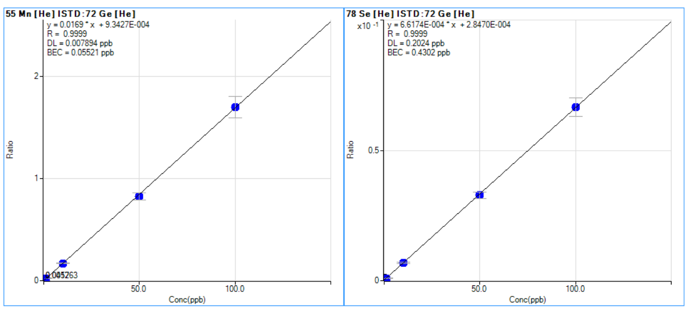

Figure 2. Calibration curves for low level elements Mn and Se, showing excellent linearity up to 100 µg/L

Method validation

Seven separate digests of NIST 1549a were analyzed as an instrument check before starting the analysis of the commercial milk product samples. The results in Table 3 show that good accuracy was achieved for all of the certified elements, with recoveries within ± 5% of the certified values. For most elements, the precision was around 3% RSD or better. The results confirm the suitability of the 7900 ICP-MS for the routine measurement of major and trace elements in digested milk samples. No special settings - such as attenuating the signal using lens or cell voltages or detuning the detector gain - were required to measure the major elements at high ppm levels.

Table 3. Quantitative results, recoveries and precision for 7 separate digests of NIST 1549a (all results in mg/kg (ppm) in the original sample)

	NIST 1549a			
Element	Measured conc. n=7 (mg/kg)	RSD (%)	Certified conc. (mg/kg)	Recovery (%)
23 Na [He]	3,176	2.43	3,176 ± 58	99.99
24 Mg [He]	865	1.54	892 ± 62	97.02
31 P [He]	7,751	1.99	7,600 ± 500	101.99
39 K [He]	11,837	2.31	11,920 ± 430	99.30
44 Ca [He]	8,798	2.12	8,810 ± 240	99.86
55 Mn [He]	0.179	3.07	0.184 ± 0.024	97.03
66 Zn [He]	32.6	1.74	33.8 ± 2.3	96.44
78 Se [He]	0.241	2.36	0.242 ± 0.026	99.78
137 Ba [He]	0.575	3.02	0.566 ± 0.039	101.58

A Continuing Calibration Verification (CCV) standard was measured every 10 samples during the entire sequence. CCV recoveries for all elements were within ± 10% limits, as shown in Figure 3.

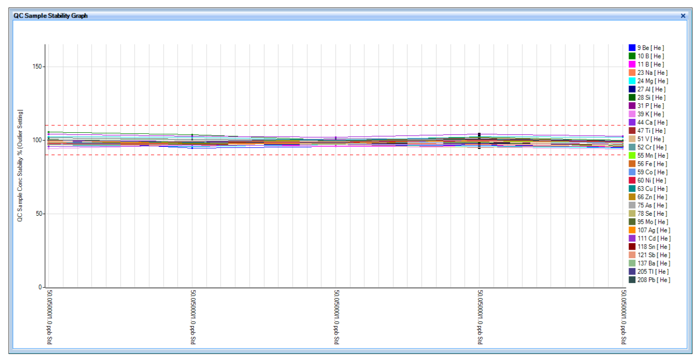

Figure 3. CCV recoveries for the 3 hour sequence. The red lines show the ± 10 % control limits.

Analysis of real samples

The method was applied to the analysis of 24 elements in seven commercial milk and milk product sample digests. Concentrations for elements detected at a concentration greater than the detection limit (DL) are shown in Table 4. Comparison of the data to the published literature (*1*) shows that the results from the commercially available whole milk and fat free milk are within ranges previously published. Khan et al. (*1*) reported values for the minor elements Zn (3535.6–4754.3 ng/g), Se (679.1–1424.8 ng/g), Cu (84.5–718.3 ng/g), Mn (64.1–236.9 ng/g) and Ba (91.0–163.1 ng/g). The authors noted that the values they found for Se, Mn and Cu in milk samples were relatively high compared to the literature values they quoted, which also matches with the results obtained in this study.

Table 4. Quantitative results (average concentration (n=3) in the original samples) for major and trace elements in commercially available milk and milk powders. Results in shaded rows in mg/kg (ppm). All other results in µg/kg (ppb).

Element	Instant Non Fat Dry Powdered Milk	Buttermilk Powder Milk	Whole Powdered Goat Milk	Sweet Cream Buttermilk Powder	Non Fat Dry Milk Powder	Whole Milk	Fat Free Milk
11 B	3,053	2,931	2,337	2,490	2,182	443.5	406.4
23 Na	3,919	3,870	2,804	4,335	3,871	371	378
24 Mg	1,152	1,017	1,094	931	1,091	106	107
31 P	10,215	90,965	8,221	8,161	9,845	965	985
39 K	15,827	30,554	15,912	14,590	17,195	1,519	1,560
44 Ca	11,762	9,963	8,486	7,950	11,077	1,104	1,123
47 Ti	442.5	221.2	201.3	256.3	253.2	<DL	<DL
51 V	24.40	25.55	27.95	28.97	15.29	9.51	9.70
52 Cr	<DL	<DL	<DL	712.7	<DL	<DL	<DL
55 Mn	170.1	220.3	292.9	193.7	219.2	20.20	19.86
56 Fe	1,836	6,468	2,401	9,760	1,935	285.0	306.7
59 Co	5.90	5.75	<DL	8.45	<DL	<DL	<DL
63 Cu	308.1	609.5	899.6	485.8	391.7	35.94	66.12
66 Zn	41	30	27	28	41	4.0	4.0
75 As	<DL	<DL	<DL	<DL	<DL	<DL	<DL
78 Se	365.8	349.8	188.0	418.3	526.4	31.15	28.91
95 Mo	319.7	1946	104.7	2,440	299.1	39.92	34.33
111 Cd	<DL	<DL	<DL	<DL	<DL	<DL	<DL
118 Sn	3.98	18.23	12.56	5.59	12.36	<DL	2.89
121 Sb	<DL	<DL	<DL	<DL	<DL	<DL	<DL
137 Ba	862.0	970.9	523.7	498.7	694.9	77.87	85.69
202 Hg	<DL	<DL	<DL	<DL	<DL	<DL	<DL
205 Tl	3.49	2.34	4.87	2.46	2.57	0.58	0.49
208 Pb	2.39	3.39	3.85	3.03	1.96	0.61	1.27

Conclusions

The Agilent 7900 ICP-MS with UHMI and optional ISIS 3 discrete sampling accessory was used successfully for the rapid, routine analysis of a variety of milk and milk product samples. The 7900 ICP-MS has the largest operating dynamic range of any quadrupole ICP-MS at 11 orders of magnitude, combined with high sensitivity, low background, and effective control of polyatomic interferences. This combination allows major elements such as Na, K and Ca to be determined in the same analytical run as trace elements, using a single set of operating conditions.

The 7900 ICP-MS offers:

- Simple method development and improved ease-of-use with autotune and preset plasma mode.
- Single mode of analysis and reliable interference removal for key elements: He mode provides absolute confidence in data quality.
- Excellent accuracy and precision for all certified major and trace elements in NIST SRM 1549a Whole Milk Powder.
- High speed, with a sample run time of 150 sec per sample for the analysis of 24 analytes and 6 internal standard elements, ideal for high throughput labs.

Reference

1. 1. Khan, N.; Jeong, I. S.; Hwang, I. M.; Kim, J. S.; Choi, S. H.; Nho, E. Y.; Choi, J. Y.; Park, K. S.; Kim, K. S. *Food Chem.* **2014**, 147, 220–224.

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