Accurate and reliable analysis of food samples using ICP-MS

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Abstract

Purpose: Optimization of inductively coupled plasma mass spectrometry (ICP-MS) in combination with argon gas dilution (AGD) to minimize matrix effects for the robust, sensitive and reproducible analysis of major and ultra-trace elements in a wide variety of foods and beverages.

Methods: A method based on ICP-MS technology using additional argon gas was successfully developed for the analysis of acid digests of the different types of samples. The method performance was thoroughly evaluated by continuous analysis of certified reference materials (CRM), quality control (QC) standards and various samples over a period of several days.

Results: The results demonstrate that the developed method delivered highly sensitive and accurate data continuously over several days with minimal user interaction and no need for maintenance steps between sequences.

Introduction

Food and beverage products available on the global market are regularly monitored for nutritional contents as well as toxic elements and metals. Compliance to local regulations such as EC No 1881/2006[1] in the EU, and GB-2762-2017[2] in China, which specify permissible limits of such elements in food, is compulsory for public health safety. Thus, analytical testing laboratories engaged in food sample measurements regularly analyze large numbers of different sample types to provide results to manufacturers, food retailers and regulatory authorities. This study reports a robust, reliable, sensitive, accurate, and high throughput method for the simultaneous analysis of a wide range of elements at different concentrations in a variety food and beverage matrices.

Methods and materials

Test methods

A Thermo Scientific™ iCAP™ RQ ICP-MS instrument (Figure 1) was used with argon gas dilution (AGD) for all analysis (instrument parameters in Table 1).

The additional argon gas, provided directly from the instrument, dilutes the samples and minimizes matrix effects without additional sample preparation. The AGD was optimized such that achieved detection limits were still satisfactory for food analysis.

Table 1. Instrument parameters for ICP-MS used for food measurements.

Instrument Parameter	Setting
Instrument	iCAP RQ ICP-MS
Nebulizer	Borosilicate glass MicroMist™, 400 µL·min^{-1}
Spraychamber	Quartz cyclonic, cooled at 2.7˚C
Injector	2.5 mm i.d., quartz
Interface	Nickel sampler and skimmer cone, high matrix insert
Plasma power	1550 W
Nebulizer gas	0.39 L·min^{-1}
CRC conditions	4.3 mL·min^{-1} at He, 3V KED
AGD setting	55% of maximum capacity of mass flow controller
Scan setting	Dwell times - 0.2 s for Hg, Pb, Se; 0.1 s for As, Cd, Ni, Cu, Fe, Zn; 0.05 s for others; 5 sweeps, 3 main runs
Lens setting	Optimized using autotune

Figure 1. The Thermo Scientific iCAP RQ ICP-MS

Data analysis

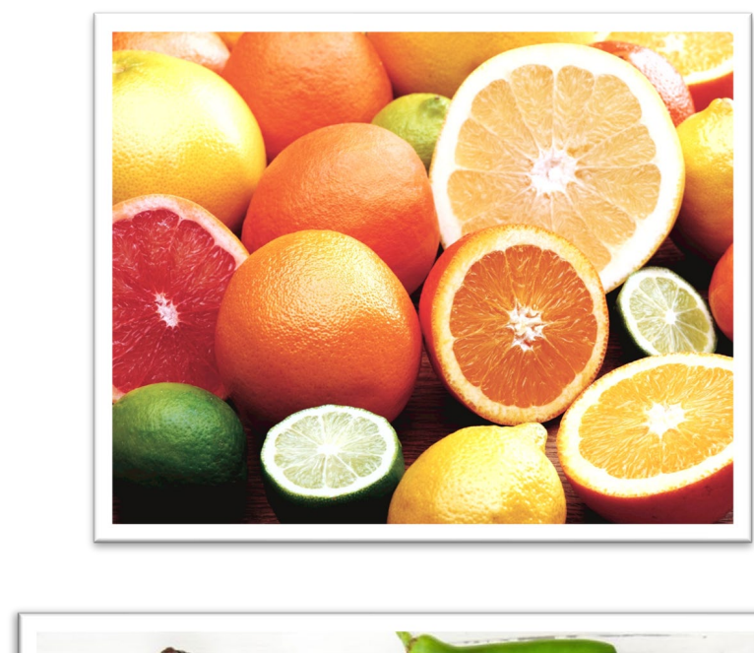
The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used for setting up LabBook and for all data acquisition, processing, and reporting in this study.

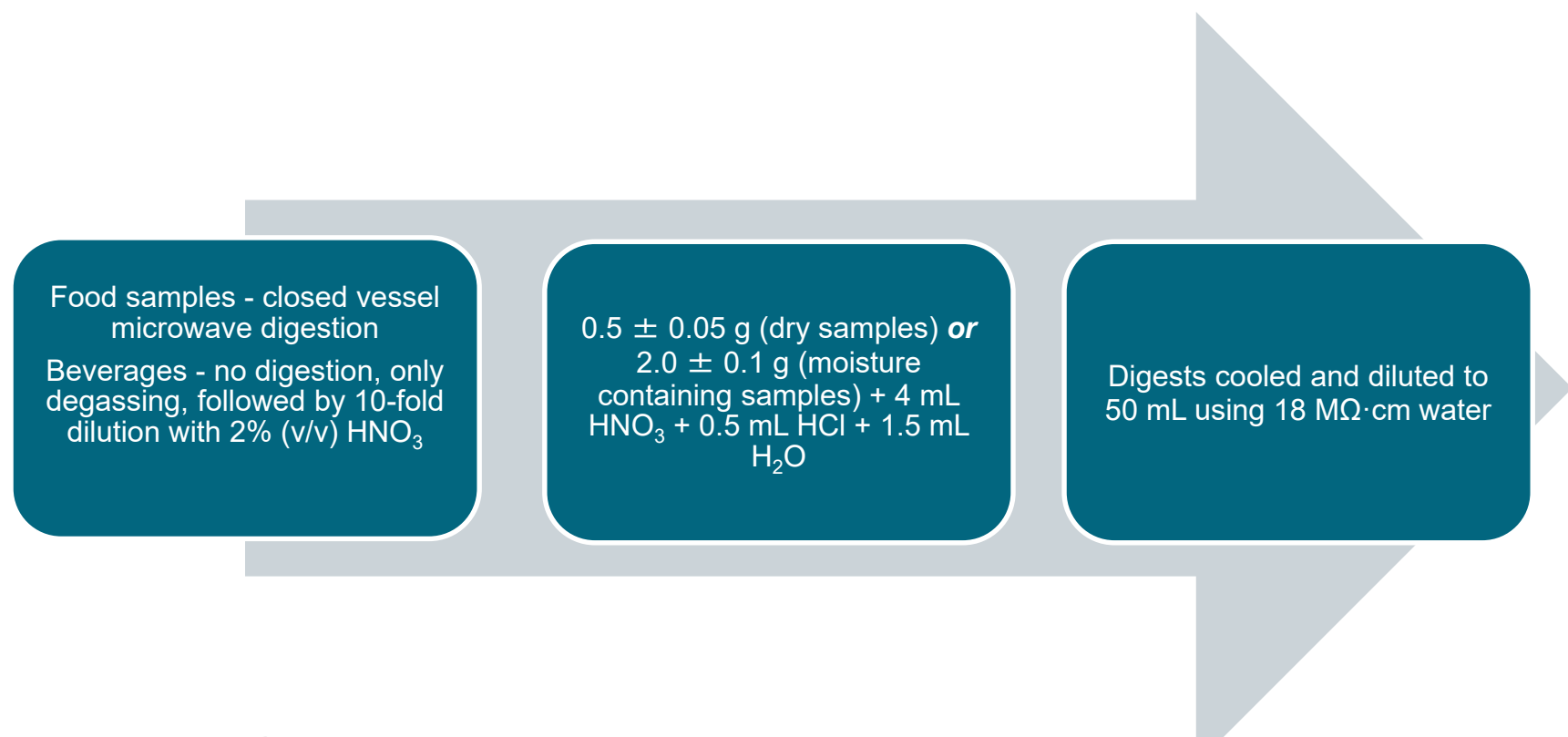
Sample preparation

Twenty-five different food and beverage samples, categorized broadly into five different groups, were selected for analysis in this study (details in Table 2). The sample preparation steps are summarized in Figure 2. Gold (200 µg·L^{-1}) was added to all final solutions including blanks, standards, and amples as a stabilizer for mercury.

Table 2. List of samples and certified reference materials (CRM) measured

Index	Sample group	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
1	Carbohydrate and protein rich	Rice	Cereal	White flour	Spelt flour	Fish (sardines)
2	Vegetable and fruits	Puree-1	Puree-2	Tomato	Spinach	Carrot
3	Spices	Mustard sauce	Pepper	Coriander	Basil	Cinnamon
4	Milk and high fat	Infant formula	Milk powder	Sesame seed biscuits	Cocoa powder	Drinking chocolate
5	Beverages	Apple juice	Orange drink	Cola	Flavoured water	Energy drink
CRMs	Biscuit CRM LGC-7103	Rice Flour SRM 1568b	Milk powder CRM BCR-063	NIST 2383a Baby food composite	Fish CRM DORM-3	Infant Formula RM TYG082





Food samples - closed vessel microwave digestion
Beverages - no digestion, only degassing, followed by 10-fold dilution with 2% (v/v) HNO_3

0.5 ± 0.05 g (dry samples) ***or*** 2.0 ± 0.1 g (moisture containing samples) + 4 mL HNO_3 + 0.5 mL HCl + 1.5 mL H_2O

Digests cooled and diluted to 50 mL using 18 MΩ·cm water

Figure 2. Sample preparation steps

Calibration standards

The developed method was verified for sensitivity and accuracy by using appropriate calibration and quality control (QC) standards prepared in 2% (v/v) HNO_3, online internal standard (IS) addition (Table 3), and CRMs. HCl (2%, v/v) was included in all rinse solutions.

Table 3. Calibration standards used and linear dynamic range achieved for different elements. The concentration units for rows in blue text (Std 1-3) is µg·kg^{-1} and the rest is mg·kg^{-1}.

Group	Elements	Std 1	Std 2	Std 3	Std 4*	Std 5	Std 6
1	Hg	0.005	0.01	0.05	0.1	0.5	1
2	Ag, As, Cd, Ce, Co, Cr, Cu, Li, Mo, Ni, Pb, Sb, Se, Sn	0.05	0.1	0.5	1	5	10
3	Mn	0.5	1	5	10	50	200
4	B, Be, Fe, Zn	0.005	0.01	0.05	0.1	0.5	1
5	Al	0.025	0.05	0.25	0.5	2.5	5
6	P, Mg	1	2	10	20	100	200
7	Ca, K	1.5	3	15	30	150	300
8	Na	3	6	30	60	300	600
IS	Sc, Y, Rh, Lu, Tl via T-piece; additionally, 4% IPA in IS solution for beverage samples						

* Also used as quality control standard

Results

Linearity, sensitivity, and accuracy

A wide linear dynamic range was achieved covering the concentration ranges for the analytes, ranging from 0.005 µg·kg^{-1} for mercury (Hg) up to 600,000 µg·kg^{-1} for sodium (Na) (Table 3). Excellent detection limits were achieved for all analytes, including the four most critical toxic elements – arsenic, cadmium, lead, and mercury (Table 4). All analytes in the study could be detected with high sensitivities that easily enable detection of extremely low amounts of the same in the final samples. The method limits of quantifications (MLOQ) were always well below regulatory limits globally.

Table 4. Instrument detection limits (IDL), limits of quantification (LOQ), and method limit of quantifications (MLOQ) in final dry, wet, and beverage samples (dilution factors: 100x, 25x, and 10x, respectively). All units in µg·kg^{-1}.

Analyte	IDL	R^2	LOQ (3 x IDL)	MLOQ for dry samples	MLOQ for wet samples	MLOQ for beverages
As*	0.004	0.9996	0.012	1.3	0.3	0.1
Cd	0.005	0.9997	0.015	1.5	0.4	0.2
Hg	0.003	0.9996	0.009	0.9	0.2	0.1
Pb	0.001	0.9999	0.003	0.30	0.08	0.03

IDL = 3 x standard deviation of repeat blank runs, LOQ = 3 x IDL, MLOQ = dilution factor x LOQ
*with IPA

The accuracy and precision of the analytical method was assessed by analyzing commercially available CRMs and RMs. A very good agreement was obtained between certified and measured values for all analytes, within acceptable range, over multiple hours and days of measurements of these materials (Table 5).

Table 5. Mean recoveries (in % vs certified value) and associated standard deviations for "n" number of individual measurements of CRMs in the long experiments

	Biscuit CRM LGC-7103		Rice Flour SRM 1568b		Fish CRM DORM-3		Infant Formula RM TYG082		NIST 2383a Baby food		Milk powder CRM BCR-063	
n	40		21		10		50		16		16	
	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev
Na	96	7	-	-	-	-	93	6	94	9	102	8
Mg	92	6	91	7	-	-	92	6	106	7	108	9
Al	-	-	96	8	-	-	-	-	-	-	-	-
P	91	5	83	6			90	11	90	9	93	8
K	98	5	95	5	-	-	91	6	102	6	102	7
Ca	-	-	103	10	-	-	95	4	102	11	103	8
Mn	100	8	93	6	-	-	87	11	93	5		
Fe	-	-	99	8	92	3	94	5	104	5	93	4
Cu	-	-	96	9	96	11	101	5	94	6	115	5
Zn	113	5	101	9	91	3	115	5	88	2	82	6
As	-	-	93	6	91	10			-	-		
Se	-	-	95	9	-	-	104	10	-	-	92	14
Cd	-	-	91	5	104	4	-	-	-	-	-	-
Ba	-	-			-	-	-	-	-	-	-	-
Hg	-	-	102	15	109	8	-	-	-	-	-	-
Pb	-	-			96	6	-	-	-	-	107	10

Robustness experiments

In order to demonstrate the suitability of this method for analyzing high number of food samples with different matrix compositions, as is the situation in a typical food testing laboratory, several experiments were run on consecutive days, over a period of nearly two weeks. Initially, the samples belonging to the respective sample groups (as in Table 2) were run on separate days (Days 1 to 5). Thereafter, the different samples from the different groups were run together for four more days (Days 6, 7, 8, and 9).

Daily experiments consisted of 8 to 10 hours of uninterrupted measurements (~240 samples/day) with a single calibration block at the beginning of the entire sequence which was found to be sufficient for accurate data throughout the run. The calibration block was followed by QC standards (Std 4) repeated after every ten unknown samples to check for calibration validity. CRM samples were interspersed throughout the sequence in order to provide further evidence for measurement accuracy.

No deterioration in performance was noted over the several consecutive days of running >200 unknown food samples per day. The response remained stable and well within 80-120% recovery tolerance range for all internal standards (Figure 3, Table 6), QC (Figure 4), and CRM samples (Table 5). No maintenance or cleaning was required throughout the entire study which demonstrates the robustness of the analytical method for measuring different food samples with widely different compositions using the same method (Figure 5).

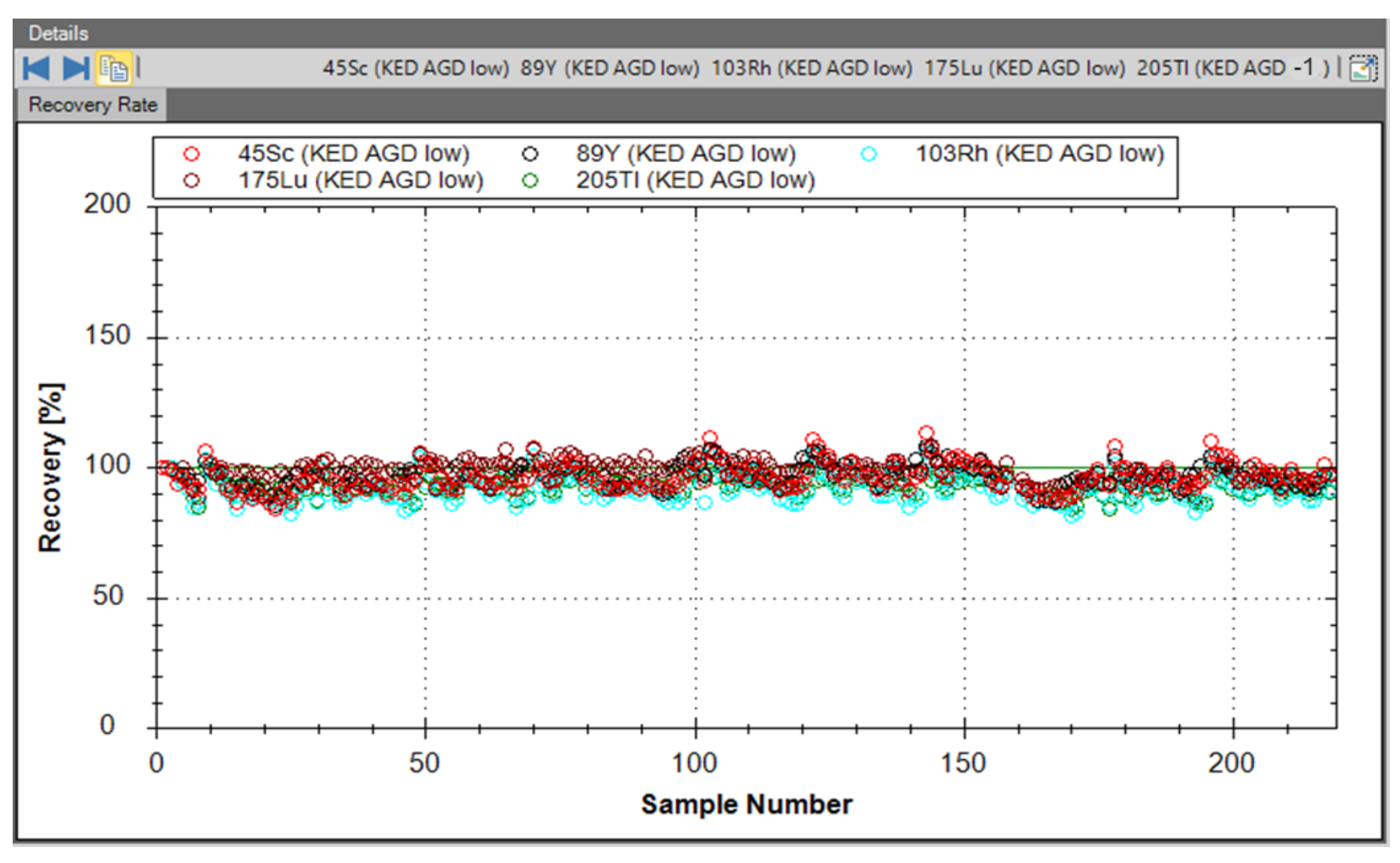


Figure 3. Stable response of the internal standards Sc, Y, Rh, Lu, and Tl of 85-110% during 11.5 h of uninterrupted measurement of food samples from different food groups in the same sequence

Table 6. Internal standard recovery (%) compared to first blank of the sequence during the 8-10 hours long food experiments run daily. The number of total samples run, including standards, CRMs, and unknowns is denoted by n.

Day	Group	n	Sc		Y		Rh		Lu		Tl	
			Recovery (%)	Stdev	Recovery (%)	Stdev	Recovery (%)	Stdev	Recovery (%)	Stdev	Recovery (%)	Stdev
1	1	216	85	8.1	90	7.9	90	7.3	96	8.0	108	8.9
2	2	249	101	4.5	99	4.1	96	3.5	95	3.4	102	3.6
3	3	216	87	3.5	95	4.3	90	3.4	96	2.9	101	5.0
4	4	255	88	8.9	89	8.9	88	9.0	90	9.3	90	9.1
5	5	214	96	8.7	98	8.6	96	8.9	98	7.9	102	9.6
6	1-4	253	107	9.8	106	9.6	100	8.5	104	7.5	106	9.2
7	1-4	216	96	8.4	96	8	91	7.9	99	7.8	92	7.2
8	1-4	244	97	5.2	96	4.1	94	5.0	99	3.6	95	3.8
9	1-5	265	94	4.7	100	4.2	93	4.9	100	2.8	97	3.6
Average of 1878 samples			**95**		**97**		**93**		**97**		**99**	

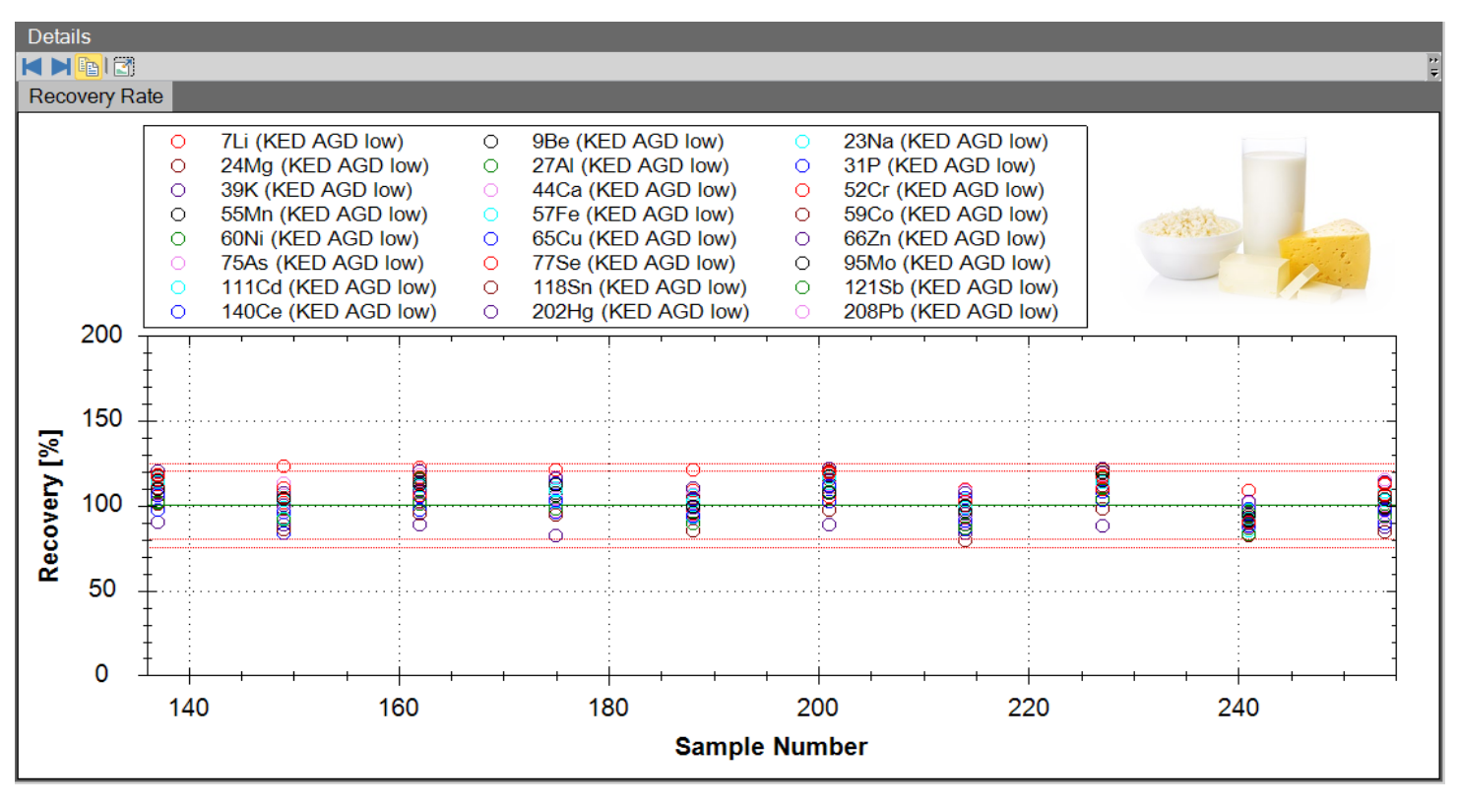


Figure 4. Accuracy of quality control standards (Continuing Calibration Verification, CCV, n = 14) spanning ~ 11 hours of continuous measurements of milk and high fat samples (Day 4, Group 4).

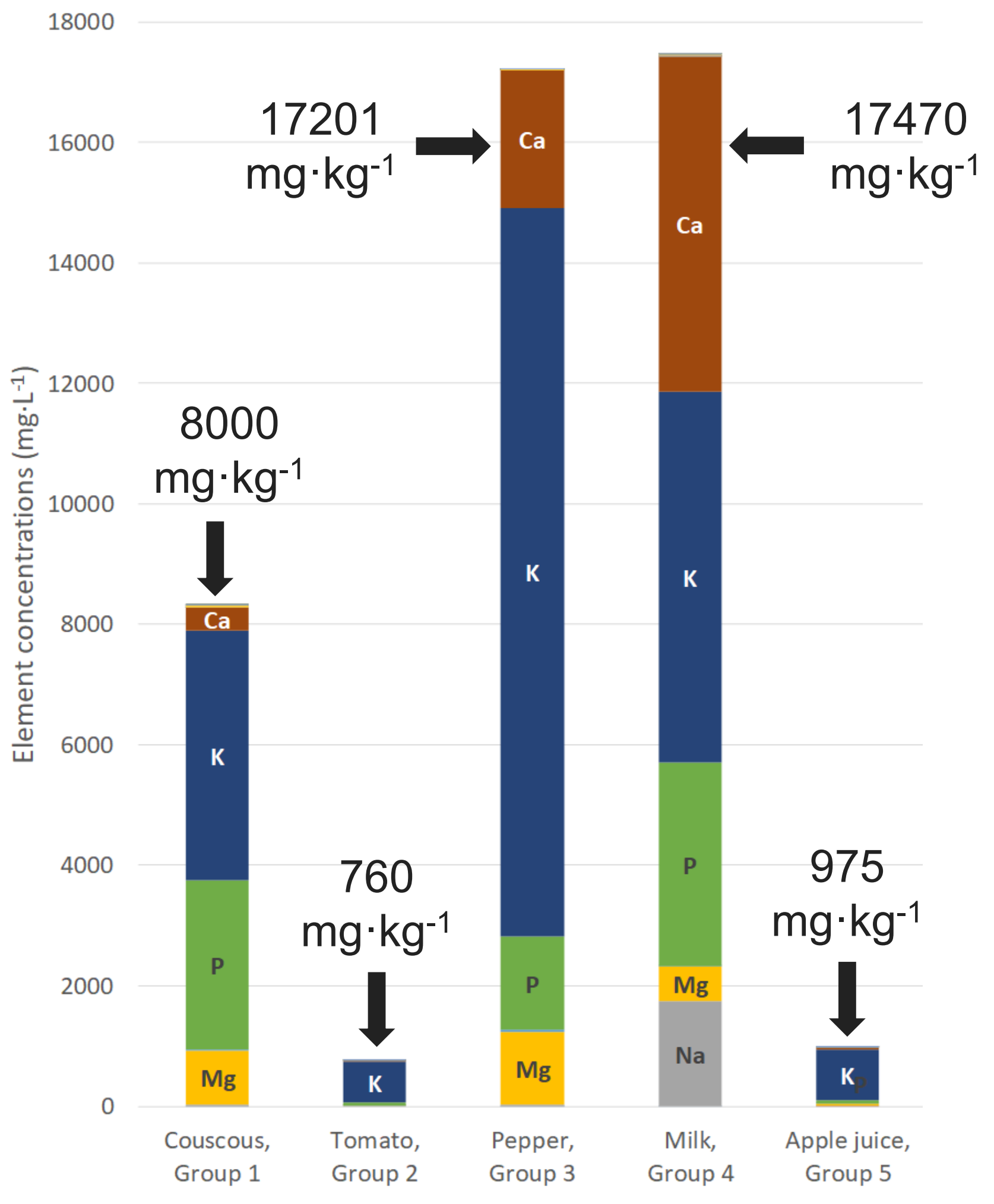


Figure 5. Elemental compositions of representative samples from Groups 1–5

Conclusions

- This study proposes a single ICP-MS and AGD method for the accurate, precise and efficient quantitation of a wide range of analytes, from high concentration nutritional elements to extremely low-level toxic metals in a variety of both food and beverage samples.
- The dilution of all samples inside the ICP-MS with direct argon gas supply is an easy and convenient approach to achieving required dilution levels that minimizes matrix effects. This is demonstrated by excellent internal standard stability over the entire mass range and consecutive days of analysis with each day comprising > 200 samples and > 8 hours of data acquisition. A total of 1878 sample measurements were made, with the quality control standard run every ten unknowns.
- Excellent sensitivity and a wide linear dynamic range was achieved even with AGD settings, enabling the user to easily comply with global regulations and ensure the safety and quality of the food supply.
- The method was validated with six different CRM samples run 153 times during the different experiments to establish the accuracy of the measurements
- Minimal user interaction and no cleaning steps were necessary during the measurements made in this study which continued for almost two weeks, thus making this approach ideal for an analytical testing facility.

References

1. Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.
2. GB-2762-2017 National Food Safety Standard for Maximum Levels of Contaminants in Foods, China.

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