From Routine Multi-element Analysis to Detecting Nanoparticles: using 7800 ICP-MS to Fully Characterize Infant Formula

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Introduction

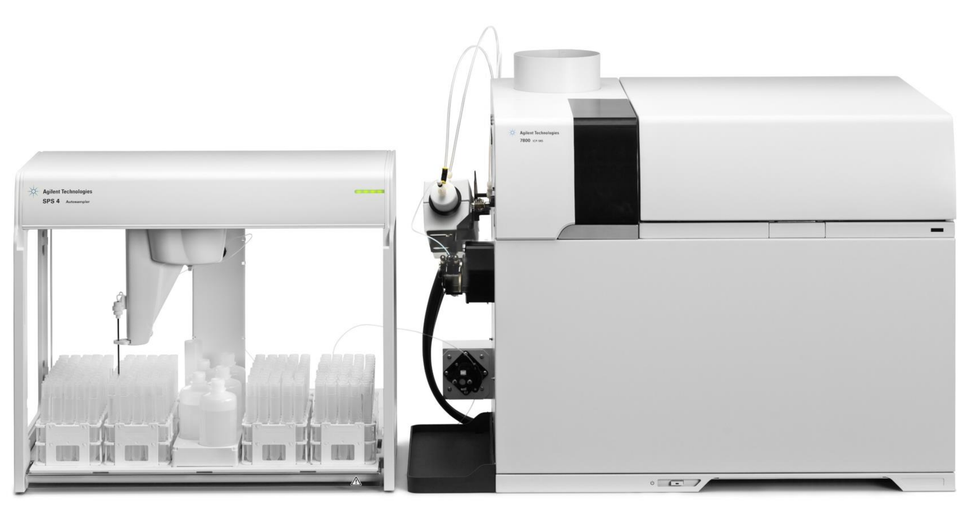
As the market for infant formula continues to grow worldwide, advances are being made in the methods used for elemental analysis of commercial products. Many countries regulate the composition of infant foods and formulas. Typically, the regulations state minimum and maximum levels of minerals, including Na, K, Cu, Mg, Fe, Zn, Mn, Ca, P, I, Cl, and Se. Producers must also adhere to regulations for maximum concentrations of potentially toxic elements, including As, Cd, Hg, Pb, Ni, Sn, and Cr. Since toxic elements are only likely to be present in food samples at low concentrations, ICP-MS is increasingly used for the high throughput, routine analysis of infant formula. ICP-MS is suited to the application since it is a fast, multi-element analysis technique with the necessary sensitivity and dynamic range to measure nutrient and toxic elements in the same sample. ICP-MS can also be used to measure nanoparticles (NPs) using a single particle ICP-MS (spICP-MS) method. spICP-MS is a powerful technique that is used increasingly to detect metal-containing nanoparticles in various matrices, including foods.

In this study, a simple and robust quantitative workflow was developed using ICP-MS for the simultaneous analysis of 28 nutrient and toxic elements in fully digested infant formula samples. A qualitative multi-element workflow using spICP-MS was also used to scan for 13 major and trace element-containing NPs in the same samples.

Experimental

Samples and reagents

- All samples were bought off-the-shelf from markets in the USA and China, included 3 infant formula products from USA, and 4 infant formula products from China;
- A milk-based NIST SRM 1849a Infant/Adult Nutritional Formula I was used to validate the analytical method for element concentration;
- A 60nm Ag nanoparticle suspension (BBI Solutions, UK) was used to spike into de-ionized water (DIW) dissolved infant formula to determinate the matrix effect;
- Nitric acid (≥ 65%, Sigma-Aldrich) was used for microwave digestion and standard/sample preparation;
- All dilutions were done using 18.2 MΩ·cm DIW (Millipore, USA).

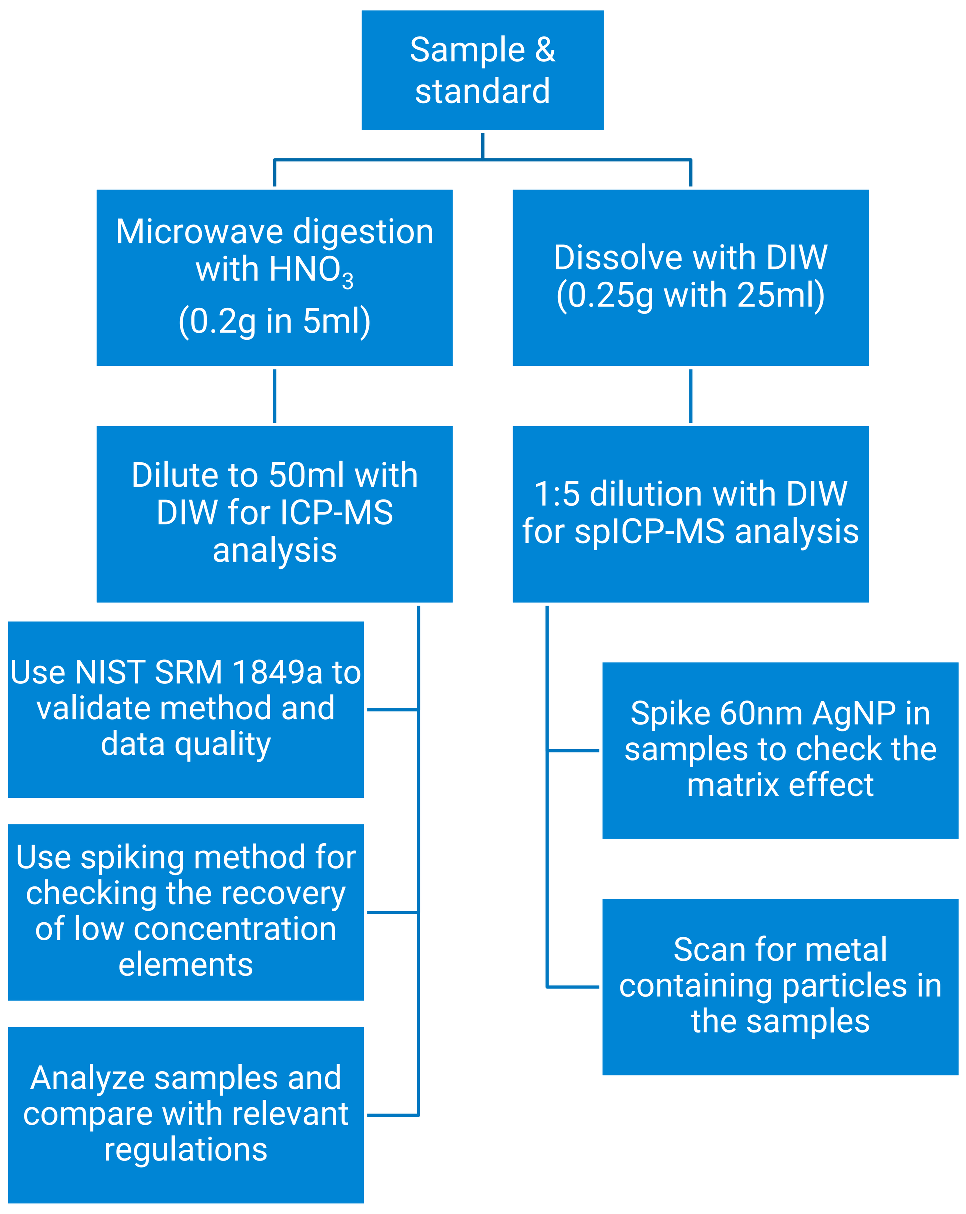


Agilent 7800 ICP-MS with Agilent SPS4 Autosampler.

Instrument settings

- Used a standard Agilent 7800 ICP-MS (with Fast TRA and single particle module activated for spICP-MS, which gives access to 0.1 ms dwell time);
- Configured with standard sample introduction system consisting of a MicroMist glass concentric nebulizer, quartz spray chamber, quartz torch with 2.5 mm i.d. injector (for spICP-MS, the injector was 1.0 mm i.d.), and nickel interface cones;
- The ICP-MS was optimized using autotuning functions within the ICP-MS MassHunter software;
- An Agilent SPS4 autosampler was used as the sample introduction system for concentration analysis, but introduced manually during spICP-MS, due to the need for shaking the sample solution before analysis.
- In the element concentration analysis, all elements, except Se, were measured in He mode with a flow rate of 5 mL/min. Se was measured in High Energy He (HEHe) mode, using a cell gas flow rate of 10 mL/min. In spICP-MS scanning analysis, He mode was used for Al, Si, Ca, Ti, Cr, Mn, Fe, Ni, Cu and Zn, 'No Gas' mode was used for Ag, Ba and Pb.

Experiment workflow



Results and Discussion

28 nutrient and toxic elements analysis

- The details of detection limits (DLs), background equivalent concentrations (BECs), method DLs (MDLs) and limits of quantitation (MLOQs) are listed elsewhere [1]. All MLOQs are lower than listed in GB 5009.268 [2].
- Table 1 shows the mean measured concentrations for all elements were in excellent agreement with the certified values of NIST SRM 1849a, with all mean recoveries well within ±10% of the expected value.

	Certified mass fraction values	Measured values		
		Mean value	RSD (n=6)	Recovery
	(mg/kg)		(%)	
Calcium (Ca)	5253 ± 51	5278	0.6	101
Copper (Cu)	19.78 ± 0.26	19.58	0.2	99
Chromium (Cr)	1.072 ± 0.032	1.124	1.2	105
Iodine (I)	1.29 ± 0.11	1.34	0.3	104
Iron (Fe)	175.6 ± 2.9	175.3	0.7	100
Magnesium (Mg)	1648 ± 36	1653	0.1	100
Manganese (Mn)	49.59 ± 0.97	49.15	0.5	99
Molybdenum (Mo)	1.707 ± 0.040	1.706	0.8	100
Phosphorus (P)	3990 ± 140	3890	0.5	98
Potassium (K)	9220 ± 110	9279	0.3	101
Selenium (Se)*	0.812 ± 0.029	0.842	2.1	104
Sodium (Na)	4265 ± 83	4268	0.1	100
Zinc (Zn)	151.0 ± 5.6	153.7	0.5	102

*Se was determined in high energy He (HEHe) mode.

Table 1. Mean recovery data for 13 elements present in the NIST SRM 1849a nutritional formula

- Spike recovery test of regulated elements in food (As, Cd, Hg, Pb, Ni, Sn, and Cr) was carried out in three infant formula products, spiked at two concentrations, The recoveries for all elements at all concentrations ranged between 95 and 109%. The details are listed elsewhere [1].
- Quantitative analysis results shown that potentially toxic elements, were well below regulatory or guideline levels [3-5]. Mineral and nutrition elements required in infant formula, such as Na, K, Ca, Mg, Fe, Zn, Mn, P, and Se, were within the ranges listed in the guidelines.

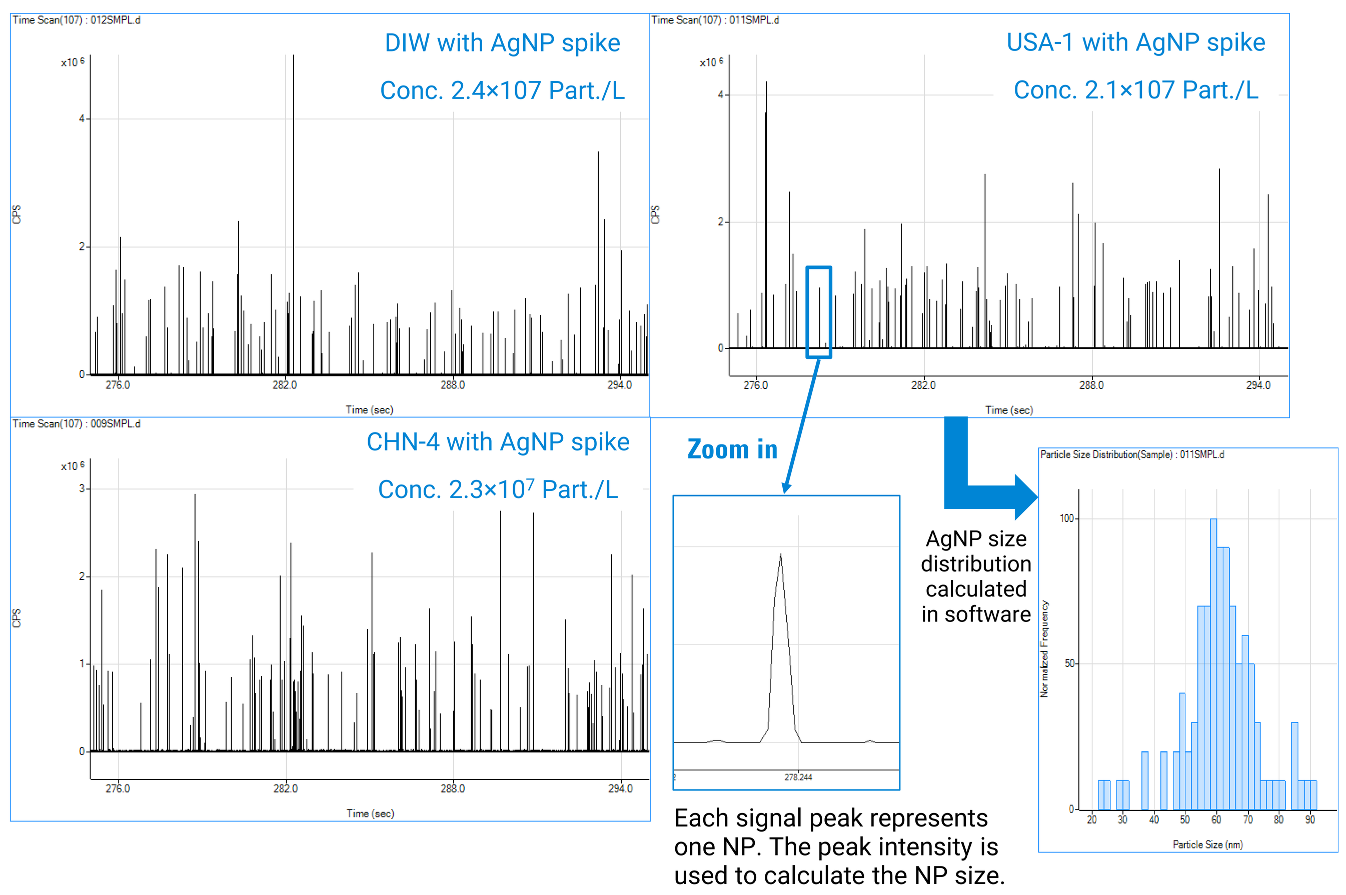
	USA-1		CHN-3		CHN-4	
	Mean (mg/kg)	RSD (%, n=3)	Mean (mg/kg)	RSD (%, n=3)	Mean (mg/kg)	RSD (%, n=3)
B	0.450	4.3	0.505	3.9	0.551	5.4
Na	1366	0.8	1560	0.8	1533	0.7
Mg	385.7	0.4	504.0	0.7	530.4	0.4
Al	0.527	5.3	2.60	0.1	1.22	3.3
P	2115	0.2	4304	0.8	4497	0.2
K	5633	0.4	7042	0.2	7668	0.4
Ca	3990	0.4	6065	0.2	6812	0.4
V	0.002	5.3	0.012	0.6	0.004	0.5
Cr	<MDL	NA	0.065	0.6	<MDL	NA
Mn	1.23	0.3	0.816	0.1	0.455	0.3
Fe	90.93	0.7	69.36	0.9	74.74	0.1
Co	0.004	4.7	0.008	2.8	0.007	2.4
Ni	<MDL	NA	0.049	1.4	0.019	3.4
Cu	4.91	0.2	2.84	0.1	3.65	0.3
Zn	48.51	0.6	46.07	0.1	39.49	0.6
As	0.007	11.3	0.005	3.7	0.004	7.2
Se	0.249	2.9	0.080	0.1	0.088	1.9
Sr	4.62	0.4	2.82	0.1	2.50	0.1
Mo	0.193	0.8	0.127	0.1	0.183	1.5
Cd	0.003	3.6	0.001	2.7	0.0002	18.5
Sn	0.106	0.4	0.003	1.9	0.003	2.5
Sb	0.002	13.7	0.001	8.3	0.001	2.1
I	1.37	1.1	0.862	2.0	0.848	0.1
Ba	0.098	1.8	0.456	1.4	0.370	0.6
Hg	0.0002	45.2	0.0001	22.5	<MDL	NA
Tl	0.002	9.5	0.001	4.2	0.0003	3.4
Pb	0.004	3.3	0.006	1.0	0.003	2.3
U	0.001	1.9	0.005	3.0	0.0003	4.8

Table 2. Quantitative data for 3 out of 7 infant formula samples, details are listed elsewhere [1]. NA: not applicable.

Results and Discussion

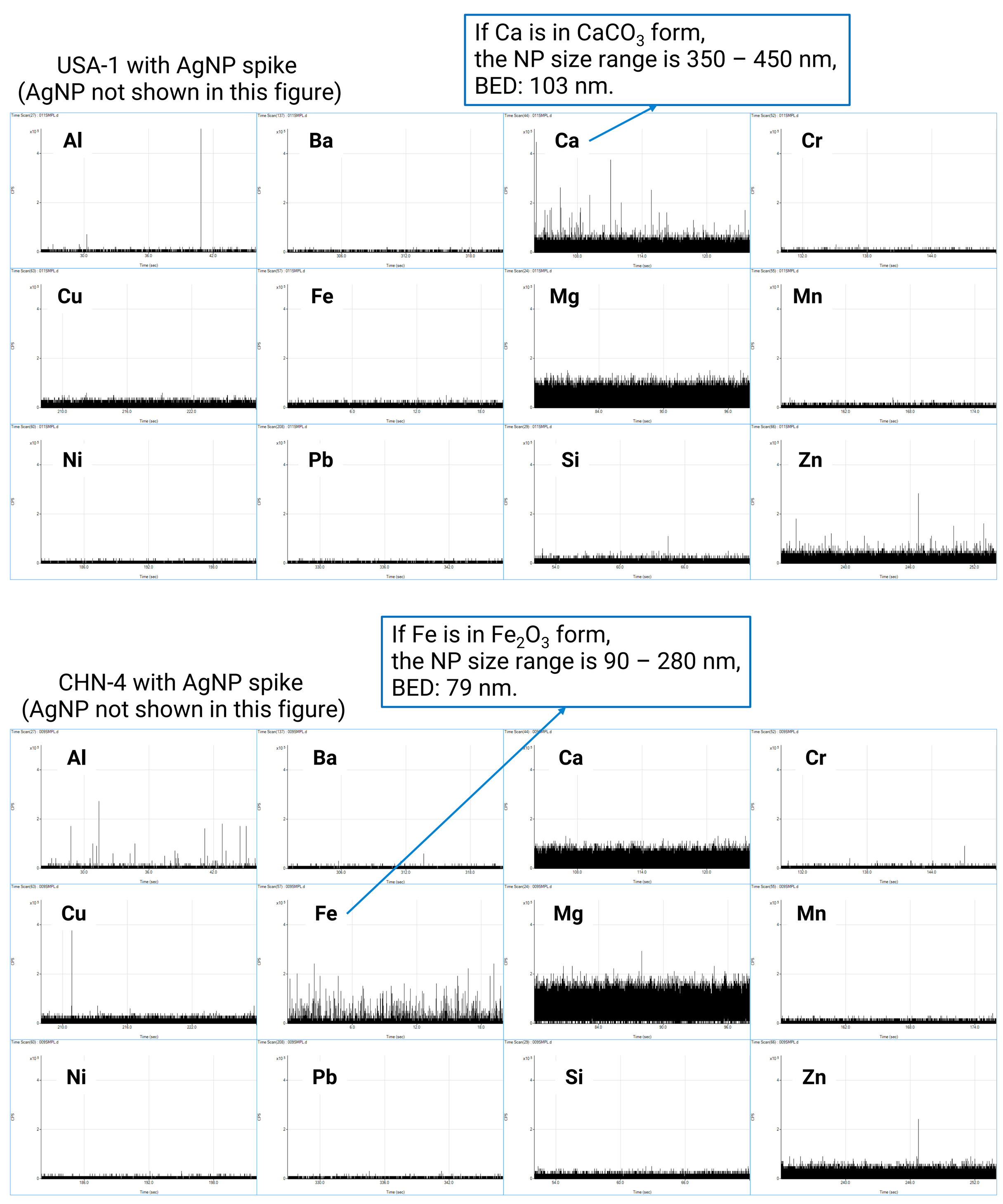
Scanning for 13 metal containing nanoparticles

- Matrix evaluation. DIW and samples were all spiked with the same amount of 60 nm AgNP. No matrix effect was observed in the DIW diluted infant formula samples. The recovery of AgNP in the infant formula sample is greater than 87%.



Distribution of the spiked AgNP in DIW and infant formula samples.

- From the qualitative multi-element scanning, particle form of Al, Ca, Fe, Zn, and Ba could be observed in the some of the samples. The scanning results of 2 out of 7 samples are shown below. By estimating the possible component of the metal containing nanoparticles, we could calculate the size distribution of the them.



Scanning results for Al, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Si, and Zn containing particles in infant formula samples.

- The Al, Ca, Fe, Zn, and Ba containing particles could be an indicator of raw material input, manufacturing technique, and/or packaging material effect.
- This method has potential to be used in manufacturing quality control and authenticity applications.

Conclusions

- The Agilent 7800 ICP-MS can analysis major, mineral elements such as Na, K, Ca, and Mg with trace elements including Cr, As, Cd, Pb, and Hg in the same analytical run.
- The method is suitable for the routine, multi-element screening of trace level elements and high concentration mineral elements in foods, ensuring quality control of elemental nutrients as well as contaminants.
- By activating the spICP-MS function on Agilent 7800 ICP-MS, with a simple dilution method, routine scanning of unknown metal containing NPs in foods could be achieved. The method has the potential to be used in manufacturing quality control and authenticity applications.

References

1) Agilent application note 5994-0842EN, Routine Analysis of Fortified Foods using the Agilent 7800 ICP-MS (2019); 2) GB 5009.268-2016, National food safety standard Determination of multi-elements in food (2016); 3) China's GB 2762–2017 National Food Safety Standard for Maximum Levels of Contaminants in Foods; 4) EU's Commission Regulation (EC) No 1881/2006 setting maximum levels for certain contaminants in foodstuffs; 5) CODEX Standard 193-1995 General Standard for Contaminants and Toxins in Food and Feed, amended 2018.