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Application News

No.J116

Inductively Coupled Plasma Atomic Emission Spectrometry

Analysis of Nutritional and Harmful Elements in Powdered Milk by ICPE-9820 / HVG-1

■ Introduction

Minerals required for infant growth are well balanced in powdered infant formula. According to Japan's Health Promotion Law, a specific formulation of essential minerals, including calcium (Ca), iron (Fe) and copper (Cu), etc., has been established for infant formula as a special-use food, and is required to be displayed on the product label.[1]

However, the potential adverse effects of certain harmful elements such as arsenic (As) on infant growth and development is of utmost concern, accentuating the importance of strict safety management in the production of infant formula from the raw material stage to the finished product.

Here, using the Shimadzu ICPE-9820 simultaneous ICP atomic emission spectrometer, we conducted simultaneous analysis of elements in powdered milk (NMIJ-certified reference material). In addition, high-sensitivity analysis using an HVG-1 hydride vapor generator was conducted for the detection and quantification of the minute levels of arsenic in the sample.

The ICPE-9820 permits analysis using both high-sensitivity axial (AX) direction observation and high-concentration radial (RD) observation, thereby allowing simultaneous analysis of elements present at concentrations ranging from very low to high levels. As for detection of arsenic, the HVG-1 permits detection of As at the several tens ng/L trace level.

■ Sample

NMIJ-certified reference material; Trace Elements in Milk Powder (NMIJ CRM 7512-a: No. MI-040)

■ Sample Preparation

(1) Acid Digestion

Sample decomposition was conducted using a microwave sample digestion system. Each sample was weighed out to approximately 0.5 g, and digestion was conducted by adding 5 mL nitric acid, 2 mL hydrochloric acid and 1 mL hydrogen peroxide. Table 1 shows the sample digestion conditions. Following sample digestion, 0.5 mL of perchloric acid was added, and after conducting digestion again using the same digestion conditions, the total volume was adjusted to 20 mL using purified water. At this time, yttrium (Y) and indium (In) were added as internal standard elements to the measurement solution to obtain concentrations of 0.5 mg/L for Y, and 5.0 mg/L for In.

Table 1 Digestion Conditions Using Microwave Digestion System

STEP	Temperature (°C)	Time (Minutes)	Power (W)
1	50	2	1000
2	30	3	0
3	180	25	1000
4	150	1	0
5	180	4	1000
6	180	15	1000

(2) Pretreatment for High-Sensitivity Analysis of As Using HVG-1

After conducting digestion as described in step (1), the sample was heated (180 °C) to near-dryness on a hot plate. Then, 3 mL hydrochloric acid, 2 mL potassium iodide (200 g/L) and 0.4 mL ascorbic acid (100 g/L) were added, and the mixture was left standing for 60 minutes. The total volume was then adjusted to 20 mL using purified water.

In addition, as reagents for operation of the HVG-1, 6 M hydrochloric acid solution and sodium borohydride solution were prepared.

(3) Validation

For validation of the analytical values, a spike and recovery test sample spiked with the standard solution containing the trace-level analyte elements (As, Cd, Cr, Pb) was prepared prior to digestion.

■ Instrument and Analytical Conditions

Measurement was conducted using the Shimadzu ICPE-9820 simultaneous ICP atomic emission spectrometer and the HVG-1 hydride vapor generator. The typical measurement conditions are shown in Table 2, and the measurement conditions using the HVG-1 are shown in Table 3.

Constituents present at high and trace level concentrations were measured using radial (RD) and high-sensitivity axial (AX) observation, respectively. This all-at-once analysis of both high-concentration components and trace components is possible due to the automatic switching between the radial and axial observation directions featured in the ICPE-9820.

The HVG-1 permits analysis of As with sensitivity that is several hundred times higher than that possible using typical measurement. Moreover, the proprietary design of the gas-liquid separator permits acquisition with stable analytical results over an extended period of time.

Table 2 Analytical Conditions

Instrument	: ICPE-9820
Radio Frequency Power	: 1.20 kW
Plasma Gas Flowrate	: 10.0 L/min
Auxiliary Gas Flowrate	: 0.60 L/min
Carrier Gas Flowrate	: 0.70 L/min
Sample Introduction	: Nebulizer 10
Misting Chamber	: Cyclone chamber
Plasma Torch	: Mini torch
Observation	: Axial (AX) / Radial (RD)

Table 3 Analytical Conditions (HVG-1)

Instrument	: ICPE-9820, HVG-1
Radio Frequency Power	: 1.20 kW
Plasma Gas Flowrate	: 10.0 L/min
Auxiliary Gas Flowrate	: 0.60 L/min
Carrier Gas Flowrate	: 0.80 L/min
Plasma Torch	: Mini torch

■ Analysis

The calibration curve method (internal standard method) was used to conduct simultaneous analysis of the minerals and harmful elements in powdered milk.

[Reference]
1) Allowable Standard for Component Composition and Display of Breast Milk and Infant Formula (published by Japan's Ministry of Health, Labour and Welfare)

■ **Analytical Results**

The analytical results are shown in Table 4. The results for the mineral elements were within the certification range, and good spike and recovery test results were obtained for the trace level toxic elements.

Table 5 shows the analysis result and spike and recovery test result for As using the HVG-1. The As detection limit in aqueous solution was 0.04 µg/L, and in powder, 2 µg/L. As for the spike and recovery test, excellent result of 99 % was obtained.

Fig. 1 shows the results of continuous analysis of a standard solution of As over a 4-hour period. The relative standard deviation (RSD) was 1.6 %, demonstrating stable results over an extended period.

■ **Conclusion**

These results demonstrate that the ICPE-9820 can be used for simultaneous analysis of the elements in powdered milk, from the minerals present at high concentrations to the toxic substances present at trace levels. Further, in combination with the HVG-1, measurement of As at trace levels is also possible.

Table 4 Analytical Results for Powdered Milk (NMIJ CRM 7512-a)

Element	Unit	Analytical Value in Powder	NMIJ-Certified Value	Expanded Uncertainty	Detection Limit in Powder (DL: 3σ)	Analytical Value in Measurement Solution mg/L	Spike Concentration mg/L	Spike and Recovery %	Detection Limit in Measurement Solution (DL: 3σ) mg/L
Ca	g/kg	8.63	8.65	0.38	0.0000002	211	-	-	0.000005
Fe		0.100	0.104	0.007	0.000006	2.45	-	-	0.0001
K		8.66	8.41	0.33	0.00002	215	-	-	0.0004
Mg		0.838	0.819	0.024	0.0000002	20.5	-	-	0.000005
Na		1.78	1.87	0.09	0.00001	50.2	-	-	0.0003
P		5.52	5.62	0.23	0.0002	135	-	-	0.005
Cu	mg/kg	4.70	4.66	0.23	0.02	0.115	-	-	0.0005
Mn		0.957	0.931	0.032	0.002	0.023	-	-	0.00005
Mo		0.229	0.223	0.012	0.02	0.006	-	-	0.0006
Sr		5.89	5.88	0.20	0.0008	0.144	-	-	0.00002
Zn		40.9	41.3	1.4	0.01	1.00	-	-	0.0003
Cd	µg/kg	<DL	-	-	10	<DL	0.5	98	0.0002
Cr		<DL	-	-	15	<DL	0.5	100	0.0004
Pb		<DL	-	-	97	<DL	0.5	100	0.002

<DL: Below detection limit (3σ) (concentration in measurement solution)

Spike and Recover Rate (%) = (Analytical value of spike-and-recovery test solution – Analytical Value) / Spike Concentration × 100

Table 5 Results of Analysis of As in Powdered Milk Using HVG-1 and Results of Spike and Recovery Test

Element	Unit	Analytical Value in Powder	NMIJ Reference Value	Detection Limit in Powder (DL: 3σ)	Analytical Value in Measurement Solution µg/L	Spike Concentration µg/L	Spike and Recovery %	Detection Limit in Measurement Solution (DL: 3σ) µg/L
As	µg/kg	(2.5)	2.1	2	(0.06)	4	99	0.04

Reference values in ( ) indicate value greater than detection limit, and value less than the lower limit of quantitation.
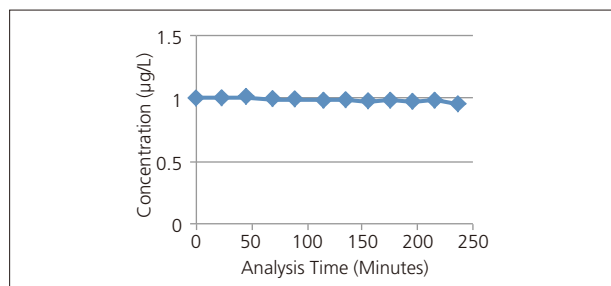

Fig. 1 Long Term Stability of As Value Using HVG-1

Continuous measurement of As 1 µg/L solution (10 % HCl-based) measured continuously every 20 minutes for four hours.
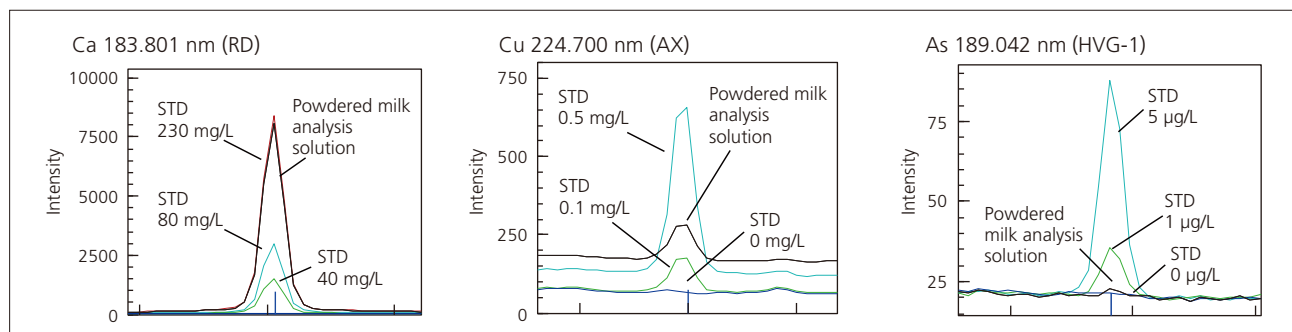

Fig. 2 Spectral Profiles of Ca , Cu, and As

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