FOOD ANALYSIS

MEASURING MAJOR AND MINOR ELEMENTS IN MILK USING THE AGILENT MP-AES 4200

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ABSTRACT

This application note presents the analytical performance of the Agilent 4200 MP-AES for the analysis of milk. Both major elements Ca, K, Mg, Na and P and minor elements Fe, Zn and Cu were determined in a standard reference material of non-fat milk powder, which had been diluted in an aqueous solution containing 0.5% TMAH, 0.5% Triton X-100, 0.03% EDTA and 1 g/L CsNO3. The 4200 MP-AES combined with the flow blurring nebulization system minimizes matrix effects allowing excellent accuracy and precision of data. Robust long term stability was achieved with RSD's between 0.7 - 2.8 % making this method applicable for routine analysis.

INTRODUCTION

Accurate routine testing of major and minor elements in milk is a critical indicator to the quality and nutritional content of the product. Commonly, milk samples have been prepared by either wet digestion or dry ashing [1]. However these methods have proven to be time consuming and involve handling potentially hazardous chemicals. Direct analysis of milk would obviously be preferable but issues relating to the uneven distribution of analytes within the different phases of the semi-homogenous mixture of milk [2], combined with reduced nebulization efficiency can lead to poor accuracy and precision of data [3].

Milk is a challenging matrix but elemental stabilization and homogenization can be achieved by a simple dilution into an aqueous diluent containing Tetramethylammonium Hydroxide (TMAH), Triton X-100 surfactant and Ethylenediaminetetraacetic Acid (EDTA). This combination of reagents solubilizes the sample allowing chelation of metal ions whilst reducing the likelihood of precipitative and/or adsorptive losses. The inert OneNeb operates on flow blurring nebulization technology that allows greater tolerance to total dissolved solids, whilst also improving nebulization efficiency compared to conventional nebulizers [4]. Many of the major components in milk including Ca, K, Mg and Na are easily ionizable elements (EIE) and exhibit ionization interferences [5]. To overcome this problem the addition of another EIE element such as Caesium Nitrate (CsNO3), an ionization suppressant, at 1 g/L to all solutions is sufficient to reduce ionization effects. This saturates the plasma of free electrons and drives the equilibrium between the ionization state of the metal back into the ground state. Caesium was chosen as an ionization suppressant as it has a low first ionization energy and spectral interference is generally not a problem.

This application note describes the analytical methodology for the multielement determination of both major elements (Ca, K, Mg, Na and P) and minor elements (Fe, Zn and Cu) found in milk using the Agilent 4200 Microwave Plasma-Atomic Emission Spectrometer (MP-AES). Accuracy and precision of the method were assessed by the use of European Reference Material (ERM) BD151 milk powder.

ANALYTICAL TECHNIQUE

Instrumentation

All measurements were performed using an Agilent MP-AES 4200 instrument equipped with the standard sample introduction system consisting of the OneNeb nebulizer, double pass cyclonic spray chamber and easy fit torch. The Agilent SPS-3 autosampler was used to deliver samples to the instrument allowing unattended operation. Selection of optimal lines depended on wavelengths that were free from spectral interference and matched the appropriate sensitivity. Spectral and background interferences could be simultaneously and accurately corrected for using the MP software. Tables 1 and 2 list the instrument operating parameters.

Element	Wavelength (nm)	Nebulizer Flow (L/min)
Ca	612.222	0.95
Na	568.820	0.9
Cu	327.395	0.65
Fe	371.993	0.65
Zn	213.857	0.3
K	404.414	0.75
P	214.915	0.4
Mg	518.360	0.75

Table 1. Wavelength, nebulizer flow for Ca, K, Mg, Na, P, Fe, Zn and Cu.

Instrument Parameter	Setting
Number of Replicates	3
Stabilization Time	20
Background Correction	AUTO
Flow rate into plasma (sec)	24
N2 (psi)	82
Air (psi)	60

Reagents and standard solutions

Single element stock solutions (Agilent Technologies) containing 10 g/L of Ca, K, Mg, Na, P, Fe, Zn and Cu were used to prepare the calibration standards. The standards were made up in 18 MΩ Milli-Q water with 0.5% v/v TMAH (Alfa Aesar), 0.05% Triton X-100 (BDH Laboratory Supply) and 0.03% v/v EDTA (Sigma Aldrich) prepared from a stock solution containing 1% v/v TMAH, 0.1% w/v Triton X-100 and 0.06% v/v EDTA. CsNO3 99.8% (Alfa Aesar) was used as the ionization buffer.

Sample preparation

A standard reference material of skimmed milk powder ERM-BD151 was obtained from LGC standards and used to validate the accuracy of the method. Aliquots of 0.5 g of milk powder were dissolved in 25 mL containing 1% TMAH, 0.1% Triton X-100, 0.06% EDTA and 5 mL of 10 g/L CsNO3. They were then made up to 50 mL with 18 MΩ Milli-Q water. To ensure sufficient mixing, the vessels were placed in an ultrasonic bath for 10 minutes followed by vigorous shaking for another minute.

RESULTS AND DISCUSSION

The standard reference material was analyzed for all elements in a single measurement and accuracy of the MP-AES results were evaluated by comparing with the reference values for ERM-BD151. Table 3 shows good accuracy was achieved for all elements over a wide concentration range with all results being obtained within 5% of the certified concentration. The standard reference material was repeatedly analyzed for over a period of 2 hours achieving excellent stability results for all elements. The results of this stability test are shown in Figure 1 and Table 4.

To sustain the plasma, nitrogen is extracted straight from the air using the Agilent 4107 Nitrogen generator. Microwave plasma eliminates the need for expensive and hazardous analytical grade gases such as acetylene used in Flame Atomic Absorption Spectrometry (FAAS), resulting in lower running costs [6].

Element	Certified Values [g/kg]	Uncertainty [g/kg]	Result [g/kg]	Recovery [%]
Ca	13.9	0.7	14.21	102
K	17	0.8	16.66	98
Mg	1.26	0.07	1.31	104
Na	4.19	0.23	4.25	101
P	11	0.6	11.27	102
	Certified Values [mg/kg]	**Uncertainty [mg/kg]**	**Result [mg/kg]**	**Recovery [%]**
Zn	44.9	2.3	45.89	102
Fe	53	4	50.51	95
Cu	5	0.23	5.13	103

Table 3. Determination of Ca, K, Mg, Na, P, Fe, Zn and Cu in TMAH, Triton X-100, EDTA and ionization buffer by MP-AES 4200.

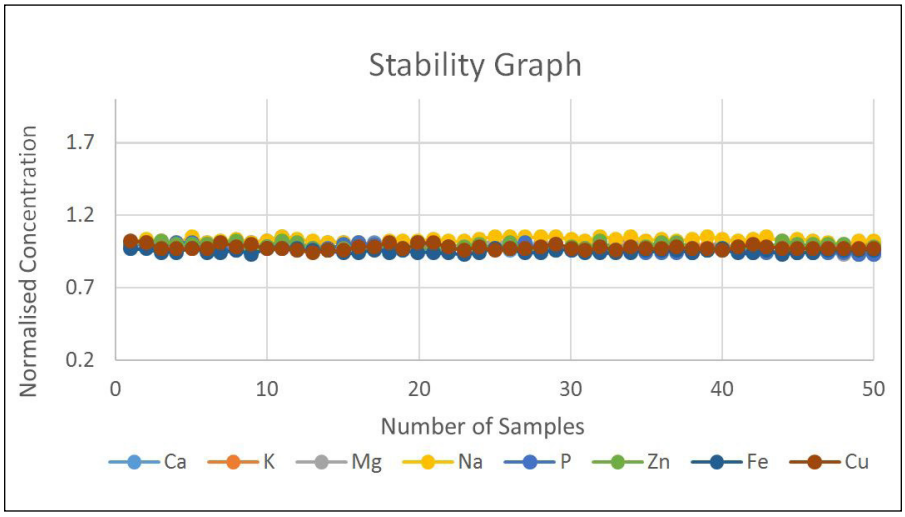

Figure 1. Stability plot for all elements. Reference material was repeatedly analyzed for a period of 2 hours. Please note that the sample solution was exhausted after 53 measurements.

Element	Ca	K	Mg	Na	P	Zn	Fe	Cu
%RSD	1.84	0.69	2.77	1.38	2.37	2.19	1.31	1.75

Table 4. Stability study RSDs for Ca, K, Mg, Na, P, Fe, Zn and Cu.

CONCLUSION

The direct analysis of the total metal content of a skimmed milk reference material, following dilution in a mixture of TMAH, Triton X-100, EDTA and an ionization buffer, is a simple and effective method that can easily be implemented in routine analysis. All measurements are in very good agreement with the certified values of the ERM, validating the accuracy of the method. Excellent long term stability was achieved. RSDs ranged from 0.7% for K to 2.8% for Mg making this method applicable for routine analysis. The MP-AES 4200 combined with the flow blurring nebulization meets the challenges of routine milk analysis whilst achieving excellent precision and accuracy.

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