Direct analysis of milk using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES)

Application note

Food Testing

Authors

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Abstract

Milk samples, which had been diluted in aqueous solutions containing 10% v/v of a mixture of tertiary amines at pH 8.0, were analyzed using an Agilent 4100 MP-AES. Al, Cr, Cu, Fe, Mg, Mn and Zn were determined in a non-fat liquid milk sample and in a standard reference material of non-fat milk powder. Sample introduction via a OneNeb nebulizer, which incorporates the Flow Blurring technology, and automatic background correction with the MP Expert software, contributed to minimizing matrix effects and background emission and to improving sensitivity and accuracy. Limits of detection are between 0.8–76 µg/L and adequate accuracies were obtained using either external calibration or the method of standard additions (MSA). In addition to the lower operational and maintenance costs of MP-AES, the detection limits achieved by the new method are comparable to ICP-OES and significantly superior to FAAS.

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Introduction

The direct analysis of milk is an intuitively attractive sample preparation choice considering its relatively high solubility in water. However, milk is a complex colloidal system with distinct components such as fat emulsion, casein micelle suspension and aqueous phase [1]. It has been demonstrated that some analytes can be distributed differently in each of these phases [2] and problems related to sample nebulization and atomization interferences may compromise accuracy and precision in the direct analysis of milk solutions [3,4].

An interesting strategy to overcome some of these problems is to dilute samples in a mixture of tertiary amines [5,6]. This reagent can dissociate casein micelles and stabilize cations present in the aqueous phase [5]. Another approach to improve precision and accuracy is to employ efficient nebulization systems. Recent studies have demonstrated that nebulizers based on the Flow Blurring nebulization technology, such as the OneNeb nebulizer, can produce smaller, narrowly-distributed aerosol particles, resulting in better sensitivity, precision and accuracy [7,8].

In this application note we describe the determination of Al, Cr, Cu, Fe, Mg, Mn and Zn in milk using an Agilent 4100 MP-AES. The nitrogen used to generate the plasma can be supplied via a simple air compressor and nitrogen gas generator. A clear advantage of in-house gas generation is the reduced costs of operation and maintenance compared to conventional gas resupply. In addition, the superior stability of the microwave-induced plasma, combined with the OneNeb nebulizer, allow sensitive and accurate determinations in milk samples following a simple dilution in a mixture of tertiary amines.

Experimental

Instrumentation

All measurements were performed using an Agilent 4100 MP-AES. The sample introduction system consisted of a double-pass cyclonic spray chamber and the OneNeb nebulizer. The Agilent MP Expert software was used to automatically subtract the background signal from the analytical signal. In this case, a background spectrum from a blank solution is recorded and subtracted from each reference and sample solution that is analyzed. This software was also used to optimize the nebulization pressure and the viewing position for each analyte. Because of this optimization, and considering that all determinations are carried out sequentially, each analyte is determined under optimized conditions rather than under compromised acquisition conditions.

Tables 1 and 2 list the instrumental operating conditions used in the direct analysis of milk.

Table 1. Agilent 4100 MP-AES operating conditions

Instrument parameter	Operating condition
Nebulizer	OneNeb
Spray chamber	Cyclonic double-pass
Read time (s)	5
Number of replicates	3
Stabilization time (s)	15
Background correction	Auto

Table 2. Wavelengths, viewing positions, nebulizer pressures for Al, Cr, Cu, Fe, Mg, Mn and Zn determinations by MP-AES

Element	Wavelength (nm)	Viewing position (nm)	Nebulizer pressure (kPa)
Al	396.152	0	240
Cr	425.433	-10	220
Cu	324.754	-20	240
Fe	385.991	10	80
Mg	285.213	-10	200
Mn	403.076	0	220
Zn	213.857	10	100

Reagents and standard solutions

Nitric acid (Merck, Darmstadt, Germany) previously purified by a sub-boiling distillation system (Milestone, Sorisole, Italy) was used in the preparation of all solutions. Stock monoelement solutions containing 1000 mg/L of Al, Cr, Cu, Fe, Mg, Mn and Zn (Tec-Lab, Hexis, São Paulo, SP, Brazil) were used to prepare standard reference solutions and to carry out spike experiments. The analytical blank was a solution containing 10% v/v of a water-soluble mixture of tertiary amines, which was prepared by diluting the stock solution (CFA-C, Spectrasol, Warwick, NY, USA) with distilled-deionized water (18.2 MΩ cm, Milli-Q, Millipore, Bedford, MA, USA) and adjusting the pH to 8.0 with ultrapure HNO_3. The analytical blank was used to prepare all of the reference standard solutions that were analyzed to generate an analytical calibration curve for each element.

Samples and sample preparation

A standard reference material of non-fat milk powder (SRM 1549) from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) was used to check the accuracy of the procedure. Aliquots of approximately 0.1 g of milk powder were dissolved in 10% v/v CFA-C at pH 8.0 to a final volume of 10 mL. A relatively translucent solution was obtained after vortex mixing for 2 minutes.

A non-fat liquid milk sample obtained in a local market was also analyzed. Sample aliquots of 0.5 mL were diluted with 10 % v/v CFA-C at pH 8.0 to a final volume of 10 mL. Spike experiments were also carried out to check the accuracy of the procedure. Standard reference solutions of Al, Cr, Cu, Fe, Mg, Mn and Zn were added to the sample to a final concentration of 20 µg/L (Al, Cr and Cu), 500 µg/L (Mg), or 2500 and 5000 µg/L (Fe, Mn and Zn).

Results

Limits of detection (LOD) and quantification (LOQ) were calculated from three and ten times the standard deviations for 16 consecutive blank measurements divided by the calibration curve slope, respectively. Table 3 presents the values obtained for all analytes. The results highlight the high detection power of the 4100 MP-AES. The microwave plasma is especially advantageous when compared to methods such as flame atomic absorption spectrometry (FAAS) in which an oxidizing gas such as nitrous oxide would be required to determine Cr and Al. In addition, the LODs obtained using the 4100 MP-AES are almost one order of magnitude lower than those typically obtained by FAAS.

Table 3. Limits of detection and limits of quantification for Al, Cr, Cu, Fe, Mg, Mn and Zn determined by MP-AES

Element	LOD[a] (µg/L)	LOQ[a] (µg/L)	LOD in liquid milk sample[b] (µg/L)
Al	1.4	4.5	28
Cr	0.8	2.8	16
Cu	2.4	7.9	48
Fe	0.4	1.5	8.0
Mg	76	250	1500
Mn	3.8	13	76
Zn	28	95	560

[a] Instrumental limits of detection and quantification
[b] Limits of detection considering sample dilution (1:20 v/v milk in CFA-C 10% v/v, pH 8.0)

To evaluate the accuracy of the method, a non-fat milk powder (NIST SRM 1549) standard reference material was analyzed. Recoveries of 100% and 108% were obtained for Al and Mg, respectively (Table 4). Concentrations for Cr, Cu, Fe, Mn and Zn in this SRM were below the LODs, therefore spike experiments were also carried out using a non-fat liquid milk sample. Adequate accuracies were observed for Cu, Fe and Mg. However, recoveries for Al, Cr, Mn and Zn were poor using external calibration, indicating the occurrence of matrix interferences on these elements. It must be pointed out that external calibration was performed without any matrix matching. Adequate recoveries were also obtained for these elements by applying the method of standard additions (MSA). (Table 4).

Table 4. Determination of Al, Cr, Cu, Fe, Mg, Mn and Zn in CFA-C-diluted milk by MP-AES

Sample	Analyte	Reference/ added (µg/L)	Measured (µg/L)	Recovery (%)
NIST SRM 1549[a]	Al	2.0	2.0 ± 0.2	100
	Mg	1200 ± 30	1300 ± 60	108
Non-fat liquid milk	Al[b]	0	< 1.4	-
		20	21 ± 6	105
	Cr[b]	0	< 0.8	-
		20	18 ± 1	90
	Cu	0	216 ± 8	-
		20	20 ± 1	100
	Fe	0	< 0.4	-
		2500	2688 ± 0.2	107.5
		5000	4807 ± 0.2	96.1
	Mg	0	138000 ± 2000	-
		500	480 ± 60	96
	Mn[b]	0	< 3.8	-
		2500	2506 ± 0.06	100.3
		5000	5141 ± 0.02	102.8
	Zn[b]	0	0.131 ± 0.002	-
		2500	2809 ± 0.008	112.4
		5000	5339 ± 0.117	106.8

[a] Values in mg/kg
[b] Values determined using the method of standard additions (MSA)

Conclusion

The direct analysis of milk combining sample dilution in CFA-C, the OneNeb nebulizer with the Flow Blurring nebulization technology and determination with the Agilent 4100 MP-AES is a simple and effective procedure that can be easily implemented in routine analysis. In addition to the relatively low costs of operation and maintenance, the powers of detection achieved using the 4100 MP-AES are comparable to ICP-OES, and significantly better than FAAS methods.

Considering the complexity of the milk colloidal system and that no internal standardization or matrix matching was applied, adequate accuracies were obtained using either external calibration or the standard additions method depending on the analyte.

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Published April 10, 2013
Publication number: 5991-2071EN

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