Bromine and Iodine Determination in Milk Powder Samples by ICP-MS after Digestion using Microwave-Induced Combustion

Morgana Doneda[1] (PG), Larissa T. Bruschi[1] (IC), Rochele S. Picoloto[2] (PQ), Cezar A. Bizzi[1] (PQ), Paola A. Mello[1] (PQ), Érico M. M. Flores[1*](PQ)

[1] *Departamento de Química, Universidade Federal de Santa Maria, 97105-900, Santa Maria, RS, Brasil*
[2] *Núcleo de Química, Universidade Tecnológica Federal do Paraná, 85884-000, Medianeira, PR, Brasil*

Keywords: *bromine, iodine, milk powder, microwave-induced combustion, ICP-MS.*

Introduction

Information about Br and I concentration in milk is important because their excess or deficiency can cause serious damages to human organism. Intake of high amount of I can lead to disorders mainly related to thyroid gland. Bromine can cause hematologic diseases if combined with hemoglobin. Moreover, Br can reduce the capability of I accumulation and can also contribute to I elimination by human organism.[1] However, the determination of Br and I in milk powder samples is not a simple task mainly because this kind of sample is particularly difficult to bring into solution due to the high fat content. Considering the feasibility of microwave-induced combustion (MIC) for efficient digestion of organic samples, in this work MIC was applied for digestion of milk powder for further simultaneous Br and I determination by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).[2]

Results and Discussion

Samples of whole, semi-skimmed and skimmed milk powder were used. In this procedure, sample was pressed as pellet and a disc of filter paper with 50 µL of 6 mol L^{-1} NH_4NO_3 solution were placed on a quartz holder. Sample holder was introduced into the quartz vessel, previously filled with 6 mL of absorbing solution (water or 10 to 100 mmol L^{-1} NH_4OH solution). Digestion vessels were closed and pressurized with 20 bar of oxygen. Heating program used for MIC was (*i*) 1400 W for 5 min and (*ii*) 0 W for 20 min (cooling step). Pellets of milk powder sample (500 to 800 mg) were used to evaluate the sample mass that could be efficiently digested by MIC. For comparison of results, Br and I were also determined by ICP-MS after Microwave- Assisted Alkaline Extraction (MW-AE) method. In the last method, samples (700 mg) were weighted and placed directly to the digestion vessels and 6 mL of 25 mmol L^{-1} NH_4OH were used for analyte extraction. Heating program was (*i*) 1400 W for 50 min (ramp of 10 min) and (*ii*) 0 W for 20 min (cooling step). Using MIC it was possible to efficiently digest up to 700 mg of milk powder (residual C < 25 mg L^{-1}), reducing interferences during ICP-MS determination caused by excessive carbon content in solution. Taking into account the use of 25 mmol L^{-1} NH_4OH as absorbing solution, recoveries were better than 95% for Br and I. Moreover, both analytes were stable in this solution up to 30 days. Results obtained by ICP-MS after MW-AE and MIC are shown in Table 1.

Table 1. Results obtained by MIC and MW-AE for Br and I in milk powder. Determination by ICP-MS. Results in µg g^{-1}, n=3.

Milk powder	Method	Bromine	Iodine
Whole	MIC	23.0 ± 1.1	0.450 ± 0.024
	MW-AE	20.8 ± 2.5	0.486 ± 0.066
Semi-skimmed	MIC	12.7 ± 0.6	1.86 ± 0.09
	MW-AE	11.1 ± 1.4	1.77 ± 0.26
Skimmed	MIC	54.2 ± 2.7	0.584 ± 0.031
	MW-AE	49.9 ± 4.9	0.563 ± 0.083

According to the results shown in Table 1, no statistical difference (t-test, 95% confidence level) was observed for Br and I using MIC and MW-AE. However, solutions obtained after digestion by MIC presented lower residual C content (25 mg L^{-1}) while solutions obtained after MW-AE presented about 8000 mg L^{-1} of C. Limits of detection (LODs) for MIC were 0.007 and 0.003 and for MW-AE they were 0.122 and 0.054 µg g^{-1} for Br and I, respectively. Accuracy of MIC method was evaluated using reference material of milk powder (NIST RM 8435, whole milk powder) and standard reference material (NIST SRM 1549, non-fat milk powder) and agreement better than 95% was obtained for both analytes.

Conclusions

MIC method was suitable for digesting milk powder samples for further simultaneous Br and I determination by ICP-MS. Complete oxidation of the organic matrix was obtained using a relatively high sample mass (700 mg) that allowed obtaining low LODs. In addition, MIC avoided the use of concentrated alkaline solutions or excessive amount of reagents, reducing blank values and residues generation according to the green chemistry recommendations.

Acknowledgments

CNPq, CAPES, FAPERGS and UFSM

[1]Mello, P.A.; Barin, J.S.; Duarte, F.A.; Bizzi, C.A.; Diehl, L.O.; Muller, E.I.; Flores, E.M.M, Anal. Bional. Chem.. **2013**, *405*, 7615.
[2]Mesko, M.F.; Moraes, D.P.; Barin, J.S.; Dressler, V.L.; Knapp, G.; Flores, E.M.M., **2006**, *82*,183.