Chlorine and Sulfur Volatilization from Eggshell Using Microwave-Induced Combustion (MIC)

Gilberto da Silva Coelho Junior[1] (IC), Rodrigo M. Pereira[1] (PG), Vanize C. Costa[1] (PG), Carla A. Hartwig[1] (PG), Filipe S. Rondan[1] (IC), Márcia F. Mesko[1] (PQ)* - (marcia.mesko@pq.cnpq.br)

[1]Centro de Ciências Químicas, Farmacêuticas e de Alimentos, Universidade Federal de Pelotas, Pelotas/RS, Brazil.

Keywords: *Volatilization, Eggshell, MIC.*

Abstract

Chlorine and S volatilization from eggshells was performed by MIC. Analytes were absorbed in water and determined by IC.

Introduction

Due to a Ca deficiency in humans, non-governmental organizations have recommended eggshells as a low-cost dietary supplement, once 38% of the eggshell's Ca content is bioavailable.[1] Moreover, eggshells may be a source of other micro or macronutrients, such as Cl and S. Thus, the evaluation of Cl and S concentration in eggshell is very important because an inadequate intake of these elements can cause disorders in humans. Due to the inorganic composition of eggshells, sample preparation can be difficult, especially when the objective is determination of elements in low concentration. An alternative to sample preparation of inorganic matrices is the volatilization of analytes by microwave-induced combustion (MIC). For this purpose, high-purity microcrystalline cellulose was used as a combustion aid, promoting energy in the combustion process and causing analyte volatilization.[2] Therefore, this study aimed evaluate the MIC method for volatilization of Cl and S from eggshells and further determination (Cl^- and SO_4^{2-}) by ion chromatography (IC).

Results and discussions

Brown, white and organic eggs were purchased in markets from Pelotas/RS/Brazil. Initially, eggshells were washed with ultrapure water, dried at 60 ºC for 4 h and ground. Brown eggshells were chosen randomly in initial studies using the procedure described by Pereira et al. (2016). Then, sample masses (100 to 600 mg) were mixed with 200 mg of high-purity microcrystalline cellulose, which was used as a combustion aid. From this, it was observed that Cl and S concentration were highest when 100 (Cl: 119.4 ± 14.4 mg kg^{-1} and S: 1350 ± 99 mg kg^{-1}) or 200 mg (Cl: 107 ± 12.4 mg kg^{-1} and S: 1344 ± 193 mg kg^{-1}) of sample mass were used. In these conditions, were not observed significant differences (Student's t-test, confidence level of 95%) in analyte concentrations and the higher mass (200 mg) was selected. Moreover, in order to reduce the blank values, lower cellulose masses (50 and 100 mg) were evaluated. No statistical differences for Cl and S concentrations were observed when 100 or 200 mg of cellulose were used. For 50 mg of cellulose, the concentrations for both analytes were about 2 times lower. Probably, the mass of cellulose used did not provide enough energy for analyte volatilization. In order to increase the concentration of both analytes in the solution and reduce the blank values, using 200 mg of sample mixed with 100 mg of cellulose was considered a suitable ratio of sample/cellulose. Posteriorly, ultrapure water and NH_4OH (50, 100 and 150 mmol l^{-1}) were evaluated for analyte absorption. The results for Cl and S using water or 50 mmol l^{-1} NH_4OH did not show significant differences. However, when using 100 or 150 mmol l^{-1} NH_4OH, Cl concentration was lower, due to interference in chlorine peak, which can be caused by the use of more-concentrated NH_4OH solutions. Therefore, water was selected as the absorbing solution, aiming to minimal reagent consumption and suitable relative standard deviation (< 9%) for both analytes. Taking into account that there are no certified reference material (CRM) for eggshells or similar matrices, 50 mg of CRM NIST 8435 (whole milk powder) or CTA-OTL-1 (oriental tobacco leaves) were mixed with the sample (200 mg) and cellulose (100 mg) and submitted to MIC for the accuracy evaluation. The recoveries for Cl and S were about 96% for both analytes. In addition, the limits of detection (LODs) were 42.3 mg kg^{-1} and 69.6 mg kg^{-1} for Cl and S, respectively. Finally, the proposed method was applied for other eggshells. For brown (Cl: 121 ± 10.9 mg kg^{-1} and S: 1201 ± 107 mg kg^{-1}) and white (Cl: 111 ± 8.61 mg kg^{-1} and S: 1188 ± 95.5 mg kg^{-1}) eggshells, the concentrations for both analytes did not show significant differences. For organic eggshells, the analyte concentrations (Cl: 69.8 ± 5.72 mg kg^{-1} and S: 866 ± 67.3 mg kg^{-1}) were lower, probably due to a lack of added minerals in the diets of the chickens.

Conclusion

The MIC method was efficient for Cl and S volatilization from eggshells, showing accuracy and suitable LODs. Moreover, the proposed method showed a high throughput (16 samples/h) and quantitative recoveries for Cl and S.

Acknowledgements

Capes, CNPq, Fapergs and UFPel.

[1]Naves, M. M. V.; Fernandes, D. C. *Ciên. e Tec. de Alim*. **2007**, *27*, 99.
[2]Pereira et al. *Talanta*, **2016**, *147*, 76.