Br, Cl AND I DETERMINATION IN FOOD SAMPLES VIA MICROWAVE-ASSISTED WET DIGESTION WITH SINGLE REACTION CHAMBER

This work describes a new method for the determination of Cl, Br and I in food, mineralizing samples in a mixture composed exclusively of H_2O_2 in an alkaline medium. The high performances of ultraWAVE system allow to obtain high quality digested solutions with low Residual carbon content (RC). This innovative protocol allows to decrease the analysis process thanks to the fast sample preparation procedure performed with Single Reaction Chamber (SRC) technology.

| INTRODUCTION

Halogens are a group of reactive elements, which are capable of creating stable bonds in different types of food. They play an important biochemical role in living organisms as there are some forms of elements such as Cl and I, which are essential for humans, while others, such as Br, could be toxic and cause damage to the organism.

This is the main reason why this group of elements has been extensively studied in food and biological materials, especially in recent years.[2]

The sample preparation step and subsequent determination of halogens by inductively coupled plasma (ICP) based techniques have been a challenging analytical task due to the problems related to analyte losses, contamination and interference.

In this work, a new method using a Single Reaction Chamber (SRC) was evaluated for Honey, Corn bran (NIST 8433) and Rice flour (NIST 1568a) digestion using only H_2O_2 in an alkaline medium for subsequent Br, Cl and I determination by ICP-based techniques.

The accuracy of the proposed method was assessed using the previously described certified reference materials.

| EXPERIMENTAL

EQUIPMENT

- Milestone ultraWAVE
- 5 position racks
- Quartz vials (40 mL)
- Analytical balance
- ICP-OES for determination of RC and Cl
- ICP-MS for determination of Br and I

APPLICATION REPORT

Br, Cl and I determination in food samples

Figure 1. Milestone's ultraWAVE

MATERIAL AND REAGENTS

- Water was purified using a distillation and subsequent deionization process in an ion exchange column and then further purified in a Milli-Q system (Millipore Corp., USA, 18.2 MU cm). It was utilized to prepare all reference solutions and reagents during this work.
- Stabilized 50% H_2O_2 (Sigma Aldrich, USA)
- Ammonium hydroxide (28%) (Merck, Germany).
- Citric acid (Vetec, Brazil) was dissolved in water to provide final solution with 10 000 mg L-1 of C.
- Yttrium (1 mg L-1, SpexCertPrep, Metuchen, USA) was used as an internal standard.
- Stock solutions (1000 mg L-1) were obtained by dissolution of NaCl, KBr and KI salts (Merck) in water.

SAMPLES

Four commercial samples of honey obtained from different regions of Rio Grande do Sul State (Brazil) were used. The accuracy of the proposed method was evaluated using a reference material (NIST RM 8433, corn bran) and a certified reference material (NIST CRM 1568a, rice flour) provided by National Institute of Standards and Technology.

SAMPLE PREPARATION

An amount of 0.5 g of honey were weighed inside the quartz vessels and 8 mL of 50% H_2O_2 mixed with 500 µL of 28% NH_4OH were added to the quartz vessel containing the sample.

The rack with the five quartz vessels was positioned inside the SRC system, which was previously filled with 120 mL of H_2O and 5 mL of H_2SO_4 (a mixture of 150 mL DI H_2O and 5 ml HNO_3 can be also used). The SRC system was pressurized up to 40 bar with Argon (Nitrogen can be also used) to close the quartz vials. The following microwave heating program was applied.

Step	Time (min)	Power (W)	T1 (°C)	T2 (°C)	P (bar)
1	10	1500	250	60	100
2	20	1500	250	60	100

Table 1 - Microwave Program

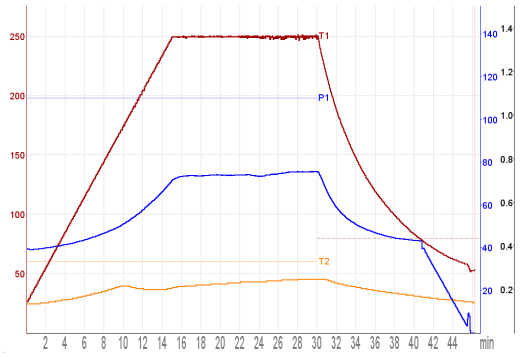

Figure 2 – Microwave run profile

After cooling the sample digests were diluted with water up to 25 mL.

Digests were analyzed for Cl using ICP-OES while Br and I determination was carried out using ICP-MS.

Determination of interference caused by C on ICP based techniques was carried out by analysis of standard solutions with C concentration ranging from 50 to 2000 mg L^{-1}, in citric acid form (alkalized with NH_4OH). Each of these solutions was spiked with 5, 5000 and 0.50 mg L^{-1} of Br, Cl and I, respectively.

RESULTS AND DISCUSSION

It is well known that residual carbon (RC) presents in digested solutions can cause interferences on halogens determination carried out by ICP-based techniques. In this sense standard solutions

containing C concentration ranging from 50 to 2000 mg L^{-1} and spiked with Cl (5000 mg L^{-1}), Br (5 mg L^{-1}) and I (0.50 mg L^{-1}) were analysed by ICP-based techniques.
For Cl, evaluation of interferences caused by C was performed in ICP-OES and significant interferences were not observed for standard solutions with C concentration up to 2000 mg L^{-1}.
In the same way, enhancement or suppression of the analytical signal was not observed for Br determination by ICP-MS for standard solutions containing up to 2000 mg L^{-1} of C.
On the other hand, a concentration higher than 500 mg L-1 of C caused enhancement of the analytical signal for I in determination by ICP-MS.

The microwave sample preparation protocol developed in this study has been optimized working on the following variables:

- Temperature
- Sample mass
- H_2O_2 concentration

The optimized method is the one reported in Sample preparation section, for additional information please, refer to the original article[1].

This method delivers digested solutions with a RC lower than 220 mg L^{-1}, enabling determination of I by ICP-MS. This analysis can be performed without interference caused by C, because RC concentration in digests is 2-fold lower than the minimum required to observe enhancement of the analytical signal for I.

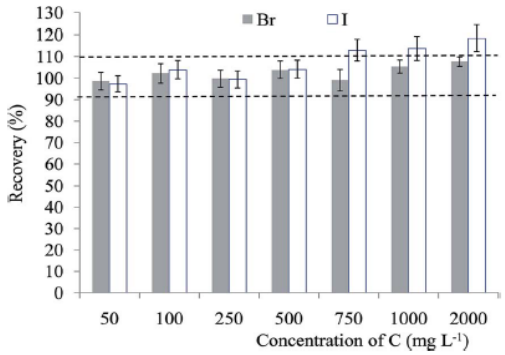

Figure 3 - Influence of C concentration on Br and I determination by ICP-MS

Four honey samples were analyzed by ICP-based techniques after previous digestion using the optimized method. These samples were also digested by microwave-induced combustion (MIC) and analyzed by ICP-OES and ICP-MS in order to evaluate the accuracy of the digestion using ultraWAVE and H_2O_2 in an alkaline medium.
As shown in Table 2, 3 and 4 no significant differences were observed in comparison of results obtained for Br, Cl and I using the proposed method and MIC technique.

Sample	Br recovery (average, n=3)	
	ultraWAVE	MIC
A	1.51 ± 0.12	1.51 ± 0.12
B	0.26 ± 0.02	0.27 ± 0.02
C	0.51 ± 0.05	0.50 ± 0.06
D	0.81 ± 0.08	0.85 ± 0.10

Table 2 – Br concentration (µg g^{-1}) obtained by MIC and the ultraWAVE digestion method

Sample	Cl recovery (average, n=3)	
	ultraWAVE	MIC
A	321 ± 9	338 ± 15
B	70 ± 6	68 ± 7
C	161 ± 12	167 ± 10
D	235 ± 17	232 ± 18

Table 3 – Cl concentration (µg g^{-1}) obtained by MIC and the ultraWAVE digestion method

Sample	Cl recovery (average, n=3)	
	ultraWAVE	MIC
A	0.040 ± 0.010	0.042 ± 0.011
B	< 0.005	< 0.005
C	< 0.005	< 0.005
D	< 0.005	< 0.005

Table 4 – I concentration (µg g^{-1}) obtained by MIC and the ultraWAVE digestion method

Moreover, the developed protocol is applicable to a wide range of food samples and to prove that, two reference materials Corn bran NIST 8433 and Rice flour NIST1568a were digested and analysed applying the same protocol (Table 5 and 6)

Element	Corn bran (NIST 8433) average, n=3	
	Found	Reference
Cl	25 ± 10	31 ± 21
Br	2.1 ± 0.2	2.3 ± 0.5
I	0.025 ± 0.005	0.026 ± 0.006

Table 5 - Halogens concentration (µg g^{-1}) in NIST 8433 reference materials using ultraWAVE

Element	Rice flour (NIST 1568a) average, n=3	
	Found	Reference
Cl	267 ± 30	300
Br	8.3 ± 1.2	8
I	0.012 ± 0.004	0.009

Table 6 - Halogens concentration (µg g^{-1}) in NIST 1568a reference materials using ultraWAVE

All the results obtained for the certified reference materials did not present a significant difference when compared with certified values.

CONCLUSION

Thanks to the high performance of ultraWAVE it is possible to obtain a complete mineralization of food samples using only a mixture of hydrogen peroxide and alkaline solution.

Tests show that the ability to reach a digestion temperature of 250 ° C, it is crucial to obtain the proper quality of digestion and ensures a reliable analysis of halogens especially for Iodine.

Additionally, ultraWAVE offers a much simpler approach than other sample preparation techniques commonly used for this type of analysis.

Other important advantages of this method are the formation of water as a product of digestion and the minimal memory effect of the analyses in ICP by the alkaline pH of the final solutions digested.

ACKNOWLEDGEMENTS

We would like to thank the authors of the Chemistry Department of Universidade Federal de Santa Maria for the realization of this innovative microwave protocol of huge benefits for halogens determination in food samples.

REFERENCES

1. *Determination of Br, Cl and I in honey using ICP based techniques following microwave-assisted wet digestion with alkaline H2O2 in a single reaction chamber* Edson I. Muller, Juliana P. Souza, Kellen F. Anschau, Michele S. P. Enders, Aline L. H. Muller, Sergio R. Mortari and Fabio A. Duarte Analytical Methods, 2017, 9, 649
2. *Halogen determination in food and biological materials using plasma-based techniques: challenges and trends of sample preparation* Marcia F. Mesko, Vanize C. Costa, Rochele S. Picoloto, Cezar A. Bizzi and Paola A. Mello Journal of Analytical Atomic Spectrometry, 2016,31, 1243-1261

ABOUT MILESTONE

At Milestone we help chemists by providing the most innovative technology for metals analysis, direct mercury analysis and the application of microwave technology for extraction, ashing and synthesis. Since 1988, Milestone has helped chemists to enhance food, pharmaceutical and consumer product safety, and to improve our world by controlling pollutants in the environment.