

Determination of trace elements in agglomerated cork stoppers using ICP-MS and ICP-OES



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Introduction

Quercus Suber L. is a native species of the Mediterranean region yielding a thick bark, known as cork. These trees grow in Mediterranean areas such as Spain, Italy, France, Morocco, Algeria and above all in Portugal that produces 50% of the worldwide cork. Economically this industry is very important for the country. Cork is used for many purposes like fishing floats and buoys, musical instruments, floor tiles and bulletin boards. Granules of cork can also be mixed with concrete to form bricks. However the first use of cork is still cork stoppers which can be made of natural cork or agglomerated cork. In general natural cork stoppers are used for better quality wines while agglomerated cork stoppers are used in current and sparkling wines.

The levels of trace elements are an important component of quality, safety and origin of the agglomerated corks stoppers in contact with food. In the present work the concentration of the following elements was determined: Chromium (Cr), Nickel (Ni), Arsenic (As), Cadmium (Cd), Selenium (Se), Lead (Pb), Iron (Fe), Zinc (Zn), Copper (Cu) and Manganese (Mn). Since almost no published work can be found on this subject it was necessary to study all stages of the process.

Material and Methods

Since agglomerated cork stoppers are a complex matrix, two sample preparation methods to destroy the organic matrix were compared: dry ashing and microwave digestion. Also several $\text{HNO}_3:\text{H}_2\text{O}_2$ ratios and different time and temperature conditions were studied to optimize the closed vessel microwave digestion.

Afterwards samples were analysed by two different techniques, trace elements were determined by ICP-MS and the remaining ones by ICP-OES.

Because no reference materials for this matrix could be found, spiked samples were used for assessment of accuracy. Sampling was made by the producer who sent representative bagged samples to the laboratory.

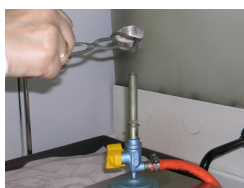
Table 1 - Microwave Digestion:

Step	Time	Temperature	Pressure
1	3 min	80 °C	250 W
2	5 min	80 °C	250 W
3	10 min	180 °C	1000 W
4	10 min	180 °C	1000W



Table 2 - Dry ashing:

Step	Procedure
1	Weight 0.5g of cork
2	Burn to ashes using a Bunsen burner
3	Place samples in muffle furnace at 470°C for 40 hours
4	Add 1ml of H_2O and 1ml of HCL
5	Put on water bath for 3 minutes without complete dry
6	Transfer to volumetric flask and complete with H_2O
7	Filter with paper filter and transfer to analysing tubs



Results and Discussion

Table 3 - Method: Dry Ashing / ICP-OES (concentration (mg/kg), repeatability (%), LoQ (mg/kg):

	Concentration (mg/kg)			
	Cu	Fe	Zn	Mn
AG210 (1)	21	144	28	50
AG210 (2)	582	623	246	204
Repeatability (%)	131,6	97,7	112,5	85,7
LoQ (mg/kg)	0,33	0,27	1,31	0,03

Table 4 - Method: Dry Ashing / ICP-MS (concentration ($\mu\text{g}/\text{kg}$), repeatability (%), LoQ ($\mu\text{g}/\text{kg}$):

	Concentration ($\mu\text{g}/\text{kg}$)					
	Cr	Ni	As	Se	Cd	Pb
AG210 (1)	661	854	20	31	35	630
AG210 (2)	859	64	30	55	21	<LoQ
Repeatability (%)	18,4	121,7	28,3	39,5	35,4	---
LoQ ($\mu\text{g}/\text{kg}$)	3,3	1,5	5,7	17,2	0,5	8,1

Table 5 - Method: Microwave digestion / ICP-OES (concentration (mg/kg), repeatability (%), LoQ (mg/kg):

	Concentration (mg/kg)			
	Cu	Fe	Zn	Mn
AG210 (1)	76	1466	37	212
AG210 (2)	77	1364	35	210
Repeatability (%)	0,9	5,1	3,9	0,7
LoQ (mg/kg)	0,2	0,9	1,0	0,1

Table 6 - Method: Microwave Digestion / ICP-MS (concentration ($\mu\text{g}/\text{kg}$), repeatability (%), LoQ ($\mu\text{g}/\text{kg}$):

	Concentration ($\mu\text{g}/\text{kg}$)					
	Cr	Ni	As	Se	Cd	Pb
AG210 (1)	317	293	26	59	22	131
AG210 (2)	321	269	41	107	20	118
Repeatability (%)	0,9	6,0	31,7	40,9	6,7	7,4
Recovery (%)	107	127	98	89	71	111
LoQ ($\mu\text{g}/\text{kg}$)	7,3	2,3	6,4	16,5	2,4	2,3

Conclusions

Regarding closed vessel microwave digestion the best results were obtained with the combination of 6ml HNO_3 with 2ml H_2O_2 .

Cork is a very light material. Dry ashing is a method that involves many steps including burning samples to ashes with a Bunsen burner which in the case of cork easily leads to sample losses. So as expected, microwave digestion proved to be the best sample preparation method since the results from repeatability were better.

Several elements were found in the sample. These elements may originate from the cork or by contamination of the manufacturing process of agglomerated cork stoppers. The presented method still requires further work in development and optimization. Also migration studies using wine must be implemented.

References

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