



University of Agricultural Sciences and Veterinary Medicine of  
Cluj-Napoca  
ROMANIA

Faculty of Food Science and Technology

## LC-MS method applied for analysis of phenolic compounds in aged brandy

Teodora Emilia Coldea  
Elena Mudura  
Carmen Socaciu  
Floricuța Ranga  
Carmen Pop  
Timea Horvath



# Self presentation

**Bachelor** - Food Science and Technology, 2008

**Food Engineer** – Alcoholic beverages Company, 2008-2012

**Master** – Food Quality Management, 2010

**Doctorate** - Comparative Study of Quality, Safety and Authenticity Biomarkers for Traditional Romanian Distilled Beverages, 2011

**Postdoc** - Metabolomic and Chemometric Analysis Applied for Identification of Biological and Geographical Biomarkers in Different Fruit Brandies Produced in Romania, 2012

**Assist Lecturer** since 2013 Fermentative Technologies (Brewing, Winery, Alcoholic beverages), Animal Raw Material

# Pilot plants

## Pilot plant for beer and wine

Assist. Prof. dr. eng. Elena Mudura

Assist. Lect. dr. eng. Teodora Coldea



**It is possible to sell the non-alcoholic beverages produced by these University pilot plants**

# Index

- Transylvanian traditional fruit brandies
- Assessment of fruit brandies authenticity
- Factors influencing their quality
- Ageing practices
- Polyphenols from fruit
- Polyphenols from wood
- Studies conducted on the effects of rapid inducing ageing character to fruit brandies

# Transylvanian traditional fruit brandies

The Central and East European countries have an old tradition in producing different types of fruit brandies.

In Romania, there is a great interest to produce home-made traditional fruit brandies obtained by a double distillation of fermented fruits.



# Transylvanian traditional fruit brandies

- *Țuica* – from plums
- *Pălinca* – from all other fruits



Besides their volatile composition, the principal differences of *țuica* and *pălinca* are the ethanol content:

*Țuica*: 24 up to 86%;

*Pălinca*: 40-70%

Current regulation about quality & safety analysis of spirits (alcoholic

# Assessment of fruit brandies authenticity

Bulletin UASVM Agriculture, 68(2)/2011  
Print ISSN 1843-5246; Electronic ISSN 1843-5386

## **Phenolic Derivatives as Authenticity Markers of Traditional Homemade Brandies from Different Counties of Transylvania, Using UV-VIS and HPLC Analysis**

**Teodora Emilia RUSU (COLDEA), Carmen SOCACIU, Florinela FETEA, Floricuța RANGA, Raluca PÂRLOG**



Available online: [www.notulaebotanicae.ro](http://www.notulaebotanicae.ro)

Print ISSN 0255-965X; Electronic 1842-4309

Not Bot Horti Agrobo, 2014, 42(2):530-537. DOI:10.1583/nbha4229607



## **Minor Volatile Compounds in Traditional Homemade Fruit Brandies from Transylvania-Romania, as Determined by GC-MS Analysis**

**Teodora Emilia COLDEA<sup>1</sup>, Carmen SOCACIU<sup>1\*</sup>,  
Zaharie MOLDOVAN<sup>2</sup>, Elena MUDURA<sup>1</sup>**

# Assessment of fruit brandies authenticity



Available online at [www.notulaeobotanicae.ro](http://www.notulaeobotanicae.ro)

Print ISSN 0255-965X; Electronic 1842-4309

Not Bot Horti Agrobo, 2013, 41(1):143-149



## Rapid Quantitative Analysis of Ethanol and Prediction of Methanol Content in Traditional Fruit Brandies from Romania, using FTIR Spectroscopy and Chemometrics

Teodora Emilia COLDEA<sup>1</sup>, Carmen SOCACIU<sup>1</sup>, Florinela FETEA<sup>1</sup>,  
Floricuța RANGA<sup>1</sup>, Raluca Maria POP<sup>1</sup>, Mira FLOREA<sup>2\*</sup>



Available online at [www.notulaeobotanicae.ro](http://www.notulaeobotanicae.ro)

Print ISSN 0255-965X; Electronic 1842-4309

Not Bot Horti Agrobo, 2011, 39(2):109-116



## Gas-Chromatographic Analysis of Major Volatile Compounds Found in Traditional Fruit Brandies from Transylvania, Romania

Teodora Emilia RUSU COLDEA, Carmen SOCACIU\*, Maria PÂRV, Dan VODNAR



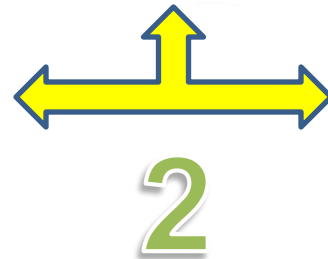
## **Factors influencing the quality of fruit brandies**

# Factors influencing the quality of aged fruit brandies

1



3



2



**Ageing practices made on fruit  
brandies**

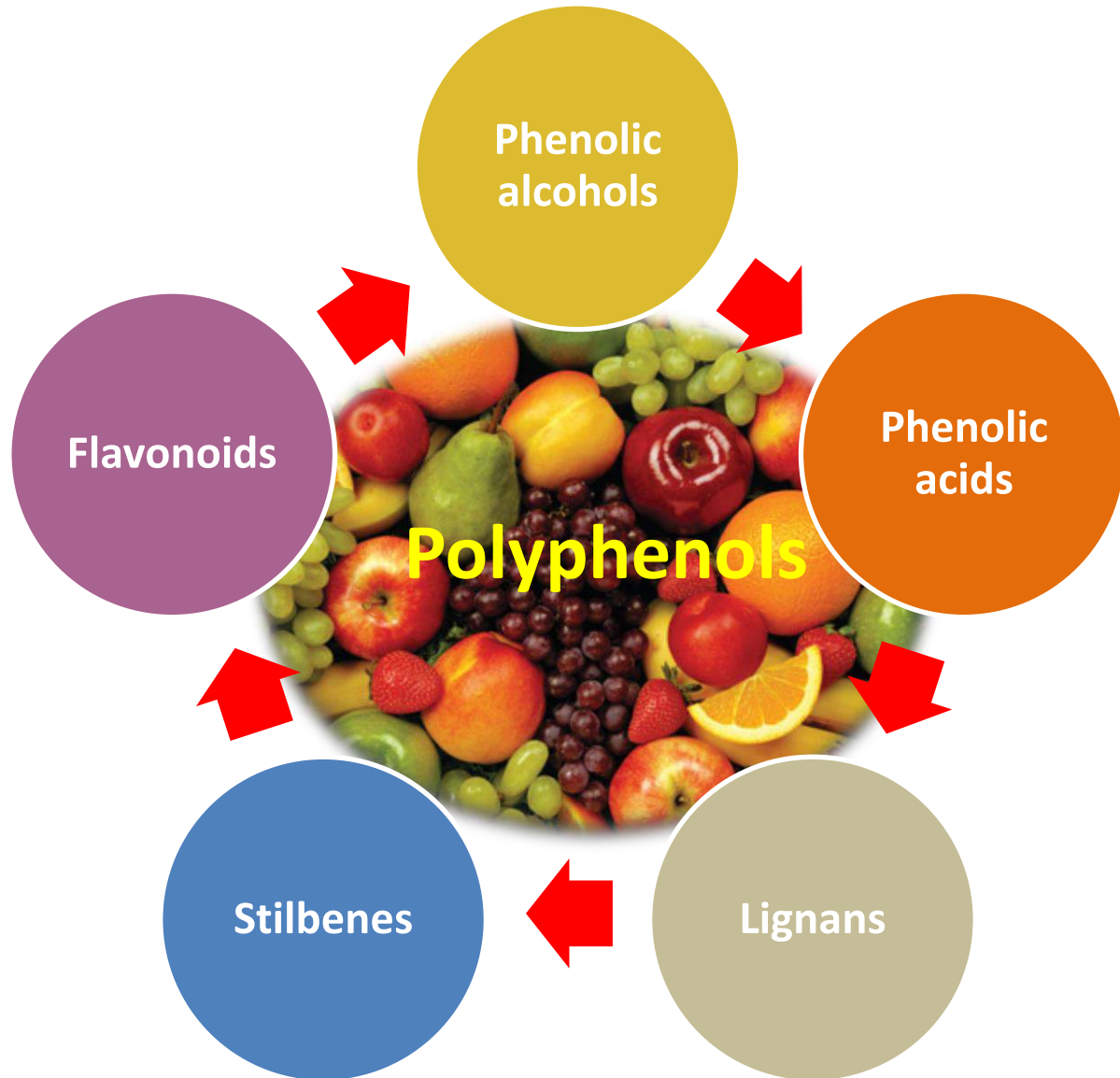
# Ageing practices of fruit brandies



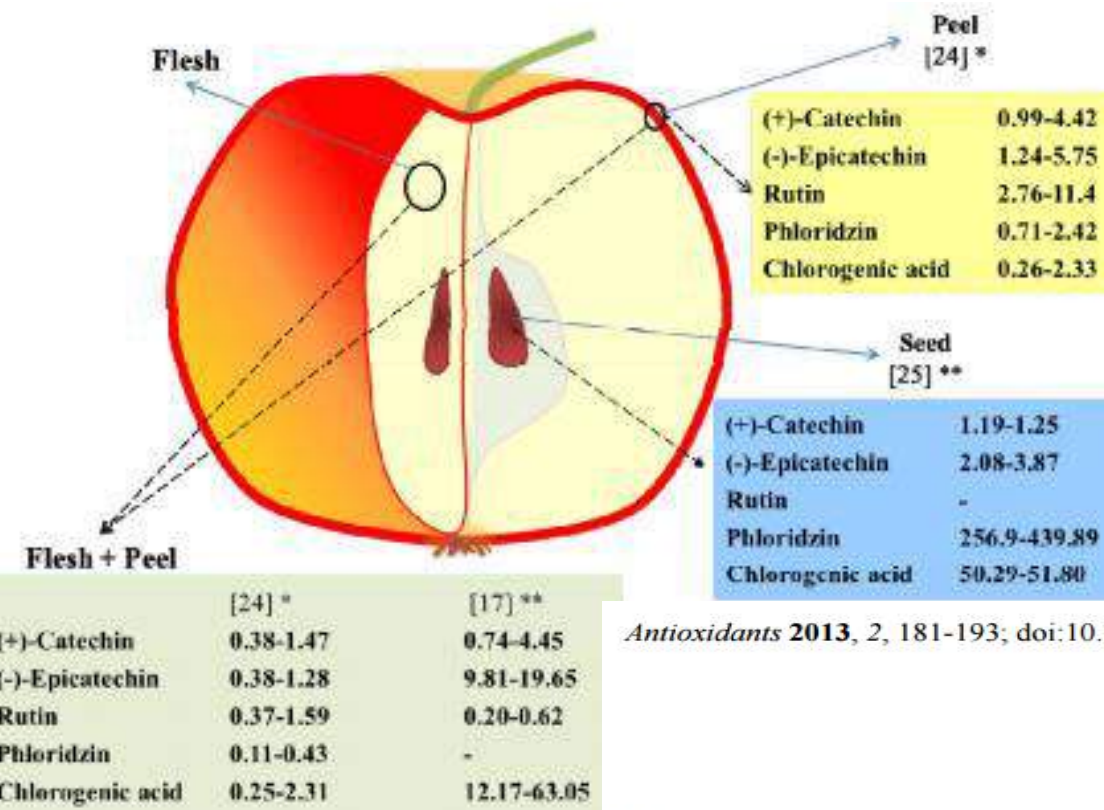
# Wood components dissolved in brandy during ageing process

- Aroma compounds
- Polyphenols and pectic substances
- Minerals
- Amino acids





# Polyphenols in fruit brandy related to raw material (apple)



*Antioxidants* 2013, 2, 181-193; doi:10.3390/antiox2030181

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*antioxidants*

ISSN 2076-3921

www.mdpi.com/journal/antioxidants

Review

## Phenolic Compounds in Apple (*Malus x domestica* Borkh.): Compounds Characterization and Stability during Postharvest and after Processing

Alessandra Francini and Luca Sebastiani \*

# Wood related polyphenols found in fruit brandy

Croat. J. Food Sci. Technol. (2012) 4 (2) 102-111

Spirit drinks: a source of dietary polyphenols

Jasna Mrvcic<sup>1\*</sup>, Sanja Posavec<sup>1</sup>, Snježana Kazazic<sup>2</sup>, D. Stanzer<sup>1</sup>,  
Andrea Peša<sup>1</sup>, Vesna Stehlik-Tomas<sup>1</sup>



J. Serb. Chem. Soc. 79 (12) 1537–1543 (2014)  
JSCS–4686

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543.544-14:547.576  
Short communication

Development and validation of an LC–MS/MS method with a multiple reactions monitoring mode for the quantification of vanillin and syringaldehyde in plum brandies

VELE TEŠEVIĆ<sup>1\*</sup>, IVANA ALJANČIĆ<sup>2</sup>, VLATKA VAJS<sup>1,2</sup>, MARIJANA ŽIVKOVIĆ<sup>2</sup>,  
NINOSLAV NIKIČEVIĆ<sup>3</sup>, IVAN UROŠEVIĆ<sup>3</sup> and LJUBODRAG VUJISIĆ<sup>1</sup>

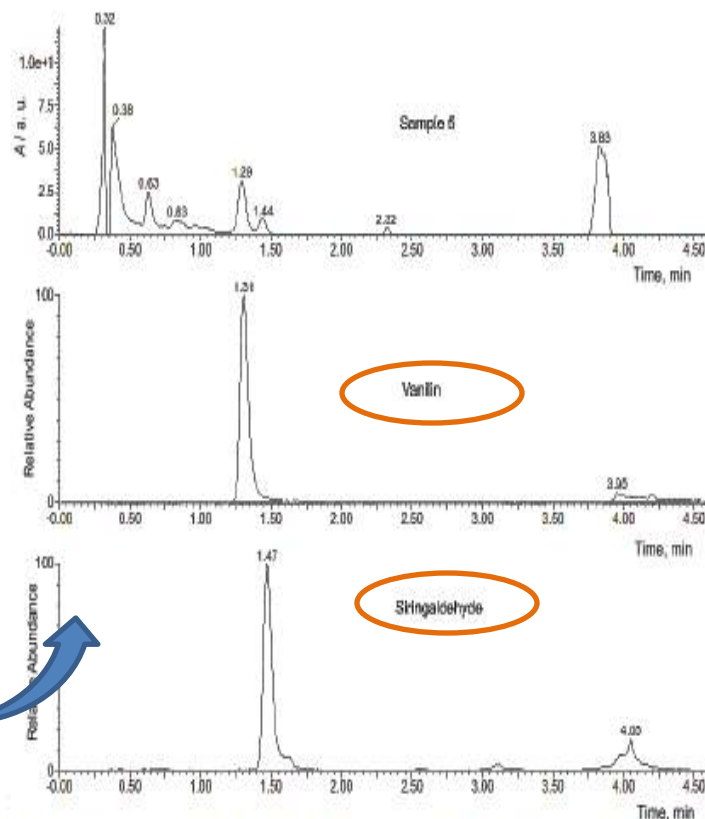


Fig. 1. DAD chromatogram of a plum brandy and extracted MRM chromatograms of vanillin and syringaldehyde, a) HPLC–UV–DAD chromatogram of plum brandy (Sample 5), b and c) extracted MRM chromatograms of vanillin and syringaldehyde in the ES<sup>+</sup> mode, respectively.

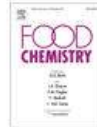


# Wood related polyphenols found in fruit brandy



Food Chemistry

Volume 129, Issue 4, 15 December 2011, Pages 1584–1590



Antioxidant capacity and phenolic composition of different woods used  
in cooperage

M.E. Alaion<sup>a</sup>, L. Castro-Vázquez<sup>a</sup>, M.C. Díaz-Maroto<sup>b</sup>, I. Hermosín-Gutiérrez<sup>b</sup>, M.H. Gordon<sup>c</sup>,  
M.S. Pérez-Coello<sup>a</sup>

*J Agric Food Chem.* 2010 Apr 28;58(8):4907-14. doi: 10.1021/jf100236v.

**Phenolic compounds in cherry (*Prunus avium*) heartwood with a view to their use in cooperage.**

Sanz M<sup>1</sup>, Cadahía E, Esteruelas E, Muñoz AM, Fernández De Simón B, Hernández T, Estrella I.

*Int. J. Mol. Sci.* 2015, 16, 6978-7014; doi:10.3390/ijms16046978

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International Journal of  
**Molecular Sciences**

ISSN 1422-0067

www.mdpi.com/journal/ijms

Review

**A Review of Polyphenolics in Oak Woods**

Bo Zhang<sup>1,2</sup>, Jian Cai<sup>1,3</sup>, Chang-Qing Duan<sup>1</sup>, Malcolm J. Reeves<sup>1,4</sup> and Fei He<sup>1,\*</sup>

# Experimental design

## Ageing process of apple brandy

Apple brandy  
+  
5 varieties of wood chips

## UV-VIS Spectra

UV-Vis spectra recorded  
(250-550 nm)

## Total Phenolic Content

Folin-Ciocalteu Method  
Gallic acid calibration  
curve

$$y = 1,11780x + 0.00000;$$
$$R^2 = 0.99748$$

## HPLC-DAD Chromatography

- Thermo Scientific HPLC UltiMate 3000 system
- quaternary pump delivery system Dionex UltiMate 3000 (UHPLC+ focused),
- Dionex Ultimate 3000 photodiode array detector, -Dionex Ultimate 3000 column oven and Dionex Ultimate 3000 autosampler

# Ageing technique



Oak  
(*Quercus robur*)  
wood chips

White  
mulberry  
(*Morus alba*)  
wood chips

Walnut  
(*Juglans regia*)  
wood chips

Chestnut  
(*Castanea sativa*)  
wood chips

Cherry  
(*Prunus avium*)  
wood chips



AO



AM



AW



AC



ACE



2 Months

LC-MS Analysis

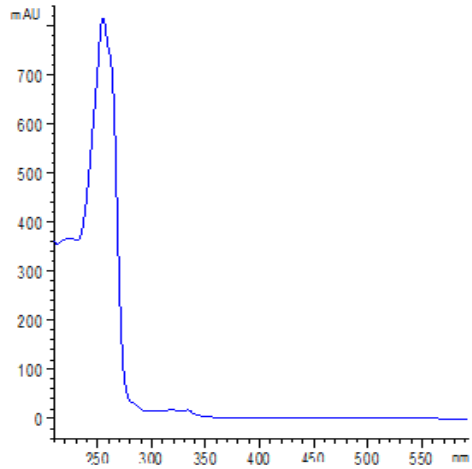


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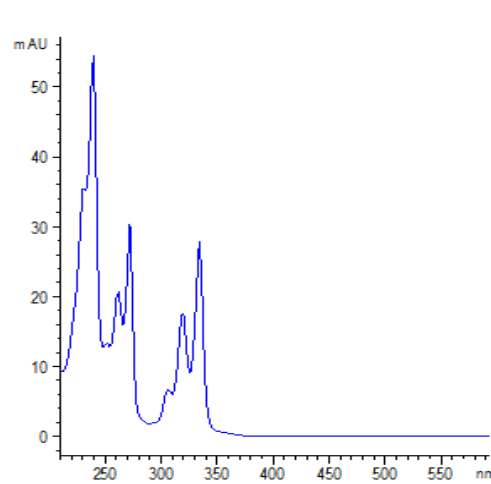
Since 1869



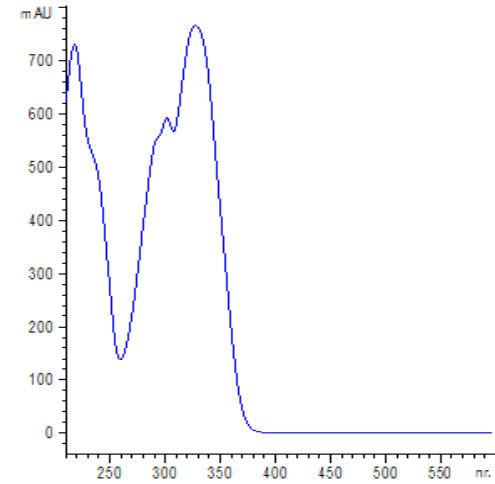
# UV-Vis spectra of studied apple brandies



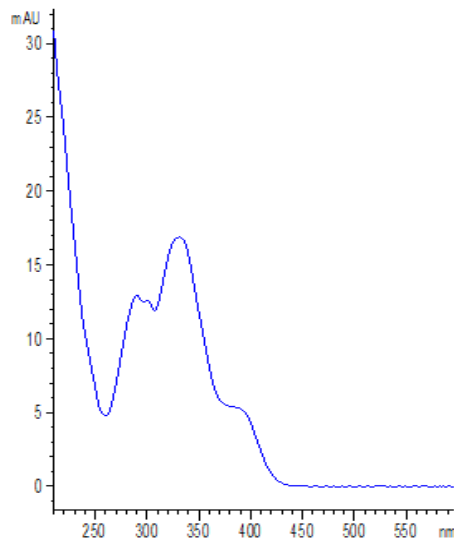
**Blank (B)**



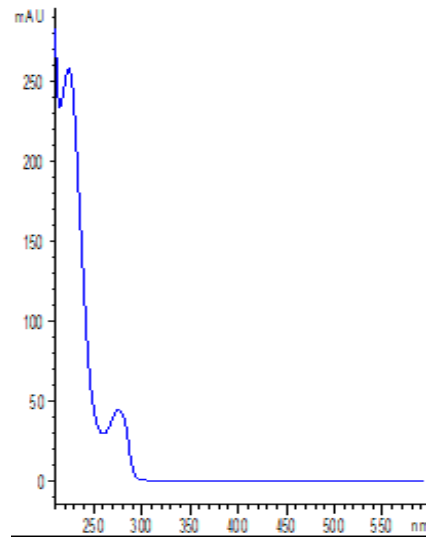
**AW**



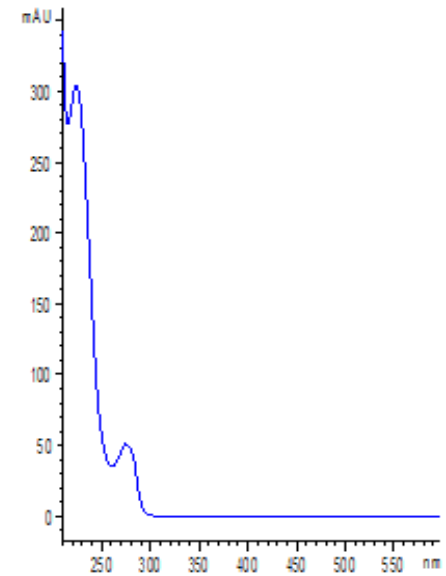
**AM**



**ACE**

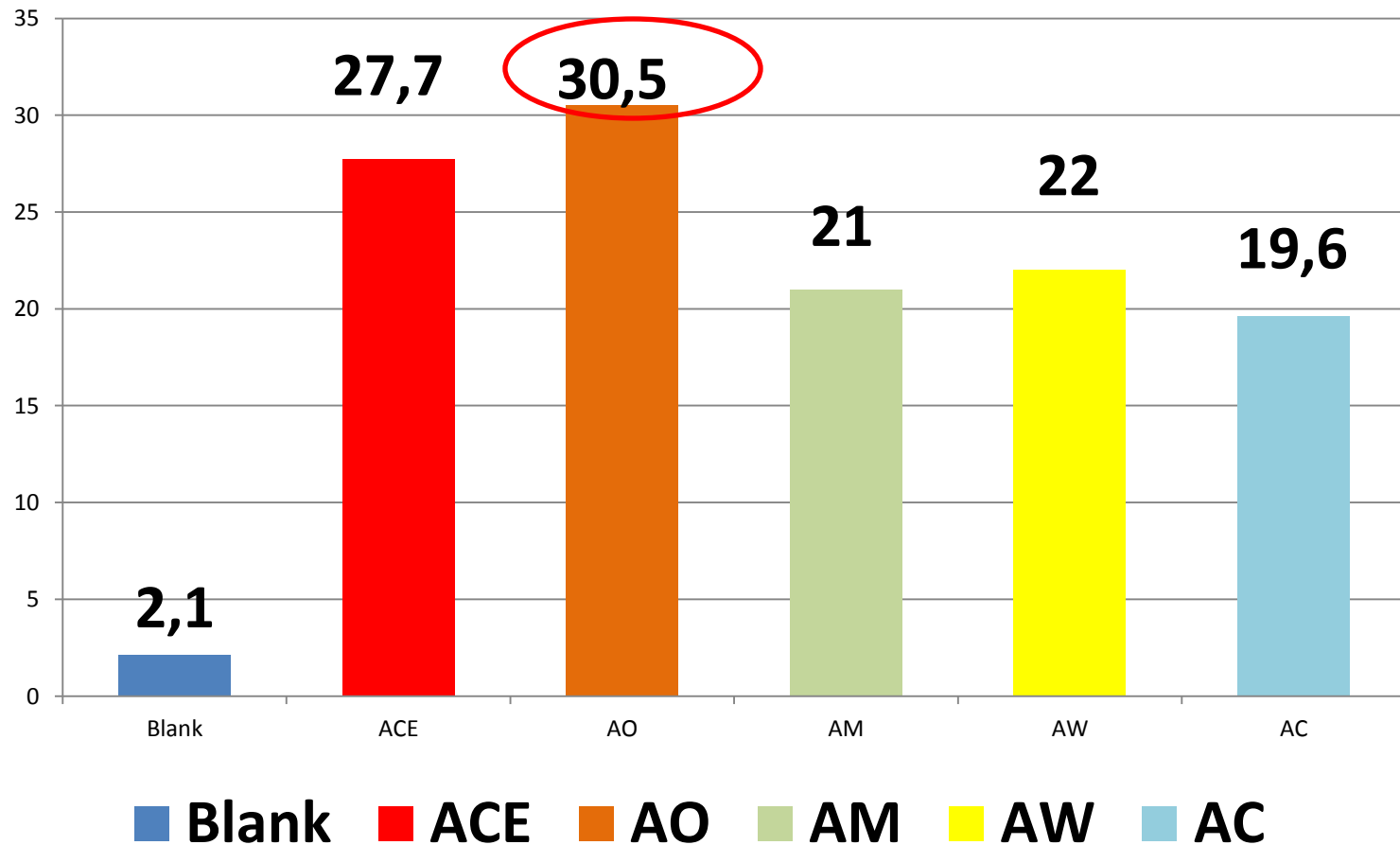


**AC**



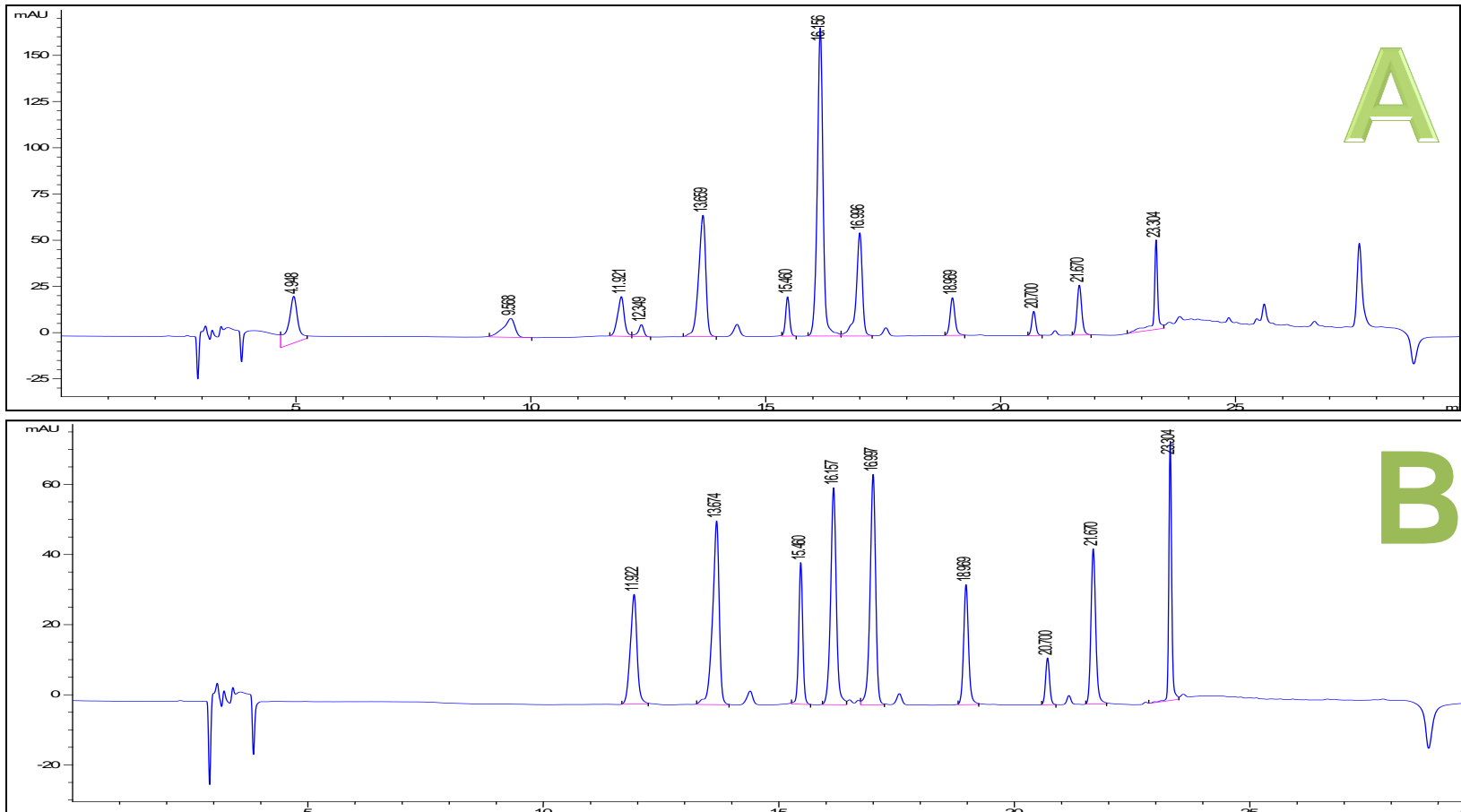
**AO**

# Total phenolic content (Folin-Ciocalteu method)



Representation of total phenolic content, mg GAE / 100 mL

# HPLC-DAD chromatograms recorded at 280 nm (A) and 340 nm (B)



Phenolic compounds standard mixture RT= 4,9 min-gallic acid; RT=9,5 min-acid protocatechuic; RT=11,9 min- chlorogenic acid; RT=12,3 min- catechin; RT=13,6 min-caffeic acid + vanillic acid; RT=15,4 min-rutin; RT=16,1 min-ellagic acid + p-coumaric acid; RT=16,9 min- ferullic acid; RT=18,9 min-myricetin, RT=20,7 min-tiliroside; RT=21,6 min-quercetin; RT=23,3 min-kaempherol

# Phenolic compounds identified in apple brandy by LC-QTOF-MS

[M+H] <sup>+</sup> m/z	Phenolic compound	Class of phenolic compound	Brandy where was identified	[M+H] <sup>+</sup> m/z	Phenolic compound	Class of phenolic compound	Brandy where was identified
162.0316	Umbelliferone	Hydroxycoumarines	Blank, AW, AO	244.0735	Piceatannol	Stilbenes	AM
442.3723	Catechin 3-O-gallate	Flavanols	Blank, AW	337.0923	3-p-Coumaroylquinic acid	Hydroxycinnamic acids	ACE
543.1508	3,4-di-O-feruloylquinic acid	Hydroxycinnamic acids	Blank, AW	358.3905	Pinoresinol	Lignans	ACE
367.0929	3-O-feruloylquinic acid	Hydroxycinnamic acids	Blank	256.0735	Pinocembrin	Flavanones	ACE
174.0316	5-Hydroxy-1,4-naphthoquinone	Naphtoquinones	AW	182.0579	Syringaldehyde	Hydroxybenzaldehydes	AC
224.0684	Sinapic acid	Hydroxycinnamic acids	AW	302.0062	Ellagic acid	Hydroxybenzoic acids	AC
198.1727	Ethyl gallate	Hydroxybenzoic acids	AM, ACE	164.1620	o-Coumaric acid	Hydroxycinnamic acids	AO
158.0367	1,4-Naphtoquinone	Naphtoquinones	AM, ACE, AC	390.3839	Resveratrol 3-O-glucoside	Stilbenes	AO
198.0528	Syringic acid	Hydroxybenzoic acids	AM, ACE				

# Conclusion

- Using LC-QTOF-MS the main biomarkers of aged apple brandies were determined
- The main biomarkers of apple brandy were: **flavanones** (pinocembrin), **flavanols** (catechin 3-O-gallate), **hydroxycinnamic acids** (3,4-di-O-feruloylquinic acid, 3-O-feruloylquinic acid, sinapic acid, 3-p-coumaroylquinic acid, o-coumaric acid), **hydroxybenzoic acids** (ethyl gallate, syringic acid, ellagic acid), **stilbenes** (piceatannol, resveratrol 3-O-glucoside), which may confer the antimicrobial and antioxidant potential, fact that would be evaluated in our future research
- Combined UV-Vis and LC-QTOF-MS spectrometry is recommended as a reliable and sensitive tool, to be used for quality control and authentication of fruit brandies



Thank  
you



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