The quality of extravirgin olive oil obtained by an innovative extraction technology

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The product: what is the extravirgin olive oil ?

The extravirgin olive oil (EVOO) is obtained only by physical processes, without using any treatment different from washing, settling, centrifugation and filtration.

This product has to reach a score ≥ 6.5 during official sensorial tasting session (in a range between 0 and 9) and be lacking in defects; at the same time, its free acidity (expressed like oleic acid grams vs 100 g of oil) has to be lower than 0.8.

(Reg. CE 1513/2001, 23th July 2001)

Extraction technology

Quality of extracted oil

Why EVOO represents one of the main elements in the Mediterranean diet?

Its daily intake produces several health benefits



- ✓ Anti-inflammatory effect
- ✓ Cardiovascular protection
- ✓ Digestive health benefits
- ✓ Anti-cancer activity

Only some references (among many papers):

Huang, C.L., Sumpio, B.E. "Olive oil, the mediterranean diet, and cardiovascular health" ***J. Am. Coll. Surg.*** **207, 407–416 (2008).**

V. Llorente – Cortes, R. Estruch, MP Mena, E. Ros, MA Gonzales, M. Fitò, RM Lamuela-Raventòs, L. Badimon, "Effect of Mediterranean diet on the expression of pro-atherogenic genes in a population at high cardiovascular risk", Atherosclerosis, August 2009.

Reduction in the incidence of the type Diabetes 2

With the Mediterranean diet Salas-Salvado et al, *Diabetes Care*, 34: 14-19, 2011

What was the idea? Knowing that the addition of carbonic snow to grapes let to produce high quality wines …







Our research group decided to apply this technology to extravirgin olive oil extraction





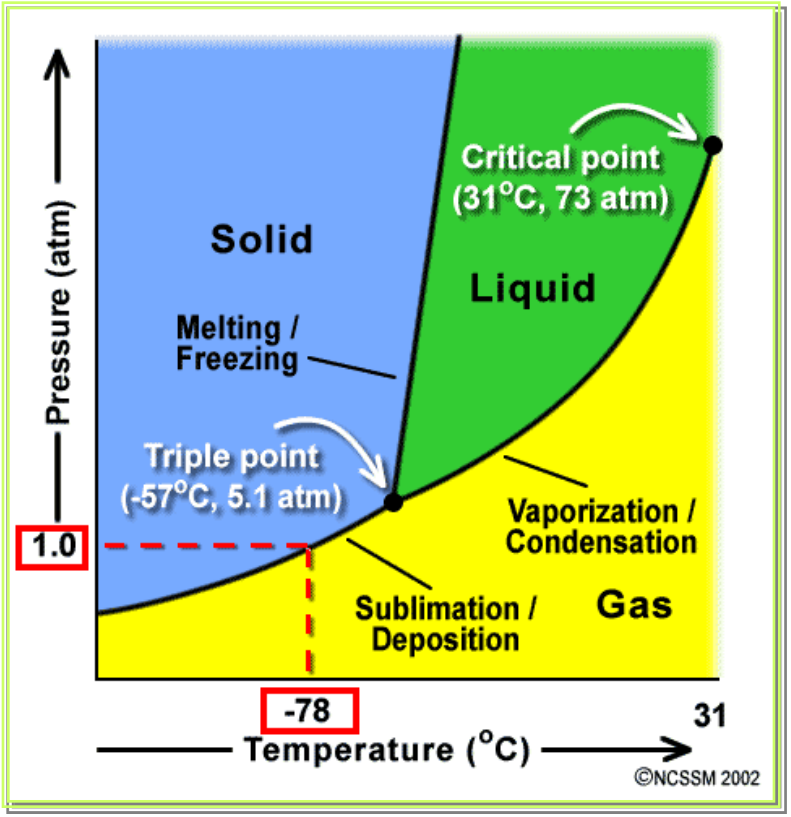




The method? An innovative EVOO extraction technology (Patent n° IT1405173-B) involving the addition of a cryogen (ex: solid CO_2) to the olives was developed, in order to increase the extraction yield and obtain an oil characterized by an higher concentration of its health compounds (ex: phenols, tocopherols) and a stronger link with its production area.

Among all the possible cryogens suitable for food technology ($N_{2,L}$, He_L, Ar_L etc)

$CO_{2,s}$ (or carbonic snow) shows a lot of advantages



- *Nontoxic and don't leave residues*
- *Not inflammable*
- *Good solvent (non-polar)*
- *Inert by an organoleptic point of view*
- *Triple point easy to reach (-57.5°C; 5.1atm)*
- *Easy to find and use*
- *low costs*
- *Anti-microbial and anti-oxidant action*
- *Enzymes inhibitor (ex: lypoxidase)*

$-\Delta Q$

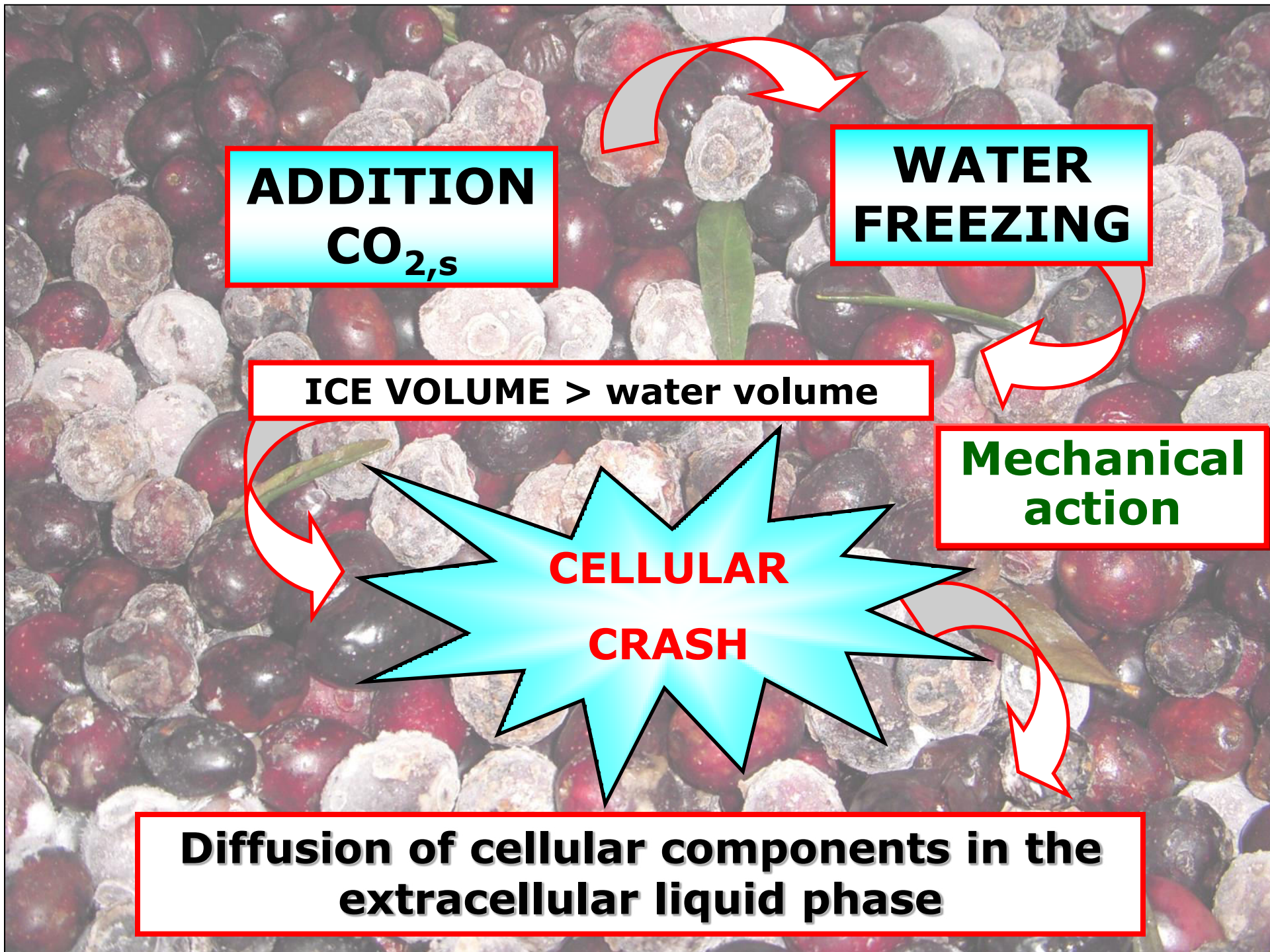
$CO_{2,s}$ (-78°C ; 1 atm)





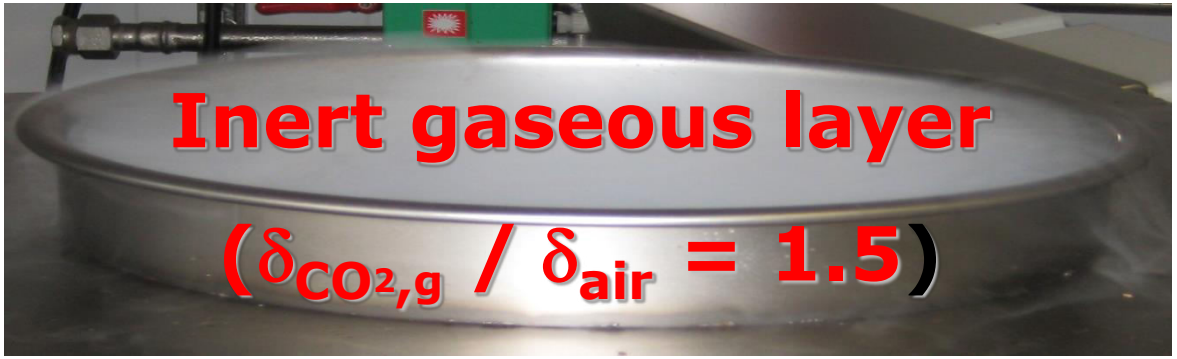
Olives (T= 12-16°C)

$+\Delta Q$


ADDITION
$CO_{2,s}$
WATER
FREEZING
ICE VOLUME > water volume
Mechanical
action
CELLULAR
CRASH
Diffusion of cellular components in the
extracellular liquid phase

$CO_{2,s}$ + Olives/olive paste

$CO_{2,g}$



Able to prevent the possible oxidation of extracted oil

Modulation of the working variables related to the MALAXATION

Increase of the extraction yield

Higher antioxidant content

Wished aromatic profile



What was done?

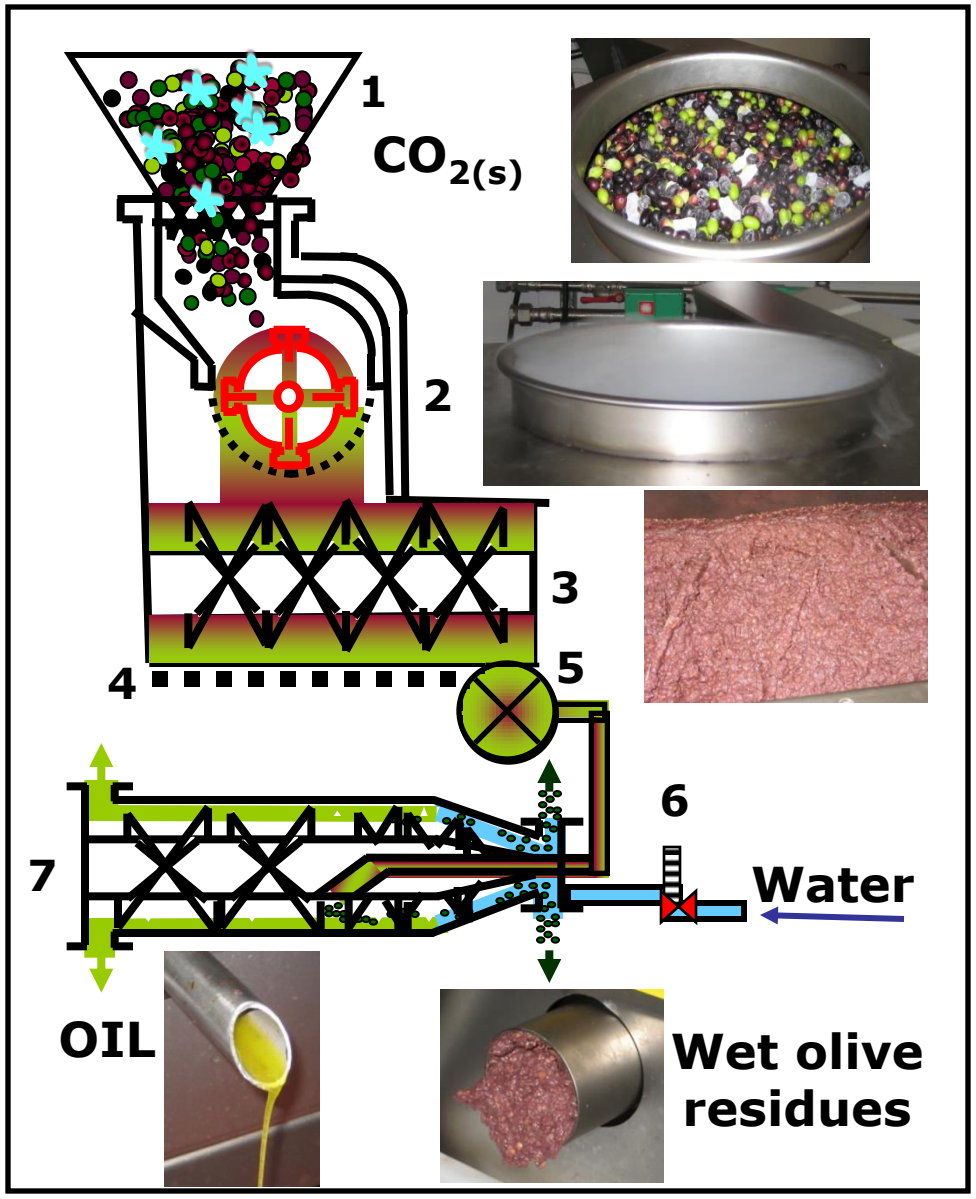
- they were determined the values for the main parameters (no reference are available) to use for the extraction of oil

- It was verified the influence of cryogen addition ($CO_{2,s}$), to the olives, during pre-milling phase, on the yield of the oil obtained and on oil quality in order to evaluate the suitability of the new method for EVOO production.



Our research group

The micro oil mill used: Oliomio Baby ® (T.E.M.)



20-30 kg of olives

Receiving hopper(1)

Knives crusher (2)

Horizontal continuous malaxer (3)

2-phases decanter (7)

Where did the olives come from? They are monovarietal and polyvarietal (*mix of some varieties*) olives collected from Tuscany olive-yards in two different years



The olives utili… experimental runs (~ 60 kg) were … mixed to ensure homogeneous feeds. Each sample was split in two fractions (30 kg)

Traditional extraction process

Addiction of $CO_{2,s}$

Origin and cultivar of the raw matter utilized

Sample ID		Geographical origin	Cultivar
Traditional	Cryo		
A	1	Tuscany (GR 2010)	Frantoio
B	2	Tuscany (SI 2010)	*mix* *
C	3	Tuscany (SI 2010)	*mix* *
D	4	Tuscany (SI 2010)	*mix* *
E	5	Tuscany (GR 2014)	Leccino
F	6	Tuscany (GR 2014)	Frantoio
G	7	Tuscany (GR 2014)	Moraiolo

* Frantoio, Leccino, Correggiolo

Main operating variables adopted during the experimental runs

		Cryo	Traditional
Cryogen/olives (w/w)		0.1 ÷ 0.2	0
Temperature of olives	(°C)	~-2	11.5
Temperature of paste	(°C)	~24.0	~24.0
Time of Malaxation	(s)	2400	2400
Time of Extraction	(s)	4900	4300
Water added/olives	(%)	8.5	9.3



In order to evaluate the effect induced by the addition of the cryogen on the oil extraction yield, it was determined the Extractability Index Variation (EIV) as the ratio between the difference of the oil extracted using $CO_{2,s}$ and that obtained by a traditional extraction process and the amount of product obtained by traditional method:

$$EIV = (EC-ET)/ET \cdot 100$$

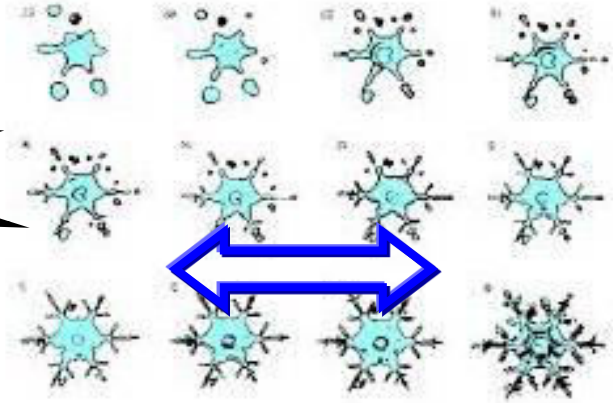
Oil extraction yield

Run	EC	ET	[(EC-ET)/ET]*100
1/A	85.8	82.5	4.0 %
2/B	85.5	77.2	10.8 %
3/C	91.2	82.7	10.3 %
4/D	84.1	74.8	12.4 %
5/E	80.8	79.3	1.9 %
6/F	73.6	68.9	6.8 %
7/G	84.4	77.4	9.4 %

The direct addition of cryogen to the olives during pre-milling phase could induce a general increase in the oil extraction yield

What's about the oil extraction yield?

CELLULAR CRASH



Water content inside the fruit

❖If it's necessary, this method allows to harvest olives early in order to reduce greatly the damages due to the third fly attack of *Bactrocera oleae* that can induce a significant loss in oil production (up to 60%) as well as a decrease in oil quality









Effects on oil quality of the new extraction method

Percentage Increase (%) in tocopherols content (PITC)	***6.0 ± 0.6***
Percentage Increase in Total phenols (PITPh)	***5.1 ± 10.6***

p=0.05



Oil general chemical parameters:

There aren't reliable differences due to the new extraction method

This evidence is probably due to the high efficience of the extraction plant (even in absence of cryogen addition)

Oil general chemical parameters

Run	Free acidity (% oleic acid)	Peroxide value (meq O_2/Kg)	K_{232}	K_{270}	ΔK
A	0.3 a*	6.26 a	1.52 a	0.09 a	0.00
1	0.3 a	6.75 a	1.45 a	0.09 a	0.00
B	0.6 a	6.53 a	1.44 a	0.10 a	0.00
2	0.4 b	4.82 b	1.37 a	0.07 a	0.00
C	0.7 a	6.52 b	1.27 a	0.12 a	0.00
3	0.7 a	7.68 a	1.26 a	0.10 a	0.00
D	0.5 a	6.80 a	1.04 b	0.11 b	0.00
4	0.5 a	7.14 a	1.78 a	0.17 a	0.00
E	0.6 a	6.11 a	1.48 b	0.11 b	0.00
5	0.6 a	5.21 b	1.57 a	0.15 a	0.00
F	0.5 a	10.67 b	1.66 a	0.13 b	0.00
6	0.5 a	11.27 a	1.68 a	0.14 a	0.00
G	0.5 a	9.72 a	1.60 a	0.12 a	0.00
7	0.5 a	8.47 b	1.62 a	0.11 a	0.00
Limit value for EVOO	≤ 0.8	≤ 20	≤ 2.5	≤ 0.22	0.00

***In relation to each couple of runs (A/1÷G/7), for each parameter, values not sharing the same letter have significantly different mean concentration**



CONCLUSIONS

- **The general analytical parameters (Reg 2568/91) don't show reliable differences due to the new extraction process and prove the efficiency of micro oil mill used (Oliomio Baby®)**

- **The concentration of PHENOLS tends to increase but there is a great variability in experimental data (this variability doen't seem to be related to the amount of water remaining in the oil).**

- **The concentration of TOCOPHEROLS increases using the new extraction method**



CONCLUSIONS

- **The $CO_{2,s}$ addition seems to increase the extraction yield (this effect is greater when the olives water content is greater).**
- **The extraction yield is greater when it's used an higher ration between $CO_{2,s}$ added / olives squeezed**
- **The possibility of using olives early harvested could limit the losses due to *Bactrocera oleae* (*this can be useful in "difficul year"*)**



CONCLUSIONS

- **The new extraction method could allow to obtain an EVOO with an higher concentration in bioactive compounds**

EVOO can increases its nutritional properties and its antioxidant activity,

and so its SHELFLIFE.



What will be done?

- to control the changes in chemical and sensory qualities both for oil extracted with the new system and the traditional one as a function of storage time;

- To set up a "more complex" innovative plant to verify the possibility to introduce other modifications to the extraction process (ex: verify if the cryogen addition can be done even (or) during the malaxation)

This project was selected for the presentation at Expo, Milan, 24th August 2015, Italian Pavillon



References

Solid carbon dioxide to promote the extraction of extra virgin olive oil

A. Zinnai, F. Venturi, C. Sanmartin, F. Favati, G. Andrich

Grasas y Aceitas (in press)

Extra-virgin olive oil production with the addition of solid CO_2

A. Zinnai, F. Venturi, C. Sanmartin, I. Taglieri, G. Andrich

Agro FOOD Industry Hi Tech - vol 26(3) - May/June 2015

Preliminary results on the influence of carbonic snow addition during the olive processing: oil extraction yield and elemental profile.

C. Zoani, G. Zappa, F. Venturi, C. Sanmartin, G. Andrich and A. Zinnai

Journal of Nutrition and Food Sciences 4: 277 (2014).

doi: 10.4172/2155-9600.1000277

Thanks to …

- *Research groups of Prof Fabio Favati and Dr.ssa Susanna Bartolini for their useful collaboration in the analytical phase of this research*

- *“Sara Arrigoni” farm - La Spezia (Italy) that took part in the experimental activity*.



SEE YOU IN MILAN, TO EXPO 2015

Research supported by

MINISTERO DELLE POLITICHE AGRICOLE ALIMENTARI E FORESTALI





MASS BALANCE during extraction process:

Total OIL entrance

(kg of crushed fruits x % of oil inside the olives)

=

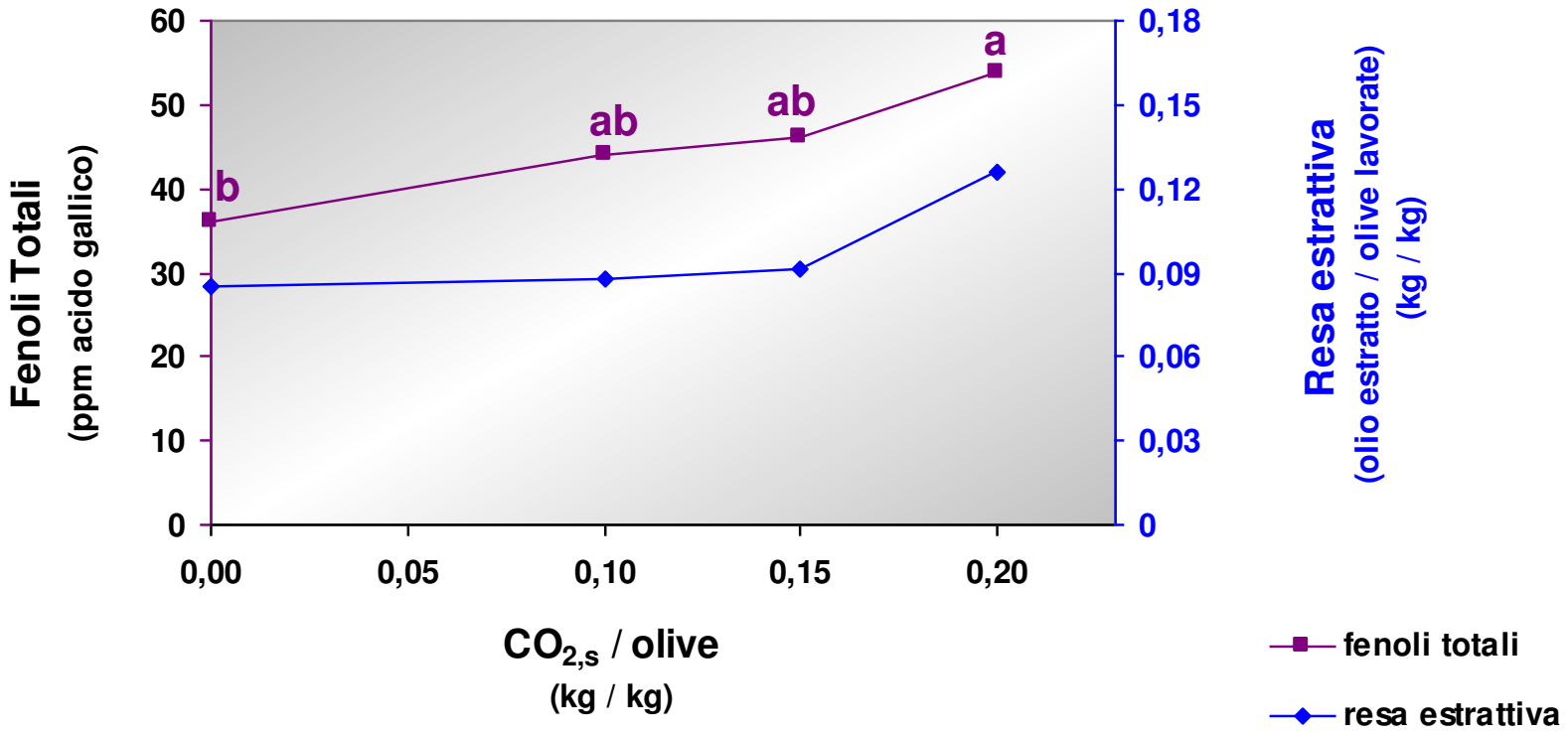
Total OIL output

(kg of the olive residues x % of oil inside the olive residues)

+

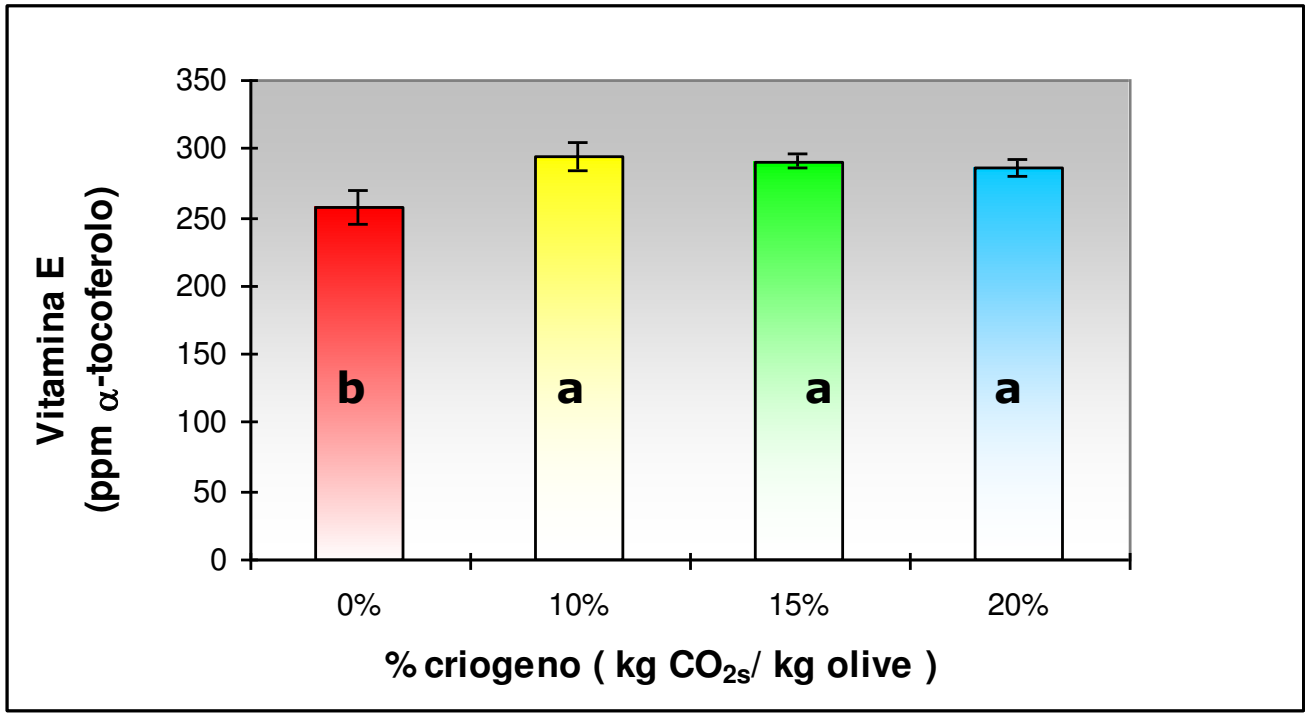
EXTRACTED OIL

Fenoli totali (ppm acido gallico) e rese estrattive (kg olio estratto/ kg olive lavorate) ottenute aggiungendo o meno diverse quantità di criogeno alle olive processate (0; 0.10; 0.15; 0.20 kg criogeno / kg olive lavorate).



lettere diverse sottolineano l'esistenza di differenze statisticamente significative (p = 0.05)

Vitamina E (ppm di α-tocoferolo) presente negli oli estratti ottenuti addizionando diverse quantità di criogeno alle olive (0; 0.10; 0.15; 0.20 kg di criogeno / kg olive lavorate).



lettere diverse sottolineano l'esistenza di differenze statisticamente significative (p = 0.05)

We need 0.8 kg of CO_{2s} to lower 100 kg of olives temperature by 1°C.

Cost of 1 kg of CO_{2s}= €0.50

Cost to turn down the average temperature of 100 kg of olives by 10°C

(15°C → 5°C)

0.8kg/°C x 10°C x 0.50 €/kg

=

4€

Considering an average oil yield of 15%,

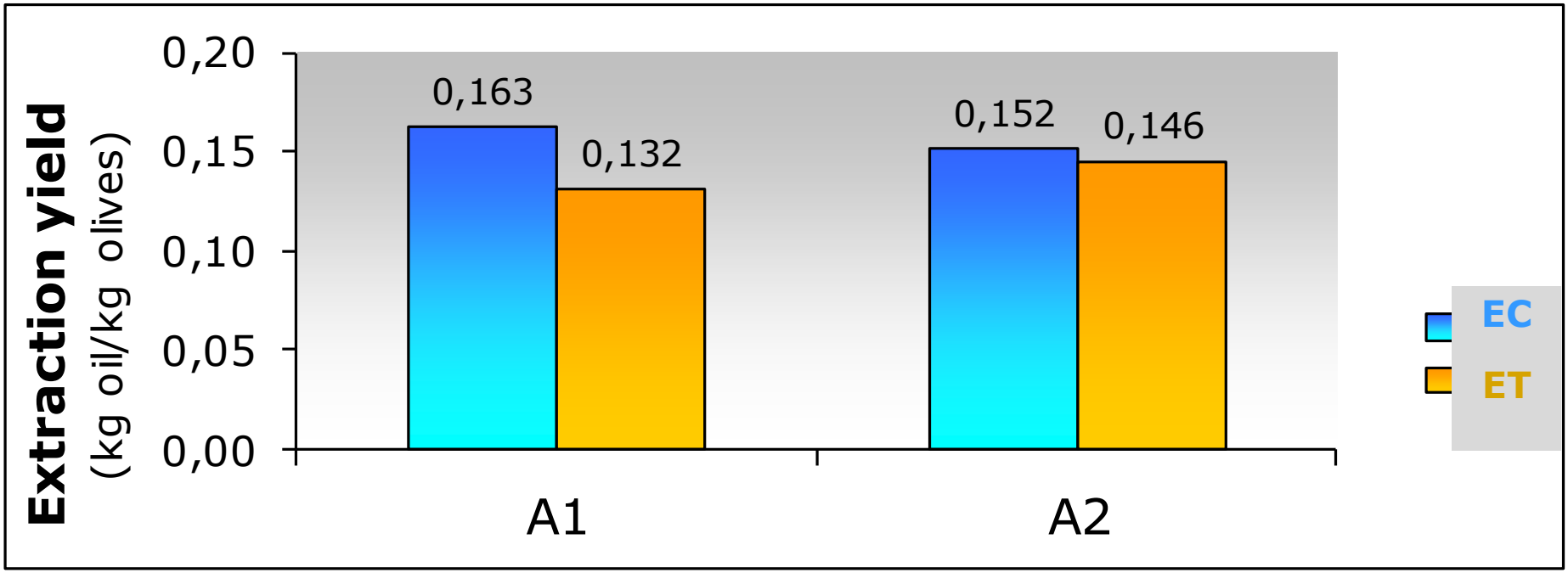
The addition cost for a kg of extravirgin olive oil is

4 €/100 kg olives x 15/100kg oil/kg olives

< 0.3€/kg oil



Extraction yield



The $CO_{2,s}$ addition is more useful if the olives have a greater content in water (fruits less ripe)

Run	CRIO Yield	TRAD Yield	EIV
A1,1	12.2	11.0	10.9
A1,2	13.0	11.8	10.2
A2	16.3	13.2	23.5
A3	15.5	15.7	-1.3
A4	16.0	14.2	12.7
A5	15.2	14.6	4.1
B1	15.8	15.2	4.0
C1	12.0	12.8	-6.2
D1	14.8	14.5	2.2
D2	16.4	15.0	9.3
D3	17.3	16.2	6.8
Ea	8.8	8.5	3.5
Eb	9.2	8.5	8.2
Ec	12.6	8.5	48.2

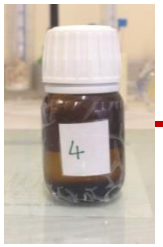
Ripe index increasing

$CO_{2,g}$ added increasing

Determination of oil elemental profile: sample pre-treatment

Different mixtures tested:
H_2O_2 30%$_{v/v}$ (1 ÷ 2 ml)+ HNO_3 69.9%$_{v/v}$ (2 ÷ 6 ml)

0.5 g olive oil



Total dissolution

2 ml H_2O_2 + 6 ml HNO_3

High Pressure Microwave Digestion



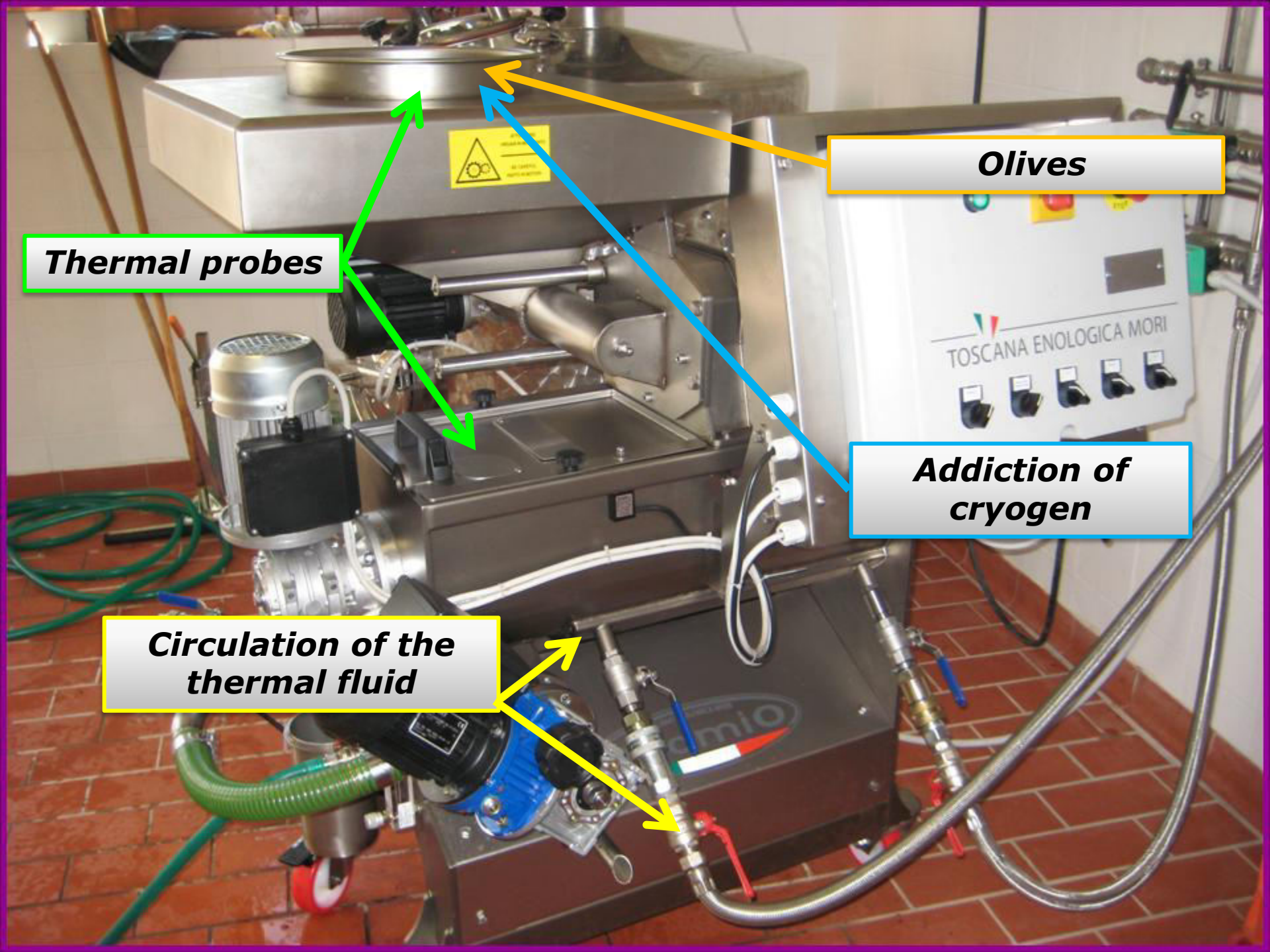
Milestone 1200 Mega

time	Power	Pressure
1 min	250 W	Free pressure race
1 min	0 W	
5 min	400 W	
5 min	650 W	
Vent = 5 min		

high-purity water (> 18 MΩ)



Mineralized oil sample (final V = 25 ml)


Olives
Thermal probes
Addiction of cryogen
Circulation of the thermal fluid
TOSCANA ENOLOGICA MORI

Preliminary results about oil extraction yield: discussion

The number of the experimental runs carried out until now is quite reduced.

BUT

The results appear very encouraging and the new method seem very suitable for olive oil extraction

- During the next crop season we will increase the number of experimental runs adopting several combinations of the working parameters (i.e. amount of cryogen/amount of olives, fruit ripening stage, etc.).

ICP-AES Analysis

Varian Vista MPX
(axial configuration,
simultaneous 1.12 Mpixel CCD detec





TQ mineralized olive oil solution

Analytical wavelengths (nm)		
Al - 396.152 nm	K - 766.491 nm	Rb - 780.026 nm
As - 188.980 nm	Li - 670.783 nm	S - 181.972 nm
B - 249.772 nm	Mg - 279.553 nm	Sb - 206.834 nm
Ba - 455.403 nm	Mn - 257.610 nm	Si - 251.611 nm
Ca - 396.847 nm	Na - 589.592 nm	Sr - 407.771 nm
Cr - 267.716 nm	Ni - 231.604 nm	Ti - 334.941 nm
Cu - 327.395 nm	P - 213.618 nm	V - 311.837 nm
Fe - 238.204 nm	Pb - 220.353 nm	Zn – 206.200 nm

Gas flows optimization ba
signal-to-background rati

		Auxiliary flow (l/min)			N
		1.0	1.5	0.9	
S/B	Mg	3.296	11.720	13.948	1
	Mn	0.128	0.197	0.245	
	Na	1.827	1.940	1.827	

Operating parameters for ICP-AES quantitative analysis

Instrumental conditions	
RF Frequency	40 MHz (free running, air-cooled)
RF Power	1.2 kW
Gas (plasma, auxiliary, nebulizer)	Argon
Plasma flow	15.0 l/min
Auxiliary flow	1.5 l/min
Nebulizer flow	1.10 l/min
Replicates	5
Replicate read time	5 s

ICP-MS Analysis

Bruker Aurora M90 (90 degree ion mirror ion optics, Collision Reaction Interface)

1:10 diluted mineralized olive oil solution





Tuning with a 5 µg/l Be, Mg, Co, In, Ba, Ce, Ti, Pb and Th solution for sensitivity and resolution optimization and mass calibration

Check of the level of **oxide ions** by the CeO^+/Ce^+ ratio: < 2%

Monitoring of double charged ions by the signal $^{137}Ba^{++}/^{137}Ba^+$: < 3%

Check/Correction of isobaric interferences:

- examination of more isotopes of the same element(e.g.: Rb85, Rb 87; Sr88,Sr87; Nd142, Nd146, Nd144; Se77, Se78; Sn147, Sm148, Sm152; Gd157, Gd154; Er166, Er168; Yb170, Yb172)
- application of correction equations with respect to isotopes of other elements potentially interfering (e.g.: Nd142 corrected by analyzing Ce140, Nd144 by Sm147, Sm152 by Gd157, Rb87 by Sr88)
- use of the Collision Reaction Interface – CRI (for As and Se)

Normal Sensitivity Mode (without CRI), High Sensitivity Mode
As and Se – Normal mode with CRI

Working ranges:

- 0.05 ÷ 5 µg/l - As, Cd, Ce, Er, Eu, Gd, La, Mn, Nd, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sr, Th, V, Y, Yb
- 0.1 ÷ 10 µg/l - Co, Cr, Cu, Mg, Ni

External calibration
5 standard solutions + blank
Curve Fit: Linear
Weighted Fit: No
Correlation coefficients:
R > 0.9999

