Geographical identification of Chianti red wine based on ICP-MS element composition

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Trace elements in food: applications with ICP-MS and ICP-MS/MS
21 Giugno 2019

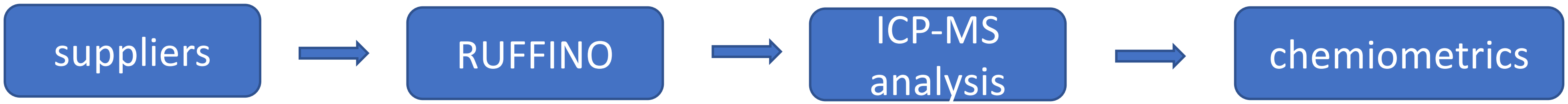
motivation

Chianti is a precious red wine and enjoys a high reputation for its high quality in the world wine market. Despite this, the production region is small.

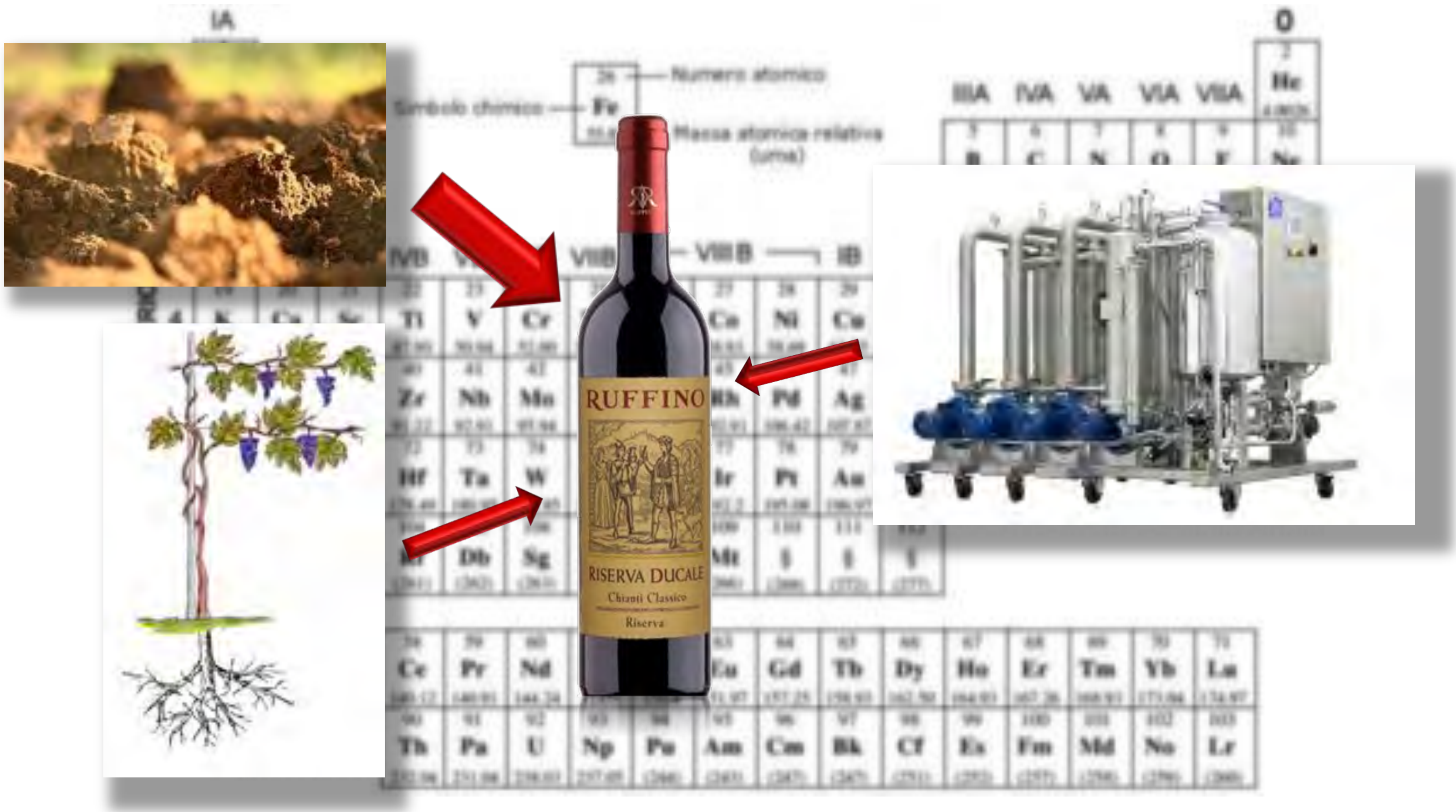
grape production areas

the aim of the project

investigate the elemental profile of Chianti and differentiate it from wines of other Italian regions provided by suppliers



wine element composition



wine element composition

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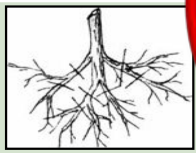
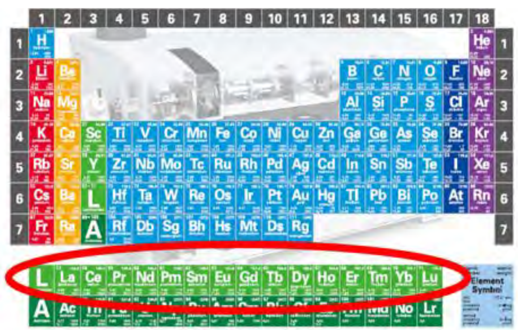
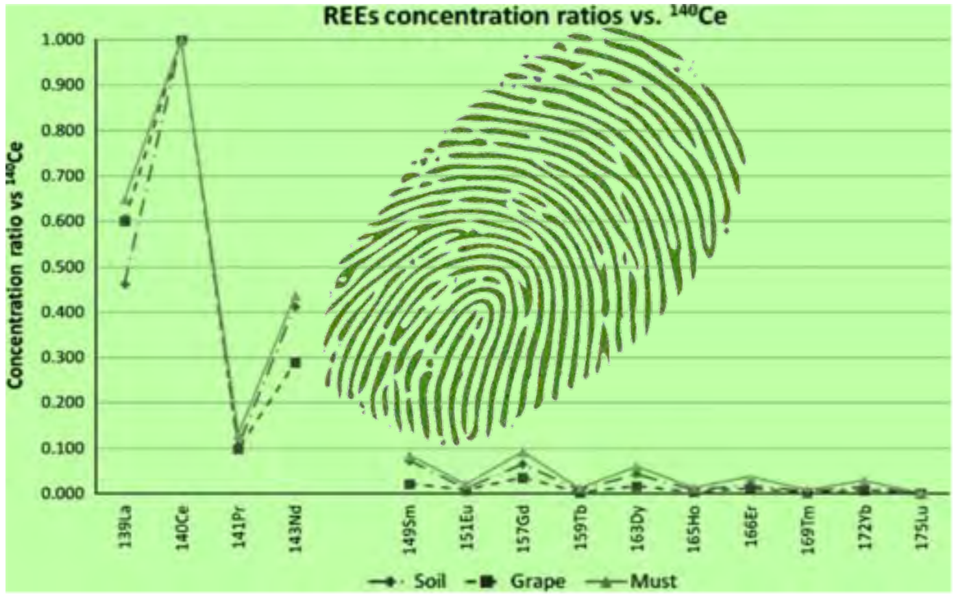
	☑	☑	
		☑	☑

could be possible markers for discriminating the geographical origin

wine element composition

traceability seems possible from soil to must since the REEs distribution is maintained from soil to grape and must Aceto et al., *Food Chemistry*, 2013





phases of the project

sites
↓ **1** SAMPLING
grapes
↓ **2** MICRO-VINIFIED
wine
↓ **3** ICP-MS
analysis
↓ **4** CHEMOMETRICS
model
↓ **5** VALIDATION
results

PARTNERS

- ❑ RUFFINO
- ❑ Agilent Technologies, Italy
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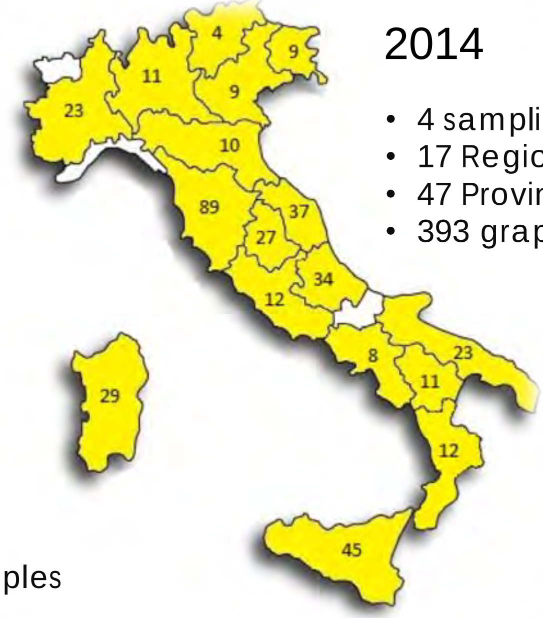
- ❑ Dept. of Mathematical and Statistical Sciences, University of Colorado Denver, CO, USA

1 sampling

2013

- 4 sampling teams
- 16 Regions
- 41 Provinces
- 246 grape samples



2014

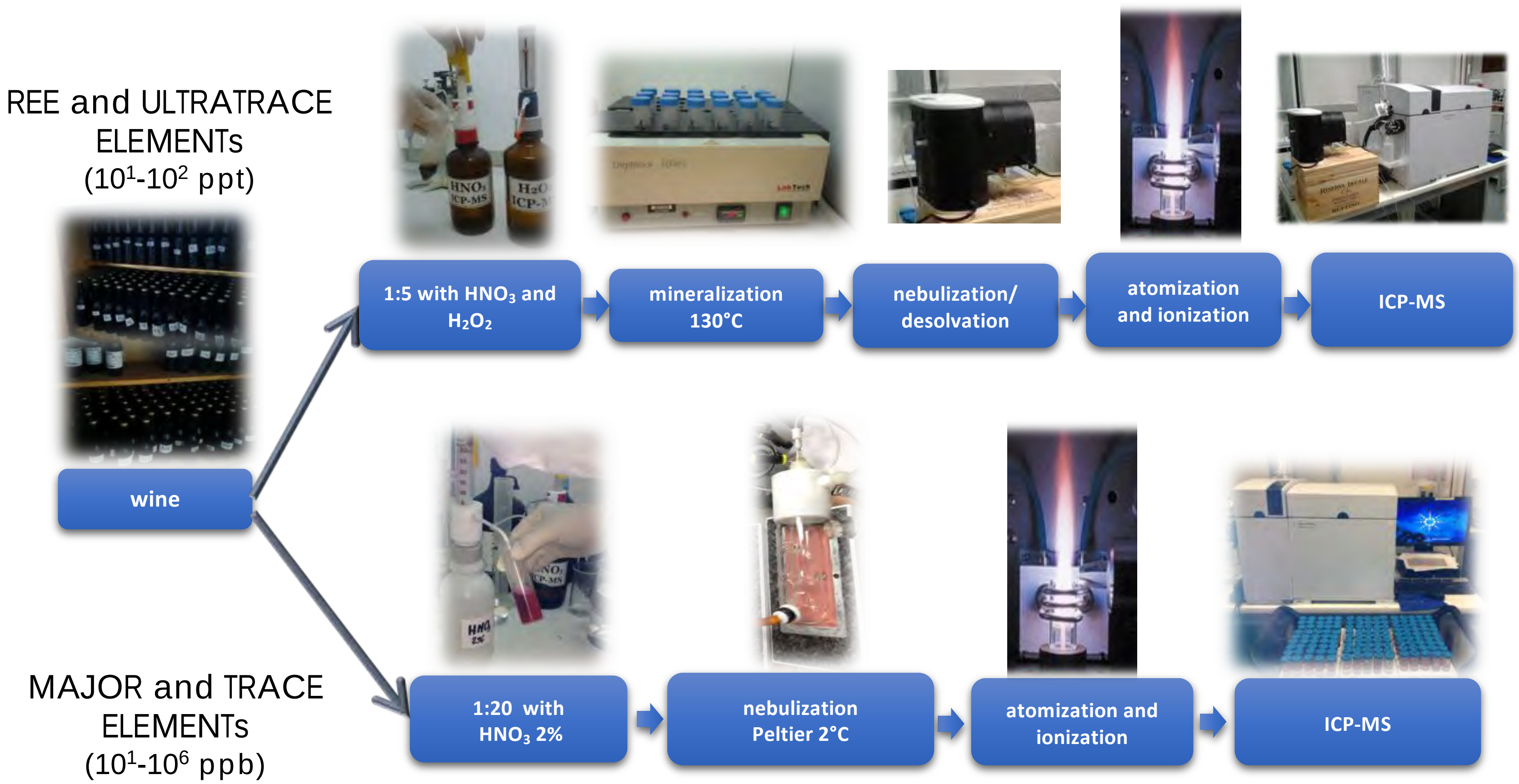
- 4 sampling teams
- 17 Regions
- 47 Provinces
- 393 grape samples

639 samples

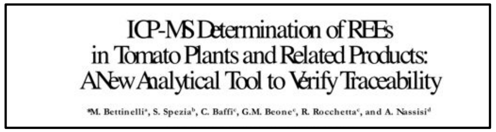
122 Sangiovese
95 Merlot
68 Montepulciano
42 Cabernet Sauvignon
33 Barbera,
32 Aglianico
28 Syrah
21 Nebbiolo
20 Nero d'Avola
17 Petit Verdot
15 Cannonau
13 Croatina,
10 Bovale Sardo
123 of 34 other varieties

2 micro-vinified

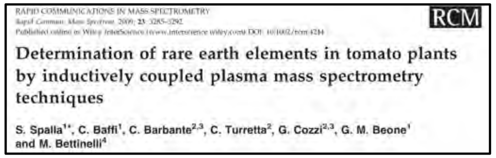
3 analytical procedures



3 sample introduction system


ICP-MS Determination of REEs in Tomato Plants and Related Products: A New Analytical Tool to Verify Traceability

*M. Bettinelli[a], S. Spezia[b], C. Baffi[c], G.M. Beone[c], R. Rocchetta[c], and A. Nassisi[d]

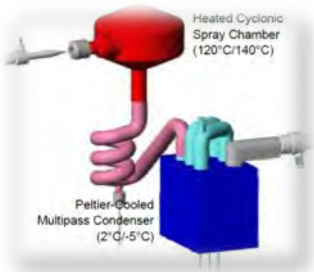

RAPID COMMUNICATIONS IN MASS SPECTROMETRY

Rapid Commun. Mass Spectrom. 2009; 23: 3285–3292

RCM

Determination of rare earth elements in tomato plants by inductively coupled plasma mass spectrometry techniques

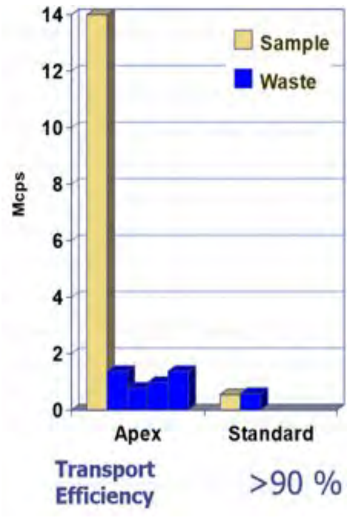
S. Spalla[1*], C. Baffi[1], C. Barbante[2,3], C. Turretta[2], G. Cozzi[2,3], G. M. Beone[1] and M. Bettinelli[4]



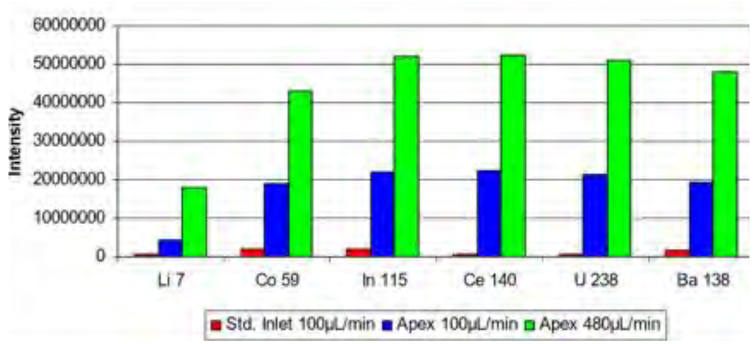
APEX Q
nebulizer has an o-ring-free Quartz flow path for high sensitivity and low background

Spiro TMD
heated macro-porous PTFE membrane desolvation module that reduces solvent derived polyatomic interferences

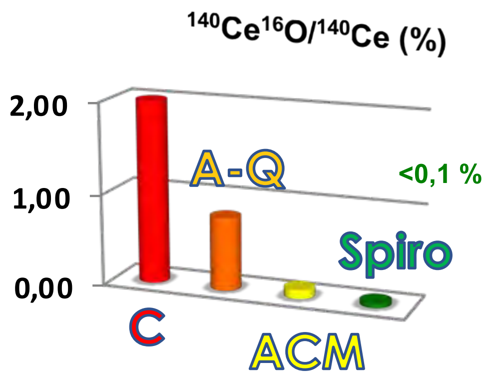
3 sample introduction system



preconcentration of the sample improves sensitivity 3-10 fold



reduces solvent derived oxide, hydride and carbide polyatomic interferences



element	interference
^{155}Gd	$^{139}La^{16}O$
^{156}Gd	$^{140}Ce^{16}O$
^{157}Gd	$^{141}Pr^{16}O$
^{158}Gd	$^{142}Ce^{16}O$, $^{142}Nd^{16}O$
^{159}Gd	$^{143}Nd^{16}O$

3 analytical method

Campione	Tipo	Vial
Lavaggio	sample	0
CAL 0	cal level 1	1
CAL 1	cal level 2	2
CAL 1’	cal level 3	3
CAL 1’’	cal level 4	4
Lavaggio	sample	0
ICB 1	sample	5
ICB 2	sample	6
ICB 3	sample	7
ICB 4	sample	8
ICV	sample	9
ICV’	sample	10
CCV	QC1	25
CAMP 1	sample	11
CAMP 2	sample	12
CAMP 3	sample	13
CAMP 4	sample	14
CAMP 5	sample	15
CAMP 6	sample	16
CCB	QC2	5
CCV	QC1	25
Batch di circa 30-40 campioni		

x6

UNI EN ISO 17294-2 (2005)

- linearity: 5 levels, $R^2>0.998$
- daily calibration: wine +STD
- checks:
  - ✓ ICB ≤ MDL
  - ✓ ICV ±10%
  - ✓ CCB < MDL (memory effect)
  - ✓ CCV ±10% (drift)
  - ✓ ISTD ±20%

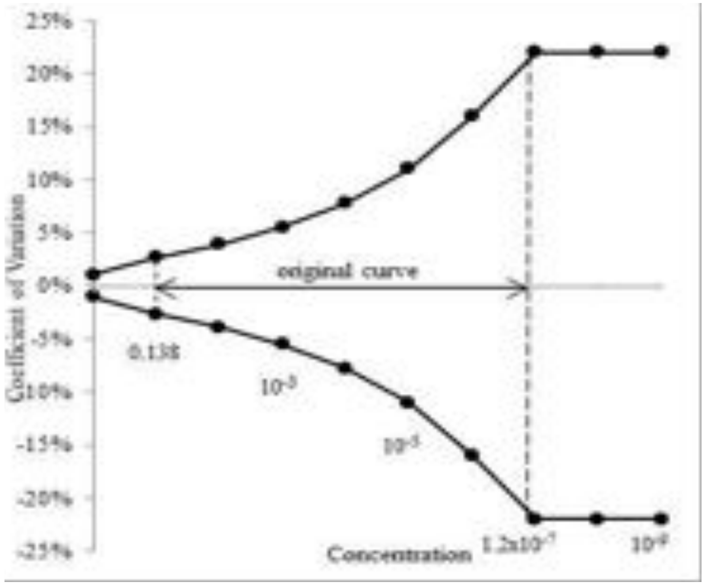
solutions	
CAL 0	wine
CAL 1, 1’, 1’’	wine + STD
ICB 1 (CCB), 2, 3, 4	analytical blank
ICV, ICV’	RM + STD (ML)
CCV	RM + STD (HL)

3 precision

HORWITZ -THOMPSON

equation	
$\sigma = 0{,}22C$	$C < 1{,}2 * 10^{-7}$
$\sigma = 2^{(1-0{,}5logC)}$	$1{,}2 * 10^{-7} \leq C \leq 1{,}38 * 10^{-1}$
$\sigma = 0{,}01\sqrt{C}$	$C > 1{,}38 * 10^{-1}$

C = concentrazione dell'analita
σ = reproducibility std dev



3 precision

repeatibility: 5 wine samples and 3 batch

			wine 1			wine 2			wine 3			wine 4			wine 5		
m/z	eement	u	CV (%)	R(%)	r(%)	CV (%)	R(%)	r(%)	CV (%)	R(%)	r(%)	CV (%)	R(%)	r(%)	CV (%)	R(%)	r(%)
7	Li	ppb	4,5	22,0	14,3	2,5	22,0	14,3	3,0	22,0	14,3	3,2	22,0	14,3	4,8	22,0	14,3
23	Na	ppm	4,2	10,4	6,8	5,5	11,3	7,4	4,5	10,7	6,9	3,1	10,5	6,8	3,6	10,9	7,1
26	Mg	ppm	2,5	7,8	5,1	2,7	7,6	5,0	2,4	7,7	5,0	1,7	7,6	5,0	2,0	7,7	5,0
48	Ti	ppb	3,0	22,0	14,3	3,3	22,0	14,3	3,0	22,0	14,3	2,4	22,0	14,3	2,6	22,0	14,3
55	Mn	ppb	2,3	14,8	9,6	2,3	14,0	9,1	2,2	13,7	8,9	1,5	15,0	9,8	2,4	15,4	10,0
59	Co	ppb	2,9	22,0	14,3	2,4	22,0	14,3	2,9	22,0	14,3	3,1	22,0	14,3	3,3	22,0	14,3
60	Ni	ppb	3,0	22,0	14,3	2,6	22,0	14,3	2,7	22,0	14,3	3,6	22,0	14,3	2,4	22,0	14,3
75	As	ppb	22,9	22,0	14,3	16,8	22,0	14,3	23,2	22,0	14,3	23,2	22,0	14,3	34,1	22,0	14,3
85	Rb	ppb	2,2	14,2	9,2	2,2	14,4	9,4	2,0	14,4	9,4	2,0	14,6	9,5	2,0	14,9	9,7
88	Sr	ppb	1,9	16,3	10,6	2,1	16,4	10,6	1,9	16,4	10,6	1,9	16,6	10,8	7,1	17,7	11,5
135	Ba	ppb	3,1	20,5	13,4	2,3	20,0	13,0	2,5	18,6	12,1	13,8	22,0	14,3	2,8	19,8	12,8

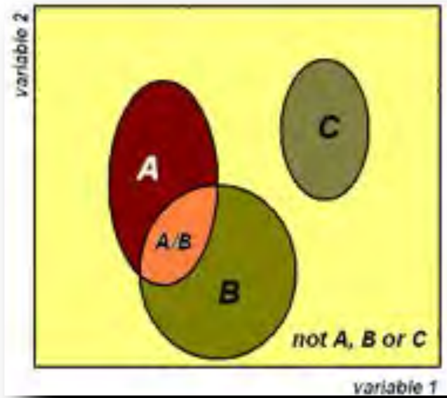
R%: reproducibility % (Horwitz-Thompson)
r%: repeatibility % (Horwitz-Thompson)

$$\mathbf{RSD \leq \sigma_{Horwitz\text{-}Thomson}}$$

4 chemometrics – data set

- 31 elements As, Ba, Co, Fe, Li, Mg, Mn, Na, Ni, Rb, Sr, Ti, Tl, V, Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Re, Sm, Ta, Tb, Tm, V, Y, and Yb
- 23 element ratios ^{140}Ce/La, ^{141}Pr/La, ^{144}Nd/La, ^{147}Sm/La, ^{151}Eu/La ^{152}Sm/La, ^{159}Tb/La, ^{160}Gd/La, ^{163}Dy/La, ^{164}Dy/La, ^{165}Ho/La, ^{166}Er/La, ^{169}Tm/La, ^{172}Yb/La, ^{175}Lu/La, ^{160}Gd/Er, ^{166}Er/Yb, ^{141}Pr/Lu, ^{140}Ce/Y, ^{141}Pr/Th, ^{172}Yb/Te, ^{172}Yb/Eu, ^{125}Te/Er
- Log transformation
- autoscaling (Partial Least Squares - Discriminant Analysis PLS-DA)
- range scaling (FF_Sin e N3_JT)

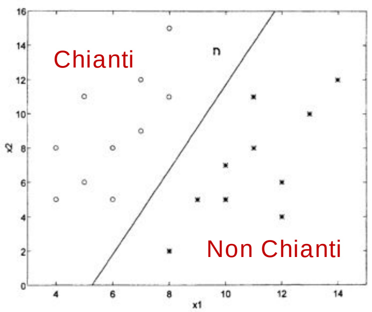
training set



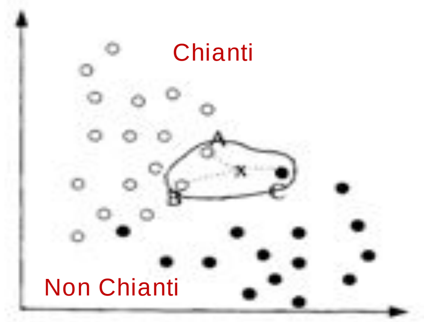
model

4 chemometrics – models

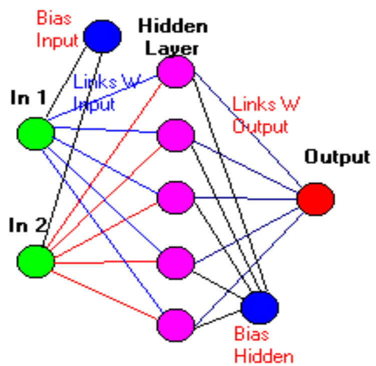
1. Linear model
(PLS-DA)



2. similarity model
(N3_JT)

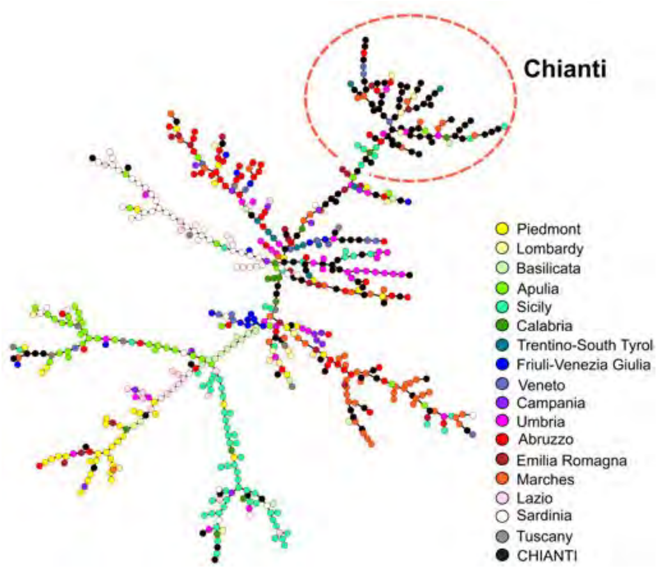


3. non-linear model
(FF_Sn)



4. consensus model
aritmetic mean of PLSDA, N3_JT e FF_Sn

5 results



the tree nodes represent the wine samples, colored according to the provenance regions

random selection of test samples• 639 samples:

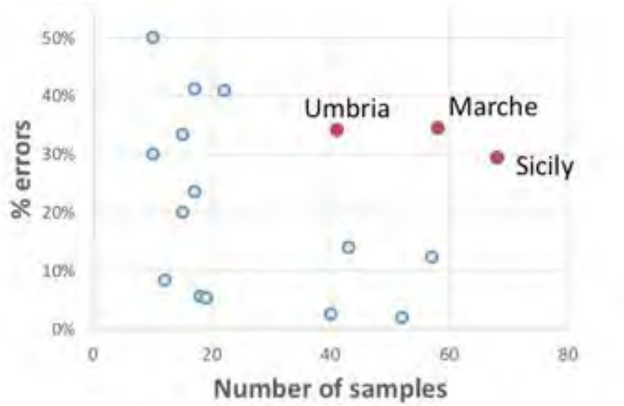
75% training + 25% test

	sensitivity	specificity
training	80%	79%
test	71%	79%

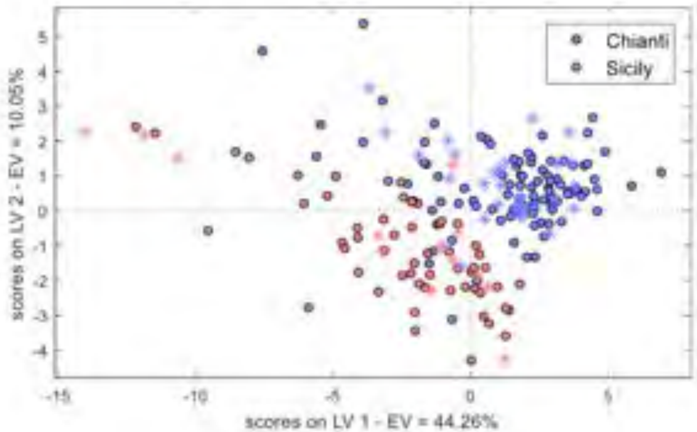
sensitivity: % of correctly predicted Chianti
specificity: % of correctly predicted non-Chianti

5 results

identification of regions with significant overlaps to Chianti



partial models (PLS-DA) to discriminate overlapping regions



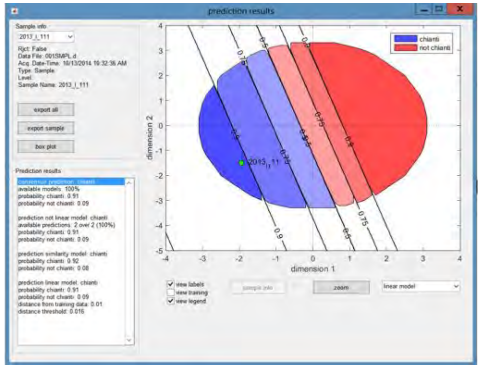
	Sicily	Marche	Umbria
training set	92%	87%	83%
test set	89%	72%	74%

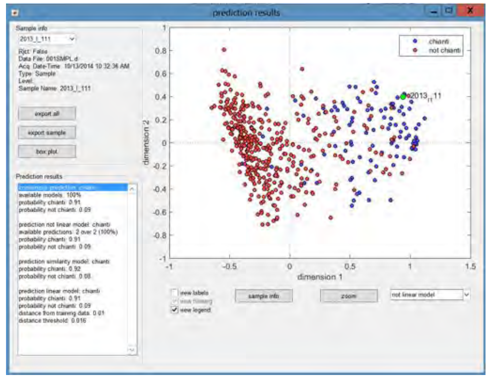
5 chemometrics – software

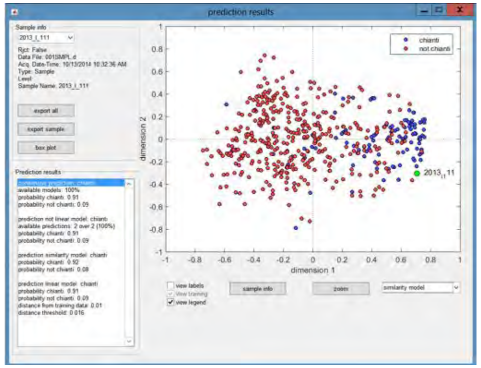
Chianti vs non-Chianti

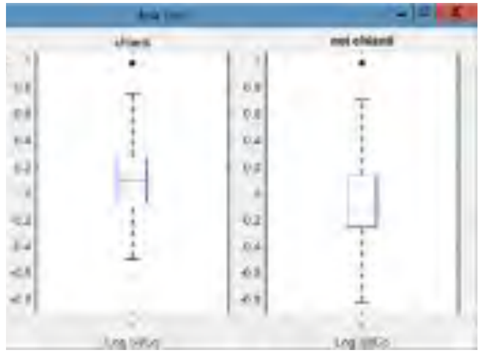
Additional information to support the prediction of each sample

- Applicability Domain estimation
- list of neighbors (most similar training samples)
- predictions of partial models (Sicily, Umbria, Marche, if predicted "Chianti")
- Batch analysis in terms of similarity of chemical profiles









conclusions

«General» models

Mg, Ti, and Co have large positive coefficients, while V, Li, As negative ones
REEs and ultratrace elements have lower weights. Tb, Gd, Dy and Re have positive contribution while Ta, Lu, Yb and Tm have negative coefficients

Most of the regions (i.e. Abruzzo, Sardinia, Apulia and Piedmont) with a large number of samples are characterised by a small degree of overlap with respect to Chianti

«Region-based» model

Sicily Ni; Marches Na and Rb; Sicily, Marches and Umbria Sr

These specific models increase the discriminant potentiality

Thank you
for your attention