

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

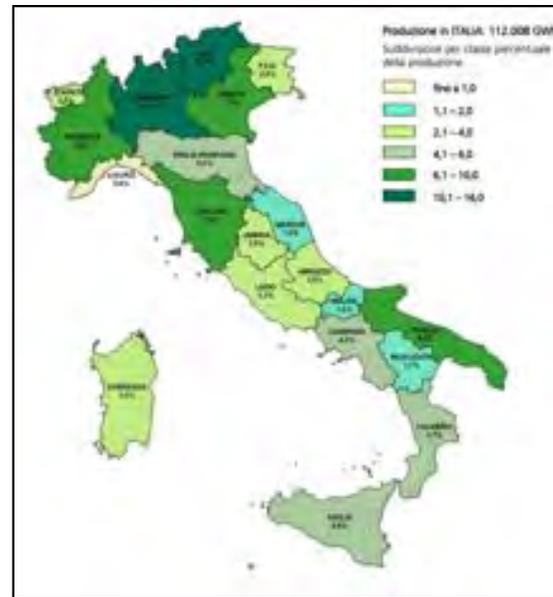
B BRONZI, C BRILLI, GM BEONE, MC FONTANELLA, D BALLABIO, R TODESCHINI, V CONSONNI, F GRISONI, FPM BUSCEMA



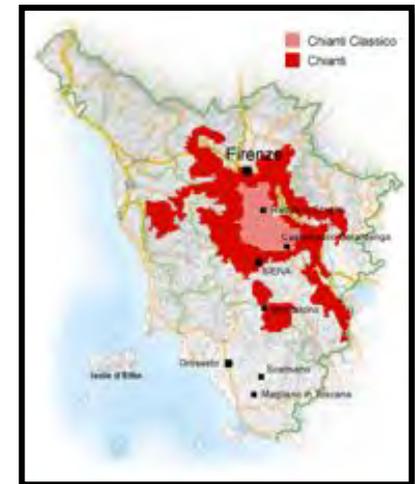
Trace elements in food: applications with ICP-MS and ICP-MS/MS
21 Giugno 2019

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.

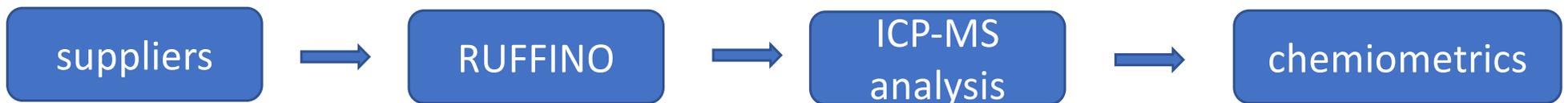


grape production areas



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

The image is a composite illustrating the connection between wine, soil, and analytical chemistry. It features a bottle of Ruffino wine, a soil sample, a grapevine, and an ICP-MS instrument, all overlaid on a periodic table of elements. Red arrows point from the soil, the bottle, and the instrument to the periodic table.

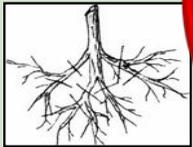
The periodic table includes the following labels and data:

- IA, 0, IIA, IVA, VA, VIA, VIIA, He
- 26 Fe, Numero atomico, Massa atomica relativa (uma)
- 25, 26, 27, 28, 29
- 21, 22, 23, 24, 25, 26, 27, 28, 29
- Ti, V, Cr, Mn, Ni, Cu
- 47, 48, 49, 50, 51, 52, 53, 54, 55, 56
- Zr, Nb, Mo, Rh, Pd, Ag
- 72, 73, 74, 75, 76, 77, 78, 79
- Hf, Ta, W, Ir, Pt, Au
- 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111
- Rf, Db, Sg, Mt, H, I, J
- 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111
- Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
- 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 250, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 273, 274, 275, 276, 277, 278, 279, 280, 281, 282, 283, 284, 285, 286, 287, 288, 289, 290, 291, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353, 354, 355, 356, 357, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419, 420, 421, 422, 423, 424, 425, 426, 427, 428, 429, 430, 431, 432, 433, 434, 435, 436, 437, 438, 439, 440, 441, 442, 443, 444, 445, 446, 447, 448, 449, 450, 451, 452, 453, 454, 455, 456, 457, 458, 459, 460, 461, 462, 463, 464, 465, 466, 467, 468, 469, 470, 471, 472, 473, 474, 475, 476, 477, 478, 479, 480, 481, 482, 483, 484, 485, 486, 487, 488, 489, 490, 491, 492, 493, 494, 495, 496, 497, 498, 499, 500, 501, 502, 503, 504, 505, 506, 507, 508, 509, 510, 511, 512, 513, 514, 515, 516, 517, 518, 519, 520, 521, 522, 523, 524, 525, 526, 527, 528, 529, 530, 531, 532, 533, 534, 535, 536, 537, 538, 539, 540, 541, 542, 543, 544, 545, 546, 547, 548, 549, 550, 551, 552, 553, 554, 555, 556, 557, 558, 559, 560, 561, 562, 563, 564, 565, 566, 567, 568, 569, 570, 571, 572, 573, 574, 575, 576, 577, 578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588, 589, 590, 591, 592, 593, 594, 595, 596, 597, 598, 599, 600, 601, 602, 603, 604, 605, 606, 607, 608, 609, 610, 611, 612, 613, 614, 615, 616, 617, 618, 619, 620, 621, 622, 623, 624, 625, 626, 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650, 651, 652, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 692, 693, 694, 695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708, 709, 710, 711, 712, 713, 714, 715, 716, 717, 718, 719, 720, 721, 722, 723, 724, 725, 726, 727, 728, 729, 730, 731, 732, 733, 734, 735, 736, 737, 738, 739, 740, 741, 742, 743, 744, 745, 746, 747, 748, 749, 750, 751, 752, 753, 754, 755, 756, 757, 758, 759, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 783, 784, 785, 786, 787, 788, 789, 790, 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 825, 826, 827, 828, 829, 830, 831, 832, 833, 834, 835, 836, 837, 838, 839, 840, 841, 842, 843, 844, 845, 846, 847, 848, 849, 850, 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879, 880, 881, 882, 883, 884, 885, 886, 887, 888, 889, 890, 891, 892, 893, 894, 895, 896, 897, 898, 899, 900, 901, 902, 903, 904, 905, 906, 907, 908, 909, 910, 911, 912, 913, 914, 915, 916, 917, 918, 919, 920, 921, 922, 923, 924, 925, 926, 927, 928, 929, 930, 931, 932, 933, 934, 935, 936, 937, 938, 939, 940, 941, 942, 943, 944, 945, 946, 947, 948, 949, 950, 951, 952, 953, 954, 955, 956, 957, 958, 959, 960, 961, 962, 963, 964, 965, 966, 967, 968, 969, 970, 971, 972, 973, 974, 975, 976, 977, 978, 979, 980, 981, 982, 983, 984, 985, 986, 987, 988, 989, 990, 991, 992, 993, 994, 995, 996, 997, 998, 999, 1000

Trace elements in food: applications with ICP-MS and ICP-MS/MS
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wine element composition

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	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	
		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>

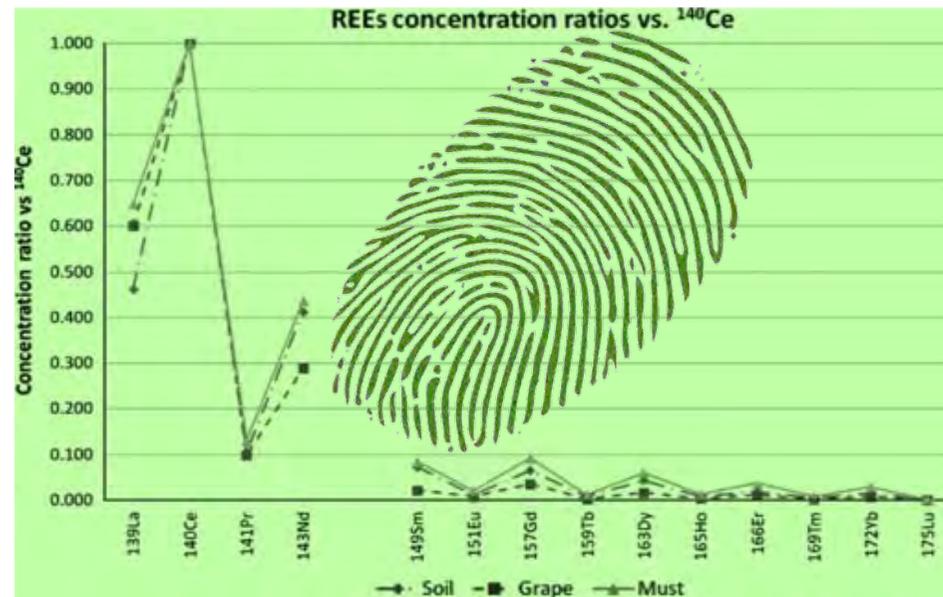
could be possible markers for discriminating the geographical origin



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

PARTNERS

grapes



2

MICRO-VINIFIED

- RUFFINO
- Agilent Technologies, Italy
- SRA Instruments, Italy
- DISTAS, UCSC, Piacenza, Italy
- DISAT - Chemometrics and QSAR - UNIMI Bicocca, Italy
- Semeion, RCSC, Rome, Italy
- Dept. of Mathematical and Statistical Sciences, University of Colorado Denver, CO, USA



wine



3

ICP-MS

analysis



4

CHEMOMETRICS



model



5

VALIDATION



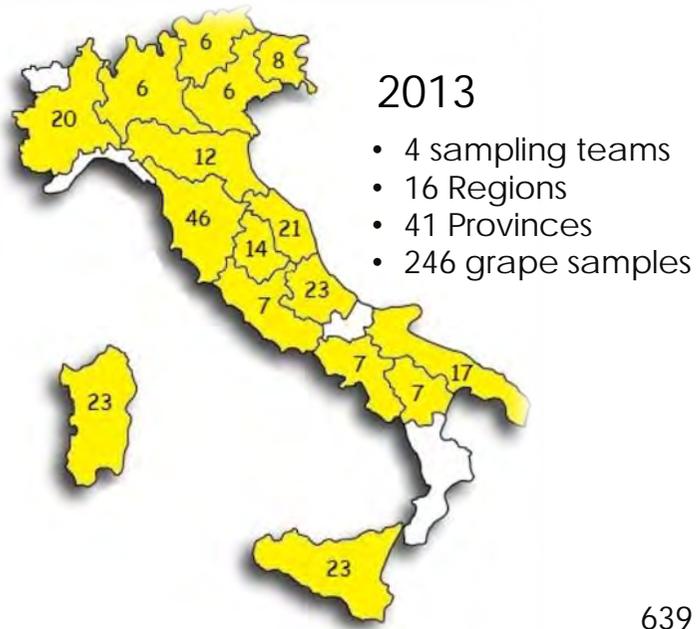
results



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

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1 sampling



639 samples



2 micro-vinified

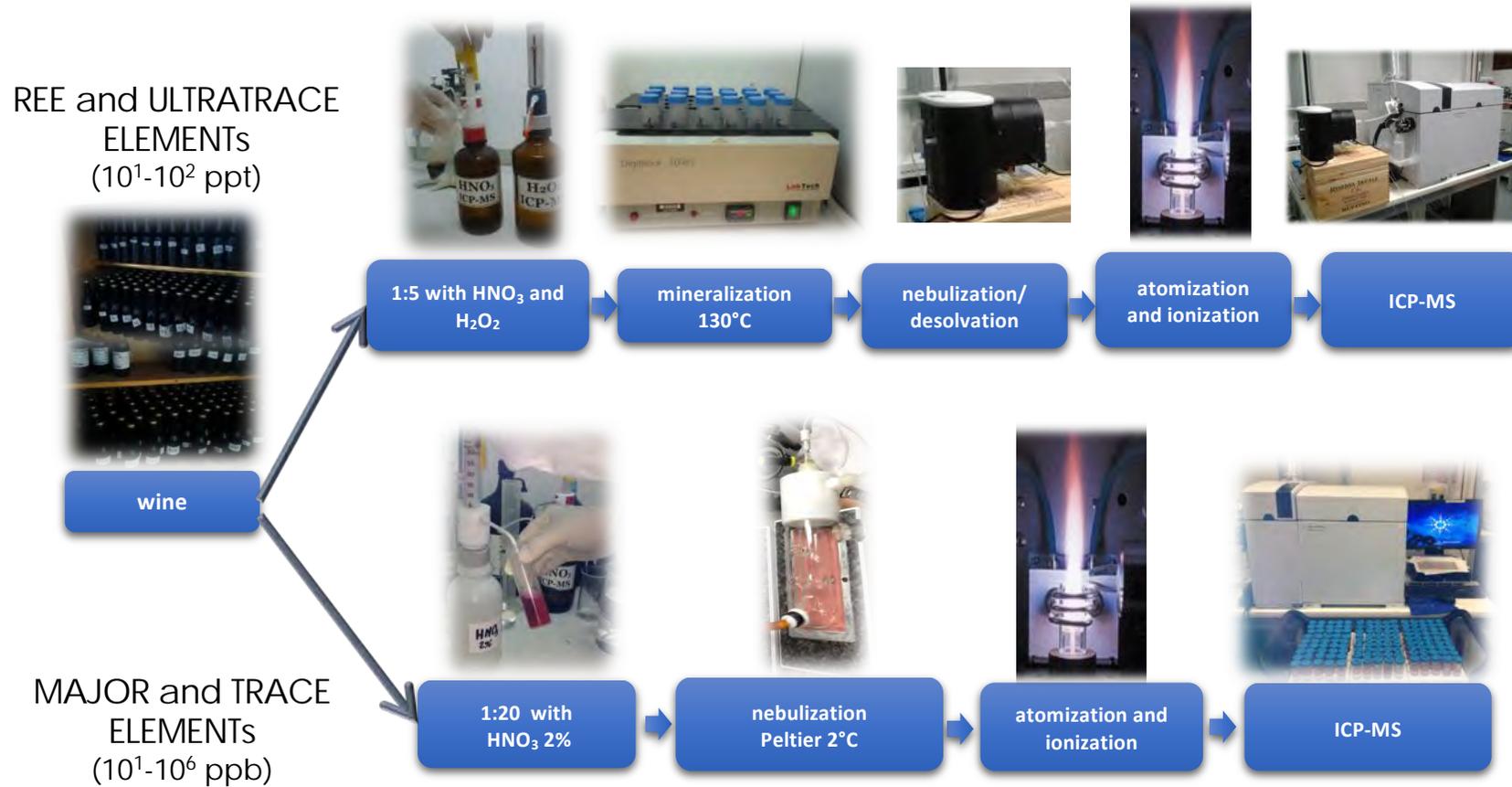


Trace elements in food: applications with ICP-MS and ICP-MS/MS
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3

analytical procedures



3 sample introduction system

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

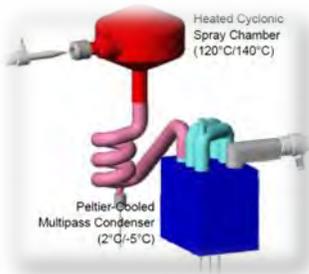
*M. Bettinelli¹, S. Spialà², C. Baffi¹, G.M. Beone¹, R. Rocchetta¹, and A. Nassisi¹

RAPID COMMUNICATIONS BY MASS SPECTROMETRY
Rapid Commun. Mass Spectrom. 2009, 23, 2285–2292
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/rcm.4214

RCM

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

S. Spialà^{1*}, C. Baffi¹, C. Barbante^{2,3}, C. Turretta², G. Cozzi^{2,3}, G. M. Beone¹ and M. Bettinelli¹



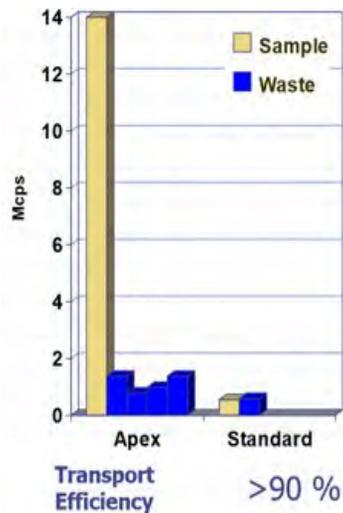
APEX Q nebulizer has an o-ring-free Quartz flow path for high sensitivity and low background



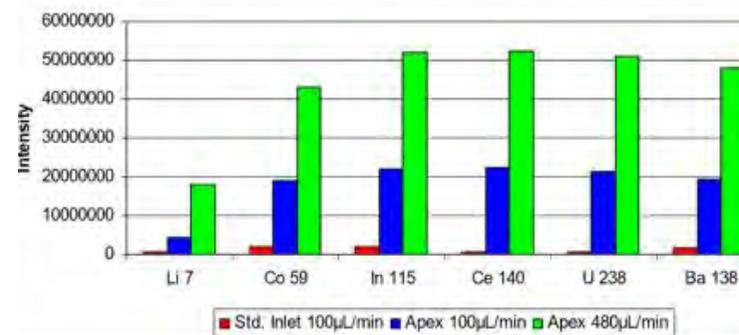
Spiro TMD heated macro-porous PTFE membrane desolvation module that reduces solvent derived polyatomic interferences



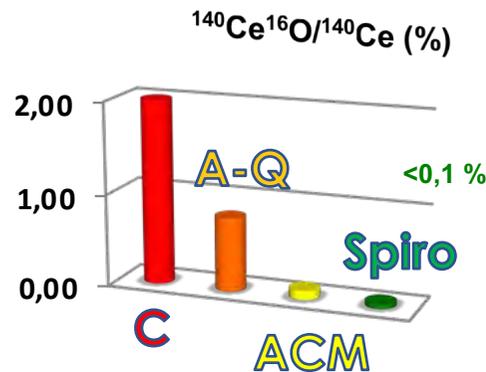
3 sample introduction system



preconcentration of the sample improves sensitivity 3-10 fold



reduces solvent derived oxide, hydride and carbide polyatomic interferences



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



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

UNI EN ISO 17294-2 (2005)

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

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)

x6

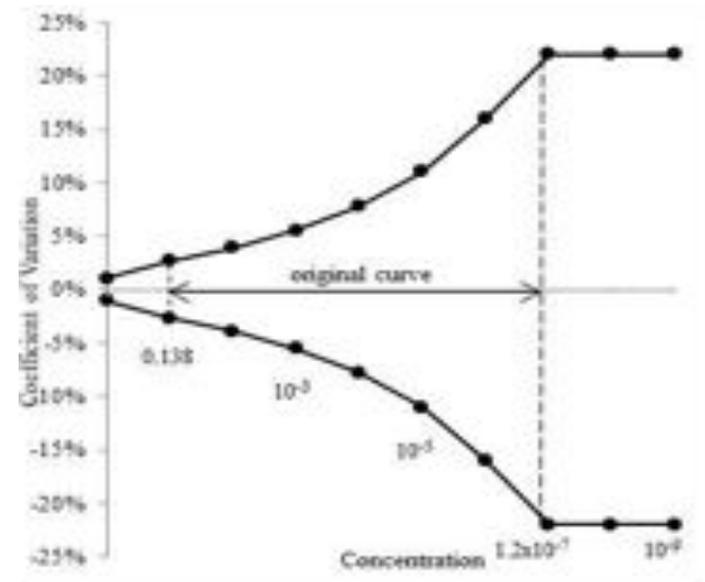


3 precision

HORWITZ -THOMPSON

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

C = concentrazione dell'analita
 σ = reproducibility std dev



3 precision

repeatability: 5 wine samples and 3 batch

m/z	element	u	wine 1			wine 2			wine 3			wine 4			wine 5		
			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%: repeatability % (Horwitz-Thompson)

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

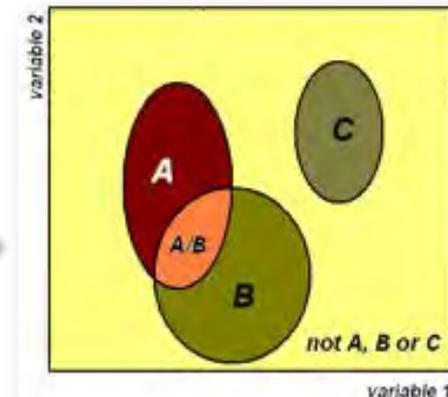


4 chemometrics – data set

- ❑ 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 $^{140}\text{Ce}/\text{La}$, $^{141}\text{Pr}/\text{La}$, $^{144}\text{Nd}/\text{La}$, $^{147}\text{Sm}/\text{La}$, $^{151}\text{Eu}/\text{La}$, $^{152}\text{Sm}/\text{La}$, $^{159}\text{Tb}/\text{La}$, $^{160}\text{Gd}/\text{La}$, $^{163}\text{Dy}/\text{La}$, $^{164}\text{Dy}/\text{La}$, $^{165}\text{Ho}/\text{La}$, $^{166}\text{Er}/\text{La}$, $^{169}\text{Tm}/\text{La}$, $^{172}\text{Yb}/\text{La}$, $^{175}\text{Lu}/\text{La}$, $^{160}\text{Gd}/\text{Er}$, $^{166}\text{Er}/\text{Yb}$, $^{141}\text{Pr}/\text{Lu}$, $^{140}\text{Ce}/\text{Y}$, $^{141}\text{Pr}/\text{Th}$, $^{172}\text{Yb}/\text{Te}$, $^{172}\text{Yb}/\text{Eu}$, $^{125}\text{Te}/\text{Er}$
- ❑ Log transformation
- ❑ autoscaling (Partial Least Squares - Discriminant Analysis PLS-DA)
- ❑ range scaling (FF_Sin e N3_JT)



training set

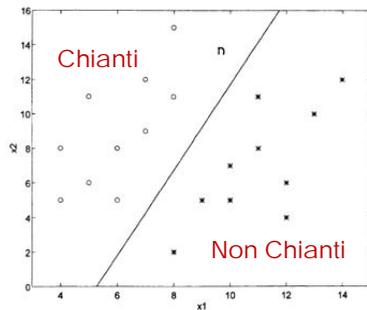


model

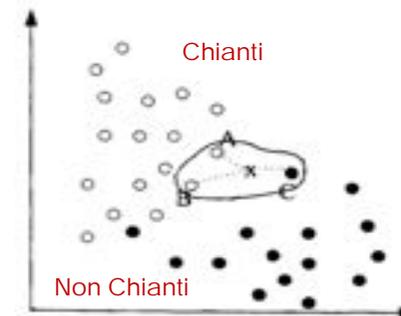


4 chemometrics – models

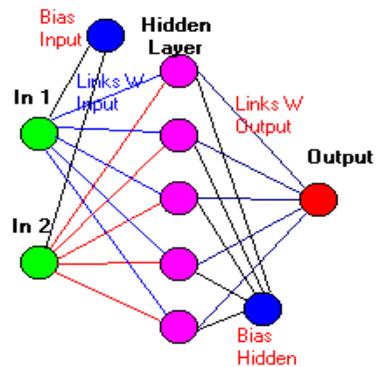
1. Linear model
(PLS-DA)



2. similarity model
(N3_JT)



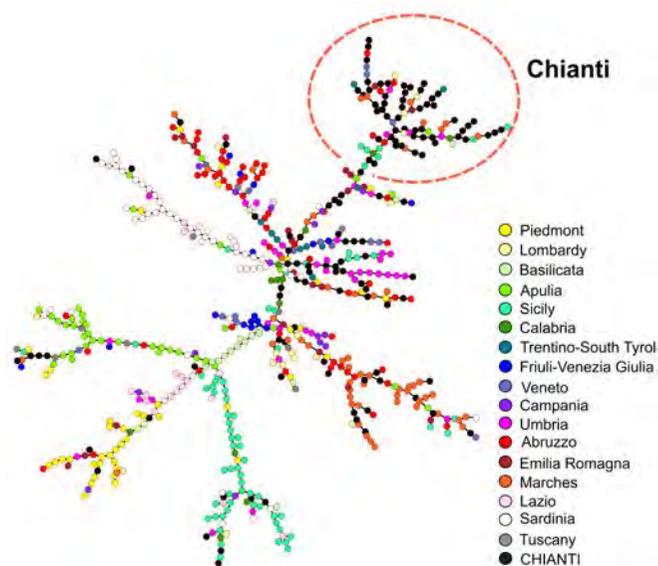
3. non-linear model
(FF_Sn)



4. consensus model
arithmetic 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

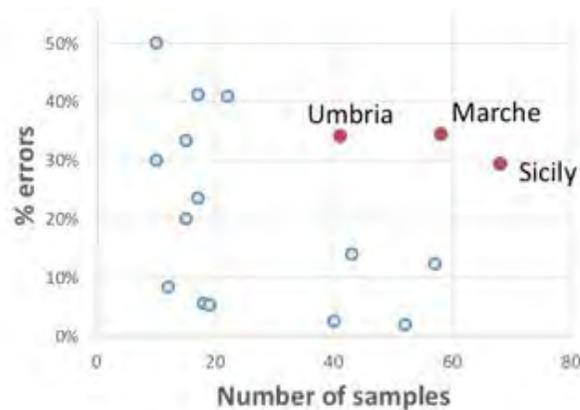
	sensitivity	specificity
training	80%	79%
test	71%	79%

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

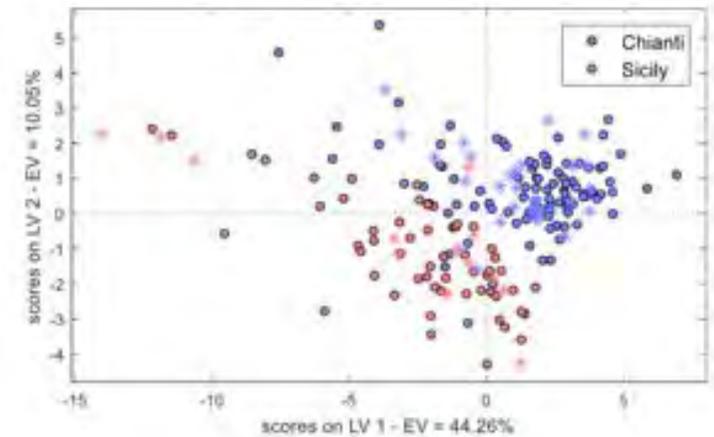


5 results

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%

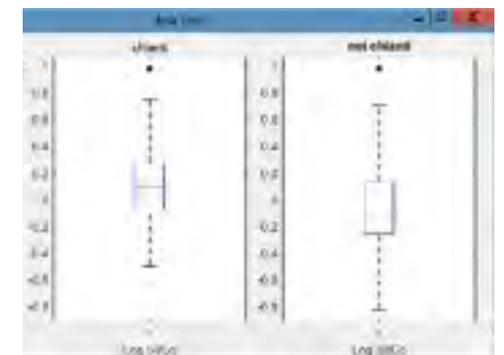
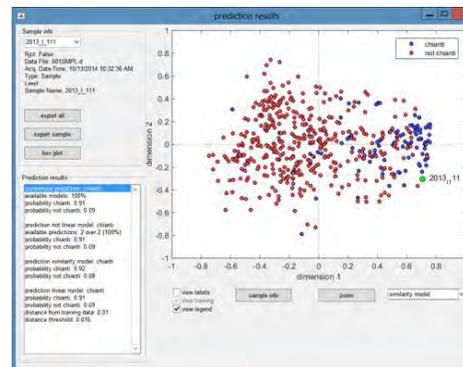
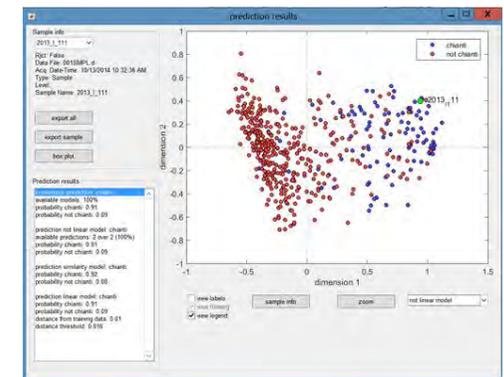
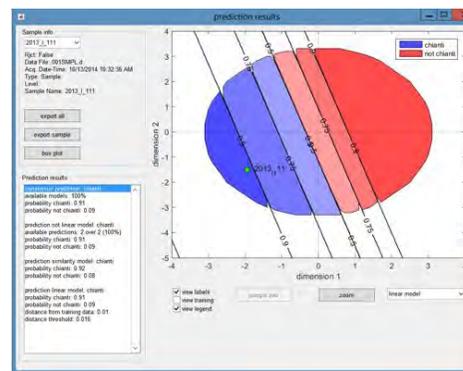


5 chemometrics – software

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



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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**

RUFFINO
LA VITA RUFFINO

RUFFINO
RISERVA DUCALE
Chianti Classico
Riserva

