DETECTION OF ADULTERATIONS IN COFFEE WITH BARLEY USING NEAR INFRARED SPECTROSCOPY AND CHEMOMETRIC TECHNIQUES

R. Leardi[1], H. Ebrahimi-Najafabadi[2], P. Oliveri[1], C. Casolino[1], M. Jalali-Heravi[2], S. Lanteri[1]

[1] Department of Drug and Food Chemistry and Technology, University of Genoa, Italy
[2] Department of Chemistry, Sharif University of Technology, Tehran, Iran

GOAL OF THE STUDY

The addition of **barley** is one of the most common adulterations of **coffee**.

Is it possible to detect and quantify it by using

NIR spectroscopy

and **multivariate calibration methods**?

THE DATA SET

A **representative and well-structured training set** is a fundamental condition for obtaining a stable and efficient model.

A **suitable test set** is essential for a thorough validation.

- Nine different types of coffee including pure *Arabica*, *Robusta* and mixtures of them at different roasting degrees, selected as to represent the most common coffee types available on the Italian market

- Four types of barley

- Ten different amounts of barley in coffee (2%, 4%, …, 20%)

360 possible combinations: too many!

Only 100 possible experiments: how to select the most informative ones?

By applying of a D-OPTIMAL DESIGN

THE TRAINING SET

exp.	coffee	barley	conc.	exp.	coffee	barley	conc.	exp.	coffee	barley	conc.
1	E	D	4	35	H	B	20	69	B	B	2
2	G	C	14	36	C	A	14	70	I	A	4
3	B	C	8	37	E	C	16	71	F	B	8
4	H	A	12	38	F	C	12	72	E	D	10
5	A	B	14	39	A	D	8	73	A	B	2
6	D	A	4	40	F	D	4	74	E	A	12
7	E	B	6	41	H	B	14	75	D	A	2
8	C	A	2	42	A	A	10	76	C	B	18
9	G	C	10	43	C	D	12	77	C	C	6
10	E	B	18	44	H	A	10	78	A	B	12
11	I	D	18	45	E	A	2	79	I	D	12
12	E	C	14	46	C	D	10	80	D	D	16
13	F	D	2	47	F	A	18	81	G	D	6
14	H	D	6	48	G	C	2	82	B	A	18
15	I	C	6	49	H	C	16	83	C	C	4
16	B	B	8	50	A	A	6	84	D	D	14
17	B	C	6	51	I	B	10	85	D	B	10
18	A	C	18	52	I	C	2	86	F	C	16
19	H	D	2	53	F	A	20	87	D	B	6
20	I	B	2	54	G	D	16	88	E	C	8
21	G	B	18	55	B	D	10	89	B	A	12
22	C	A	8	56	A	C	4	90	F	D	6
23	G	B	8	57	G	B	12	91	G	A	4
24	C	C	12	58	D	C	12	92	F	B	10
25	A	C	20	59	H	B	4	93	A	D	20
26	D	D	8	60	D	C	20	94	G	D	20
27	C	B	16	61	I	A	8	95	H	A	18
28	A	A	16	62	B	B	16	96	A	D	18
29	I	A	20	63	I	B	14	97	B	C	4
30	I	D	16	64	D	A	6	98	D	C	18
31	B	D	20	65	G	A	14	99	E	A	20
32	E	B	4	66	C	B	20	100	B	D	14
33	F	C	14	67	F	A	16				
34	H	D	8	68	H	C	10				

Each coffee present 11 times (except A, 12 times)

Each barley present 25 times

Each concentration present 10 times

The 9 pure coffees were also considered

THE TEST SET

Thirty mixtures, selected again by D-Optimal Design:

exp.	coffee	barley	conc.
1	B	D	4
2	F	B	2
3	G	C	18
4	A	D	12
5	C	C	2
6	C	D	14
7	C	D	20
8	E	D	12
9	F	A	8
10	H	D	18
11	E	C	20
12	F	C	4
13	I	C	10
14	A	B	6
15	I	A	16
16	B	A	10
17	E	D	14
18	H	A	8
19	H	B	12
20	D	B	20
21	B	A	14
22	E	B	16
23	G	D	2
24	G	B	4
25	D	A	10
26	A	C	16
27	D	C	8
28	I	B	18
29	H	C	6
30	G	A	6

Each coffee present 3 or 4 times
Each barley present 7 or 8 times
Each concentration present 3 times

THE EXPERIMENTAL PROCEDURE

The coffee and barley toasted beans were ground with an electric coffee grinder for about 60 s and, afterward, passed through a 0.3 mm sieve.

Mixtures at different concentrations were prepared by separately weighting and accurately mixing the finely ground pure samples.

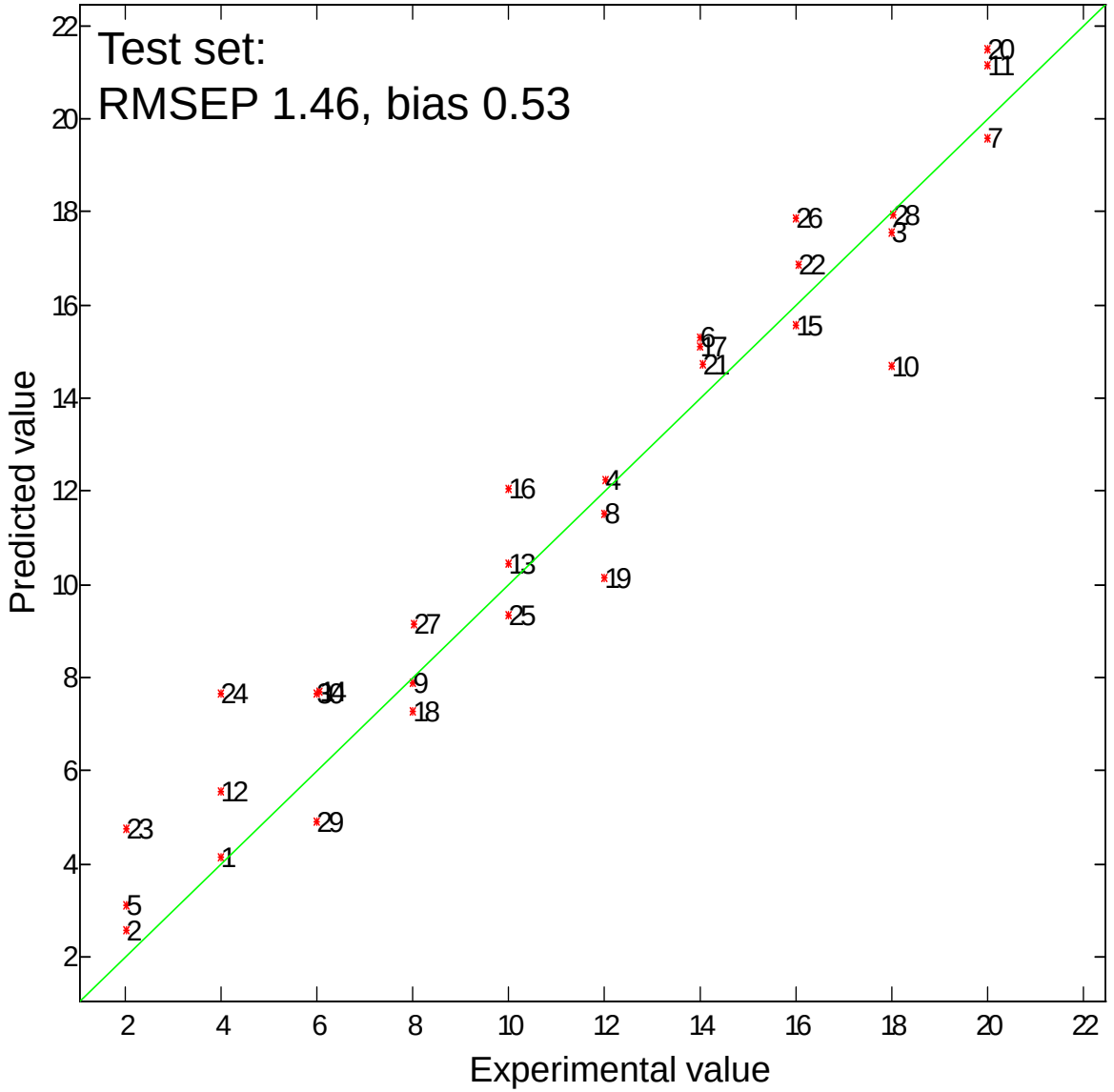
Spectral profiles of powder samples were recorded in the reflection mode in the range 4,000-10,000 cm^{-1}, with a resolution of 4 cm^{-1}, by an FT-near infrared spectrophotometer based on a polarization interferometer (Buchi NIRFlex N-500). Spectra were recorded on two grams of powder sample placed into a cylindrical quartz holder. Each spectrum recorded was the average of 32 successive scans.

For each experiment three acquisitions were performed, each time manually rotating the cell.

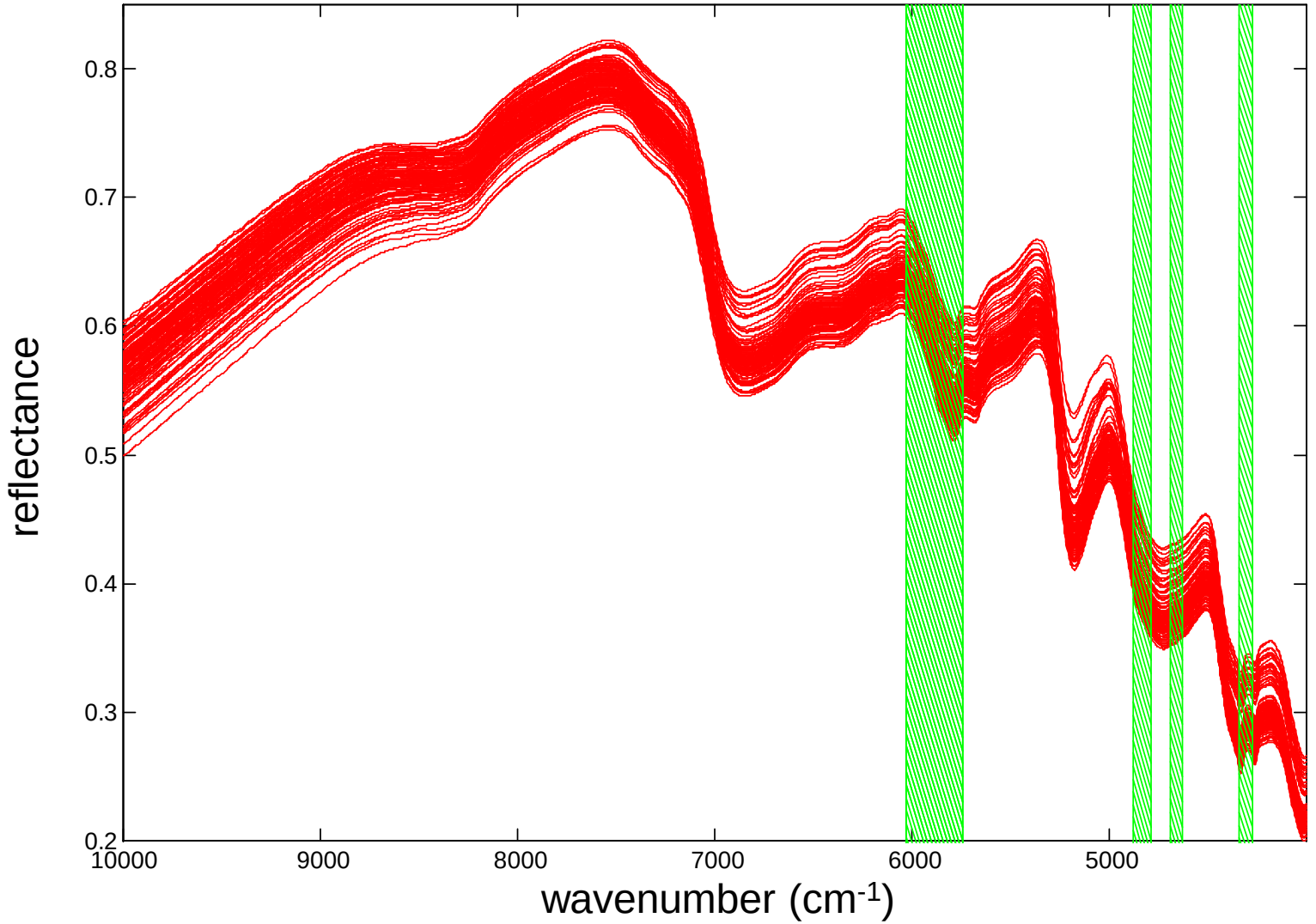
The experiments were carried out in a random order (first the training set, then the test set).

THE FULL-SPECTRUM PLS MODEL

(1501 wavenumbers, 12 components)



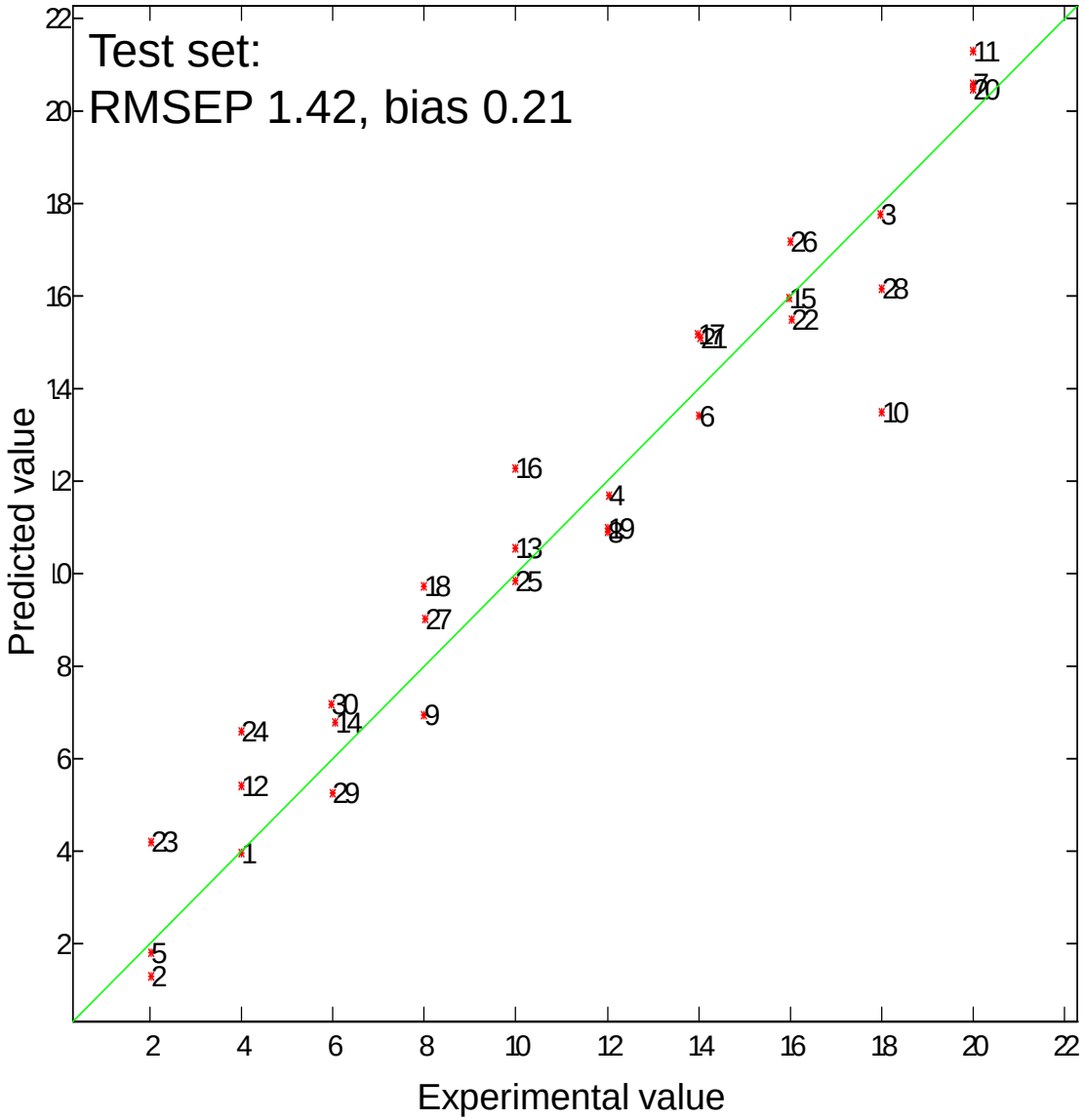
VARIABLE SELECTION BY GA



GA selected 4 regions, for a total of 128 wavenumbers: 6032-5748, 4880-4788, 4688-4628, 4336-4276 cm^{-1}.

THE GA-PLS MODEL

(128 wavenumbers, 8 components)



The results on the test set are **very good** (RMSEP 1.5%, << human sensitivity).

Can we say that the model is **properly validated**?

NO!!!

WHY???

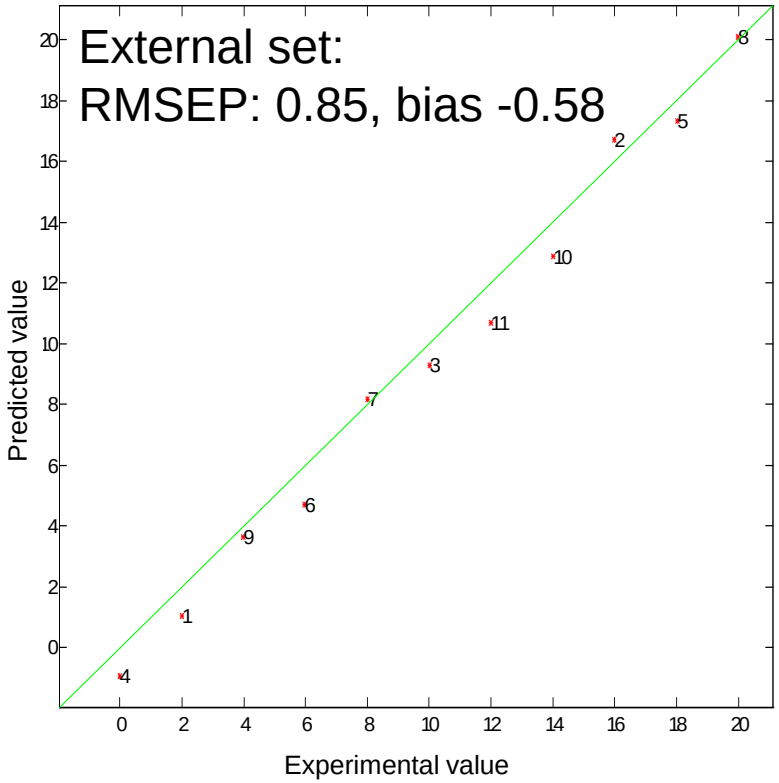
Because the types of coffee and barley of the test set are **THE SAME TYPES** that have been used in the training set.

To correctly validate the model an **INDEPENDENT (EXTERNAL)** test set is **REQUIRED**

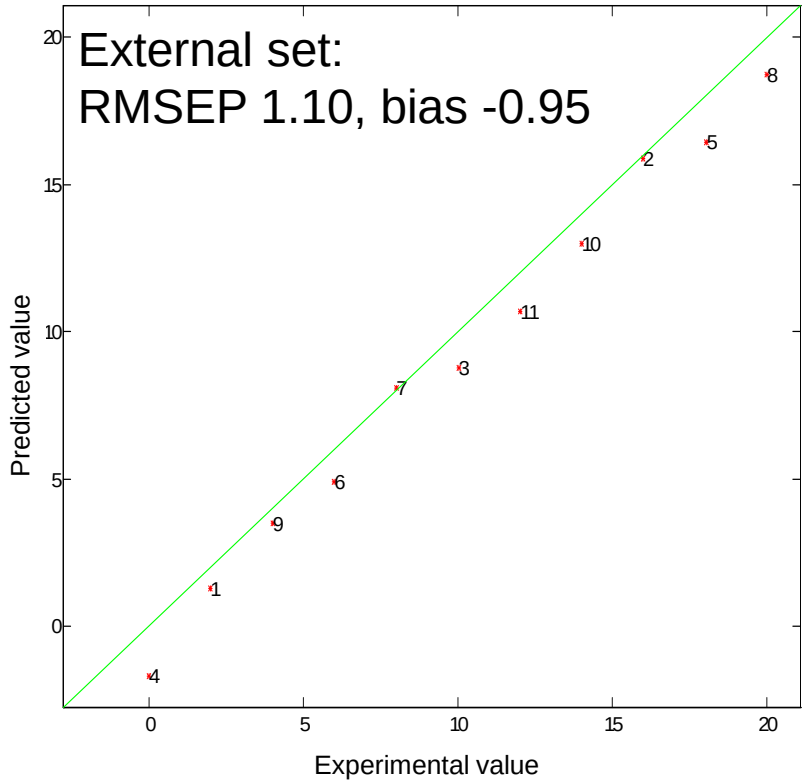
EXTERNAL TEST SET

Mixtures made by a type of coffee and a type of barley that were **NOT PRESENT** in the training set, prepared and analyzed **AFTER** the mixtures of the training set

Full-spectrum (1501 var.)



GA-PLS (128 var.)



CONCLUSIONS

It has been demonstrated that by applying methods of multivariate calibration it is possible to detect fraudolent addition of barley to coffee.

The application of a method of variable selection allowed to obtain a much simpler model with the same performances of the full-spectrum model.

The good predictive ability of the obtained model on an external test set showed that it can be efficiently applied to the products of the **ITALIAN MARKET**.