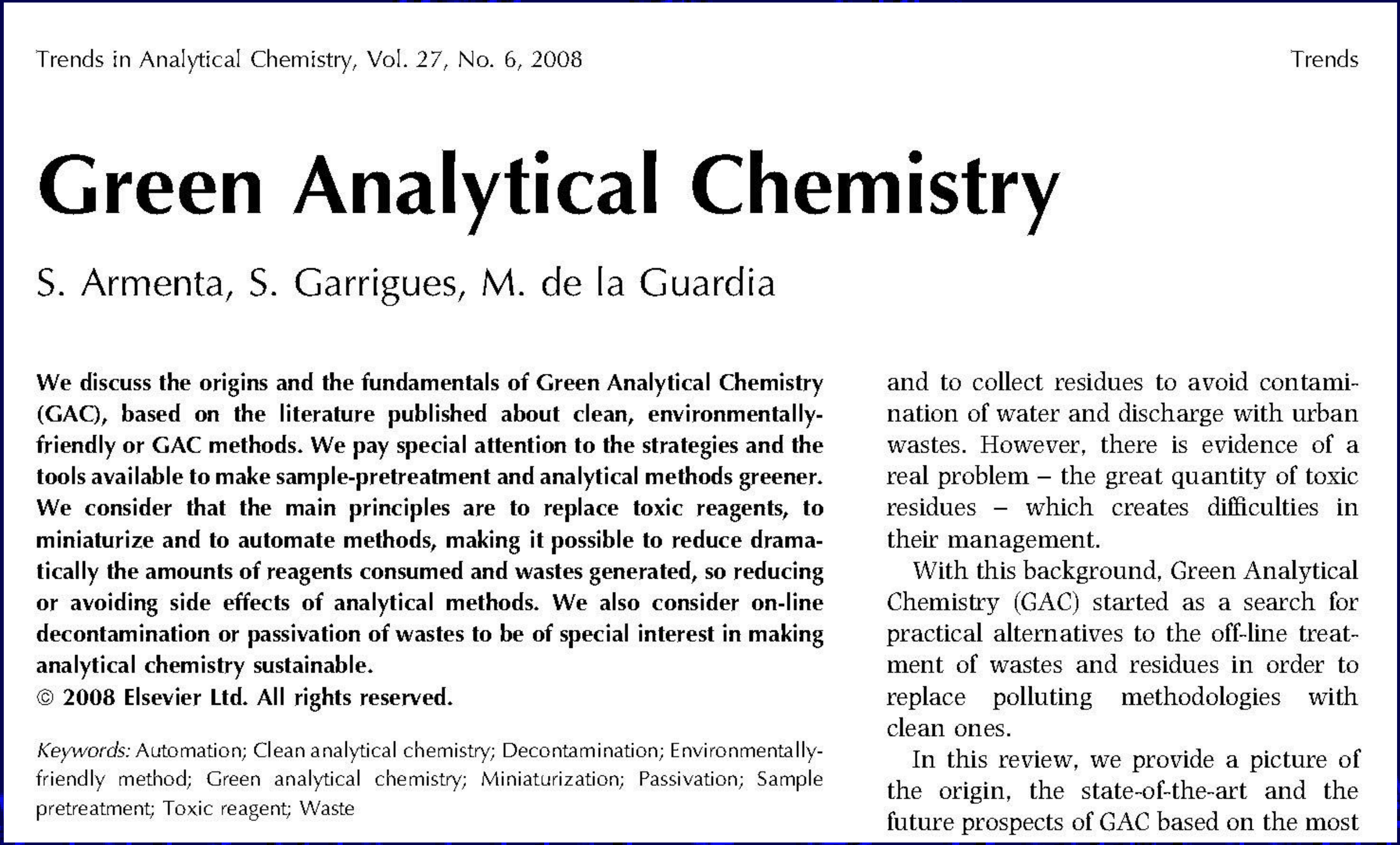
Química Analítica Democrática

Miguel de la Guardia

SOLINQUIANA

Department of Analytical Chemistry
University of Valencia



Trends in Analytical Chemistry, Vol. 27, No. 6, 2008

Green Analytical Chemistry

S. Armenta, S. Garrigues, M. de la Guardia

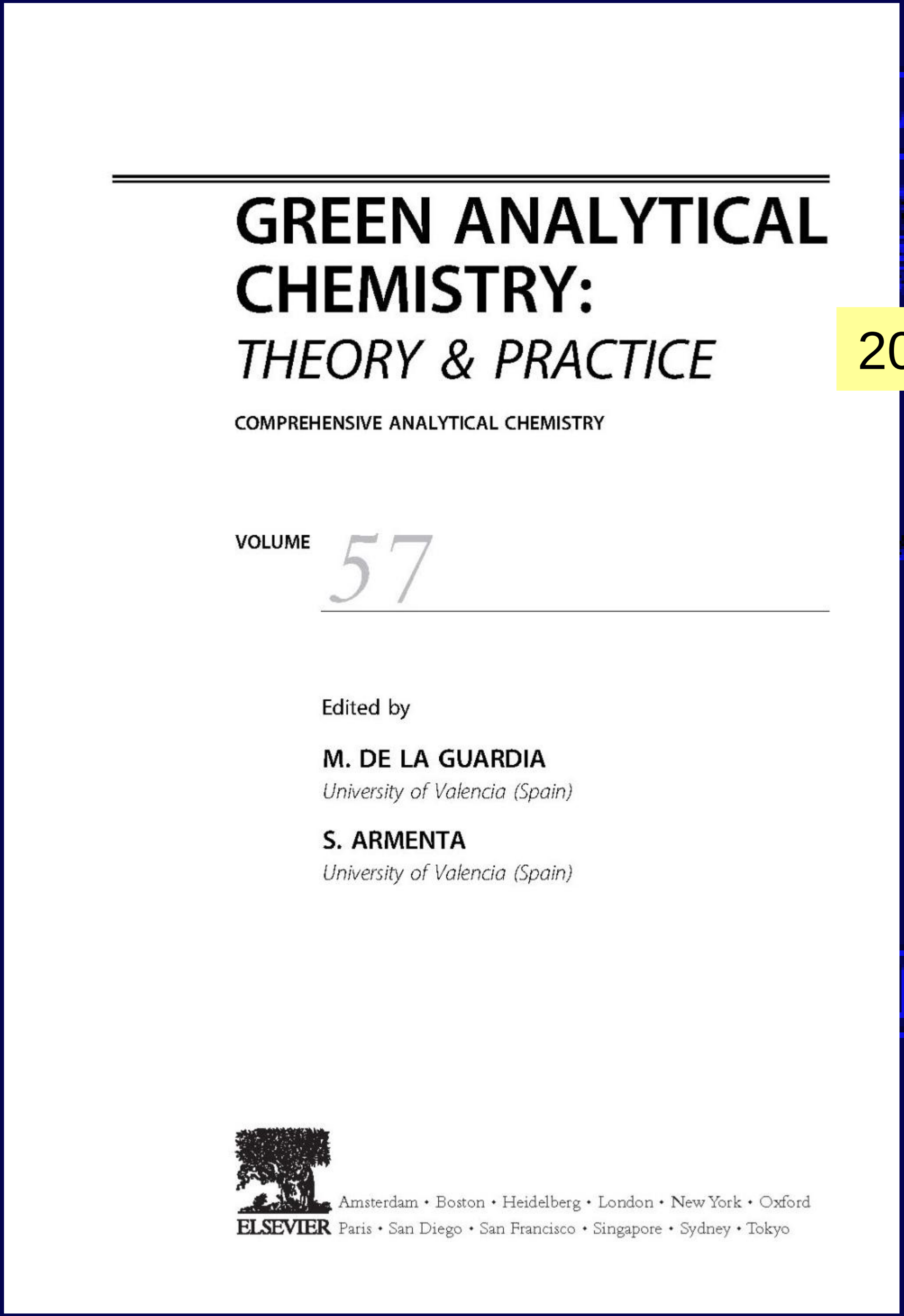
We discuss the origins and the fundamentals of Green Analytical Chemistry (GAC), based on the literature published about clean, environmentally-friendly or GAC methods. We pay special attention to the strategies and the tools available to make sample-pretreatment and analytical methods greener. We consider that the main principles are to replace toxic reagents, to miniaturize and to automate methods, making it possible to reduce dramatically the amounts of reagents consumed and wastes generated, so reducing or avoiding side effects of analytical methods. We also consider on-line decontamination or passivation of wastes to be of special interest in making analytical chemistry sustainable.

Keywords: Automation; Clean analytical chemistry; Decontamination; Environmentally-friendly method; Green analytical chemistry; Miniaturization; Passivation; Sample pretreatment; Toxic reagent; Waste

and to collect residues to avoid contamination of water and discharge with urban wastes. However, there is evidence of a real problem – the great quantity of toxic residues – which creates difficulties in their management.

With this background, Green Analytical Chemistry (GAC) started as a search for practical alternatives to the off-line treatment of wastes and residues in order to replace polluting methodologies with clean ones.

In this review, we provide a picture of the origin, the state-of-the-art and the future prospects of GAC based on the most



GREEN ANALYTICAL CHEMISTRY:
THEORY & PRACTICE

COMPREHENSIVE ANALYTICAL CHEMISTRY

VOLUME 57

Edited by

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University of Valencia (Spain)

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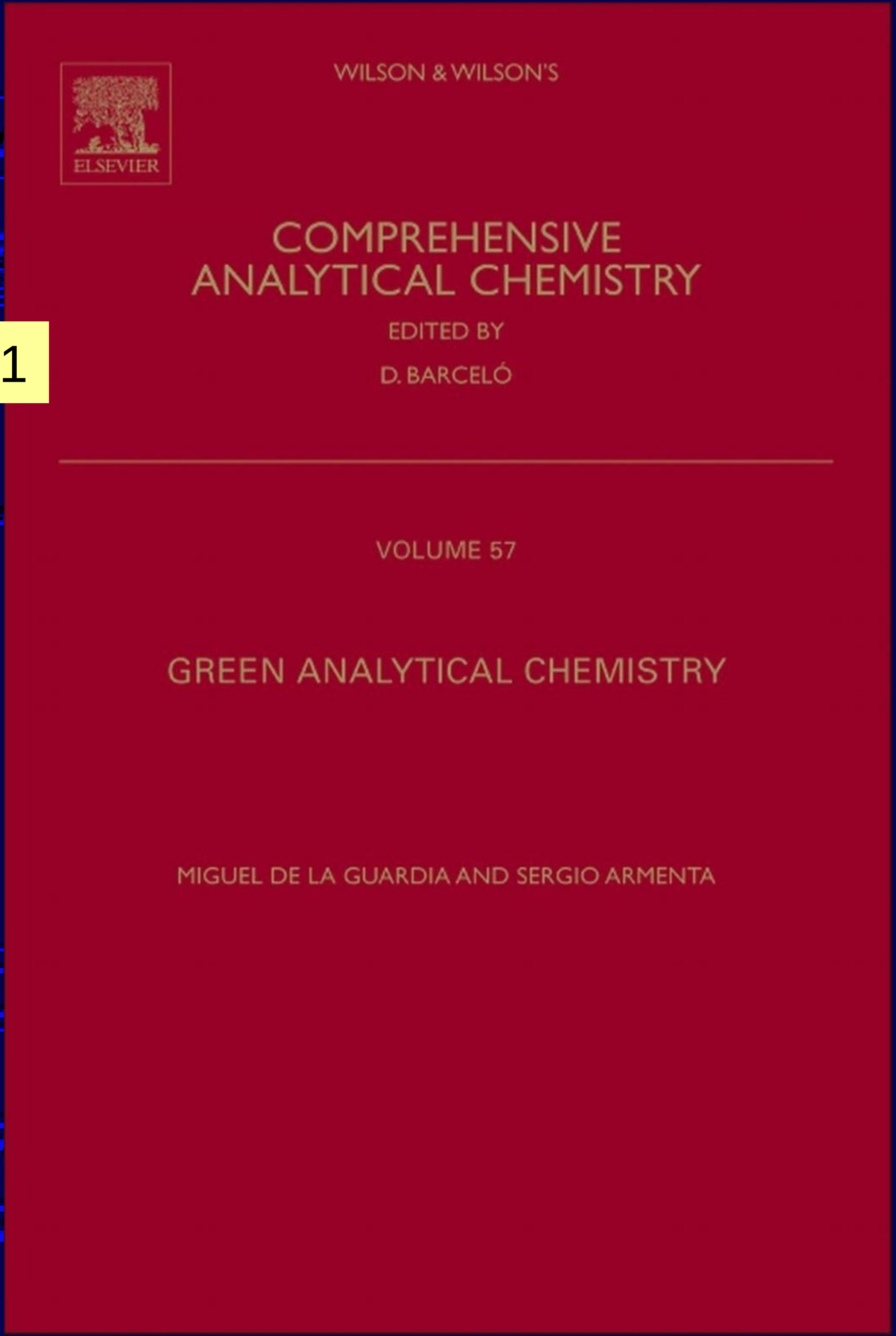

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VOLUME 57

GREEN ANALYTICAL CHEMISTRY

MIGUEL DE LA GUARDIA AND SERGIO ARMENTA

2011

Concerns about environmental pollution, global climate change and hazards to human health have increased dramatically. This has lead to a call for change in chemical processes including those that are part of chemical analysis.

The development of analytical chemistry continues and every new discovery in chemistry, physics, molecular biology, and materials science brings new opportunities and challenges.

Yet, contemporary analytical chemistry does not consume resources optimally. Indeed, the usage of toxic chemical compounds is at the highest rate ever. All this makes the emerging field of green chemistry a "hot topic" in industrial, governmental laboratories as well as in academia.

This book starts by introducing the twelve principles of green chemistry. It then goes on to discuss how the principles of green chemistry can be used to assess the 'greenness' of analytical methodologies. The 'green profile' proposed by the ACS Green Chemistry Institute is also presented. A chapter on "Greening" sample preparation describes approaches to minimizing toxic solvent use, using non-toxic alternatives, and saving energy.

The chapter on instrumental methods describes existing analytical approaches that are inherently green and making non-green methods greener. The final chapter on signal acquisition describes how quantitative structure-property relationship (QSPR) ideas could reduce experimental work thus making analysis greener. The book concludes with a discussion of how green chemistry is both possible and necessary.

Challenges in Green Analytical Chemistry is aimed at managers of analytical laboratories but will also interest teachers of analytical chemistry and green public policy makers.

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Green Chemistry is one of the most important and rapidly growing concepts in modern chemistry. Through national awards and funding programmes, national and international course, networks and conferences, and a dedicated journal Green Chemistry is now widely recognised as being important in all of the chemical sciences and technologies, and in industry as well as in education and research

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Challenges in Green Analytical Chemistry

de la Guardia & Garrigues

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Challenges in Green Analytical Chemistry

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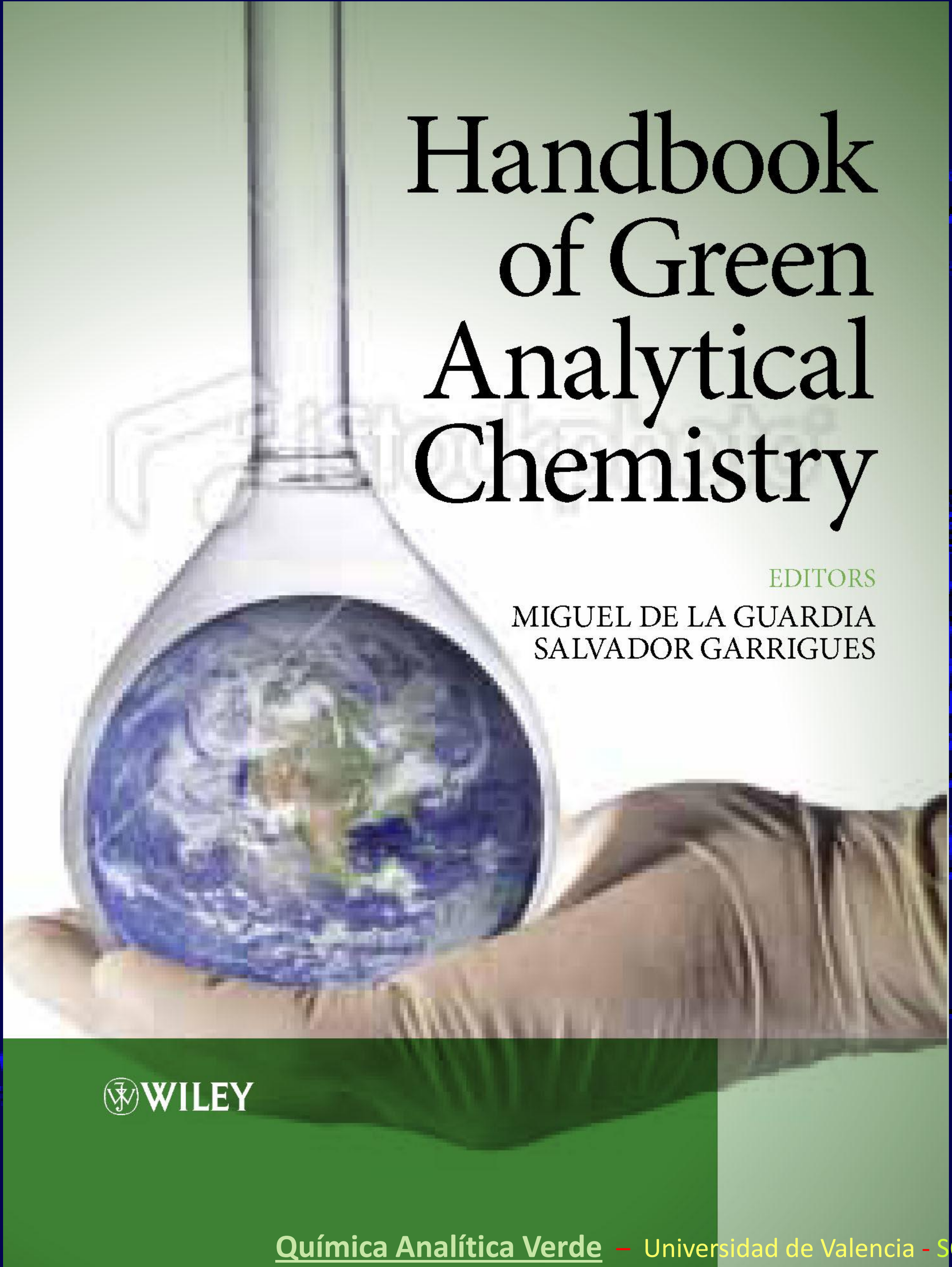
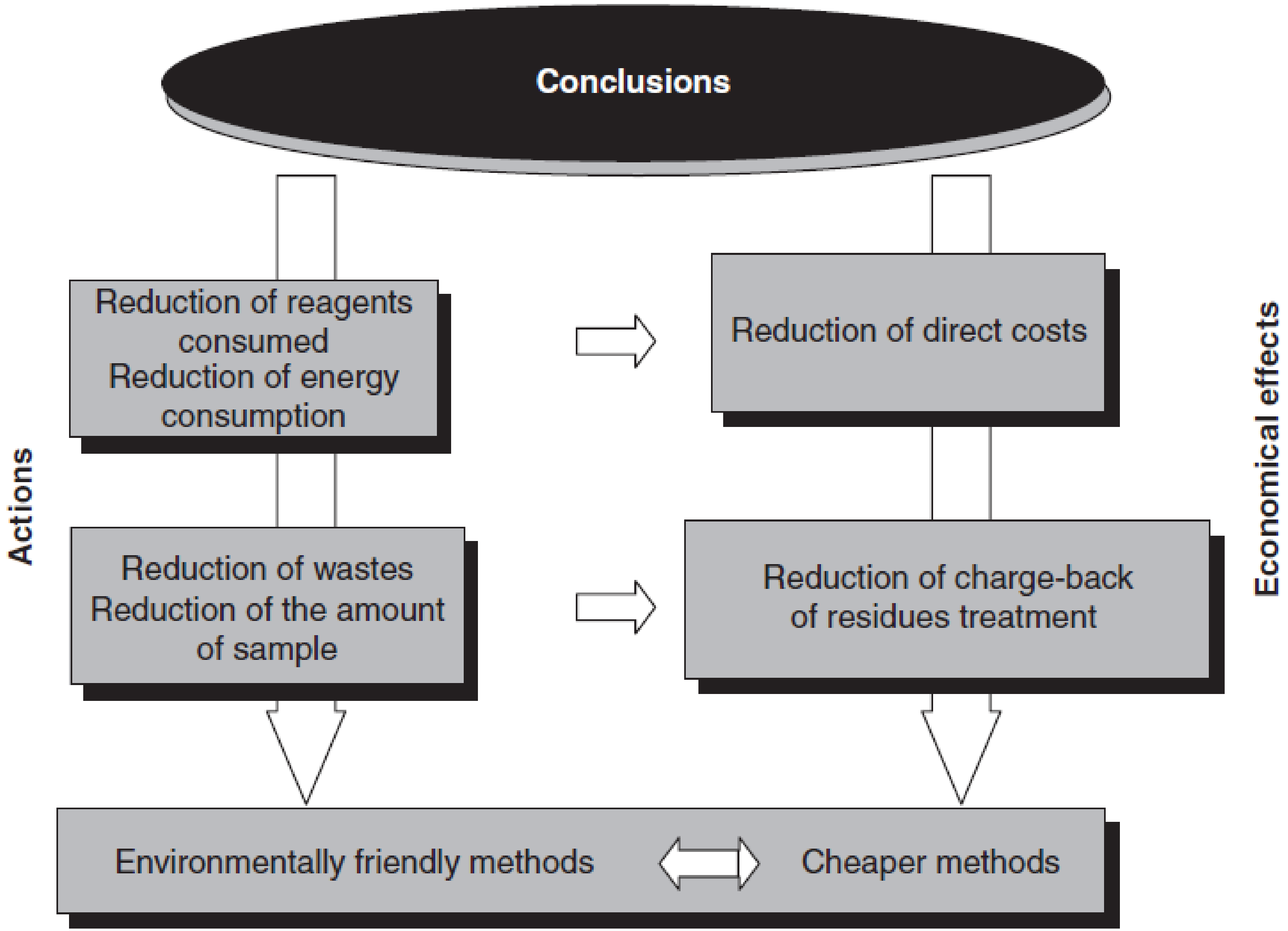


Handbook of Green Analytical Chemistry

EDITORS
MIGUEL DE LA GUARDIA
SALVADOR GARRIGUES

WILEY

2012



Conclusions

Actions

Reduction of reagents consumed
Reduction of energy consumption

Reduction of wastes
Reduction of the amount of sample

Economical effects

Reduction of direct costs

Reduction of charge-back of residues treatment

Environmentally friendly methods ⇔ Cheaper methods

Figure 9.4 Correlation between downsizing environmental side effects of analytical methods and their costs.

USO DE HORNOS DE MICROONDAS

Digestión de muestras en línea

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DIGESTIONES "ON-LINE"

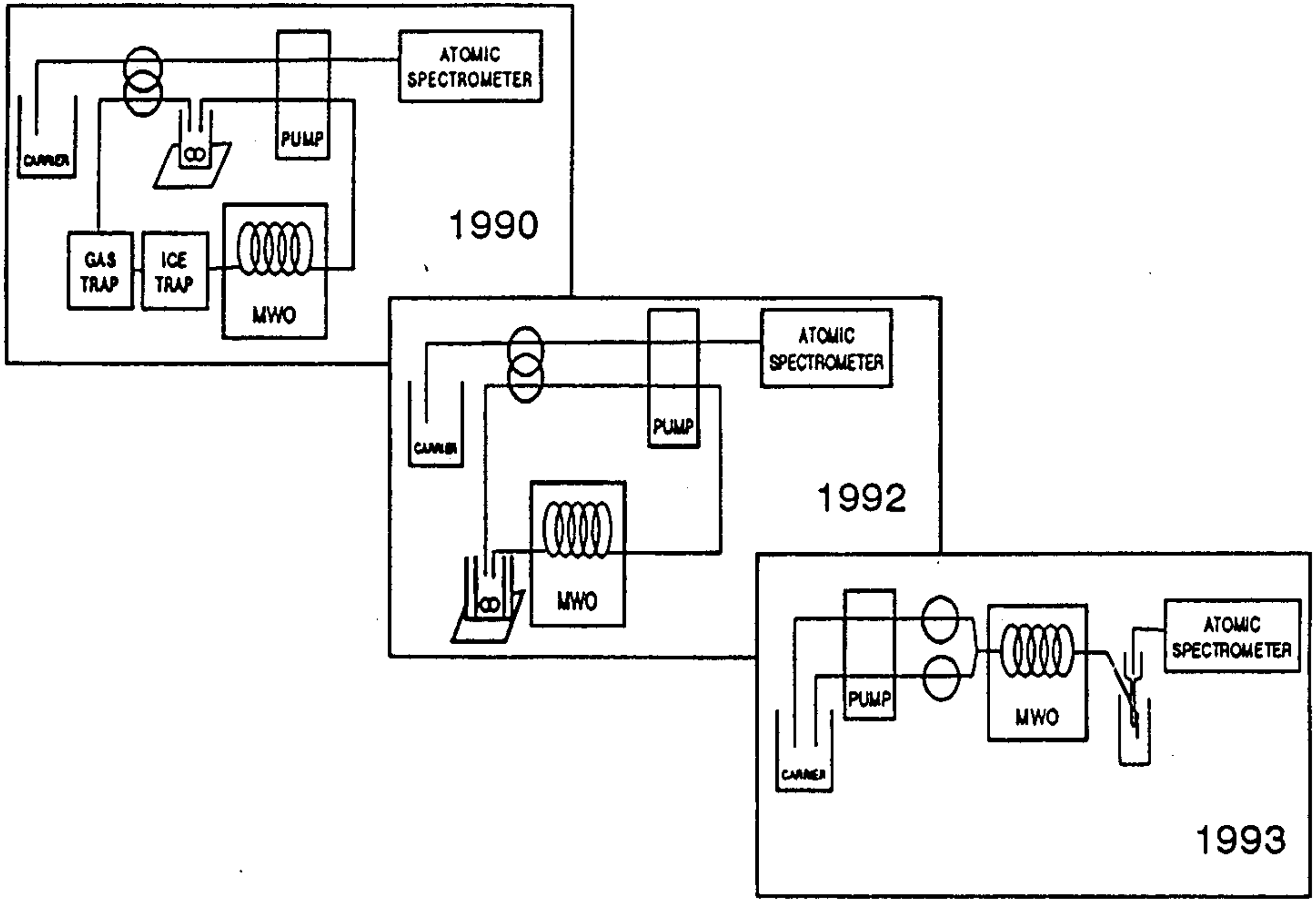
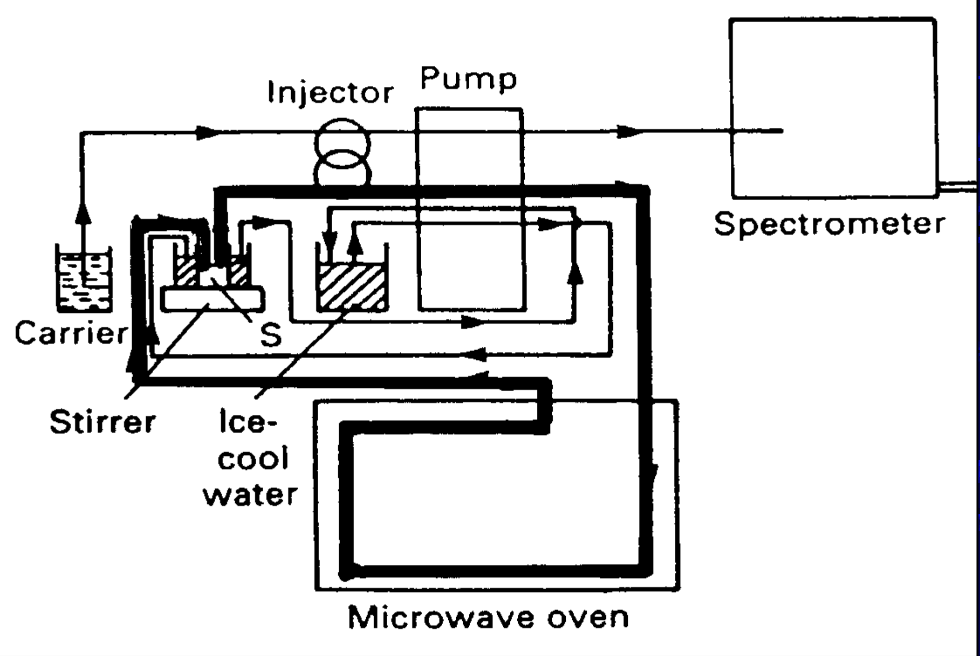
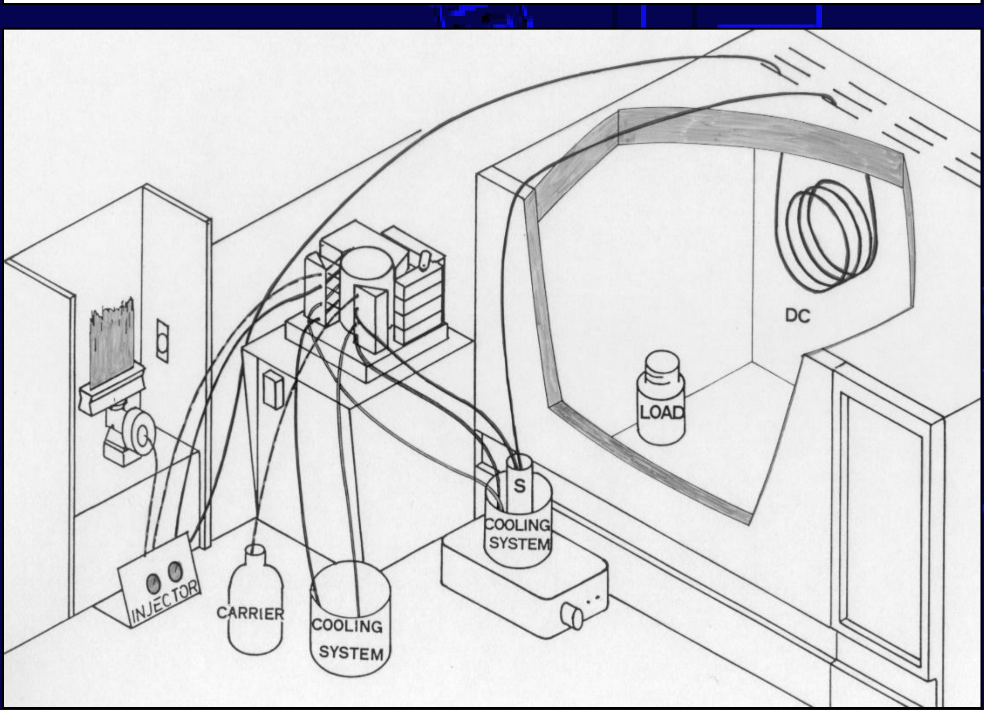
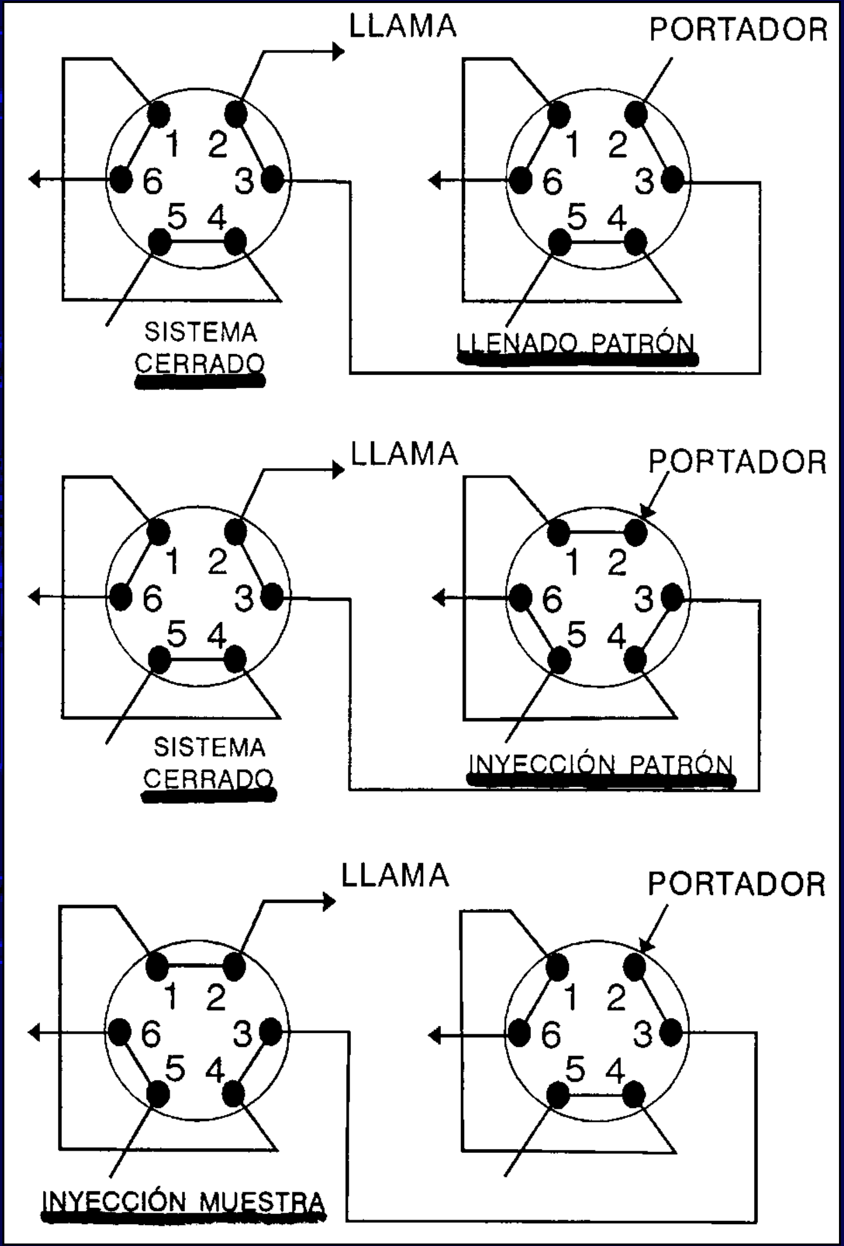


Fig. 4. Evolution of manifolds employed in our laboratory for the on-line sample digestion and atomic spectrometric determination of metals in sewage sludges (MWO = microwave oven).


Injector
Pump
Spectrometer
Carrier
S
Stirrer
Ice-cool water
Microwave oven


DC
LOAD
S
COOLING SYSTEM
INJECTOR
CARRIER
COOLING SYSTEM


LLAMA
PORTADOR
1 2 3 4 5 6
SISTEMA CERRADO
LLENADO PATRÓN
LLAMA
PORTADOR
1 2 3 4 5 6
SISTEMA CERRADO
INYECCIÓN PATRÓN
LLAMA
PORTADOR
1 2 3 4 5 6
INYECCIÓN MUESTRA

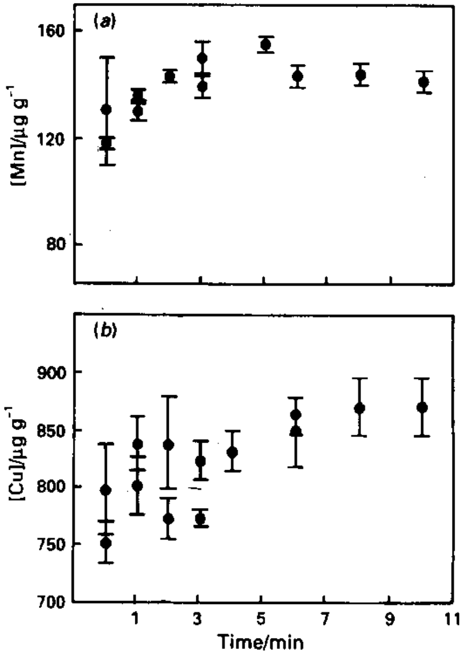


Fig. 2 Effect of the digestion time on the determination of (*a*) Mn and (*b*) Cu in sewage sludge samples. The different points indicated, for the same time value, correspond to independent experiments carried out in different work sessions. For each time the average concentration and the corresponding standard deviation are indicated

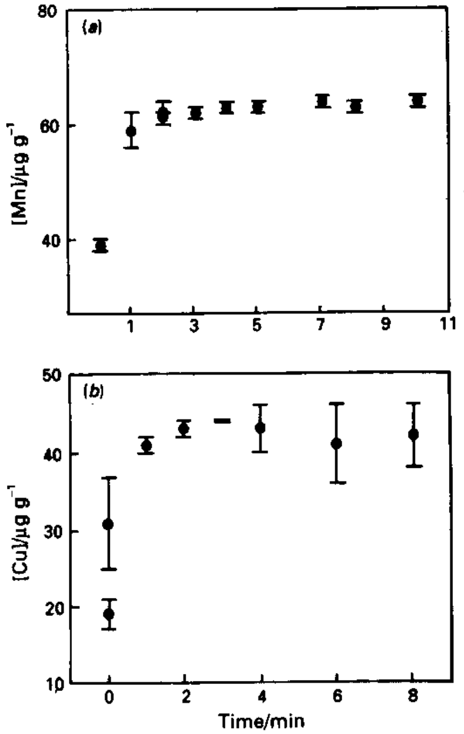


Fig. 3 Effect of the digestion time on the determination of (*a*) Mn and (*b*) Cu in diet chocolate samples

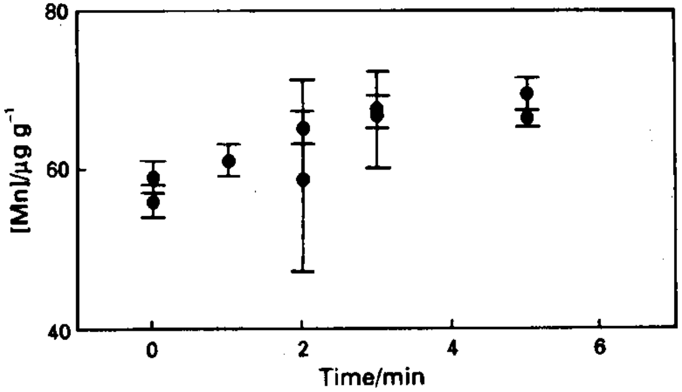
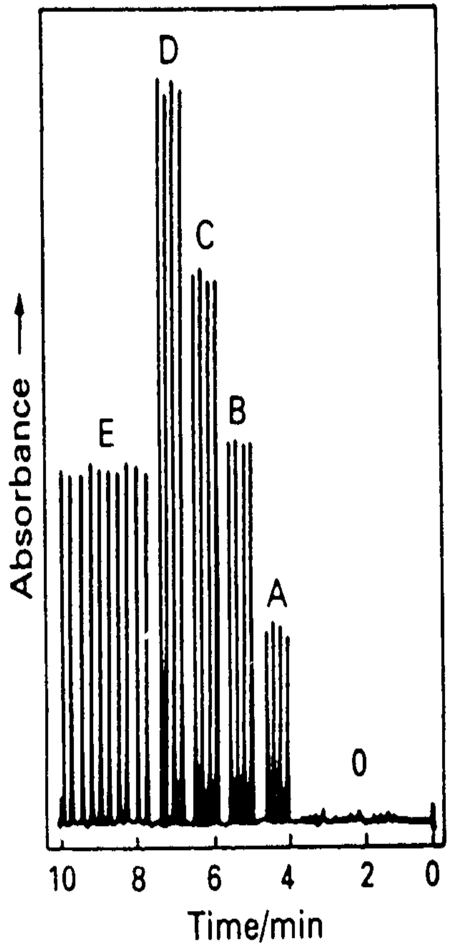


Fig. 4 Effect of the digestion time on the determination of Mn in artichoke samples



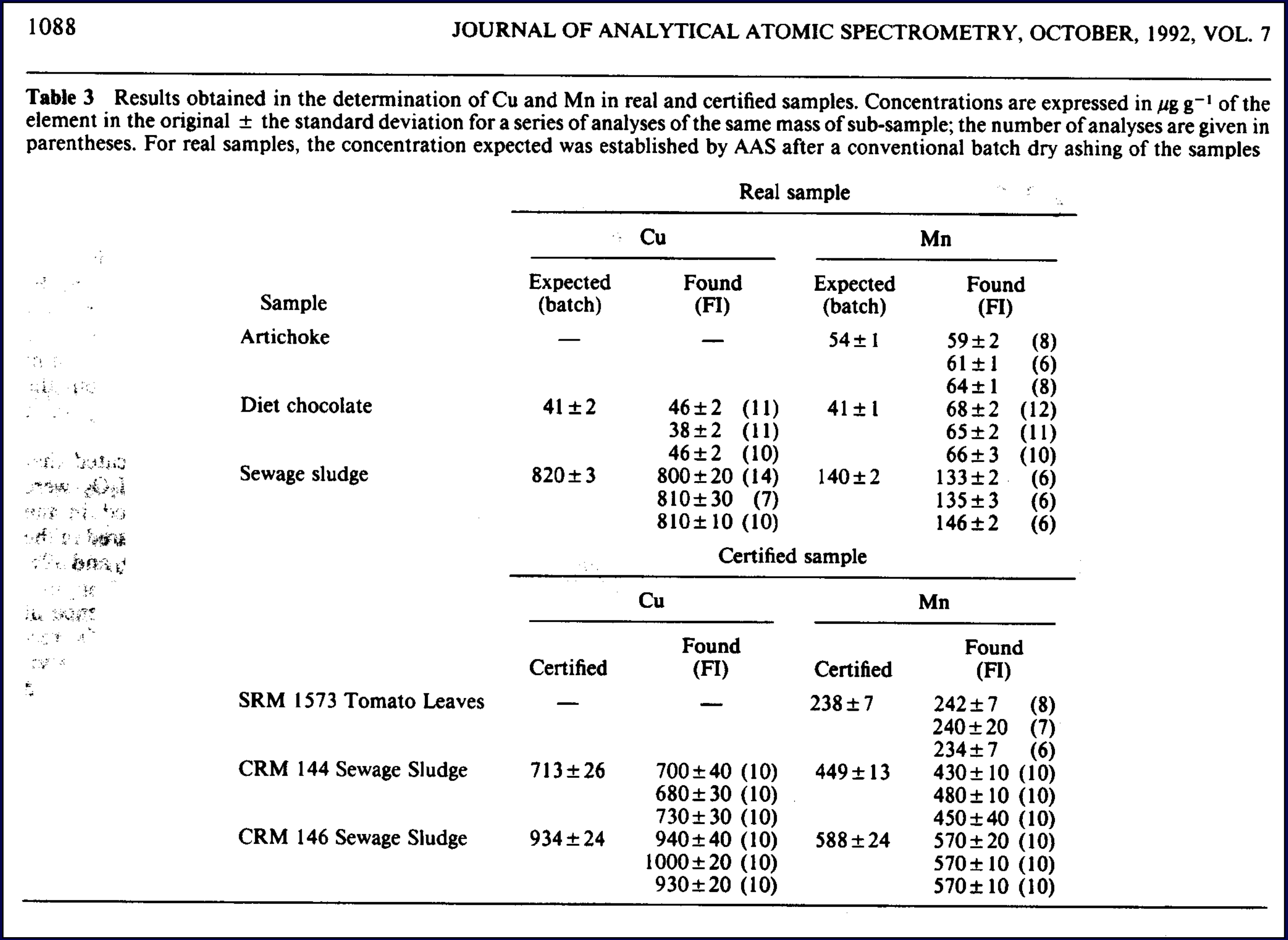
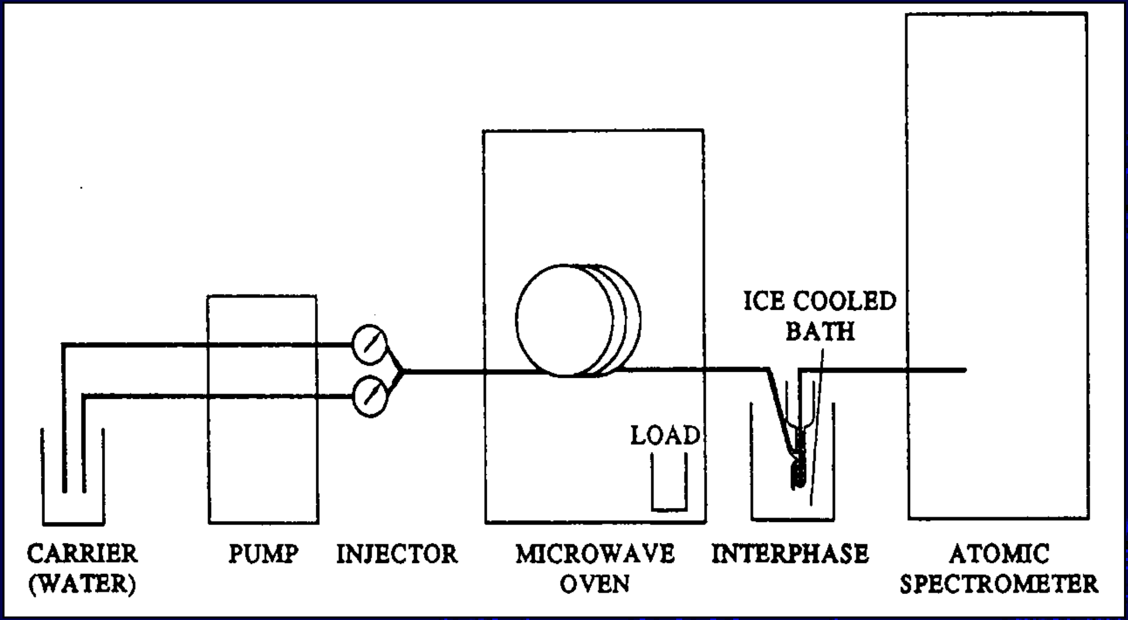


Table 3 Results obtained in the determination of Cu and Mn in real and certified samples. Concentrations are expressed in μg g^{-1} of the element in the original ± the standard deviation for a series of analyses of the same mass of sub-sample; the number of analyses are given in parentheses. For real samples, the concentration expected was established by AAS after a conventional batch dry ashing of the samples

	Real sample			
	Cu		Mn	
Sample	Expected (batch)	Found (FI)	Expected (batch)	Found (FI)
Artichoke	—	—	54 ± 1	59 ± 2 (8)
				61 ± 1 (6)
				64 ± 1 (8)
Diet chocolate	41 ± 2	46 ± 2 (11)	41 ± 1	68 ± 2 (12)
		38 ± 2 (11)		65 ± 2 (11)
		46 ± 2 (10)		66 ± 3 (10)
Sewage sludge	820 ± 3	800 ± 20 (14)	140 ± 2	133 ± 2 (6)
		810 ± 30 (7)		135 ± 3 (6)
		810 ± 10 (10)		146 ± 2 (6)
	Certified sample			
	Cu		Mn	
	Certified	Found (FI)	Certified	Found (FI)
SRM 1573 Tomato Leaves	—	—	238 ± 7	242 ± 7 (8)
				240 ± 20 (7)
				234 ± 7 (6)
CRM 144 Sewage Sludge	713 ± 26	700 ± 40 (10)	449 ± 13	430 ± 10 (10)
		680 ± 30 (10)		480 ± 10 (10)
		730 ± 30 (10)		450 ± 40 (10)
CRM 146 Sewage Sludge	934 ± 24	940 ± 40 (10)	588 ± 24	570 ± 20 (10)
		1000 ± 20 (10)		570 ± 10 (10)
		930 ± 20 (10)		570 ± 10 (10)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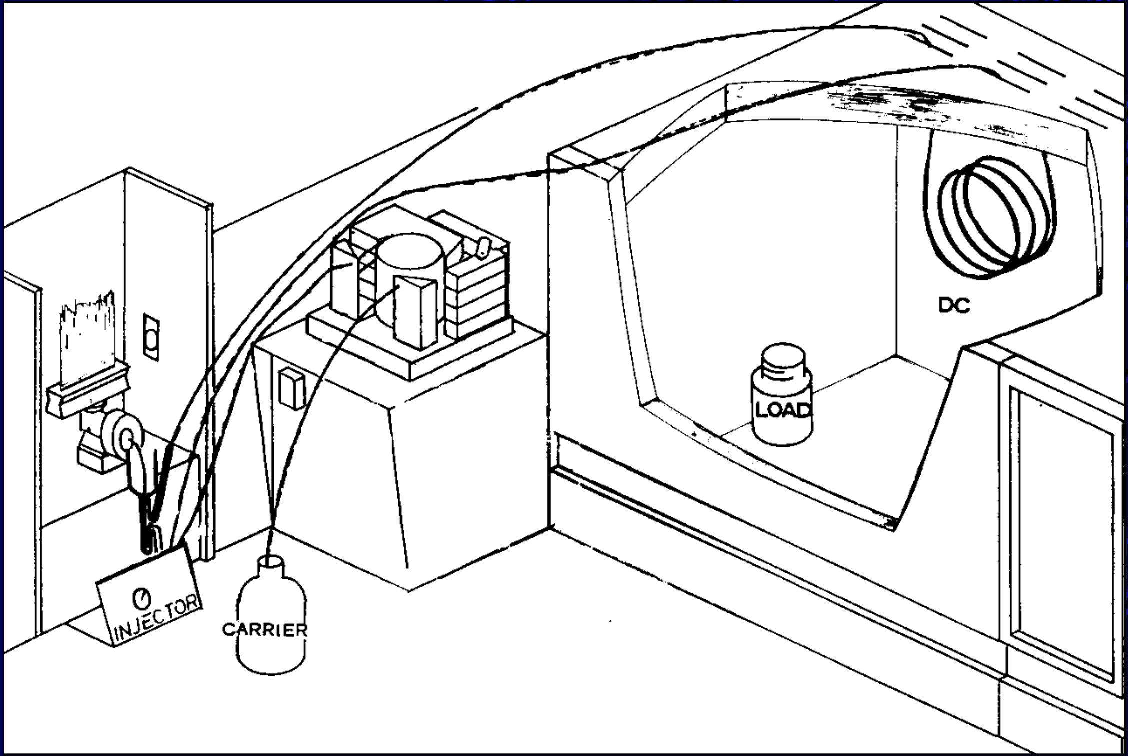
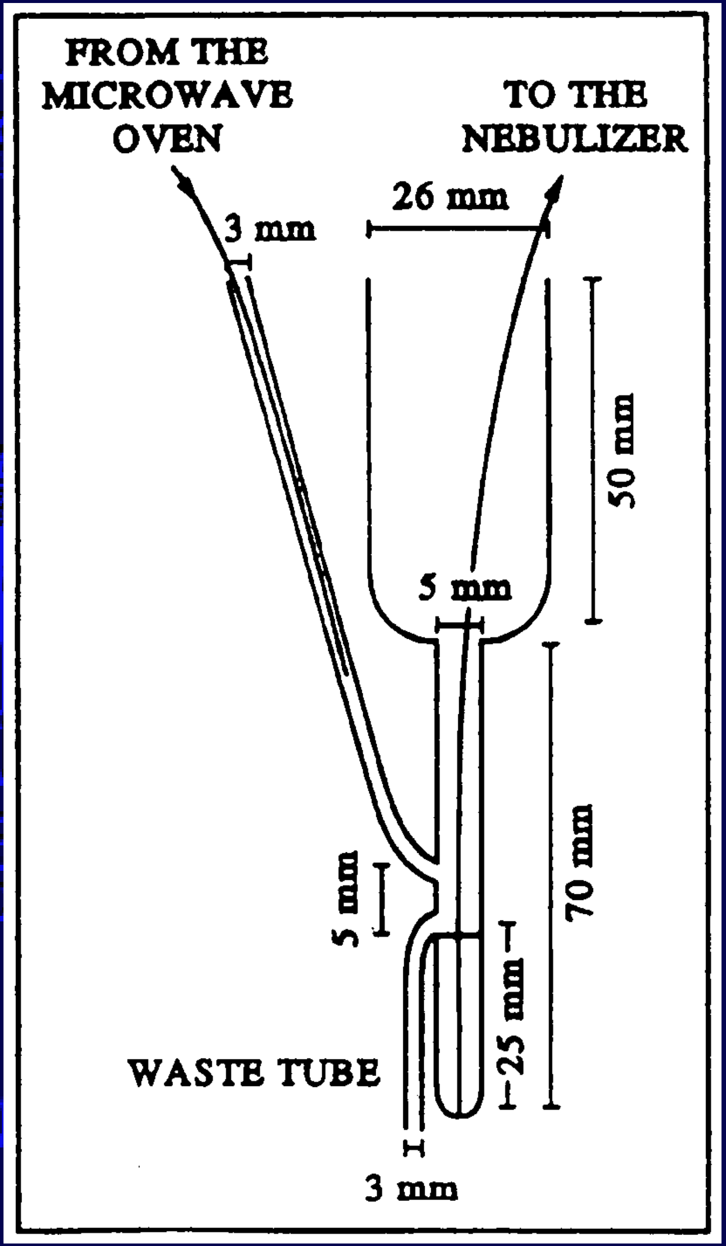
LOAD
CARRIER (WATER)
PUMP
INJECTOR
MICROWAVE OVEN
INTERPHASE
ATOMIC SPECTROMETER


DC
LOAD
INJECTOR
CARRIER


FROM THE MICROWAVE OVEN
TO THE NEBULIZER
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50 mm
5 mm
70 mm
5 mm
25 mm
WASTE TUBE
3 mm

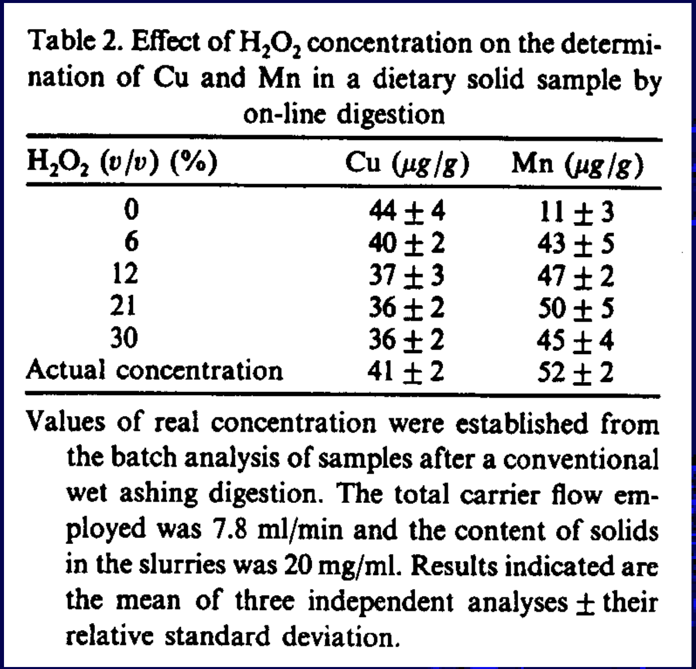


Table 2. Effect of H_2O_2 concentration on the determination of Cu and Mn in a dietary solid sample by on-line digestion

H_2O_2 (*v*/*v*) (%)	Cu (*µg*/*g*)	Mn (*µg*/*g*)
0	44 ± 4	11 ± 3
6	40 ± 2	43 ± 5
12	37 ± 3	47 ± 2
21	36 ± 2	50 ± 5
30	36 ± 2	45 ± 4
Actual concentration	41 ± 2	52 ± 2

Values of real concentration were established from the batch analysis of samples after a conventional wet ashing digestion. The total carrier flow employed was 7.8 ml/min and the content of solids in the slurries was 20 mg/ml. Results indicated are the mean of three independent analyses ± their relative standard deviation.

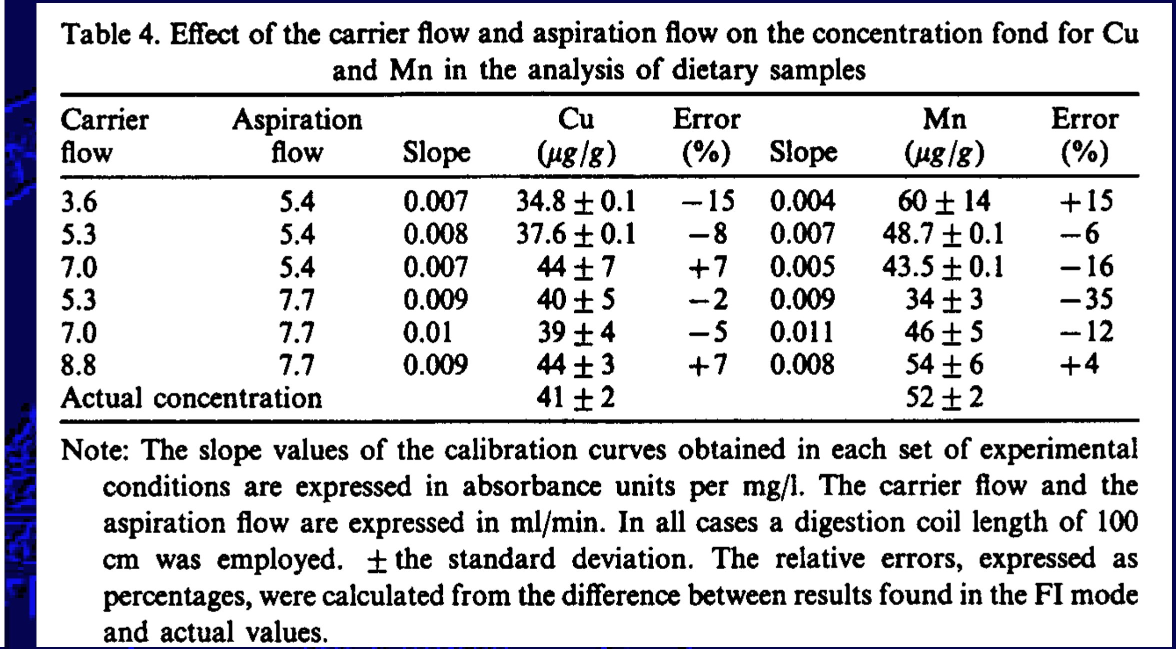


Table 4. Effect of the carrier flow and aspiration flow on the concentration fond for Cu and Mn in the analysis of dietary samples

Carrier flow	Aspiration flow	Slope	Cu (*µg*/*g*)	Error (%)	Slope	Mn (*µg*/*g*)	Error (%)
3.6	5.4	0.007	34.8 ± 0.1	−15	0.004	60 ± 14	+15
5.3	5.4	0.008	37.6 ± 0.1	−8	0.007	48.7 ± 0.1	−6
7.0	5.4	0.007	44 ± 7	+7	0.005	43.5 ± 0.1	−16
5.3	7.7	0.009	40 ± 5	−2	0.009	34 ± 3	−35
7.0	7.7	0.01	39 ± 4	−5	0.011	46 ± 5	−12
8.8	7.7	0.009	44 ± 3	+7	0.008	54 ± 6	+4
Actual concentration			41 ± 2			52 ± 2	

Note: The slope values of the calibration curves obtained in each set of experimental conditions are expressed in absorbance units per mg/l. The carrier flow and the aspiration flow are expressed in ml/min. In all cases a digestion coil length of 100 cm was employed. ± the standard deviation. The relative errors, expressed as percentages, were calculated from the difference between results found in the FI mode and actual values.

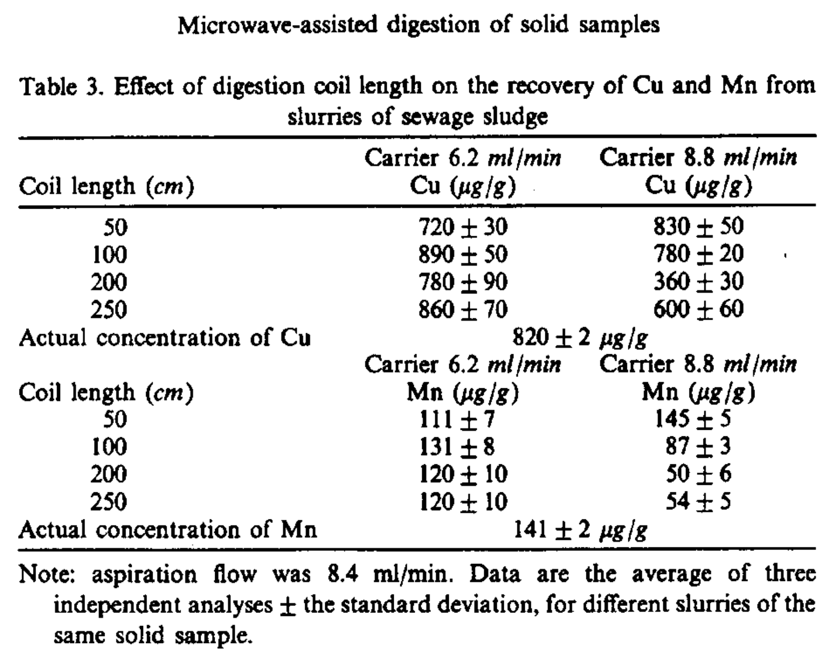


Table 3. Effect of digestion coil length on the recovery of Cu and Mn from slurries of sewage sludge

Coil length (*cm*)	Carrier 6.2 *ml*/*min* Cu (*µg*/*g*)	Carrier 8.8 *ml*/*min* Cu (*µg*/*g*)
50	720 ± 30	830 ± 50
100	890 ± 50	780 ± 20
200	780 ± 90	360 ± 30
250	860 ± 70	600 ± 60
Actual concentration of Cu	820 ± 2 *µg*/*g*	
Coil length (*cm*)	Carrier 6.2 *ml*/*min* Mn (*µg*/*g*)	Carrier 8.8 *ml*/*min* Mn (*µg*/*g*)
50	111 ± 7	145 ± 5
100	131 ± 8	87 ± 3
200	120 ± 10	50 ± 6
250	120 ± 10	54 ± 5
Actual concentration of Mn	141 ± 2 *µg*/*g*	

Note: aspiration flow was 8.4 ml/min. Data are the average of three independent analyses ± the standard deviation, for different slurries of the same solid sample.

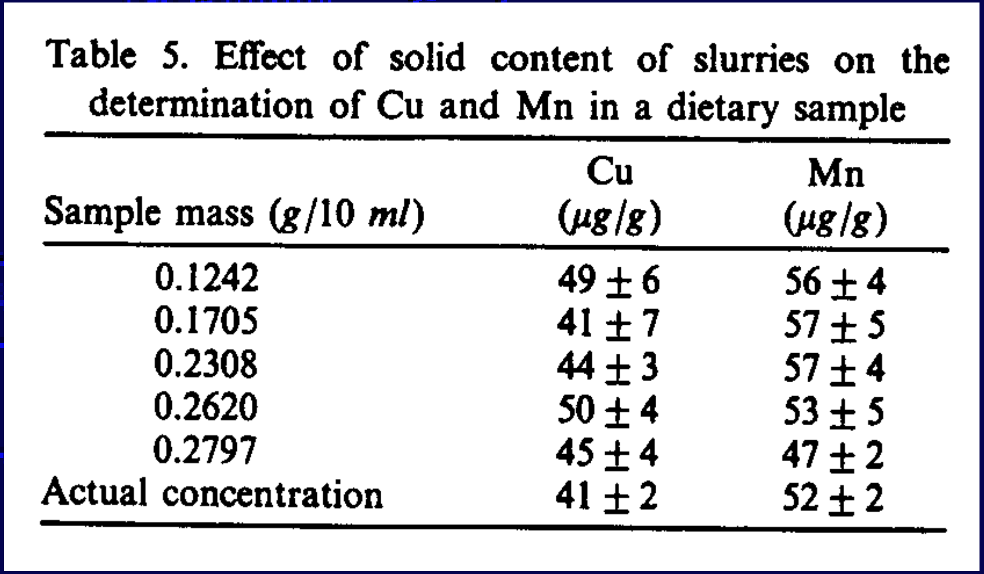


Table 5. Effect of solid content of slurries on the determination of Cu and Mn in a dietary sample

Sample mass (*g*/10 *ml*)	Cu (*µg*/*g*)	Mn (*µg*/*g*)
0.1242	49 ± 6	56 ± 4
0.1705	41 ± 7	57 ± 5
0.2308	44 ± 3	57 ± 4
0.2620	50 ± 4	53 ± 5
0.2797	45 ± 4	47 ± 2
Actual concentration	41 ± 2	52 ± 2

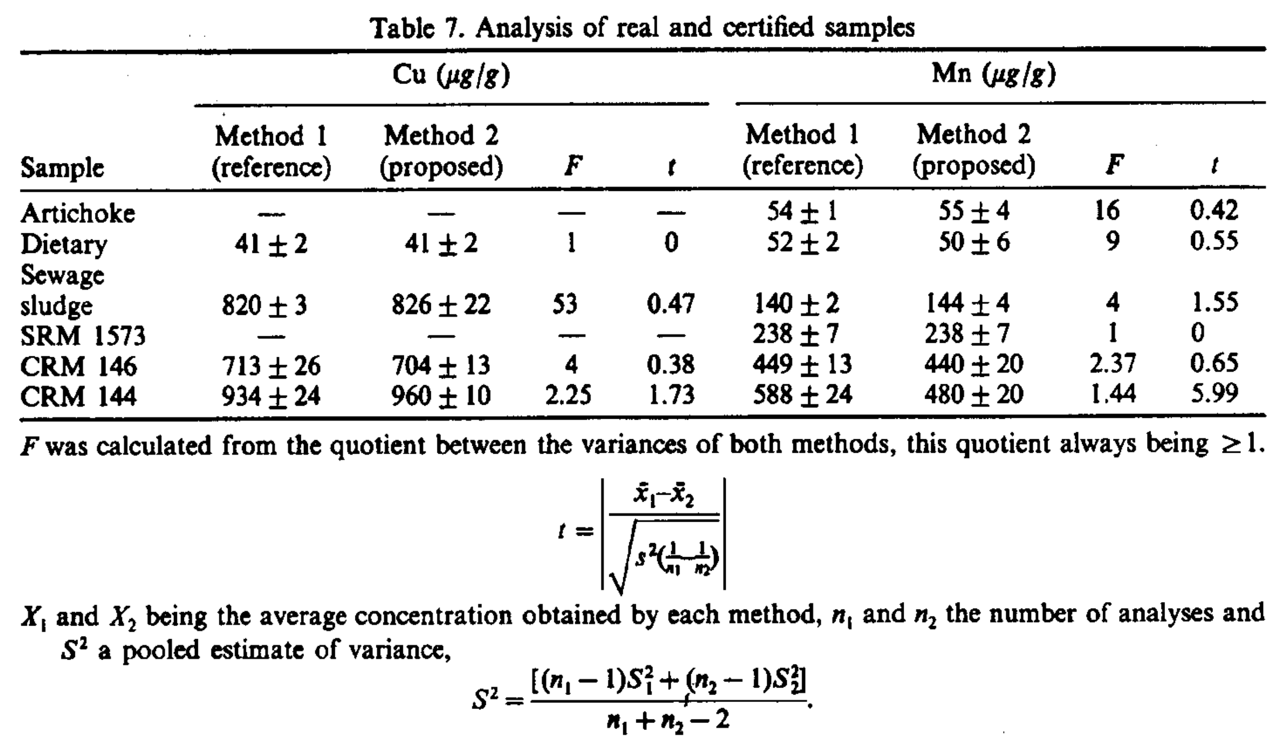


Table 7. Analysis of real and certified samples

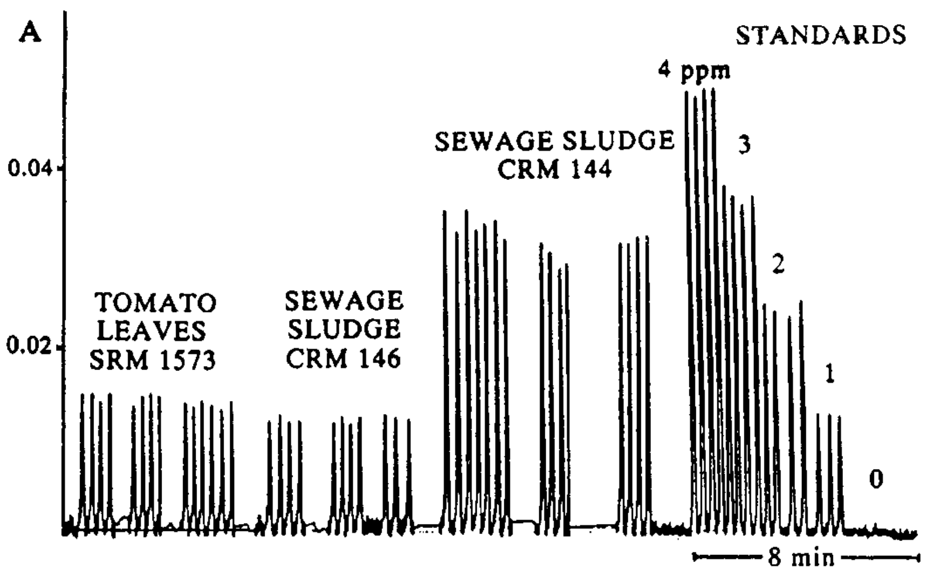
Sample	Cu ($\mu g/g$) Method 1 (reference)	Cu ($\mu g/g$) Method 2 (proposed)	Cu *F*	Cu *t*	Mn ($\mu g/g$) Method 1 (reference)	Mn ($\mu g/g$) Method 2 (proposed)	Mn *F*	Mn *t*
Artichoke	—	—	—	—	54 ± 1	55 ± 4	16	0.42
Dietary	41 ± 2	41 ± 2	1	0	52 ± 2	50 ± 6	9	0.55
Sewage sludge	820 ± 3	826 ± 22	53	0.47	140 ± 2	144 ± 4	4	1.55
SRM 1573	—	—	—	—	238 ± 7	238 ± 7	1	0
CRM 146	713 ± 26	704 ± 13	4	0.38	449 ± 13	440 ± 20	2.37	0.65
CRM 144	934 ± 24	960 ± 10	2.25	1.73	588 ± 24	480 ± 20	1.44	5.99

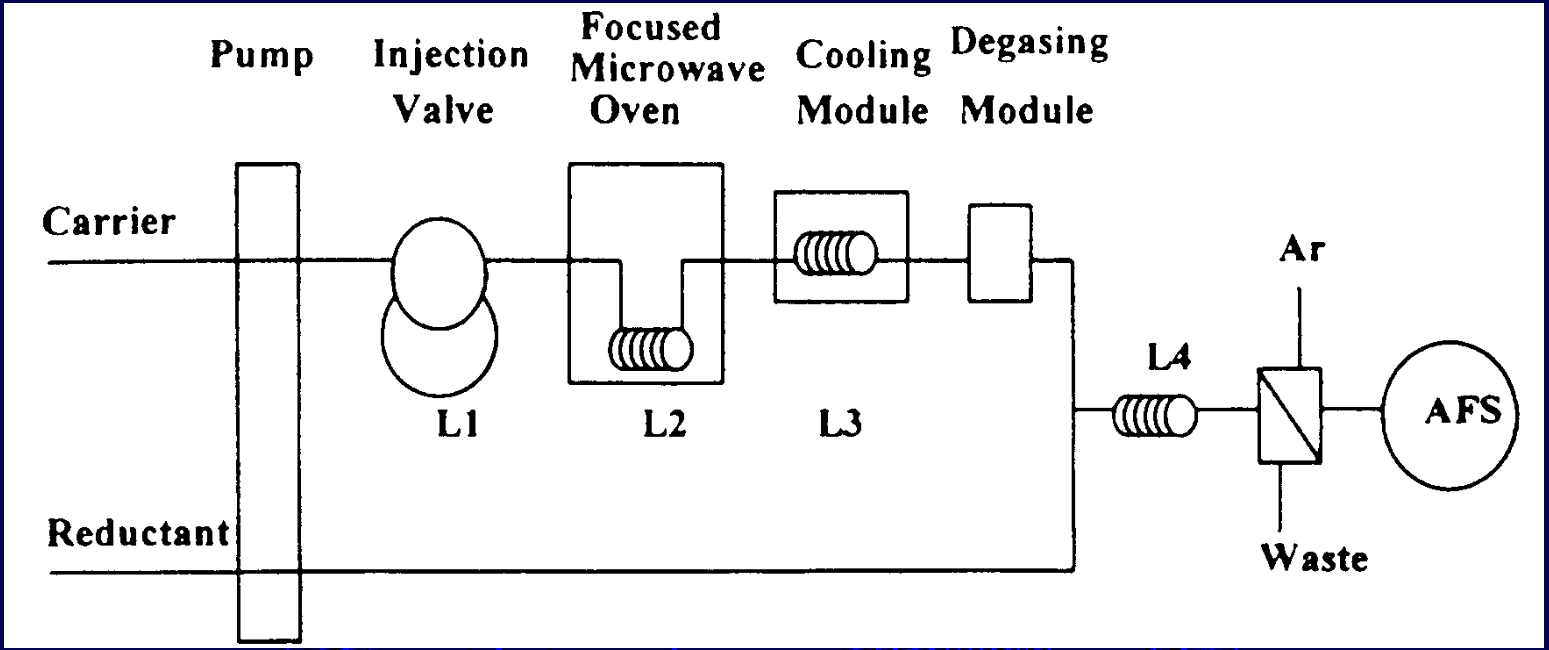
F was calculated from the quotient between the variances of both methods, this quotient always being ≥ 1.

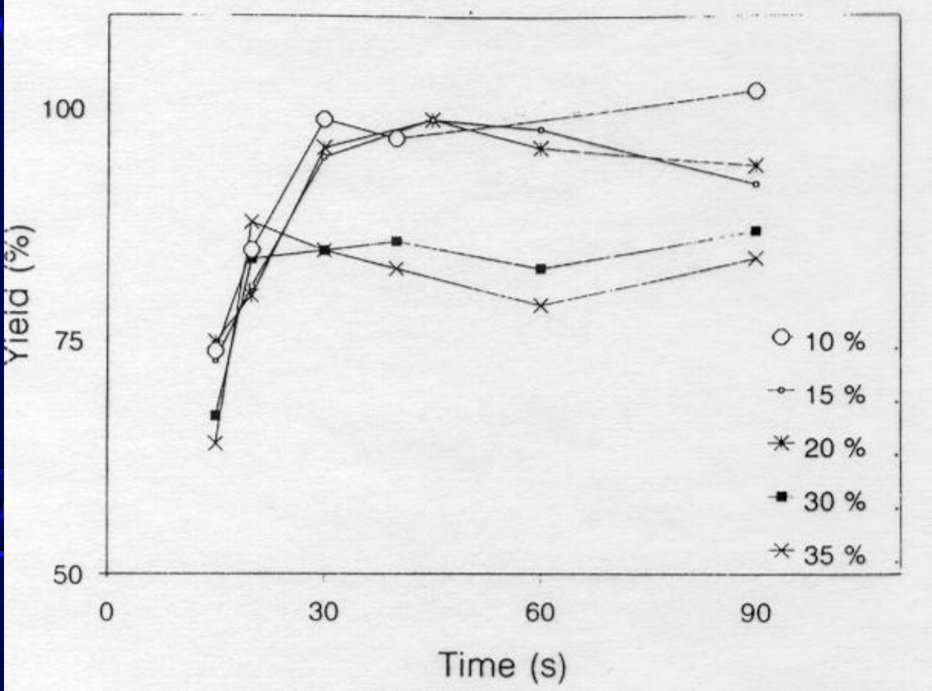
$$t = \left| \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{s^2\left(\frac{1}{n_1} - \frac{1}{n_2}\right)}} \right|$$

X_1 and X_2 being the average concentration obtained by each method, n_1 and n_2 the number of analyses and S^2 a pooled estimate of variance,

$$S^2 = \frac{[(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2]}{n_1 + n_2 - 2}.$$



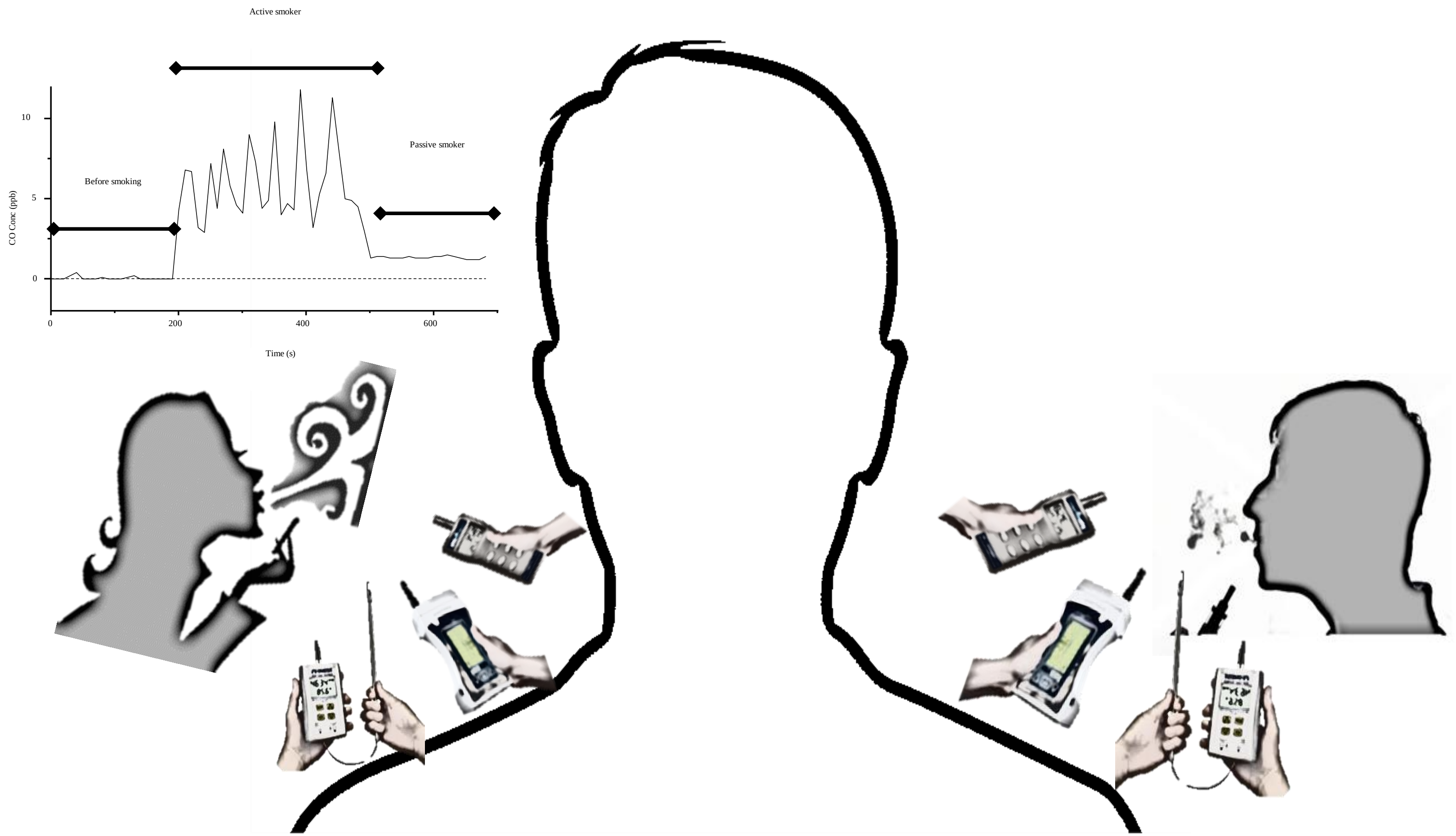

Pump
Injection Valve
Focused Microwave Oven
Cooling Module
Degasing Module
Carrier
Reductant
L1
L2
L3
L4
Ar
AFS
Waste


Yield (%)
100
75
50
0
30
60
90
Time (s)
10 %
15 %
20 %
30 %
35 %

LOW COST GAS SENSORS

New applications for available devices

VNIVERSITAT DE VALÈNCIA


Active smoker
10
5
0
CO Conc (ppb)
Before smoking
Passive smoker
0
200
400
600
Time (s)

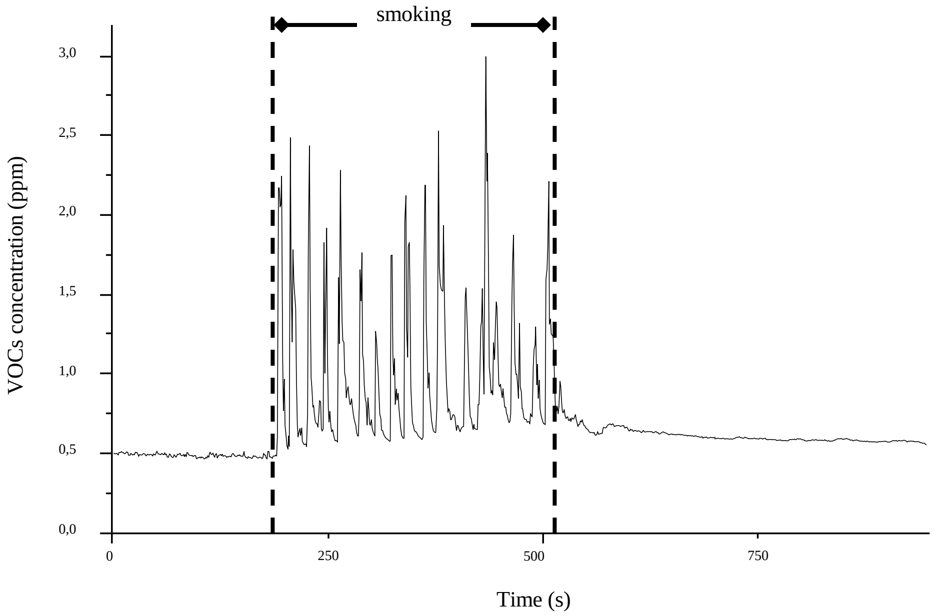


Figure 1. VOCs monitoring before, during and after smoking classical cigarette.

Note: Changes in the measurements during smoking correspond to different puffs.

Table 2. Results obtained for the quality of indoor air, active and passive agents before and after smoking. n indicates the number of experiments performed to obtain the average and the standard deviation values.

		Active		**Passive**	
	Indoor	Before	Smoking	Before	After
PM (µg m^{-3})	14 ± 4 (n=4)	32 ± 18 (n=2)	18589 ± 639 (n=3)	15 ± 4 (n=5)	1269 ± 295 (n=6)
CO_2 (ppm)	880 ± 522 (n=3)	1793 ± 690 (n=2)	1505 ± 82 (n=3)	1861 ± 812 (n=7)	2050 ± 611 (n=7)
CO (ppm)	<LOD (n=3)	0.13 ± 0.07 (n=3)	8 ± 5 (n=3)	<LOD (n=7)	1.3 ± 0.2 (n=7)
VOC (ppm)	0.50 ± 0.03 (n=3)	0.52 ± 0.02 (n=2)	1.0 ± 0.1 (n=3)	0.488 (n=1)	0.614 (n=1)
Formaldehyde (ppb)	<LOD (n=1)	<LOD (n=1)	134 (n=1)	<LOD (n=1)	<LOD (n=1)

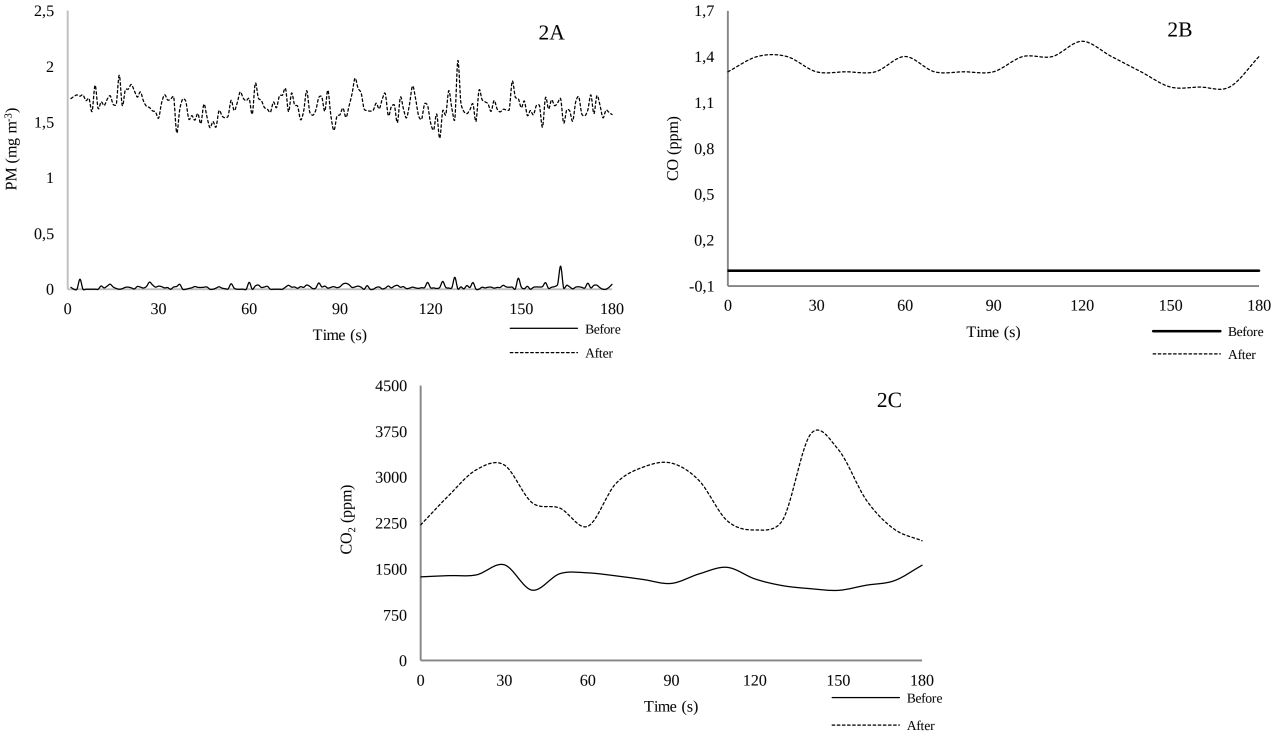


Figure2. Examples of continuous monitoring for passive smoker breath before and after exposition to cigarette smoke of PM (Figure 2A), CO_2 (Figure 2B) and CO (Figure 2C).

Table 3. Results obtained for the quality of indoor air, active and passive agents before and after vaping.

n indicates the number of experiments performed to obtain the average and the standard deviation values.

	Active		**Passive**	
	Before	Vaping	Before	After
PM (µg m^{-3})	24 ± 3 (n=2)	5134 ± 1096 (n=3)	19 ± 4 (n=5)	21 ± 7 (n=5)
CO_2 (ppm)	1992 ± 409 (n=2)	1502 ± 134 (n=4)	2208 ± 812 (n=3)	3327 ± 909 (n=3)
CO (ppm)	<LOD (n=2)	0.58 ± 0.13 (n=3)	<LOD (n=5)	<LOD (n=5)
VOC (ppm)	0.47 ± 0.03 (n=2)	0.55 ± 0.04 (n=2)	0.49 (n=1)	0.47 (n=1)
Formaldehyde (ppb)	<LOD (n=1)	35 (n=1)	<LOD (n=1)	<LOD (n=1)

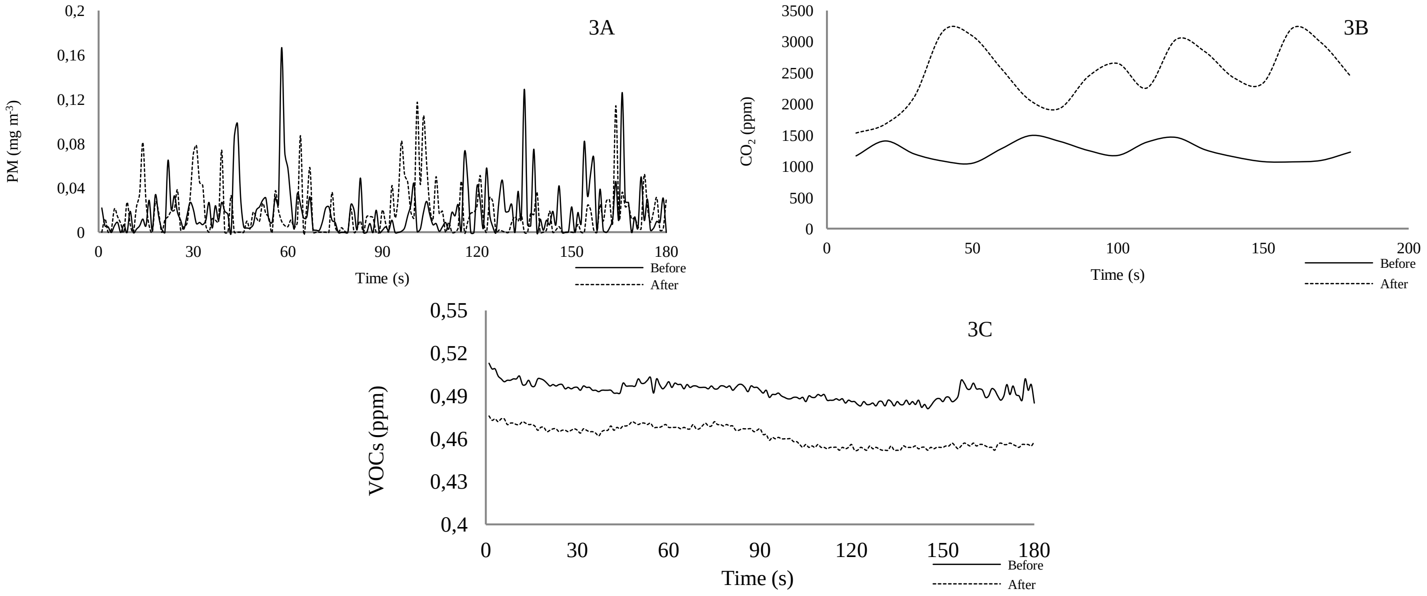
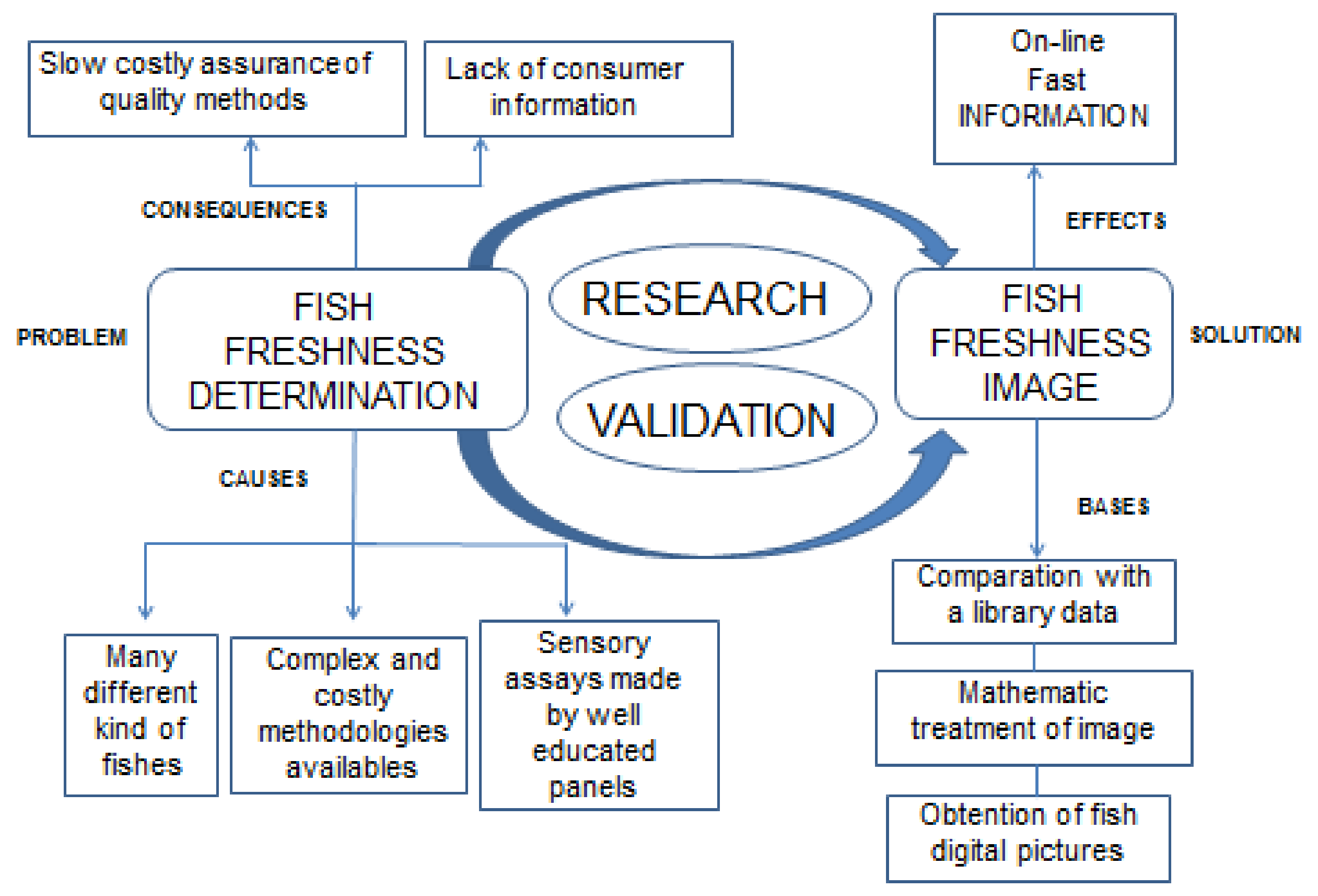


Figure 3. Examples of continuous monitoring for passive vaper breath before and after exposition to EC vapor of PM (Figure 3A), CO_2 (Figure 3B) and VOCs (Figure 3C).

IMAGE TREATMENT

Global analytical parameters determination

F.F.I as a potential solution of problems involved in fish freshness determination by using the available methodologies



PROBLEM

FISH FRESHNESS DETERMINATION

CONSEQUENCES

Slow costly assurance of quality methods

Lack of consumer information

CAUSES

Many different kind of fishes

Complex and costly methodologies availables

Sensory assays made by well educated panels

RESEARCH

VALIDATION

SOLUTION

FISH FRESHNESS IMAGE

EFFECTS

On-line
Fast
INFORMATION

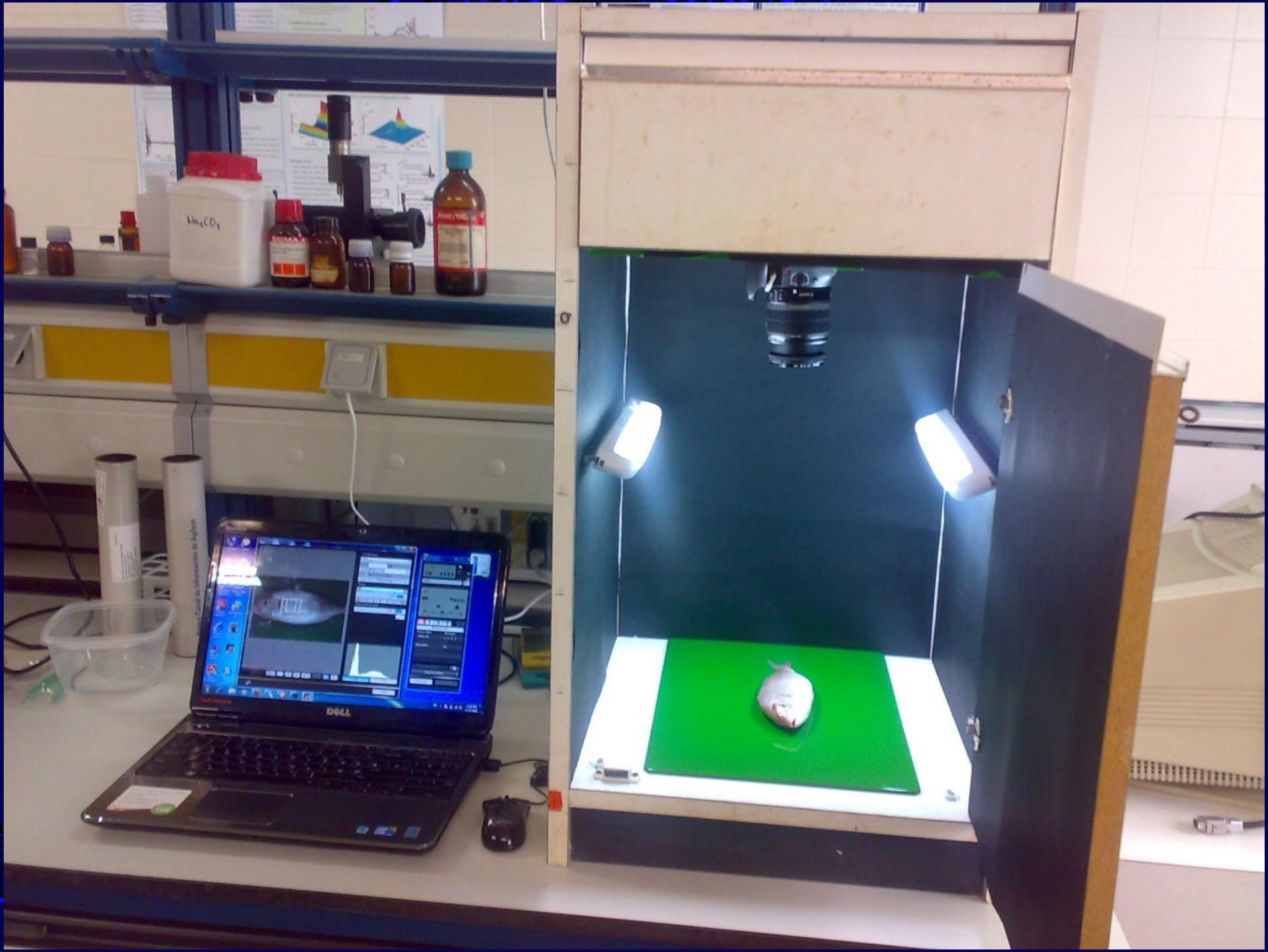
BASES

Comparation with a library data

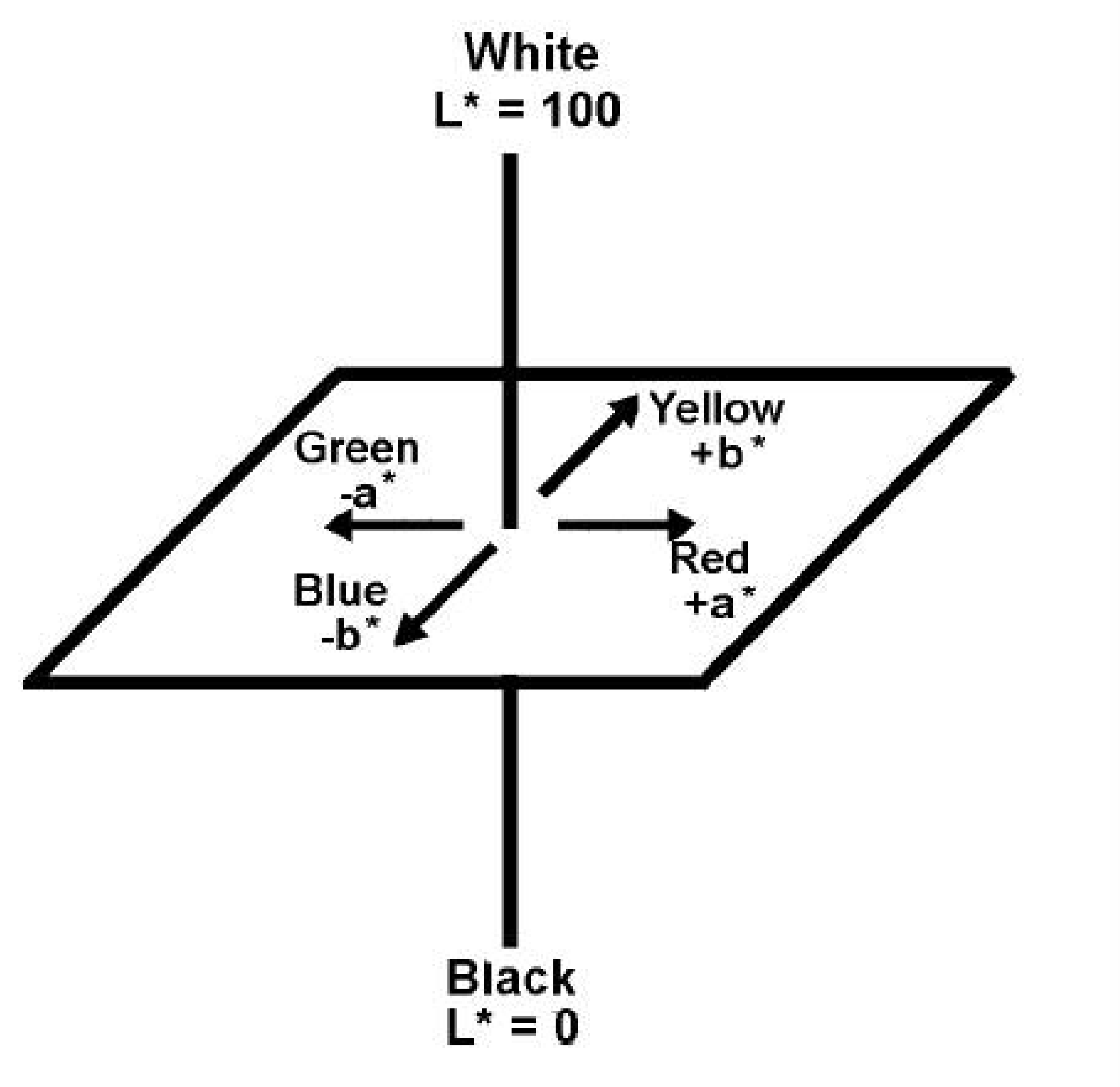
Mathematic treatment of image

Obtention of fish digital pictures

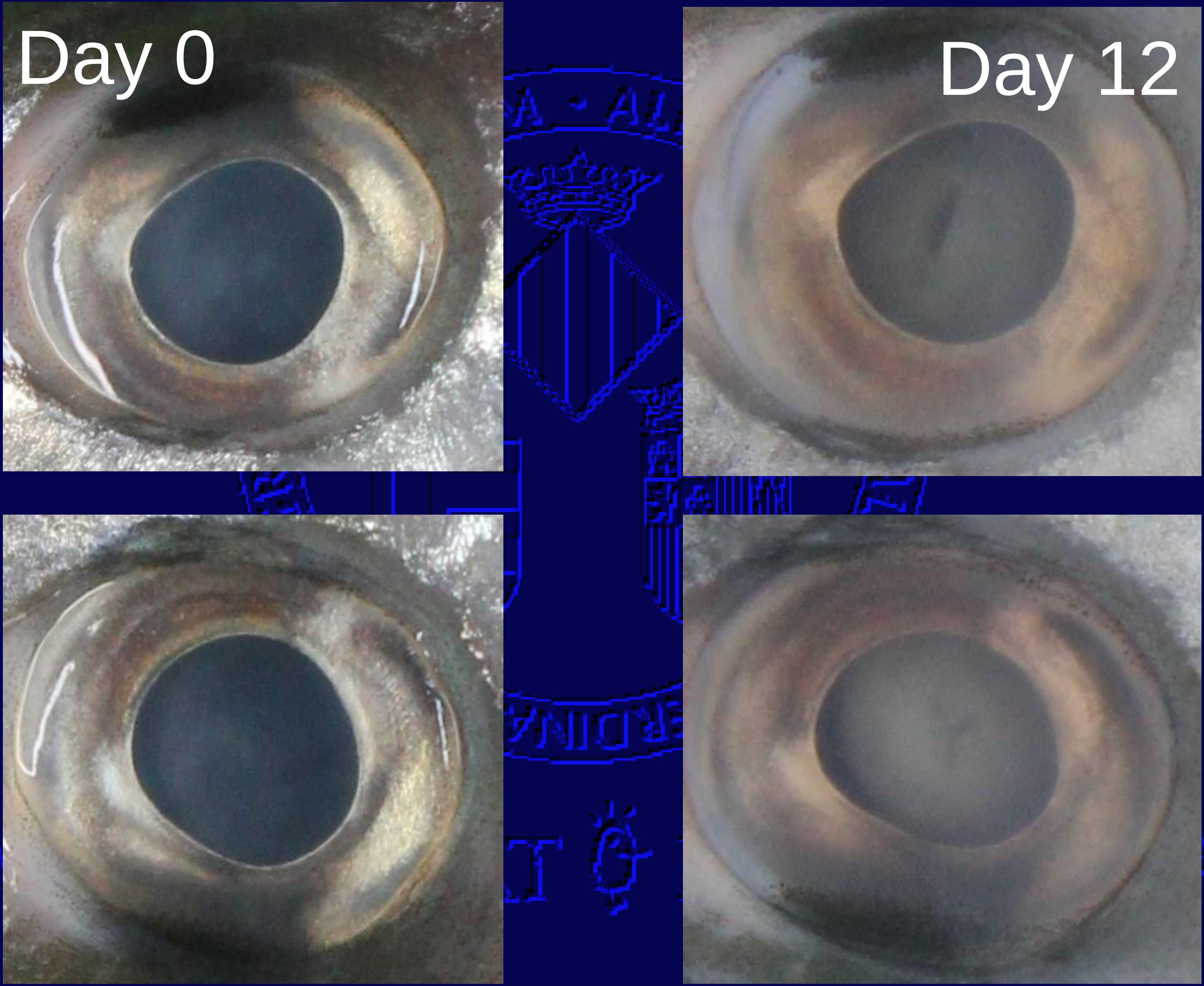
Image acquisition system



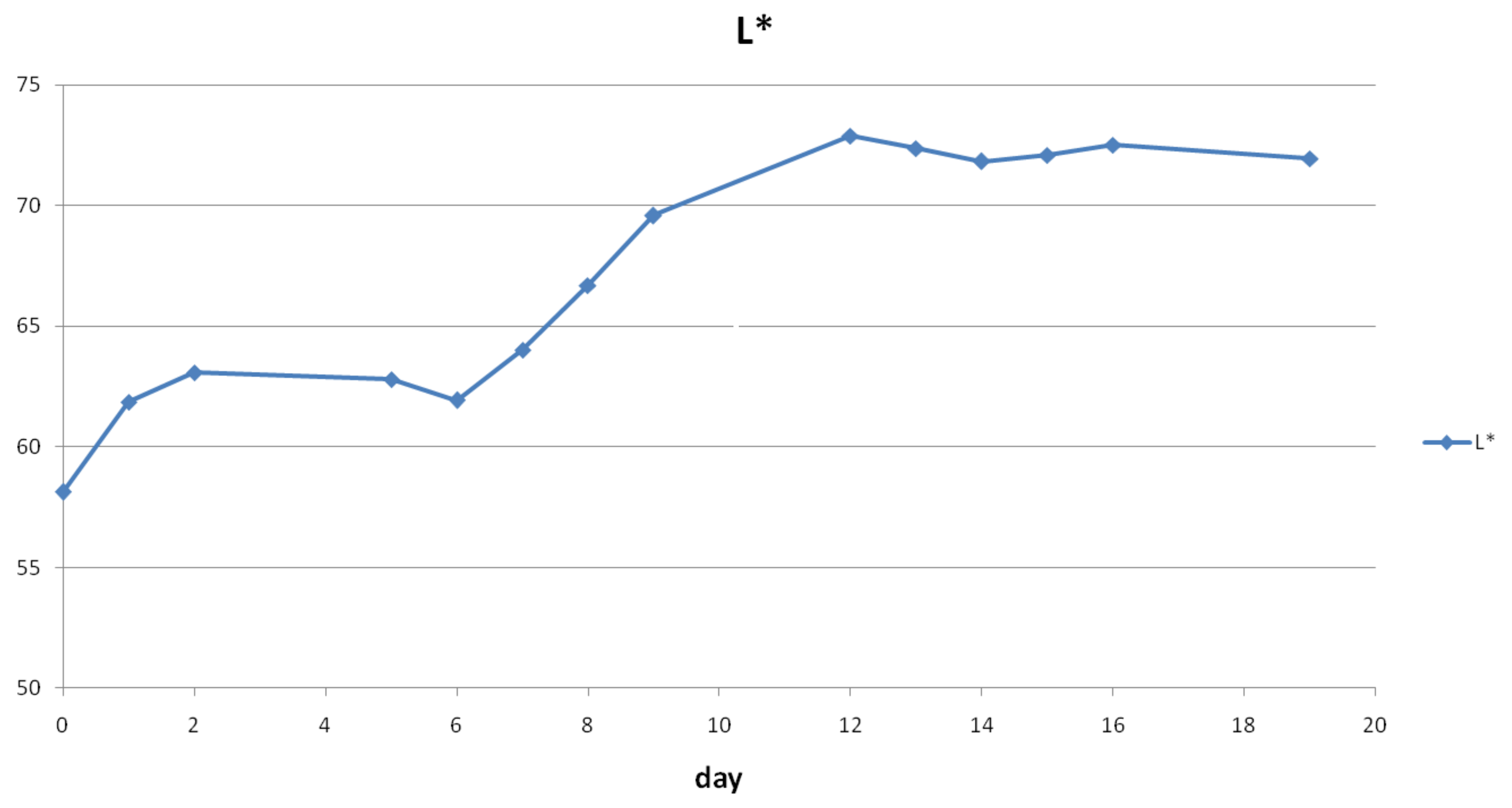
CIELAB coordinate system



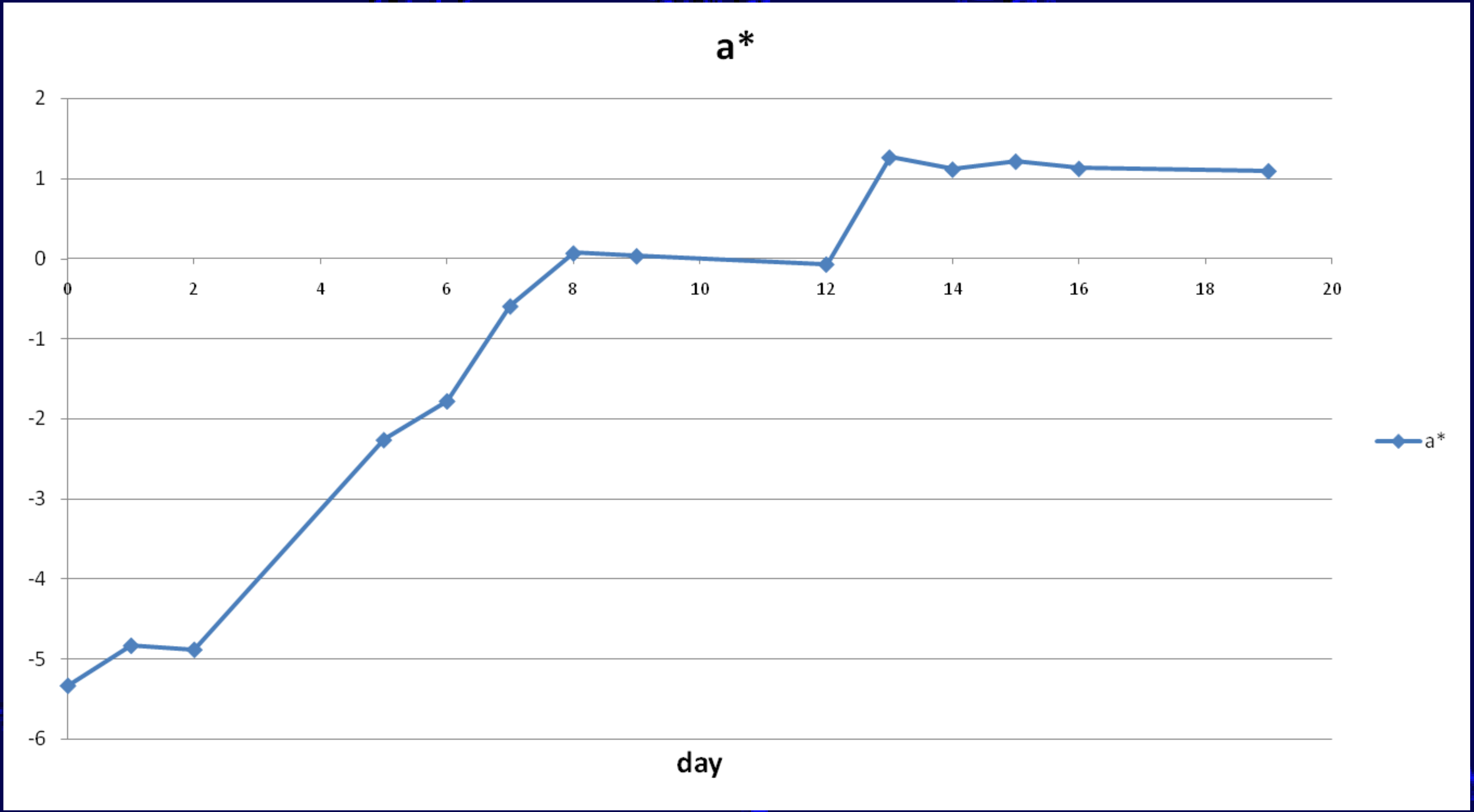
Changes in *Sparus aurata* (Dorada) eyes during ice storage


Day 0
Day 12

Evolution of parameter L*



Evolution of parameter a*



Evolution of parameter b*

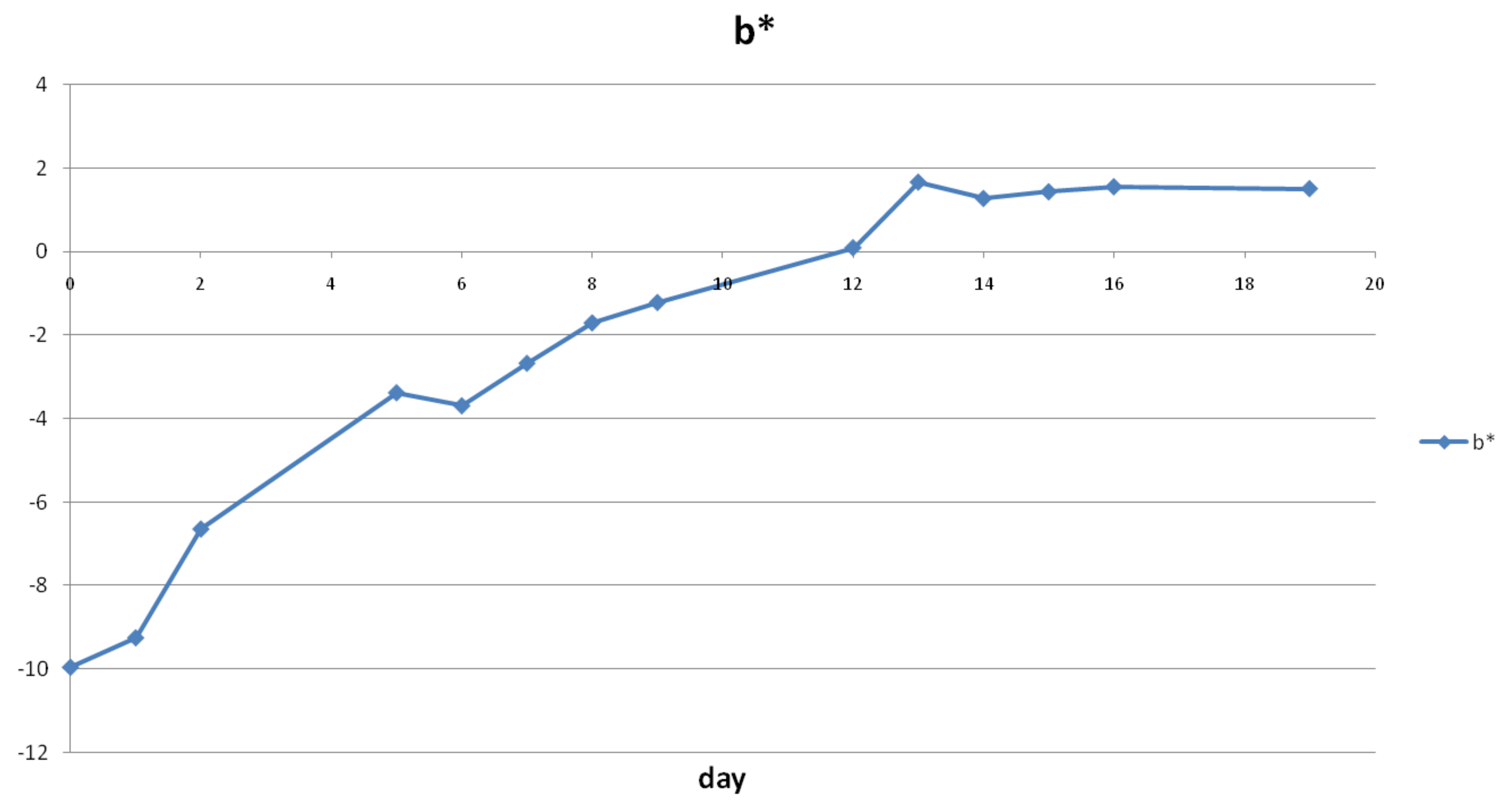
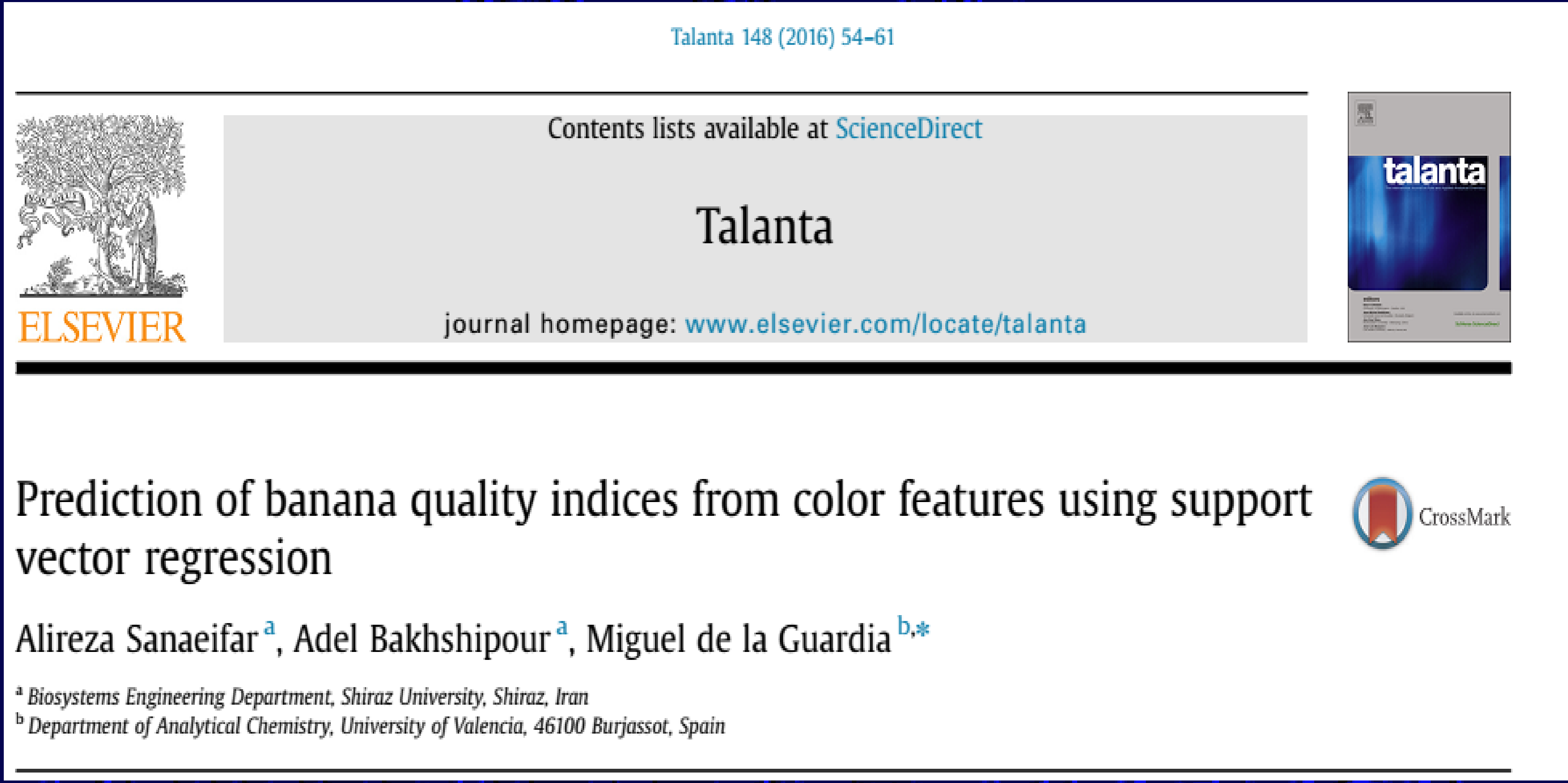


IMAGE TREATMENT

A bit of Chemometrics

VNIVERSITAT DE VALÈNCIA



Talanta 148 (2016) 54–61

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journal homepage: www.elsevier.com/locate/talanta

Prediction of banana quality indices from color features using support vector regression

Alireza Sanaeifar [a], Adel Bakhshipour [a], Miguel de la Guardia [b,*]

[a] *Biosystems Engineering Department, Shiraz University, Shiraz, Iran*
[b] *Department of Analytical Chemistry, University of Valencia, 46100 Burjassot, Spain*

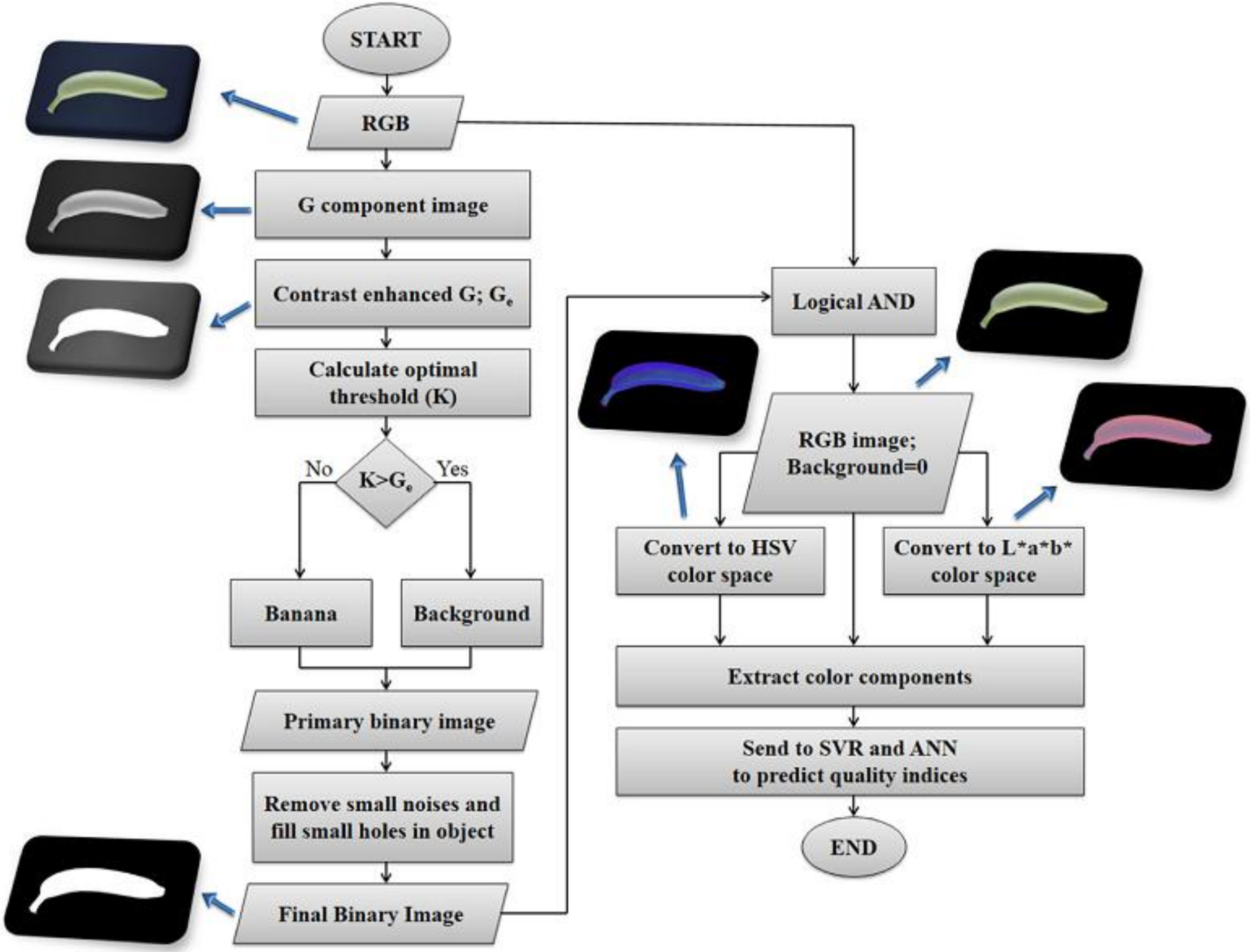


Fig. 1. Flowchart of the algorithm employed for color measurement of banana samples.

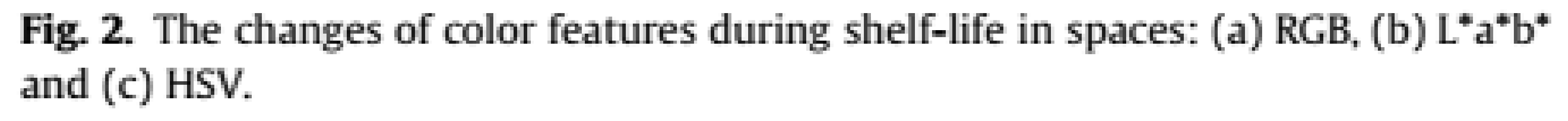


Fig. 2. The changes of color features during shelf-life in spaces: (a) RGB, (b) L*a*b* and (c) HSV.

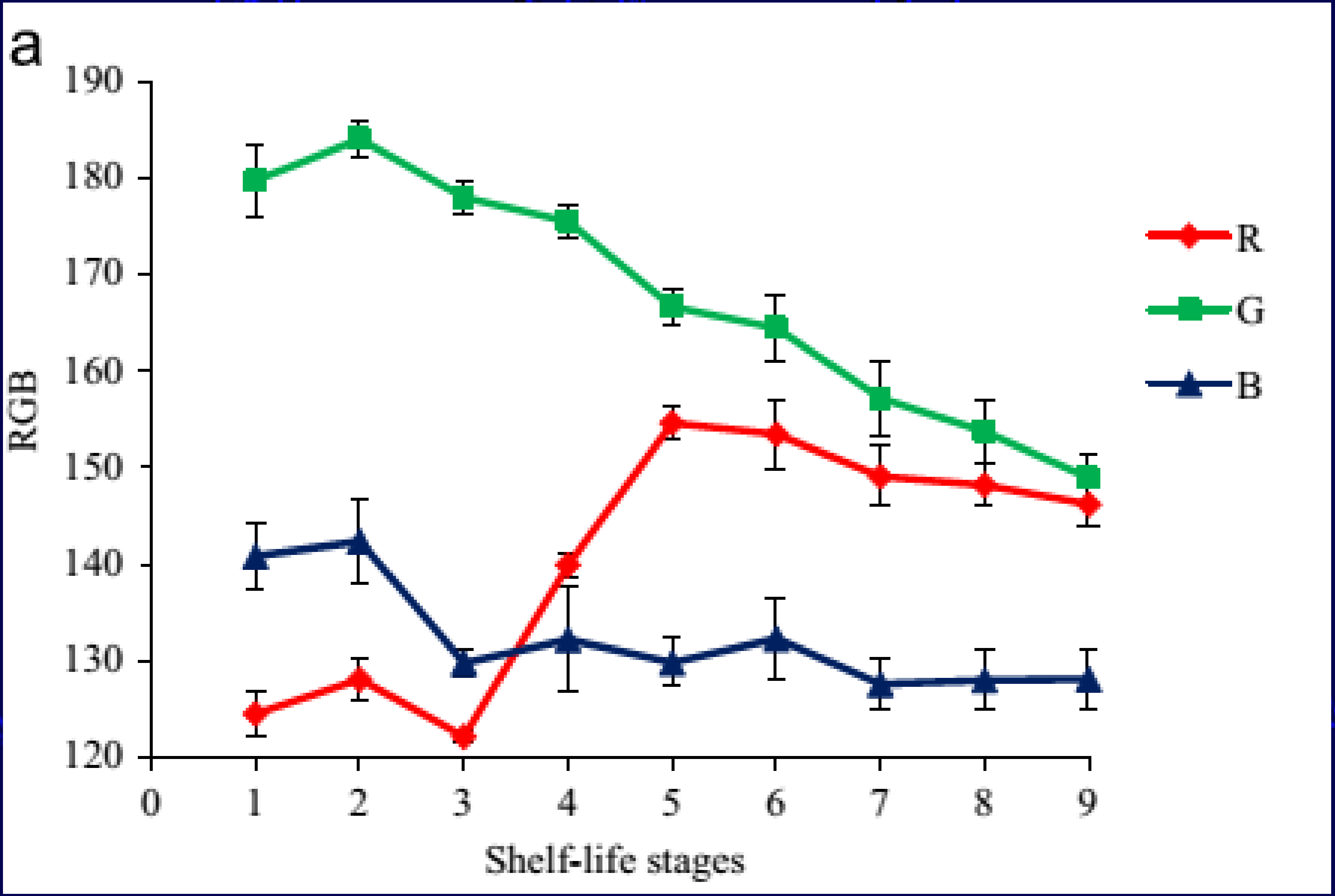


Fig. 2. The changes of color features during shelf-life in spaces: (a) RGB, (b) L*a*b* and (c) HSV.

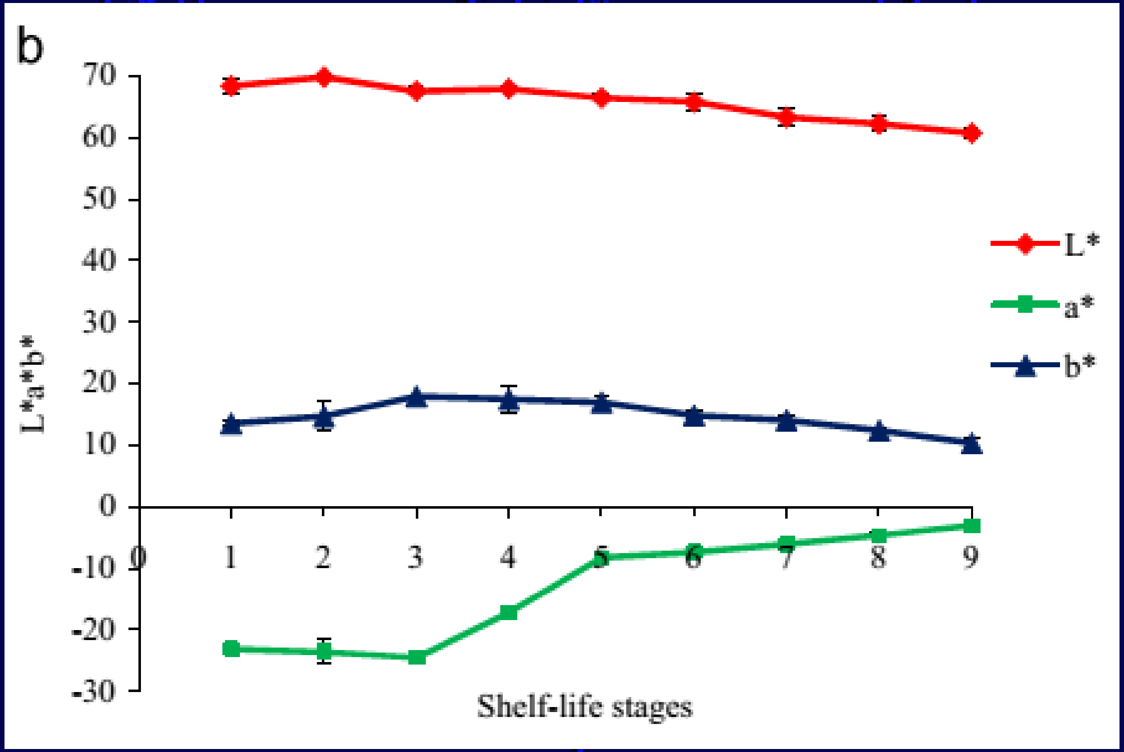
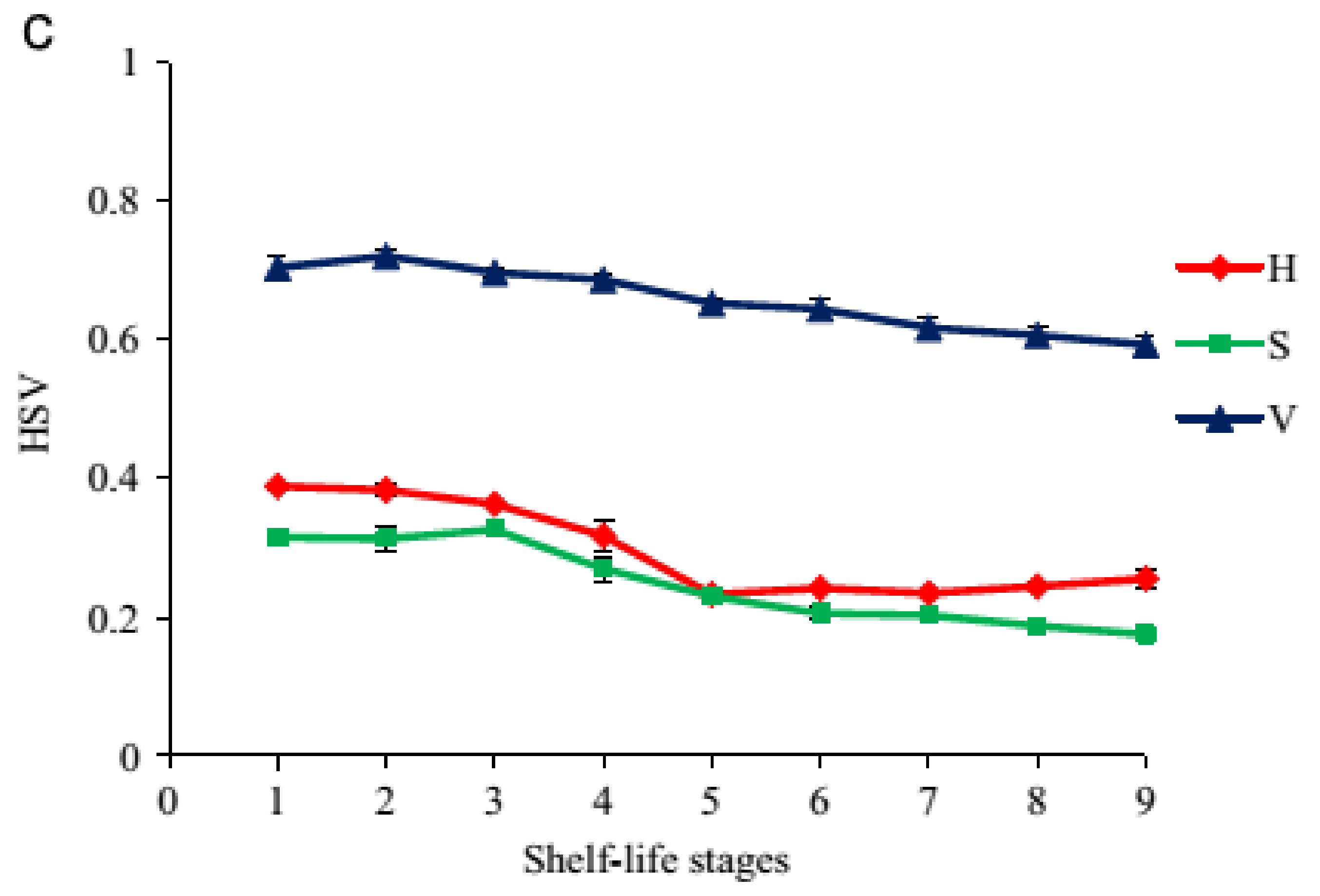


Fig. 2. The changes of color features during shelf-life in spaces: (a) RGB, (b) L*a*b* and (c) HSV.



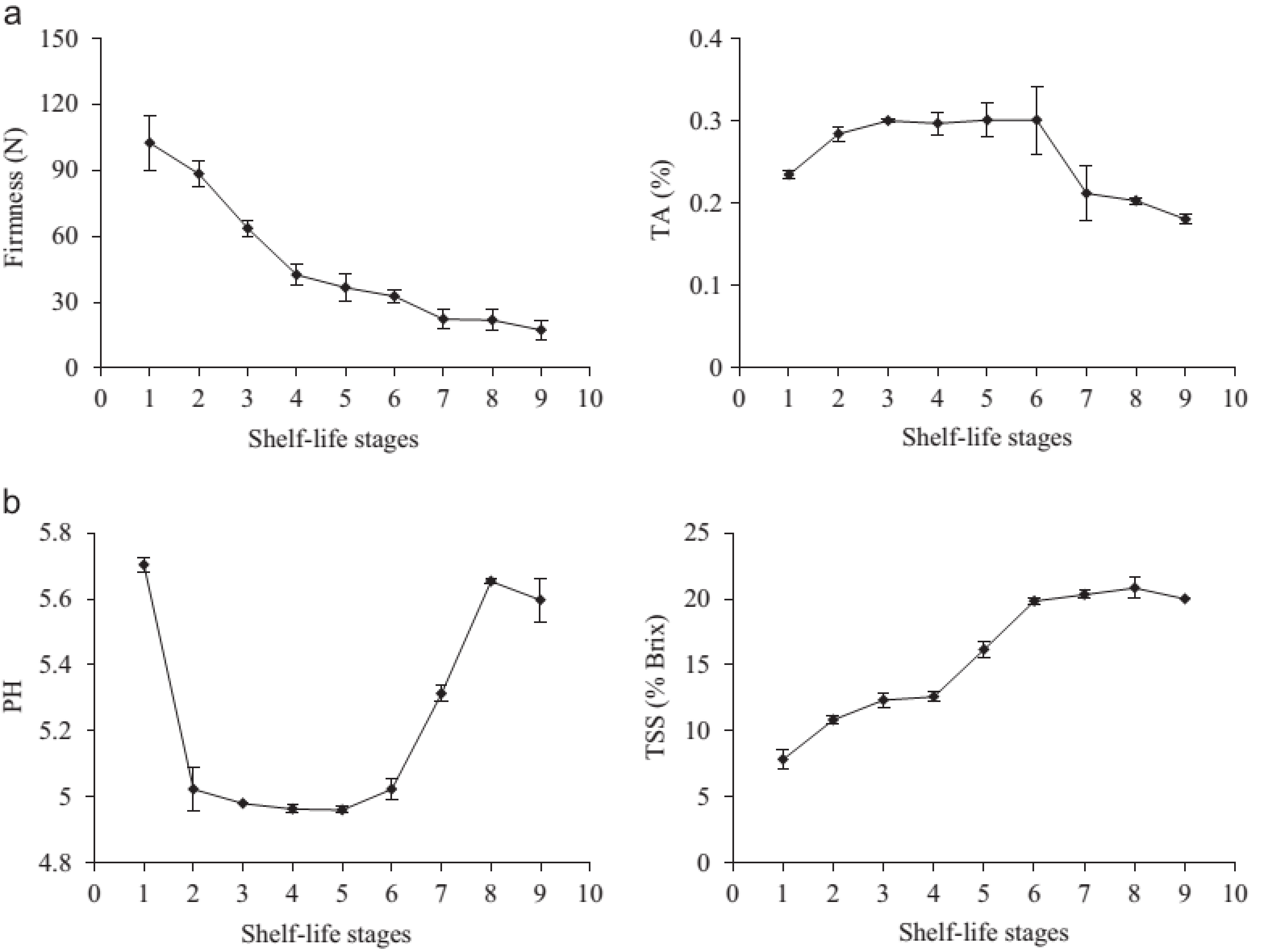


Fig. 3. The changes of the banana quality indices during shelf-life stages.

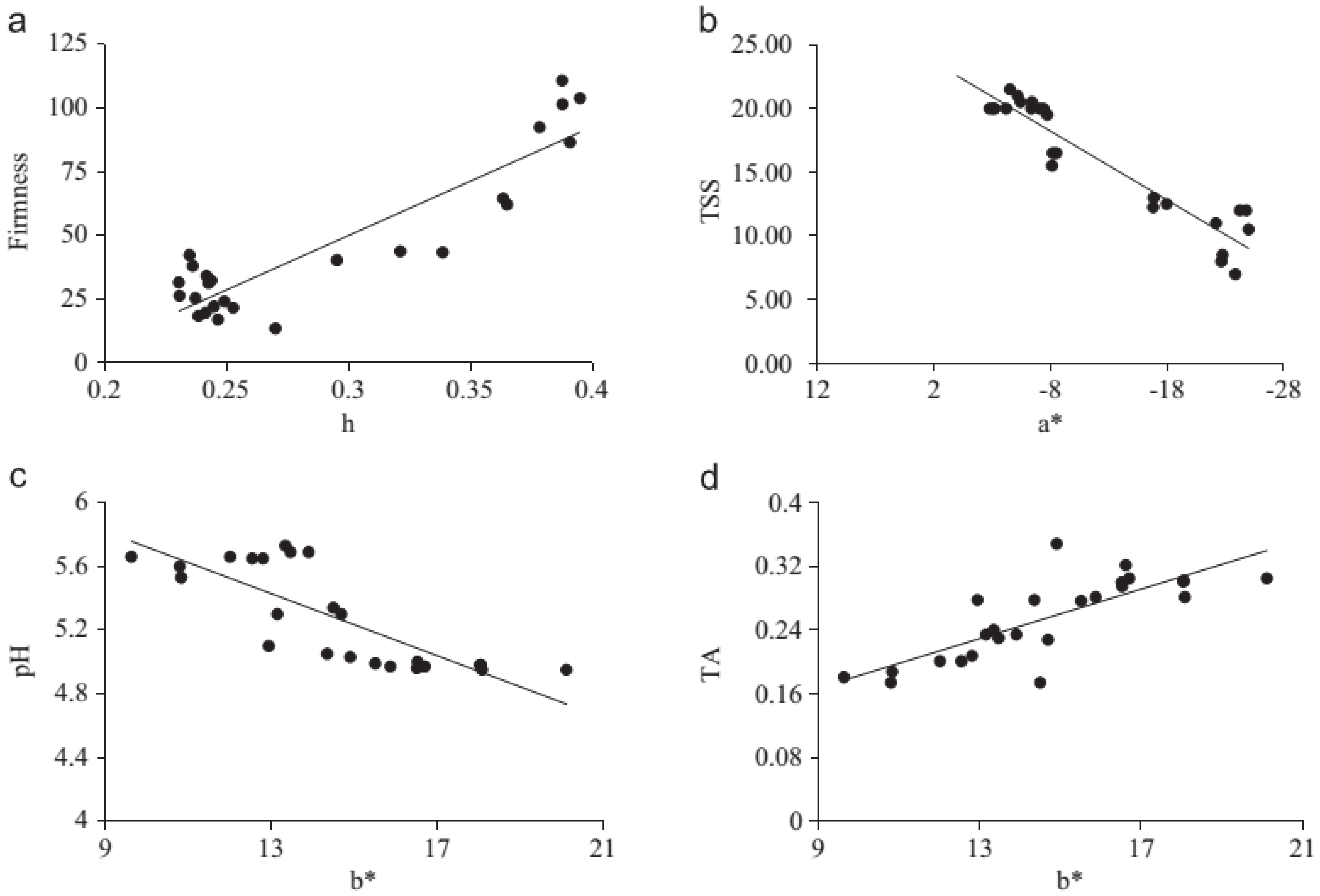


Fig. 4. Change of quality indices vs. color features.

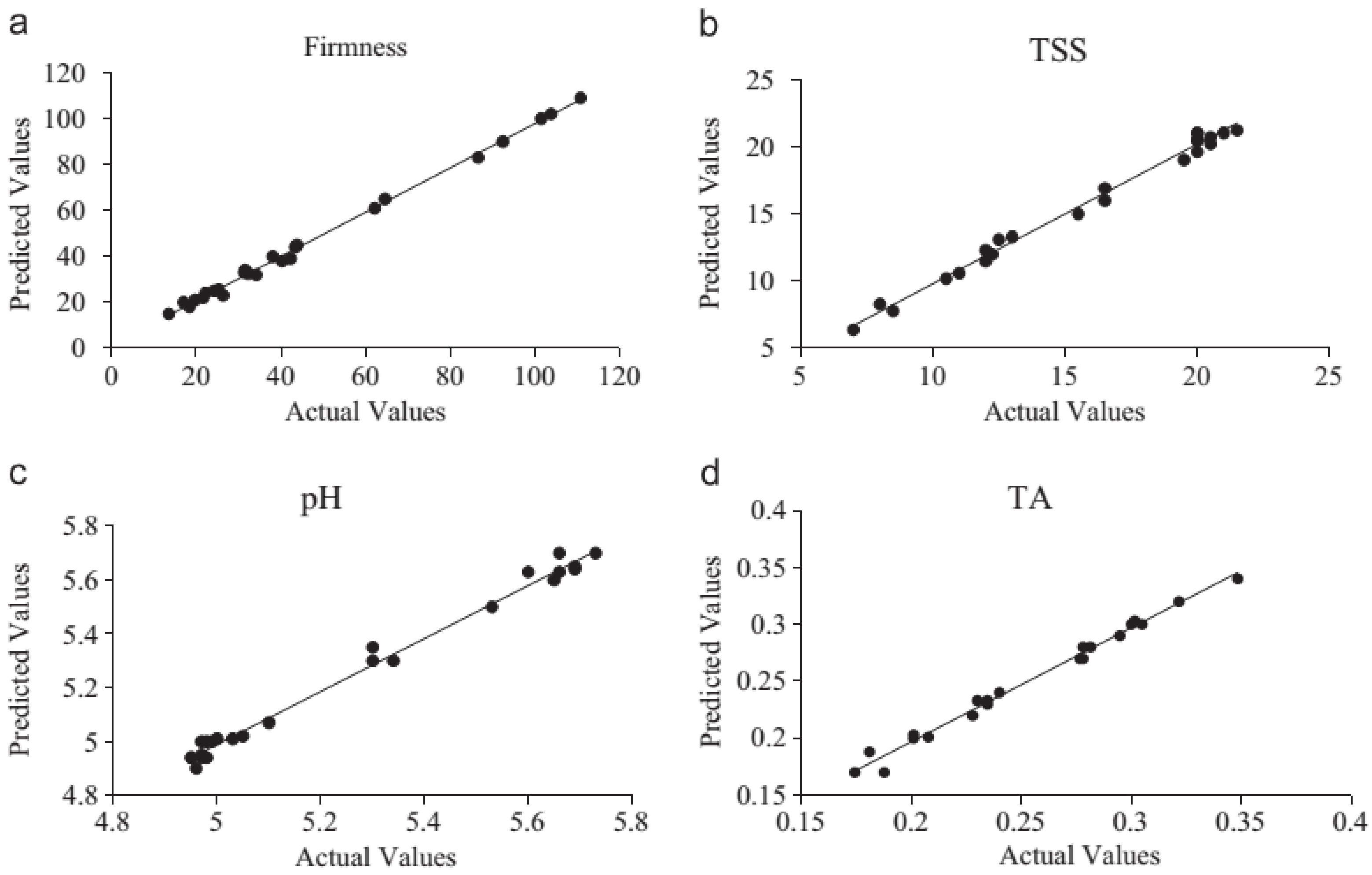


Fig. 5. Plots of the regression between observed and predicted banana quality indices obtained by using the original color data set and SVR_rbf model.

SMARTPHONE IMAGE TREATMENT

Fat determination in meat products

Universitat de València


BOILING
SAMPLE
EXTRACTION
MODE
RINSING
137.4
OPERATOR'S INSTRUCTIONS
PRESS
PRESS
SOXTEC SYSTEM HT 2
1043 Extraction Unit

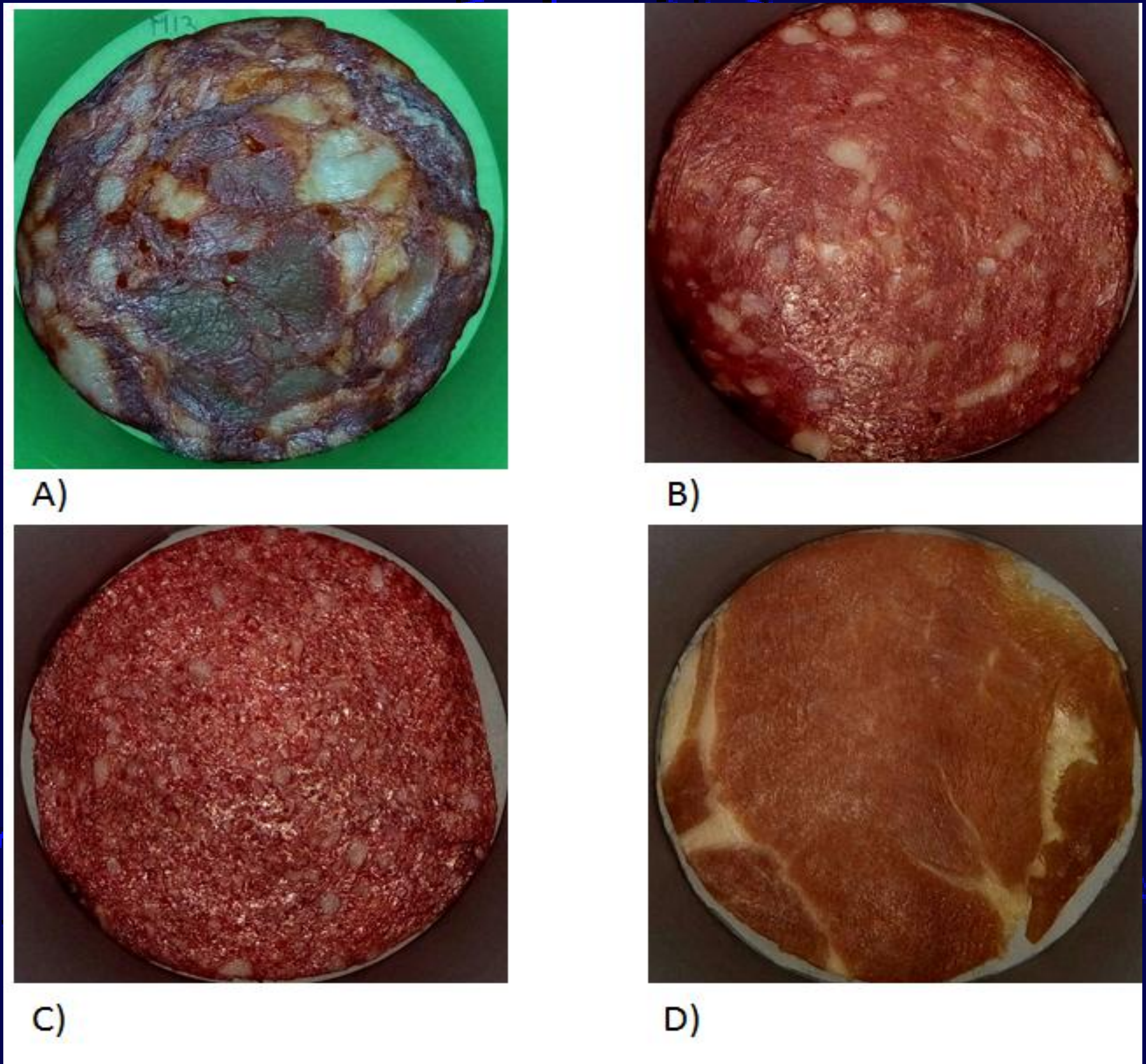
Figura 3. 1 Smartphone utilizado para la obtención de imágenes

Para la adquisición de las imágenes se empleó la cámara de un Smartphone modelo Meizu M2 Mini

Tabla 3. 1 Características de la cámara

13 megapíxeles
Apertura f/2.2
lentes
Lente panorámica
Flash LED

Figura 1. 1 Lonchas de las muestras empleadas: A) Chorizo, B) Salchichón, C) Salami, D) Jamón serrano



Universitat de València

Unconventional uses for conventional things: the use of domestic coffee machines as analytical tool

SOLINQUIANA

Department of Analytical Chemistry, University of Valencia

Introduction – Organic Analytes Extraction

USE

PSE

SOLID SAMPLES

Soxhlet

MAE

Shaking

SFE

Introduction

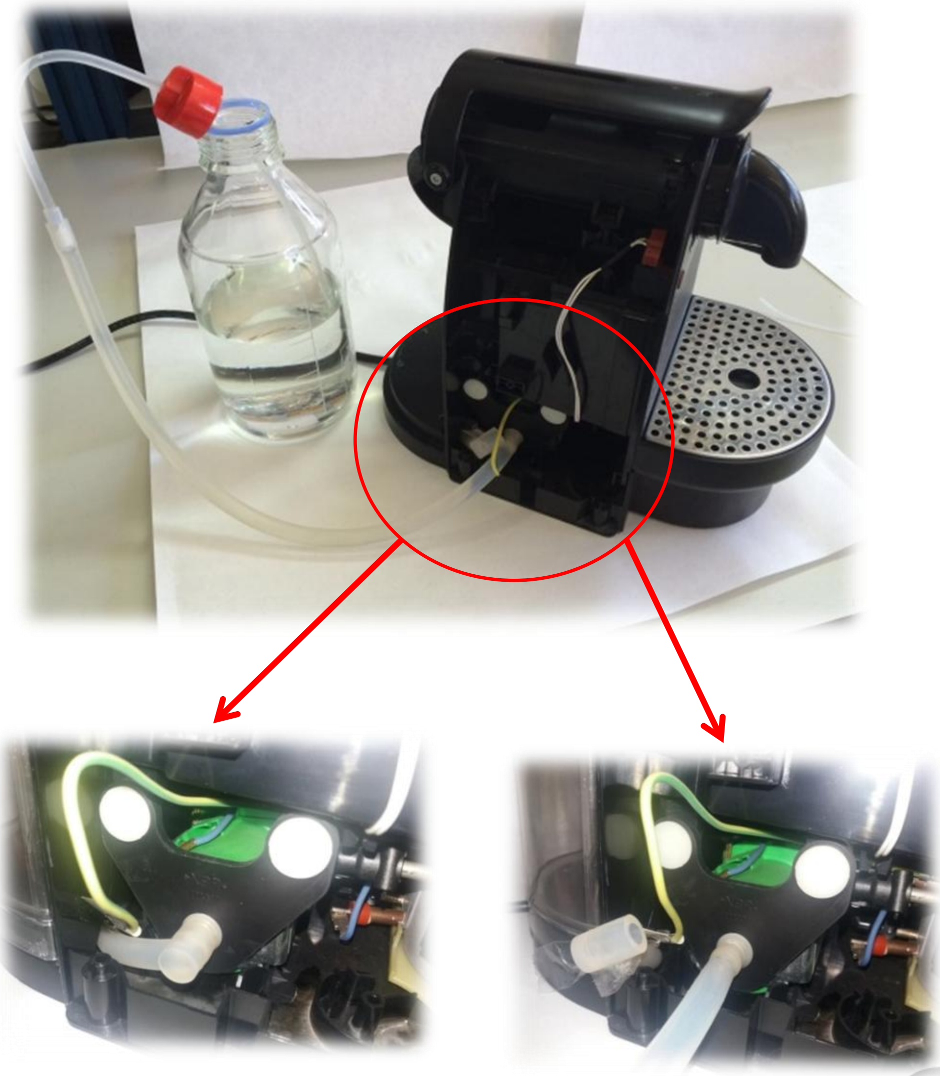
One afternoon…

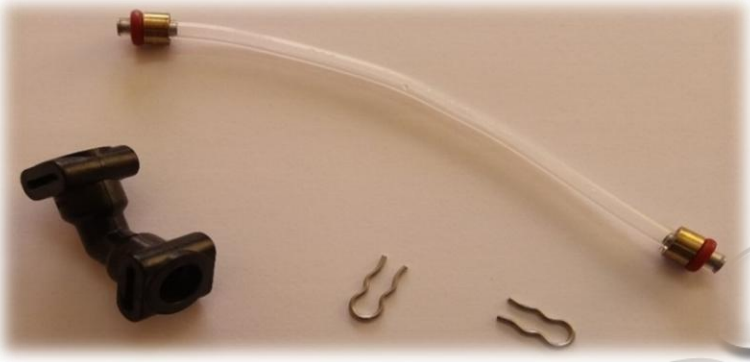
so…

If we use…?

assisted by:
-pressure
-temperature

Modification & Safety Conditions

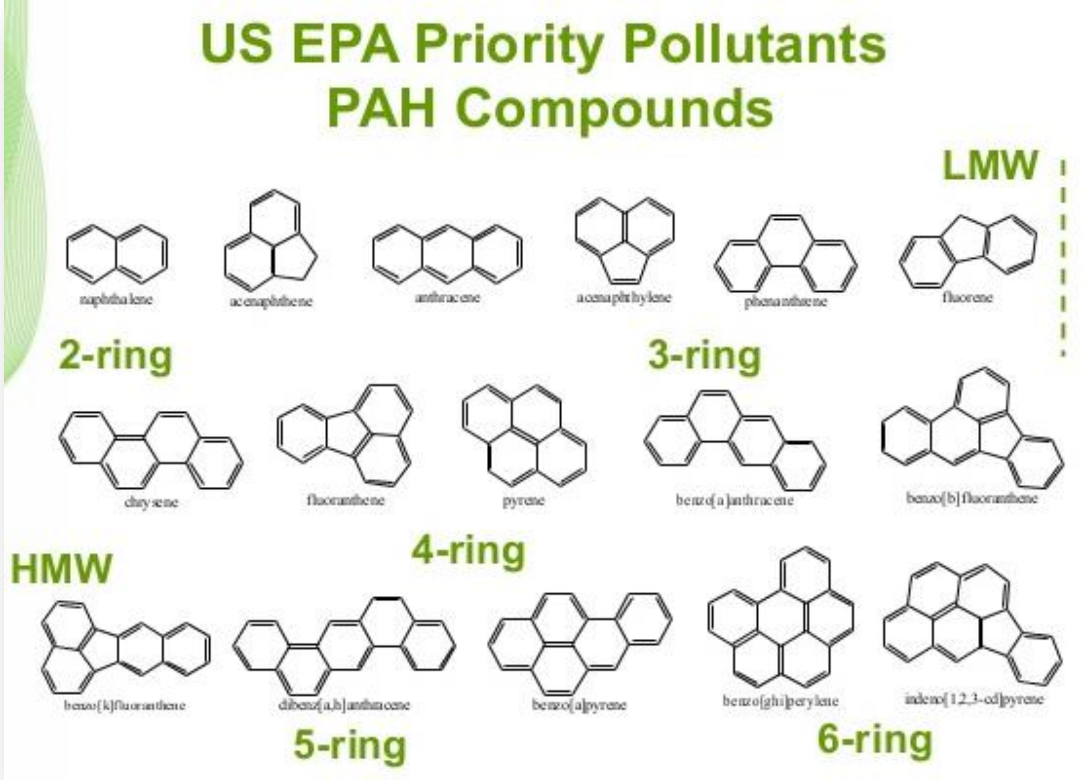




Experimental Procedure

Results – Polycyclic aromatic hydrocarbons

Hard cap espresso extraction



US EPA Priority Pollutants PAH Compounds

LC-FD

Armenta et al. *Anal. Chem*. **2016**, 88, 6570.

Results – Selection of Extraction Solvent

Water

Low recovery

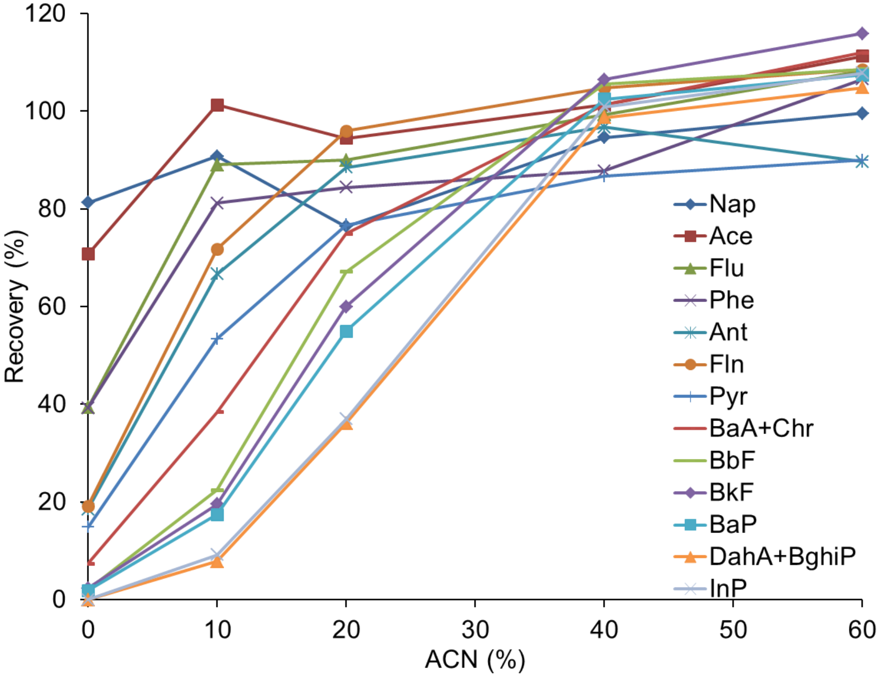
✗

Acetonitrile

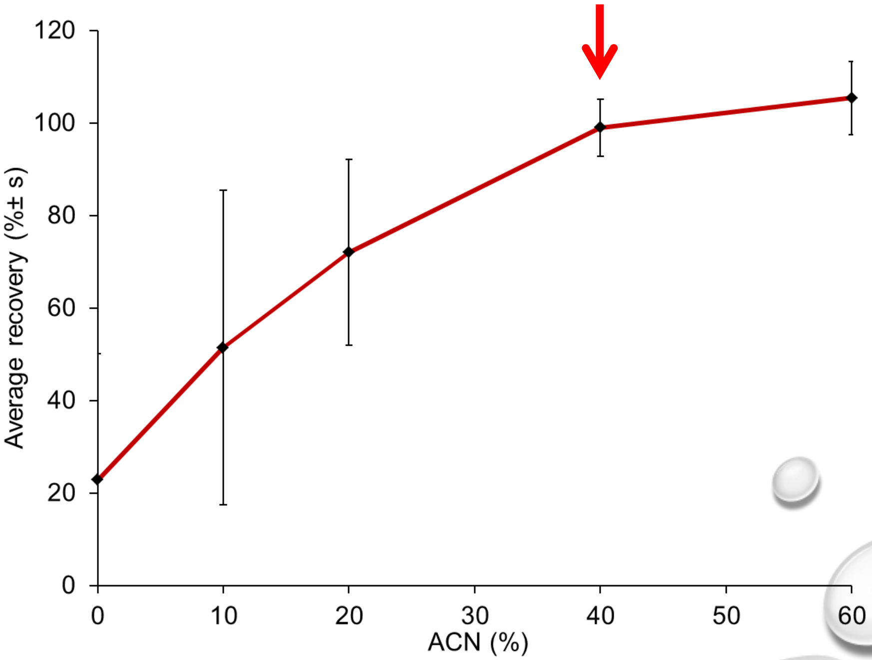
Ethanol

- water miscibility
- dielectric constant
- boiling point
- compatibility with LC

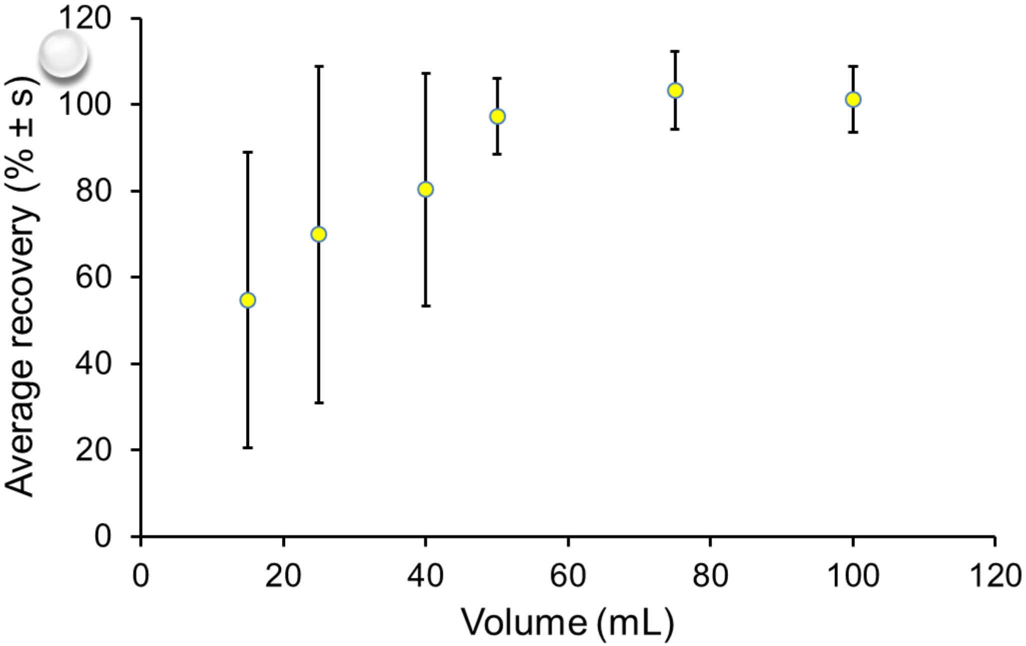
✓

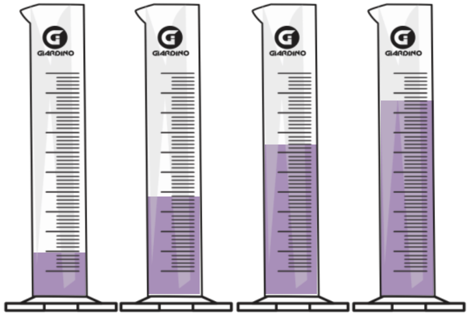


5 g soil spiked at 1000 µg Kg^{-1} PAHs



Results – Extraction Volume





5 g soil spiked at 1000 µg Kg^{-1} PAHs

40 % acetonitrile
50 mL
11 seconds

Dilution factor 10
No clean-up
Direct LC-FD injection

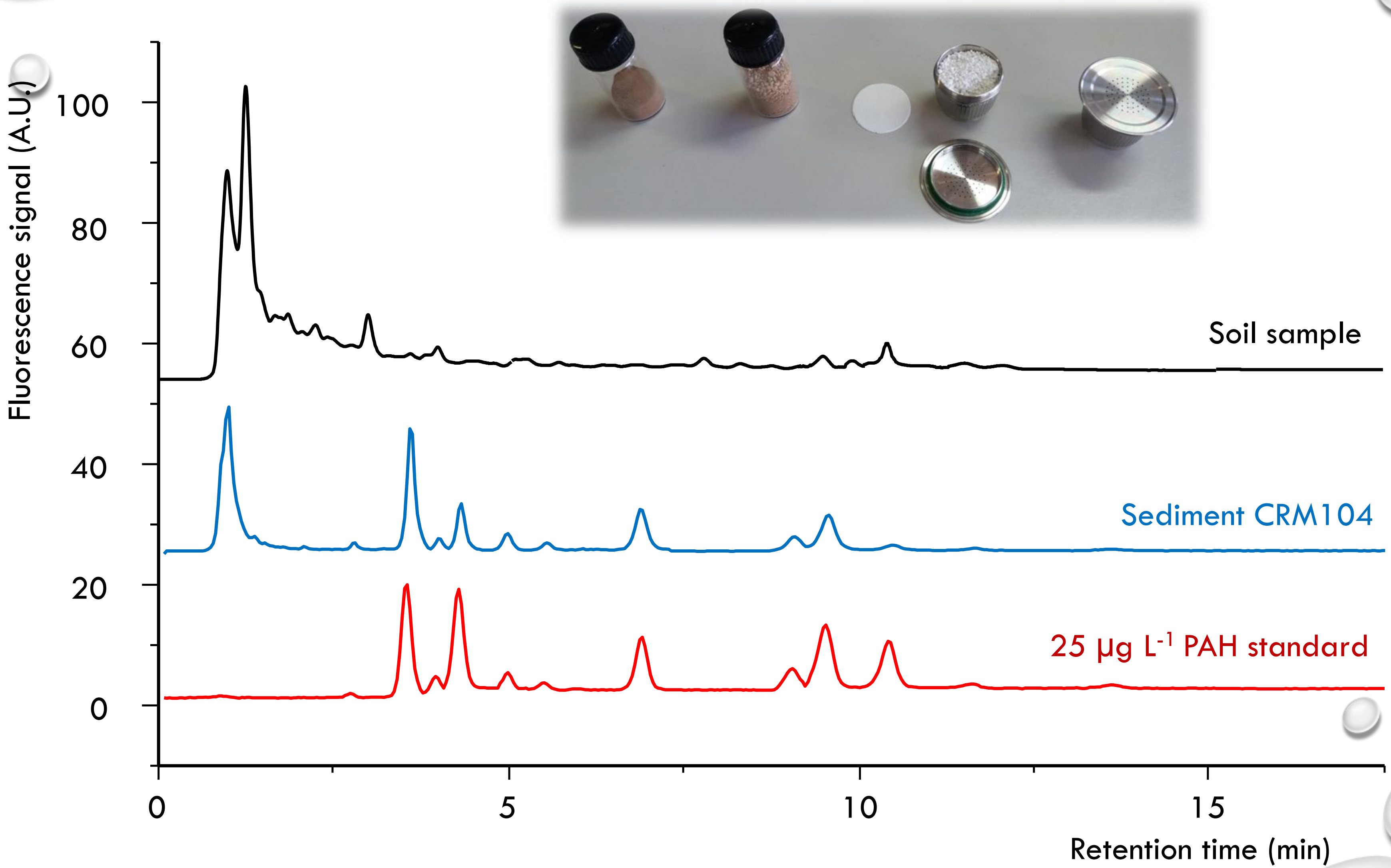
LOD = 2 - 85 ng g^{-1} PAHs

Results – Refillable Capsules

Characteristics	mycoffeestar	Seal Pod	Coffee duck	Capsule'in	Self cap
Capsule size (mm)	26 x 25 x 23	29 x 24 x 21	27 x 26 x 23	29 x 27 x 23	28 x 26 x 23
Internal volume (mL)	8.84	9.53	10.30	12.60	12.20
Capsule material	Stainless steel	Stainless steel	Plastic	Plastic	Plastic
Sealing material	Stainless steel	Aluminium	Plastic	Aluminium	Aluminium
Average recovery (% ± s) [a]	105 ± 12	111 ± 7	102 ± 10	112 ± 13	106 ± 10
Maximum recovery (%)[a]	119 (Pyr)	122 (BbF)	115(InP)	121 (InP)	117 (Fln)
Minimum recovery (%)[a]	81 (Phe)	93 (Phe)	77 (Phe)	86 (Phe)	78 (Phe)

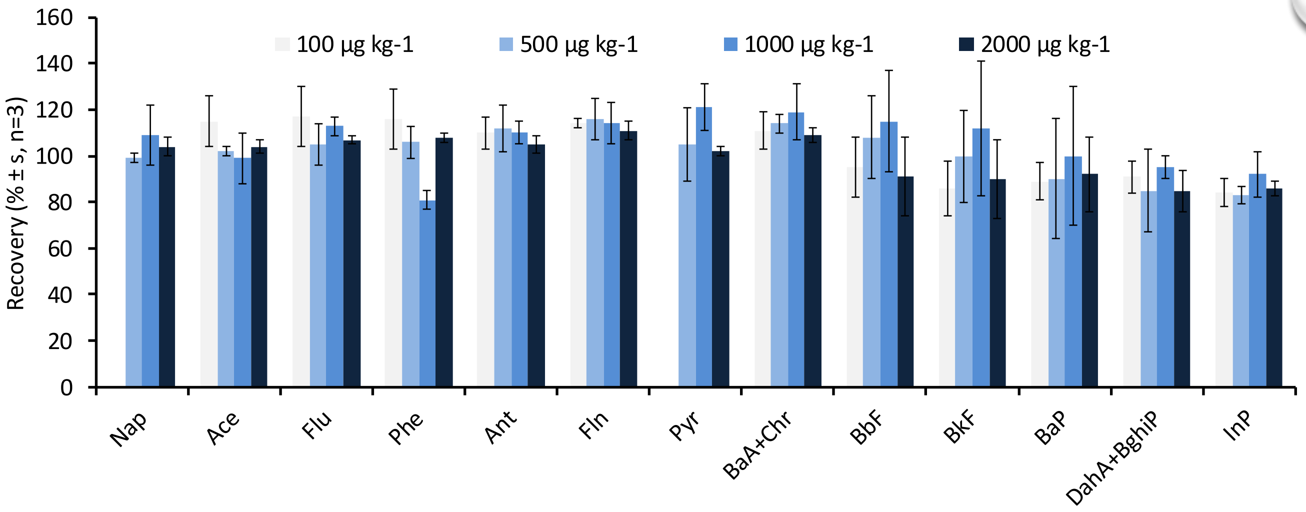
[a] Recovery values were calculated for 5.0 g of soil spiked with 1000 µg kg^{-1} PAHs

Results – LC-FD Chromatogram



Results – Method Validation

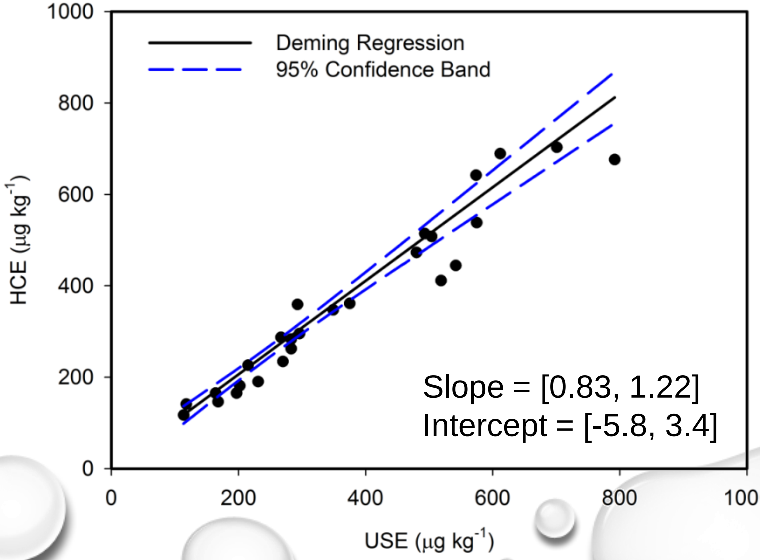
Recoveries in spiked soil



Certified reference material

CRM170 clay soil
CRM104 sediment

Method comparison (USE)



Slope = [0.83, 1.22]
Intercept = [-5.8, 3.4]

Results – Hard cap espresso machine extraction

Advantages

Fast

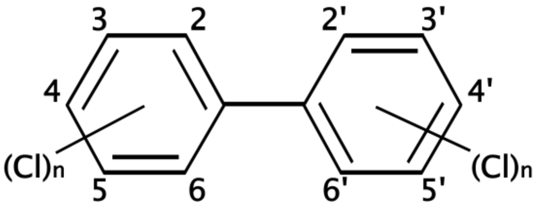
Quantitative

Drawbacks

Lack in sensitivity

High water content

Results – Polychlorinated biphenyls



Hard cap espresso extraction

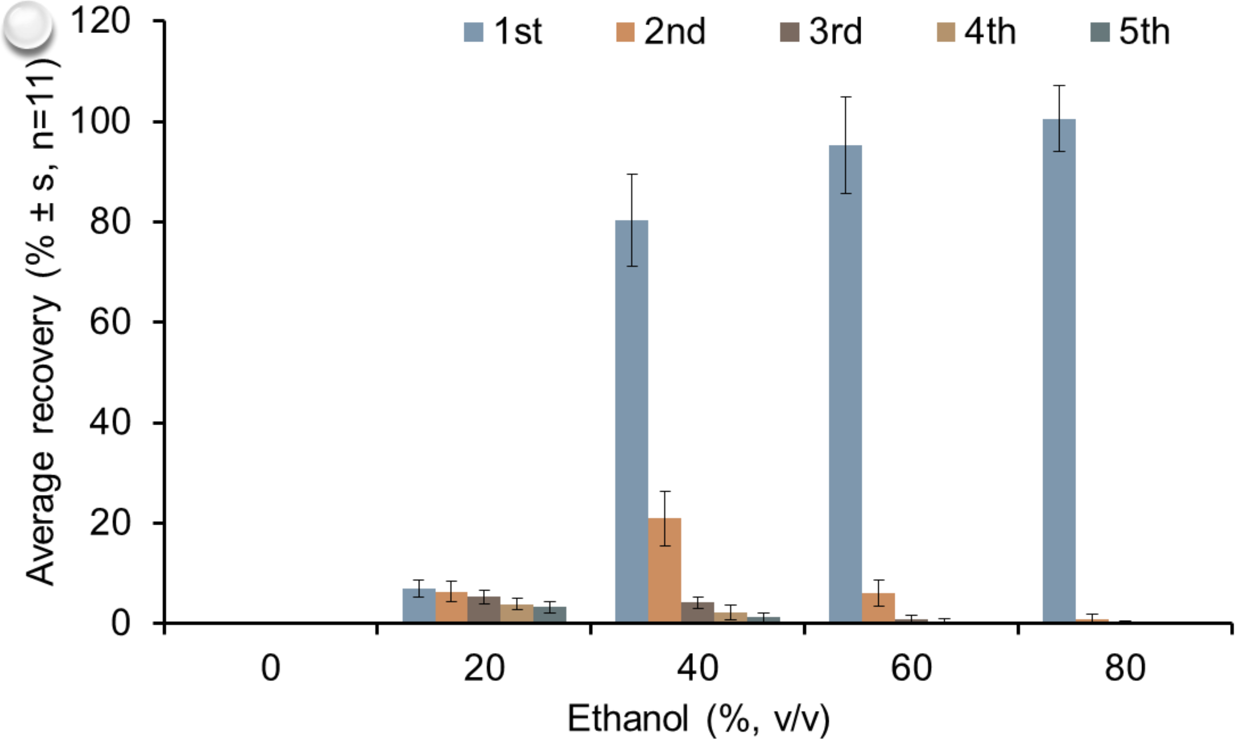
Stir bar sorptive extraction

90 min stirring

TD-GC-MS-MS

Gallart-Mateu et al. *Anal. Chim. Acta* **2017**,41, 952

Results – Hard cap espresso extraction efficacy



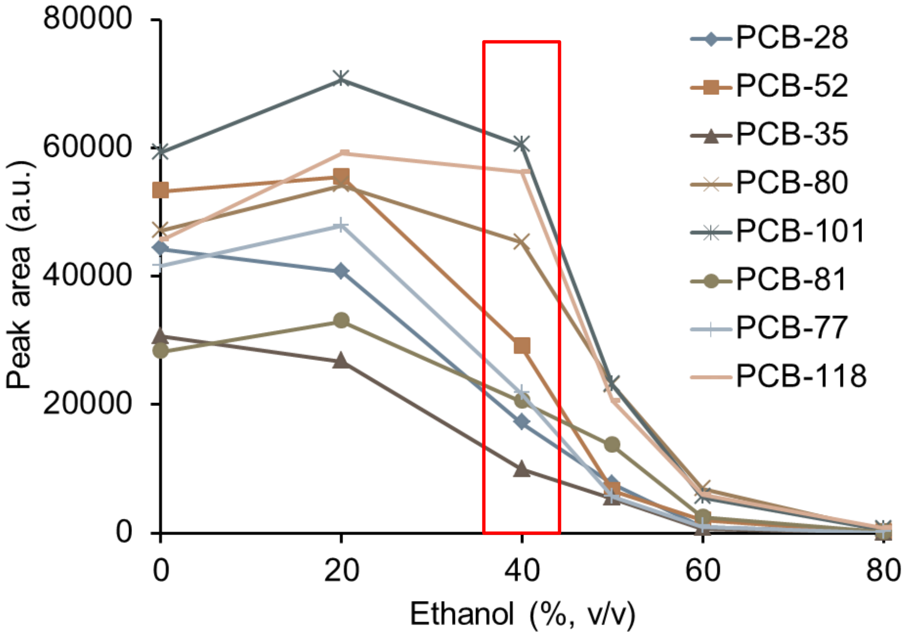
40 % ethanol
200 mL
39 seconds

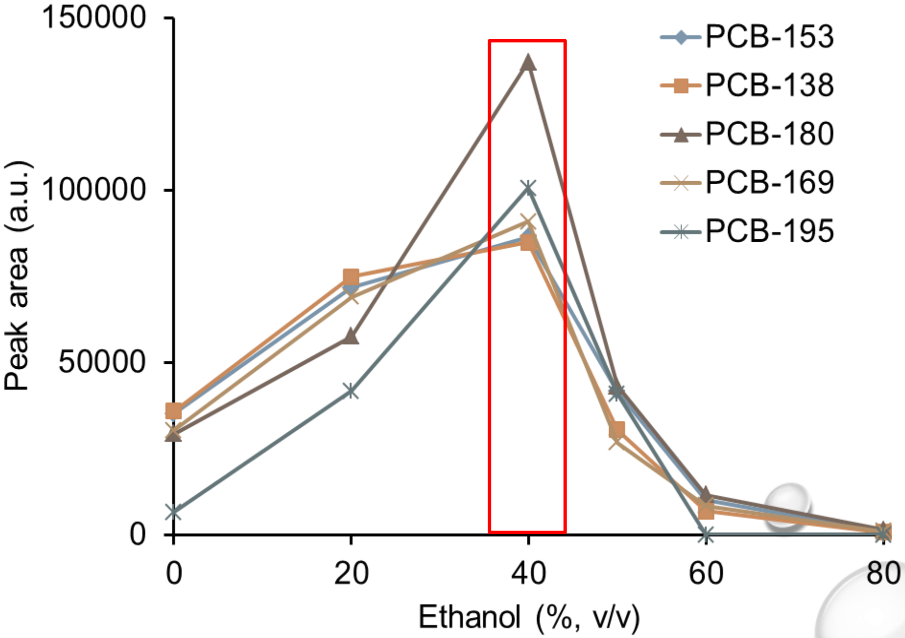
5 g soil spiked at 10 ng g^{-1} PCBs extracted by 5 x 100 mL of ethanol:water mixtures and analyzed by SBSE and TD-GC-MS-MS

Results – Stir bar sorptive extraction efficacy

40 % ethanol
200 mL
90 minutes

250 °C
20 min
75 mL min^{-1} helium

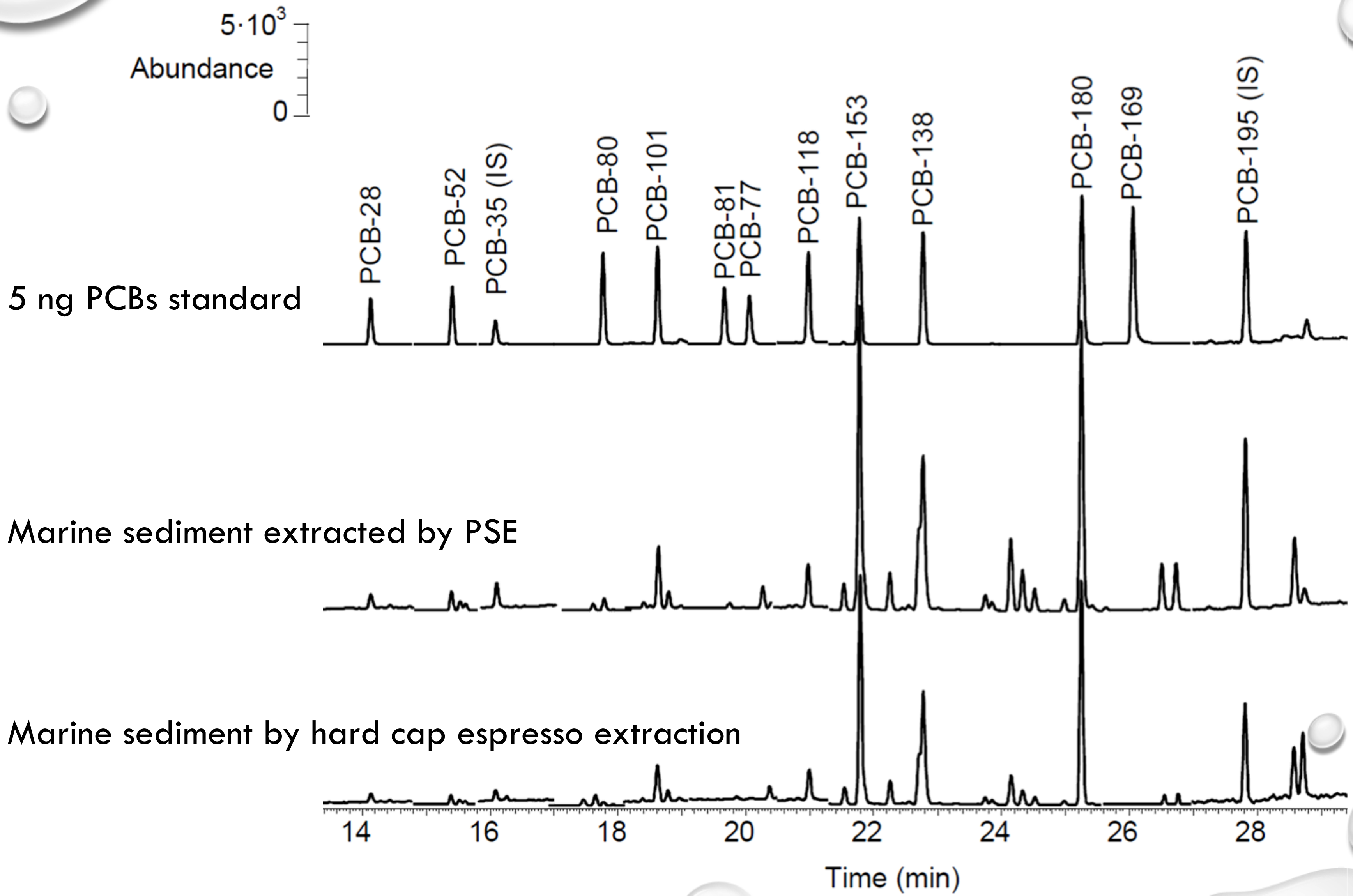




200 mL of ethanol:water mixtures spiked at 0.25 μg L^{-1} PCBs

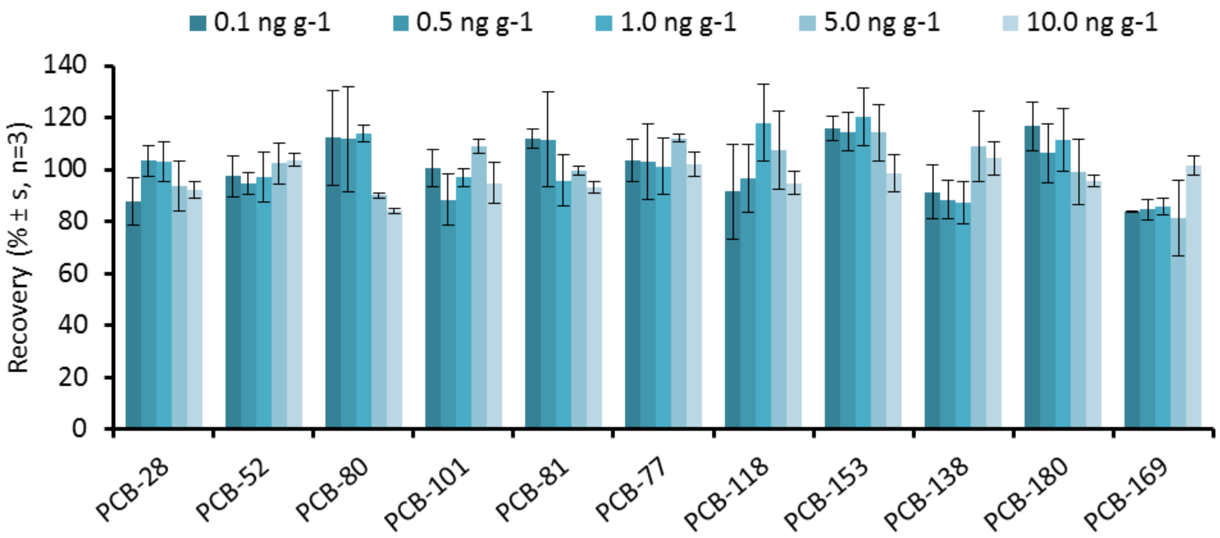
LOQ : 30 – 80 pg g^{-1}

Results – TD-GC-MS-MS chromatograms



Results – Method Validation

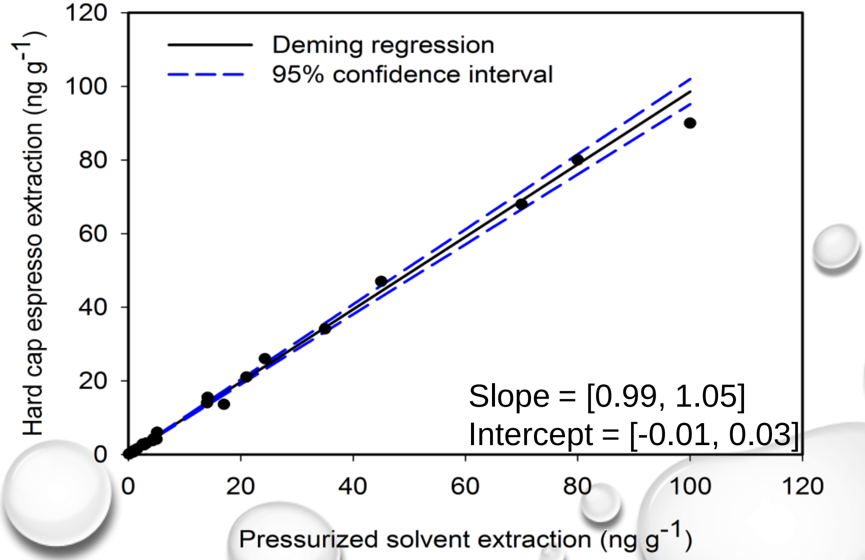
Recoveries in spiked soil



Certified reference material

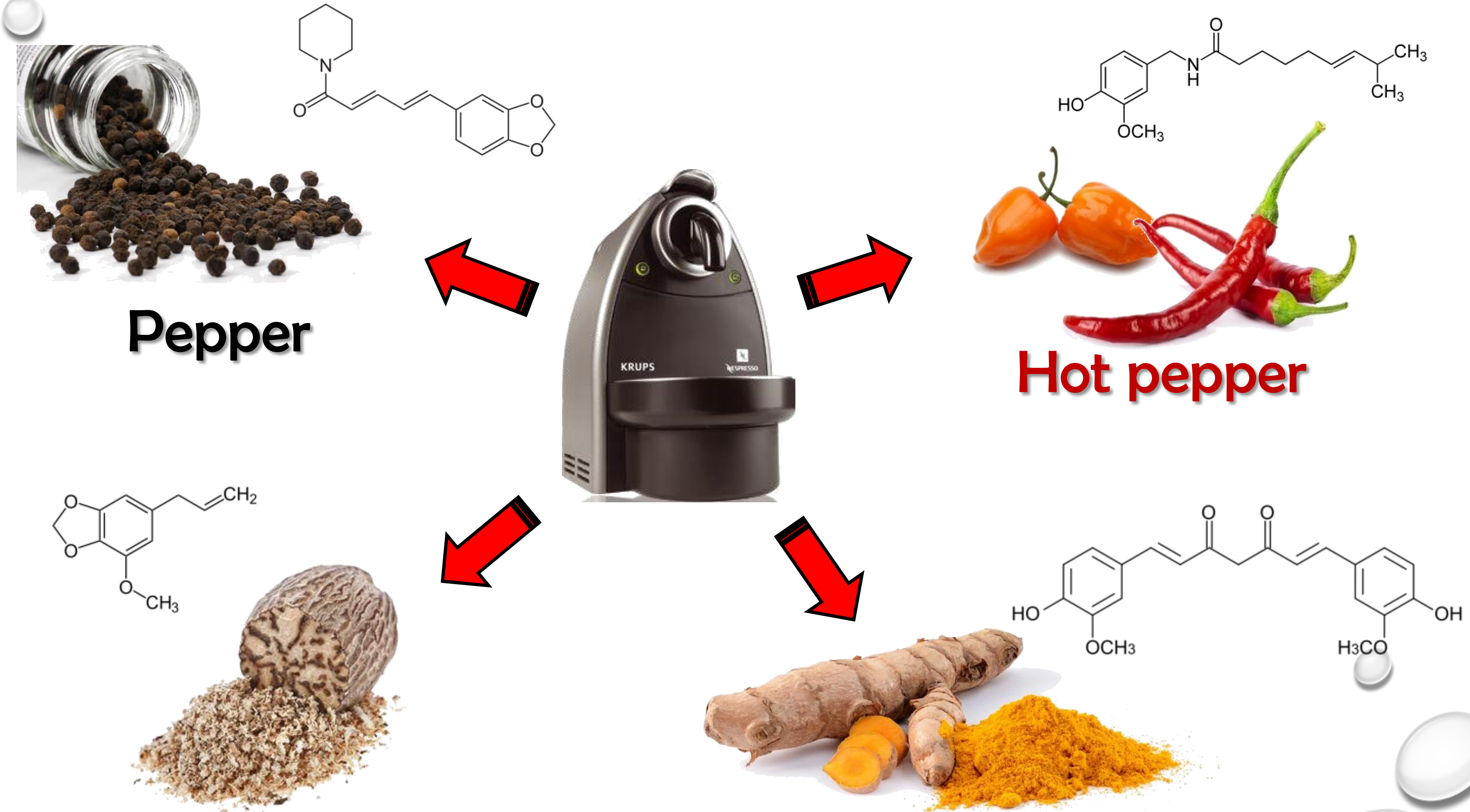
IAEA 357 homogenized marine sediment

Method comparison (PSE)



Slope = [0.99, 1.05]
Intercept = [-0.01, 0.03]

Results – What else?
Bioactive compounds from spices and herbs



Pepper

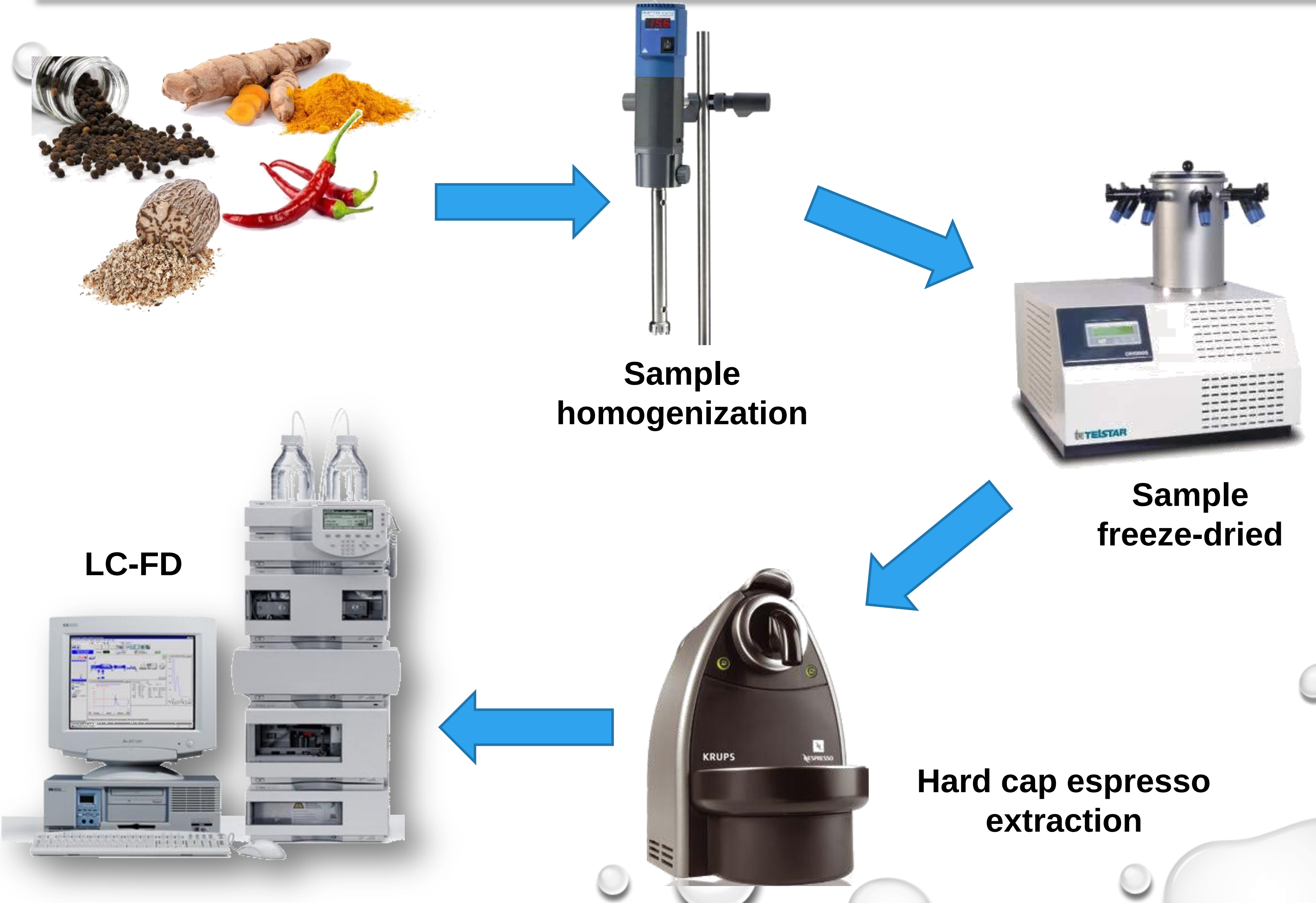
Hot pepper

Nutmeg

Turmeric

Martínez-Sena et al. *Food Chem.* **2016** Submitted

Results – Bioactive compounds from spices and herbs



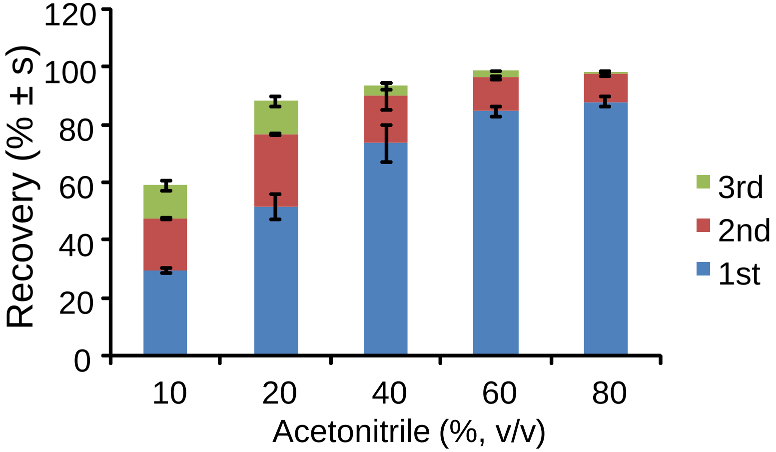
Sample homogenization

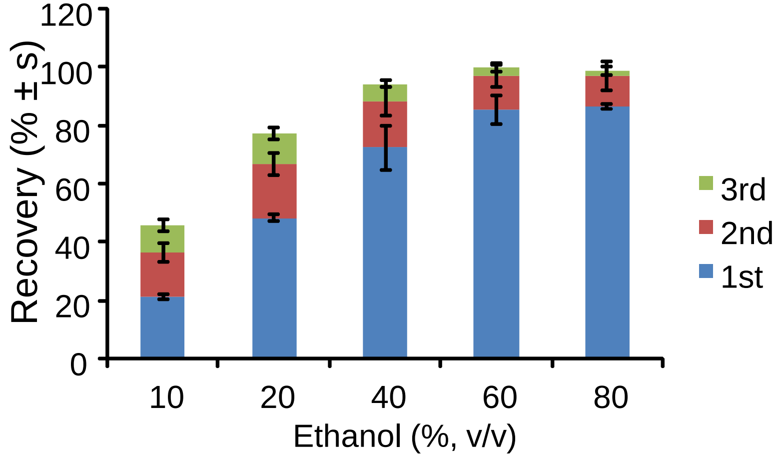
Sample freeze-dried

Hard cap espresso extraction

LC-FD

Results – Solvent selection





2 g cayenne chilli, total capsaicin extracted with 3 x 50 mL of ethanol:water mixtures and analyzed HPLC-FLD

Quantitative recoveries obtained

↓

100 mL 60% solvent

Total capsaicin

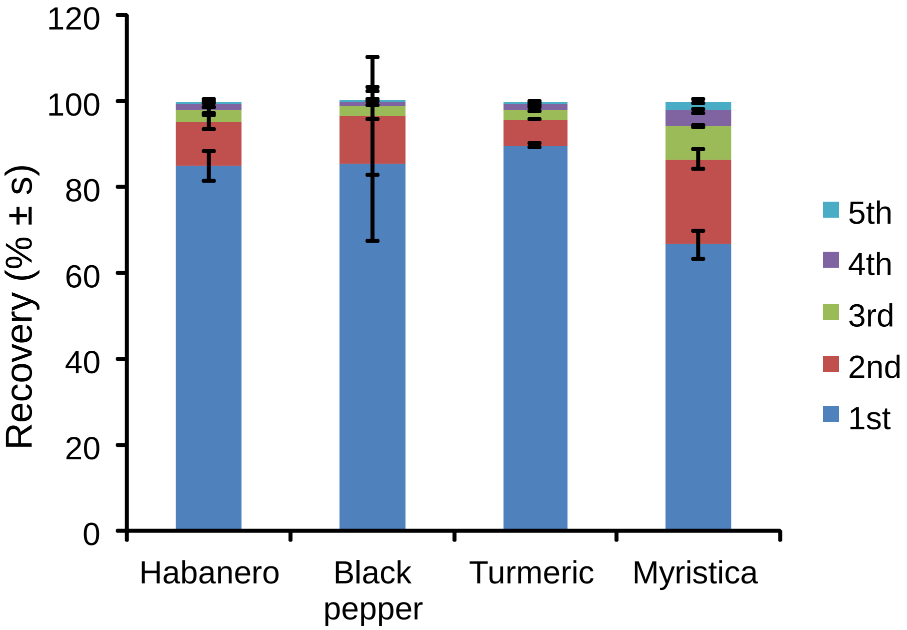
97 ± 9 ACN:H_2O

96 ± 2 EtOH:H_2O

↓

60 %EtOH
100 mL
20 sec

Results – Extraction efficiency

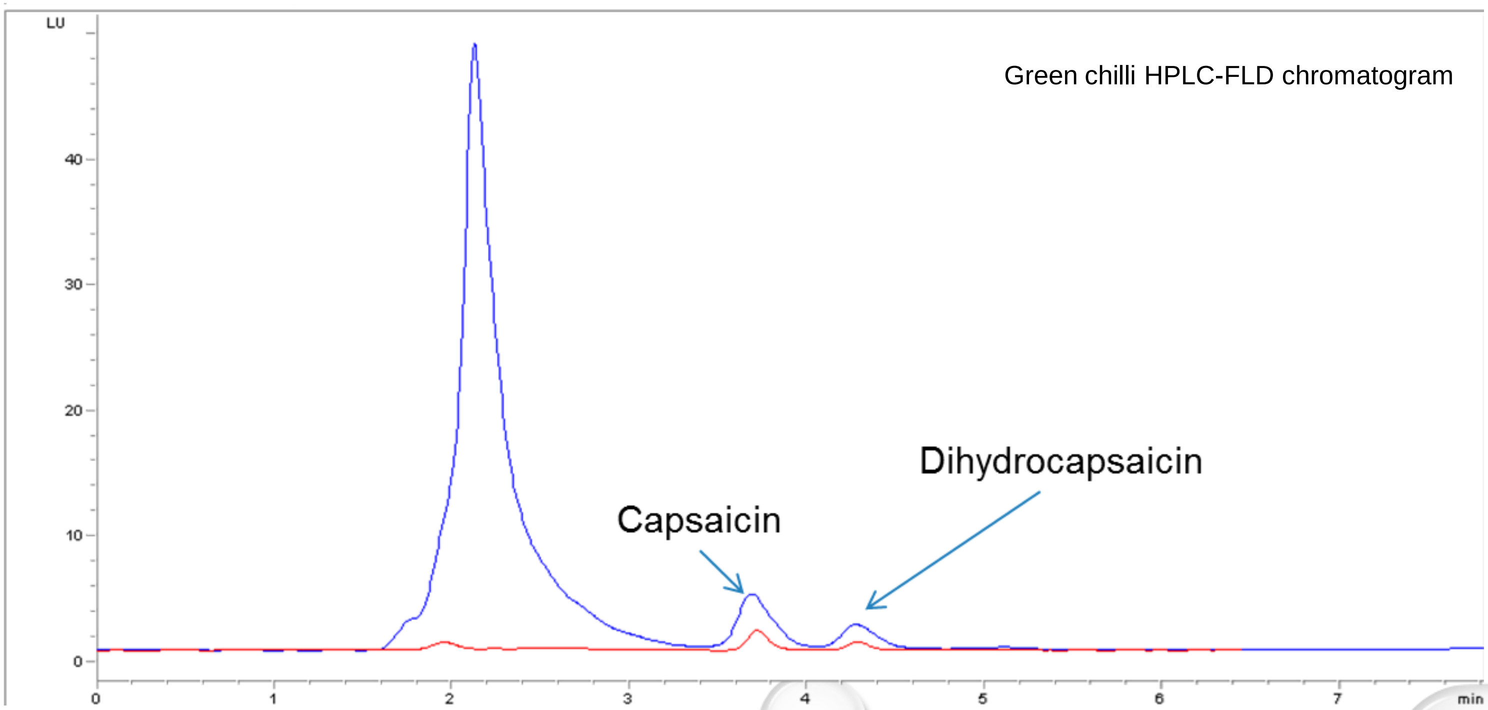


2 g sample, total capsaicin, piperine, curcumin and myristicin extracted with 5 x 50 mL of ethanol:water mixtures and analyzed HPLC-FLD

LOQ 0.07 to 0.31 mg g^{-1}

Results – HPLC-FLD cromatograms

Compound	RT (min) [b]	UV λ (nm)	FD λ (nm)	LOD (mg L^{-1})	LOQ (mg L^{-1})	LOQ_{AM}(mg g^{-1})
Curcumin	8.3	420	420 → 525	1.0	3.3	0.16
Piperine	8.8	340	350 → 435	1.9	6.3	0.31
Capsaicin	8.8	280	230 → 323	0.4	1.4	0.07
Dihydrocapsaicin	9.2	280	230 → 323	0.8	2.6	0.13
Myristicin	9.9	240	230 → 400	1.2	4.0	0.30


Green chilli HPLC-FLD chromatogram

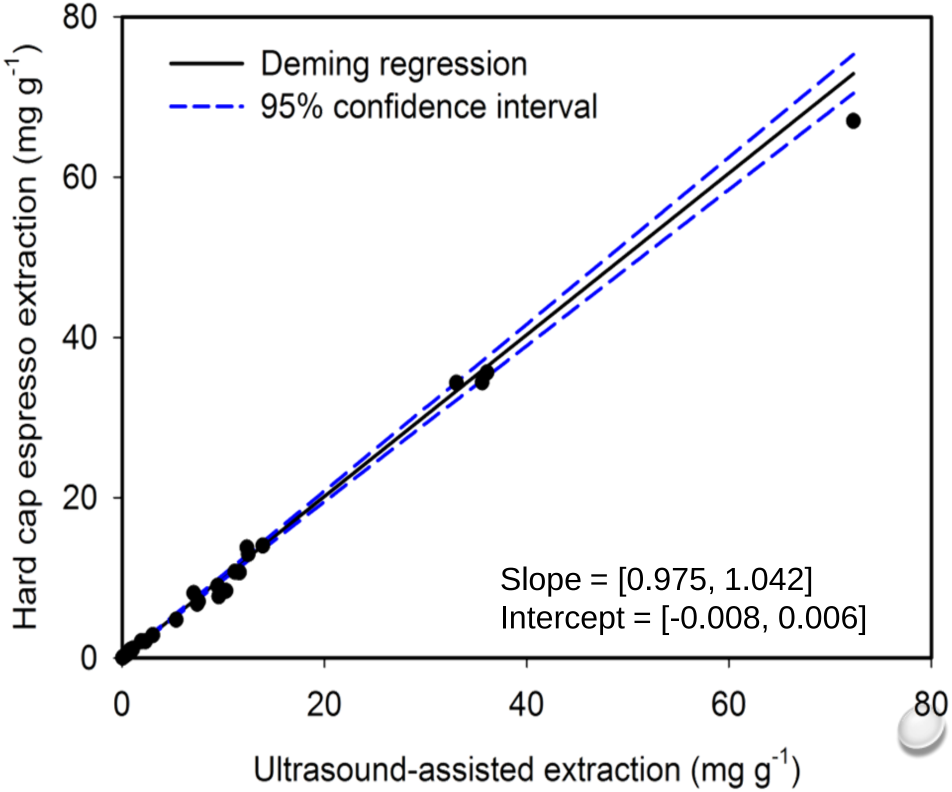
Results – Method Validation

28 commercial spice samples

Hard cap extraction

Ultrasounds assisted extraction

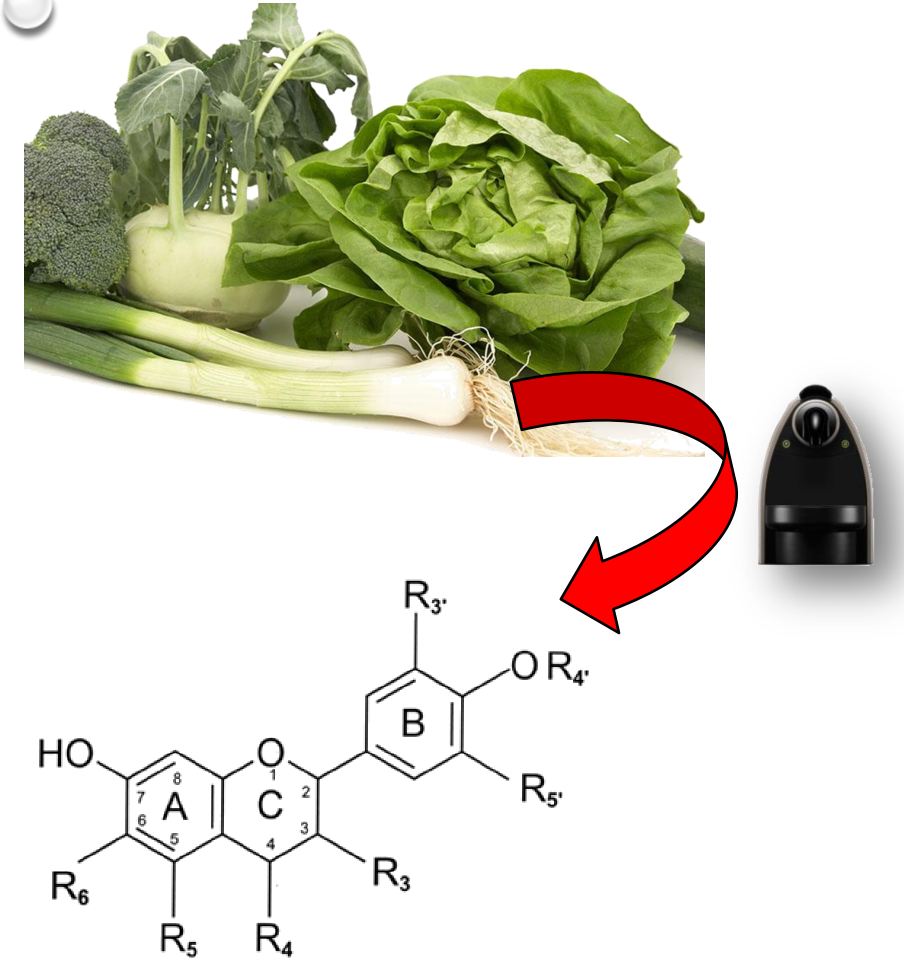
Method comparison (UAE)



Slope = [0.975, 1.042]
Intercept = [-0.008, 0.006]

Conclusions – What more?

Flavonoids in vegetables



Pesticides in air filters

Conclusions

- ✓ Easy, rapid, and low cost extraction.
- ✓ High sensitivity and compatibility with gas chromatography techniques.
- ✓ Hard cap espresso machine has been employed for the efficient extraction of PAHs, PCBs and bioactive compounds.
- ✓ Results statistically comparable with reference extraction methods.

Low-cost serum analysis

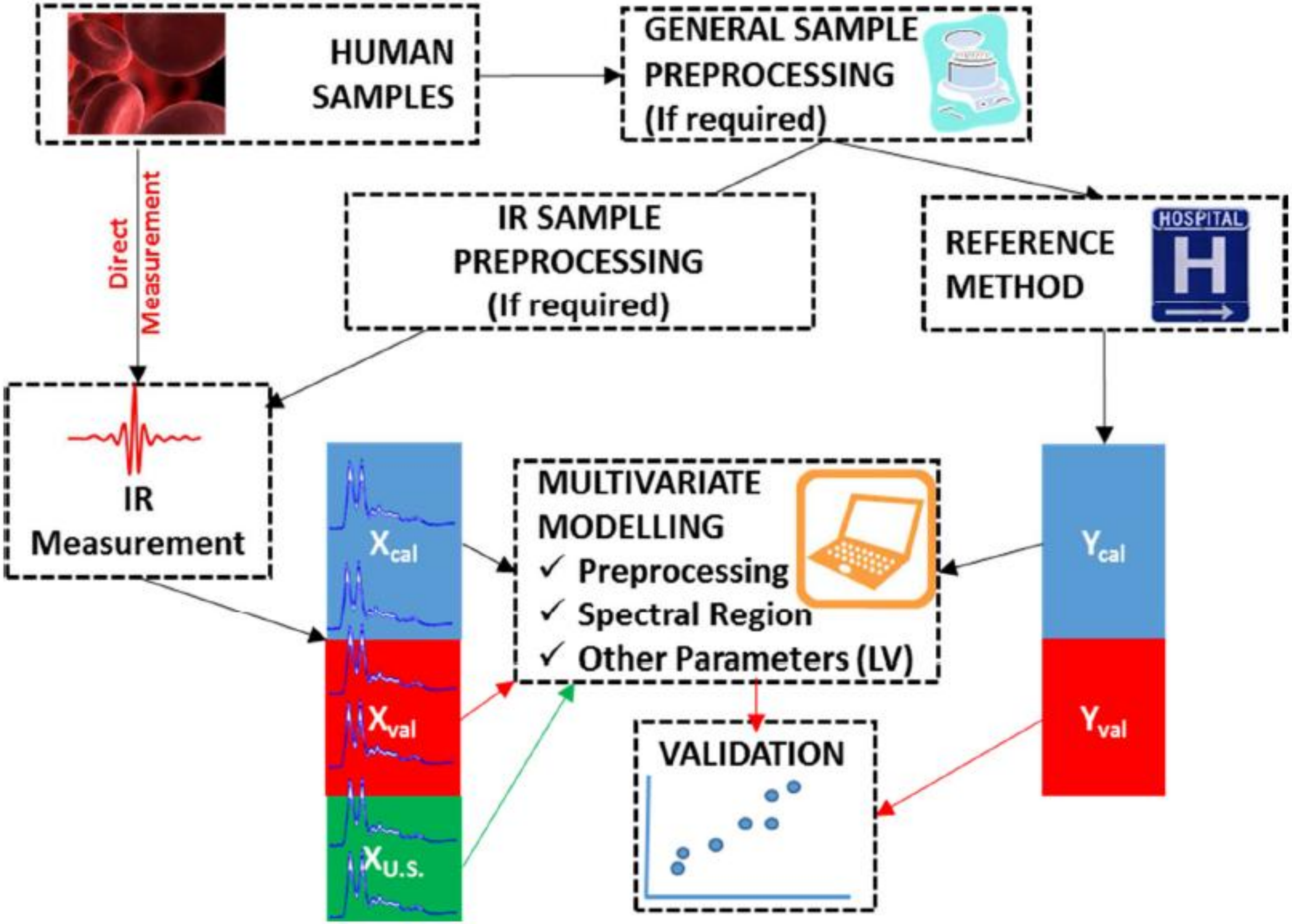


Figure 1.3: *The general process employed for performing and validating an IR based clinical method.* ***Note:*** *LV, latent variables; X_{cal}, spectra of the calibration set; X_{val}, spectra of the validation set; $X_{U.S}$, spectra of the unknown samples; Y_{cal}, reference data of the calibration set; Y_{val}, Reference data of the validation set.*

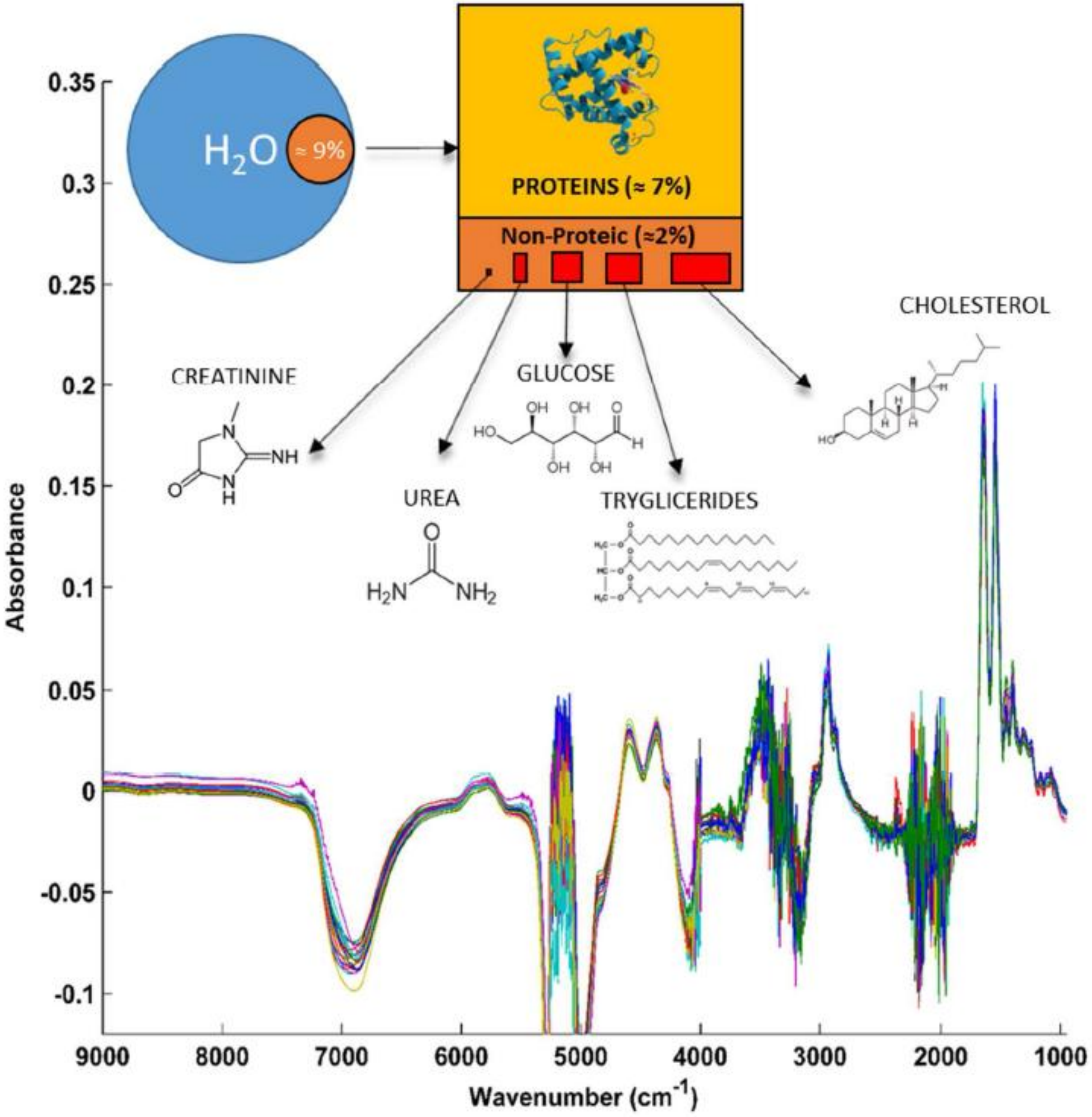


Figure 3.1: *MIR and NIR spectra of serum samples and images of the structure of the main analytes which are found in serum.*

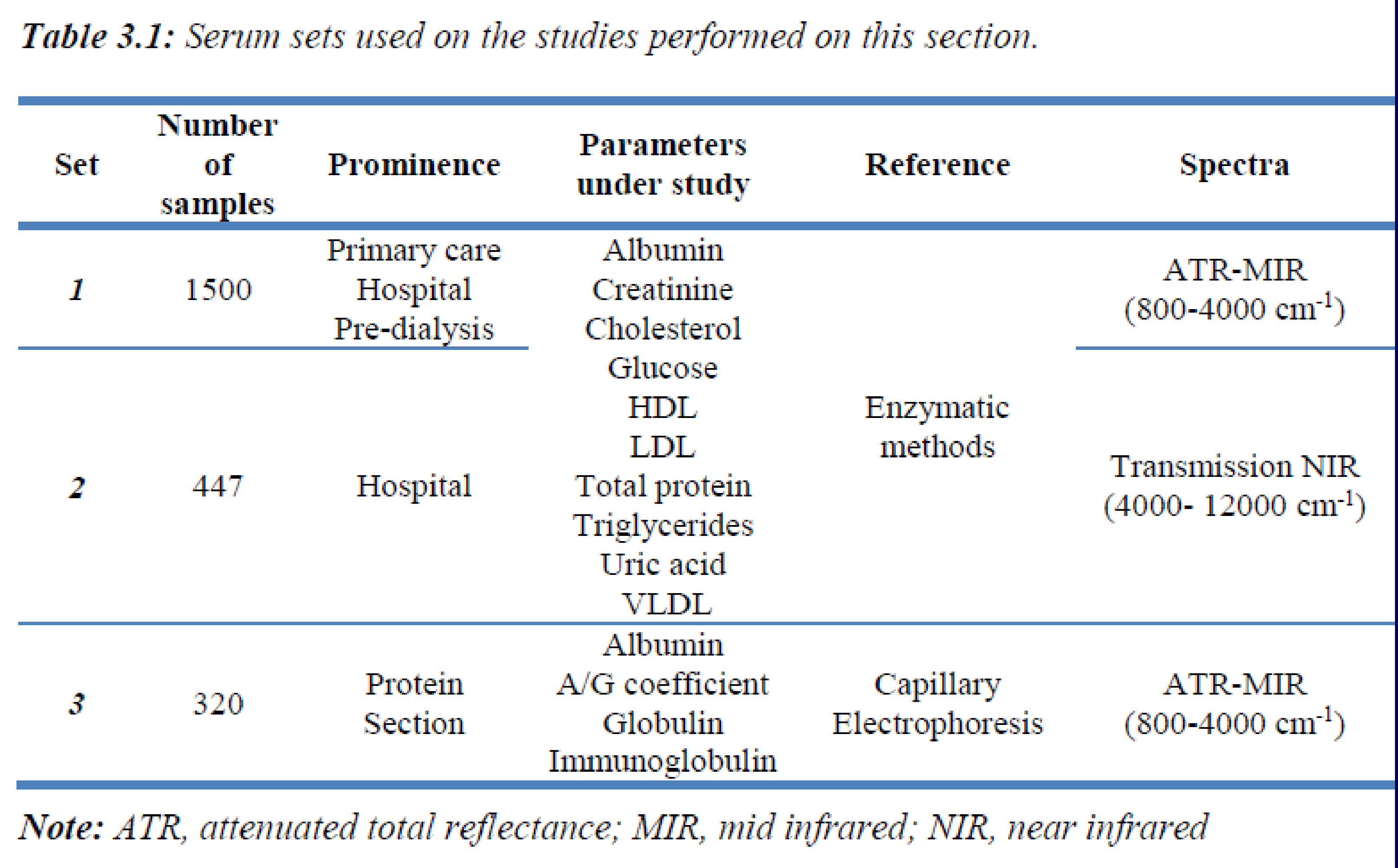


Table 3.1: *Serum sets used on the studies performed on this section.*

Set	**Number of samples**	**Prominence**	**Parameters under study**	**Reference**	**Spectra**
1	1500	Primary care Hospital Pre-dialysis	Albumin Creatinine Cholesterol Glucose HDL LDL Total protein Triglycerides Uric acid VLDL	Enzymatic methods	ATR-MIR (800-$4000\ cm^{-1}$)
2	447	Hospital			Transmission NIR (4000- $12000\ cm^{-1}$)
3	320	Protein Section	Albumin A/G coefficient Globulin Immunoglobulin	Capillary Electrophoresis	ATR-MIR (800-$4000\ cm^{-1}$)

Note: *ATR, attenuated total reflectance; MIR, mid infrared; NIR, near infrared*

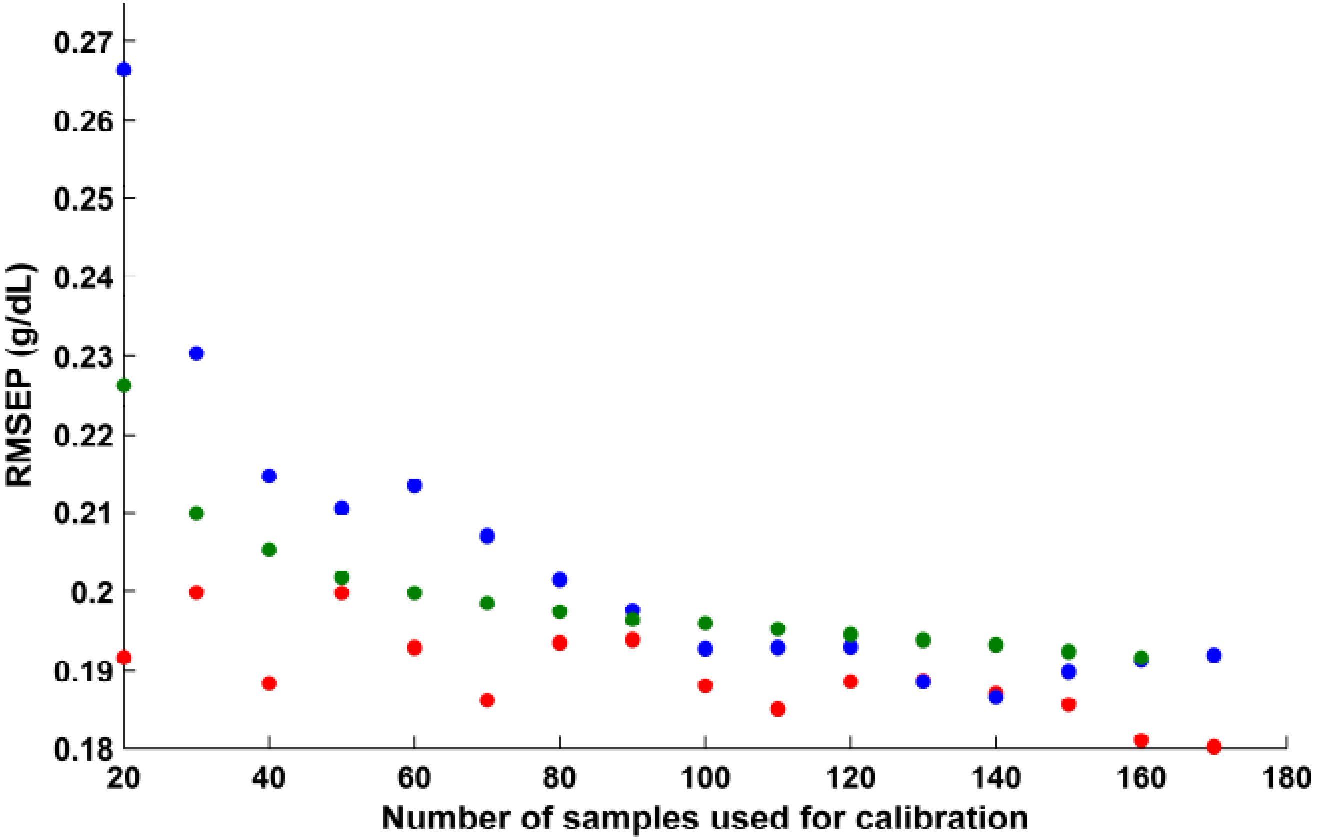


Figure 3.2: *Evolution of the RMSEP on the prediction of albumin as a function of the size of the calibration set for different strategies used for its selection: randomly selection (green), Kennard–Stone (red), and SPA (blue).*

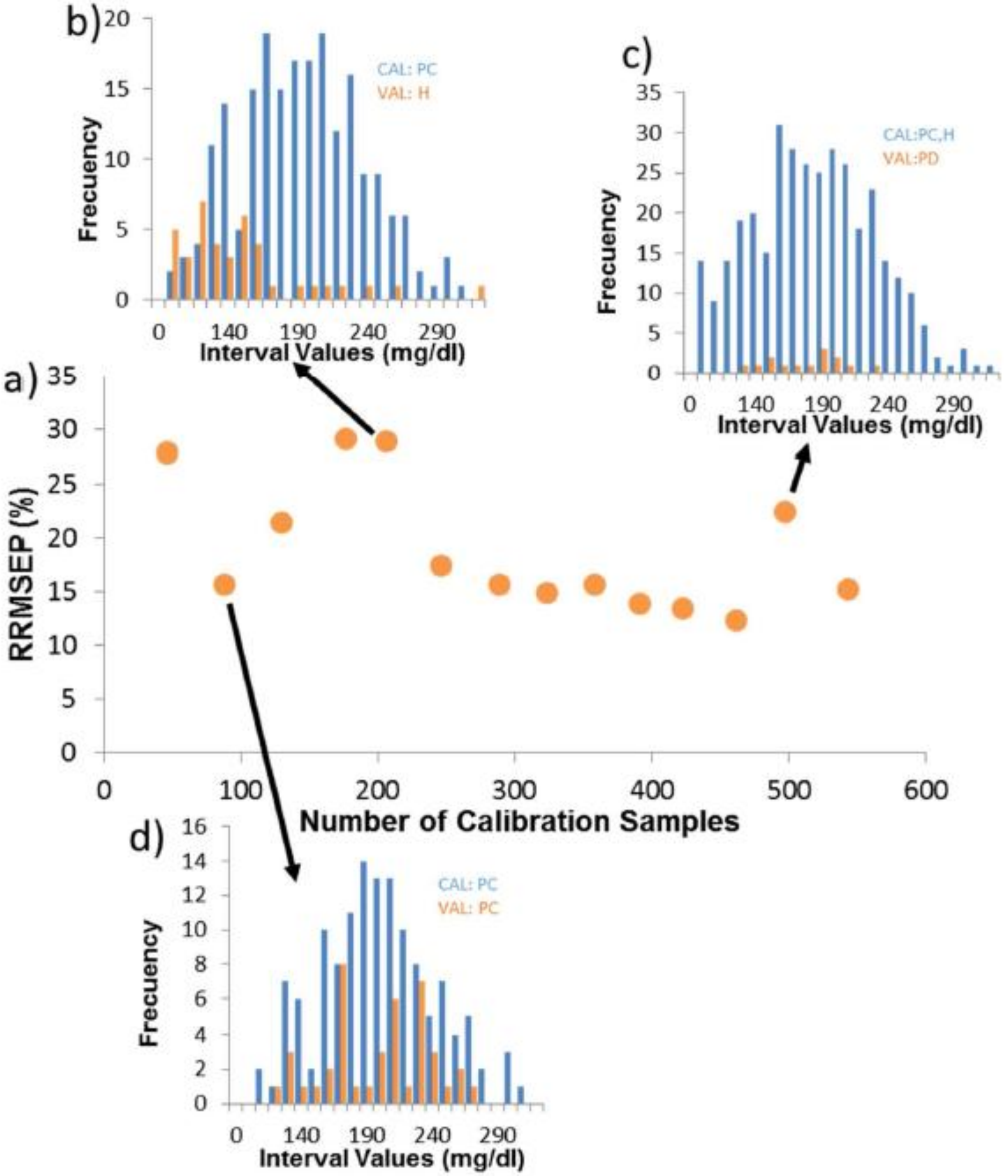


Figure 3.4 Evolution of the RRMSEP of the PLS-FTIR model with the size of the calibration set for the prediction of cholesterol from the MIR spectra (a). Distribution of sample reference values of calibration (blue) and validation (orange) for model 2, validated with a primary care sample set (b), model 4, validated with a hospital sample set (c) and model 13 validated with a pre-dialysis sample set (d). ***Note:*** *PC; primary care; H, hospital; PD, pre-dialysis.*

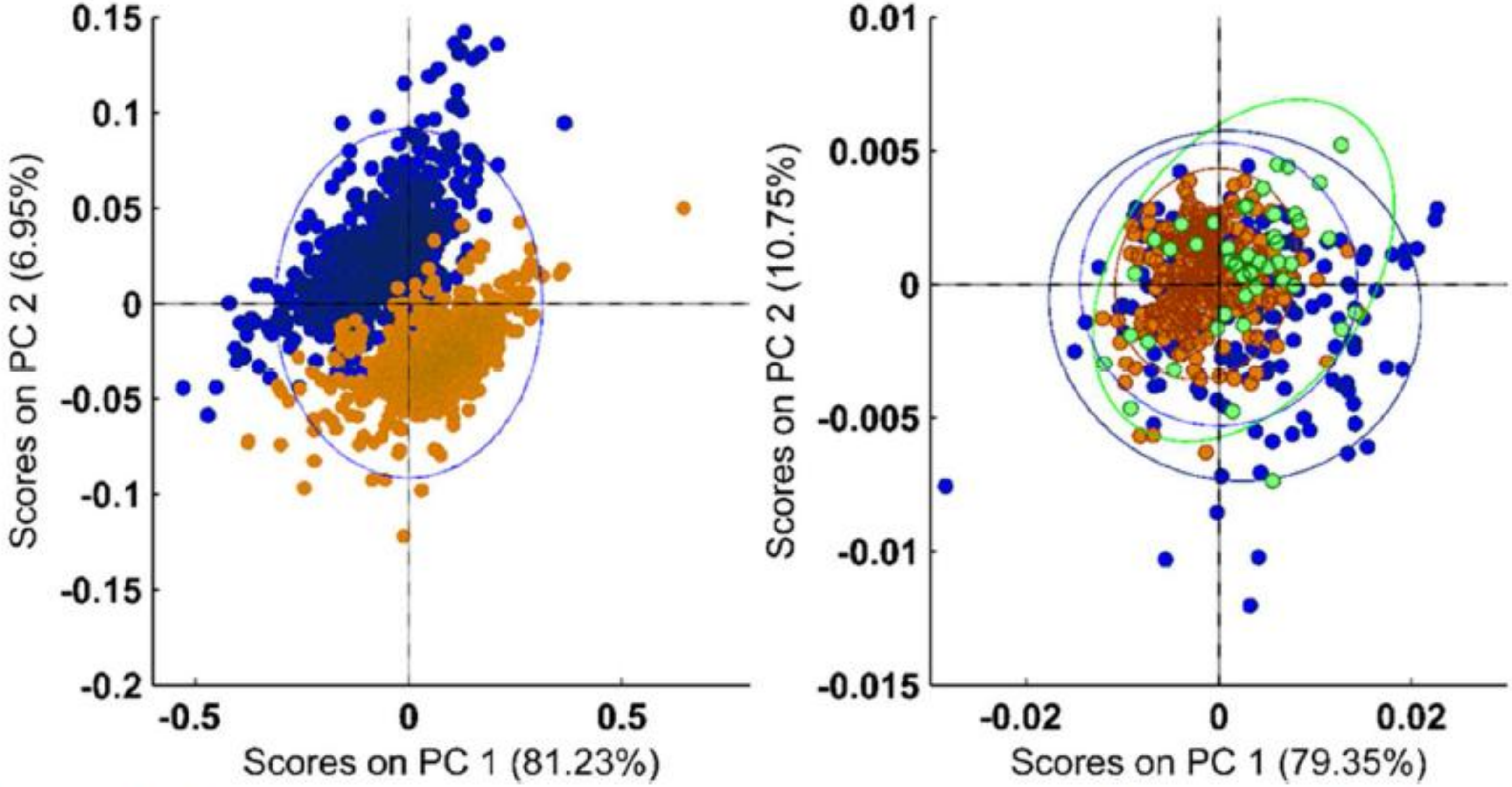


Figure 3.5. *PCA score plots of the PCA performed on the spectra of serum samples from different origins measured in different years. Left: Comparison of the spectra acquired the first year (blue) and those acquired the second year (orange). Right: Spectra of samples obtained the first year, colored according to their origin: Primary care (orange), hospital (blue) and pre-dialysis (green).*

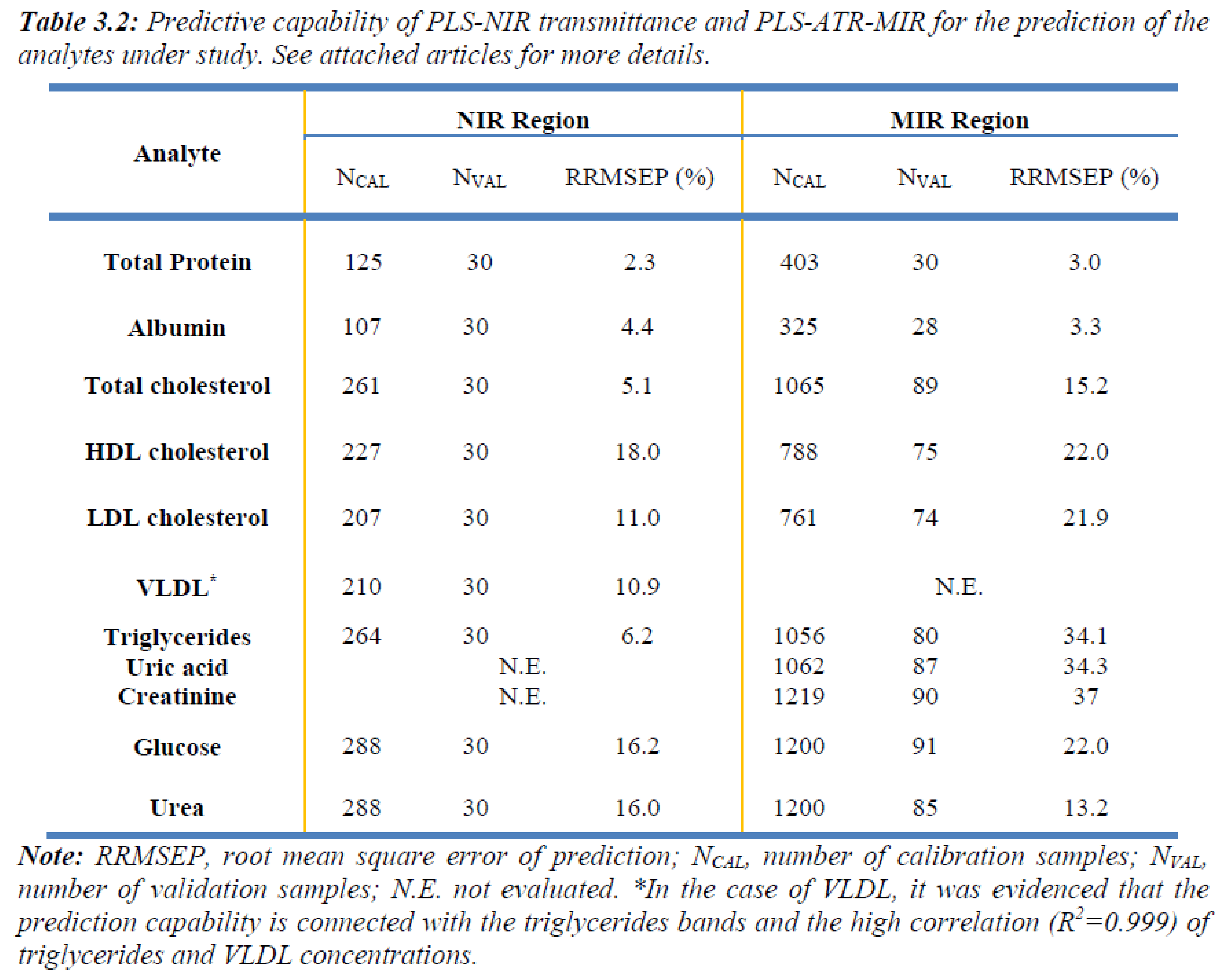


Table 3.2: *Predictive capability of PLS-NIR transmittance and PLS-ATR-MIR for the prediction of the analytes under study. See attached articles for more details.*

Analyte	NIR Region			MIR Region		
	N_{CAL}	N_{VAL}	RRMSEP (%)	N_{CAL}	N_{VAL}	RRMSEP (%)
Total Protein	125	30	2.3	403	30	3.0
Albumin	107	30	4.4	325	28	3.3
Total cholesterol	261	30	5.1	1065	89	15.2
HDL cholesterol	227	30	18.0	788	75	22.0
LDL cholesterol	207	30	11.0	761	74	21.9
VLDL*	210	30	10.9	N.E.		
Triglycerides	264	30	6.2	1056	80	34.1
Uric acid	N.E.			1062	87	34.3
Creatinine	N.E.			1219	90	37
Glucose	288	30	16.2	1200	91	22.0
Urea	288	30	16.0	1200	85	13.2

Note: *RRMSEP, root mean square error of prediction;* N_{CAL}*, number of calibration samples;* N_{VAL}*, number of validation samples; N.E. not evaluated. *In the case of VLDL, it was evidenced that the prediction capability is connected with the triglycerides bands and the high correlation (*$R^2=0.999$*) of triglycerides and VLDL concentrations.*

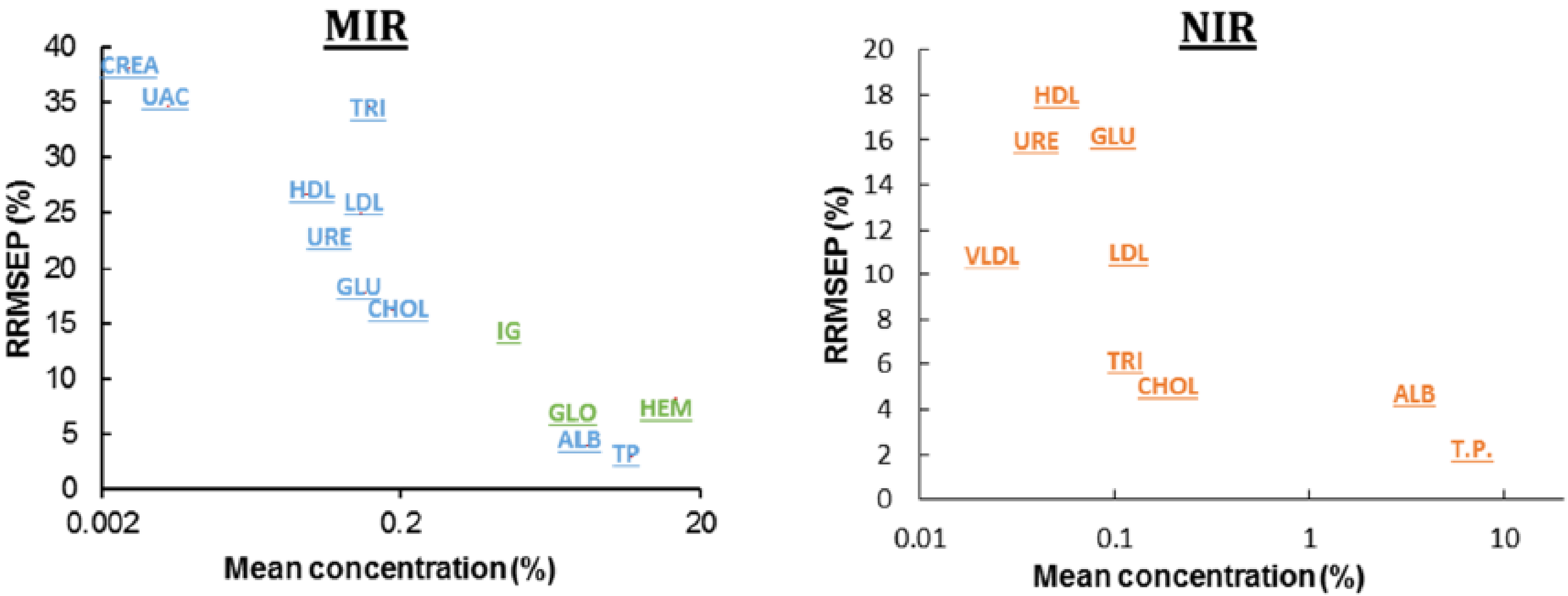


Figure 3.6: *Representation of the relative root mean square error of prediction (RRMSEP) of PLS-IR models built as a function of the mean concentration of the target analyte for the studies performed using the MIR range (left) and the NIR (right) ranges. Blue indicates results from the* ***Article 1****, green indicates results from the* ***Article 3*** *and orange indicates results from the* ***Article 2****.* ***Note:*** *ALB, albumin; CHOL, cholesterol; CRE, creatinine; GLB, globulin; GLU, glucose; HDL, high density lipoprotein; HEM, hemoglobin; Ig, immunoglobulin; LDL, low density lipoprotein; TRI, triglycerides; T.P., total protein; UAC, uric acid; URE, urea.*

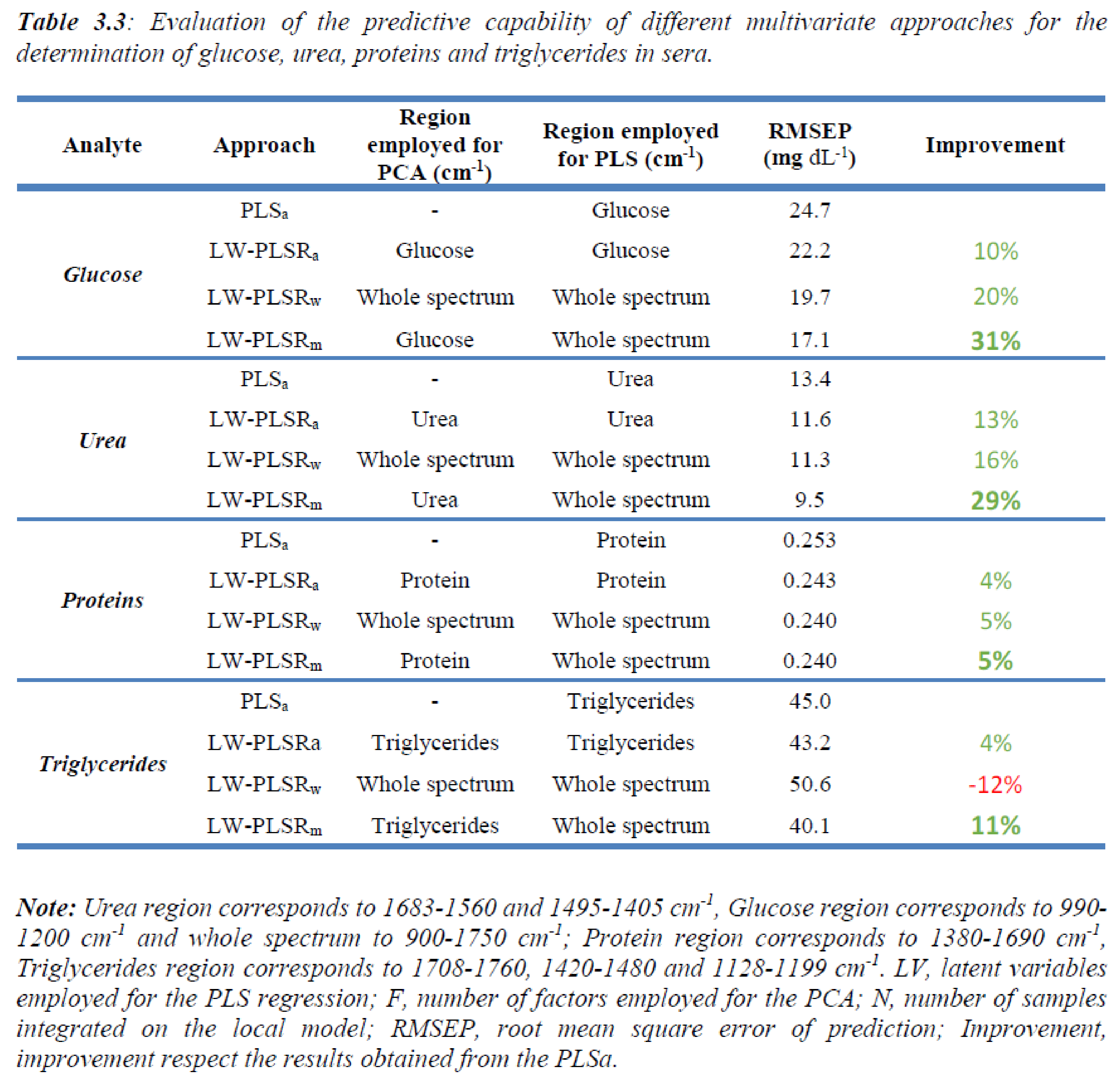


***Table 3.3**: Evaluation of the predictive capability of different multivariate approaches for the determination of glucose, urea, proteins and triglycerides in sera.*

Analyte	Approach	Region employed for PCA (cm^{-1})	Region employed for PLS (cm^{-1})	RMSEP (mg dL^{-1})	Improvement
Glucose	PLS$_a$	-	Glucose	24.7	
	LW-PLSR$_a$	Glucose	Glucose	22.2	10%
	LW-PLSR$_w$	Whole spectrum	Whole spectrum	19.7	20%
	LW-PLSR$_m$	Glucose	Whole spectrum	17.1	**31%**
Urea	PLS$_a$	-	Urea	13.4	
	LW-PLSR$_a$	Urea	Urea	11.6	13%
	LW-PLSR$_w$	Whole spectrum	Whole spectrum	11.3	16%
	LW-PLSR$_m$	Urea	Whole spectrum	9.5	**29%**
Proteins	PLS$_a$	-	Protein	0.253	
	LW-PLSR$_a$	Protein	Protein	0.243	4%
	LW-PLSR$_w$	Whole spectrum	Whole spectrum	0.240	5%
	LW-PLSR$_m$	Protein	Whole spectrum	0.240	**5%**
Triglycerides	PLS$_a$	-	Triglycerides	45.0	
	LW-PLSRa	Triglycerides	Triglycerides	43.2	4%
	LW-PLSR$_w$	Whole spectrum	Whole spectrum	50.6	-12%
	LW-PLSR$_m$	Triglycerides	Whole spectrum	40.1	**11%**

***Note:** Urea region corresponds to 1683-1560 and 1495-1405 cm^{-1}, Glucose region corresponds to 990-1200 cm^{-1} and whole spectrum to 900-1750 cm^{-1}; Protein region corresponds to 1380-1690 cm^{-1}, Triglycerides region corresponds to 1708-1760, 1420-1480 and 1128-1199 cm^{-1}. LV, latent variables employed for the PLS regression; F, number of factors employed for the PCA; N, number of samples integrated on the local model; RMSEP, root mean square error of prediction; Improvement, improvement respect the results obtained from the PLSa.*

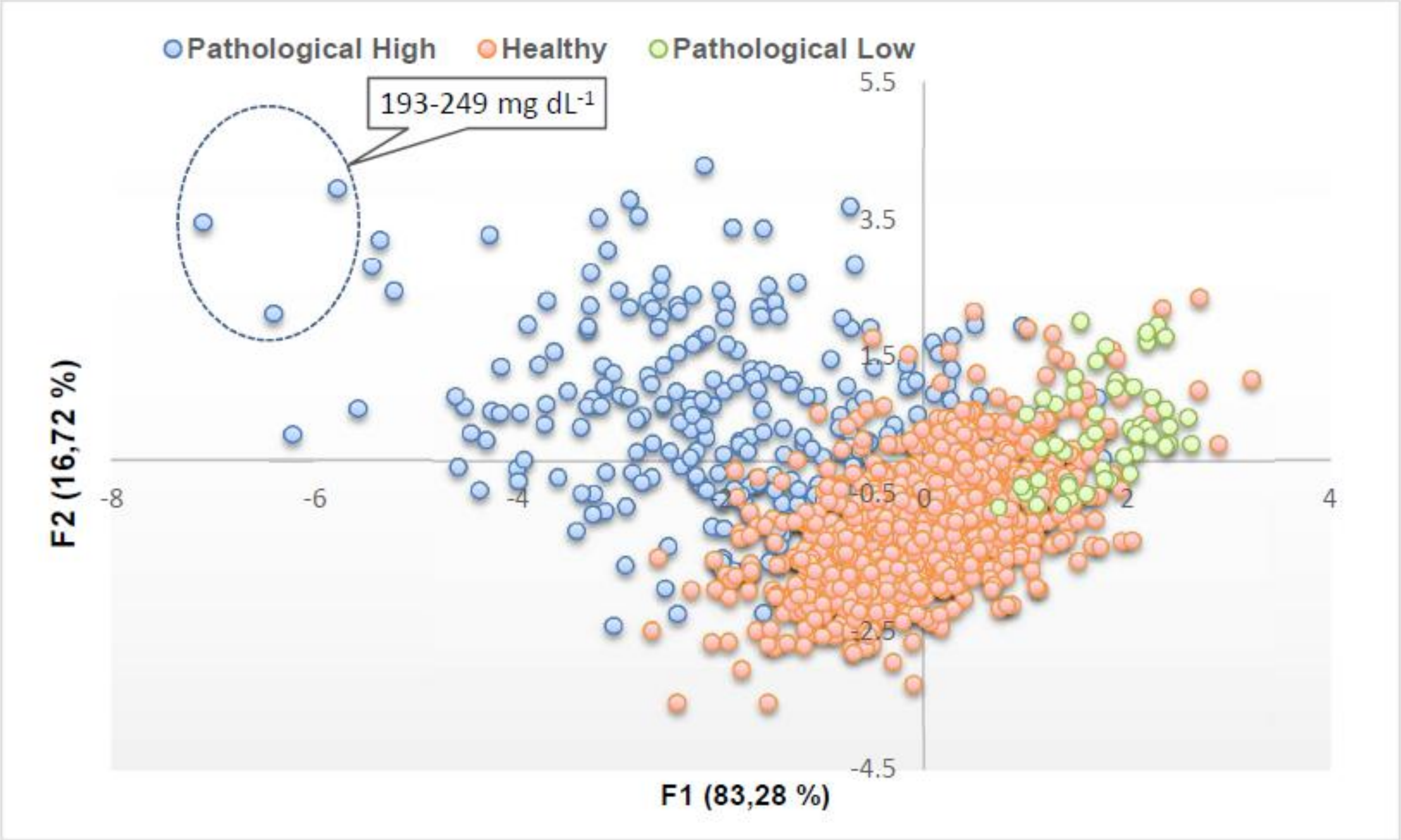


Figure 3.9: *Canonical coordinates for LDA discrimination of sera samples based on urea values.* ***Note:*** *samples indicated with arrows on the blue circle correspond to those with concentrations from 193 till 249 mg dL^{-1}.*

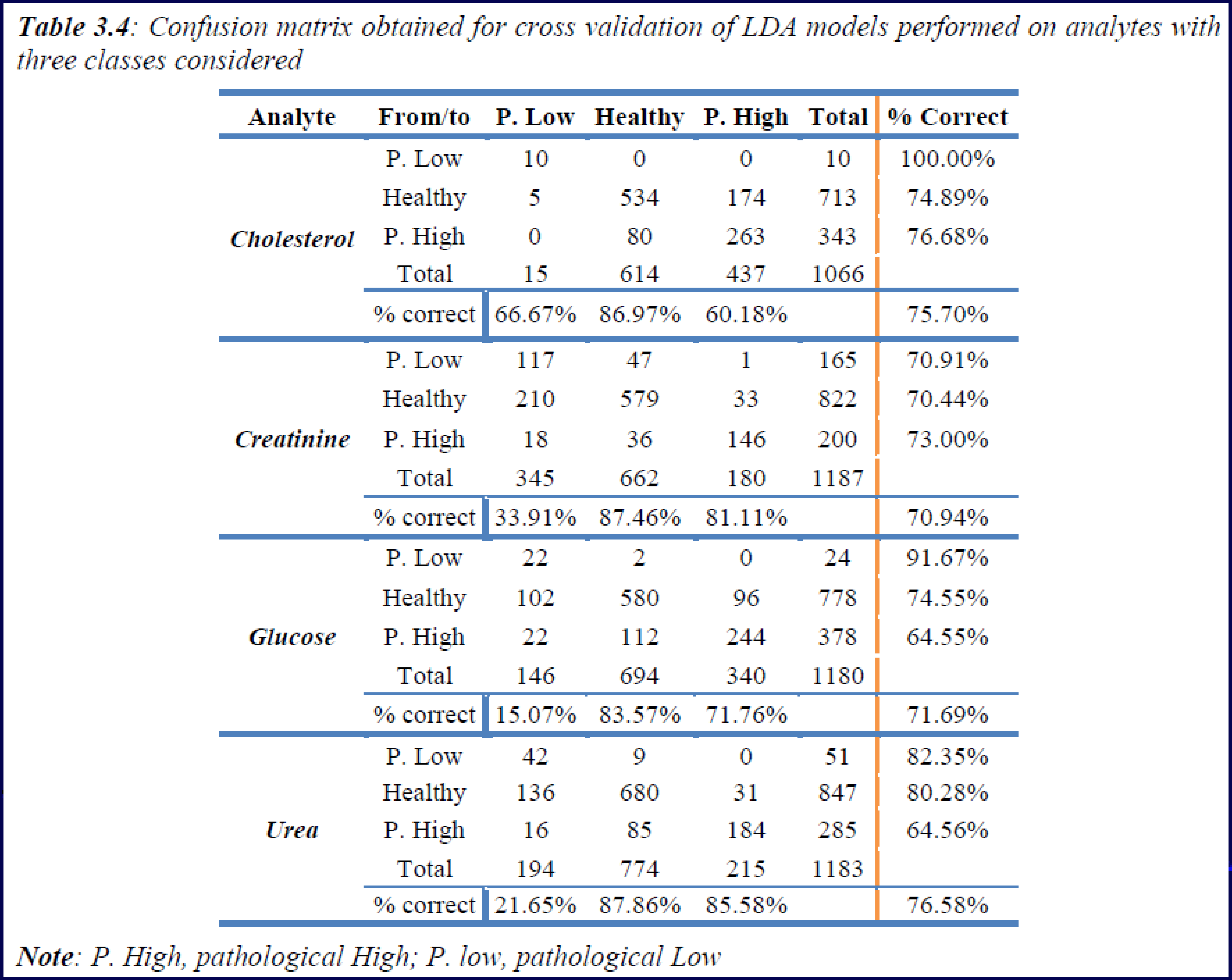


***Table 3.4**: Confusion matrix obtained for cross validation of LDA models performed on analytes with three classes considered*

Analyte	From/to	P. Low	Healthy	P. High	Total	% Correct
Cholesterol	P. Low	10	0	0	10	100.00%
	Healthy	5	534	174	713	74.89%
	P. High	0	80	263	343	76.68%
	Total	15	614	437	1066	
	% correct	66.67%	86.97%	60.18%		75.70%
Creatinine	P. Low	117	47	1	165	70.91%
	Healthy	210	579	33	822	70.44%
	P. High	18	36	146	200	73.00%
	Total	345	662	180	1187	
	% correct	33.91%	87.46%	81.11%		70.94%
Glucose	P. Low	22	2	0	24	91.67%
	Healthy	102	580	96	778	74.55%
	P. High	22	112	244	378	64.55%
	Total	146	694	340	1180	
	% correct	15.07%	83.57%	71.76%		71.69%
Urea	P. Low	42	9	0	51	82.35%
	Healthy	136	680	31	847	80.28%
	P. High	16	85	184	285	64.56%
	Total	194	774	215	1183	
	% correct	21.65%	87.86%	85.58%		76.58%

***Note**: P. High, pathological High; P. low, pathological Low*

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Evaluation of infrared spectroscopy as a screening tool for serum analysis Impact of the nature of samples included in the calibration set

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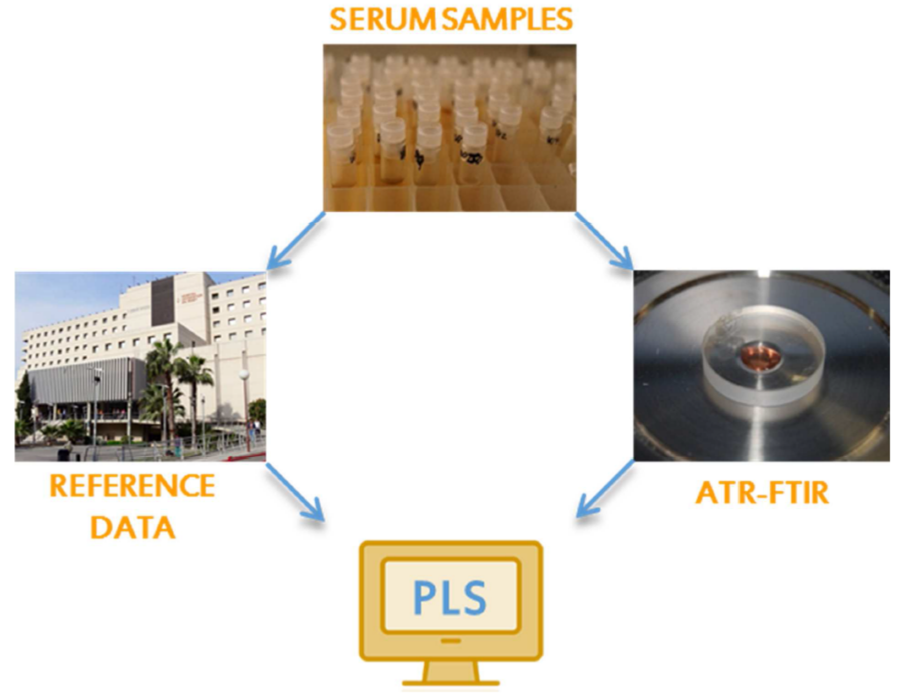

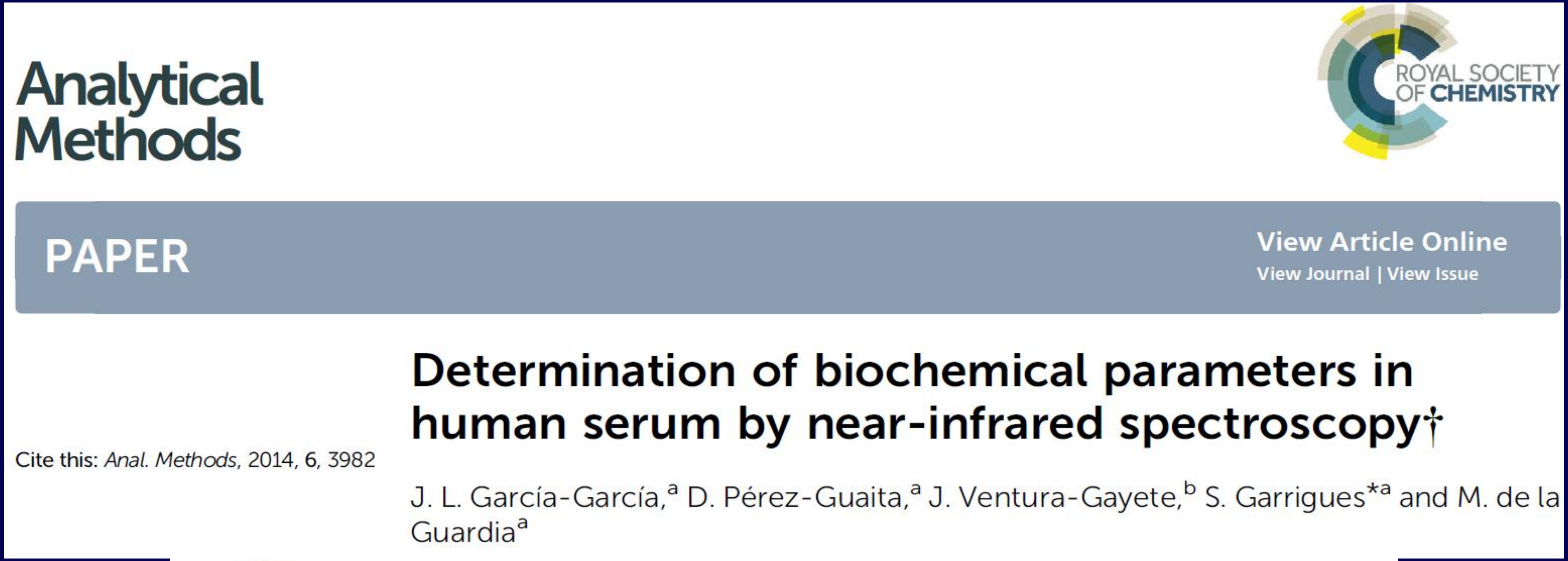

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Determination of biochemical parameters in human serum by near-infrared spectroscopy†

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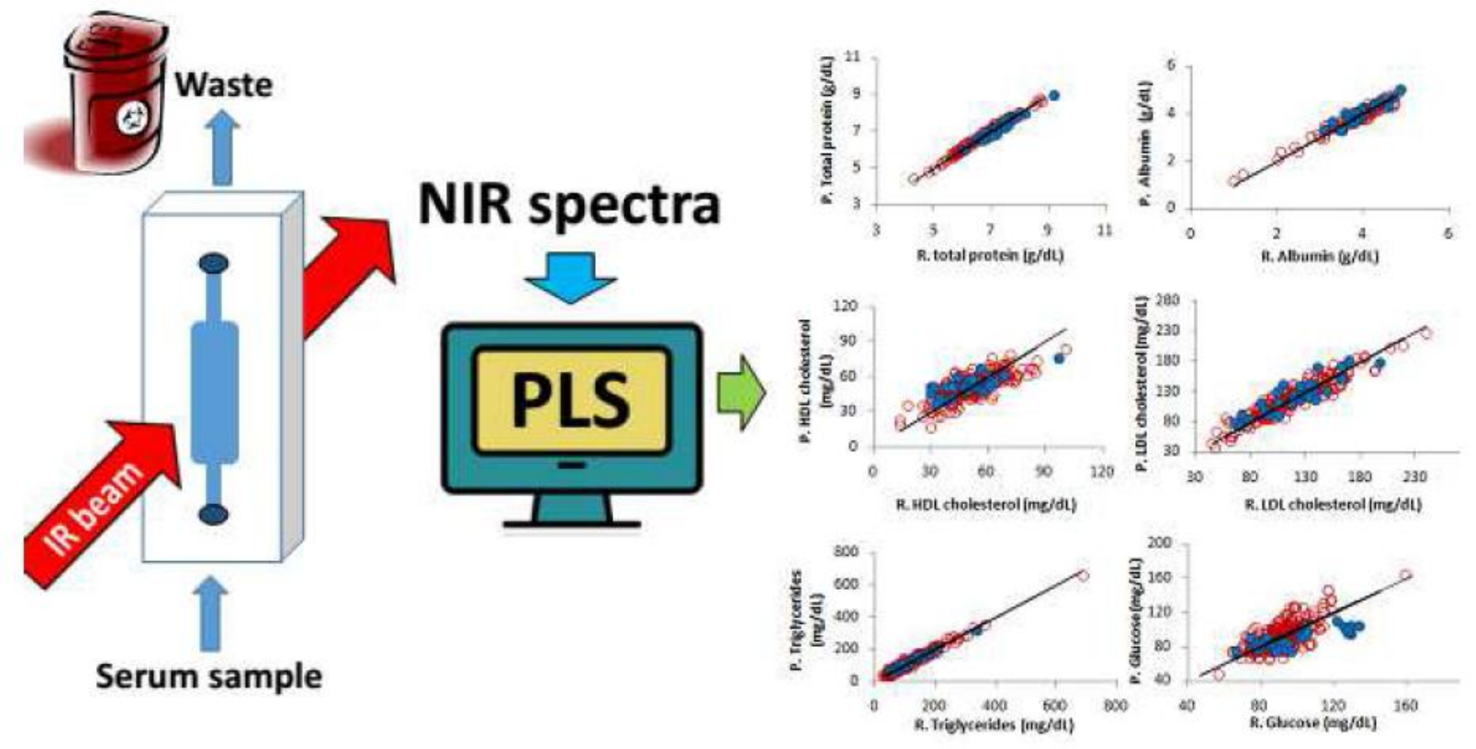
J. L. García-García,[a] D. Pérez-Guaita,[a] J. Ventura-Gayete,[b] S. Garrigues*[a] and M. de la Guardia[a]



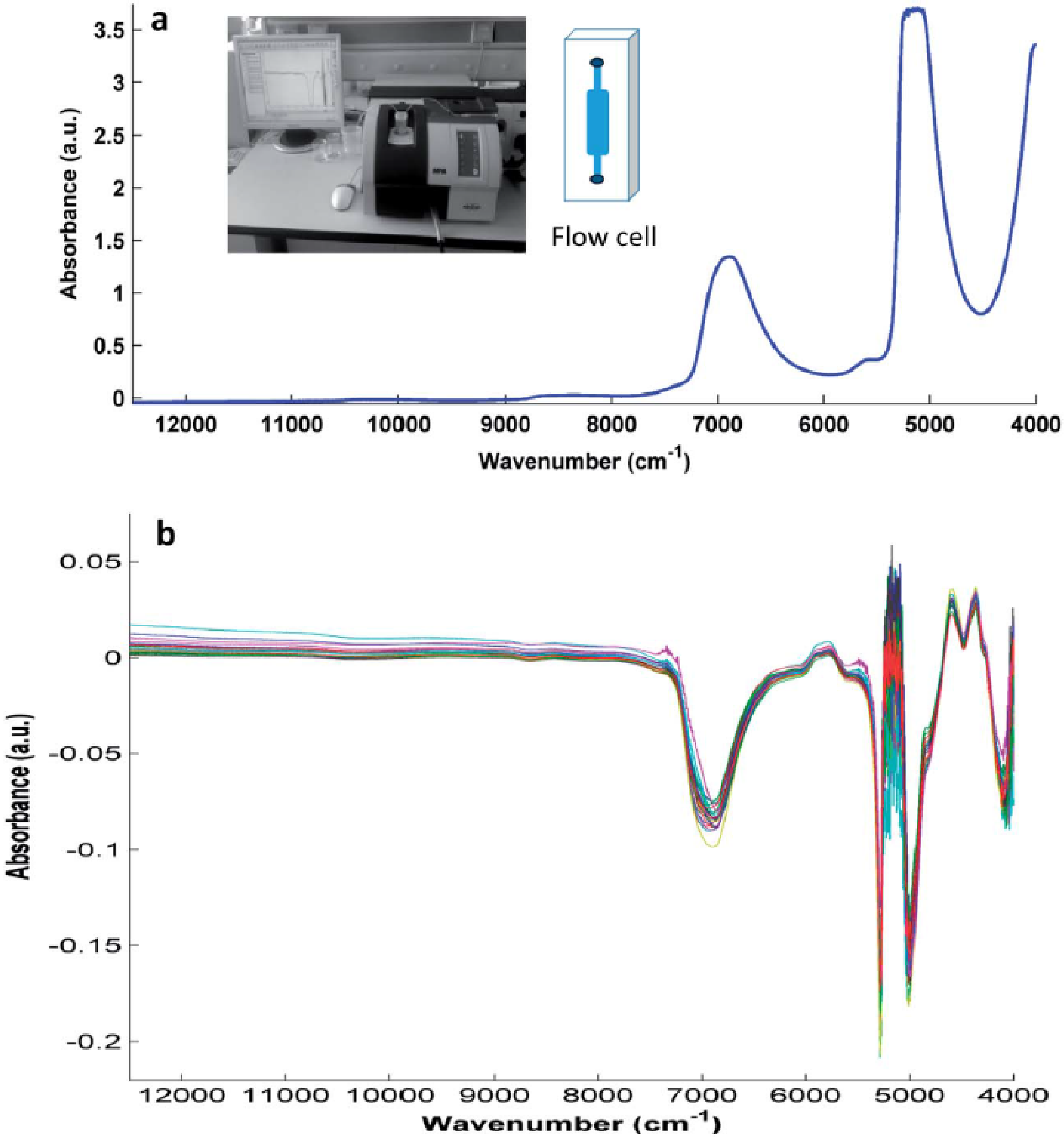


Fig. 1 NIR spectrum of a serum sample obtained using an empty flow cell as the background (a) and some serum absorption spectra after water subtraction (b). Inset: the setting and the cell employed for NIR spectra acquisition.

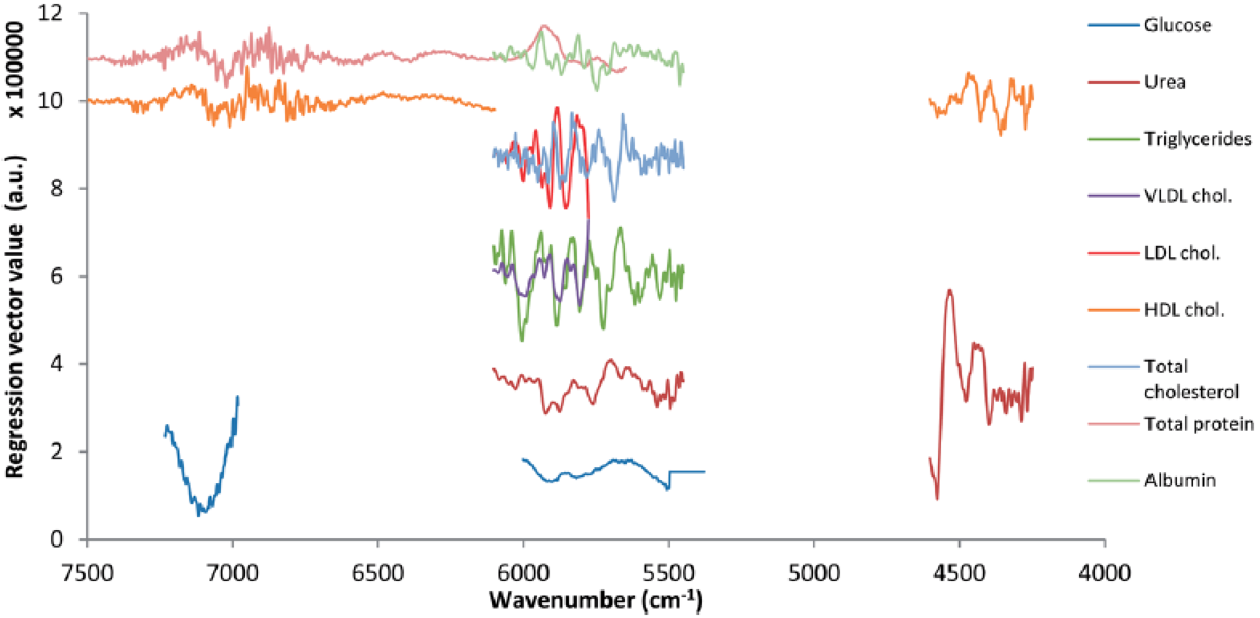


Fig. 3 Regression vectors of the models built through this study, with the analytes with higher correlation placed on the same *y*-axis. Note: spectra have been shifted on the *y*-axis and expanded in some cases for clarification. The region between 7500 and 10 000 cm^{-1} for albumin is available in SM2.†

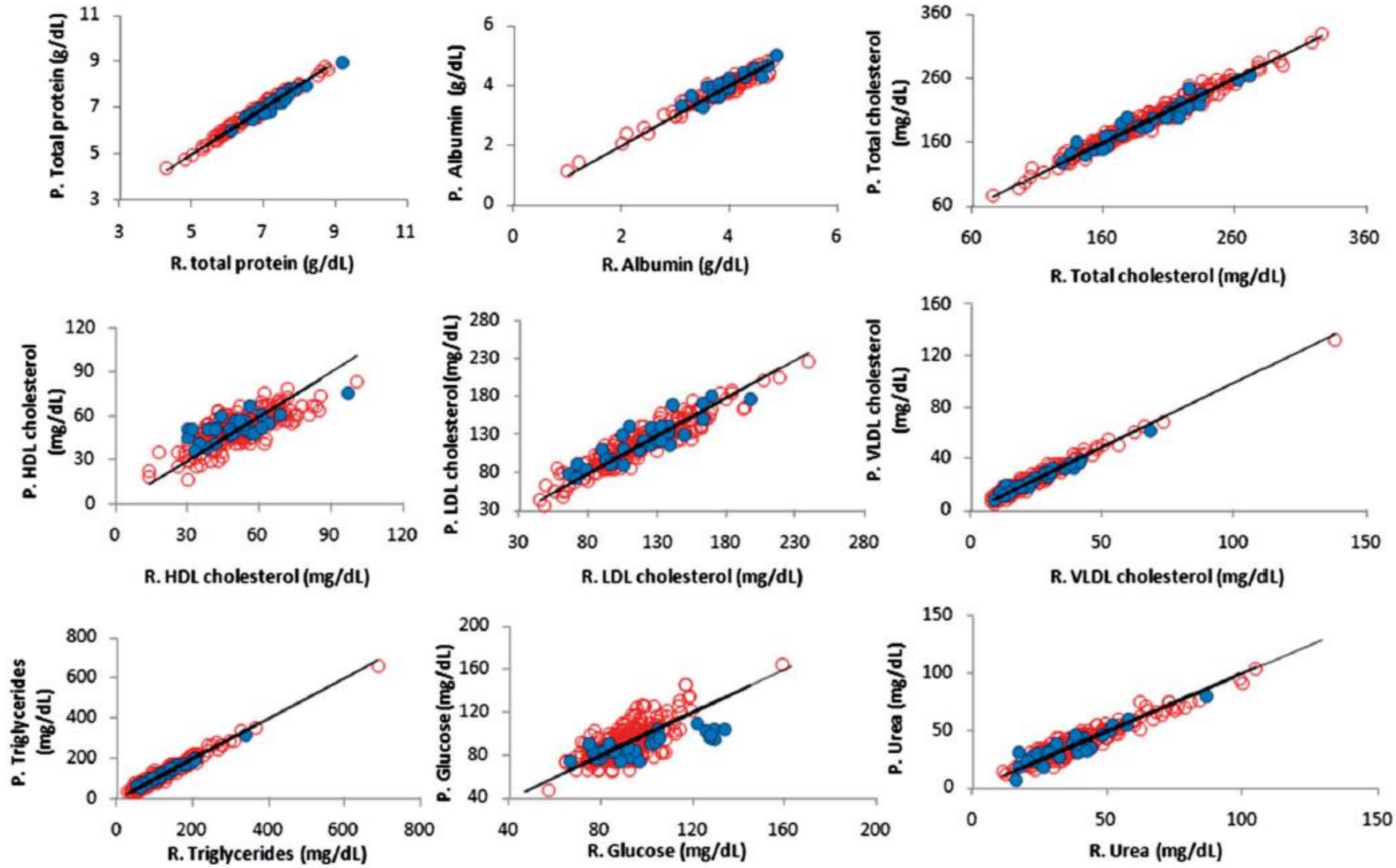


Fig. 4 Scattering plot showing a correlation between reference concentrations and NIR measurements for all the parameters under study. Red open and blue filled circles indicate the calibration and validation set respectively.

DEMOCRATIC ANALYTICAL CHEMISTRY

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CONCEPT of
DEMOCRATIC ANALYTICAL CHEMISTRY

from BENEFITS to DATA PRODUCTION

- Improved ACCES to low-cost ANALYTICAL METHODS
- POINT of CARE methodology
- REMOTE SENSING

- EASY AVAILABLE INSTRUMENTATION
- FREE ACCESS SOFTWARE in the CLOUD
- RESPONSIBLE DISTRIBUTION of DATA through SOCIAL NETWORKS

A SINGLE WORLD at HUMAN SCALE

OLD CONCEPTS

- COMPLEX & EXPENSIVE methodology
- Academic obscurantism
- Protected software
- Slow data transmission
- Closed & Protective reactionary mentalities
- LABORATORY as space of science production
- Sacred JOURNALS and academical sites

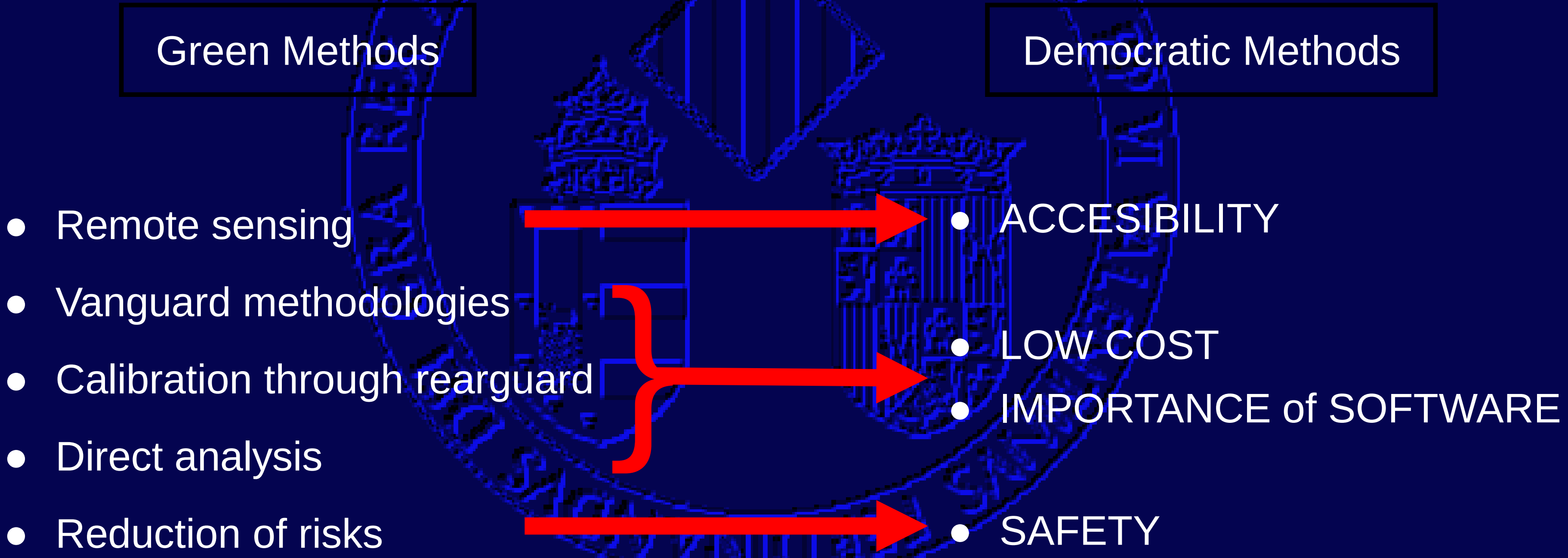
NEW SCENARIO

- Low cost instrumentation
- Easy measurement
- Free access software in the cloud
- Light speed data sharing
- Solidarity & Globalization
- On-site & Point-of-care data acquisition
- OPEN DIFUSSION of data & opinion

RISKS of DEMOCRATIC ANALYTICAL CHEMISTRY

- False data distribution → SELF CONTROL & POLICY
- Unexperienced data acquisition → IMPROVED EDUCATION
- Lack of representative data → IMPORTANCE of ANALYTICAL CHEMISTRY EDUCATION
- Irresponsible distribution of non-rigurous data → SOCIAL RESPONSIBILITY
- Misuse of true data → CRITICAL ATTITUDE of data receptors

FROM **GREEN** to **DEMOCRATIC** **ANALYTICAL CHEMISTRY**



Green Methods

- Remote sensing
- Vanguard methodologies
- Calibration through rearguard
- Direct analysis
- Reduction of risks

Democratic Methods

- ACCESIBILITY
- LOW COST
- IMPORTANCE of SOFTWARE
- SAFETY

INTERNET

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