Development of two methods for monitoring codfish desalting process based on flow injection analysis and Fourier-mid infrared spectroscopy

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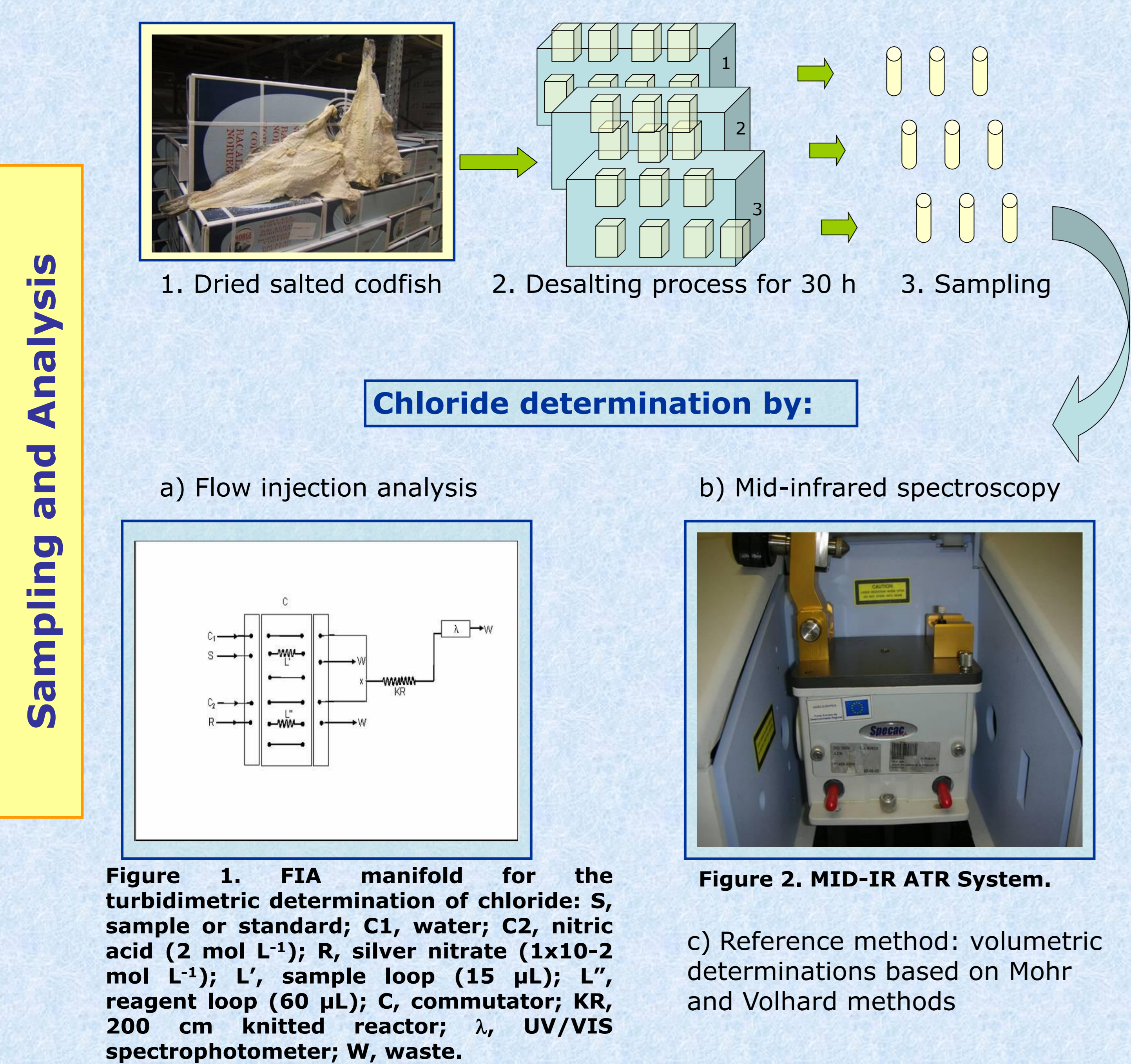[d]Pascoal e Filhos S.A. Gafanha da Nazaré, Aveiro, Portugal

Traditional analytical determinations for chloride are precise but are time consuming and difficult to perform for routine analysis.

A pronounced tendency towards "clean methods" was observed in the recent years:

Flow injection analysis (FIA) technique permits: automatic sample processing, high repeatability, adaptability to miniaturization, waste and reagent reduction.

Mid-infrared spectroscopy (MID-IR) allows in-situ monitoring and real-time analytical determinations.

The main objective of the present work was to compare the performance of a flow-injection (FIA) system and a mid-infrared (MID-IR) spectroscopy procedure for the determination of sodium chloride in the cod muscle and desalting solutions during cod desalting process.

Sampling and Analysis

1. Dried salted codfish   2. Desalting process for 30 h   3. Sampling

Chloride determination by:

a) Flow injection analysis

Figure 1. FIA manifold for the turbidimetric determination of chloride: S, sample or standard; C1, water; C2, nitric acid (2 mol L^{-1}); R, silver nitrate (1x10^{-2} mol L^{-1}); L', sample loop (15 µL); L'', reagent loop (60 µL); C, commutator; KR, 200 cm knitted reactor; λ, UV/VIS spectrophotometer; W, waste.

b) Mid-infrared spectroscopy

Figure 2. MID-IR ATR System.

c) Reference method: volumetric determinations based on Mohr and Volhard methods

Operation Conditions

Table 1. Characteristics of the FIA and IR-Spectroscopy methods

|	FIA	FT-MID
Mode	Turbidimetric	Attenuated total reflection
Detection system	Spectrophotometer (CCD-array detector, Ocean Optics)	Fourier Infrared – Spectrometer (Spectrum BX, Perkin–Elmer)
Spectral range	9090 – 50000 cm^{-1} (λ=425 nm)	600 – 4000 cm^{-1}
Accessories	Peristaltic pump (Gilson, Manipuls 3)	ATR Golden Gate (Specac)
	Cuvette holder (Ocean Optics)	
	Optical fibers (i.d: 300 µm)	
	Tungsten/halogen light source (DH-200, Mikropack)	
Software	SpectraSuite	Spectrum v.5.3.1 and CATS program[1]

Figures of Merit

Table 2. Analytical characteristics of the FIA and MID-IR ATR systems for the determination of sodium chloride.

|	FIA	FT-MID
LOD (g L^{-1})	0.04	5.0
LOQ (g L^{-1})	0.13	16.0
Working range (g L^{-1})	0.05 – 0.6	0 – 200
Determination rate / h	40	20
Reagent consumption per assay		Not used
Silver Nitrate	6.0 mg	
Polyvinyl alcohol	3.0 mg	
Nitric acid	3.1 g	

LOD: limit of detection
LOQ: limit of quantification

Results
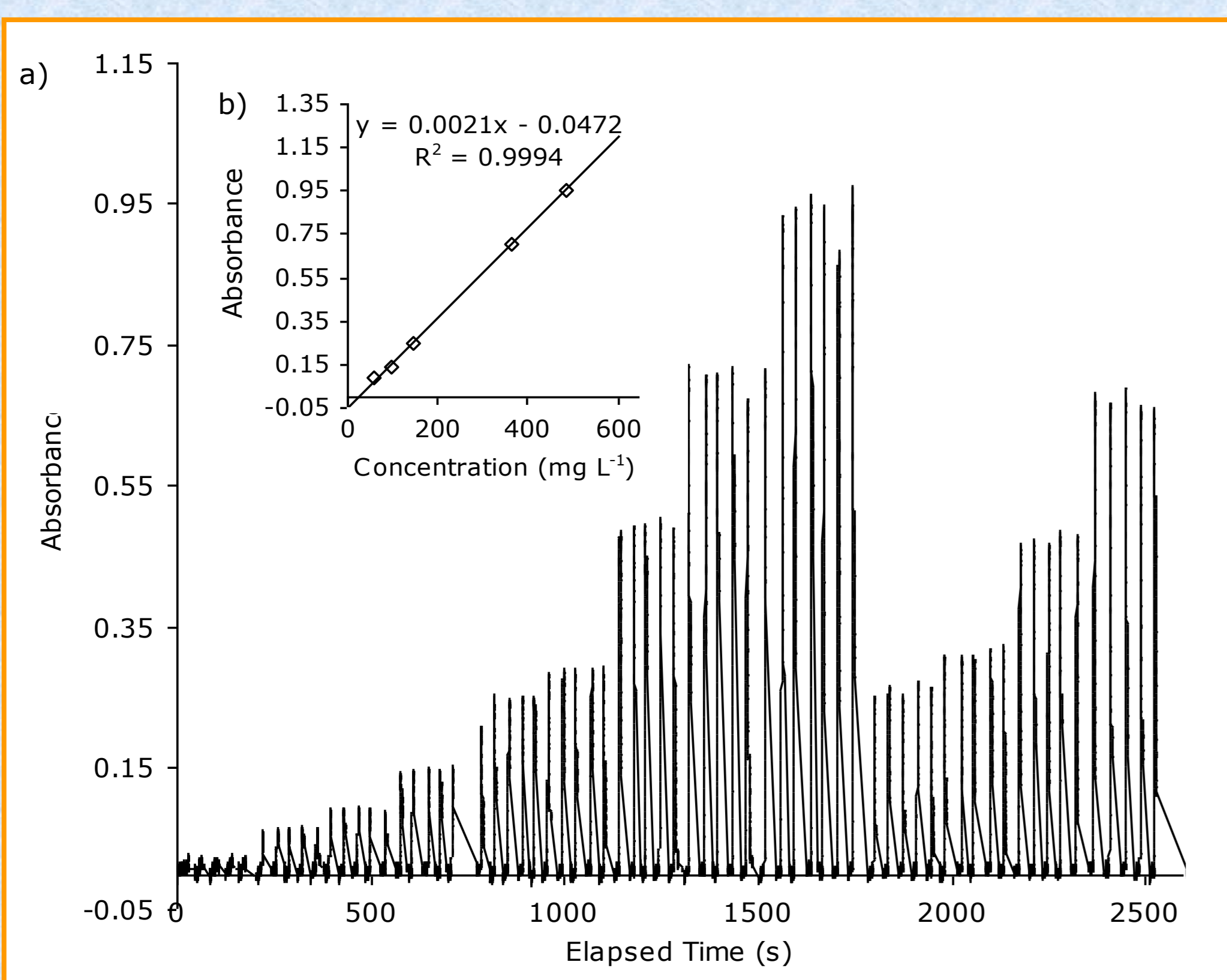
Figure 3. Flow injection peaks (a) of chloride working standard solutions and codfish extracts; calibration curve (b) from 0.05 to 0.6 g L^{-1} NaCl.

y = 0,991x + 0,460
LV = 2
R^2 = 0,981
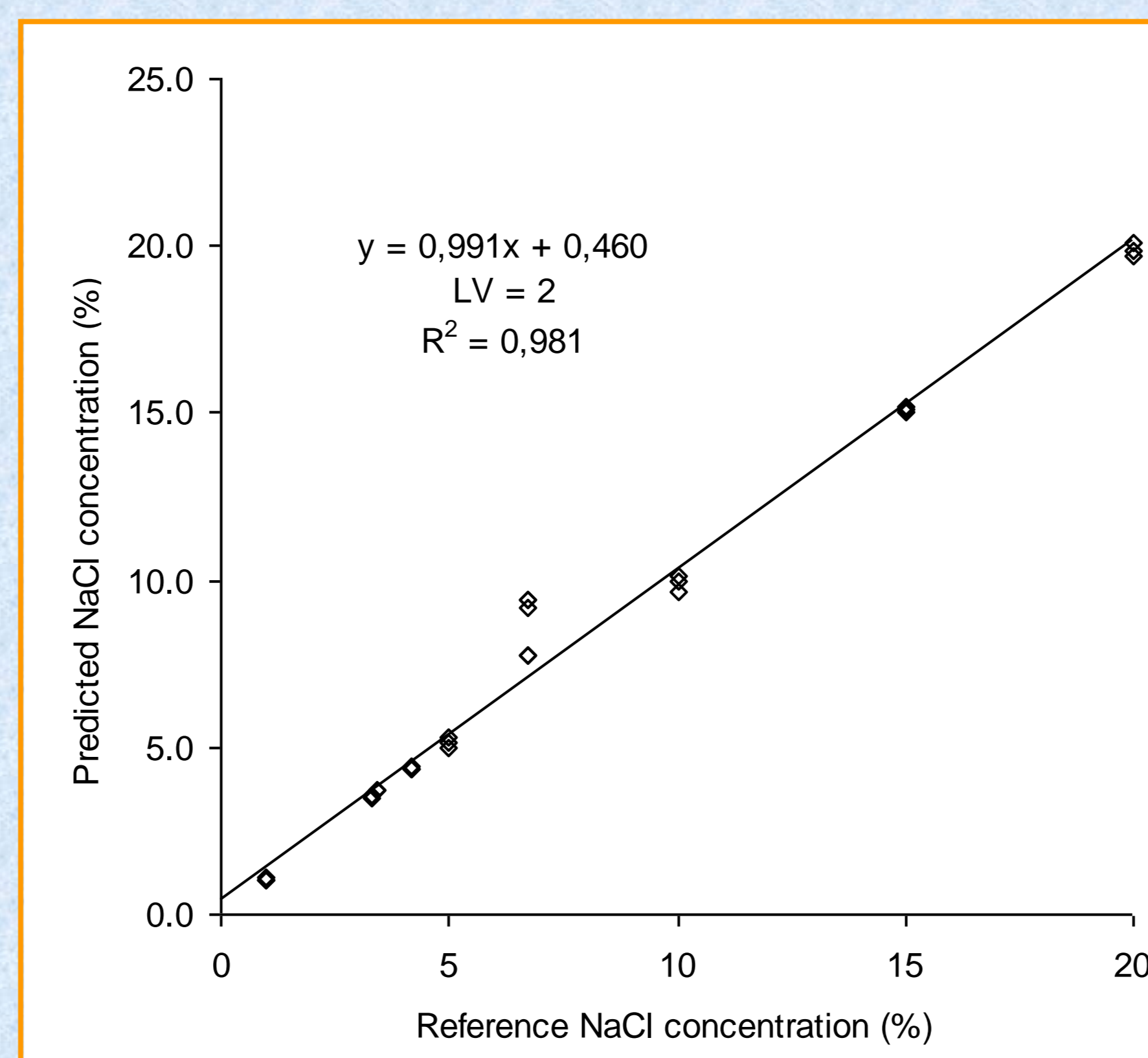
Figure 4. PLS1 regression of spectral data of sodium chloride in cod fish extracts.

y = 1,002x - 0,051
LV = 4
R^2 = 0,930
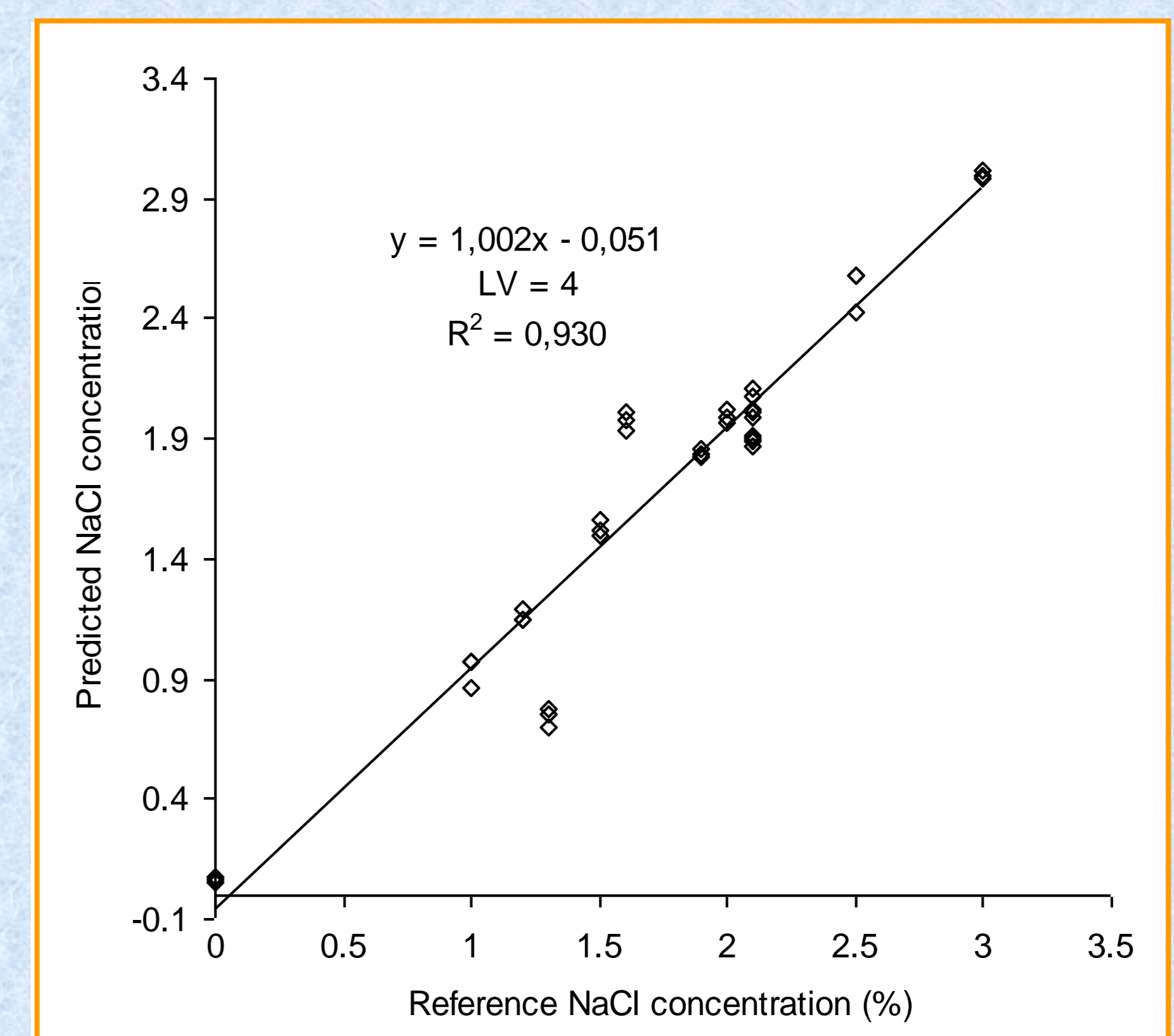
Figure 5. PLS1 regression of spectral data of sodium chloride in desalting solution samples.

Conclusions:

➢ The flow analysis system was shown to be an accurate methodology, rapid and convenient alternative, when applied to the determination of chloride in the desalting solutions. Technological aspects associated to codfish processing (i.e. cod freshness, salting and drying methods) will influence the desalting process and might also affect the turbidimetric NaCl determination.

➢ Salt content in cod fish and desalting cod solutions was predicted with good results by using MID-IR, however more data should be incorporated into the models in order to create a robust way of prediction of the NaCl concentration.

Reference
[1] Barros, A. 1999. Contribution à la sélection et la comparaison de variables caractéristiques. Ph. D. Thesis. Institut National Agronomique Paris-Grignon Paris. France.