Pretreatments by means of orthogonal projections

J.C. Boulet, J.M. Roger

► To cite this version:

J.C. Boulet, J.M. Roger. Pretreatments by means of orthogonal projections. Chemometrics and Intelligent Laboratory Systems, 2012, 117, p. 61 - p. 69. 10.1016/j.chemolab.2012.02.002 . hal-00842452

HAL Id: hal-00842452

<https://hal.science/hal-00842452>

Submitted on 8 Jul 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Pretreatments by means of orthogonal projections

Jean-Claude Boulet¹

INRA, UMR1083 Sciences Pour l'Oenologie, 2 place Viala, F-34060 Montpellier, France

Jean-Michel Roger²

IRSTEA, UMR ITAP Information Technologies Analyse environnementale Procédés agricoles, F-34196 Montpellier, France

Abstract

This article describes several linear pretreatments based on orthogonal projections. The main differences of these pretreatments lie in the way the information to be removed is identified, using calibration dataset, pure spectra, experimental designs or mathematical models. Removing all the undesired spectral information yields spectra proportional to the net analyte signal, so it is important to collect the most complete information possible, using the complementarities of different approaches. The correction should then be processed with a single Euclidian orthogonal projection that gathers all the information, rather than with successive operations. By embedding Euclidian orthogonal projections into the calibration, it is not necessary to reapply them to new datasets.

Keywords: orthogonal projection, pretreatment, preprocessing, subspace, linear model

1. Introduction

Spectroscopy has spread throughout many industries as an on-line process control tool because calibration models are able to extract quantitative information about a compound of interest from the spectra. Among the models proposed, regressions or inverse calibrations such as partial least square regression (PLSR) (1), extract the relevant spectral information by means of a calibration dataset. The term "partial" recalls that just a few dimensions or latent variables are used, and thus the information related to the other variables is dropped. Pretreatments or preprocessings are positioned prior to calibration. Their purpose is to identify and to remove spectral information that interferes

Email addresses: bouletjc@supagro.inra.fr (Jean-Claude Boulet),
jean-michel.roger@irstea.fr (Jean-Michel Roger)

¹Tel.(33)499613148 Fax (33)499612857 (corresponding author)

²Tel.(33)467046383 Fax (33)467166440

with the desired prediction. Pretreatments and regressions share a same objective, so pretreatments allow regressions to perform better. Many different pretreatments are available. This paper focuses on describing the ones based upon orthogonal projections and complements a recent review by Rinnan et al (2). After introducing the notations, we describe several pretreatments focused on orthogonal projections, and then discuss their properties. We propose a clarified view of several pretreatments by putting forward their resemblances and complementarities and suggesting the best methods for their use. The detailed relationships of these pretreatments with other pretreatments (e.g. Savitsky-Golay (SG), standard normal variate) and with other calibration methods are outside the scope of this article.

1.1. Notations

Vectors are noted in bold lowercase, matrices in bold uppercase, and scalars in uppercase characters. Vectors are arranged in columns, except in matrices $\mathbf{X}$ and $\mathbf{X}_G$ where the lines represent the spectra. The transposed forms of vector $\mathbf{a}$ and matrix $\mathbf{A}$ are noted $\mathbf{a}'$ and $\mathbf{A}'$, respectively. The main notations are gathered in Table 1, and a glossary is also available in Table 2.

2. Pretreatments based on orthogonal projections

Pretreatments based on orthogonal projections deal with the correction of additive effects. For example, suppose that for sample i the observed spectrum $\mathbf{x}_{i,obs}$ is the sum of the expected spectrum $\mathbf{x}_i$ plus an unwanted contribution $\mathbf{h}_i$:

$$\mathbf{x}_{i,obs} = \mathbf{x}_i + \mathbf{h}_i \quad (1)$$

If a good estimation of $\mathbf{h}_i$ is available, the first possibility would be to perform a subtraction, and so $\mathbf{x}_i$ is estimated as:

$$\hat{\mathbf{x}}_i = \mathbf{x}_{i,obs} - \hat{\mathbf{h}}_i$$

Unfortunately, because $\mathbf{h}_i$ is not well estimated for each spectrum i , this configuration is very uncommon in spectrometry. Nevertheless, it is possible to obtain a good estimation of the subspace $\mathcal{E}^D$ spanned by the different vectors $\{\mathbf{h}_i\}$. Thus it becomes possible to build a projector orthogonal to this subspace. Let $\mathbf{P}$ be a matrix of dimensions $P \times A$ whose column-vectors $\{\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_A\}$ form a basis of $\mathcal{E}^D$. Let $\mathbf{I}_P$ be the identity matrix of dimensions $P \times P$. The Euclidian orthogonal projector to $\mathbf{P}$ is:

$$\mathcal{P}_P^\perp = \mathbf{I}_P - \mathbf{P}(\mathbf{P}'\mathbf{P})^{-1}\mathbf{P}'$$

A spectrum $\mathbf{x}_{i,corr}$ corrected from the information due to any $\mathbf{h}_i$ is obtained after a projection of $\mathbf{x}_{i,obs}$ orthogonally to $\mathbf{P}$:

$$\mathbf{x}_{i,corr} = \mathcal{P}_P^\perp \mathbf{x}_{i,obs} = \mathcal{P}_P^\perp \mathbf{x}_i \quad (2)$$

Note that the vector $\mathbf{x}_{i,corr}$ that is obtained after an orthogonal projection is very different from $\hat{\mathbf{x}}_i$ obtained when a subtraction is possible. However in both cases, the influence of $\mathbf{h}_i$ has been reduced to nought. The orthogonal projector $\mathcal{P}_P^\perp$ is symmetrical: $\mathcal{P}_P^{\prime\perp} = \mathcal{P}_P^\perp$, so for N spectra forming the matrix $\mathbf{X}$ of dimensions $N \times P$:

$$\mathbf{X}_{corr} = \mathbf{X} \mathcal{P}_P^\perp = \mathbf{X}(\mathbf{I}_P - \mathbf{P}(\mathbf{P}'\mathbf{P})^{-1}\mathbf{P}') \quad (3)$$

The performances of the different pretreatments are directly explained by their ability to obtain a good approximation of a basis of $\mathcal{E}^D$. Different approaches are possible: using pure spectra, information extracted from experimental design, models, and calibration datasets. For each method, matrix $\mathbf{X}$ represents centered or uncentered data, depending on the centering option chosen. In order to simplify the presentation, all pretreatments presented here are for correcting spectra in which just one compound of interest is to be quantified. However, some pretreatments can also be written for the correction of several compounds of interest.

2.1. Pretreatment using pure spectra

A basis of the space spanned by chemical components is given by their pure spectra. A method derived from hyperspectral imaging uses this property.

2.1.1. Orthogonal subspace projection

The orthogonal subspace projection (OSP) use pure spectra, called undesired signatures, which are associated with all the chemical influences present except the one of the compound of interest. These undesired signatures form matrix $\mathbf{K}$. They can be determined after a clustering process (3; 4), in which homogeneous groups of spectra are obtained, followed by selection of a spectrum representative of each group. However in Harsanyi et al (5) they were chosen within the image. The OSP correction is a projection that is orthogonal to $\mathbf{K}$, in accordance with equation 3:

$$\mathbf{X}_{OSP} = \mathbf{X}(\mathbf{I}_P - \mathbf{K}(\mathbf{K}'\mathbf{K})^{-1}\mathbf{K}')$$

In Harsanyi et al (5), the OSP method was applied to an hyperspectral image from an airborne VIS-IR spectrometer using the radiance spectra directly. Several end members were identified and alternatively chosen as the compound of interest. An OSP was performed for each endmember. For each OSP, the corrected spectra were used to classify the pixels, and the results were in accordance with the measured values, or ground truth. However, the limits of this method are such that all the pure spectra must be known in advance and they cannot be collinear. In addition, influences such as temperature are not taken into account.

78 2.2. Pretreatments using spectra issued from an experimental design

79 If pure spectra are not available due to the chemical complexity of the sam-
80 ples or because the influence to be removed is physical and no pure spectrum
81 exists, OSP cannot be applied. It is possible to construct experimental designs
82 to obtain a matrix $\mathbf{X}_G$ whose spectra contain targeted spectral perturbations
83 without any useful information. A singular value decomposition (SVD) or a
84 principal component analysis (PCA) applied to $\mathbf{X}_G$ gives a matrix of eigenvec-
85 tors $\mathbf{P}$ of dimensions $(P \times A)$ whose columns represent an orthonormal basis of
86 the subspace to be removed. The matrix $\mathbf{X}$ is corrected to $\mathbf{X}_{corr}$ by a projection
87 orthogonal to $\mathbf{P}$. The following formula is the same as equation 3 and can be
88 simplified to:

$$\mathbf{X}_{corr} = \mathbf{X}(\mathbf{I}_P - \mathbf{P}(\mathbf{P}'\mathbf{P})^{-1}\mathbf{P}') = \mathbf{X}(\mathbf{I}_P - \mathbf{P}\mathbf{P}')$$

89 Several methods have been based on this principle, but they differ in the
90 way $\mathbf{X}_G$ is obtained, and in how the dimension of the SVD or the PCA applied
91 to $\mathbf{X}_G$ is determined.

92 2.2.1. Independent interference reduction

93 The independant interference reduction method (IIR), Hansen (6) uses spec-
94 tra from samples where the compound of interest is null and these spectra are
95 gathered into the matrix $\mathbf{X}_G$. The IIR method implies that such samples should
96 be easy to collect in large numbers. This was the case in the reported applica-
97 tion, due to the absence of acetone for the milk of healthy cows. IIR yielded
98 models that were more interpretable and predictions that were more stable. IIR
99 removes more interferences with higher numbers of PCA factors and thus the
100 PLSR needs fewer latent variables.

101 2.2.2. External parameter orthogonalization and transfer orthogonal projection

102 External parameter orthogonalization (EPO), Roger et al (7) and transfer
103 orthogonal projection (TOP), Andrew et al (8) are two closely related methods.
104 For the same set of M samples, M spectra are acquired at R levels of one phys-
105 ical influence. Thus, each sample is associated with R spectra. Centering each
106 set of R spectra removes chemical information to leave only the information
107 from the physical influence remaining. Matrix $\mathbf{X}_G$ of dimensions $(MR \times P)$
108 is obtained by merging the R centered spectra from each of the M samples.
109 EPO was first applied to correct temperature effects when predicting the sugar
110 concentration in apples in the near infrared. Ten apples were set at different
111 temperatures between 5°C and 40°C. The spectra of the ten apples were centered
112 for each temperature level, and then merged, to yield $\mathbf{X}_G$. The PCA and PLSR
113 dimensions were determined using either cross validation or Wilks Λ . The EPO
114 method produced a dramatic drop in the root mean square error of prediction
115 ($RMSEP$) value compared to that obtained without any pretreatment. TOP
116 aims at transferring calibrations from one instrument to another, and was used
117 in two applications: to determine the protein content in barley and moisture

in corn. Near infrared (NIR) spectra of the same five samples of barley were acquired onto seven spectrometers, and the NIR spectra of five samples of corn were acquired onto three spectrometers. Spectra were centered for each instrument, and then merged into two matrices $\mathbf{X}_G$ associated with barley and corn respectively. The PCA dimensions were determined such that 98 – 99 % of the variance was captured. For barley and corn, the TOP-PCR and TOP-PLSR models were determined on one instrument and then applied to the others. The low *RMSEP* values produced by the analysis demonstrated the value of using TOP for calibration transfer. Calibration was also successfully transferred to an unseen instrument (not used for the calculation of TOP).

2.2.3. Dynamic orthogonal projection

Dynamic orthogonal projection (DOP), Zeaiter et al (9) was inspired by EPO. The aim of DOP is the on-line correction of unexpected disruptive influences. The spectra and reference values of a few disturbed samples are assumed to be known. Let $(\mathbf{X}, \mathbf{y})$ be the calibration dataset, $\mathbf{x}_1$ a spectrum acquired after the appearance of a disruptive influence, and y_1 the reference value associated with $\mathbf{x}_1$. The ideal spectrum $\hat{\mathbf{x}}_1$ which would have been obtained without the disturbance is estimated by a kernel function or weighted mean of spectra from $\mathbf{X}$ chosen for their proximity to y_1 . The difference between the spectra $(\hat{\mathbf{x}}_1 - \mathbf{x}_1)$ characterizes the disturbance. The same operation is repeated with other measurement points $\mathbf{x}_2, \mathbf{x}_3$, etc., and spectral differences are gathered into $\mathbf{X}_G$. The method was applied to the prediction of ethanol in wine fermentations, and aimed at correcting the temperature effects. A calibration database was first obtained during an isothermal fermentation. Then, temperature was monitored during a second fermentation. Five reference points were acquired during the increase of temperature and the NIR predictions of ethanol were corrected using DOP. A Gaussian kernel function was used to build virtual spectra of the available reference points, and the database was successively corrected from one to five points. Ethanol predictions were well-corrected by DOP, even at the end of the fermentation when the temperature had decreased to its initial value. It was also shown that DOP was able to capture the vertical (baseline) and horizontal (wavelength) shifts due to the temperature.

2.2.4. Error removal by orthogonal subtraction

Error removal by orthogonal subtraction (EROS), Zhu et al (10) is a method derived from TOP. EROS takes into account and then corrects variations due to repetitions. Several spectra acquired from a same sample are centered. The centered spectra associated with the different samples are gathered into a matrix $\mathbf{X}_G$ which contains only information due to the repetitions and in which the row mean is null. EROS was applied to the diagnosis of precancerous polyps using visible-NIR spectroscopy. The repeatability of the spectra was poor due to different angles, pressures or locations at which the optical probe was used during the *in vivo* data acquisitions. EROS was able to correct these influences using five repetitions for each analysis. Normal and precancerous polyps were classified by principal component discriminant analysis (PCDA), the dimensions

were tuned using cross-validation. EROS enabled the accuracy of the classification to be slightly increased. However, the models generated were expected to be more robust because they had been simplified and because EROS+PCDA needed fewer components than PCDA alone.

2.3. Pretreatments using a polynomial model

Let λ be the vector of dimensions $P \times 1$ composed of values $\{v_1, v_2, \dots, v_P\}$. The i° column of the matrix $\mathbf{\Lambda}_R$ of dimensions $(P \times R + 1)$ is obtained by raising each term of λ to the power i . A vector $\mathbf{z}$ can be written in a polynomial form if it exists as vector $\mathbf{a}$ such that:

$$\mathbf{z} = \mathbf{\Lambda}_R \mathbf{a} \quad (4)$$

If an observed spectrum $\mathbf{x}_{obs}$ is the sum of the expected spectrum $\mathbf{x}$ plus the contribution of an unexpected influence (e.g. scattering), which is represented by a polynomial vector $\mathbf{z}$, then:

$$\mathbf{x}_{obs} = \mathbf{x} + \mathbf{z} = \mathbf{x} + \mathbf{\Lambda}_R \mathbf{a}$$

An estimation of $\mathbf{x}$, corrected from the polynomial, is obtained after $\mathbf{x}$ is projected orthogonally to $\mathbf{\Lambda}_R$:

$$\hat{\mathbf{x}}_{corr} = (\mathbf{I}_P - \mathbf{\Lambda}_R (\mathbf{\Lambda}'_R \mathbf{\Lambda}_R)^{-1} \mathbf{\Lambda}_R) \mathbf{x}_{obs}$$

The following pretreatments: detrend, constrained principal spectra analysis (CPSA) and iterative polynomial fitting, are based on polynomial corrections.

2.3.1. Detrend

Detrend was proposed by Barnes et al(11; 12) to correct baselin distortions due to scattering effects able to be modeled by a polynomial. These situations are very common in spectroscopy and are difficult to model due to the variability of particle sizes (2). Detrend calculates a matrix $\mathbf{\Lambda}_2$ of dimensions $(P \times 3)$ as described above, to model second-order polynomials. A detrend correction consists of an orthogonal projection of the raw spectra to $\mathbf{\Lambda}_2$. Detrend was applied to spectra from crystalline and powder forms of sucrose (11), and the corrected spectra of the same component were nearly identical. However, as expected for an orthogonal projection, they had lost the classical shape of the sucrose spectra. Other authors have proposed modeling baselines with polynomials having orders up to two (13; 14) and with solutions for the choice of the polynomial order. However the corrections were done using subtraction and an orthogonal projection was also possible, at least for the spectra.

2.3.2. Constrained principal spectra analysis

CPSA addresses the correction of influences unrelated to the chemical composition of the sample (15). As for detrend, scattering is modeled by a matrix $\mathbf{\Lambda}_2$. Spectra from external influences such as water and carbon dioxide gas, form matrix $\mathbf{K}$. Matrices $\mathbf{\Lambda}_2$ and $\mathbf{K}$ are merged to yield matrix $\mathbf{R}$. The CPSA correction consists of projecting raw spectra $\mathbf{x}_i$ orthogonally to $\mathbf{R}$.

2.4. Pretreatments using data compression methods

The main goal of data compression methods is to obtain fewer numbers of new variables A such that $A \ll P$, where P is the dimension of a spectrum. These variables form the best basis (BB) (16), in that they span the subspace of $\mathbb{R}^P$ containing the most relevant information. However a consequence of this pretreatment is that information is dropped while projecting onto the BB.

Let $\mathbf{W}$ be a $P \times P$ matrix in which column-vectors constitute an orthonormal basis of $\mathbb{R}^P$. Thus $\mathbf{W}'\mathbf{W} = \mathbf{I}_P$. The projection of any vector $\mathbf{x}_i$ of dimension P onto $\mathbf{W}$ is invariant and gives $\mathbf{x}_i$:

$$\mathbf{W}(\mathbf{W}'\mathbf{W})^{-1}\mathbf{W}'\mathbf{x}_i = \mathbf{W}\mathbf{W}'\mathbf{x}_i = \mathbf{x}_i \quad (5)$$

The scores of $\mathbf{x}_i$ in the basis represented by the column-vectors of $\mathbf{W}$ are represented by a unique vector $\mathbf{t}_i$, which by definition verifies:

$$\mathbf{x}_i = \mathbf{W}\mathbf{t}_i \quad (6)$$

Thus, from equations 5 and 6:

$$\mathbf{t}_i = \mathbf{W}'\mathbf{x}_i$$

$\mathbf{W}$ is split into two matrices: $\mathbf{W}_{1:A}$ containing A selected vectors of $\mathbf{W}$ (the BB); and $\mathbf{W}_{A+1:P}$ containing the last $P - A$ vectors of $\mathbf{W}$. The spectrum $\mathbf{x}_i$ is rebuilt using $\mathbf{W}_{1:A}$ and the A first scores of $\mathbf{t}_i$, noted $\mathbf{t}_{i,1:A}$, into equation 6:

$$\mathbf{x}_{i,corr} = \mathbf{W}_{1:A}\mathbf{t}_{i,1:A} = \mathbf{W}_{1:A}\mathbf{W}'_{1:A}\mathbf{x}_i$$

It can easily be deduced that $\mathbf{x}_{i,corr}$ is also the orthogonal projection of $\mathbf{x}_i$ to $\mathbf{W}_{A+1:P}$:

$$\mathbf{x}_{i,corr} = (\mathbf{I}_P - \mathbf{W}_{A+1:P}\mathbf{W}'_{A+1:P})\mathbf{x}_i$$

The equation obtained is equivalent to equation 2 with $\mathbf{W}_{A+1:P}$ replacing $\mathbf{P}$. The $\mathbf{W}_{1:A}$ and $\mathbf{W}_{A+1:P}$ matrices can be obtained using several compression methods. The simplest way is to perform a PCA, then select respectively the A first and $P - A$ last components. Discrete Fourier transform (DFT) is used in signal processing. However in chemometrics more attention has been paid to wavelet transforms. Thus a discrete wavelet transform (DWT) and a wavelet packet transform (WPT) offer alternative solutions.

222 2.5. The wavelet packet transform and the discrete wavelet transform

223 All of the vectors of $\mathbf{W}$ are calculated using a WPT, whereas only a few of
224 them are obtained with DWT (16). Thus DWT is a particular case of WPT.

225 Two parameters must be determined for a WPT: (1) an orthonormal wavelet
226 basis of $\mathbb{R}^P$, represented by the columns of $\mathbf{W}$; and (2) the A vectors from $\mathbf{W}$
227 which form the BB (16). Examples of orthonormal wavelet families of bases
228 are Haar-Daubechie, Symmlet, and Coiflet (16; 17; 18). The vectors forming
229 the BB are determined using a threshold. Several methods are available to
230 obtain the value of the threshold: predetermined (16); minimum description
231 length (MDL), which is a compromise between A and the percent of spectral
232 reconstruction (16; 19); and universal thresholding (ThU) (20). Cross-validation
233 on a calibration dataset $(\mathbf{X}, \mathbf{y})$ can help to determine these parameters (19; 21).
234 A WPT-DWT can be used for data compression and for smoothing, denoising
235 and baseline corrections. Smoothing consists of removing high frequency signals
236 (16; 19; 22), regardless of their amplitudes (23). Denoising consists in removing
237 the lower coefficients in the frequency domain, regardless of their frequencies
238 (23). Smoothing and denoising are different, but high frequencies are often
239 associated with low coefficients, so in practice both denoising and smoothing
240 are performed in the same operation. Baseline can also be removed. Hu et al
241 (20) applied DWT to Raman spectra for baseline and noise corrections.

242 DWT-WPT performance can be very good in terms of signal reconstruction
243 and data compression. Barclay et al obtained corrections which overwhelmed
244 the DFT and the SG method (23). Trygg et al obtained quite the same in-
245 formation after a compression rate of 30 (17). However, when associated with
246 PLSR, DWT-WPT did not significantly improve the quality of prediction (17).

247 2.6. Pretreatments using a calibration dataset

248 Orthogonal signal correction (OSC) methods are based on a calibration
249 dataset $(\mathbf{X}, \mathbf{y})$ and do not need any additional information. Several methods
250 have been proposed for removing the spectral information orthogonal to $\mathbf{y}$ from
251 $\mathbf{X}$: Wold et al OSC (24); Sjoblom et al OSC (25); Wise et al OSC (cited in (26));
252 Andersson direct orthogonalization (DO) (27); Fearn's OSC (28); Westerhuis et
253 al direct orthogonal signal correction (DOSC) (26); Goicoechea net analyte pre-
254 processing (NAP) (29); and Trygg orthogonal projection to latent structures
255 (OPLS) (30). These methods have been reviewed previously (26; 31) and have
256 been cited extensively in the litterature. OSC methods are not reviewed here
257 but will be discussed briefly to clarify their relationships with orthogonal pro-
258 jections.

259 2.6.1. Overview of the OSC methods

260 All OSC methods aim at determining scores $\mathbf{T}$ containing information or-
261 thogonal to $\mathbf{y}$. The correction can be written as an orthogonal projection into
262 $\mathbb{R}^N$:

$$\mathbf{X}_{OSC} = (\mathbf{I}_N - \mathbf{T}(\mathbf{T}'\mathbf{T})^{-1}\mathbf{T}')\mathbf{X} \quad (7)$$

263 The methods differ in the way $\mathbf{T}$ is obtained.

264 • Wold's OSC

$$\begin{aligned}
\mathbf{X}_{1:0} &= \mathbf{X}; \text{ for step } i : \\
\mathbf{t} &= \text{first score of a PCA onto } \mathbf{X}_{1:i-1} \\
\mathbf{t}_o &= (\mathbf{I}_N - \mathbf{y}(\mathbf{y}'\mathbf{y})^{-1}\mathbf{y}')\mathbf{t} \\
\mathbf{T}_{PLSR} &= \text{first scores of a PLSR calculated with } (\mathbf{X}_{1:i-1}, \mathbf{t}_o) \\
\mathbf{t}_{o,new} &= \mathbf{T}_{PLSR}(\mathbf{T}'_{PLSR}\mathbf{T}_{PLSR})^{-1}\mathbf{T}'_{PLSR}\mathbf{t}_o \\
\mathbf{t} &= \mathbf{t}_{o,new} \text{ then repeat until convergence of } \mathbf{t} \rightarrow \mathbf{t}_i \\
\mathbf{p}_i &= \mathbf{X}'_{1:i-1}\mathbf{t}_i(\mathbf{t}'_i\mathbf{t}_i)^{-1} \\
\mathbf{X}_{1:i} &= (\mathbf{I}_N - \mathbf{t}_i(\mathbf{t}'_i\mathbf{t}_i)^{-1}\mathbf{t}'_i)\mathbf{X}_{1:i-1}
\end{aligned}$$

265 At each loop, the projection of $\mathbf{t}_o$ onto $\mathbf{T}_{PLSR}$ means that $\mathbf{t}_{o,new}$ lies in
266 the subspace spanned by the columns of $\mathbf{X}_{1:i-1}$. Thus the $\mathbf{t}_i$ are orthog-
267 onal. After A iterations, they form matrix $\mathbf{T}$ and the OSC correction is
268 performed according to equation 7.

269 • Sjöblom and Wise OSCs

$$\begin{aligned}
\mathbf{X}_{1:0} &= \mathbf{X}; \text{ for step } i : \\
\mathbf{t} &= \text{first score vector of a PCA onto } \mathbf{X}_{1:i-1} \\
\mathbf{t}_o &= (\mathbf{I}_N - \mathbf{y}(\mathbf{y}'\mathbf{y})^{-1}\mathbf{y}')\mathbf{t} \\
\mathbf{w}_i &= \mathbf{X}'_{1:i-1}\mathbf{t}_o \text{ then } \mathbf{w}_i \text{ is normed} \\
\mathbf{t}_1 &= \mathbf{X}_{1:i-1}\mathbf{w}_i \\
\mathbf{t} &= \mathbf{t}_1 \text{ then repeat until convergence of } \mathbf{t}_1 \\
\mathbf{T}_{PLSR} &= \text{first scores of a PLSR calculated with } (\mathbf{X}_{1:i-1}, \mathbf{t}_1) \\
\mathbf{t}_i &= \mathbf{T}_{PLSR}(\mathbf{T}'_{PLSR}\mathbf{T}_{PLSR})^{-1}\mathbf{T}'_{PLSR}\mathbf{t}_1 \\
\mathbf{p}_i &= \mathbf{X}'_{1:i-1}\mathbf{t}_i(\mathbf{t}'_i\mathbf{t}_i)^{-1} \\
\mathbf{X}_{1:i} &= (\mathbf{I}_N - \mathbf{t}_i(\mathbf{t}'_i\mathbf{t}_i)^{-1}\mathbf{t}'_i)\mathbf{X}_{1:i-1}
\end{aligned}$$

270 This is Sjöblom's OSC. Wise' OSC is similar, with an additional step
271 consisting of orthogonalizing $\mathbf{t}_i$ to $\mathbf{y}$ (26). By construction each score-
272 vector $\mathbf{t}_i$ lies in the $\mathbf{X}_{1:i-1}$ subspace, so the $\mathbf{t}_i$ vectors are orthogonal. After
273 A iterations, they form matrix $\mathbf{T}$ and the OSC correction is performed into
274 $\mathbb{R}^N$ according to equation 7.

275 • Andersson's DO and Goicoechea's NAP

$$\begin{aligned}\mathbf{Z} &= (\mathbf{I}_N - \mathbf{y}(\mathbf{y}'\mathbf{y})^{-1}\mathbf{y}')\mathbf{X} \\ \mathbf{P} &= \text{A first loadings of a PCR calculated with } \mathbf{Z} \\ \mathbf{T} &= \text{A first scores of a PCR calculated with } \mathbf{Z}\end{aligned}$$

276 DO and NAP are the same method. The correction is performed into
277 $\mathbb{R}^N$ according to equation 7, but also into $\mathbb{R}^P$ using $\mathbf{P}$:

$$\mathbf{X}_{DO-NAP} = \mathbf{X}(\mathbf{I}_P - \mathbf{P}\mathbf{P}')$$

278 • Fearn's OSC

$$\begin{aligned}\mathbf{M} &= \mathbf{I}_P - \mathbf{X}'\mathbf{y}(\mathbf{y}'\mathbf{X}\mathbf{X}'\mathbf{y})^{-1}\mathbf{y}'\mathbf{X} \\ \mathbf{W} &= \text{A first eigenvectors of a PCA calculated with } \mathbf{M}\mathbf{X}'\mathbf{X} \\ \mathbf{T} &= \mathbf{X}\mathbf{W}\end{aligned}$$

279 As the $\mathbf{t}_i$ are orthogonal (28), the correction is performed into $\mathbb{R}^N$ accord-
280 ing to equation 7.

281 • Westerhuis' DOSC

$$\begin{aligned}\mathbf{y}_1 &= \mathbf{X}(\mathbf{X}'\mathbf{X})^+\mathbf{X}'\mathbf{y} \\ \mathbf{X}_1 &= (\mathbf{I}_N - \mathbf{y}_1(\mathbf{y}_1'\mathbf{y}_1)^{-1}\mathbf{y}_1')\mathbf{X} \\ \mathbf{T} &= \text{A first scores of a PCA calculated with } \mathbf{X}_1\end{aligned}$$

282 The scores of a PCA are orthogonal, so the correction is performed into
283 $\mathbb{R}^N$ according to equation 7.

284 • Trygg's OPLS

$$\begin{aligned}\mathbf{X}_{1:0} &= \mathbf{X}; \text{ for step } i : \\ \mathbf{w}_{PLS}, \mathbf{p}_{PLS} &= \text{first weight and loading vectors of a PLSR calculated with } (\mathbf{X}_{1:i-1}, \mathbf{y}) \\ \mathbf{w}_i &= \mathbf{p}_{PLS} - (\mathbf{w}'_{PLS}\mathbf{p}_{PLS})(\mathbf{w}'_{PLS}\mathbf{w}_{PLS})^{-1}\mathbf{w}_{PLS} \text{ then } \mathbf{w}_i \text{ is normed} \\ \mathbf{t}_i &= \mathbf{X}_{1:i-1}\mathbf{w}_i \\ \mathbf{p}_i &= \mathbf{X}'_{1:i-1}\mathbf{t}_i(\mathbf{t}_i'\mathbf{t}_i)^{-1} \\ \mathbf{X}_{1:i} &= (\mathbf{I}_N - \mathbf{t}_i(\mathbf{t}_i'\mathbf{t}_i)^{-1}\mathbf{t}_i')\mathbf{X}_{1:i-1}\end{aligned}$$

285 Each vector $\mathbf{t}_i$ lies in the column space of $\mathbf{X}_{1:i-1}$. Thus the $\mathbf{t}_i$ vectors are
286 orthogonal and can be gathered into a matrix $\mathbf{T}$ for the OPLS correction
287 into $\mathbb{R}^N$ according to equation 7.

2.6.2. Properties of the OSC methods

OSC methods were created to improve inner properties (26), such as: no (or nearly no) correlation between the OSC scores $\mathbf{t}_i$ and the reference values $\mathbf{y}$; removal of the largest variability in $\mathbf{X}$; belonging of the $\mathbf{t}_i$ to the column space; and more direct calculation. In order to prevent overfit, just a few dimensions are usually removed. The usefulness of OSC has been widely discussed, and many authors agree that OSC does not improve accuracy (26; 27; 28; 29; 30; 31). Several OSC methods are connected with PLSR. For example, Wold's OSC is derived from PLSR, and OPLS can be obtained from PLSR (32). Often the same calibrations obtained after OSC would be obtained without OSC, but the latter calibrations contain more PLSR latent variables. Nevertheless OSC improves the interpretability of the calibrations by identifying outliers (27) and explaining the regression model obtained after OSC, by analyzing the information removed by OSC (30; 31).

OSC models can always be presented as a subtraction: $\mathbf{X}_{OSC} = \mathbf{X} - \sum \mathbf{t}_i \mathbf{p}'_i$ (31). The calculations of these models are similar to orthogonal projection into the individual space $\mathbb{R}^N$. It is less obvious to link OSC to orthogonal projections into the variable space $\mathbb{R}^P$, but it is possible in some instances. For example, DO and NAP are Euclidian orthogonal projections into $\mathbb{R}^P$, whereas Fearn's OSC is an oblique orthogonal projection into $\mathbb{R}^P$, see Appendix A. These mathematical considerations are of importance for the embedded or not embedded properties of OSCs, and also for their compatibilities with other orthogonal projection methods (see below).

3. Discussion

Orthogonal projections are common to the main linear pretreatment methods. We discuss several of their properties, including the relationship to the net analyte signal, the complementarity and the association of different pretreatments, and the correction of additive and multiplicative effects. We also propose for practical rules using orthogonal projections.

3.1. Net analyte signal and pretreatments in the calibration process

Calibration consists of two steps: an optional pretreatment or preprocessing step, and a mandatory calibration step. The aims of pretreatments and linear calibrations are linked.

A linear multivariate calibration extracts the spectral information produced by the compound of interest, and uses this information to predict the concentration of the compound. From a mathematical point of view, it is a function from $\mathbb{R}^P$ to $\mathbb{R}$, represented by a vector $\mathbf{b}$, called the regression or b-coefficients vector. Let $(\mathbf{X}, \mathbf{y})$ be a calibration dataset, $(\mathbf{X}_c, \mathbf{y}_c)$ be the calibration dataset after mean centering, and let $\mathbf{b}$ and $\mathbf{b}_c$ be the models obtained from raw or centered data. For a spectrum $\mathbf{x}_i$ from $\mathbf{X}$ acquired on sample i , an estimation $\hat{y}_i$ for the concentration of the compound of interest is given by the following equations, depending on the centering option:

$$\begin{aligned}\hat{y}_i &= \mathbf{x}'_i \mathbf{b} \text{ (no centering)} \\ \hat{y}_i &= \mathbf{x}'_{i,c} \mathbf{b}_c + y_0 \text{ (centering)}\end{aligned}$$

330 The intercept y_0 is induced by the centering. A good calibration model gives
331 a prediction close to the true values of y_i , so $|y_i - \hat{y}_i|$ is minimized under different
332 constraints. For that purpose, it is able to extract only the relevant information
333 from $\mathbf{x}_i$ (or $\mathbf{x}_{i,c}$ if centered). The most condensed relevant spectral information
334 is called the net analyte signal (NAS). Lorber et al (33) introduced the NAS (a
335 vector of the same dimension as a spectrum) in multivariate calibration. For
336 one component of interest, two definitions were proposed:

- 337 • First definition
338 "NAS is the part of the spectrum of the component of interest which, is
339 orthogonal to the spectra of the other components" (33; 34)
- 340 • Second definition
341 "NAS is the part of the raw signal that is useful for prediction of the
342 component of interest" (34)

343 Suppose that all of the contributions to the spectra, except the contribution
344 of the compound to be predicted, span a subspace $\mathcal{E}^D$. Let the column-vectors
345 of a matrix $\mathbf{P}$ be a basis of $\mathcal{E}^D$. Thus the NAS part of a spectrum $\mathbf{x}_i$, called
346 $\mathbf{x}_{i,nas}$, is obtained as an orthogonal projection of $\mathbf{x}_i$ to $\mathbf{P}$ (35), so that the NAS
347 is in the null space of $\mathcal{E}^D$:

$$\mathbf{x}_{i,nas} = (\mathbf{I}_P - \mathbf{P}(\mathbf{P}'\mathbf{P})^{-1}\mathbf{P}')\mathbf{x}_i \quad (8)$$

348 The net sensitivity vector (NSV) $\mathbf{s}_{nsv}$ is the NAS for a compound of interest
349 whose concentration is one. The vectors $\mathbf{s}_{nsv}$ and $\mathbf{b}$ are collinear and they verify,
350 for direct and inverse calibrations (34):

$$\mathbf{s}_{nsv} = \mathbf{b}(\mathbf{b}'\mathbf{b})^{-1} \quad (9)$$

351 For the same compound of interest, the NAS is strongly dependent on the
352 experiment. For instance, glucose presents different NAS, when measured in
353 fruit juices or blood. If a new compound whose spectra is close to that of glucose
354 is added either to juice or blood, the glucose NAS is immediately modified.
355 Thus, the NAS is conceptual rather than actual and is difficult or impossible
356 to measure. However, the NAS can be estimated. From equation 9, the best
357 calibration models are expected to be the best NAS estimates.

358 Equations 8 and 9 also clarify the relationships among orthogonal pretreat-
359 ments, NAS and calibrations. The definitions of the NAS and a pretreatment
360 based on orthogonal projections are very similar. The differences lie in the in-
361 formation represented by the matrices $\mathbf{P}$. For the NAS, $\mathbf{P}$ contains the vectors

spanning *all* the spectral contributions to be removed. In general pretreatment cases, $\mathbf{P}$ contains the vectors spanning *only a part* of the space containing the contributions to be removed. The extent to which pretreatments are able to gather the comprehensive information to be removed determines how close corrected spectra will be to their NAS. And from equation 9, determining regression vector $\mathbf{b}$ is straightforward. The relationship between the NAS and $\mathbf{b}$, along with the calculation of the NAS using Euclidian orthogonal projections, has at least two consequences.

A first consequence is the embedded / not embedded property of pretreatments. A pretreatment is embedded into the calibration if it is not necessary to apply the pretreatment to a new spectrum $\mathbf{x}_{i, val}$ before using it for prediction. If Euclidian orthogonal projection is applied, e.g. to correct the spectra from $\mathbf{P}$, the regression vector $\mathbf{b}$ of the subsequent calibration is built in a subspace already orthogonal to $\mathbf{P}$: $\mathbf{b} = \mathcal{P}_{\mathbf{P}}^{\perp} \mathbf{b}$. Thus, it is not necessary to apply the same pretreatment to $\mathbf{x}_{i, val}$. However this property is not verified for non-Euclidian orthogonal projections. For example, OSC methods have different behaviors. Fearn's OSC is not embedded because it is an *oblique* rather than an Euclidian projection. In contrast, the DO and NAP OSCs, which are written as Euclidian orthogonal projections, are embedded. No conclusions can be drawn for the other OSC methods because they have not yet been rewritten as projections into $\mathbb{R}^P$.

A second consequence is an identification of the useful and detrimental spaces within the variables space $\mathbb{R}^P$ (Fig.2). The useful space $\mathcal{E}^U$ contains informations for the prediction of the compound of interest. Its dimension is one according to the first definition, but can be greater than one according to the second definition. The subspace related to other compounds or chemical influences is detrimental ($\mathcal{E}^D$) if it shares common information with the useful space. The information from $\mathcal{E}^U$ which is not shared by $\mathcal{E}^D$ is the NAS, i.e. the NAS is orthogonal to $\mathcal{E}^D$. All the information from $\mathbb{R}^P$ which does not belong to $\mathcal{E}^U$ or $\mathcal{E}^D$ is useless information because it is already orthogonal to $\mathcal{E}^U$. Pretreatments have different strategies to remove $\mathcal{E}^D$. OSC methods rely on the information provided by $\mathbf{y}$. However, as PLSR uses the same approach, there is no added value, at least for prediction. Nevertheless OSCs calculated using other data (e.g. pure spectra or experimental design) and then applied to the calibration data $\mathbf{X}$ can increase the accuracy of measurement (36; 37) because the two sets of spectral informations are complementary. On the other hand, the non OSC orthogonal projections (OSP, IIR, EPO, TOP, DOP, EROS, detrend, CPSA, DWT-WPT) rely on additional information, and various sources of information can be withdrawn. The disadvantages of the methods are: (1) except for DWT-WPT, a prior knowledge is necessary, such as a model, pure spectra or information that can be used to build an experimental design; and (2) non OSC orthogonal pretreatments *may* remove information from the NAS subspace, contributing to a drop in the accuracy of prediction. Therefore, choosing the correct pretreatments and tuning and applying them properly, are very important for optimizing their predictive value.

3.2. Pretreatment complementarity

A spectrum can be viewed as the sum of signals of different frequencies: low, medium, and high (38).

Baseline shifts correspond to low frequencies. They can be modeled and removed either by detrend and related methods or by data compression methods such as WPT. Detrend is used more often than WPT. One reason for this may be that the polynomials used are based on models of low rank (e.g. 2). These models may already fit well with the observed deviations of the baseline, and thus detrend is more parsimonious.

Noise corresponds to high frequencies, usually removed using the SG algorithm. However WPT also removes noise, smooths the spectra and is more compatible with the other orthogonal projections.

Most of the relevant spectral information corresponds to medium frequencies, such as the information from the component of interest and the information to be removed. Orthogonal projections perform best in these situations.

Therefore different pretreatments should be selected according to their complementarity; that is, their ability to represent the whole space to be removed (Fig. 2, hatched part). Pretreatment choice is guided by the data to be processed and also by the available information. However, disrupting information can be expected in all frequency ranges. Thus, a relevant association of several methods, such as detrend + EPO + WPT, would respectively be able to remove the low, medium and high frequency spectral perturbations. How can several projection methods be used to produce the best results?

3.3. Association of pretreatments

Using successively two or more orthogonal projections is not equivalent to performing a single orthogonal projection containing all the information to be removed. An example is given in Fig. 1. Suppose that the spectral information from water and ethanol are to be removed from the spectrum of a sample that is half ethanol and half water. The expected result is the null vector. It is obtained if the orthogonal projection to ethanol and water is done in one step, but not if two orthogonal projections, one for ethanol and one for water, are done separately. Moreover, successive orthogonal projections are not commutative, so different orders lead to different results.

Let $\mathbf{P}$ and $\mathbf{Q}$ be two matrices whose column-vectors span the subspaces $\mathcal{E}_P$ and $\mathcal{E}_Q$. Let $\mathcal{P}_P$ and $\mathcal{P}_Q$ be the orthogonal projectors for $\mathcal{E}_P$ and $\mathcal{E}_Q$, respectively. The combined orthogonal projector for the $\mathcal{E}_P$ and $\mathcal{E}_Q$ subspaces is called $\mathcal{P}_{P+Q}$. According to Piziak et al (39):

$$\mathcal{P}_{P+Q} = (\mathcal{P}_P + \mathcal{P}_Q)(\mathcal{P}_P + \mathcal{P}_Q)^+$$

The orthogonal projector to $\mathcal{E}_P$ and $\mathcal{E}_Q$ is $\mathcal{P}_{P+Q}^\perp$ defined as:

$$\mathcal{P}_{P+Q}^\perp = \mathbf{I}_P - (\mathcal{P}_P + \mathcal{P}_Q)(\mathcal{P}_P + \mathcal{P}_Q)^+ \quad (10)$$

445 If $\mathcal{E}_P$ and $\mathcal{E}_Q$ are orthogonal, equation 10 is simplified:

$$\mathcal{P}_{P+Q}^\perp = \mathbf{I}_P - \mathcal{P}_P - \mathcal{P}_Q = (\mathbf{I}_P - \mathcal{P}_P)(\mathbf{I}_P - \mathcal{P}_Q) = \mathcal{P}_P^\perp \mathcal{P}_Q^\perp$$

446 However, in the other cases where $\mathcal{E}_P$ and $\mathcal{E}_Q$ are not orthogonal, $\mathcal{P}_{P+Q}^\perp \neq$
447 $\mathcal{P}_P^\perp \mathcal{P}_Q^\perp$. So, if several Euclidian orthogonal pretreatments must be applied, it
448 is strongly recommended to merge their respective $\mathbf{P}$ matrices into a matrix $\mathbf{R}$
449 and then performing a single orthogonal projection to $\mathbf{R}$. For example, suppose
450 that spectra are to be corrected from scattering and from chemical components
451 whose pure spectra are known. The best choice is to merge the $\mathbf{A}_2$ to the
452 pure spectra, yielding $\mathbf{R}$, and to orthogonalize to $\mathbf{R}$. This is also the option
453 recommended by Brown (15). In the case of successive orthogonal projections,
454 calculations will be erroneous if the bases of the different subspaces are not
455 orthogonal.

456 3.4. Limits of orthogonal projections

457 Orthogonal projections have at least two limits: the number of dimensions
458 of the spectra to be processed and the correction of multiplicative effects.

459 3.4.1. Reduction of dimensions and number of variables

460 Orthogonal projection to a subspace of dimension A retains the number of
461 variables but reduces the mathematical dimension of the spectra by A , which
462 cannot exceed the dimension P of the spectra. This is not a problem if spectra
463 contain hundreds of variables, because A remains lower than P . However, if
464 the spectra contain only a few variables (e.g. between 10 and 20), then only a
465 few dimensions can be removed by orthogonal projections, and often orthogonal
466 projection cannot be applied.

467 3.4.2. Additive and multiplicative effects

468 Orthogonal projection methods correct additive effects according to equation
469 1. Suppose that the spectral perturbations also induce a multiplicative effect
470 α_i , such that Eq. 1 can be written:

$$\mathbf{x}_{i,obs} = \alpha_i(\mathbf{x}_i + \mathbf{h}_i) = \alpha_i\mathbf{x}_i + \alpha_i\mathbf{h}_i \quad (11)$$

471 An orthogonal projector $\mathcal{P}_R^\perp$ can be obtained such that:

$$\mathbf{x}_{i,corr} = \mathbf{x}_{i,obs} \mathcal{P}_R^\perp = \alpha_i\mathbf{x}_i \mathcal{P}_R^\perp \quad (12)$$

472 Orthogonal projections are able to remove the term $\alpha_i\mathbf{h}_i$, but are not able to
473 correct the value α_i associated with $\mathbf{x}_i$; they cannot handle multiplicative effects.
474 Thus, methods such as standard normal variate (SNV) proposed by Barnes (11),
475 or (extended) multiplicative signal correction proposed by Martens (40; 41) do
476 not use orthogonal projections to correct multiplicative effects.

477 4. Conclusion

478 All the pretreatments presented here are based on orthogonal projections.
479 Some pretreatments that also use the principle of orthogonal projection were
480 not addressed because they do not fulfill all the conditions. The MSC and EMSC
481 methods perform a corrections using subtraction and division. SG is a piecewise
482 orthogonal projection. Even variable selection is an orthogonal projection into
483 the variables space, but in practice, variables are dropped by reshaping the
484 spectra rather than by setting them to 0. Thus, the orthogonal projection
485 principle, which is directly associated with the least squares approximation, is
486 used extensively and its prevalence is a confirmation of its power. Projections
487 are performed usually in a *Euclidian* space but at least one OSC is an oblique
488 projection performed in a *non-Euclidian* space.

489 The information used by calibrations is actually an estimation of the NAS.
490 A very important issue for pretreatments is identifying the detrimental infor-
491 mation to be removed by orthogonal projection. Two opposing strategies are
492 used: supervised and unsupervised. On one hand, OSC methods are supervised,
493 the information to be removed is chosen orthogonal to the reference values $\mathbf{y}$.
494 These methods obey the definition of the NAS, and thus OSC methods should
495 perform very well. However, due to OSC's redundancy with PLSR, which is
496 based on the same principles its accuracy has not improved substantially. On
497 the other hand, information removed by unsupervised orthogonal projection
498 methods is chosen based on prior knowledge of the experimental conditions and
499 the analyzed samples. All the available information, pure spectra, spectra from
500 an experimental design, and models (such as polynomials), should be consid-
501 ered to correct the detrimental information as comprehensively as possible. It is
502 important to avoid removing any information about the compound of interest,
503 which would lead to worse calibration models. Thus, proper use of orthogonal
504 projections requires being very careful about the quality and the completeness
505 of the removed information.

506 Orthogonal projections have practical properties. Information from different
507 origins should be merged in order to process only one orthogonal projection. Eu-
508 clidian orthogonal projections are embedded; they are applied only once when
509 building the calibration model. There is no need to apply them to new spec-
510 tra. Orthogonal projections also have limits. They cannot be applied in good
511 conditions for spectra containing just a few variables, and they do not correct
512 multiplicative effects. Nevertheless, orthogonal projections have proven to be
513 valuable tools when building the calibration models of many applications.

514 5. Acknowledgements

515 The authors would like to thank the reviewers whose relevant remarks were
516 very helpful for the improvement of this paper.

$\mathbf{X}$	matrix $N \times P$, N samples and P spectral variables
$\mathbf{y}$	vector $N \times 1$, the reference values
$\mathbf{X}_{1:i}$	projection of $\mathbf{X}$ orthogonally to $\{\mathbf{t}_1, \mathbf{t}_2, \dots, \mathbf{t}_i\}$
$\mathbf{T}$	matrix $N \times A$, scores for $\mathbf{X}$
$\mathbf{P}$	matrix $P \times A$, loadings for $\mathbf{X}$
$\mathbf{W}$	matrix $P \times A$, weights for $\mathbf{X}$
Σ	Moore-Penrose pseudo-inverse of $(\mathbf{X}'\mathbf{X})$; $\Sigma = (\mathbf{X}'\mathbf{X})^+$
$\mathbf{I}_N, \mathbf{I}_P$	identity matrices for $\mathbb{R}^N$ and $\mathbb{R}^P$ spaces
$\mathcal{P}_P$	Euclidian orthogonal projector $P \times P$ onto $\mathbf{P}$; $\mathcal{P}_P = \mathbf{P}(\mathbf{P}'\mathbf{P})^{-1}\mathbf{P}'$
$\mathcal{P}_P^\perp$	Euclidian projector $P \times P$ orthogonally to $\mathbf{P}$; $\mathcal{P}_P^\perp = \mathbf{I} - \mathcal{P}_P$
$\mathbf{t}_i$	i^{eme} column vector of $\mathbf{T}$
$\mathbf{p}_i$	i^{eme} column vector of $\mathbf{P}$
$\mathbf{w}_i$	i^{eme} column vector of $\mathbf{W}$
$\mathcal{E}_X$	subspace of $\mathbb{R}^P$ spanned by the line vectors of $\mathbf{X}$
$\mathcal{E}^U, \mathcal{E}^D$	useful / detrimental subspaces of $\mathbb{R}^P$

Table 1: Main notations

BB	best basis
CPSA	constrained principal spectra analysis
DFT	discrete Fourier transform
DO	direct orthogonalization
DOP	dynamic orthogonal projection
DOSC	direct orthogonal signal correction
DWT	discrete wavelet transform
EMSC	extended multiplicative signal correction
EPO	external parameter orthogonalization
EROS	error removal by orthogonal subtraction
IIR	independent interference reduction
MSC	multiplicative signal correction
MDL	minimum description length
NAP	net analyte preprocessing
NAS	net analyte signal
NSV	net sensitivity vector
OPLS	orthogonal projection to latent structures
OSC	orthogonal signal correction
OSP	orthogonal subspace projection
PCA	principal component analysis
PCDA	principal component discriminant analysis
PLSR	projection to latent structures regression
RMSEP	root mean square error of prediction
SG	Savitsky-Golay
SNV	standard normal variate
SVD	singular value decomposition
TOP	transfer by orthogonal projection
WPT	wavelet packet transform

Table 2: Glossary

Figure 1: Water and ethanol spectra, and their orthogonal projection. (1) From top to bottom, spectra of water, water+ethanol, ethanol. (2) Projection of the (water+ethanol) spectrum orthogonally to: ethanol then water (thick line), water then ethanol (dashed line), and a matrix containing water and ethanol spectra (horizontal light line)

Figure 2: Different subspaces of $\mathbb{R}^P$. The useful subspace $\mathcal{E}^U$; the detrimental subspace $\mathcal{E}^D$; the NAS; the common part of $\mathcal{E}^U$ and $\mathcal{E}^D$ to be removed (hatched); and the information represented by three orthogonal pretreatments (grey) are depicted in the figure. Information inside of and outside of each subspace are orthogonal

517 References

- 518 [1] S.Wold, A.Ruhe, H.Wold, W. D. III, The collinearity problem in linear
519 regression, the partial least square (pls) approach to generalized inverses, J.
520 Sci Stat. Comput. 5 (1984) 735–743.
- 521 [2] A.Rinnan, F.VanDenBerg, S. Engelsen, Review of the most common pre-
522 processing techniques for near infrared spectra, TrAC 28(10) (2009) 1201–
523 1222.
- 524 [3] C.I.Chang, M.L.G.Althouse, Unsupervised interference rejection approach
525 to target detection and classification for hyperspectral imagery, Opt. Eng.
526 37(3) (1998) 735–743.
- 527 [4] C.I.Chang, Hyperspectral imaging, Kluwer academic / Plenum, N.Y., 2003.
- 528 [5] J.C.Harsanyi, C.I.Chang, Hyperspectral image classification and dimen-
529 sionality reduction: an orthogonal subspace projection approach, IEEE
530 Trans. Geosci. Rem. Sens. 32(4) (1994) 779–786.
- 531 [6] P.W.Hansen, Pre-processing method minimizing the need for reference
532 analyses, J. Chemom. 15 (2001) 123–131.
- 533 [7] J.M.Roger, F.Chauchard, V.Bellon-Maurel, Epo-pls external parameter or-
534 thogonalisation of pls, application to temperature-independant measure-
535 ment of sugar contents in fruits, Chemom. Intell. Lab. Syst. 66 (2003)
536 191–204.
- 537 [8] A.Andrew, T.Fearn, Transfer by orthogonal projection: making near infra-
538 red calibrations robust to between-instrument variation, Chemom. Intell.
539 Lab. Syst. 72 (2004) 51–56.
- 540 [9] M.Zeaiter, J.M.Roger, V.Bellon-Maurel, Dynamic orthogonal projection, a
541 new method to maintain the on-line robustness of multivariate calibration,
542 application to nir-based monitoring of wine fermentations., Chemom. Intell.
543 Lab. Syst. 80 (2006) 227–235.
- 544 [10] Y.Zhu, T.Fearn, D.Samuel, A.Dhar, O.Hameed, S.G.Brown, L.B.Lovat, Er-
545 ror removal by orthogonal subtraction (eros): a customised pre-treatment
546 for spectroscopic data, J. Chemom. 22 (2008) 130–134.
- 547 [11] R.J.Barnes, M.S.Dhanoa, S.J.Lister, Standard normal variate transforma-
548 tion and de-trending of near-infrared diffuse reflectance spectra, Appl. Spec-
549 trosc. 43 (1989) 772–777.
- 550 [12] R.J.Barnes, M.S.Dhanoa, S.J.Lister, Correction to the description of stan-
551 dard normal variate (snv) and de-trend (dt) transformations in practical
552 spectroscopy with applications in food and beverage analysis, 2nd edition,
553 J. Near Infrared Spectrosc. 1 (1993) 185–186.

- 554 [13] V.Mazet, C.Carteret, D.Brie, J.Idier, B.Humbert, Background removal
555 from spectra by designing and minimizing a non-quadratic cost function,
556 Chemom. Intell. Lab. Syst. 76 (2005) 121–133.
- 557 [14] F.Gan, G.Ruan, J.Mo, Baseline correction by improved iterative polyno-
558 mial fitting with automatic threshold, Chemom. Intell. Lab. Syst. 82 (2006)
559 59–65.
- 560 [15] J.M.Brown, Method for correcting spectral data for data due to the spec-
561 tral measurement process itself and estimating unknown property and/or
562 composition data of a sample using such method, U.S. patent 5.121.337
563 (1992).
- 564 [16] B.Walczak, D.L.Massart, Noise suppression and signal compression using
565 the wavelet packet transform, Chemom. Intell. Lab. Syst. 36 (1997) 81–94.
- 566 [17] J.Trygg, S.Wold, Pls regression on wavelet compressed nir spectra,
567 Chemom. Intell. Lab. Syst. 42 (1998) 209–220.
- 568 [18] L.Eriksson, J.Trygg, E.Johansson, R.Bro, S.Wold, Orthogonal signal cor-
569 rection, wavelet analysis and multivariate calibration of complicated pro-
570 cess fluorescence data, Anal.Chim. Acta 420 (2000) 181–195.
- 571 [19] L.Pasti, B.Walczak, D.L.Massart, P.Reschiglian, Optimization of signal de-
572 noising in discrete wavelet transform, Chemom. Intell. Lab. Syst. 48 (1999)
573 21–34.
- 574 [20] Y.Hu, T.Jiang, A.Shen, W.Li, X.Wang, J.Hu, A background elimination
575 method based on wavelet transform for raman spectra, Chemom. Intell.
576 Lab. Syst. 85 (2007) 94–101.
- 577 [21] R.K.H.Galvao, G.E.Jose, H.A.D.Filho, M.C.V.Aranjo, E.C.DaSilva,
578 H.M.Paiva, T.C.B.Saldanha, E.S.O.N.DeSouza, Optimal wavelet filter con-
579 struction using x and y data, Chemom. Intell. Lab. Syst. 70 (2004) 1–10.
- 580 [22] B.K.Alsberg, A.M.Woodward, D.B.Bell, An introduction to wavelet trans-
581 form for chemometricians: a time-frequency approach, Chemom. Intell.
582 Lab. Syst. 37 (1997) 215–239.
- 583 [23] V.J.Barclay, R.F.Bonner, I.P.Hamilton, Application of wavelet transforms
584 to experimental spectra: smoothing, denoising and data compression, Anal.
585 Chem. 69 (1997) 78–90.
- 586 [24] S. Wold, H. Antti, F. Lindgren, J. Ohman, Orthogonal signal correction of
587 near infra-red spectra., Chemom. Intell. Lab. Syst. 44 (1998) 175–185.
- 588 [25] J.Sjöblom, O.Svensson, M.Josefson, H.Kullberg, S.Wold, An evaluation of
589 orthogonal signal correction applied to calibration transfer of near infrared
590 spectra, Chemom. Intell. Lab. Syst. 44 (1998) 229–244.

- 591 [26] J.A.Westerhuis, J.DeJong, A.K.Smilde, Direct orthogonalization,
592 Chemom. Intell. Lab. Syst. 56 (2001) 13–25.
- 593 [27] C.A.Andersson, Direct orthogonalization, Chemom. Intell. Lab. Syst. 47
594 (1999) 51–63.
- 595 [28] T.Fearn, On orthogonal signal correction., Chemom. Intell. Lab. Syst. 50
596 (2000) 47–52.
- 597 [29] H.C.Goicoechea, A.C.Olivieri, A comparison of orthogonal signal correction
598 and net analyte preprocessing methods, theoretical and experimental study,
599 Chemom. Intell. Lab. Syst. 56 (2001) 73–81.
- 600 [30] J.Trygg, S.Wold, Orthogonal projection to latent structures (o-pls), J. of
601 Chemom. 16(3) (2002) 119–128.
- 602 [31] O.Svensson, T.Kourti, J.F.MacGregor, An investigation of orthogonal sig-
603 nal correction algorithms and their characteristics, J. of Chemom. 16(4)
604 (2002) 176–188.
- 605 [32] E.K.Kemsley, H.S.Tapp, Opls filtered data can be obtained directly from
606 non-orthogonalized pls1, J. Chemom. 23 (2009) 518–529.
- 607 [33] A.Lorber, N.K.M.Faber, B.R.Kowalski, Net analyte signal calculation in
608 multivariate calibration, Anal. Chem. 69(8) (1997) 1620–1626.
- 609 [34] J.Ferre, N.K.M.Faber, Net analyte signal calculation for multivariate cali-
610 bration, Chemom. Intell. Lab. Syst. 69 (2003) 123–136.
- 611 [35] R.Bro, C.M.Andersen, Theory of net analyze signal vectors in inverse re-
612 gression, J. of Chemom. 17 (2003) 646–652.
- 613 [36] J.C.Boulet, T.Doco, J.M.Roger, Improvement of calibration models using
614 two successive orthogonal projection methods, application to quantification
615 of wine mannoproteins., Chemom. Intell. Lab. Syst. 87 (2007) 295–302.
- 616 [37] S.Preys, J.M.Roger, J.C.Boulet, Robust calibration using orthogonal pro-
617 jection and experimental design, application to the correction of the light
618 scattering effect on turbid nir spectra., Chemom. Intell. Lab. Syst. 91 (2006)
619 28–33.
- 620 [38] K.H.Liland, T.Almoy, B.H.Mevik, Optimal choice of baseline correction
621 for multivariate calibration of spectra, Appl. Spectrosc. 64(9) (2010) 1007–
622 1016.
- 623 [39] R.Piziak, P.L.Odell, R.Hahn, Constructing projections on sums and inter-
624 sections, Comput. Math. Appl. 37 (1999) 67–74.
- 625 [40] P.Geladi, D.MacDougall, H.Martens, Linearization and scatter-correction
626 for near infrared reflectance spectra of meat, Appl. Spectrosc. 39(3) (1985)
627 491–499.

- [41] H.Martens, E.Stark, Extended multiplicative signal correction and spectral interference subtraction: new preprocessing methods for near infrared spectroscopy, J. Pharm. Biomed. Anal. 9 (1991) 625–635.
- [42] R.DeMaesschack, D.JouanRimbaud, D.L.Massart, The mahalanobis distance, Chemom. Intell. Lab. Syst. 50 (2000) 1–18.

Appendix A. Writing Fearn’s OSC in the form of an orthogonal projection into $\mathbb{R}^P$

Two equations are extracted from Fearn’s text:

$$\mathbf{t}_i = \mathbf{X}\mathbf{w}_i \quad (\text{A.1})$$

$$\mathbf{p}_i = \mathbf{X}'\mathbf{t}_i(\mathbf{t}_i'\mathbf{t}_i)^{-1} \quad (\text{A.2})$$

Let Σ be $(\mathbf{X}'\mathbf{X})^+$, the Moore-Penrose pseudo-inverse of $(\mathbf{X}'\mathbf{X})$. Our first goal is to write $\mathbf{w}_i$ using $\mathbf{p}_i$ and Σ . The calculation of the product $\mathbf{p}_i'\Sigma\mathbf{p}_j$ is performed using equations A.1 and A.2 :

$$\begin{aligned} \mathbf{p}_i'\Sigma\mathbf{p}_j &= (\mathbf{t}_i'\mathbf{t}_i)^{-1}\mathbf{w}_i'\mathbf{X}'\mathbf{X}\Sigma\mathbf{X}'\mathbf{w}_j(\mathbf{t}_j'\mathbf{t}_j)^{-1} \\ &= (\mathbf{t}_i'\mathbf{t}_i)^{-1}\mathbf{w}_i'\mathbf{X}'\mathbf{X}\mathbf{w}_j(\mathbf{t}_j'\mathbf{t}_j)^{-1} \\ &= (\mathbf{t}_i'\mathbf{t}_i)^{-1}\mathbf{t}_i'\mathbf{t}_j(\mathbf{t}_j'\mathbf{t}_j)^{-1} \end{aligned}$$

If $i \neq j$, because of the orthogonality of the $\mathbf{t}_i$:

$$\mathbf{p}_i'\Sigma\mathbf{p}_i = (\mathbf{t}_i'\mathbf{t}_i)^{-1} \quad (\text{A.3})$$

$$\mathbf{p}_i'\Sigma\mathbf{p}_j = 0 \quad (\text{A.4})$$

After multiplying on the left by $\Sigma\mathbf{X}'$, a different combination of equations A.1 and A.2, completed with equation A.3, yields:

$$\Sigma\mathbf{X}'\mathbf{X}\mathbf{w}_i = \Sigma\mathbf{X}'\mathbf{t}_i = \Sigma\mathbf{p}_i(\mathbf{t}_i'\mathbf{t}_i) = \Sigma\mathbf{p}_i(\mathbf{p}_i'\Sigma\mathbf{p}_i)^{-1} \quad (\text{A.5})$$

The left term is the projection of $\mathbf{w}_i$ onto the space spanned by $\mathbf{X}'\mathbf{X}$, which is also the space spanned by the lines of $\mathbf{X}$ (39), called $\mathcal{E}_X$. On the other hand, the $\mathbf{w}_i$ are the eigenvectors of the matrix $\mathbf{M}\mathbf{X}'\mathbf{X}$, where $\mathbf{M}$ is the projector orthogonal to $\mathbf{X}'\mathbf{y}$, which belongs to $\mathcal{E}_X$. Thus, $\mathbf{w}_i$ also belongs to $\mathcal{E}_X$, it is not modified after projection onto $\mathbf{X}'\mathbf{X}$ and equation A.5 is simplified:

$$\mathbf{w}_i = \Sigma\mathbf{p}_i(\mathbf{p}_i'\Sigma\mathbf{p}_i)^{-1} \quad (\text{A.6})$$

647 The $\mathbf{p}_i$ are Σ - orthogonal according to equation A.4, and therefore $(\mathbf{P}'\Sigma\mathbf{P})$
648 is a diagonal matrix of full rank. Thus, equation A.6 can be written in a matrix
649 form:

$$\mathbf{W} = \Sigma\mathbf{P}(\mathbf{P}'\Sigma\mathbf{P})^{-1}$$

650 The OSC correction is:

$$\begin{aligned}\mathbf{X}_{OSC} &= \mathbf{X} - \mathbf{X} \sum_{i=1}^A \mathbf{w}_i \mathbf{p}'_i \\ &= \mathbf{X} - \mathbf{X} \mathbf{W} \mathbf{P}' \\ &= \mathbf{X} (\mathbf{I}_P - \Sigma \mathbf{P} (\mathbf{P}' \Sigma \mathbf{P})^{-1} \mathbf{P}')$$

651 To conclude, Fearn's OSC can be also expressed into $\mathbb{R}^P$ as an oblique (not
652 Euclidian) projection to the space spanned by the column-vectors of $\mathbf{P}$. If $\mathbf{X}$
653 has been centered, Σ is a metric associated to a Mahalanobis distance (42).