Are standard sample measurements still needed to transfer multivariate calibration models between near-infrared spectrometers? The answer is not always

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Are standard sample measurements still needed to transfer multivariate calibration models between near-infrared spectrometers? The answer is not always

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ABSTRACT

Calibration transfer (CT) refers to the set of chemometric techniques used to transfer (near-infrared) calibration models between spectrometers. The requirement of traditional CT methods to measure calibration standard samples has been a challenge as such measurements are difficult in real-world applications, e.g. when the instruments are located far apart or chemically stable standard samples are not available. In recent years, major developments have taken place in the domain of CT, hence, this work provides a concise but critical review of all the main recent chemometric techniques available to perform CT. Particularly this work explains some newer concepts for standard-free CT, where the standard samples are not required to attain the CT. We conclude that CT approaches that do not rely on standard sample measurements hold promise to help making calibration models sharable between similar analytical devices and to increase the applicability of CT to real-world problems in the analytical sciences.

1. Introduction

A substantial proportion of chemometric applications to real-world problems deals with the possibility of predicting qualitative and quantitative sample properties based on some analytical measurements [1–3]. However, the generalizability of predictive models, i.e., the extent to which such models can be applied to new data, depends on how much of the variability spanned by the future samples is represented in the calibration set [4,5]. A direct consequence of this is that the use of multivariate chemometric models is often limited to data collected on the same instrument that was used to measure the calibration samples. Different instruments have intrinsic differences, due to i) different technical components in the instrument such as the detector or the illumination source ii) differences in the spectral range, resolution or wavelength axis registry or iii) due to differences in the environment surrounding the instrument [6,7], e.g. temperature or humidity. To cope with this limitation, several so-called calibration transfer (CT) strategies have been proposed in the literature [7,8].

An exemplary overview of the need for CT is illustrated in Fig. 1, where the scenario of model transfer from a lab-based primary instrument to similar lab-based instruments and portable spectrometers is presented. Such model transfer is required e.g. after instrument maintenance, when a new similar instrument is used, or the same type of instrument is deployed at a different location to analyze similar samples. In another scenario, model transfer is

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Abbreviations

AI	Artificial intelligence
CARS	Competitive adaptive reweighted sampling
CCA	Canonical component analysis
CH	Carbon hydrogen
CT	Calibration transfer
CTAI	Calibration transfer with affine invariance
CTWM	Calibration transfer using weight matrix
DA	Domain adaption
di-PLS	Domain invariant partial least square
DL	Deep learning
DOP	Dynamic orthogonal projection
DOP	Dynamic orthogonal projections
DS	direct standardization
ELM	Extreme learning machine
FIR	Finite impulse response
GCT-PLS	Graph based calibration transfer partial least square
JUMBA	Joint and unique multi-block analysis
JY-PLSR	Joint Y partial least square regression
LMC	Linear model correction
LVs	Latent variables
MSCA	Multi-level simultaneous component analysis
MWMSC	Moving window multiplicative scatter correction
NAS	Net analyte signal
NIR	Near-infrared
NPE	Neighborhood preserving embedding
O2PLS	2-block orthogonal partial least square
OH	Oxygen hydrogen
OLS	Ordinary least square
OnPLS	n-block orthogonal partial least square
OSC	Orthogonal signal correction
OSR	Orthogonal signal regression
PCA	Principal component analysis
PDS	Piecewise direct standardization
PLS	Partial least square
RKSPDS	Rand Kennard Stone piecewise direct standardization
SCA	Simultaneous component analysis
SDPDS	Standard deviation of precision detection spectra
SR	Selectivity ratio
SST	Spectral space transformation
SWCS	Screening wavelengths with consistent and stable signals
TCA	Transfer component analysis
TOP	Transfer by orthogonal projection
TSR	Trimmed score regression
TL	Transfer learning
UVE	Uninformative variable elimination
VIP	Variable importance in projection
VPdtw	variable penalty dynamic time warping
WMSC	Window multiplicative scatter correction

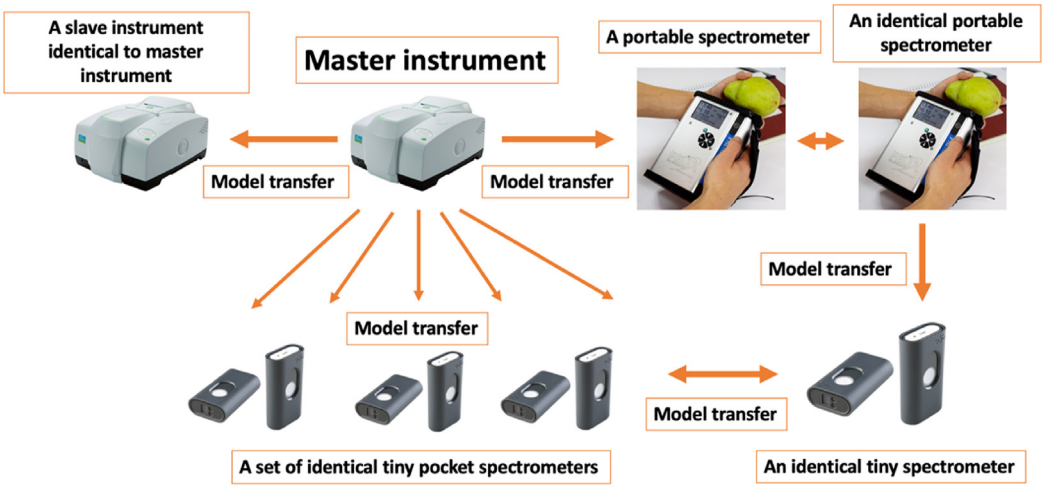

Fig. 1. An example of potential scenarios where CT might be employed to transfer calibration models between analytical devices. The portable, handheld spectrometer is the Felix portable spectrometer from Felix Instruments, USA and the pocket spectrometer are the SCiO, Consumer physics, Israel.

required when aiming to use advanced portable spectrometers for field analyses. Furthermore, model transfer may be required to transfer models between portable spectrometers. Similarly, a model established on a lab-based or portable spectrometer might need to be transferred to multiple pocket spectrometers. Lastly, multiple pocket spectrometers may share a model between different pocket spectrometers of the same (or different) type.

CT refers to chemometric techniques that allow adaption of a calibration model developed using a spectral database acquired on one instrument to enable inference (i.e. prediction) on spectra acquired on other instruments with similar accuracy and precision [6,7,9]. In this context, the most adopted strategy requires calibration standard samples to be measured on both instruments to model the instrumental differences and/or to compensate for them [7]. For example, the most widely used CT techniques i.e., direct standardization (DS) [10] and piecewise direct standardization (PDS) [11], require measurement of the same set of standard samples on the different instruments. Since the samples are the same, it is assumed that the resulting differences in the signals are due to the intrinsic differences between the instruments. The inequality between a primary instrument (for which an initial calibration model has been established) and a secondary instrument (to which

a calibration model should be transferred) can be modelled by means of a transfer function. Once the transfer function is parameterized, it can be used to transform the data from the secondary instrument to make them look as if they were recorded on the primary instrument, so that the primary calibration model can be directly employed for inference on the data from the secondary instrument (forward standardization). Alternatively, the primary calibration database is transformed to match the secondary spectra and the model is rebuilt using the transformed data (backward standardization) [10,11].

CT based on calibration standards may not always be feasible [12–14], e.g. if the instruments are in remote locations, if stable calibration standards with appropriate spectral properties are not available or, more recently, in the case of portable spectroscopy where spectrometers are sold as consumer products. There is an increasing demand for methods which reduce the need for standard samples measurements in order to facilitate sharing of chemometric models across different instruments (or analytical platforms). Recently, the development of CT strategies that do not require standard samples has gained attention and several approaches have been proposed in the literature [8]. These approaches range from techniques such as dynamic orthogonal projection (DOP) [15], where the need of paired measurements of standard samples is replaced by the measurement of occasional standard samples on the secondary instrument only, to advanced variable selection techniques such as double competitive adaptive reweighted sampling (double CARS) [16], which selects the variables that retain the predictive performance of models on a new instrument, to domain-adaption techniques such as domain-invariant partial least-squares (di-PLS) regression [13,14] which aims at extracting domain-invariant latent variables (LVs) to attain generalized models that can be used on multiple instruments.

With the present article we aim at providing a concise, easy to understand but critical review of all the main recent chemometric concepts and techniques available to perform CT between instruments. Successively, a summary and a critical comparison of different CT methods that do not require standard samples are presented and innovative applications of standard-free CT methods are reviewed. A key point to note is that this review focuses on the transfer of regression models dealing with continuous responses and that the transfer of classification models is outside the scope of this review.

2. Why calibration models cannot be used directly on a new instrument?

Multivariate regression/calibration models are often required to relate the instrument/sensor responses to some property(-ies) of interest [1]. Due to the usually large number of highly correlated variables present in the signals from modern near-infrared (NIR) equipment, methods based on the extraction of latent variables (LVs), such as partial least squares (PLS) regression, are frequently used for this purpose [17]. The calibration model identifies a function which approximates the relationship between the instrument/sensor signals and the property(-ies) of interest. For example, if NIR spectroscopy is used to predict the fat content in meat, then the corresponding calibration model will identify the bands around 1200 nm to be the most correlated to the fat content, as these wavelengths correspond to the second overtone of C–H stretching vibrations. In principle, one would expect this same relation to hold for any other NIR instrument. However, due to instrument-specific sources of additional variability such as differences in light source, the sensitivity of the detectors or in the measurement mode, the same model, if used on a different instrument, will lead to over- or under-estimation of the property of interest. Sometimes it is not only the instrument itself but the environmental condition in which the measurements are performed that can play an important role in affecting the generalizability of chemometric models. For example, in the case of NIR spectroscopy, the temperature at which the measurements are conducted is known to play a crucial role and often leads to model failure if not properly accounted for in advance. The influence of temperature can be noticed as baseline shifts for the complete spectra or peak shifts near the O–H absorption bands, especially in high moisture products. Sometimes the CT problem can become even more challenging when the state of the samples is different, for example, when the samples on the primary instruments are measured in solid form while in the secondary they are measured as powders, as is the case when the model developed on rice kernels is to be transferred to rice flour samples [18]. Such a change in the physical state of the samples can cause differences between the spectra from two instruments. Finally, the most complicated scenario arises when there are intrinsic differences in the instruments as well as differences in the surrounding environment and the samples' physical or chemical (i.e. matrix effects) properties. For example, when a calibration for solid rice kernels established on one instrument for a certain temperature range needs to be transferred to a new instrument that operates at different temperature levels on rice flour. The differences that a CT method needs to account for include the intrinsic difference between the instruments, the shifts in peak positions and baselines due to temperature effect and the scattering effects due to interaction of light with samples corresponding to different physical forms.

3. Recent development in calibration transfer methods

CT using standard samples has been a field of interest in chemometrics for a long time [6,9,10]. The procedure usually involves measuring the same set of samples on the two instruments between which the calibration model is to be transferred. Later, either a (correction) function is modelled based on the differences between the responses of the two instruments or these differences are compensated [7]. In both cases, CT methods work well and are widely used in industrial settings, even if their good performances have not stopped the innovation and the development of novel approaches based on standard samples. The traditional standard-based CT methods can be broadly classified into three subgroups:

1. Methods that deal with the complete multivariate signal from the primary and the secondary instrument at once, such as DS.
2. Methods dealing with local differences between primary and secondary instruments such as PDS.
3. Methods that perform standardization in latent spaces to attain generalized performance of the models such as spectral space transform (SST) [19].

A summary of recent techniques for CT is provided in Table 1. In terms of local approaches, two types of methods are available. The first type, such as Rank Kennard- Stone Piecewise Direct Standardization (RKSPDS) [20], extends the classical PDS approach, whereas the second type aims to select a subset of variables and their combinations that support the generalization of models to a new instrument [21–23]. The RKSPDS methods include a transfer sample selection step based on the Rank Kennard-Stone approach [24] prior to applying PDS to select transfer samples of greater representativeness and wider coverage with respect to the property of interest. The main benefit of the RKSPDS over its predecessor PDS is that it achieves high precision model transfer with fewer transfer samples [20]. In relation to the methods based on the selection of subsets of variables, the major innovation can be noted

Table 1
A summary of recent calibration transfer techniques.

Type	Technique	Background	Key features	Ref.
Local modelling	Double competitive adaptive reweighted sampling (double CARS)	• Extension of CARS algorithm to multi-instruments scenario • Variable importance is considered for both primary and secondary instrument	• Identifies the key subset of variables that lead to minimum error in both the instrument • Suitable when model transferred between different number of spectral variables	[16]
	Rank Kennard Stone Piecewise Direct Standardization (RKSPDS)	• RKSPDS methods just includes a transfer sample selection step based on Rank Kennard-Stone approach before the PDS operation to select transfer samples of greater representativeness and wider coverage over the property of interest	• The transfer samples selected by Rank-KS have greater representativeness and wider coverage • Required the least number of transfer samples in the model transfer • Selected transfer samples selected can be directly applied to model transfer related to other properties e.g., sample selected during transferring a fat prediction model and later be used to transfer a protein prediction model	[20]
	CT by optimizing wavelengths combination based on stable spectral signals	• Wavelength combinations were screened by different methods such as, uninformative variable elimination, selectivity ratio and variable importance in projection, to obtain robust and simple calibration models that can be shared by secondary spectrometers	• Simplify PLS models and improve the models' efficiency such that when the models can be transferred to secondary spectrometers	[21]
	Correlation analysis-based wavelength selection for CT	• Aims to selects the variables at which the spectral responses from different instruments are well correlated	• Integrates the variable selection and CT in single technique • Selected variables are adjusted based on the instrument to maintain the predictive performance	[22]
Sub-space modelling methods	CT with canonical correlation analysis	• Utilizes canonical component analysis as a dimensionality reduction technique prior to computing transfer function	• Useful when instruments provide signals at different resolution, without any interpolation or extrapolation of signals	[23]
	Direct CT to principal components via canonical component analysis (PCA-CCA)	• PCA-CCA based CT extracts the PCs from secondary spectra and then CCA is used to transfer the PCs of secondary to the latent variables of PLS developed on the primary instrument	• A fast alternative to classical CT methods such as piecewise direct standardization (PDS) and spectral space transformation (SST)	[25]
	CT via extreme learning machine auto encoders	• Utilizes extreme learning machine auto encoders as a dimensionality reduction and difference learning technique	• A non-linear approach to CT	[26]
	CT with neighborhood-preserving embedding	• Utilizes neighborhood preserving embedding as a dimensionality reduction technique prior to computing transfer function	• Neighborhood preserving embedding (NPE) allows capturing the nonlinearity in data which improves the transform function for CT	[27]
	Cross-component CT with PCA and weighted ELM-based TrAdaBoost algorithm	• Combines principal component analysis (PCA) for dimensionality reduction with the weighted extreme learning machine (ELM) and TrAdaBoost algorithm	• Allow to transfer model between different components to be predicted	[28]
	PLS subspace-based CT	• The data from primary and secondary instrument are transferred to the PLS subspace spanned by the PLS model developed between spectra of primary instrument and the response variables, later a feature transfer relationship model is constructed by ordinary least-square regression at PLS feature space	• PLS-based subspace transfer provides an efficient method for performing CT with only a small number of standard samples • Can correct for complex distortions	[29]
	CT using weight matrix of partial least squares	• Two version were proposed namely CTWM1 and 2 • CTWM1 uses PLS to build a linear regression model between the secondary spectra of standardization samples and the low-dimensional information extracted from the primary spectra of standardization samples using the weight matrix of the original calibration model. • CTWM2 retains the weight matrix but uses ordinary least squares (OLS) to update the y-weight vector using the secondary spectra and property values of standardization samples.	• CTWM1 can be applied to the occasion when both the primary and secondary spectra of standardization samples can be obtained. • CTWM2 can be applied to the occasion when the primary spectra of standardization samples cannot be obtained but the observed property values can be.	[30]
	Trimmed score regression and joint Y regression	• Permit to exploit the specific relationships between instruments for imputing new unmeasured spectra, which will be then	• Utilizes data imputation concept to simulate unmeasured spectra and	[31]

Table 1 (*continued*)

Type	Technique	Background	Key features	Ref.
		resorted to for building an improved predictive model, suitable for the analysis of future incoming data	late use it to adjust the model to be used on a new instrument.	
	A two-level strategy for standardization of near infrared spectra by multi-level simultaneous component analysis	• Uses a two-level MSCA model to capture the difference between instruments (the first level) and samples (the second level)	• Both the instrument difference and the spectral variation caused by operation and measurements conditions can be corrected, simultaneously.	[32]
	A dual model strategy for CT	• A primary calibration model is built using the spectra of a primary instrument and a correction model is established to describe the ratios between the predicted results from the spectra of different instruments • The prediction for the spectra of secondary instrument are achieved by correcting the prediction of the primary model	• Does not rely on the transfer function	[33]
	Robust calibration model transfer to deal with outliers and noise in the samples	• Cauchy estimator are employed to learn common subspace from primary and secondary spectra robustly. Transformation matrix is calculated with the two corresponding coefficient matrices.	• Useful in automatically dealing with outliers present in data which may affect the performance of transferred model	[34]
	Multi-instrument CT using independent component analysis	• Performs independent component analysis on variable domain concatenated spectral matrix to obtain the mixing matrix and the independent components of different spectrometers. • Spectrometers can then be standardized by correcting the coefficients within the independent components	• Models can be transferred to multiple instruments in one go	[35]
	Common quantitative model generation for models to be used on multiple instruments	• Utilizes Tchebichef image moment method based on the near infrared (NIR) three-dimensional spectra constructed based on multiple instruments and later uses stepwise regression to attain generalized models	Generalized multi-instrument models can be obtained	[36]
	Joint and unique multiblock analysis for CT	• Exploits the common and distinct information to perform extracted by multi-block data analysis to perform the CT	• Models can be transferred simultaneously to multiple instruments	[37]
	Graph-based CT	• Utilizes manifold regularization on the PLS objective to reduce between-device variation	• Does not require that calibration standards share similar (spectral) features with the calibration samples	[12]

in the development of methods that extend standard variable selection techniques to multi-instrument scenarios allowing CT when the number of variables recorded by the instruments involved are different (i.e., spectrometers generating signals with different spectral resolutions). For example, a recent extension of competitive adaptive reweighted sampling (CARS), called Double-CARS, allows CT by selecting variables from primary and secondary spectra that lead to low prediction errors [16]. The other recent variable selection approaches for CT aim to build robust PLS calibrations by identifying consistent and stable spectral regions using traditional strategies such as uninformative variable elimination (UVE), variable importance in projection (VIP) and selectivity ratio (SR) [21]. The application of models based on selected variables has shown better performance compared to the standard PDS approach to CT. There can also be the possibility of adopting a coupled strategy where a preliminary variable selection is followed by traditional CT approaches on the identified subset of predictors. For example, the recently proposed correlation-based approach to variable selection can be combined with the classical CT approaches to enhance the efficiency of CT [22].

Although there have been several developments in the extension of local modelling strategies, most of the recent ones are related to subspace modelling approaches (Table 1). The general idea of subspace-based CT methodologies is to perform the standardization after transformation, e.g., using traditional chemometric approaches such as principal component analysis (PCA) [25] or advanced non-linear approaches such as autoencoders [26], neighbor embeddings [27] or extreme learning machines [26,28]. Canonical correlation analysis (CCA) has played a major role in the development of subspace-based CT methods, and particularly methods that allow transferring models between instruments having different spectral resolutions [23]. CCA is a popular technique from multivariate statistics that allows modelling multivariate relationships among different data blocks, which, in the case of CT, may correspond to different instruments. Basically, the CCA-based methods operate on subspaces and thus eliminate the need for interpolation of signals, representing a generic solution for CT problems [23]. Development in CCA-based methods can also be noted where CCA is combined with PCA to attain even more efficient CT [25]. The PCA-CCA-based CT methods extract the PCs from the signals collected on the secondary device and then CCA is used to transfer the PCs of the secondary to the latent variables of a PLS model developed on the primary instrument [25]. PCA-CCA-based CT methods have already proven to be better than those based on CCA alone [25]. PLS-based CT methods are also emerging where at first the primary and secondary profiles are projected onto the subspace spanned by the primary's PLS model [29]. Later, the projected secondary spectra are transformed by ordinary least squares to match the projections of the primary spectra, i.e. a direct standardization is performed in the PLS subspace. Application of PLS subspace-based methods has proven to be better than those solely based on CCA [29]. The superior performance of PLS subspace-based CT methods can be explained by the fact that PLS identifies subspaces that are most correlated to the property of interest. Instead of performing the standardization on

the projections of primary and secondary spectra, Zhang et al. proposed to apply the transformation on the PLS weight matrix in order to update the y-regression weights by using the spectra from the secondary instrument and the corresponding property of interest [30]. Advances can also be noted in the use of methodologies such as the trimmed scores regression (TSR) and the joint-Y PLS (JYPLS) regression where the data from the primary and secondary instruments are jointly explored with the aim to attain CT [31]. In particular, the idea behind both approaches is that CT can be seen as a missing data imputation problem, where the information in the paired profiles acquired with both instruments can be exploited to reconstruct the signals which were not measured on the secondary device. A recent approach to subspace modelling utilizes a multilevel simultaneous component analysis approach (MSCA) [32], where the spectra of the same samples measured on two instruments are modelled with a two-level MSCA model to capture both the difference between instruments (the first level) and among samples (the second level). The MSCA scores of the first level model the spectral difference between instruments, whereas the inter-sample variability is captured by the scores of the second level. Later, the spectral difference due to the instrument and measurement can be corrected by adjusting the coefficients in the scores of the two-level models, respectively [32]. A recent approach also utilizes a dual modelling approach where the aim is not to attain a CT but to correct the predictions from the model made on the primary instrument to match the predictions on the secondary instrument's spectra [33].

The presence of outliers negatively affects chemometric models in general and, specifically, CT methods. Consequently, new developments in CT methods have emerged from the area of robust techniques, which can detect and reduce the influence of outlying samples. One such new technique utilizes the Cauchy estimator to reduce the influence of the outlying samples [34]. Robust CT methods have already outperformed the traditional CT methods such as DS and PDS as well as advanced subspace-based methods based on CCA [34]. Apart from the robust methods, key developments can also be noted with methods that allow the transfer of calibrations to multiple instruments. Traditionally, methods for CT are limited to two instruments. However, recent advancements in NIR technology and the increasing availability of low-cost sensors have led to the development of methods that allow multi-instrument CT, i.e., from one primary device to multiple secondary instruments. In the domain of multi-instrument CT, there are currently three types of methods: simultaneous subspace modelling methods [35], methods that aim at developing generalized common quantitative models to be used on multiple instruments [36] and methods extending multi-block chemometric strategies to model the distinct and unique subspaces in a multi-instrument scenario [37]. Liu et al. have recently introduced a simple subspace-based multi-instrument CT method using independent component analysis on the concatenated data matrices (in the variable domain) [35], where measurements on different spectrometers are standardized by correcting the coefficients within the independent components [35]. In the framework of developing common quantitative models for multi-instrument scenarios, the use of Tchebichef image moments to extract relevant chemical features has been studied in Ref. [36]. In the framework of multi-block chemometric methods [38], joint and unique multi-block analysis (JUMBA), where orthogonal n-blocks partial least-squares (OnPLS) [39] is used to extract common and unique information from data acquired on the same samples with different spectrometers, has been successfully applied to CT problems [37].

Although several new standard-based calibration methods were developed in recent years, all these methods require that the transfer standard samples share similar characteristics with the calibration samples. In many cases, however, it might be difficult to find standard samples that are chemically stable and at the same time share similar spectral features with the calibration samples. Towards enabling CT with arbitrary CT standards, Nikzad-Langerodi and Sobieczky recently proposed a manifold regularization method for PLS regression [12]. Their approach, termed GCT-PLS, shares some similarity with other subspace-based CT techniques such as PLSCT proposed in Ref. [24]. However, instead of first constructing the PLS subspace and standardizing primary and secondary signals in that space, GCT-PLS implicitly standardizes the instruments while deriving a subspace that is predictive with respect to the response and at the same time-invariant with respect to between-instrument variation.

4. Standard-free calibration transfer and methods

The main limitation of “classical” CT methods is that they require standard samples that must be measured on all the instruments [8]. Such extra measurements can be time-consuming, labor intensive and inconvenient (e.g., when the model must be transferred from the laboratory to an in-line process spectroscopic sensor), and, sometimes, not possible as either the instruments are based in locations far from one another, or the primary instrument is damaged. Further, most CT methods need the standard samples to have similar or the same spectral properties as the calibration samples. At the same time, the standards should also be chemically stable, otherwise each time a different signal will be measured from the same sample. Over the past years, several standard-free CT techniques have been proposed to deal with this issue. In the following subsections, the major concepts related to standard-free CT are discussed and a summary of available methods is provided in Table 2.

4.1. Domain adaption-based standard-free calibration transfer

While having already been widely explored in the context of machine learning, domain adaption (DA) is a new term in chemometrics and analytical chemistry. DA is the branch of machine learning that is concerned with learning (classification/regression) models from data that follow different distributions (i.e., data from different domains). The most frequent setting in DA is when substantial amounts of labelled data are available in one (source) domain, whereas label information for data from some related (target) domain(s) is either missing or scarce. The goal of DA is then to leverage the source domain information to support learning in the target domain(s). In the case of CT, data acquired on different instruments usually follow different distributions and DA techniques might be employed to leverage the calibration set from a primary instrument to establish a calibration model using unlabelled secondary instrument data (e.g., spectra where the reference values are unknown).

Many works on DA-based CT employed the domain-invariant representation learning paradigm, where the idea is to derive (latent) representations of the input data (e.g. spectra) where the distributional differences between the domains are small (Fig. 2). The rationale behind this approach is to make the source and target domain data look as if they were sampled from the same underlying distribution, in which case (according to statistical learning theory) generalization from the source to the target domain(s) should succeed (within the usual error bounds). In one of the first studies of its kind, Andries [40] employed transfer- (TCA) [41] and scatter component analysis (SCA) [42], two well-established methods from the DA community, to study CT on the Corn dataset [40]. Both methods construct subspaces of the input data where between-domain scatter is small. Subsequently, linear regression is employed on the (domain-invariant) LVs to establish the

Table 2
A summary of recent standard free calibration transfer techniques.

Type	Technique	Background	Key features	Ref.
Domain adaption-based standard-free transfer	Transfer component analysis (TCA)/Scatter Component Analysis (SCA)	• Both methods aim at finding a subspace, where the distributional difference between samples belonging to different conditions is small and the amount of explained variance is large.	• Extraction of LVs that are invariant w.r.t. the different conditions (i.e. domains) • Allows linear or non-linear (kernel-based) embedding of the domains • The subspace is not necessarily predictive w.r.t. the response	[41]
	Domain-invariant partial least squares regression (di-PLS)	• Finds a subspace that is predictive w.r.t. a response y and at the same time minimizes the distributional difference between the domains in terms of co-variances.	• Applicable to (semi-) supervised and unsupervised domain adaptation scenarios • Assumes normal distributed domains	[40]
	Domain adaptive partial least squares regression	• Similar to di-PLS but can handle more complicated distributional differences beyond co-variances.	• Handles more complicated (i.e. beyond co-variance related) domain shifts. • Allows linear or non-linear (kernel-based) embedding of the domains.	[14]
	Semi-supervised covariate shift modelling for spectroscopic data	• Implicitly removes the influence of mean and co-variance differences between labelled and unlabelled data on the model predictions.	• Model agnostic correction of covariate shifts	[76]
Methods based on orthogonal projections	Orthogonal space regression	• Uses OSC to estimate the Net Analyte Signal (NAS) of each domain (primary and secondary) • Estimates a linear model to turn a NAS into the other one	• Provides an explicit correction of the spectra • Assumes a simple linear distortion between the two domains	[54]
	Dynamic orthogonal projection	• Builds virtual standards based on some control points on the secondary • Estimates the subspace of spectral distortions and remove it by means of an orthogonal projection	• Makes the same model efficient on both domains • Provides insights on the spectral differences	[15]
	Dual-Domain CT Using Orthogonal Projection	• Calculates specific frequency components of each domain by means of wavelet transform • Projects the frequency components of the primary spectra onto the subspace orthogonal to the mean difference between the domains	• The model generalizes better on new instruments • Provides insights on the spectral differences	[56]
Methods relying on variable subset modelling	Stacked PLS for CT without standards	• Partition data in spectral domain and developed several stacked models. • The models were then weighted to emphasize the spectral region the most related to the property of interest.	• Allows to prefilter variables that are not related to the property of interest.	[65]
	Screening wavelengths with consistent and stable signals	• Used the standard deviation of difference spectra between the primary and secondary instruments to select key wavelengths invariant to instrumental differences	• Lead to simplified and robust models based on a few variables.	[66]
Methods exploring relationship between the prediction error and the spectral difference of the instruments	Partial-least square model correction by modelling prediction error and the spectral difference of the instruments	• Develops an extra PLS model between the prediction error obtained from the application of model made on primary instrument and the spectral difference of the instruments • The new error based PLS model is used to correct the predication of the model made on primary instrument and used for prediction on secondary instrument	• No such specific feature apart from possibility to perform standard free CT	[59]
	Affine invariance-based CT	• Utilizes angles and biases between the regression coefficients of the primary instrument and the secondary instrument	• Performs better when the concentration ranges of spectra measured on primary and secondary instrument are in similar range	[60]
Constrained optimization-based methods	Tikhonov regularization	• Utilizes Tikhonov regularization to transfer the coefficients of the primary model by optimizing the regression coefficients and minimizing the prediction errors of secondary spectra	• Requires some samples measured on secondary instrument to be augmented to the primary instrument prior to regularization	[57]
	Linear model correction	• Utilizes a few spectra measured on secondary instrument together with the constrained optimization, to transfer the model coefficients of the primary instrument to the secondary instrument	• Useful when the spectra measured on different instruments are linearly correlated	[58]
Transfer learning	Deep learning for non-translational data	• Develops several 1-dimensional convolutional neural networks with data from different spectral and variable size to learn generalized features	• Allows development of generalized models which can be used in scenarios with different signal resolution and variables. • Useful in cases when huge data is available.	[70]
	Transfer learning for spectral modelling	• Utilizes the concept of model fine-tuning by replacing the output layer of models	• Requires a few new measurements to update model weights	[71]
Other methods	Finite impulse response		• Useful in dealing with localized differences between spectra form primary and secondary instrument	[72,73]

(*continued on next page*)

Table 2 (*continued*)

Type	Technique	Background	Key features	Ref.
		• Utilizes finites impulse response filters to remove non-relevant information from the spectra of secondary instrument		
	Windowed MSC (W-MSC) and moving window MSC (MW-MSC)	• Extend the concept of multiplicative scatter correction to correct for localized differences in the spectra from different spectrometers	• The approach is useful when the differences in the instrument signals are local	[74]
	Variable penalty dynamic time warping	• Performs alignment of peaks between primary and secondary instruments	• Useful in cases when the main difference between primary and secondary instrument in the peak shifts	[75]

calibration. However, neither method can incorporate information about the response (i.e. the *y*-values) while deriving the corresponding subspace and could not significantly outperform local mean centring approaches. To overcome this limitation, Nikzad-Langerodi et al., 2018 proposed a domain-regularization approach for PLS to derive domain-invariant PLS (di-PLS) models which showed promising results on the same dataset [10]. di-PLS solves a non-convex optimization problem and is thus difficult to handle in practice. In Refs. [9,43], the same authors propose a convex relaxation of the original objective function of di-PLS which improves both applicability and performance of the method for CT and sample matrix compensation problems. Huang et al. subsequently extended the idea of domain-regularization for PLS regression problems to handle non-linearities (using a kernel-based approach) and non-Gaussian domains [37].

The main advantage of DA-based CT approaches is that no standardization set is required to transfer calibrations to another instrument if a representative set of samples from the corresponding "primary and secondary domains" are available. However, several pitfalls can make DA-based CT difficult in practice, in the cases when only input data are available from the secondary instrument (i.e., unsupervised DA). For unsupervised DA to succeed, the so-called covariate shift assumption must hold, which states that the domains must differ only in the marginal distribution of the input data (i.e., $P(X)$). This means that the relationship between instrumental response and property of interest must be the same in both domains, i.e., the conditional probability (i.e., $P(Y|X)$) must not change across the domains. Secondly, the distribution of the response (i.e., $P(Y)$) must be similar for the primary and secondary data, since models based on domain-invariant representations also give rise to predictions which are invariant w.r.t. the *y*-distributions (Fig. 3).

Other DA approaches to handle covariate shifts are the extension of the Linear Joint Training Framework proposed in Ref. [38] as well as the sample and feature augmentation approaches described in Ref. [44]. Both aim at orthogonalizing the regression vector away from between-domain differences.

4.2. Methods based on orthogonal projections

Orthogonal projections are immensely popular in the domain of chemometric data analysis [45]. Orthogonal projection can be understood as a "multivariate subtraction" and it is usually performed to subtract the already explained or irrelevant information. The use of orthogonalization is deep-rooted in chemometrics: the most popular chemometric methods such as principal component analysis (PCA) [46] and partial least-squares (PLS) regression [17] involve several orthogonalization steps to extract the un-correlated latent variables. Moreover, the current trends in multi-block chemometric data processing [47] also rely to a substantial extent on orthogonal projections which are used to remove the redundant information from several data blocks to model only unique information [38,48–50]. Fig. 4 provides an insight into the concept of orthogonal projections. Let S1 and S2 be two sets of spectra that should be similar, because they were acquired on the same samples, or because they correspond to the same reference value. These spectra differ because of a change in the measurement environment. Orthogonalization correction involves identifying the spectral subspace caused by these differences and removing it from the calibration base. Thus, a model calibrated on the modified base will

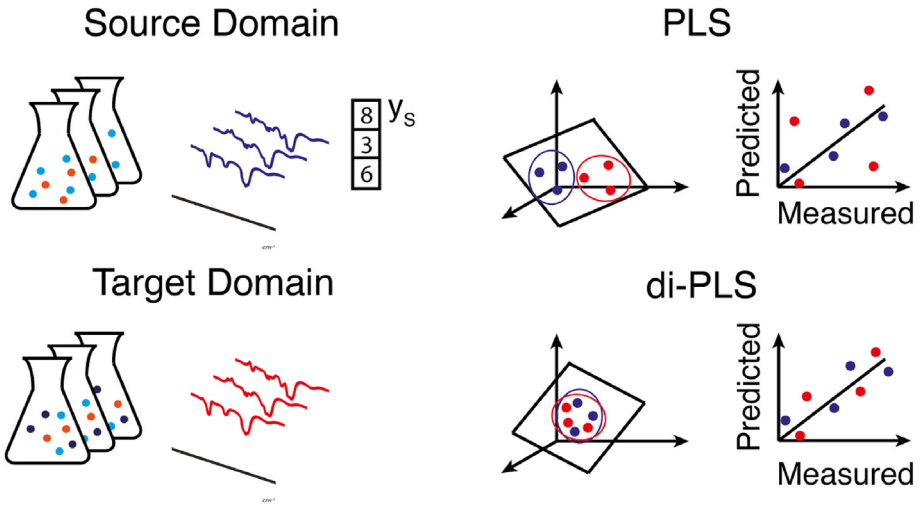

Fig. 2. An illustration of the concept of domain-invariant partial least squares (di-PLS) regression [14]. In the di-PLS, domain-invariant subspaces are learned which allows the model to be generalized to a previously unmodeled variation.

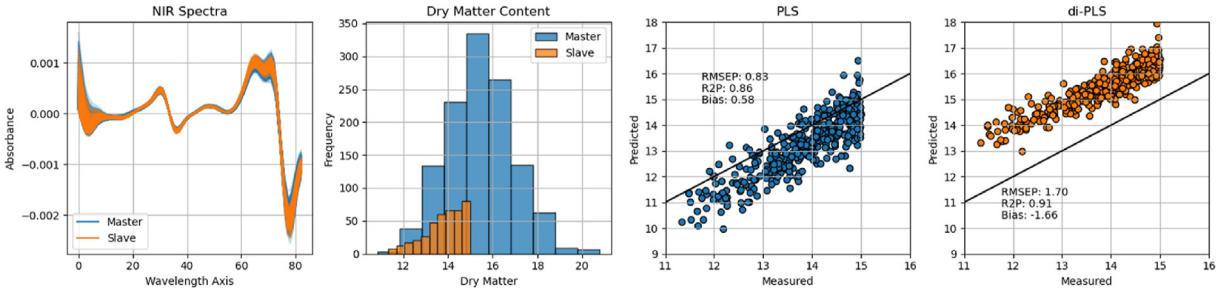

Fig. 3. What can go wrong with DA-based CT. From left to right: Primary (blue) and secondary (orange) NIR spectra of fruit, distribution of the corresponding dry matter (DM) contents, measured vs. predicted values of the primary PLS model applied to secondary instrument spectra and measured vs. predicted values of di-PLS model on the secondary instrument spectra. Note that the predicted values for the di-PLS model vary between 13 and 18, i.e. within the same range of DM contents from the samples recorded on the primary instrument.

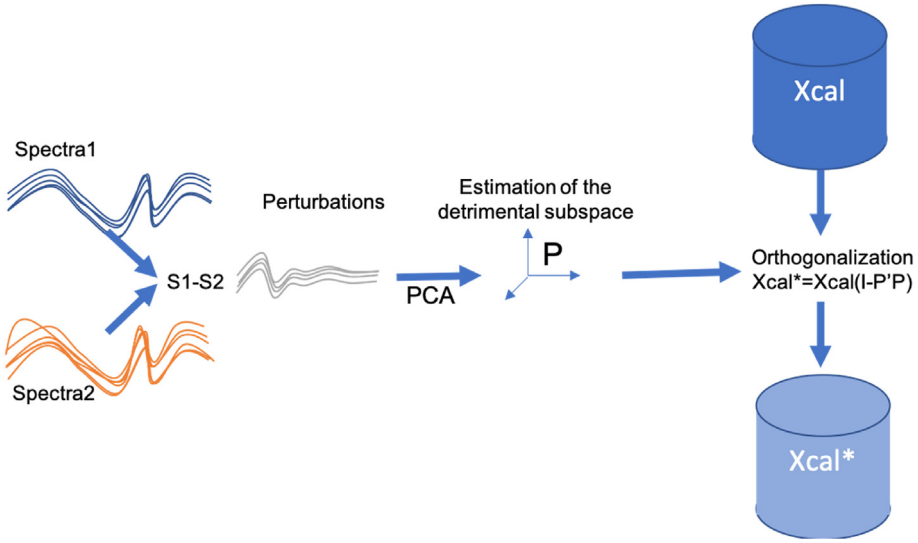

Fig. 4. Illustration of the calibration transfer by orthogonal projection. Two sets of spectra S1 and S2, measured on two different instruments are at first use to model the difference and later the spectra are transformed by removing this difference using orthogonal projections.

be insensitive to the spectral variations observed, whatever their level [51].

The use of orthogonal methods for CT started with a method called transfer by orthogonal projection (TOP) [52]. TOP attains the CT by orthogonalizing the calibration spectra with respect to directions in the spectral space in which most of the between-instrument variability lies. However, the main drawback of the TOP approach was that it required the standard samples to be measured on both primary and secondary instruments to estimate the between-instrument variability. To remove the dependence of TOP on the requirement of standard samples, new standard-free orthogonal methods were proposed. Although the standard-free orthogonal methods were first proposed with the aim of model maintenance [15], they have been finding increased application for CT purposes [53]. There are two different scenarios where the orthogonal projection-based methods can be used to perform standard-free CT. The first is where a small set of spectra and reference measurements are available from the secondary instrument, and in that case, the methods dynamic orthogonal projection (DOP) [15] and orthogonal space regression (OSR) [54] can be implemented. The second scenario is when the reference values for the secondary instrument are not available; in this case, methods such as orthogonal signal correction (OSC) [55] and dual-domain CT using orthogonal projection [56] are of high interest. DOP and OSR rely on the same principle of developing virtual standard spectra to account for response changes between instruments or batches. The aim is to identify the detrimental subspace which captures the differences between the instruments. This detrimental subspace is also unrelated to the property of interest, hence, their removal from the model does improve the prediction of the property of interest when the orthogonalized model from the primary instrument is tested on a secondary instrument. However, the main limitation of DOP and OSR is that they both require some spectra from the secondary instrument along with the values of the corresponding reference measurements. To deal with this, the dual-domain CT using orthogonal projection, which combines wavelet prism decomposition with the TOP approach to CT, was proposed [56]. The new dual-domain method projects the frequency components of the signals from the primary instrument onto the subspace orthogonal to the mean difference between the profiles from the primary and the secondary instrument. Then, each frequency component model is weighted according to the cross-validation error of the frequency components of the projected primary instrument's spectra to generate a stacked ensemble model robust to contributions to the spectra from instrumental variations [56]. By doing this, the dual-domain method allows suppression of the instrumental or physical phenomena (i.e., instrumental baseline shifts or discretized intensity changes which may be attributed to scattering), and enhancing of the chemical phenomena useful to explain the property of interest [56]. The dual-domain approach

has already outperformed the other orthogonal projection methods that require property values for spectra from the secondary instrument [56].

4.3. Constrained optimization-based methods

Constrained optimization is the process of optimizing an objective function with respect to some variables in the presence of constraints on those variables. A constrained optimization-based method such as utilizing Tikhonov regularization also gained popularity for standard-free CT. Tikhonov regularization transfers the coefficients of the primary model by optimizing the regression coefficients and minimizing the prediction errors of the secondary spectra [57]. Inspired by the Tikhonov regularization, a new constrained optimization method called linear model correction (LMC) was proposed [58]. LMC assumes that the spectra measured on different instruments for samples with similar physical and chemical properties are linearly dependent. Hence, the coefficients of the linear models constructed by the spectra measured on different instruments are similar. Using a few spectra measured on the secondary instrument together with the constrained optimization method, the coefficients of the primary model can be transferred to those of the secondary instrument [58].

4.4. Methods exploring the relationship between prediction error and spectral differences between instruments

When the same sample is measured using two different instruments under the same chemical, physical and environmental conditions, the differences in the spectra from the two instruments are due to differences between the instruments. In the case of spectrometers, these can be termed as spectral differences of the instruments. Similarly, when a model made on one instrument is used on a different instrument it may result in high prediction errors. However, it is a well-documented fact that the differences between the two instruments are proportional to the prediction error of the model made on the first instrument and used on the other [59,60]. For example, if the spectral differences between the data from two spectrometers are large, the prediction error resulting from applying a model trained on one instrument to signals acquired with the other will be large as well. Considering this relationship between signal differences and prediction error, two different standard-free CT methods were recently proposed [59,60]. The first method is based on the correction of the PLS models made on the primary instrument assuming a linear relationship between the spectral difference and the prediction error. The method uses the PLS model built on the primary instrument to make predictions for the signals acquired with the secondary instrument. Later, the error in the predictions is used to build a new PLS correction model relating the error itself to the spectral differences. The predicted error obtained with the correction model can be used to amend that of the primary model [59]. The second method, called CT based on affine invariance (CTAI), establishes a PLS model on the primary instrument to obtain score matrices and predicted values of the primary and secondary instruments, and then the regression coefficients between each of the score vectors and predicted values are computed for the primary instrument and the secondary instrument, respectively. Later, angles and biases are calculated between the regression coefficients of the primary instrument and the secondary instrument. Finally, by introducing an affine transformation, new samples are predicted based on the obtained angles and biases [60]. Both approaches showed a comparative performance to the standard-based CT methods such as DS and PDS.

4.5. Methods relying on variable subset modelling

Multivariate signals generated by analytical instruments, such as spectrometers, often contain many collinear variables [61]. Furthermore, in many cases signals ascribable to the chemical analytes that are targeted can be localized in specific regions of the multivariate profiles [62,63]. Hence, in chemometrics, variable selection is widely used to identify key spectral intervals or bands most related to the property of interest, to gain insight into the background chemistry and to improve the predictive performance of calibration models [62–64]. Dealing with the importance of localized regions or variables, two standard-free CT methods were recently proposed [65,66]. The first method is based on the concept of stacked PLS regression analysis, where several PLS models are built by partitioning the data into a set of disjoint regions to emphasize the portions of the signal related to a property of interest to be predicted [65]. By emphasizing those regions of the profiles, the technique correspondingly down-weights intervals with little or no predictive information. The models made with stacked PLS were comparable in performance to traditional standard-based CT methods, with the major advantage that spurious variation due to irrelevant variables was pre-eliminated [65]. Another recent method assumes that there can be a subset of variables that is invariant to the differences in the instruments so that a model made on the data from the primary instrument using only those variables can be directly used on the secondary instrument. The method called screening wavelengths with consistent and stable signals (SWCS) eliminates the wavelengths at which the standard deviation of the difference between the signals of the primary and secondary instruments is higher than the standard deviation of precision detection spectra (SDPDS, i.e., the standard deviation of the profile of a sample measured on the primary instrument several times), and the wavelengths with the highest SDPDS values. For the examples discussed in the paper, the NIR calibration built with fewer variable was found to be robust with good prediction results for the samples from secondary instruments [66].

4.6. Deep learning-based transfer learning

Deep learning (DL) is an emerging field in the domain of machine learning where advanced neural networks are employed to learn hidden data representations to enhance the performance of predictive models. DL has outperformed all classical machine learning and image processing algorithms in the domain of computer vision and image analysis. The main advantage of deep learning (DL) comes into play when huge data sets are available (in the order of thousands of samples). Application of DL in chemometrics is still in its infancy and only a few works can be found such as the development of 1-D convolutional networks for multivariate calibration [67] and the use of stacked auto-encoders for feature extraction from highly multivariate spectral datasets [68].

Since DL requires huge data sets and training new models from scratch is usually not feasible for small calibration sets, a popular practice in DL is to employ transfer learning (TL) [69]. TL aims to fine-tune the weights of an existing model for a similar problem by including a few samples from the new application (i.e. the target domain). An analogy to CT can be understood as a DL model trained on a primary instrument that needs to be transferred to a secondary instrument, where the weights of the model trained for the primary instrument are used to initialize the model for the secondary instrument. In chemometrics, there are currently two studies that report on the application of transfer learning in the framework of reusing the model weights between spectral data sets with different numbers of variables [70,71]. In the new

chemometric framework proposed for non-translation data, several spectral datasets with different numbers of variables can contribute to learning an optimal (latent) representation. Learning from several spectral data sets allows learning higher-level representations that generalize over multiple data sets regardless of the data sets having different input sizes [70]. Although, the new deep learning framework for non-translational data does not deal directly with the standard-free CT problem and practical applications of it is still awaited, the development of generalized models with this or similar approach may allow models to be sharable between instruments of different resolution. Recently, the use of transfer learning (TL) was proposed for updating DL models [71]. The TL approach was based on the idea of fine-tuning of DL models, where the old DL model is complemented by new dense layers to adapt to the variability present in the new scenario. The idea of TL is inspired from the reuse of models and to avoid the training of models from scratch. A summary of the three recent TL approaches to fine-tune DL models is shown in Fig. 5. In TL, an existing model architecture (Fig. 5A) is first modified by removing the output layer. Then, the modified architecture is complemented by either adding only a new output layer (Fig. 5B) or multiple dense layers (Fig. 5C and D) to learn complex patterns specific to the new instrument. Later, with the help of some new data, the model is retrained and ready to be used on a new instrument. In a recent study, the TL approaches allowing retraining of the old model weights (Fig. 5B and C) were found to achieve better predictive performance compared to a model where the training was only performed on the new dense layers (Fig. 5D). More extended details on the TL approaches to updating DL models can be found elsewhere [71].

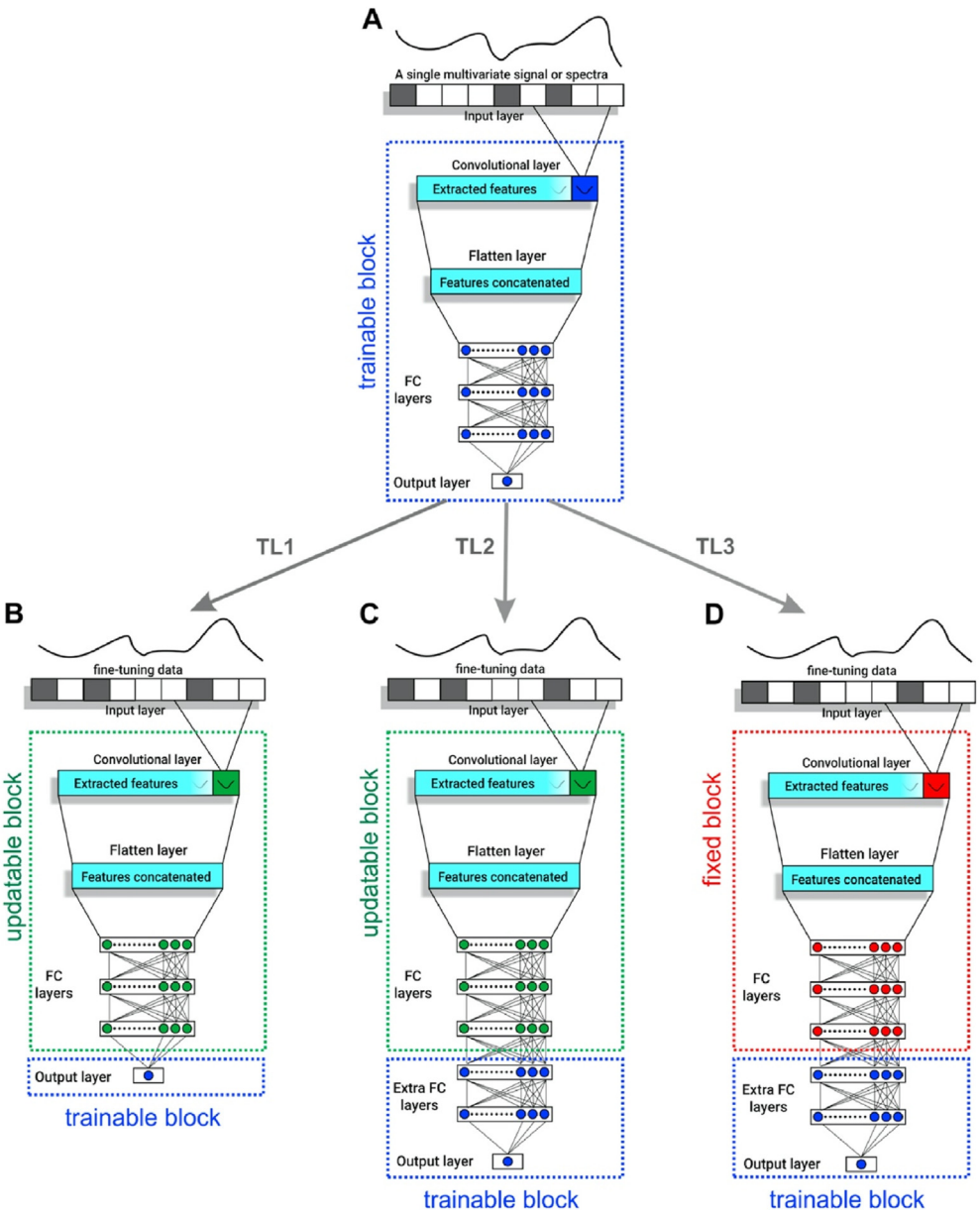

Fig. 5. A summary of the transfer learning approach from Ref. [71] for model transfer. (A) The primary deep learning (DL) model architecture. (B) The output layer of the primary DL model is replaced by a new output layer to learn the variability in the new instrument data; the old model weights were allowed to be retrained. (C–D) The output layer of the primary DL model is replaced by a new output layer and two dense layers to learn the variability in the new instrument data and the old model weights were allowed to be retrained (C) or kept frozen (D).

4.7. Other methods

The first seed of standard-free CT in chemometric was sowed 2 decades ago when a finite impulse response (FIR) filtering approach was proposed [72] which performed equally well as standard-based CT methods such as PDS. The basic principle of FIR-based CT was to map the response obtained on one spectrometer to the response from a second spectrometer. Furthermore, since only the instrument variation was reduced, the FIR-based method does not require standard samples but just a spectrum from the secondary instrument to filter the spectra of the primary. A major challenge with the FIR-based CT approach was that it led to artefacts in the transferred spectra due to the nonlinearity between the spectra. Hence, the FIR method was improved to make the transfer more robust and general by avoiding transfer artefacts in the filtered spectra [73]. Later, methods based on the adaption of preprocessing methods such as windowed MSC (W-MSC) and moving window MSC (MW-MSC) were proposed to do the CT without standard samples [74]. The aim of the methods was to locally standardize the spectra from primary and secondary instruments so that the model developed on the primary can be used efficiently. One of the challenges of the MSC preprocessing-based methods is to choose the right window size. Although the authors proposed a strategy based on sample leverage to decide the optimal window size, the method failed to find widespread and successful applications in the scientific domain [74].

In some cases, the instrumental differences can manifest themselves mainly as shifts in the peaks of the resulting signals [75]. In that case, the alignment of peaks may be sufficient to maintain the predictive performance of models on a new instrument. To deal with such peak shifts, a dynamic time wrapping-based method for standard-free CT was recently proposed [75]. The method utilizes the variable penalty dynamic time warping (VPdtw) for peak alignment of spectral data and has proved superior in performance to the traditional standard-based CT methods as well as standard-free techniques, such as di-PLS, particularly on data sets with shifted peaks [75].

5. When to use which standard-free CT techniques

To this end, a summary of recent developments in the domain of CT techniques has been provided. The number of techniques presented in Tables 1 and 2 suggests that an exponential development of both standard-based and standard-free CT techniques has occurred in recent decades. On the one hand, the development of a large number of techniques provides practical users, such as analytical chemists, with multiple options to explore in order to solve their model transfer problems, while on the other hand, the availability of multiple techniques makes the decision regarding the choice of a particular technique more difficult. There is currently no single golden technique that is suitable for all cases, and indeed, the development of different techniques is the result of the different challenges usually associated with different scenarios of CT. Standard-free CT techniques emerged to cope with the main constraint associated with the standard-based techniques which is the need to perform the measurements of standard samples on the primary as well as on the secondary instruments. In a practical scenario, an analytical chemist can expect that in many cases the measurement of standard samples will not be possible. For example, when the primary instrument is located in a distant location or even damaged. Furthermore, in many cases, it sometime becomes difficult to find standard samples that are stable in terms of their physico-chemical properties. For standard-based methods, the measurements performed to do CT requires physico-chemically stable samples, otherwise the difference modelled by CT techniques is not purely the instrument difference but also includes physico-chemical changes. Hence, in the scenario, when the primary instrument is not available, the analytical chemist has no option other than using one of the standard-free CT methods. Because of the wide range of standard-free CT techniques available (Table 2), the analytical chemist first needs to check if the model created on the primary instrument is a multivariate, such as a PLS regression, or a (deep) neural network-based model. If the model is a DL model, then the user should follow either the DL approach to non-translation data [70] or the recently proposed transfer learning approach [71] where only some data from the new instrument are required and the model weights can be updated to be used on the new instrument. A key point to note is that the model transfer approach based on DL requires both the spectra and the reference property of interest to be measured on the new instrument. On the other hand, when the model to be transferred is a multivariate model like a PLS regression, the user can follow traditional standard-free CT approaches based on domain adaption, such as di-PLS, or orthogonal projection-based methods such as DOP. Although there are multiple techniques mentioned in Table 2, these two methods di-PLS and DOP are particularly highlighted here due to their versatility as well as to the availability of free open-access code. However, a key point to note is that techniques like DOP do not require standard sample measurements but requires both spectra and corresponding reference property to be measured for the new instrument. Domain adaption-based techniques, such as di-PLS, allow more flexibility by allowing to perform either unsupervised (i.e. without reference measurements for samples measured on the secondary instrument) or semi-supervised (i.e. reference measurements are available for some of the samples measured on the secondary instrument) model transfer. In some cases, an analytical chemist may also note that the main differences in the spectra of the primary and the secondary instrument are the shifted peaks, in that case, the user can apply the variable penalty dynamic time wrapping technique [75] to align the shifted peaks such that the model made on the primary instrument can be well generalized to the secondary instrument data. Furthermore, there are also cases when in addition to standard-free model transfer, the user may like to gain more insight into the important spectral wavelengths that are related to the property of interest. Such additional insight into important wavelengths can serve multiple purposes, e.g. easier understanding of the underlying chemistry of the model or improvement of the predictive performance of models. There are currently two methods that rely on variable subset selection i.e. stacked PLS [65] and screening wavelengths with consistent and stable signals [66].

Although several standard-free CT techniques are now available in the scientific literature (Table 2), they are not available in commercial software packages and still outside the reach of the average analytical chemist. Following a literature search, it was found that only three methods had associated codes available for the scientific community to perform standard-free CT. The first method is di-PLS regression, which is available at: https://github.com/B-Analytics/di-PLS. The second method is the variable penalty dynamic time wrapping technique available at: https://github.com/HMzhu/CTVPdtw. The third technique is the DOP, for which the codes are available as a graphical user interface (GUI) [77]. For the transfer of DL models, the techniques for model-fine tuning are openly accessible from TensorFlow API, Google, Inc., USA [71].

In many cases, the choice of a CT technique will be more inspired by the modality of spectroscopy to be used. For example, if the CT is required to be performed in two identical, laboratory-based instruments located in the same laboratory, then the users can measure standard samples easily and can use standard CT techniques. Doing such a CT in a standard-free way can facilitate the

analysis but is not necessary. On other hand, if the aim is to transfer models between portable spectrometer such as consumer spectrometers, then standard-free CT becomes mandatory. This is because the consumer spectrometers are often used by non-experts, who do not have research facilities and chemometric expertise, and hence, cannot perform reference analysis to perform the CT. Hence, in the case of consumer spectrometers the best standard-free CT approach is the unsupervised domain adaption techniques where the users just need to measure some extra spectra and adapt the primary model with techniques such as unsupervised di-PLS [13] or TL [71].

6. Innovative applications of standard-free calibration transfer approaches

Going back to the fundamental concepts, the main aim of CT is to remove the differences between the signals acquired with two (or more) instruments. To attain the CT, either standard-based or standard-free methods can be used. However, thinking broadly, the effectiveness of CT strategies to remove the contributions to the signals ascribable to differences between two instruments can also be extended to remove spurious variability related to temperature changes, differences in the sample state, seasonal effects e.g. in agro-food products [78] and many more [15,53]. For example, it is a well-known fact that NIR spectroscopy measurements are affected by the temperature of the samples; hence, if the primary model is built on a set of signals recorded at a particular temperature, it will probably fail in providing accurate predictions when applied to data collected at a different temperature [15]. In such a case, the CT algorithms can be used to adapt the existing model to the new temperature range by removing (or accounting for) the differences in the spectra due to the temperature variations. Such applications of CT are becoming more abundant: For instance, spectral space transformation (SST) [19], DOP [15,53], transfer component analysis [41] and domain invariant partial least-square (di-PLS) [13] have recently been successfully applied to correct for unwanted variation due to temperature differences [53,79,80]. The adaptation of models to signals collected on samples in different physical forms is emerging as another interesting application of CT methods. An application where a NIR-based protein prediction model made on intact rice kernels was transferred to ground rice flour samples was recently presented by Xu et al. [18]. To do so, measurements were collected on both rice kernels and powder in order to model the discrepancies between the paired spectra acquired on the same samples in the two different physical forms. Later, the model made on rice kernels was transformed using the difference function in order to be used for the powdered samples [18]. These “out-of-the-box” applications of CT methods are still relatively new and more are to be expected in the near future.

7. Concluding remarks

CT in chemometrics holds a unique place due to its potential to make calibration models widely sharable and applicable on different instruments. In the last decade, extensive developments have taken place regarding both standard-based and standard-free CT approaches. Standard-based CT methods are still the gold standard in laboratory scenarios, however, the application of standard-free CT methods is gaining increasing attention as can be measured by the number of recent publications on the subject. For the former, in our view, important developments comprise approaches that can cope with different spectral resolutions of primary and secondary instruments as well as methods where the spectral features of CT standards and calibration samples don't need to be similar (such as with GCT-PLS proposed in Ref. [12]). Such approaches could be employed in the future for CT using calibration standards that are directly built into NIR spectrometers.

The main benefits of standard-free CT methods are the time and cost-saving related to running extra experiments for standard measurements. Furthermore, in some scenarios, standard-free CT is more practical, e.g. when aiming at transferring calibrations from a lab-based primary to a (low-cost) portable instrument that is operated by non-expert users. In such situations, an automatic standard-free CT based method could be a viable solution to allow the end-user to use calibrations developed elsewhere and to share his models as well. Out-of-the-box applications of CT are also emerging such as for transferring models between different temperature levels, between different physical forms of samples such as from solids to powders or between different sample matrices. With the recent progress pace in artificial intelligence (AI), deep learning and computing capabilities, it is foreseen that the major advantage in future years could be related to automatic standard-free CT methods which can automatically adapt between instruments of different resolutions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] W. Saeys, N.N. Do Trong, R. Van Beers, B.M. Nicolai, Multivariate calibration of spectroscopic sensors for postharvest quality evaluation: a review, Postharvest Biol. Technol. (2019) 158.
[2] S. Wold, C. Albano, W.J. Dunn, U. Edlund, K. Esbensen, P. Geladi, S. Hellberg, E. Johansson, W. Lindberg, M. Sjöström, Multivariate data analysis in chemistry, in: B.R. Kowalski (Editor), Chemometrics: Mathematics and Statistics in Chemistry, Springer Netherlands, Dordrecht, 1984, pp. 17–95.
[3] R. Bro, Multivariate calibration: what is in chemometrics for the analytical chemist? Anal. Chim. Acta 500 (2003) 185–194.
[4] K.H. Esbensen, L.P. Julius, S.D. Brown, R. Tauler, B. Walczak, 4.01 - Representative Sampling, Data Quality, Validation – A Necessary Trinity in Chemometrics, Comprehensive Chemometrics, Elsevier, Oxford, 2009, pp. 1–20.
[5] F. Westad, F. Marini, Validation of chemometric models – a tutorial, Anal. Chim. Acta 893 (2015) 14–24.
[6] R.N. Feudale, N.A. Woody, H. Tan, A.J. Myles, S.D. Brown, J. Ferré, Transfer of multivariate calibration models: a review, Chemometr. Intell. Lab. Syst. 64 (2002) 181–192.
[7] J.J. Workman, A review of calibration transfer practices and instrument differences in spectroscopy, Appl. Spectrosc. 72 (2017) 340–365.
[8] B. Malli, A. Birlutiu, T. Natschläger, Standard-free calibration transfer - an evaluation of different techniques, Chemometr. Intell. Lab. Syst. 161 (2017) 49–60.
[9] T. Fearn, Standardisation and calibration transfer for near infrared instruments: a review, J. Near Infrared Spectrosc. 9 (2001) 229–244.
[10] Y. Wang, D.J. Veltkamp, B.R. Kowalski, Multivariate instrument standardization, Anal. Chem. 63 (1991) 2750–2756.
[11] Y. Wang, B.R. Kowalski, Calibration transfer and measurement stability of near-infrared spectrometers, Appl. Spectrosc. 46 (1992) 764–771.

[12] R. Nikzad-Langerodi, F. Sobieczky, Graph-based calibration transfer, J. Chemometr. 35 (2021) e3319.
[13] R. Nikzad-Langerodi, W. Zellinger, S. Saminger-Platz, B.A. Moser, Domain adaptation for regression under Beer–Lambert's law, Knowl. Base Syst. 210 (2020) 106447.
[14] R. Nikzad-Langerodi, W. Zellinger, E. Lughofer, S. Saminger-Platz, Domain-invariant partial-least-squares regression, Anal. Chem. 90 (2018) 6693–6701.
[15] M. Zeaiter, J.M. Roger, V. Bellon-Maurel, Dynamic orthogonal projection. A new method to maintain the on-line robustness of multivariate calibrations. Application to NIR-based monitoring of wine fermentations, Chemometr. Intell. Lab. Syst. 80 (2006) 227–235.
[16] K. Zheng, T. Feng, W. Zhang, X. Huang, Z. Li, D. Zhang, Y. Yao, X. Zou, Variable selection by double competitive adaptive reweighted sampling for calibration transfer of near infrared spectra, Chemometr. Intell. Lab. Syst. 191 (2019) 109–117.
[17] P. Geladi, B.R. Kowalski, Partial least-squares regression: a tutorial, Anal. Chim. Acta 185 (1986) 1–17.
[18] Z. Xu, S. Fan, J. Liu, B. Liu, L. Tao, J. Wu, S. Hu, L. Zhao, Q. Wang, Y. Wu, A calibration transfer optimized single kernel near-infrared spectroscopic method, Spectrochim. Acta Mol. Biomol. Spectrosc. 220 (2019) 117098.
[19] W. Du, Z.-P. Chen, L.-J. Zhong, S.-X. Wang, R.-Q. Yu, A. Nordon, D. Littlejohn, M. Holden, Maintaining the predictive abilities of multivariate calibration models by spectral space transformation, Anal. Chim. Acta 690 (2011) 64–70.
[20] C. Liang, H.-f. Yuan, Z. Zhao, C.-f. Song, J.-j. Wang, A new multivariate calibration model transfer method of near-infrared spectral analysis, Chemometr. Intell. Lab. Syst. 153 (2016) 51–57.
[21] L. Zhang, Y. Li, W. Huang, L. Ni, J. Ge, The method of calibration model transfer by optimizing wavelength combinations based on consistent and stable spectral signals, Spectrochim. Acta Mol. Biomol. Spectrosc. 227 (2020) 117647.
[22] Z. Xu, S. Fan, W. Cheng, J. Liu, P. Zhang, Y. Yang, C. Xu, B. Liu, J. Liu, Q. Wang, Y. Wu, A correlation-analysis-based wavelength selection method for calibration transfer, Spectrochim. Acta Mol. Biomol. Spectrosc. 230 (2020) 118053.
[23] J. Yang, X. Lou, H. Yang, H. Yang, C. Liu, J. Wu, J. Bin, Improved calibration transfer between near-Infrared (NIR) spectrometers using canonical correlation analysis, Anal. Lett. 52 (2019) 2188–2202.
[24] W. Liu, Z. Zhao, H.F. Yuan, C.F. Song, X.Y. Li, An optimal selection method of samples of calibration set and validation set for spectral multivariate analysis, Guang Pu Xue Yu Guang Pu Fen Xi/Spectroscopy and Spectral Analysis 34 (2014) 947–951.
[25] X. Fan, H. Lu, Z. Zhang, Direct calibration transfer to principal components via canonical correlation analysis, Chemometr. Intell. Lab. Syst. 181 (2018) 21–28.
[26] W.-R. Chen, J. Bin, H.-M. Lu, Z.-M. Zhang, Y.-Z. Liang, Calibration transfer via an extreme learning machine auto-encoder, Analyst 141 (2016) 1973–1980.
[27] L. Chen, D. Liu, J. Zhou, J. Bin, Z. Li, Calibration transfer for near-infrared (NIR) spectroscopy based on neighborhood preserving embedding, Anal. Lett. (2020) 1–19.
[28] Y.-y. Chen, Z.-b. Wang, Cross components calibration transfer of NIR spectroscopy model through PCA and weighted ELM-based TrAdaBoost algorithm, Chemometr. Intell. Lab. Syst. 192 (2019) 103824.
[29] Y. Zhao, J. Yu, P. Shan, Z. Zhao, X. Jiang, S. Gao, PLS subspace-based calibration transfer for near-infrared spectroscopy quantitative analysis, Molecules 24 (2019) 1289.
[30] F. Zhang, R. Zhang, J. Ge, W. Chen, W. Yang, Y. Du, Calibration transfer based on the weight matrix (CTWM) of PLS for near infrared (NIR) spectral analysis, Analytical Methods 10 (2018) 2169–2179.
[31] A. Folch-Fortuny, R. Vitale, O.E. de Noord, A. Ferrer, Calibration transfer between NIR spectrometers: new proposals and a comparative study, J. Chemometr. 31 (2017), e2874.
[32] J. Zhang, C. Guo, X. Cui, W. Cai, X. Shao, A two-level strategy for standardization of near infrared spectra by multi-level simultaneous component analysis, Anal. Chim. Acta 1050 (2019) 25–31.
[33] J. Wang, Z. Li, Y. Wang, Y. Liu, W. Cai, X. Shao, A dual model strategy to transfer multivariate calibration models for near-infrared spectral analysis, Spectrosc. Lett. 49 (2016) 348–354.
[34] Y. Mou, L. Zhou, S. Yu, W. Chen, X. Zhao, X. You, Robust calibration model transfer, Chemometr. Intell. Lab. Syst. 156 (2016) 62–71.
[35] Y. Liu, H. Xu, Z. Xia, Z. Gong, Multi-spectrometer calibration transfer based on independent component analysis, Analyst 143 (2018) 1274–1280.
[36] J.J. Liu, B.Q. Li, H.L. Zhai, S.H. Lu, S.S. Li, The common quantitative model for the determination of multiple near infrared spectrometers, Chemometr. Intell. Lab. Syst. 182 (2018) 117–123.
[37] T. Skotare, D. Nilsson, S. Xiong, P. Geladi, J. Trygg, Joint and unique multiblock Analysis for integration and calibration transfer of NIR instruments, Anal. Chem. 91 (2019) 3516–3524.
[38] P. Mishra, J.M. Roger, D.N. Rutledge, A. Biancolillo, F. Marini, A. Nordon, D. Jouan-Rimbaud-Bouveresse, MBA-GUI: A Chemometric Graphical User Interface for Multi-Block Data Visualisation, Regression, Classification, Variable Selection and Automated Pre-processing, Chemometrics and Intelligent Laboratory Systems, 2020, 104139.
[39] T. Löfstedt, J. Trygg, OnPLS—a novel multiblock method for the modelling of predictive and orthogonal variation, J. Chemometr. 25 (2011) 441–455.
[40] E. Andries, Penalized eigendecompositions: motivations from domain adaptation for calibration transfer, J. Chemometr. 31 (2017), e2818.
[41] S.J. Pan, I.W. Tsang, J.T. Kwok, Q. Yang, Domain adaptation via transfer component analysis, IEEE Trans. Neural Network. 22 (2011) 199–210.
[42] M. Ghifary, D. Balduzzi, W.B. Kleijn, M. Zhang, Scatter component analysis: a unified framework for domain adaptation and domain generalization, IEEE Trans. Pattern Anal. Mach. Intell. 39 (2016) 1414–1430.
[43] R. Nikzad-Langerodi, W. Zellinger, S. Saminger-Platz, B. Moser, Domain-Invariant Regression under Beer-Lambert's Law, 18th IEEE International Conference On Machine Learning And Applications (ICMLA), IEEE, 2019, pp. 581–586.
[44] E. Andries, J.H. Kalivas, A. Gurung, Sample and feature augmentation strategies for calibration updating, J. Chemometr. 33 (2019), e3080.
[45] J.-M. Roger, J.-C. Boulet, A review of orthogonal projections for calibration, J. Chemometr. 32 (2018), e3045.
[46] R. Bro, A.K. Smilde, Principal component analysis, Analytical Methods 6 (2014) 2812–2831.
[47] P. Mishra, J.M. Roger, D. Jouan-Rimbaud-Bouveresse, A. Biancolillo, F. Marini, A. Nordon, D.N. Rutledge, Recent trends in multi-block data analysis in chemometrics for multi-source data integration, Trac. Trends Anal. Chem. (2021) 116206.
[48] T. Skov, D. Ballabio, R. Bro, Multiblock variance partitioning: a new approach for comparing variation in multiple data blocks, Anal. Chim. Acta 615 (2008) 18–29.
[49] A. Biancolillo, T. Næs, R. Bro, I. Måge, Extension of SO-PLS to multi-way arrays: SO-N-PLS, Chemometr. Intell. Lab. Syst. 164 (2017) 113–126.
[50] A. Biancolillo, T. Næs, Chapter 6 - the sequential and orthogonalized PLS regression for multiblock regression: theory, examples, and extensions, in: M. Cocchi (Editor), Data Fusion Methodology and Applications, Data Handling in Science and Technology, Elsevier, Amsterdam, 2019, pp. 157–177.
[51] J.-M. Roger, F. Chauchard, V. Bellon-Maurel, EPO–PLS external parameter orthogonalisation of PLS application to temperature-independent measurement of sugar content of intact fruits, Chemometr. Intell. Lab. Syst. 66 (2003) 191–204.
[52] A. Andrew, T. Fearn, Transfer by orthogonal projection: making near-infrared calibrations robust to between-instrument variation, Chemometr. Intell. Lab. Syst. 72 (2004) 51–56.
[53] P. Mishra, J.M. Roger, D.N. Rutledge, E. Woltering, Two standard-free approaches to correct for external influences on near-infrared spectra to make models widely applicable, Postharvest Biol. Technol. 170 (2020) 111326.
[54] Z. Lin, B. Xu, Y. Li, X. Shi, Y. Qiao, Application of orthogonal space regression to calibration transfer without standards, J. Chemometr. 27 (2013) 406–413.
[55] J. Sjöblom, O. Svensson, M. Josefson, H. Kullberg, S. Wold, An evaluation of orthogonal signal correction applied to calibration transfer of near infrared spectra, Chemometr. Intell. Lab. Syst. 44 (1998) 229–244.
[56] D.V. Poerio, S.D. Brown, Dual-domain calibration transfer using orthogonal projection, Appl. Spectrosc. 72 (2017) 378–391.
[57] M.R. Kunz, J.H. Kalivas, E. Andries, Model updating for spectral calibration maintenance and transfer using 1-norm variants of Tikhonov regularization, Anal. Chem. 82 (2010) 3642–3649.
[58] Y. Liu, W. Cai, X. Shao, Linear model correction: a method for transferring a near-infrared multivariate calibration model without standard samples, Spectrochim. Acta Mol. Biomol. Spectrosc. 169 (2016) 197–201.
[59] X. Li, W. Cai, X. Shao, Correcting multivariate calibration model for near infrared spectral analysis without using standard samples, J. Near Infrared Spectrosc. 23 (2015) 285–291.
[60] Y. Zhao, Z. Zhao, P. Shan, S. Peng, J. Yu, S. Gao, Calibration transfer based on affine invariance for NIR without transfer standards, Molecules 24 (2019) 1802.
[61] P. Mishra, A. Biancolillo, J.M. Roger, F. Marini, D.N. Rutledge, New data preprocessing trends based on ensemble of multiple preprocessing techniques, Trac. Trends Anal. Chem. (2020) 116045.
[62] T. Mehmood, K.H. Liland, L. Snipen, S. Sæbø, A review of variable selection methods in Partial Least Squares Regression, Chemometr. Intell. Lab. Syst. 118 (2012) 62–69.
[63] T. Mehmood, S. Sæbø, K.H. Liland, Comparison of variable selection methods in partial least squares regression, J. Chemometr. (2020) e3226.
[64] P. Mishra, E.J. Woltering, Identifying key wavenumbers that improve prediction of amylose in rice samples utilizing advanced wavenumber selection techniques, Talanta 224 (2021) 121908.
[65] W. Ni, S.D. Brown, R. Man, Stacked PLS for calibration transfer without standards, J. Chemometr. 25 (2011) 130–137.
[66] L. Ni, M. Han, S. Luan, L. Zhang, Screening wavelengths with consistent and stable signals to realize calibration model transfer of near infrared spectra, Spectrochim. Acta Mol. Biomol. Spectrosc. 206 (2019) 350–358.
[67] C. Cui, T. Fearn, Modern practical convolutional neural networks for multivariate regression: applications to NIR calibration, Chemometr. Intell. Lab. Syst. 182 (2018) 9–20.

[68] X. Yu, H. Lu, Q. Liu, Deep-learning-based regression model and hyperspectral imaging for rapid detection of nitrogen concentration in oilseed rape (Brassica napus L.) leaf, Chemometr. Intell. Lab. Syst. 172 (2018) 188–193.
[69] K. Weiss, T.M. Khoshgoftaar, D. Wang, A survey of transfer learning, J. Big Data 3 (2016) 9.
[70] J.S. Larsen, L. Clemmensen, Deep Learning for Chemometric and Non-translational Data, 2019. arXiv preprint arXiv:1910.00391.
[71] P. Mishra, D. Passos, Realizing Transfer Learning for Updating Deep Learning Models of Spectral Data to Be Used in a New Scenario, Chemometrics and Intelligent Laboratory Systems, 2021, p. 104283.
[72] T.B. Blank, S.T. Sum, S.D. Brown, S.L. Monfre, Transfer of near-infrared multivariate calibrations without standards, Anal. Chem. 68 (1996) 2987–2995.
[73] H. Tan, S.T. Sum, S.D. Brown, Improvement of a standard-free method for near-infrared calibration transfer, Appl. Spectrosc. 56 (2002) 1098–1106.
[74] K.E. Kramer, R.E. Morris, S.L. Rose-Pehrsson, Comparison of two multiplicative signal correction strategies for calibration transfer without standards, Chemometr. Intell. Lab. Syst. 92 (2008) 33–43.
[75] C. Zou, H. Zhu, J. Shen, Y. He, J. Su, X. Fan, H. Lu, Z. Zhang, Y. Chen, Scalable calibration transfer without standards via dynamic time warping for near-infrared spectroscopy, Analytical Methods 11 (2019) 4481–4493.
[76] G. Huang, X. Chen, L. Li, X. Chen, L. Yuan, W. Shi, Domain adaptive partial least squares regression, Chemometr. Intell. Lab. Syst. 201 (2020) 103986.
[77] P. Mishra, J.M. Roger, F. Marini, A. Biancolillo, D.N. Rutledge, FRUITNIR-GUI: a graphical user interface for correcting external influences in multi-batch near infrared experiments related to fruit quality prediction, Postharvest Biol. Technol. (2020) 111414.
[78] J.-M. Roger, F. Chauchard, P. Williams, Removing the block effects in calibration by means of dynamic orthogonal projection. Application to the year effect correction for wheat protein prediction, J. Near Infrared Spectrosc. 16 (2008) 311–315.
[79] Z.-P. Chen, J. Morris, E. Martin, Correction of temperature-induced spectral variations by loading space standardization, Anal. Chem. 77 (2005) 1376–1384.
[80] P. Mishra, R. Nikzad-Langerodi, Partial least square regression versus domain invariant partial least square regression with application to near-infrared spectroscopy of fresh fruit, Infrared Phys. Technol. (2020) 103547.