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Projection to latent correlative structures, a dimension reduction strategy for spectral-based classification†

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Latent variables are used in chemometrics to reduce the dimension of the data. It is a crucial step with spectroscopic data where the number of explanatory variables can be very high. Principal component analysis (PCA) and partial least squares (PLS) are the most common. However, the resulting latent variables are mathematical constructs that do not always have a physicochemical interpretation. A new data reduction strategy, named projection to latent correlative structures (PLCS), is introduced in this manuscript. This approach requires a set of model spectra that will be used as references. Each latent variable is the relative similarity of a given spectrum to a pair of reference spectra. The latent structure is obtained using every possible combination of reference pairing. The approach has been validated using more than 500 FTIR-ATR spectra from cool-season culinary grain legumes assembled from germplasm banks and breeders' working collections. PLCS has been combined with soft discriminant analysis to detect outliers that could be particularly suitable for a deeper analysis.

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Introduction

The term chemometrics was defined in 1971 by Svante Wold as “The science of relating measurements made on a chemical system or process to the state of the system *via* application of mathematical or statistical methods”.^{1,2} While many algorithms are not new, it is only in the past decade that numerical-analysis software (Python, R, MATLAB, Excel...) started to incorporate easy to use chemometrics and machine learning algorithms. Thus, there is growing interest from chemists to apply advanced chemometrics tools in their daily work to extract as much knowledge as possible from their data.^{3,4}

Spectroscopic data are particularly interesting for chemometrics techniques. Multiple applications have been developed, either for multilinear calibrations that allow qualitative analysis of the principal elements,⁵ or to identify samples *via* clustering

(unsupervised) or classification (supervised) methods. One of the key issues when working with spectral data is the high number of predictor variables (intensities as a function of wavelengths, for example) with many multicollinearities. A variable selection method (Lasso or elastic net, for example),⁶ or dimension reductions are therefore necessary.^{7,8}

Dimension reductions use latent variables (LV) to represent the original data in a more compact form with minimal information loss. The most common approaches are linear discriminant analysis (LDA), principal component analysis (PCA) and partial least squares (PLS). Each latent variable is a combination of all original variables while fulfilling a specific criterium. They are mathematical constructs and are not always sensible in a spectroscopic way. Dimension reduction is often used in conjunction with clustering or classification, allowing predicting the nature of unknown samples. In chemometrics, Partial Least-Squares Discriminant Analysis (PLS-DA) is the method of choice.⁹ However, as recently pointed out by Rodionova and co-workers, discriminant analysis (DA) and PLS-DA is not an appropriate authentication method.¹⁰ The main drawback is the inability of classical (or hard) DA to classify a sample that does not belong to one of the predefined classes. However, in chemical analysis, samples are often contaminated (willingly or not), resulting in many potential classes. In recent works, Pomerantsev and co-workers introduced soft discriminant analysis (softDA) to classify a sample to one, multiple or no classes using the Mahalanobis distances.^{11,12}

This manuscript aims to introduce a new data reduction strategy that makes use of model spectra. The latent structure is

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built as the relative correlation of the spectra with every pairing of model spectra and was named Projection to Latent Correlative Structures (PLCS). The latent structure is then used with a soft discriminant analysis to classify samples. The approach is validated with a large dataset of grains analysed by FTIR-ATR. 500 accessions of the most important European cool season culinary grain legumes, assembled from germplasm banks and breeders working collections, were analysed (LEGATO project germplasm collections). Pea (*Pisum sativum*), grass pea (*Lathyrus sativus*), chickpea (*Cicer arietinum*), lentil (*Lens culinaris*) and faba bean (*Vicia faba*) accessions spectroscopic relationships (or diversity) were cleared out.

Theory

Projection to latent correlative structures

PLCS axes aim to compare the relative similarities between an unknown spectrum and a series of pairs of reference spectra. The similarity between spectra is measured using the Pearson correlation coefficient, defined as

$$\rho_{X,Y} = \frac{\text{cov}(X, Y)}{\sigma_X \sigma_Y} \quad (1)$$

where $\text{cov}(X, Y)$ is the covariance between two spectra X and Y , and σ_X and σ_Y are the variance of spectra X and Y , respectively. $\rho_{X,Y}$ will measure the similarity between two spectra on an absolute scale of 0 to 1.

Selecting two references spectra, the dissimilarity indexes, measured as $1 - \rho_{X,Y}$, between those references and all spectra are measured. An example is shown in Fig. 1(A) with the data that will be described below. The first axis is the dissimilarity $1 - \rho(X_i, Y_{\text{lentil}})$ between the intensity at each wavelength for each sample (X_i) and the reference lentil spectrum (Y_{lentil}). The second axis is the dissimilarity $1 - \rho(X_i, Y_{\text{fababean}})$ between the intensity at each wavelength for each sample (X_i) and the reference faba bean spectrum (Y_{fababean}). Additional information about the reference spectra can be found in the Experimental section. We inferred the latent axis as the line passing through the dissimilarity indexes of the two models spectra (black line in Fig. 1A). Spectra are projected to this axis (Fig. 1B).

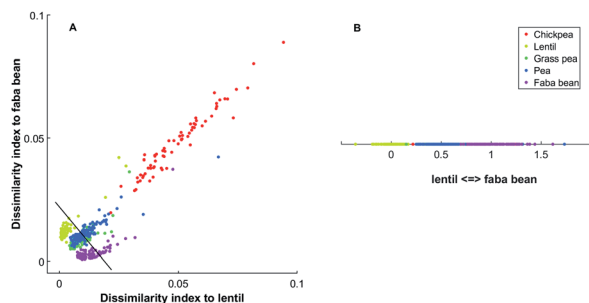


Fig. 1 (A) Projection of all spectra on the latent plane obtain by measuring the dissimilarity with the reference spectra of lentil and faba bean; (B) projection to the latent axis lentil \leftrightarrow faba bean. The black line in (A) is the vector passing through the dissimilarity indexes of the two models spectra that is the latent axis faba bean \leftrightarrow lentil.

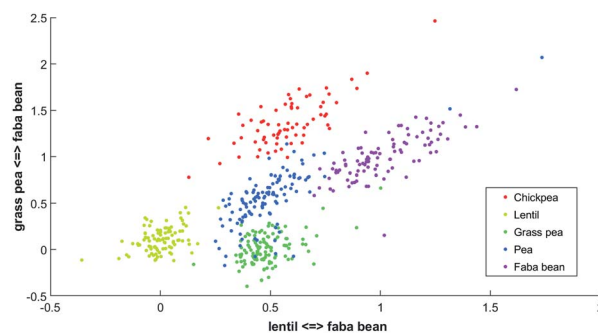


Fig. 2 Two-dimensional PLCS of the beans FTIR-ATR spectra with the lentil \leftrightarrow faba bean axis and the grass pea \leftrightarrow faba bean axis.

One latent axis is built for every possible pairing of reference spectrum. With five model spectra, ten latent axes are extrapolated. An example of a two-dimensional representation is presented in Fig. 2.

In this new representation, each spectrum is described by its relative similarity between a set of reference spectra. This representation is easy to understand; points in the bottom left correspond to spectra that will be more similar to lentil than faba bean and more similar to grass pea than faba bean.

Properties of PLCS

Unlike PCA and PLS, in PLCS there is neither ranking of the LV nor constraint of orthogonality. It is therefore important to test for every possible combination of axes. However, the number of latent variables obtained with PLCS is low. For example, with 5 model spectra, the total number of LV will be 10, whereas, with 10 model spectra, the total number of LV will be 45.

The Pearson correlation coefficient (eqn (1)) is used to measure the similarity between spectra. This is particularly suitable for spectral-based applications as it is invariant under constant shift or multiplicative factor:

$$\text{corr}(X, Y) = \text{corr}(a + bX, c + dY) \quad (2)$$

Thus, there is no need to normalise the spectra for variation of intensities nor to correct for constant baseline drift,¹³ removing potential source of error or bias.

Experimental section

Samples preparation and characterisation

The different seeds from LEGATO project (grass pea (*Lathyrus sativus* $n = 116$), chickpea (*Cicer arietinum* $n = 87$), pea (*Pisum sativus* $n = 119$), faba bean (*Vicia faba* $n = 93$) and lentil (*Lens culinaris* $n = 93$)) were dried at 40 °C and milled using a miller Retsch cyclone mill with particle size under 0.8 mm. The different flours were stored at -20 °C.

FTIR-ATR spectroscopy

The equipment used was a Thermo Scientific FTIR spectrometer (San Jose, USA) Class 1 Laser Product Nicolet 6100 using an ATR accessory with a diamond crystal. This crystal provided an angle



of incidence of 42°. The acquisition of the spectra was performed using the software OMNIC version 7.3 (Thermo Electron Corporation). The background spectrum of the air was collected before each sample spectrum acquisition. The crystal was cleaned using water and acetone and dried with a soft tissue. For the sample spectrum acquisition, the different flours were placed in the ATR crystal and the spectra were recorded with 32 scans between 4000–650 cm⁻¹ and with a resolution of 4 cm⁻¹. All data used in this work are available in the Zenodo repository at the address: https://zenodo.org/record/5075052#.YOvp_OhKiUl.¹⁴

Programming and software

Matlab R2021a (Mathworks) was used for this work; functions were programmed and run using a PC equipped with an Intel Core i7 CPU (2.80 GHz) and 18.0 GB RAM. The functions *fitcdiscr*, *plsregress*, *pca*, *cvpartition* from the Statistics and Machine Learning toolbox (Mathworks) were used for the discriminant analysis, Partial Least Squares, principal component analysis, and cross-validation, respectively. The functions *sgolay* and *isoutlier* from the Signal Processing Toolbox (Mathworks) were used to smooth and derivate the spectra and find outliers.

Data analysis

Data preparation. The FTIR spectra were smoothed, and the first, second and third derivatives were calculated. The parameters tested are detailed in Results and discussions. Best results were obtained using the second derivatives of the spectra, with a Savitzky–Golay filter and a polynomial order of 2 and a frame length of 9. Before any further analysis, data were split into a training set (75% of the data) and a test set (25% of the data) using stratified hold-up cross-validation.

Dimension reduction. Three data reduction approaches were used in this work, PCA, PLS, and PLCS.

For PCA, the Matlab function *pca* and the training set ($\mathbf{X}_{\text{training}}$) were used to calculate the matrix of loadings (\mathbf{X}_{PCL}) and the score matrix of the training set ($\mathbf{X}_{\text{PCS_training}}$). Score matrix of the test data ($\mathbf{X}_{\text{PCS_test}}$) was calculated using

$$\mathbf{X}_{\text{PCS_test}} = (\mathbf{X}_{\text{test}} - \mu)\mathbf{X}_{\text{PCL}} \quad (3)$$

where \mathbf{X}_{test} is the test data, and μ is the mean of the intensities of all samples selected in the training set at each wavelength.

For multi-class PLS, the Matlab function *plsregress*, the training set ($\mathbf{X}_{\text{training}}$), and the dummy variable \mathbf{Y} were used to calculate the predictor training score ($\mathbf{X}_{\text{PLS_training}}$) and the matrix of PLS weight \mathbf{W} . The dummy matrix \mathbf{Y} is inferred from the classes membership.¹¹ The predictor scores for the test set ($\mathbf{X}_{\text{PLS_test}}$) were calculated using:¹⁵

$$\mathbf{X}_{\text{PLS_test}} = (\mathbf{X}_{\text{test}} - \mu)\mathbf{W} \quad (4)$$

μ is the mean of the intensities of all samples selected in the training set at each wavelength.

For PLCS, the five references spectra were obtained by averaging all spectra in the training set belonging to the same class (pea, faba bean, grass pea, chickpea, and lentil). Then, the

Pearson correlation coefficients between the averaged spectrum and labelled spectra were calculated. The outliers were detected and removed using the *isoutlier* function from Matlab with the median absolute deviation (MAD).¹⁶ The final references spectra were obtained by averaging all spectra with the same label after removing the outliers. The function *PLCS_proj* was used to measure the PLCS score, α_{training} and α_{test} . α is a $m \times n$ matrix with, m the number of samples, and n the number of possible combinations of two reference spectra. The line j in α corresponds to the relative Pearson correlation of the spectra j to all combinations of two references spectra. With the beans data, the original matrix was reduced from 1734 × 491 (1734 intensities measured at different wavelength with 491 samples) to 10 × 491 (ten possible combination of reference spectra measured with 491 samples).

Soft discriminant analysis. A quadratic discriminant analysis model was obtained using the Matlab function *fitcdiscr* with the training scores obtained after dimension reduction ($\mathbf{X}_{\text{PCS_training}}$, $\mathbf{X}_{\text{PLS_training}}$ or α_{training}), and the class membership of the training set. The Mahalanobis distances, d_i ,¹⁷ between each sample and all classes centres, were calculated using the *mahal* Matlab function. d is like the univariate z-score by considering the variance and covariance of each group. The Mahalanobis distance from a vector \mathbf{V}_i , that defined the coordinate of a single point i , to the distribution of a class k with mean μ_k and covariance matrix \mathbf{S}_k is given by¹⁸

$$d_{ik} = \sqrt{(\mathbf{V}_i - \mu_k)\mathbf{S}_k^{-1}(\mathbf{V}_i - \mu_k)^T} \quad (5)$$

While in hard discriminant analysis (hardDA) and unknown sample is assigned to the closest group, with soft discriminant analysis (softDA),¹² sample i belongs to class k when the distance d_{ik} is less than the threshold $d_{\text{crit}} = \chi^{-2}(1 - \alpha, K - 1)$.¹¹ χ^{-2} is the quantile of the chi-squared distribution, with $K - 1$ degree of freedom. Value α stands for a given type I error (in this work, α has been set to 0.05). By this rule, a sample can be simultaneously attributed to one, several or no classes depending on its Mahalanobis distances to the centres of each class.

Outliers detections. DA models were refined by removing the outliers. Those were detected as samples with d to their own class centre with more than three scaled MAD from the median, with MAD (median absolute deviation) defined as

$$\text{MAD} = c \times \text{median}(|A_i - \text{median}(A)|) \quad (6)$$

where A is a variable vector with N observation, and $i = 1, 2, \dots, N$. c is a scaling factor, usually equal to 1.4826.¹⁹ An example of PLCS-softDA with and without outliers is shown in Fig. 3.

In Fig. 3A all data are used, while in Fig. 3B, the Mahalanobis distances have been recalculated after removing the outliers. In this representation, the position of the samples is the relative similarity of their spectrum to the reference spectra of chickpea and grass pea (axis 1) and the relative similarity of their spectrum to the reference spectra of lentil and grass pea. The coloured zones indicate the soft-classification zones where



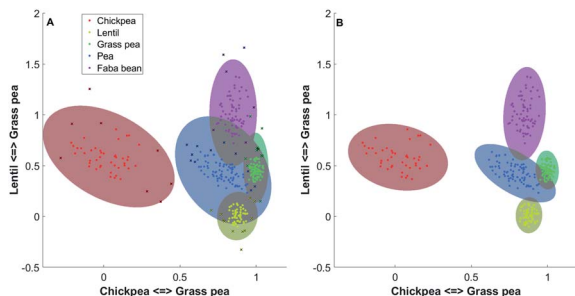


Fig. 3 (A) PLCS and superimposed soft discriminant analysis using all the data with the axis lentil \leftrightarrow grass pea and chickpea \leftrightarrow grass pea, (B) PLCS and superimposed discriminant analysis after removal of the outliers. The coloured surfaces represent, for each cluster, the zone where $d \leq d_{crit}$. Crosses in (A) indicate outliers.

samples can be classified to one of the classes ($d < d_{crit}$). Zone in grey indicates multinomial classification. Samples that do not belong to any soft-classification zones may be outliers, adulterated samples or samples that do not belong to any classes. It is evident that the soft classification areas obtained after the DA is highly dependent on the outliers detected and the value of d_{crit} . Two-dimensional projections allow confirming the outlier's selection and the soft classifications zones visually (see Fig. 3). While DA can use a high number of variables, visual validation is only possible with up to three variables.

Figures of merits. Figures of merits are calculated by comparing the predicted test class membership obtained by the DA model with the known class membership. The accuracy of the classification is assessed with four parameters: **no**, the number of samples that are in no groups with $d \leq d_{crit}$ (unclassified); **nm**, the number of samples that are in more than one groups with $d \leq d_{crit}$ (multinomial classification); **ns**, the number of samples correctly assigned to one and only one group (true positives); and **ms**, the number of samples wrongly assigned to one and only one group (false positives).

Discriminant analysis model complexity. Complexity refers to the number of variables used in the discriminant model to predict the correct output. Complexity should be as low as possible. The optimal model is a compromise between low complexity and predictivity accuracy. With PCA and PLS, the latent variables are ranked by importance through their explained variance or covariance, respectively. Optimal model is obtained by building successive models, increasing the number of LV, and measuring the accuracy of the predicted values. Such an approach cannot be used for PLCS as there is no ranking of the LV, and all combinations of axes should be tested. However, while PCA and PLS will give as many LV as the number of samples, with PLCS, the number of latent variables, n_{LV} , is the number of binary combinations of reference spectra.

$$n_{LV} = \frac{n!}{2(n-2)!} \quad (7)$$

where n is the number of reference spectra. Thus, the number of possible combinations, N , of LV to be tested for DA is given by

$$N = \frac{n_{LV}!}{C!(n_{LV}-C)!} \quad (8)$$

where C is the complexity (number of LV) of the DA. The Matlab function *OptAxis4fitdiscr* has been designed to test all possible combinations. Matlab functions and a tutorial related to this article are available free of charge in the GitHub repository (<https://zenodo.org/record/5078461#.YObPq-hKiUk>).²⁰

Results and discussion

Spectra pre-treatment

Recorded spectra are transformed from admittance to transmittance, and triplicates recordings are averaged to obtain a single spectrum. Further data transformations were assessed by their ability to classify the data better.

Savitzky-Golay (SG) smoothing and derivation filters were tested,¹³ and the best combination of axes for classification were chosen as the one that provides the highest accurate prediction (number of true positives with the test set). For each model, with five reference spectra, ten PLCS axis were obtained. Thus 45 possible combinations of axes for a two-dimensional representation (120 combinations for a three-dimensional representation) were assessed. Results with underivatised, first, second and third derivatives of the spectra are given in Table 1. Only results with the optimal Savitzky-Golay parameters are reported. However, the order of the polynomial has been varied from 1 to 3, and the frame length from 3 to 25.

While in all cases, a reasonable separation was observed, the 2nd derivative of the spectra gave the clearest representations.

Comparison with PCA and PLS

PCA-softDA and PLS-softDA were compared with PLCS-softDA. With each model, the number of true positive (ns), false positive (ms), multinomial classification (nm) and unclassified (no) were measured. Usually with PCA and PLS, variables are selected in order of explained variance or covariance. However, to be consistent with PLCS, the first ten LV (90.9% of explained

Table 1 PLCS-softDA performances with different spectra pre-treatment

	Derivative of the spectra			
	None ^a	1 ^{stb}	2 ^{ndc}	3 rd
ms	3	3	0	3
nm	60	34	7	6
ns	53	81	109	104
no	6	4	6	9

^a No derivative, no smoothing. ^b SG 1st derivative with polynomial order of 2 and frame length of 9. ^c SG 2nd derivative with polynomial order of 2 and frame length of 9. ^d SG 3rd derivative with polynomial order of 3 and frame length of 15. Ms, nm, ns and no are the number of samples assigned at $d \leq d_{crit}$ (ms: false positives, nm: multinomial classification, ns: true positives and no: unclassified).



Table 2 Comparison of PCA, PLS and PLS with softDA

	PCA-softDA	PLS-softDA	PLCS-softDA
ms	2	1	0
nm	84	57	7
ns	32	63	109
no	4	1	6

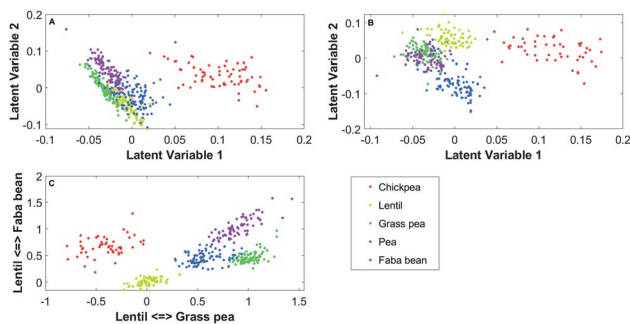


Fig. 4 (A) PCA, (B) PLS and (C) PLCS two-dimensional representations of the second derivative of the FTIR-ATR spectra.

variance in PCA) were selected, and all combinations were tested in the soft-DA model. The best combination was chosen as the one with the highest single and correct classification (ns). For PCA, best softDA model was obtained when using the first and second principal components (explaining 70.0% of the variance), and for PLS the first and third LV gave best predictability. Results are summarised in Table 2; the two-dimensional PCA, PLS and PLCS projections with the selected latent variables by softDA can be appraised in Fig. 4.

Using the second derivatives of the spectra gave the best accuracy of predictive class membership with the softDA models with any data reduction strategy. All pre-treatments described in Spectra pre-treatment were tested. For the classification of the flours, PLS performs better than PCA (32 and 63 true positives, respectively). However, PLCS is superior to both (109 true positives).

Model complexity

As final validation, the model's complexity was increased from 2 LV to 4 LV with PLCS and from 2 LV to 15 LV with PLS.

Table 3, below, summarised key results with 2 to 5 latent variables (LV). While with hardDA, the sum of true and false

Table 3 Validation

		PLCS 2 LV	PLCS 3 LV	PLCS 4 LV	PLS 2 LV	PLS 3 LV	PLS 4 LV	PLS 5 LV
Hard	True ^a	117	116	118	98	116	118	121
	False ^b	5	6	4	24	6	4	1
Soft	True ^a	109	111	107	56	101	103	101
	False ^b	4	1	1	2	3	2	0

^a Number of true positives in hard and soft classification. ^b Number of false positives with hard and soft classifications.

positives will always be equal to the number of samples, with softDA, some samples will be unclassified. As a general observation, with hard classification, the number of true positive increases as the complexity increases; however, with soft classification, the number of true positive reaches a maximum then decreases. At equivalent complexity, while a higher number of true positives is obtained with hard classification, a lower number of false positives is obtained with soft classification.

PLCS-softDA allows higher true positive and lower false positive at low complexity (91.0% true positive, 0.8% false positive, 8.2% unclassified with 3 LV). However, the complexity with PLCS is limited due to the collinearity of the LV (the correlation matrix of the latent variables obtained with PLCS are in ESI, Fig S11.tif). Consequently, models could not be built with more than four LV. On the other end, complexity with PLS and PCA can be much higher as each LV retain unique information. For example, with this data, best results using PLS were obtained with five LV (82.8% true positive, 0% false positive, 17.2% unclassified). Furthermore, with ten variable, the true positive rate of hardDA is 100%, however, while with softDA false positive rate is 0%, the true positive rate decrease to 52.2% (15.6% with 15 variables).

PCA-softDA shows the same trend as with PLS-softDA, with an increase in predictivity as the complexity increase. Best results were obtained with five LVs (73.0% true positive, 0.8% false positive and 26.2 unclassified).

Conclusions

In this manuscript, a new dimension reduction algorithm has been described. Spectra are represented in the latent structure based on their relative similarity between a series of pairs of model spectra. While results with a complete dataset of flours analysed using FTIR-ATR were extremely promising, this approach will have to be tested with other data. However, this approach is believed to be particularly interesting for spectral-based classification or clustering. The combination of PLCS with soft discriminant analysis is particularly attractive when different or contaminated samples are to be expected. While with hard classification, those samples will be assigned to a group without any warnings. With soft classification, the sample will be unclassified and thus marked for further analysis if needed.

The European grain legume germplasm has great potential for quality improvement. Spectroscopic techniques offer a reliable, cost-effective alternative approach for rapid and easy analysis of outlier genotypes with different spectroscopic



fingerprints. They require few sample preparations, therefore, are very appealing for breeders to handle large numbers of samples. The PLCS classification approach differentiated among the 5-grain legume species allowing the identification of outliers in all the species. These accessions might in the future be associated with a specific biochemical composition after further analysis and may represent interesting sources of traits to introduce in breeding programs.

Author contributions

G. E., M. P. and M. B. designed the research. G. E. programmed the Matlab functions. A. P., E. B. and A. S. analysed the samples. G. E. wrote the manuscript, all authors contributed to the redaction and revision of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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