Piece-Wise Multiplicative Scatter Correction Applied to Near-Infrared Diffuse Transmittance Data from Meat Products

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This paper presents a nonlinear scatter correction method, called piece-wise multiplicative scatter correction (PMSC), that is a further development of the multiplicative scatter correction (MSC) method. Near-infrared diffuse transmittance (NIT) data from meat and meat product samples were used to test the predictive performances of the PMSC and the MSC methods. With the use of PMSC, the prediction errors, expressed as the root mean square error of prediction (RMSEP), were improved by up to 36% for protein, up to 55% for fat, and up to 37% for water, in comparison to uncorrected data. The corresponding improvements by using PMSC compared to MSC were up to 22%, 24%, and 31% for protein, fat, and water, respectively.

Index Headings: **Near-infrared spectroscopy; Light scatter; Multiplicative scatter correction; Multiplicative signal correction; Preprocessing; NIR; NIT; MSC; EMSC; PMSC.**

INTRODUCTION

The response signals from diffuse spectroscopy are a result of the light scatter and chemically absorbed energy in the sample. The diffuse scatter of light is a result of optical inhomogeneity in the sample. Optical inhomogeneity is due to different velocity of light in the different parts of the sample, often due to particles and/or droplets and the surrounding media. The optical inhomogeneity will result in reflectance, refraction, and diffraction of the light at the particle and droplet interfaces. The scatter will consequently vary according to different sizes, shapes, and distributions of the particles and/or droplets in a sample. In quantitative determination of a chemical analyte, the analyst is most often only interested in the analyte absorbance information in the spectra. Interferences (i.e., scatter variation) must consequently be either fully modeled or eliminated to give a robust and accurate quantitative method. In multivariate regression it is often possible to model the interferences. This approach, however, gives a less parsimonious model, and the modeling of the interferences is often not good enough to give the desired accuracy. It is therefore desirable in most analyte prediction methods to eliminate interferences such as light scatter or to have control of the variation of the light scatter in the samples; also, in nondestructive and noninvasive analyses it is not possible to physically eliminate the scatter.

The most obvious way to control the light scatter is to standardize the sample preparation to get equal scatter properties in all samples. However, this is most often impossible in biological samples because of structure variation caused by chemical variation, heating from the homogenization process that can cause moisture loss, denaturation, etc. It is, however, recommended that sample preparation and presentation be standardized to minimize the scatter variation between samples before spectroscopic measurement.

The only way, other than standardization, to eliminate or reduce scatter variation is by mathematical methods. A number of mathematical pretreatments of the response signal from the diffuse near-infrared spectral measurements, prior to calibration, are reported (for overview see, e.g., Williams and Norris[1]). These methods are often divided in two groups and are performed in two steps: (1) the response transformation step and (2) the linearization step. In step 1 the data are transformed to units of: R (reflectance), T (transmittance), A (absorbance), K/S (Kubelka Munk), etc. The linearization step 2 can include (one or more): normalization, mean centering, first derivatives, second derivatives, higher derivatives, Fourier transforms, response ratios, multiplicative scatter correction [also called multiplicative signal correction (MSC)],[2,3] or extended multiplicative signal correction (EMSC).[4] The light scatter properties in biological samples will vary from sample to sample according to physical and chemical inhomogeniety, so these methods must be empirically proven. Among the transformation methods, most often the absorbance, $A = \log(1/R)$ and $A = \log(1/T)$ units are chosen in near-infrared diffuse reflectance and transmittance measurements, respectively. Among the linearization methods the choices differ more widely in the literature. Several reports show very good predictive results by use of the MSC method.[2-6]

The MSC method is motivated partly from theory, but is mainly motivated from favorable empirical prediction results. MSC is used most often to improve the predictive ability of NIR data.[5,6] Three explanations[5] of why the MSC improves the predictive ability of near-infrared diffuse reflectance data are as follows: (1) MSC gives more parsimonious models by removing irrelevant information, (2) MSC linearizes the relationship between the regressor and the regressand, and (3) MSC gives a better or more regular distribution of the samples, in comparison to non-MSC data.

The multiplicative scatter correction method corrects for a linear additive offset term and a single multiplicative term for each sample. The present paper presents a piece-wise multiplicative scatter correction (PMSC) method, which is a further development of the MSC method. The purpose in introducing PMSC is to correct

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for nonlinear additive scatter effects and to correct for nonlinear multiplicative scatter effects. Several nonlinear fitting methods exist, e.g., polynomial, artificial neural network fitting, etc. Many of these methods are complex and many parameters need to be estimated. In the present paper we have studied a local linear fitting approach.[7] The main idea for PMSC is to make linear regression fits to local regions of the spectra, assuming that the spectra are continuous and smooth. This local linear approach to model nonlinearity is also successfully used in multivariate regression.[8,9]

To illustrate the predictive performance of PMSC, we use near-infrared diffuse transmittance (NIT) spectra. Prediction results of the main constituents from products with high water content (meat and meat products) are presented.

THEORY

MSC. A diffuse transmittance or reflectance spectrum is a result of chemically absorbed and scattered light. In the multiplicative scatter correction method it is assumed that the light scatter and the chemical information can be mathematically differentiated. The scatter for each sample is assumed to be a linear deviation from a standard or ideal sample. Most often, the mean spectra are used. The remaining variation represents the chemical information according to specific absorption. Each sample is additively and multiplicatively scatter corrected in order to equalize the scatter levels. For each spectrum, x_i ($K \times 1$), where i [1, 2, . . . , i, . . . , I] represents the samples and K [1, 2, . . . , k, . . . , K] represents the wavelengths, the offset, a_i, and the slope, b_i, are estimated by a linear least-squares regression on the mean spectrum, $\bar{\mathbf{x}}$ ($K \times 1$) according to:

$$x_i = \mathbf{1}\, a_i + \bar{\mathbf{x}}\, b_i + \mathbf{e}_i \qquad (1)$$

where $\mathbf{1}$ ($K \times 1$) is a vector of ones, and $\mathbf{e}_i$ ($K \times 1$) is the residual vector. The responses, x_{ik}, at each wavelength, k, in each sample, i, are multiplicatively scatter corrected according to:

$$x_{ik,\text{corrected}} = (x_{\text{ik,noncorrected}} - a_i)/b_i. \qquad (2)$$

PMSC. The MSC and EMSC methods correct for linear baseline or additive effects by adding or subtracting one single term to the whole spectrum for each sample. The intention of the piece-wise multiplicative scatter correction method is to correct for nonlinear additive and multiplicative scatter effects. The idea is to fit a linear regression in a local wavelength region. For continuous spectra this is done by fitting Eq. 1 in a moving window of wavelengths. In the present paper, a fixed-size window is used. The x_{ik} is corrected by replacing $\mathbf{x}_i$ in Eq. 1 by the vector, $\mathbf{x}_{ik}$ ($m + n + 1 \times 1$), according to:

$$\mathbf{x}_{ik} = [x_{i,k-m}, x_{i,k-m-1}, \ldots, x_{i,k}, \ldots, x_{i,k+n-1}, x_{i,k+n}]' \qquad (3)$$

with window m and n variables on each side of variable k. The corresponding window sizes are consequently $m + n + 1$ variables. The corresponding window is taken from the mean spectrum ($\bar{\mathbf{x}}_k$), and Eq. 1 is applied for each sample and each variable, according to Eq. 4:

$$\mathbf{x}_{ik} = \mathbf{1}\, a_{ik} + \bar{\mathbf{x}}_k\, b_{ik} + \mathbf{e}_{ik}. \qquad (4)$$

Here, the $\mathbf{1}$ and $\mathbf{e}_{ik}$ are ($m + n + 1 \times 1$) vectors. The corrections are performed analogously to Eq. 2 and according to:

$$x_{ik,\text{corrected}} = (x_{ik,\text{noncorrected}} - a_{ik})/b_{ik}. \qquad (5)$$

To avoid shortening of the corrected spectra at the ends, we corrected the first m variables and the last n variables by a permanent (not moving) window, with a width of ($m + n + 1$) variables.

EXPERIMENTAL

To test the predictive performance of the PMSC method prior to calibration, we used three different sample sets; they are identified as set 1, set 2, and set 3. Two sets are from raw meat samples and the third sample set is from processed meat products. The sets are as follows:

Set 1. One hundred homogenized beef samples, divided into a 68-sample calibration set and a 32-sample test set. These samples are used and are further described by Isaksson *et al.*[10]

Set 2. One hundred and three homogenized meat samples, divided into a 70-sample calibration set and a 33-sample test set. The set consists of samples from beef and pork, and is used and further described by Næs and Isaksson[9] and also Næs *et al.*[11]

Set 3. One hundred and twenty-three homogenized cooked and smoked dinner sausage samples, 70 for calibration and 53 for the test set. This sample set was collected from many different manufacturers in Norway and is used and further described by Isaksson and Hildrum.[6]

Prior to spectral and chemical measurements, the samples were homogenized with a rotating knife homogenizer (Moulinette S653, Moulinex, Nieune, France).

Near-infrared diffuse transmittance spectra (Tecator 1225 Infratec food and feed analyzer, Höganäs, Sweden) were acquired in the 850–1050 nm region, in 2-nm intervals, giving 100 variables. Averages of five replicate samples, with one spectrum of each, were used in the calibrations.

The samples were chemically analyzed for protein, fat, water, and carbohydrate (set 3 only) with standard methods as described in Refs. 6, 9, and 10. The units used are given as weight % of the constituents relative to the sample.

The NIPALS algorithm for principal component regression (PCR)[12] was used as the multivariate regression method. The regressions were performed with the use of the principal components (PC) corresponding to the largest eigenvalues, without deletion of intermediate PCs, as advocated by Næs and Martens.[13]

As the quality measurement of the predictive ability of the different linearization methods, the independent test sets were used. The prediction errors were calculated as root mean square error of prediction (RMSEP)[11], which was defined as:

$$\text{RMSEP} = \left[I_p^{-1} \sum_{i=1}^{I_p} (y_i - \hat{y}_i)^2 \right]^{1/2}$$

where I_p [1, 2, . . . , i, . . . , I_p] denotes the number of

TABLE I. Overview of the chemical composition of the sample sets. The repeatability, minimum, maximum, average, and standard deviation (SD) values in weight % are stated.

Constituents	Repeatability[a]	Min.	Max.	Avg.	SD
Set 1					
Protein	0.13				
Calibration		16.62	22.99	20.32	1.12
Test		18.25	22.94	20.35	1.09
Fat	0.094				
Calibration		0.94	23.17	7.91	4.69
Test		1.30	17.47	7.75	4.22
Water	0.19				
Calibration		58.98	75.94	70.42	3.53
Test		62.58	75.33	70.43	3.26
Set 2					
Protein					
Calibration	...	13.86	22.50	18.56	2.20
Test		15.11	22.10	18.49	2.21
Fat	...				
Calibration		0.97	33.23	14.39	8.60
Test		1.10	28.93	15.45	8.27
Water	...				
Calibration		50.45	76.94	66.13	6.54
Test		55.74	76.51	65.21	6.10
Set 3					
Protein					
Calibration	...	9.0	12.4	10.94	0.80
Test		9.7	12.9	10.90	0.68
Fat	...				
Calibration		13.8	22.9	18.34	2.00
Test		14.3	23.1	18.97	2.03
Water	...				
Calibration		57.3	65.5	60.92	1.97
Test		56.3	65.2	60.70	2.01
Carbohydrate	...				
Calibration		4.2	6.5	5.35	0.60
Test		3.7	7.1	5.51	0.74

[a] The repeatability of the chemical reference method, calculated as standard error of three replicate measurements.

samples in the test (prediction) set used, y_i denotes the chemically measured reference value, and $\hat{y}_i$ denotes the NIT predicted chemical value of sample number i.

Prediction improvements of method 2 compared to method 1, expressed in percent, were calculated as:

$$\text{Improvement (\%)} = [(\text{RMSEP}_1 - \text{RMSEP}_2)/\text{RMSEP}_1]*100.$$

The calculations were performed on the software packages UNSCRAMBLER II, Version 3.0 (Camo AS, Trondheim, Norway), and PRO-MATLAB, Version 3.2-SUN (The MathWorks, Inc. Sherborn, MA).

RESULTS AND DISCUSSION

Below, the chemical composition of the sample sets is discussed. The prediction performance, by use of PMSC compared to MSC and noncorrected log(1/T), for the three different sample sets is discussed. To illustrate the behavior of PMSC on the spectra, we will briefly consider some spectra and some correction coefficients from set 1.

Chemical Composition. An overview of the chemical composition of the sample sets is given in Table I. Note that the largest chemical variation was in set 2. Set 2 was more heterogeneous than set 1. Sample set 3 was heterogeneous with regard to raw materials in addition to process variation but has relatively little chemical variation.

TABLE II. Sample Set 1. The standard deviation (SD) and the optimal (lowest) root mean square error of prediction (RMSEP) results in weight % (in bold). In parentheses are the number of PCs in the calibration model and, after the comma, the window size (nm) in the PMSC used.

	SD	log (1/T)	MSC	PMSC
Protein	1.08	**0.33** (23,−)	**0.27** (29,−)	**0.21** (22,42)
Improvement (%)		...	18	36
Fat	4.15	**0.75** (7,−)	**0.42** (14,−)	**0.34** (19,22)
Improvement (%)		...	44	55
Water	3.20	**0.46** (17,−)	**0.42** (14,−)	**0.29** (19,22)
Improvement (%)		...	9	37

The prediction error from a multivariate calibration of near-infrared diffuse transmittance contains errors from the reference methods, errors related to the instrument, and errors related to sampling, as well as model errors. The sizes of these terms are often difficult to determine. In Table I the repeatability for the reference method in set 1 is given. These terms relate to the reference method errors, the sampling errors (not known here), and the instrument errors (not known here), and should indicate the lowest possible prediction error expressed as RMSEP. The upper limit for the prediction errors (RMSEP) is the standard deviation (STD) of the chemical constituent values in the test sets.

Prediction Results. An overview of the prediction results for the sample sets is presented in Tables II, III, and IV. The prediction results for the beef sets show, overall, lower prediction errors for set 1 compared to set 2. This is probably due to less chemical variation in set 1. It may also be due to lower sampling error and lower reference method errors.

In general, the use of MSC improves prediction in comparison to simply using log(1/T). PMSC further improves prediction in comparison to MSC. The prediction error improvements for the use of the scatter correction methods for sample set 3 were, however, very small (and probably arbitrary). This observation is probably due to the relatively small composition variation compared to that for the other sample sets studied here and, correspondingly, less scatter variation between the samples in this set.

TABLE III. Sample Set 2. The standard deviation (SD) and the optimal (lowest) root mean square error of prediction (RMSEP) results in weight % (in bold). In parentheses are the number of PCs in the calibration model and, after the comma, the window size (nm) in the PMSC used.

	SD	log (1/T)	MSC	PMSC
Protein	2.21	**0.49** (29,−)	**0.41** (25,−)	**0.39** (35,22)
Improvement (%)		...	16	20
Fat	8.27	**1.21** (10,−)	**1.00** (5,−)	**0.76** (12,22)
Improvement (%)		...	17	37
Water	6.10	**0.98** (10,−)	**0.77** (8,−)	**0.62** (15,22)
Improvement (%)		...	21	37

TABLE IV. **Sample Set 3. The standard deviation (SD) and the optimal (lowest) root mean square error of prediction (RMSEP) results in weight % (in bold). In parentheses are the number of PCs in the calibration model and, after the comma, the window size (nm) in the PMSC used.**

	SD	log (1/T)	MSC	PMSC
Protein	0.68	**0.30** (14,–)	**0.29** (12,–)	**0.32** (13,122)
Improvement (%)		···	3	−7
Fat	2.10	**0.90** (14,–)	**0.89** (12,–)	**0.85** (23,42)
Improvement (%)		···	1	6
Water	2.00	**0.55** (13,–)	**0.51** (10,–)	**0.51** (11,42)
Improvement (%)		···	7	7
Carbohydrate	0.74	**0.70** (14,–)	**0.65** (35,–)	**0.65** (36,122)
Improvement (%)		···	7	7

The prediction errors for sample set 2 were improved from 16 to 21% by use of MSC and from 20 to 37% by use of PMSC compared to log(1/T). The lowest PMSC prediction error for fat was 0.76 weight %, with the use of 12 PCs in the model. The same data were also discussed in a paper by Næs and Isaksson,[9] where locally weighted regression (LWR) was used. In that paper the lowest prediction error for LWR was 0.91% fat, for only three PCs. The prediction of water after PMSC gave an error of 0.62 weight %, with the use of 15 principal components in the regression model. LWR provided Næs and Isaksson[9] with a prediction error for water from 0.65 to 0.69, depending on different weighting functions, with the use of three principal components. These data (every other wavelength) were also analyzed by Næs *et al.*[11] with artificial neural networks (ANN). ANN gave, in that study, a prediction error for water of 0.64 with the use of eight principal components as input variables and three nodes in the hidden layer. On the basis of these data, PMSC, prior to the linear PCR, gave lower prediction results than the nonlinear methods LWR and ANN; however, more complex regression models (i.e., more PCs) were needed.

The prediction error for sample set 1, expressed as root mean square error of prediction, as a function of the number of principal component used in the regression models, is illustrated in Figs. 1a, 1b, and 1c. The MSC and PMSC methods clearly improved the prediction ability for protein, fat, and water. Table II gives the optimal (lowest) test set prediction results. For protein, MSC improved the prediction results by 18%, and PMSC with a window size of 42 nm improved prediction by 36%, compared with noncorrected log (1/T) data. For fat, the improvements were 44% by MSC and 55% by PMSC (window size = 22 nm), compared to noncorrected data. The corresponding improvements for water were 9% and 37%. Note that the prediction errors with PMSC are very close to the reference method errors. This is particularly the case for water and protein predictions. This result means that it is not possible to improve the RMSEP much more, taking into account that sampling and instrumental errors are also present.

PMSC shows a clear tendency to give relatively low prediction errors after two PCs (Fig. 1) while MSC needs typically one extra PC and log(1/T) needs in addition

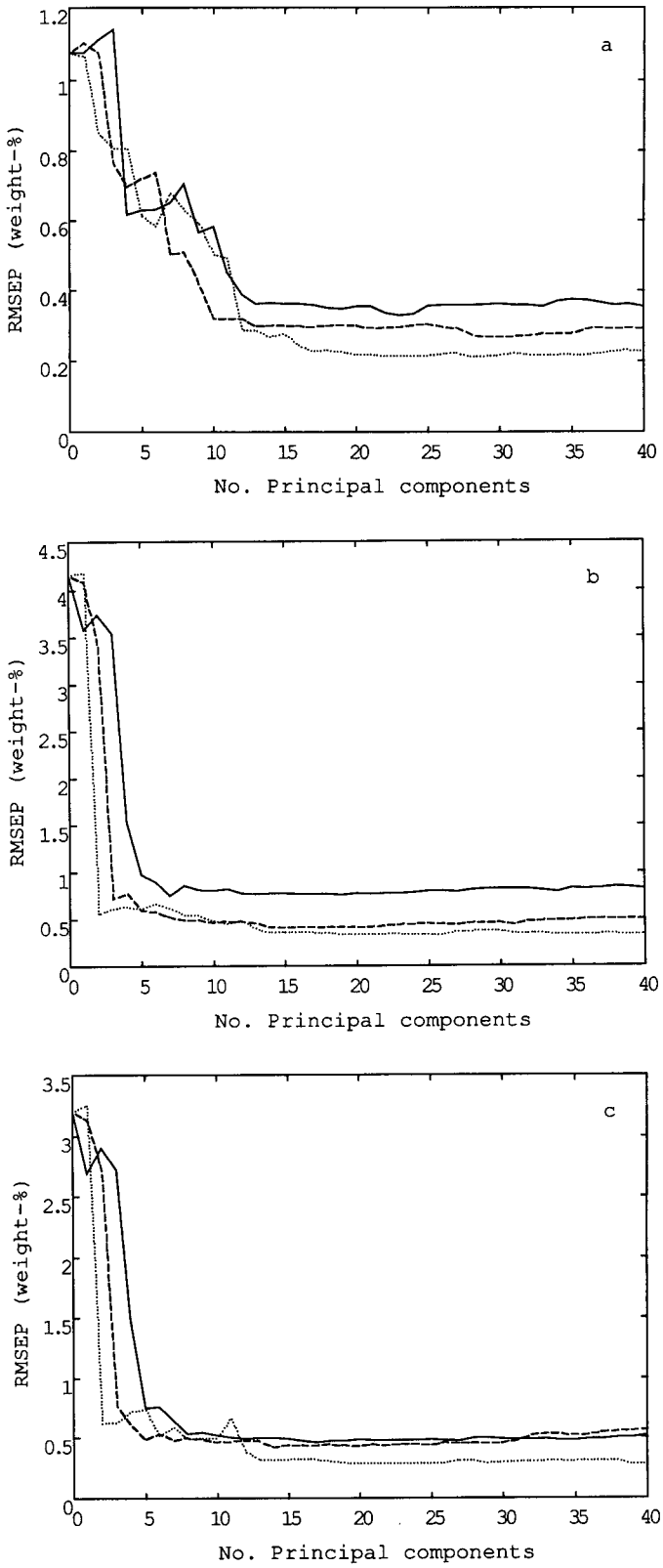

FIG. 1. Prediction errors expressed as root mean square error of prediction (RMSEP, in weight %) as a function of the number of principal components used in the regression models. (——) log(1/T); (- - - - -) MSC log(1/T); and (· · · · ·) PMSC log(1/T). (**a**) Protein, PMSC with window size = 42 nm; (**b**) fat, PMSC with window size = 22 nm; and (**c**) water, PMSC with window size = 22 nm.

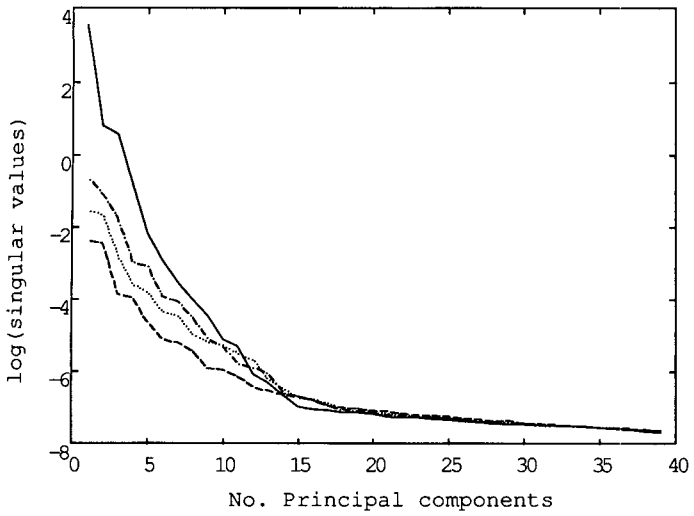

FIG. 2. Logarithms of the largest singular values. (——) log(1/T); (–·–·–) PMSC with window size = 82 nm; (·····) PMSC with window size = 42 nm; and (-----) PMSC with window size = 22 nm.

one or two extra PCs to get the same level of prediction error result. For prediction of the most varying constituent, fat, PMSC gave better prediction ability with only two PCs than log(1/T) did in any model. The same was nearly the case for the second most varying constituent, water. However, for protein, with relatively small chemical variation, a larger number of PCs are needed to get good predictive results. This observation indicates that the light scatter interferences were reduced by PMSC and also by MSC compared to PCR on the log(1/T) data.

In doing regression on log(1/T) and MSC data, we found the main predictive ability in the first eight to ten PCs, while regression on PMSC data showed additional and substantial predictive ability in PCs 12 to 17. These high-numbered PCs correspond to relatively smaller eigenvalues that correspond to relatively smaller variation in the spectra. The singular values (square roots of the eigenvalues) for the first PC were 34.70, 2.89, and 0.096 for log(1/T), MSC, and PMSC (window size = 22 nm), respectively. This result indicates the decrease of colinearity and total variation, caused mainly by light scatter, by use of the scatter correction methods. Figure 2 shows the singular values for the different PCs for log(1/T) data and PMSC data with some different window sizes. We can see (Fig. 2) that the rank is 3 to 4 higher when one is using PMSC, compared to noncorrected data. The PMSC data gave relatively larger singular values compared to log(1/T) data for PCs higher than 14—meaning that PCA extracts larger spectral variation in the PMSC data in comparison to log(1/T) data. As a consequence, by the use of PMSC, some extra PCs can be extracted for prediction. PMSC exposed these small chemically related spectral variations, while log(1/T) (and MSC) did not. The explanation of why PMSC exposes these small variations in the spectra may be that the PMSC method eliminates irrelevant (from a predictive point of view) interferences in the data, so that this minor information is extractable by the linear principal component model. These interferences may have caused nonlinearities in the spectra, making it impossible to model these nonlinearities because of the noise level or noise distribution

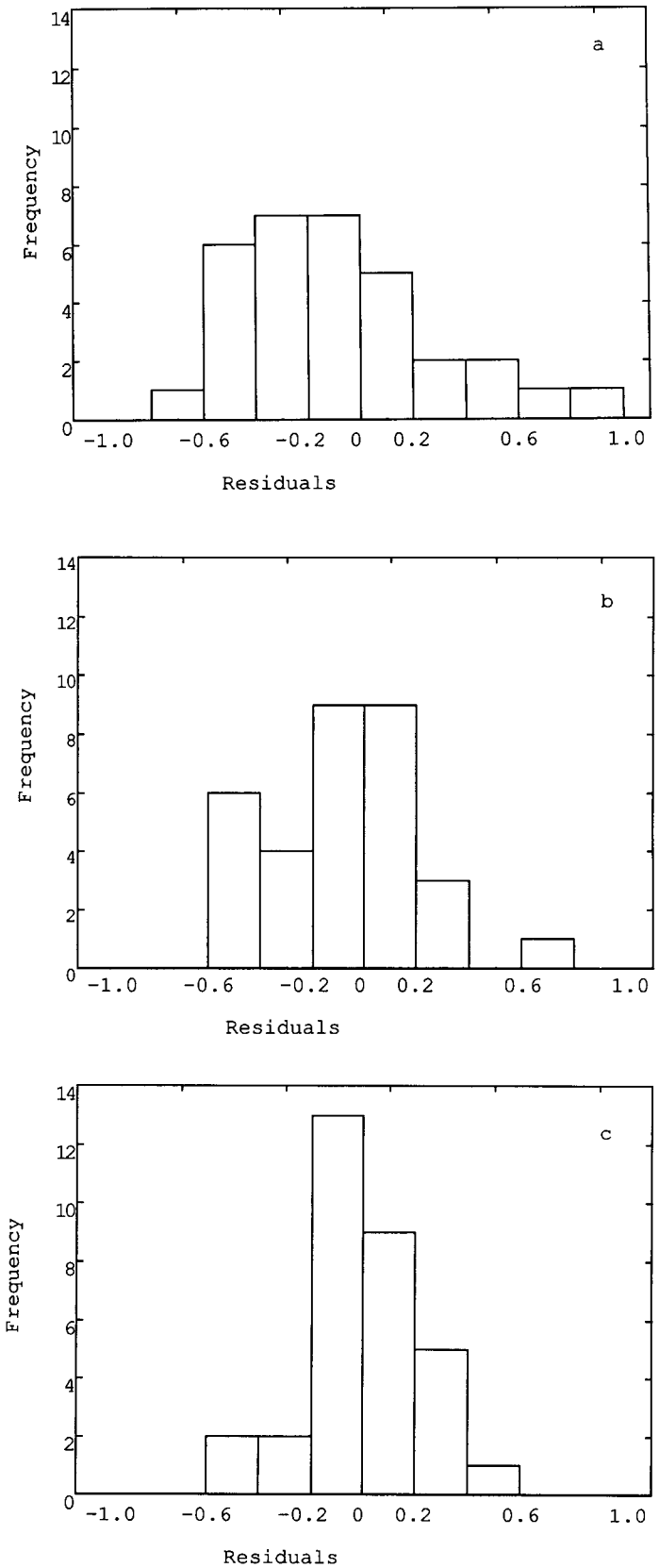

FIG. 3. The distribution of the residuals for protein, with 17 PCs in the regression models. (**a**) log(1/T); (**b**) MSC log(1/T); and (**c**) PMSC log(1/T), window size = 42 nm.

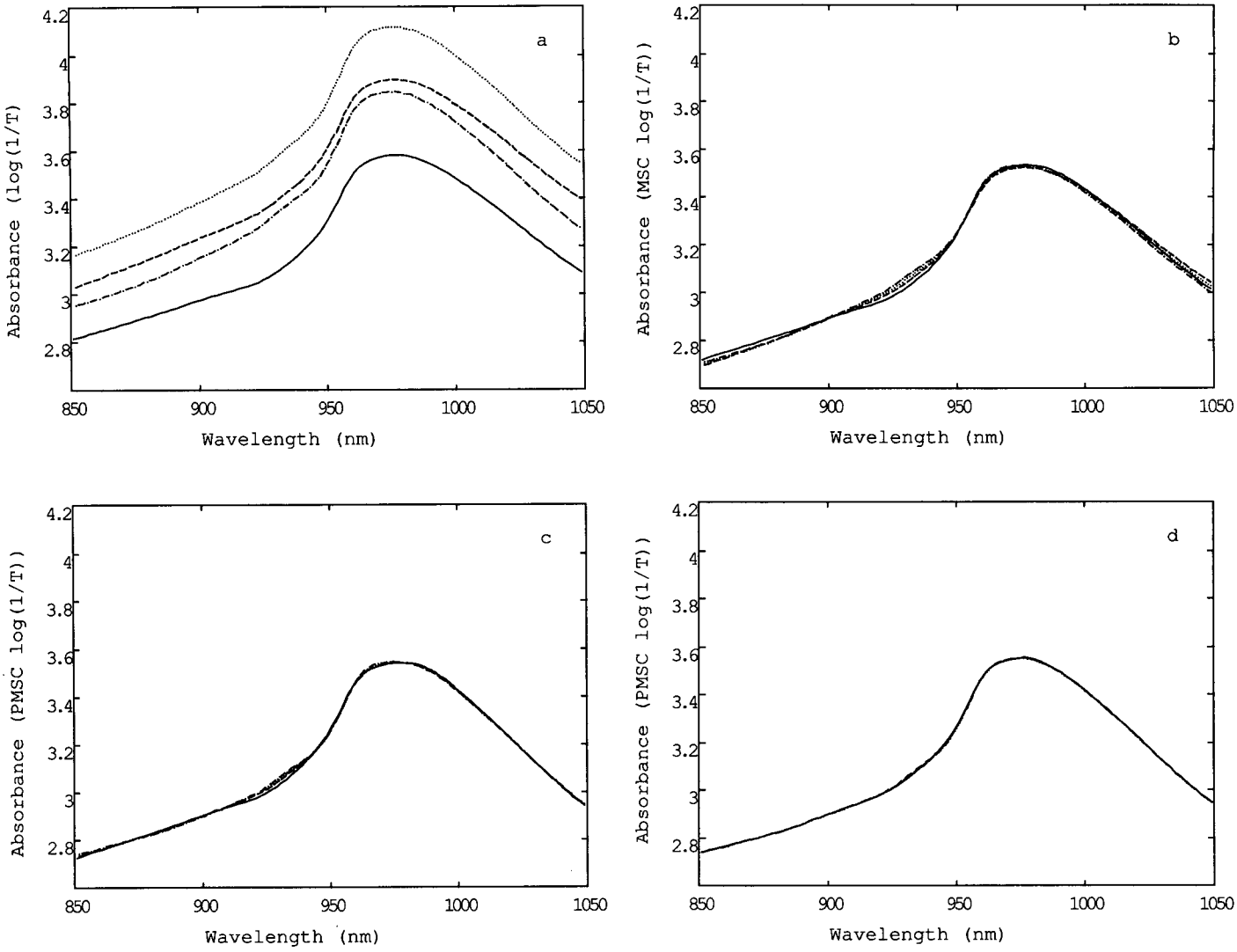

FIG. 4. NIT spectra from four randomly chosen meat samples. The samples contain from the upper to the lower spectra in **a**: 19.48, 20.80, 18.23, and 22.99% protein; 12.33, 8.10, 15.67, and 3.00% fat; and 66.71, 69.77, 65.45, and 72.44% water. (**a**) log(1/*T*); (**b**) MSC of the spectra in **a**; (**c**) PMSC of the spectra in **a** and with window size = 82 nm; (**d**) PMSC of the spectra in **a** and with window size = 22 nm.

in the data. From loading plots it can be observed (not shown here) that noise gradually started to appear, for all the studied transformations, from about PC number 12 to 14 (this observation is, however, subjective).

Regression on PMSC data gives, in addition to lower prediction errors, a narrower distribution of the residuals, as illustrated for protein (17 PCs) in Figs. 3a, 3b, and 3c. This means that the predictions of the samples with the largest residuals were improved by MSC and further improved by PMSC in comparison to uncorrected spectra. The scatter correction methods, in particular PMSC, also reduced the bias. After correction of the bias (−0.083, −0.081, and 0.018 for log(1/*T*), MSC, and PMSC, respectively), the bias-corrected standard error of performance was 0.35, 0.29, and 0.23, with the use of 17 PCs, for log(1/*T*), MSC, and PMSC, respectively. The corresponding RMSEPs were 0.36, 0.30, and 0.23 for log(1/*T*), MSC, and PMSC, respectively.

Regression models with relatively larger numbers of PCs are, in general, not preferable, because small variation due to temperature variation, instrumental drift, etc., can interfere and will consequently give less robust methods. However, modern instruments are very stable and reliable, giving excellent repeatability.

For sample set 1, we also performed the regressions on the linear first (using windows of 6, 8, 10, and 12 nm) and second (using windows of 6–6, 8–8, 10–10, and 12–12 nm) derivatives of the log(1/*T*) data. These transformations did not improve the prediction error results in comparison to log(1/*T*) data.

Spectra. As shown in Fig. 4a—four randomly chosen NIT spectra from set 1—the baselines are very different due to varying additive scatter. The spectra are mostly dominated by O-H absorbance bands from water at about 970 nm. We can also see that there is no visual selectivity for protein, fat, and water in these spectra that correlates to the chemical contents (the chemical contents are stated in the figure caption). MSC visually eliminates these substantial additive scatter differences (Fig. 4b). The methylene C-H stretch absorbance bands at about 930 nm, mainly originating from the fat, are now selectively correlated to the fat contents. PMSC reduces the visual

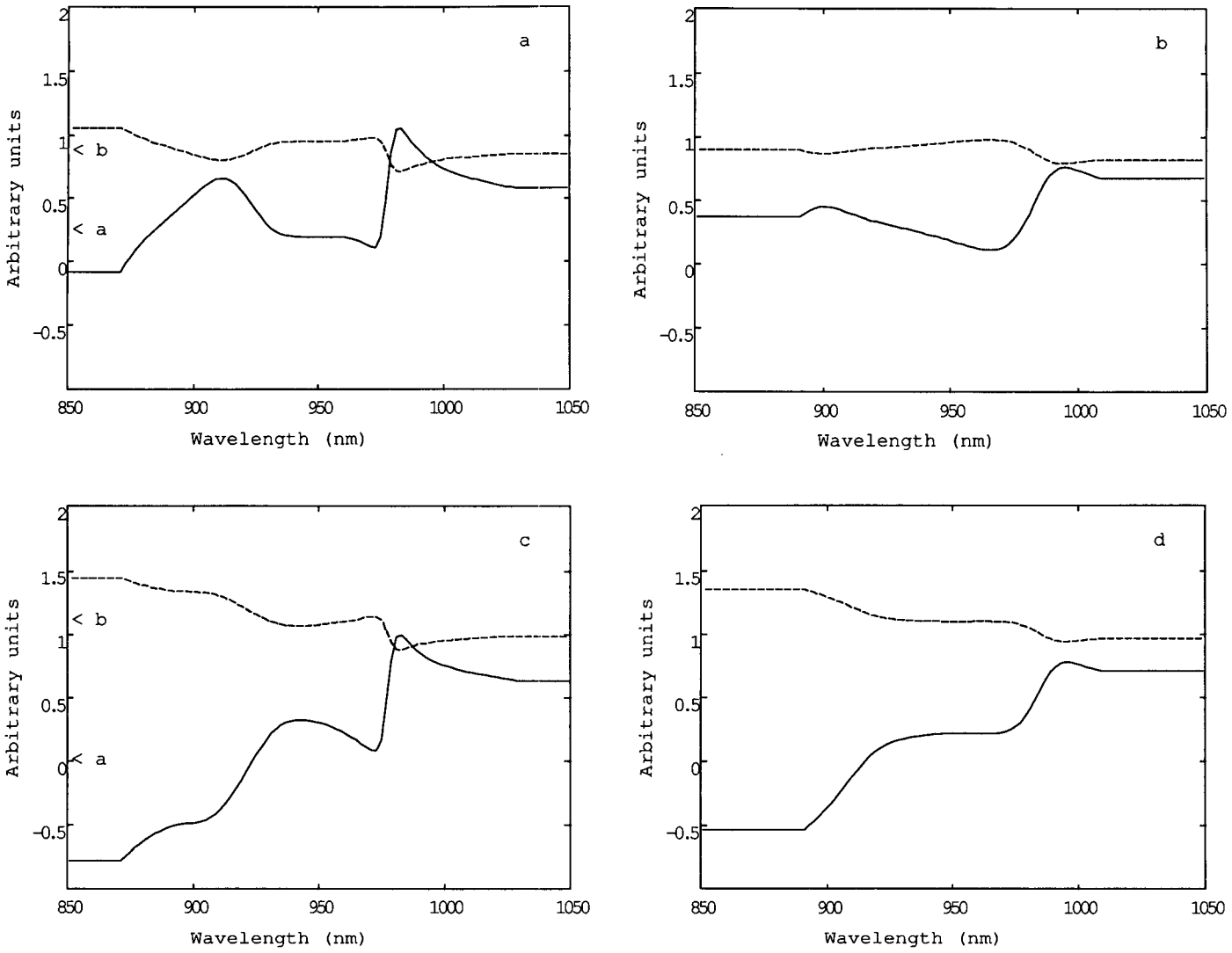

FIG. 5. The local regression-coefficients, the offset and additive coefficients (——) a_{ik}, and the slope and multiplicative coefficients (-----): b_{ik}, as a function of the wavelengths. The arrows indicates the MSC coefficients. (**a**) The lower spectrum in Fig. 1a, window size = 42 nm; (**b**) The lower spectrum in Fig. 1a, window size = 82 nm; (c) The upper spectrum in Fig. 1a, window size = 42 nm; and (**d**) The upper spectrum in Fig. 1a, window size = 82 nm.

scatter differences still further (Fig. 4c). The visual differences decrease more when smaller windows are used (Fig. 4d).

Parameters a_{ik} and b_{ik}. The smallest possible window size in the PMSC algorithm, from a regression point of view, is to use two wavelengths in a local regression. This extreme will smooth out all the chemical absorbances in the spectrum and make all samples almost identical. Consequently, no chemical information will remain, and the predictive ability will be lost. It is therefore important not to use excessively small windows. The other extreme, using all wavelengths, gives standard MSC. The window sizes must be large enough to keep the chemical-related absorbances intact and small enough to correct for nonlinear scatter effects. The optimal window size will depend on the spectral shape of the peak width compared to the scatter properties. The spectral shape will vary according to a number of different properties (e.g., optical properties of the instrument—slits, lenses, filters, etc.), the spectral region (wavelength), the sample composition, the sample preparation, and the sample presentation to the spectrophotometer. The window sizes must therefore be empirically optimized according to predictive ability.

We have studied different window sizes (22, 42, 82, and 122 nm). To give an idea of the sizes of a_{ik} and b_{ik} as a function of wavelength, two different samples (the upper and lower spectra from Fig. 4a), with two different window sizes, are illustrated in Figs. 5a, 5b, 5c, and 5d. The local regression coefficients, the offset (a_{ik}) and the slope (b_{ik}) in PMSC, were estimated for each spectrum and each variable (Fig. 5). The additive scatter according to PMSC typically gives somewhat higher baseline offsets at higher wavelength. The profiles of a_{ik} and b_{ik} vary from sample to sample and according to different window sizes. A more smooth profile is obtained for larger windows used. The profiles approach a straight line as the window size increases toward using all wavelengths, as in MSC. The offsets (a_i) and the slopes (b_i) from MSC are indicated by arrows in Fig. 5. As mentioned above, in the MSC method, only one offset (a_i) and one slope (b_i) for each spectrum are calculated.

CONCLUSIONS

PMSC $\log(1/T)$ gave improved predictive results in comparison to $\log(1/T)$, first derivatives of $\log(1/T)$, second derivatives of $\log(1/T)$, and MSC $\log(1/T)$ for the meat sets studied. PMSC gave very good results for sample sets with relatively wide chemical variations and correspondingly large scatter variation.

The window sizes in the PMSC algorithm must be chosen empirically and should be larger than the "widths" of the spectral peaks that are related to the chemical information, and smaller than the distribution of nonlinear scatter. In this study, the lowest prediction errors were obtained by using relatively small window sizes. Typically 22-nm to 42-nm window sizes gave the best prediction results.

The PMSC method is believed to be best suited for correction of spectra where the scatter variation is large in comparison to the chemical variation. In addition, the spectra should have relatively broad and strongly nonselective peaks. This is the case in near-infrared spectra, and in particular in the short-wavelength regions (700–1200 nm), of samples with high water content, as in biological solid and semi-solid samples such as meat, meat products, vegetables, etc.

Note that the term "scatter" in MSC and PMSC does not necessarily refer to the physical scatter of the light propagation in the sample. We have little physical evidence that these methods correct for light scatter effects. As mentioned above, these methods are mostly empirical methods, shown to give improved predictive results. We chose, however, to call them scatter correction methods, as originally stated by Martens *et al.*,[2] to separate this information from chemically related information. These methods can generally be considered as signal correction methods.[12]

Finally, it is well known that linear calibration methods can handle nonlinearity by adding more factors (PCs) to the model. However, calibration models with many factors are suspect because they are less parsimonious. On the other hand, using linear methods is highly desirable because of the associated outlier detection and error estimation methods not available with nonlinear calibration methods. PMSC provides data that can be modeled by linear methods, provided the noise is low enough, and therefore provides these advantages of modeling nonlinear data.

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