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Automated alignment of one-dimensional chromatographic fingerprints

M. Daszykowski[a,*], Y. Vander Heyden[b], C. Boucon[c], B. Walczak[a]

[a] Department of Chemometrics, Institute of Chemistry, The University of Silesia, 9 Szkolna Street, 40-006 Katowice, Poland
[b] Analytical Chemistry and Pharmaceutical Technology, Center for Pharmaceutical Research (CePhaR), Vrije Universiteit Brussel - VUB, Laarbeeklaan 103, 1090 Brussels, Belgium
[c] Unilever R&D Vlaardingen, Olivier van Noortlaan 120, 3130 AC Vlaardingen, The Netherlands

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ABSTRACT

A general framework for the automatic alignment of one-dimensional chromatographic signals is presented in this article. The alignment of signals was achieved by explicitly modeling the warping function. Its shape was estimated using a linear combination of several B-spline functions. The coefficients of the spline functions were found in the course of an optimization procedure to maximize the Pearson's correlation coefficient between a target chromatogram and aligned chromatogram(s). The computational requirements of the method are discussed with respect to the correlation optimized warping method, frequently used for the alignment of chromatographic signals. As illustrated with two sets of one-dimensional chromatographic fingerprints, the automatic alignment approach performs well even when non-linear peak shifts need to be corrected. It can be applied in an on-the-fly manner since the alignment of signals is rapid.

1. Introduction

Chromatographic methods are frequently used to characterize the chemical composition of samples. When optimal chromatographic conditions are maintained during a chromatographic run, components of a mixture can potentially be separated, and if necessary, identified and quantified. Nowadays, analysis of very complex mixtures such as herbal extracts, urine samples, is a direct research focus of many laboratories and it has proven to be very challenging. For complex samples it is often impossible to achieve a sufficient chromatographic resolution, while additionally identification and/or quantification of all chemical constituents may be impossible due to a lack of chromatographic standards.

On the other hand, samples can be characterized by their chromatographic signals (the so-called fingerprints). In theory, a chromatographic fingerprint has a potential to describe a sample as uniquely as a human fingerprint identifies an individual person. Using chemometric methods, including projection, clustering and modeling techniques, similarities/differences among samples can be revealed and studied [1,2]. The objective of comparative analysis is to uncover or explain variability caused by differences in the chemical composition of samples. In addition to their chemical variance, instrumental variance (induced by instrumental instability), can be a key factor. In the extreme case, the experimental variability can mask chemical differences among samples. Such a problem is often encountered in chromatography, when due to different factors, e.g. column ageing, variability in mobile phase composition, peak shifts are observed among chromatographic fingerprints. Despite the relatively wide access to advanced instrumentation, problems of peaks shifts are common for signals of other types as well, e.g. for nuclear magnetic resonance signals (^{1}H NMR) [3], two–dimensional gel electropherograms [4], signals obtained from liquid chromatography coupled with mass spectrometry [5]. To focus further by the comparative analysis of samples on underlying chemical differences, the instrumental variability manifested as peak shifts must be eliminated. This preprocessing step is crucial and considered to be a prerequisite before any multivariate chemometric analysis can successfully be applied [6].

In this article we will focus on the alignment of one-dimensional signals only. The first attempts to correct peak shifts in such analytical signals, including alignment approaches dedicated to the alignment of chromatographic signals, emerged relatively early. For a better understanding of the alignment issue, it is interesting to trace the evolution of different alignment methods and the improvements introduced over time. In the early-developed alignment approaches, chromatographic standards were considered. Information about the positions of standard peaks (the so-called marker or landmark peaks) in a target and in the signals to be aligned was used for the adjustment of time axes by means of linear interpolation. Such an approach seems to be simple and very appealing, but for complex samples many landmark peaks are necessary to achieve a satisfactory alignment, and thus it has a limited range of applications.

* Corresponding author. Tel.: +48 323591219.
E-mail address: mdaszyk@us.edu.pl (M. Daszykowski).

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The next generation of alignment methods, such as e.g. dynamic time warping (DTW) [8] and correlation optimized warping (COW) [9], have been developed with the aim to align signals without any preliminary information about the correspondence of peaks or the use of landmark peaks.

Comprehensive surveys of different alignment techniques can be found for instance in [7,10]. Independently, other alignment techniques were developed in the field of spectroscopy and signal processing, which can also be adopted for the alignment of chromatographic signals [7]. The large number of existing alignment methods indicates that a perfect one does not exist. They differ with respect to their alignment flexibility, computational time and the number of input parameters.

In addition to alignment of one-dimensional signals, alignment of two-dimensional chromatographic signals such as the ones obtained from e.g. gas or liquid chromatography coupled with mass spectrometry (GC–MS or LC–MS) steadily gains attention. Recent examples of such techniques, presenting various issues related to alignment and comparative analysis of instrumental signals, are discussed in e.g. [5,11–17].

There is a great deal of interest in developing an automatic alignment approach that is able to correct linear and non-linear peak shifts quickly and is applicable in an on-the-fly manner with little or even no input parameters. In an attempt to meet this challenge, a general alignment framework is presented in this article and extended to an automatic approach that can withstand computational time requirements and offer users an independent selection of input parameters. In order to introduce the automatic alignment method (AA), firstly fundamental alignment concepts and approaches will be reviewed. Then, performance of the automatic alignment will be compared with the correlation optimized warping and illustrated on two sets of one–dimensional chromatographic signals.

2. Theory

Chromatograms are recorded as discrete signals at certain points of a time axis, $x(t_i)$, using a fixed sampling rate:

$$t_i = ih \tag{1}$$

where t is the time at a given sampling point, $i = 1, 2, \ldots, n$, n is the number of sampling points in a signal, and h is the sampling interval.

Alignment of chromatographic signals requires finding a suitable transformation of their time axis, the so-called alignment or warping function. The warping function is determined in order to optimize a certain objective function. It is achieved by aligning signals with a particular signal called a target. Several objective functions can be used, among which the Euclidean distance and the correlation coefficient, are the most common. In general, all alignment methods aim to approximate the warping function, though not explicitly in certain methods. For instance, in DTW or COW, a suitable alignment transformation is established by means of dynamic programming without assuming any parametric form of this function. In contrast, in the parametric time warping method (PTW) [18], the alignment function has an assumed form—a polynomial of a certain degree. The success of signal alignment is mostly dependent on the type of peak shifts observed (linear or non-linear) and a sufficient flexibility of the warping function. In chromatography, peak shifts are often of a non-linear type and thus their correction may require applying a highly non-linear warping function. Therefore, to achieve a satisfactory form of the alignment function it should have no constraints. Such an idea is pursued, for instance, in the semi-parametric time warping approach (STW) [19]. The shape of the warping function is approximated by a number of B-spline functions of a given degree [19]. The spline basis consists of several polynomial fragments which are joined at certain points of the time axis. Usually, the spline functions are distributed uniformly along the time axis, but if necessary a user defined arrangement can be considered. In Fig. 1, an exemplary B-spline basis of the third degree containing eight spline functions, is presented. The consecutive spline functions are placed uniformly along a discrete grid of 1000 sampling points. The smallest spline basis with the 3rd degree splines contains four splines.

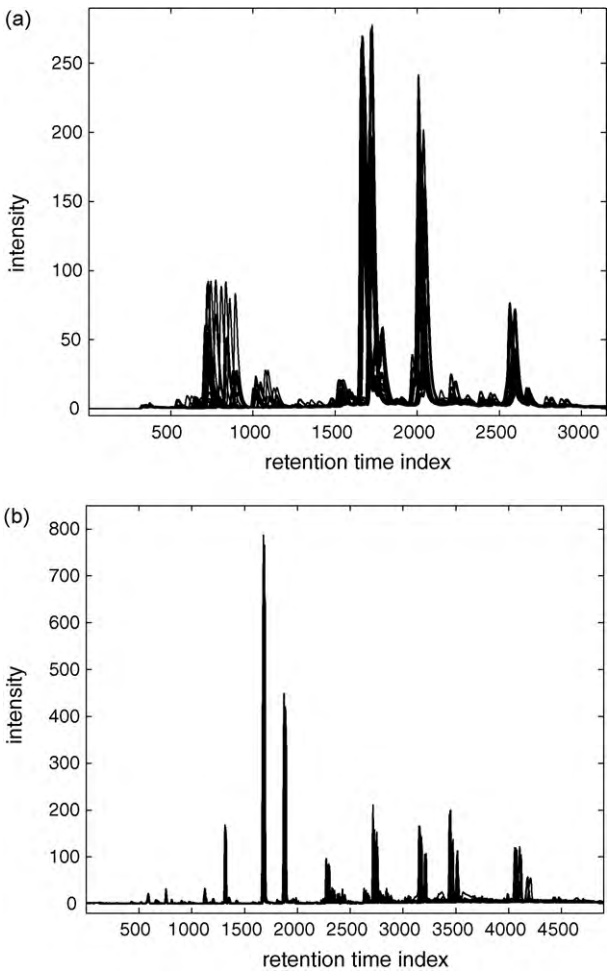

Fig. 1. (a) 30 chromatographic signals of data set 1 obtained from high-performance liquid chromatography of green tea extracts and (b) 16 gas chromatographic signals of data set 2.

In general, any function or signal, **x**, can be modeled using a linear combination of a sufficient number of spline functions, as the ones shown in Fig. 1. Bearing this in mind, the warping function, $w(t_i)$, can be estimated as follows:

$$w(t_i) = \sum_{j=1}^{k} a_j b_j(t_i) \tag{2}$$

where $j = 1, 2, \ldots, k$, k is the number of spline functions, a is a vector representing the spline coefficients, and b_j is the jth spline.

During an iterative procedure, the spline coefficients are modified, in order to minimize the cost function (in STW and PTW—sum of squared differences between a target signal, T, and the transformed signal, P).

2.1. Correlation optimized warping

A large number of articles provide evidence that correlation optimized warping is the most popular approach applied for signal alignment. It can help in aligning one- and two-dimensional signals without preliminary information about the correspondence of chromatographic peaks in signals. Alignment of two signals is achieved by means of piecewise linear stretching and compression of sections in a profile signal, so that the overall correlation coefficient between the profile signal and the target is maximized.

In COW, two input parameters control the quality of signal alignment. These are the number of segments (or the section length of a signal), N, and the slack parameter, s. At the initial step of the COW alignment, both, the target and profile are divided into a number of segments, each containing approximately the same number of sampling points. Then, during the alignment procedure, end points of the sections in a signal are allowed to change position by a specified number of points, s, the so-called slack parameter. For a given s value, the position of the end points can range from $-s$ to $+s$ including 0. This implies that the section being considered is shortened by s points ($-s$), its length is unchanged (0) or a section is extended by s points (+s). After modifying the positions of section endpoints, each section is linearly interpolated to the length of the corresponding section in the target signal.

Finding the optimal positions of section endpoints is achieved by applying the dynamic programming scheme and maximizing the sum of the correlation coefficients for warped sections for specified N and s values. This guarantees the optimality of the alignment solution for the given input parameters. An exhaustive description of the COW algorithm is provided in [9], whereas a fast implementation of the COW algorithm, programmed for a Matlab environment is available from [20].

2.2. General automatic alignment by a direct modeling of warping function

In our study, we concentrate on modeling the alignment function and propose a general framework for the automatic alignment (AA) of one-dimensional chromatographic signals. Like the STW approach, to ensure sufficient alignment flexibility of the method, no assumptions about shape of the warping function are made. It is approximated by a few B-spline functions (here, the third order splines generated uniformly along a discrete grid of sampling points as it is done in STW) the number of which is optimized. In most of our applications, the optimal number of spline functions, k, varied between 4 and 8, but anyway only a few were sufficient to obtain an acceptable alignment.

The alignment of a set of signals with the target signal can be boiled down to determining the coefficients of spline functions, a_j, which allows the warping function to be properly estimated, and thus ensures a good match between peaks in the target and aligned signal. Depending on the problem at hand, the overall quality of alignment can be judged using a few measures. Since complex samples may contain chemical components at different concentration levels, the Pearson's correlation coefficient seems to be a straightforward choice to evaluate quality of alignment. Thus, in the course of the optimization procedure, the correlation coefficient between the target and a profile is maximized.

The spline coefficients are determined using the *fminunc* optimization routine implemented in the Optimization Toolbox, version 3 and programmed in the Matlab environment (version 7.0.4.365 (R14) Service Pack 2). Depending on the input parameters passed to the *fminunc* routine, different optimization problems can be handled, including medium- and large-scale as well as those that are constrained and unconstrained. In our study, unconstrained medium-scale optimization via the quasi-Newton line search was used. A detailed description of the optimization algorithm can be found in [21]. The basic AA algorithm, including routines for generating B-splines functions and signals' interpolation (implemented in Matlab), is available from the corresponding author upon a request.

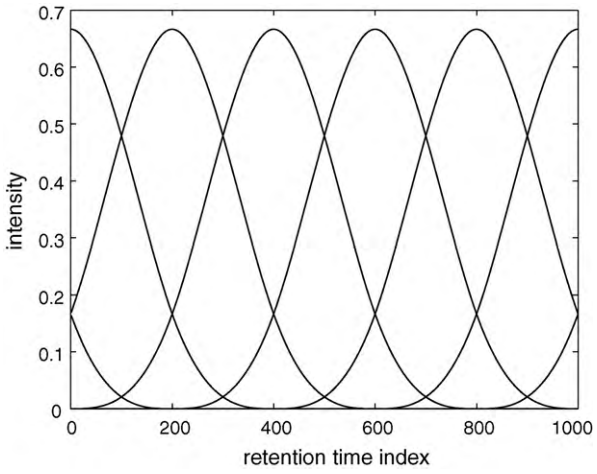

Fig. 2. B-spline basis containing 8 splines of the 3rd degree distributed uniformly over 1000 sampling points.

3. Data sets

To illustrate the performance of the AA approach, two data sets containing one-dimensional chromatographic signals were used. The collections of chromatographic signals differ to a great extent in the complexity of the retention shifts observed. Data set 1 represents very severe non-linear retention shifts due to different instrumental and experimental factors, while in data set 2 retention shifts were mainly caused by the column ageing.

Data set 1 consisted of 30 chromatographic fingerprints of green tea extracts (see Fig. 2a). The extracts were chromatographed using an HPLC system and mixture components were separated on a monolithic chromatographic column. A monolithic column allows high mobile phase flow rates during a chromatographic run, and thus it was possible to record chromatograms within ca. 2 min only. Each chromatographic signal consisted of 3151 sampling points. The chromatographic fingerprints reveal very complex non-linear peak shifts and thus pose a real alignment challenge. Experimental conditions were as in [22].

Data set 2 consisted of 16 gas chromatograms of a reference sample (see Fig. 2b). The chromatograms of the reference sample were registered over a period of time after routine analysis of a certain number of samples. Therefore, the column ageing effect contributed most to the observed retention shifts. The sample index is larger the later the analysis was carried on, and thus a more pronounced stationary phase degradation is observed. In our study, the original signals were first shrunk by removing uninformative regions at the beginning and at the end of the signals. In total, each signal contained 4901 sampling points.

4. Results and discussion

To date, many algorithms for the alignment of one-dimensional analytical signals have been proposed. In most studies, several criteria are frequently used for algorithms' comparison. They include a computational time analysis of an algorithm, the number of input parameters and the overall quality of the alignment achieved. In addition to the above-mentioned criteria, the possibility of the automatic alignment of signals should be considered.

4.1. Aspects of computational time

Due to the increasing computation power of computers and improvements introduced in algorithm implementations (e.g. vectorisation of algorithm code), most of the alignment algorithms available help to align signals within acceptable time limits. In many articles, this aspect is examined carefully because an alignment method should enable preprocessing of a large collection of signals. For instance, the current implementation of COW has been greatly speeded up by the increasing efficiency of the computation steps which are repeated many times: the interpolation step, computing the correlation coefficient and the batch processing of samples [23]. The PTW approach, when relatively simple retention shifts are considered, often requires less than one second to align signals containing ca. 3000 sampling points. Saving computational time compared to COW is possible because the warping function is modeled explicitly and its approximation requires only a few iterations of the algorithm.

When different alignment algorithms are compared, one can easily identify the fastest method. On the other hand, an alignment algorithm should be considered as computationally efficient if the alignment of two signals can be achieved in an on-the-fly manner, i.e. in the course of processing the next sample and registering its chromatogram. Such a requirement places a natural constraint on the processing time of any alignment method and it has to be shorter than the time required for recording a chromatogram. So how fast should an alignment method be?

In some studies, discussing different facets of alignment, monolithic chromatographic columns are used, e.g. in [19]. Their unique properties, compared to classic particle-based chromatographic columns, allow high flow rates to be applied, and thus separation of mixture components can be very rapid and may take even less than 2 min (see e.g. [22]). This can be considered as the maximal acceptable processing time.

In order to discuss the computational time of the AA method, let us compare the computational times of single and multiple alignment runs for two chromatograms using a different number of the B-spline functions. For illustrative purposes two chromatograms of data set 1, containing 3151 sampling points each, were used. The signals were aligned using a personal computer (Intel® Pentium®M 1.70 MHz processor, 2 Gb of RAM, Windows XP: Home Edition, service pack 3).

Generally, the computational time of AA is mostly influenced by the number of spline functions and the type of optimization applied (medium or large). However, the length of signals can also increase computational time because more spline functions may be required to obtain a satisfactory alignment. In Fig. 3, for a given number of spline functions, computational times of 30 alignment runs for obtained from unconstrained medium-scale optimization are presented as a box-plot. The number of the third order B-spline functions used to estimate the warping function was increased stepwise from 4 to 15.

From Fig. 3, it becomes apparent that computational time increases steadily with the number of spline functions, and a slight deviation from this trend is caused by fluctuations in processor workload necessary to maintain other running processes. In order to demonstrate the computational time demand of COW, implementation available from [20] was used. In general, comparison of AA with the COW approach favors the AA method as the faster one. In Fig. 4a, the computational times of the COW alignment, when different values for the input parameters were applied, are shown. The section length was chosen to contain between 30 and 100 points and extended by 10 points for each alignment step. The slack parameter was increased from 1 to 8 with a step size equal to 1. The computational time of COW depends mostly on the slack value. However, often, virtually the same align-

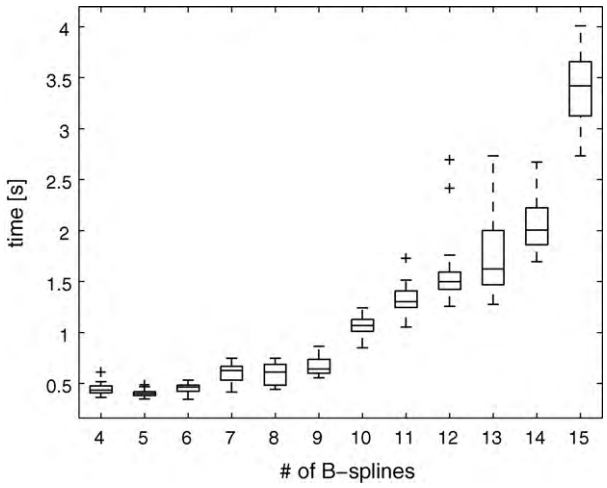

Fig. 3. Box-plots presenting 30 alignment runs of the automatic alignment approach using a given number of spline functions.

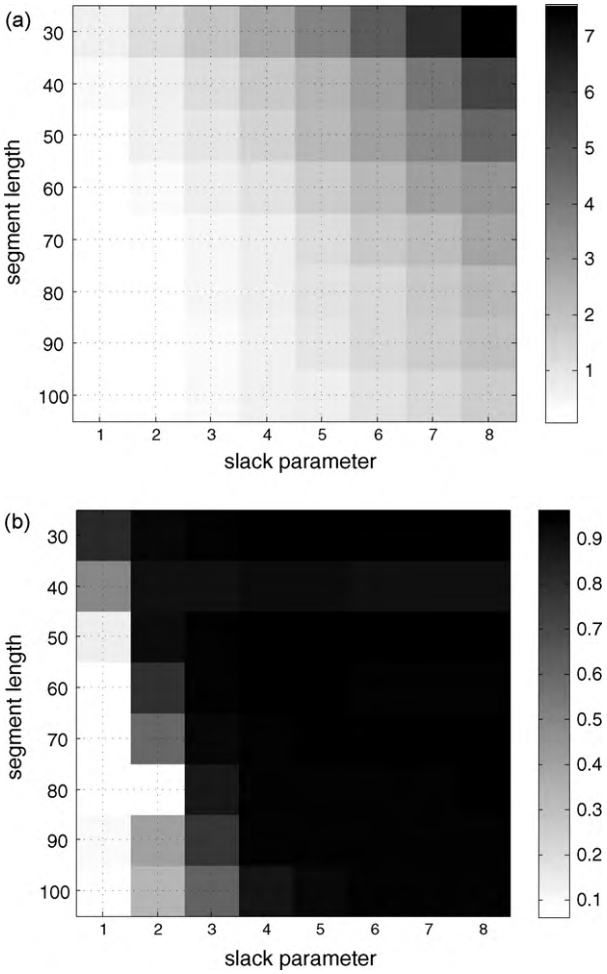

Fig. 4. Grayscale images presenting: (a) computational time(s) in seconds and (b) correlation coefficient between a target chromatogram (sample no. 22 from data set 1) and a profile (sample no. 1) obtained from correlation optimized warping using different values of the slack parameter (1, 2, . . ., 8) and the section length (30, 40, 50, 60, 70, 80, 90, and 100).

ment can be obtained for different pairs of input parameters (see Fig. 4b).

4.2. Developing the automatic alignment method

In order to achieve satisfactory and automatic alignment of chromatographic signals, two issues have to be addressed, namely maintaining a high flexibility of the warping function and selecting input parameters in an objective manner.

Correction of non-linear peak shifts requires a non-linear warping function to be applied. In the COW method, individual sections of a signal are warped and thus the overall warping function is not continuous. However, complex retention shifts can easily be processed when a sufficiently large slack parameter is used. In fact, a successful signal alignment using COW also requires dividing a signal into a sufficient number of sections.

Over the last few years we have witnessed a steadily increasing interest in developing an automatic method for the alignment of signals, i.e. limiting the number of input parameters and/or providing an objective framework for the selection of input parameters. In particular, some kind of optimization strategy in the alignment course has to be embedded in order to achieve this goal. For instance, recently an optimization procedure for the selection of COW parameters has been introduced [23]. It starts with a discrete-coordinates simplex optimization to define the most suitable range of alignment parameters, and then a further search is executed. The domain of two input parameters is sampled uniformly at discrete grid points arranged, as a default, into a 5×5 grid. However, the computational time required for identification of the optimal input parameters may exceed the satisfactory processing time limit and take more than 2 min.

Certainly, an exhaustive search for a suitable pair of input parameters is time consuming and impractical in real situations, especially when chromatograms are obtained rapidly. For a relatively narrow grid of input parameters (see Fig. 4) the total time of multiple alignments was about 110 s for a pair of signals with 3151 sampling points.

In AA, the alignment function is modeled explicitly. It is continuous and smooth, and can be approximated by several spline functions (however, it is also possible to consider other types of functions, e.g. radial basis functions, Gaussian functions, etc.). Compared to COW, only one input parameter requires selection, i.e. the number of spline functions. The order of spline functions can be set to two or three as a default, thereby offering sufficient modeling power of an alignment function. In our applications, the use of 4–8 spline functions often seems to provide a satisfactory result. In order to select a sufficient number of spline functions, the alignment result should be judged (e.g. maximizing the correlation coefficient).

In Fig. 5, correlation coefficients before and after the alignment of chromatograms from data set 1 (samples nos. 1 and 3) are presented. Each bar depicts the value of the correlation coefficient achieved when the alignment function was modeled with 5, 6, . . ., and 15 spline functions, respectively.

The larger the number of spline functions the more complex the retention shifts that can be handled. However, in case of one-dimensional chromatographic signals, an increase of the alignment flexibility can result in the misalignment of chromatographic peaks, although visual inspection of the aligned signals may be very appealing. Moreover, a large alignment flexibility can cause peak deformation too. Thus, in addition to maximizing the correlation coefficient between two chromatographic signals, peak shapes and their areas should also be preserved. To control these aspects of alignment, additional parameters can be introduced in the optimization framework and evaluated, for instance, the so-called warping effect, simplicity and the peak factor [23]. In AA, an

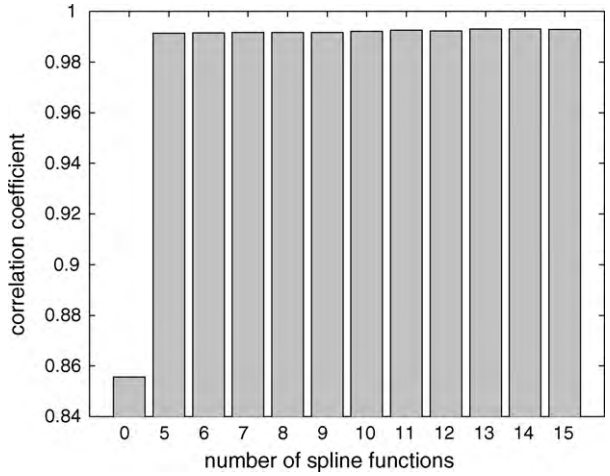

Fig. 5. Bar plot of correlation coefficients of two chromatograms from data set 1 (chromatogram no. 1—the target and chromatogram no. 3—a signal) obtained from the automatic alignment approach using 5, 6, . . ., and 15 B-spline functions; 0 spline functions = before alignment.

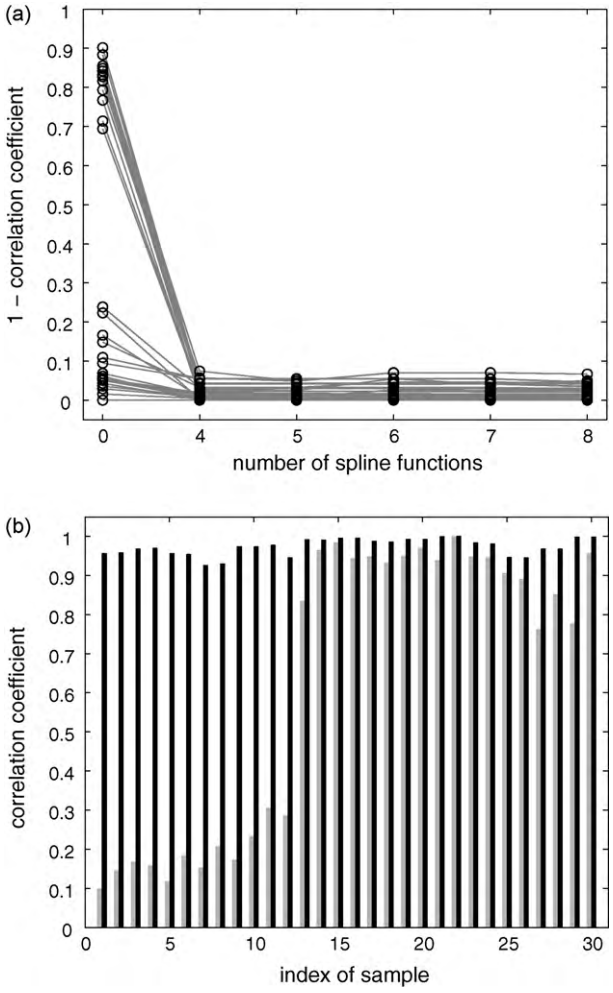

Fig. 6. Results obtained for the alignment of chromatograms of data set 1 (target chromatogram—sample no. 22) using the automatic alignment approach with different numbers of B-spline functions: (a) a scree-plot of the residual correlation coefficient (1—correlation coefficient) and (b) a bar plot of initial (gray) and final (black) correlation coefficients for the optimal number of B-spline functions.

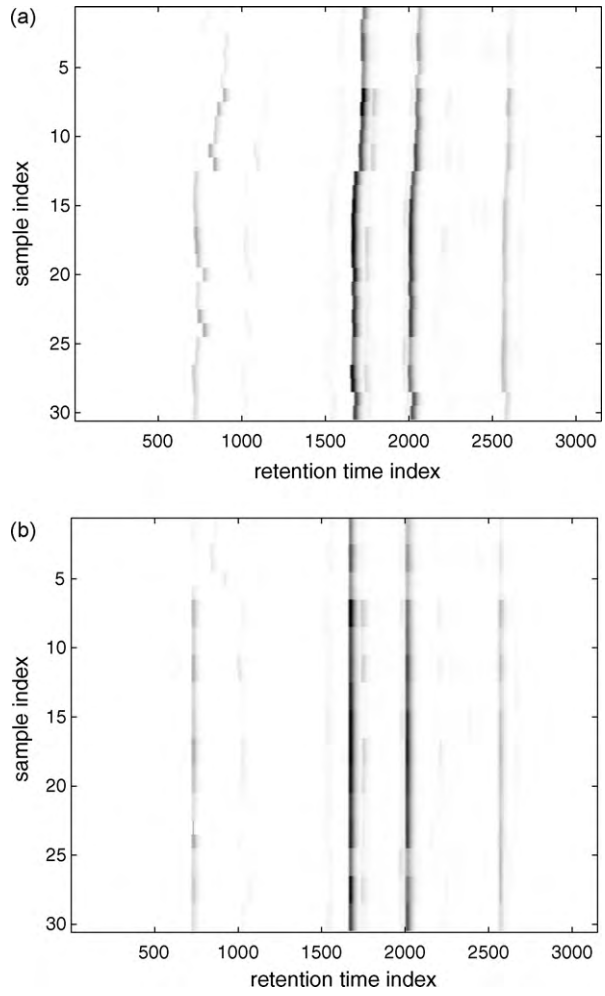

Fig. 7. A gray scale image of 30 chromatograms from data set 1: (a) before and (b) after alignment with the automatic alignment approach.

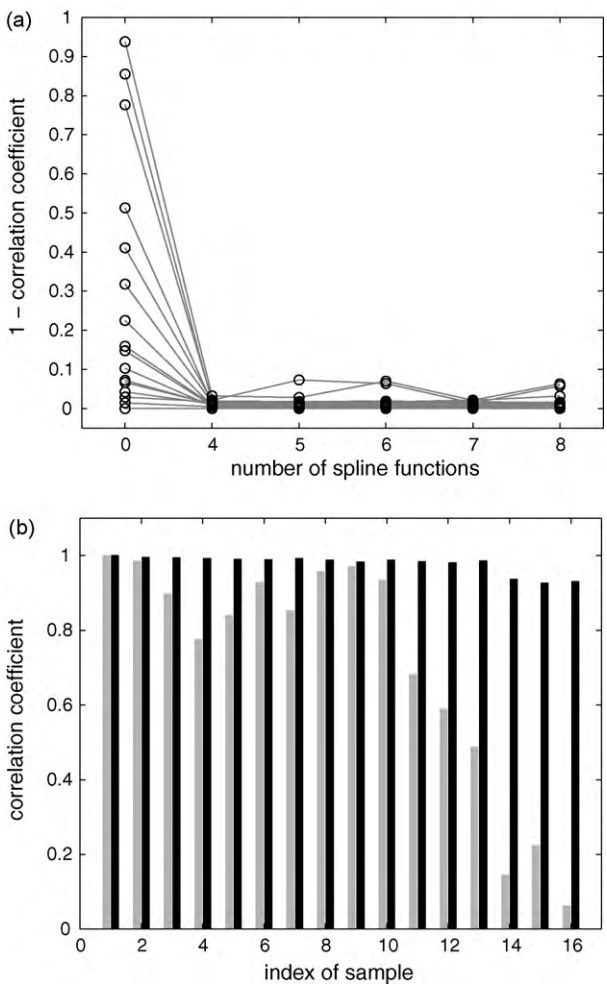

Fig. 8. Results obtained for the alignment of chromatograms of data set 2 (target chromatogram—sample no. 1) using the automatic alignment approach with different numbers of B-spline functions: (a) a scree-plot of the correlation coefficients and (b) a bar plot of initial (gray) and final (black) correlation coefficient for the optimal number of B-spline functions.

optimization procedure is used, allowing for the easy implementation of different objective functions, e.g. correlation coefficient, sum of squared differences between target and profile, etc. It is also possible to take into account the above-mentioned additional parameters.

As shown in Fig. 3, a relatively simple strategy for the selection of the number of spline functions has little impact on the overall increase in computational time. Therefore, the alignment can still be performed in an on-the-fly manner even for chromatograms recorded in less than 2 min.

4.3. Alignment of chromatographic fingerprints by AA

In this section, the application of the AA approach to two sets of chromatograms will be demonstrated.

First, 30 chromatograms of data set 1 were aligned using the AA method. In order to minimize the risk of improper alignment caused by the selection of non-representative signals, the correlation approach was used [24]. Chromatogram no. 22 was selected as the target signal, since it has the largest average correlation coefficient with respect to all chromatograms in the data set. The number of spline functions, considered to model the warping function, was varied from 4 to 8. The alignment of the 30 signals took about 79 s and for each signal 5 independent alignments were performed. It can be concluded from Fig. 6a that for fingerprints of data set 1 a relatively small number of spline functions is sufficient to model the warping function, and thus to substantially improve the correlation coefficient between the target signal and the aligned fingerprints. For a majority of signals, four splines allowed a satisfactory alignment (correlation coefficients after alignment above 0.9) and using more splines does not substantially improve correlation coefficients.

In Fig. 6b the initial (gray bar) and the final correlation coefficients (black bar) are presented for each chromatogram. For samples 1–12, the alignment was the most beneficial (see Fig. 6b), since the largest gain in correlation coefficient between target and aligned signals have been achieved. The values close to one indicate hardly any improvement after the alignment.

The gray scale image of the signals before (Fig. 7a) and after alignment (Fig. 7b) using AA with the optimal number spline functions indicates a relatively good signals' alignment, also confirmed by relatively high correlation coefficients (all above 0.92).

The alignment of 16 chromatograms from data set 2 took nearly 83 s (i.e. about one second per alignment run). Sample no. 1 has been selected as a target signal because its chromatogram has been registered at the very beginning of column usage, and thus under the most favorable conditions [18]. Like before, the number of spline functions was optimized and selected from the interval between 4 and 8. Once more, it was found that with as few as four spline functions a satisfactory alignment was achieved (see Fig. 8a). As indicated in Fig. 8b, the final correlation coefficient was higher

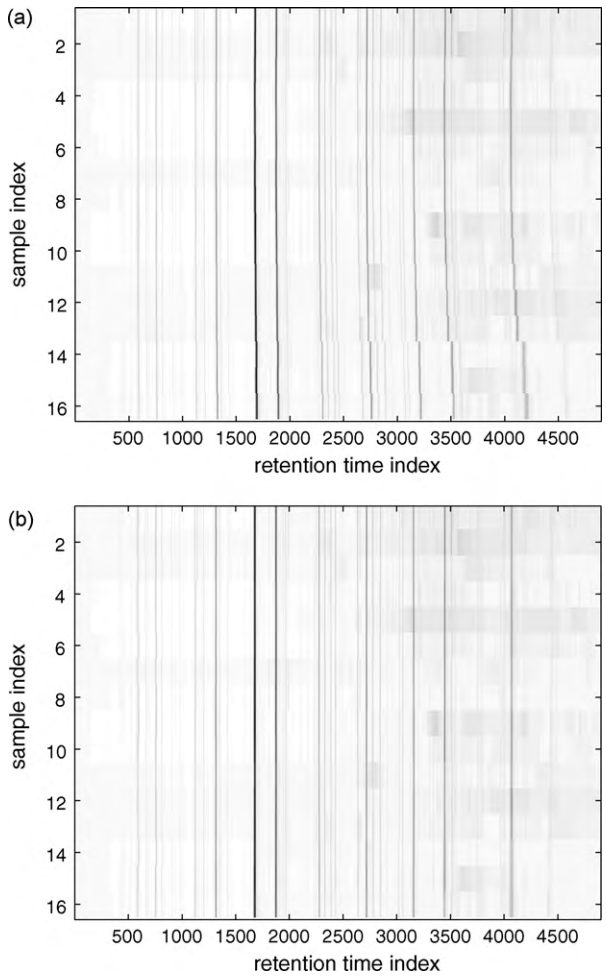

Fig. 9. A gray scale image of 16 gas chromatograms from data set 2: (a) before and (b) after alignment using the automatic alignment approach (to increase image contrast, chromatograms were transformed with the square root transform).

than 0.92 for all of the signals. The largest improvement in terms of the correlation coefficient was observed for chromatogram no. 16 (see Fig. 8b).

It is interesting to note that this chromatogram was registered after a long column usage, and thus retention shifts for this signal seem to be the most pronounced with respect to sample no. 1 (see Fig. 9).

4.4. Automatic alignment approach vs. correlation optimized warping

Both sets of signals were also aligned using the COW approach. It should be emphasized that for all of the signals the correlation coefficients between corresponding target signals and aligned signals were above 0.92. For some of chromatograms, compared to AA result, slightly higher correlation coefficients were obtained. On the other hand, COW requires optimization of two input parameters for each signal. In this study, the computational time (including selection of optimal input parameters) greatly exceeded 2 min per chromatogram. Therefore, bearing in mind on-the-fly alignment requirement, the AA approach outperformed COW.

5. Conclusions

In this article a general alignment approach was presented and adopted to support the automatic alignment of one-dimensional chromatographic signals. Using experimental chromatographic data, it was proven that the AA method is a fast alternative to popular alignment approaches. Moreover, AA can handle different types of peaks shifts, including linear and non-linear ones. The approximation of an alignment function requires the selection of a sufficient number of spline functions. However, this can be achieved by means of a simple evaluation without a substantial increase in computational time. It is important to emphasize that an increase in the flexibility of alignment can be a source of undesired peak shape changes and/or peak misalignment. Therefore, the warping function should be estimated with the smallest possible number of spline functions, but offering a satisfactory gain in terms of the correlation coefficient. The AA approach can be used in on-line settings, especially for alignment of chromatograms obtained using a fast chromatographic approach where separations are carried out on monolithic columns.

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