



Vibrational spectroscopic methods for the overall quality analysis of washing powders



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ABSTRACT

The aim of this study was to compare and evaluate the ability of near infrared- (NIR), Raman- and attenuated-total-reflection infrared (ATR-IR) spectroscopy as tools for the identification of washing powder brands as well as for an overall quantitative analysis of all ingredients of the analyzed laundry detergents. The laundry detergents used in this work were composed of 22 different ingredients.

For this purpose, principal component analysis (PCA) cluster models and partial least-squares (PLS) regression models were developed and different data pre-processing algorithms such as standard-normal-variate (SNV), multiplicative scatter correction (MSC), first derivative BCAP (db1), second derivative smoothing (ds2), smoothing Savitzky Golay 9 points (sg9) as well as different normalization procedures such as normalization between 0 and 1 (n01), normalization unit length (nle) or normalization by closure (ncl) were applied to reduce the influence of systematic disturbances. The performance of the methods was evaluated by comparison of the number of principal components (PCs), regression coefficient (r), Bias, Standard error of prediction (SEP), ratio performance deviation (RPD) and range error ratio (RER) for each calibration model. For each of the 22 ingredients separate calibration models were developed. Raman spectroscopy was suitable for the analysis of only two ingredients (dye transfer inhibitor 1 and surfactant 6) and it was not possible to record all Raman spectra due to high fluorescence.

NIR and ATR-IR are powerful methods to analyze washing detergents with low numbers of PCs being necessary, regression coefficients of only little below 1, small Biases and SEPs compared to the range and high RPDs and RERs

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1. Introduction

Washing powders play an important role in everybody's life with an average yearly consumption of 7.6 kg per capita in Germany 2001. Even if the use of washing powders decreased in the early 1990s due to an increase in the quality of washing powders and its ingredients – especially of the enzymes – it remained on a constant level since 1995. These numbers show that only in Germany more than 600,000 tons of washing powders are bought, deployed and disposed into the domestic drainage system every year [1]. Due to this enormous market volume and the competition on the market, manufacturers as well as purchasing agents require fast, selective, sensitive and economical analytical techniques for quality control during and after the production process as well as for the control of incoming goods. Modern washing powders consist of 20 or more different ingredients, which can be

categorized in different groups such as builders, bleaching agents, surfactants anti-redispersion agents or enzymes. There are even reports of counterfeit washing powders which were found on the market, especially in China [2]. This is not only a financial drawback for consumers but can also be a potential risk to human health as well as for the environment.

Established methods for the qualitative and quantitative analysis of washing powders are high performance liquid chromatography (HPLC), capillary electrophoresis (CE), gas chromatography (GC), mass spectrometry (MS) and various wet chemical methods [3]. However, these methods are time-consuming, require specially trained personal as well as they cause high costs for acquisition and operation.

Vibrational spectroscopic methods such as near-infrared (NIR) spectroscopy, attenuated total reflection infrared (ATR-IR) spectroscopy and Raman spectroscopy have been proven to be fast, sensitive and non-invasive methods for the analysis of physical as well as chemical parameters in quality control [4–9]. This is especially true when the above mentioned methods are combined

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with multivariate data analysis (MVA).

The process analytical technology (PAT) initiative launched by the US-American food and drug administration (FDA), according to which a pharmaceutical product should be monitored throughout the whole production process, pushed the development of vibrational spectroscopic methods in general and NIR spectroscopy in special [10].

There are numerous works, which show the deployment of NIR-spectroscopy, MIR-spectroscopy and Raman-spectroscopy for the qualitative and quantitative analysis on powdered samples. These methods are even capable to determine physical parameters of powders such as polymorphic forms and particle size [4,5,11–14].

Khanmohammadi et al. carried out several works using fourier-transform mid-infrared (FT-MIR) spectroscopy to analyze washing powder detergent. A FT-MIR-spectroscopy based methods for the determination of sodium percarbonate in washing powders was deployed [15]. The same technique was proven to be suitable for the simultaneous determination of sodium tripolyphosphate (STPP), sodium sulfate (SS) and linear alkylbenzenesulfonate in washing powder [16]. In a different work, they applied the Doolittle Algorithm as a multivariate calibration method to quantify STPP, SS and sodium carbonate (SC) [17]. For the determination of SS, SC and STPP a FT-MIR spectroscopic method in combination with genetic algorithm (GA) wavelength selection followed by feed forward back-propagation artificial neural networks (BP-ANN) was developed [18]. Azghandi et al. introduced LU multivariate calibration algorithm (LUMCA) to determine STPP, SS and SC in commercial washing powders deploying FT-MIR spectroscopy [19]. Khanmohammadi et al. also presented QR decomposition algorithm (QRDA) initially into the chemistry field to investigate and differentiate STPP, SS and SC [20].

Heigl et al. developed a NIR-spectroscopic method to determine silicon, phosphorus, carbonate and tenside content in washing powders [6]. Zhang et al. classified washing powder brands using NIR-spectroscopy combined with the chemometric methods partial least square discriminant analysis (PLS-DA), BP-ANN and least square support vector machine (LS-SVM) [2].

So far there is no contribution comparing the performance of different infrared and also Raman spectroscopic attempts for the overall classification and quality control of washing powders.

Therefore, in this work, vibrational spectroscopic methods (ATR-IR spectroscopy, NIR spectroscopy and Raman spectroscopy) in combination with MVA were deployed in two steps: as a first step, multivariate models to distinguish different washing powder mixtures were developed. This is of importance for quality control and to observe competitors' products on possible changes. Further, in a second step, vibrational spectroscopic methods in combination with PLS regression models were developed and evaluated for the quantitative analysis of the total composition of washing powders.

The novel established spectroscopic method described in the present work allows for the first time the overall classification and quality control using a time-saving and non-invasive spectroscopic methodology.

2. Material and methods

2.1. Samples

For the construction of a method to identify different washing powders, 59 samples (all-purpose detergents and color detergents) of seven different brands were purchased throughout Scandinavia on different dates. The samples of the same brand differed in their production codes to ensure that they do not

descend from the same production batch.

For the quantification of ingredients 54 samples of known composition were analyzed. A total of 22 ingredients were used for the preparation of the samples. The ingredients are one anti-re-deposition agent, two different bleaches, six different builders, one dye transfer inhibitor, two different enzymes, one filler, one perfume and eight different surfactants.

2.2. Sample preparation

The samples were milled with a Retsch centrifugal mill (Retsch, Haan, Germany) to a particle size of 0.5 μm prior to ATR-IR and Raman measurements. For the NIR measurements, no sample preparation was conducted.

2.3. ATR-IR spectroscopy

ATR-IR spectra were recorded using a PerkinElmer Spectrum 100 ATR-IR spectrometer with the Spectrum software version 6.3.1 (PerkinElmer, Waltham, USA). A horizontal attenuated total reflection unit (HATR) was used, where the upper side of the ATR Germanium crystal is exposed to the sample and the background was collected from the clean ATR crystal. The spectrometer is equipped with a deuterated triglycine sulfate (DTGS) detector. Wavenumbers ranged from 4000 cm^{-1} to 650 cm^{-1} with a spectral resolution of 1 cm^{-1} . The milled samples were divided into 5 subsamples and 20 scans per subsamples were collected to eliminate the effect of sample inhomogeneity. All spectra were recorded at 22 °C. The spectra are depicted in Fig. 1.

2.4. NIR spectroscopy

A Bruker Multi Purpose Analyzer (MPA) (Ettlingen, Germany) equipped with a rotating sample cup was used in combination with the OPUS software package (Bruker Optics, Billerica, USA) to record the NIR spectra. The spectrometer is equipped with a Si-diode Detector. Wavenumbers were ranging from 3.599 cm^{-1} to 12.493 cm^{-1} . Spectral resolution was at 8 cm^{-1} and one spectrum was created as an average of 32 single spectra. All measurements were performed at 22 °C. The background was recorded using a Spectralon reflector. No sample preparation was necessary. This was due to the fact that the milled samples showed no advantages and no influence from differences in particle size over the non-milled samples on the NIR spectra, respectively. The original spectra are depicted in Fig. 1.

2.5. Raman spectroscopy

For spectra collection, a PerkinElmer Raman Station 400 (PerkinElmer, Waltham, USA) was deployed. The spectrometer has a Calcium Fluoride beam splitter and a 785 nm laser as a source and is equipped with a CCD detector.

As fluorescence could be observed in a number of samples prior to the final Raman analysis, all samples were tested for fluorescence after photobleaching resulting in the elimination of around 40% of all samples. Five subsamples per sample were analyzed in super-macro-mode (seven-point-mode) with two scans and an integration time of five seconds per point. In super-macro-mode seven points arranged as six points around one point analyze a larger sample spot resulting in a spectrum which represents the large spot. This mode was chosen to eliminate the problem of getting spectra representing only a few powder particles instead of the whole sample. In addition to this, spectra were recorded several times to eliminate the effect of sample inhomogeneity. Wavenumbers ranged from 3.200 cm^{-1} to 100 cm^{-1} with a spectral resolution of 2 cm^{-1} . Prior to each measurement the samples

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