ATR-FTIR spectroscopy for the determination of Na$_4$EDTA in detergent aqueous solutions

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A B S T R A C T

Fourier transform infrared spectroscopy in the attenuated total reflectance mode (ATR-FTIR) combined with partial last square (PLS) algorithms was used to design calibration and prediction models for a wide range of tetrasodium ethylenediaminetetraacetate (Na$_4$EDTA) concentrations (0.1 to 28% w/w) in aqueous solutions. The spectra obtained using air and water as a background medium were tested for the best fit. The PLS models designed afforded a sufficient level of precision and accuracy to allow even very small amounts of Na$_4$EDTA to be determined. A root mean square error of nearly 0.37 for the validation set was obtained. Over a concentration range below 5% w/w, the values estimated from a combination of ATR-FTIR spectroscopy and a PLS algorithm model were similar to those obtained from an HPLC analysis of NaFeEDTA complexes and subsequent detection by UV absorbance. However, the lowest detection limit for Na$_4$EDTA concentrations afforded by this spectroscopic/chemometric method was 0.3% w/w. The PLS model was successfully used as a rapid and simple method to quantify Na$_4$EDTA in aqueous solutions of industrial detergents as an alternative to HPLC-UV analysis which involves time-consuming dilution and complexation processes.

1. Introduction

Aminopolycarboxylates (APCs) are used as chelating agents (also called complexing or sequestrating agents) in household and industrial cleaners and detergents. Due to their multidentate structure, they have the ability to form stable complexes with alkaline-earth and heavy metal ions in salts which prevents their precipitation in aqueous solutions. Commonly used APCs are ethylenediaminetetraacetic acid (H$_4$EDTA), nitrilotriacetic acid (NTA), diethylenetriaminepentaacetic acid (DTPA) and propylenediaminetetraacetic acid (PDTA) and sodium salts. Of these, tetrasodium ethylenediaminetetraacetate (Na$_4$EDTA) is a stable and powerful synthetic chelator used to prevent sedimentation and deposits on the surfaces of containers, pipes and nozzles in several branches of industry [1–7]. The concentration of Na$_4$EDTA in aqueous detergent formulations varies over a wide range, reaching values of up to nearly 40% w/w [8,9]. Depending on the type of industry, the soil to be removed and the surface to be cleaned, the cleaning aqueous solution can be tailored using a dilution factor, that involves concentrations of chelating agent below 5% w/w. After use, some chelating species with slow biologically degradation are discharged into the aquatic environment, affecting the distribution of metals within aquatic ecosystems and remobilizing heavy metals from sediments [3].

For specific cleaning applications, process monitoring and the quality control of detergent formulations, a simple, rapid, reproducible, environmentally friendly and low-cost method is required to determine the concentration of Na$_4$EDTA or other APCs in aqueous solutions over a broad concentration range. Several instrumental analytical techniques have been applied for determining the concentrations of EDTA and its salts in aqueous systems. In-depth descriptions of the advantages and weaknesses of applying various techniques in the field of detergents [5,10–13] and natural and processing waste waters [14–26] have been reported. Among the chromatographic methods those based on high performance liquid chromatography with UV detection (HPLC-UV), in conjunction with sample derivatization and the formation of Fe (III) complexes before analysis, have been successfully developed and applied by several authors [5,18,22,23,27–29] in order to determine the concentration of ethylenediaminetetraacetic acid (H$_4$EDTA) and metal ethylenediaminetetraacetate salts in municipal wastewaters, surface and drinking waters. The concentrations of H$_4$EDTA and its metal complexes in aqueous environmental samples are much lower than in industrial detergents. Indeed, in industrial wastewater effluents it can reach the level of mg l^{-1} whereas in drinking and surface waters the concentrations are commonly as low as µg l^{-1} [4]. For this reason, aqueous environmental samples always require a

pre-concentration step before derivatization [21,23–25]. However, in industrial detergents the levels of metal-EDTA complexes such as Na_4EDTA are usually at the g l^{-1} level and therefore the samples studied require the opposite process, i.e. dilution of the sample before derivatization.

Attenuated total reflectance coupled to Fourier transform infrared spectroscopy (ATR-FTIR) is appropriate for use with a large variety of samples. This technique can be implemented simply on an analytical routine basis. It is a versatile non-destructive analytical tool for qualitative and quantitative analysis that requires only a small quantity of sample without any pre-treatment. However, quantitative analysis is limited when there is some degree of overlapping between the selected absorption bands and those caused by the presence of other constituents. A further complication arises when water is the main component of the detergent ($>80\%$) because its strong IR absorption band obscures the functional group bands of the detergent ingredients [5]. Nevertheless, the strengths of ATR-FTIR can be reinforced and its weaknesses overcome by combining it with chemometric algorithms such as partial least squares (PLS). Such a combination provides an optimal statistical and mathematical approach for correlating spectral information with the concentration of a specific component in a complex mixture. This method of evaluation is extremely useful in the specific cases of overlapping, molecular interactions between components or non-proportional increase in absorbance with concentration [11–13,30–33].

The aim of this work is to develop a calibration model based on ATR-FTIR spectroscopy in combination with PLS analysis in order to determine the amount of Na_4EDTA in aqueous solutions of industrial detergents over a wide concentration interval ranging from 0.1 to 28% w/w. The most outstanding spectral feature of Na_4EDTA is an absorption band at 1575 cm^{-1}, which is attributed to its carboxylate groups, overlapping the band assigned to the OH bending vibration of water (1635 cm^{-1}). Depending on its concentration when air is used as a background medium, the shape of the absorption band appears as an overlapping band, a shoulder or as an unidentified contribution to the tail of the water band. Such interferences, however, can be minimized by using water as a background medium to suppress the water band. This spectral acquisition procedure is useful only for high concentrations of Na_4EDTA or other APCs. In the case of low concentrations, measurement of the area or the height of the carboxylate band suffers from a low signal-to-noise ratio, which makes it difficult to situate the region boundaries and to establish the baseline points in a noisy spectrum. PLS algorithms are then a highly effective tool for overcoming spectral-processing difficulties and for compensating for the detection limitations of Na_4EDTA quantification in detergents and their diluted solutions. In the present study, HPLC-UV in combination with dilution and sample derivatization is used as a complementary technique, special attention being paid to Na_4EDTA concentrations below 5% w/w.

2. Experimental

2.1. Reagents and sample preparation

Ethylenediaminetetraacetic acid tetrasodium salt (Na_4EDTA) was purchased from Sigma Aldrich (purity, 98%). Sixty six aqueous solutions of Na_4EDTA were prepared so as to cover a wide concentration range from 0.1 to 28% w/w. The samples were split into two groups for analysis by ATR-FTIR spectroscopy. The first group consisted of 46 standard solutions, 21 of which were used to construct the calibration model and the remaining 25 being used for validation. The latter solutions were prepared in different days in order to assess repeatability and reproducibility. The second validation group consisted of 20 aqueous solutions prepared in

concentrations of g l^{-1} and the density of each solution was measured using a portable density meter (DMA 35N, Anton Paar) in order that the concentrations could be expressed in both g l^{-1} and % w/w. From this set of samples, 13 solutions with a Na_4EDTA concentration lower than 40 g l^{-1} (3.93% w/w) were selected for analysis by HPLC. The two groups of samples were prepared over different periods of time to obtain information about the accuracy of the PLS calibration method.

To evaluate the precision, accuracy, matrix effects and quantification limit of the procedure, several aqueous solutions of a commercial liquid detergent containing Na_4EDTA in unknown concentrations were selected for analysis by ATR-FTIR and HPLC-UV.

2.2. ATR-FTIR spectroscopy and multivariate PLS algorithms

ATR-FTIR spectra of the aqueous solutions were obtained by using a Nicolet IR 8700 spectrometer equipped with a KBr beamsplitter, a deuterated triglycine sulfate (DTGS) detector and a diamond ATR crystal with a 45° incidence angle and one single bounce. Spectra were acquired between 4000 and 525 cm^{-1}, in duplicate, by applying an average of 64 scans at a nominal resolution of 4 cm^{-1}. A background spectrum was collected by using air or water before scanning each sample. The background also served as a way to check the cleanness of the crystal and to ensure that no residue from the previous sample remained on the surface. Omnic software was used to obtain the spectra and TQ Analyst software to build the partial least squares (PLS) model. Two PLS calibration models were developed. The first model was restricted to the spectral region between 1604 and 1365 cm^{-1}, —where the two carboxylate stretching vibrations of Na_4EDTA occurred—, and the second one to the area between 1604 and 1465 cm^{-1} where the most prominent carboxylate stretching vibration appeared. The best fit was obtained by selecting the band area between 1604 and 1465 cm^{-1} and a two-point baseline correction type. TQ Analyst software required the input of the spectra, a constant pathlength and the targeted Na_4EDTA concentrations. The leave-one-out cross-validation diagnostic tool was applied to verify the calibration model. Root mean square error of calibration, cross-validation and validation or prediction (RMSEC, RMSECV and RMSEP, respectively) and the correlation coefficients (r) between the predicted and real values were used as indicators of the validity of the model developed. A good model should yield low and very similar RMSEC and RMSEP values and a r value close to unity.

2.3. HPLC analysis and sample preparation

Thirteen standard Na_4EDTA solutions were analyzed by means of a Hewlett Packard 1100 series system provided with a reversed-phase column (Pursuit XRs C18, 150×4.6 mm, 5 μm particle size, Varian, USA) which was protected by a security guard column (Dionex, acclaim surfactant, 4.6×10 mm, 5 μm). The mobile phase consisted of a mixture of methanol and an ion-pair reagent solution (2:98 v/v). The flow rate was 0.9 ml min^{-1} under isocratic conditions, in accordance with the method described by Xie et al. [22]. The entire system was maintained at room temperature. The volume of every sample injected was 50 μl. Before HPLC analysis a stock Na_4EDTA standard solution (0.1 g l^{-1} equivalent to 0.01% w/w) was subjected to a pre-treatment consisting of: (1) its dilution to 4, 8, 12, 16 and 20 mg l^{-1} for calibration; and (2) derivatization of the five solutions to form a NaFeEDTA complex, $FeCl_3$ (0.05 mg ml^{-1}) being added in a proportion of 1:1 v/v. Preliminary experiments were carried out to select the appropriate quantity of Fe^{3+} solution to ensure that all the salt was transformed in the NaFeEDTA complex [22,29]. A UV detector was used at 254 nm to obtain the maximum possible absorption spectrum of the photosensitive NaFeEDTA complex. It is generally