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ATR-FTIR spectroscopy for the determination of Na_4EDTA in detergent aqueous solutions

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ABSTRACT

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_4EDTA) 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_4EDTA 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_4EDTA 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_4EDTA 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_4EDTA), nitrilotriacetic acid (NTA), diethylenetriaminepentaacetic acid (DTPA) and propylenediaminetetraacetic acid (PDTA) and sodium salts. Of these, tetrasodium ethylenediaminetetraacetate (Na_4EDTA) 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_4EDTA 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_4EDTA 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_4EDTA) and metal ethylenediaminetetraacetate salts in municipal wastewaters, surface and drinking waters. The concentrations of H_4EDTA 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 $\mu g\,l^{-1}$ [4]. For this reason, aqueous environmental samples always require a

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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 accepted that chelation with Fe^{3+} has the advantage of keeping interference from other metal ions to a minimum due to the high constant stability of the complex in water [18,22]. All the samples were filtered through a 0.45 μm nylon filter and stored in the dark at 4 °C, for at least 12 h before analysis. The quantification of Na_4EDTA was centred on the area of the unique chromatographic peak for an elution time of 6.54 min. For validation, the Na_4EDTA solutions in quantities of 0.15, 0.3, 0.6, 0.9, 1.3, 1.7, 2.5 and 4.0% w/w and the commercial detergent suitably diluted were subjected to the same pre-treatment protocol (dilution to 15 mg l^{-1} and complexation).

3. Results and discussion

3.1. *ATR-FTIR spectroscopy combined with PLS algorithm modeling*

Fig. 1 presents the mid-range ATR-FTIR spectra of Na_4EDTA in powder form and its aqueous solution at a concentration of 12% w/w as well as pure water. The spectrum of the pure Na_4EDTA is characterized by an intense absorption band centered at around 1575 cm^{-1} which is attributed to the asymmetric stretching vibration of carbonyl in the four ionic carboxylate groups (ν_{as} COO^-). The corresponding symmetric stretching vibration occurs close to 1405 cm^{-1} (ν_s COO^-), which is a less intense absorption band than the one at 1575 cm^{-1} [34–36].

To quantify the Na_4EDTA in aqueous solutions over a concentration range from 0.1 to 28% w/w, two protocols were followed to obtain the spectra: (1) the use of air as a background medium; and (2) the use of 50 μl of pure water on a diamond ATR-crystal as a background medium (spectra c and b, respectively). Both protocols present drawbacks from the point of view of the quantitative analysis of carboxylate groups. An inspection of the spectra shows that with the first method it is not possible to measure the area/height of the band at 1575 cm^{-1} due to its strong overlapping with the OH bending vibration of the water molecules at 1635 cm^{-1} (spectra c and d, Fig. 1; Fig. 2). Added to this are the problems of the decreasing intensity of the band at 1405 cm^1 (ν_s COO^-) and the non-detectable bands at relatively low concentrations (Fig. 2). Besides the problems just mentioned, the water bands dominate every spectrum. The second approach provides spectra of Na_4EDTA in aqueous solutions that are virtually unaffected by the water band (spectrum b, Fig. 1). However, removing the water increases spectral noise and prevents quantitative analysis, since the band contours and baseline are distorted or unrecognizable at the low concentrations. In neither of the cases can the classical band area or height measurement necessary for quantification be applied over the whole concentration range. However, by calibrating the PLS algorithm, it is possible to examine a specific region or regions of the calibration spectra of a compound and determine the areas or spectral regions which vary statistically as a function of the concentration of components, even when differences are not visually apparent in the spectra or the bands of two components overlap excessively (Fig. 2).

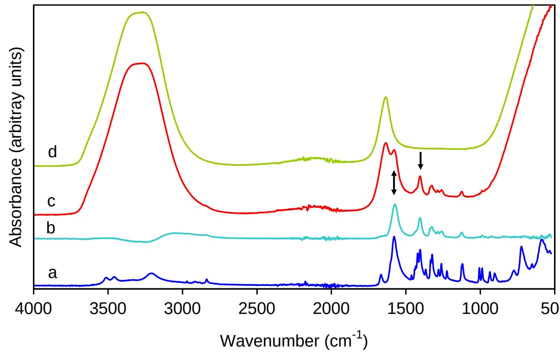

Fig. 1. ATR-FTIR spectra of (a) Na_4EDTA in powder form, (b) Na_4EDTA in aqueous solution at 12% w/w using a water background, (c) Na_4EDTA in aqueous solution at 12% w/w using an air background, (d) purified water.

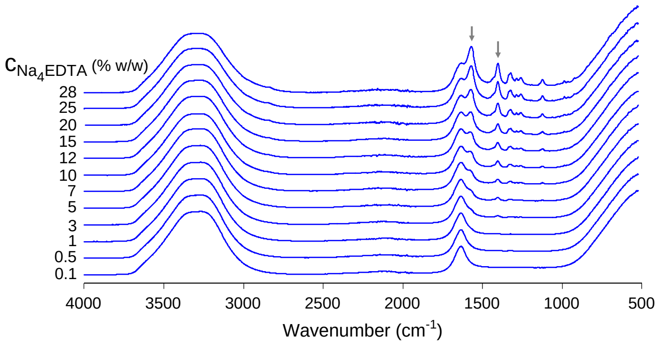

Fig. 2. ATR-FTIR spectra of several Na_4EDTA aqueous solutions in a concentration range between 0.1 and 28% w/w.

Table 1
Calibration and validation parameters for the PLS methods.

	PLS_w	PLS_a	PLS_{a5}
Two-point baseline	1741–1467	1822–1465	1822–1465
Spectrum range	1635–1467	1604–1465	1604–1465
Concentration range (% w/w)	0.1–28	0.1–28	0.1–5
Calibration samples	12	21	14
Validation samples	8	45	35
Validation spectra	16	94	66
RMSEC	0.29	0.30	0.08
Calibration coefficient correlation	0.9993	0.9991	0.9984
RMSEP	0.23	0.28	0.13
Prediction coefficient correlation	0.9997	0.9995	0.9917
RMSCV	0.37	0.37	0.09
Cross-validation coefficient correlation	0.9989	0.9987	0.9982
Slope	0.9989	1.0040	1.0038
Factors used in PLS	1	1	1

PLS: Partial least square model using air (a) or water (w) as a background over the whole concentration range or in the 0.1–5% w/w range (a5); RMSE: Root mean square error for calibration (RMSEC), validation (RMSEP) and cross-validation (RMSECV).

It is important to remark that in the range of concentrations used in this study, the pH values of all solutions were between 11 and 12.5, where Na_4EDTA presents a dissociated form. The band area at 1575 cm^{-1} is unaffected by these small variations in the assayed pH range, according with data previously reported on the quantification of carboxylate groups in NTA solutions in the same pH range [12].

Two PLS models were constructed on the basis of spectra in air or water as a background medium (PLS_a and PLS_w, respectively). A summary of the calibration and validation results is presented in Table 1. Relatively low root mean square errors of calibration and cross-validation (RMSEC and RMSECV, respectively) and a high correlation coefficient of the order of 0.999 were consistently obtained. Increasing the number of spectra for the calibration does not improve the statistical parameters significantly. In order to determine the accuracy of the calibration model, several validation solutions of known concentrations were considered using PLS_a and PLS_w, respectively. The similarity of RMSEP and the correlation coefficients indicates that the background registration mode does not affect the accuracy of the prediction. The acceptability of the prediction models is also reinforced by the close similarity between the spectral data for the Na_4EDTA, which is generated by the pure component spectra diagnostic tool of the TQ software (Fig. 3).

Fig. 4 shows that the Na$_4$EDTA concentrations obtained by the two PLS methods in the range of $<30\%$ w/w are almost the same, with linear correlation coefficients of the order of 0.999. Thus, the two methods are statistically equivalent in terms of accuracy and reproducibility. However, the predictive ability of the software is less satisfactory in the concentration range below 1% w/w. To permit a better visualization, Table 2 shows the predictive data of nine samples taken at regions close to the centre and the upper and lower ends of the calibration curve together with individual standard deviations of each concentration based on at least two spectra. From these results, it can be seen that the predictive potential of both methods fails. In order to get the best possible fit, the set of calibration standards was restricted to a Na$_4$EDTA concentration range below 5% w/w (PLS$_{a5}$ in Table 1). PLS$_{a5}$ gives much more accurate concentration values than the other models that have a wider prediction interval (Table 2). The greater accuracy of PLS$_{a5}$ may be due to the similar degrees of overlapping between the two bands, —the carboxylate groups ($\nu_{\mathrm{as\ COO^-}}$) and the OH bending vibration of the water molecule—, and the shift of the wavenumber as the concentration increases. Although the result may be sufficient for an initial screening of the highly-diluted solutions, further analysis by other analytical techniques such as HPLC is required. It is important to mention that the three PLS models are based on the area of the most prominent band corresponding to Na$_4$EDTA (1575 cm^{-1}). Predictive performance is not improved by employing the two characteristic bands associated to the carboxylate groups or multiple absorbance in a specific spectral region.

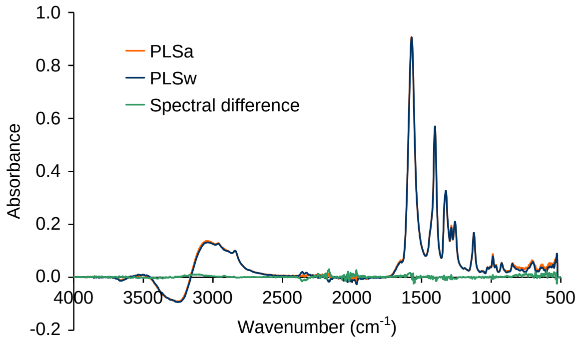

Fig. 3. Na$_4$EDTA spectra calculated by the PLS method from those obtained by using air and water as a background medium, (PLS$_a$ and PLS$_w$, respectively) and spectral differences.

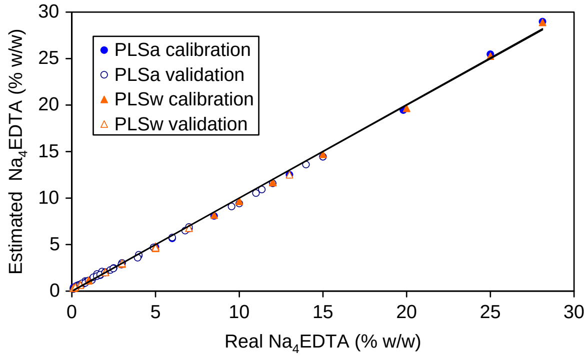

Fig. 4. Real Na$_4$EDTA concentration *vs.* estimated concentration obtained from PLS$_a$ and PLS$_w$.

Table 2
Statistical comparison of some Na$_4$EDTA aqueous solutions obtained from the PLS validation sets.

Real c_{Na4EDTA} (% w/w)	Estimated c_{Na4EDTA} (% w/w)					
	PLS$_w$		PLS$_a$		PLS$_{a5}$	
	Mean value	SD	Mean value	SD	Mean value	SD
0.20	0.43	0.02	0.32	0.01	0.09	0.01
0.30	0.68	0.02	0.58	0.03	0.37	0.03
0.50	0.67	0.03	0.70	0.06	0.50	0.06
1	1.15	0.03	1.13	0.04	0.94	0.15
1.70	1.84	0.01	nd	nd	1.65	0.06
2	2.04	0.04	2.05	0.26	2.01	0.18
5	4.75	0.11	4.74	0.08	4.97	0.10
10	9.67	0.01	9.41	0.02		
20	19.65	0.00	19.45	0.00		

PLS: Partial least square model using water (*w*) or air (*a*) as a background over the whole concentration range or in the 0.1–5% w/w range (*a*5); SD: individual standard deviation for at least two spectra; nd: not determined.

3.2. *HPLC-UV analysis*

Complexed Na$_4$EDTA solutions flowing through the HPLC system exhibit a unique peak at an elution time of 6.54 min and a good linearity between the peak areas (A) and the Na$_4$EDTA concentrations (c) over the whole range tested before complexation.

$$A=25.914c–7.896 \quad r=0.9998$$

Quantitative analysis from the five-point calibration curve provides a good agreement between the real and estimated concentrations of validation with a high degree of repeatability. A comparison between the data obtained by HPLC and by ATR-FTIR shows that ATR-FTIR combined with PLS is effective for Na$_4$EDTA quantification above 0.3% w/w (Table 3). However, below this detection limit, HPLC-UV based on the complexation process is the optimum method.

3.3. *Na$_4$EDTA in a commercial detergent*

The quantitative determination of the Na$_4$EDTA present in a caustic commercial detergent with pH nearly 13, resulted in an acceptable agreement between the concentration values obtained by HPLC-UV (20.7% w/w) and ATR-FTIR in combination with PLS$_w$ (22.6% w/w) and PLS$_a$ (23.5% w/w). Different solutions of the detergent with concentrations ranging from 0.11 to 90% w/w were

Table 3
Na$_4$EDTA concentrations estimated by ATR-FTIR in combination with PLS and HPLC-UV.

Real c_{Na4EDTA} (% w/w)	Estimated c_{Na4EDTA} (% w/w)			
	HPLC-UV		PLS$_{a5}$	
	Mean value	SD	Mean value	SD
3.93	4.04	0.54	3.71	0.06
2.48	2.49	0.05	2.42	0.18
1.69	1.69	0.03	1.69	0.01
1.30	1.36	0.13	1.39	0.05
0.90	0.91	<0.01	0.91	0.08
0.60	0.61	<0.01	0.64	0.08
0.30	0.30	0.02	0.27	0.13
0.15	0.15	<0.01	0.20	0.06

PLS: Partial least square model using air as a background over the 0.1–5% w/w concentration range (*a*5); SD: individual standard deviation for at least two spectra.

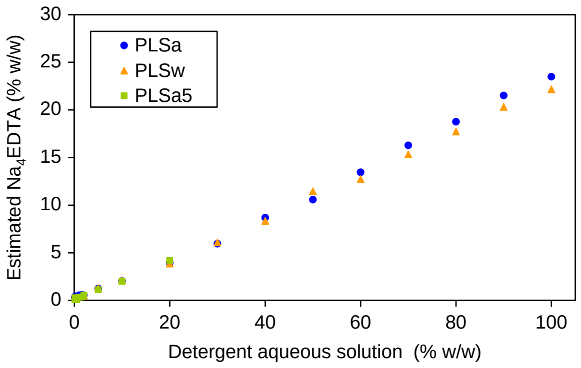

Fig. 5. Relation between the amount of detergent and the estimated amount of Na_4EDTA in aqueous solutions as determined by PLS analysis (correlation coefficients, $r_{PLSa}=0.9982$; $r_{PLSw}=0.9989$; $r_{PLSa5}=0.9981$).

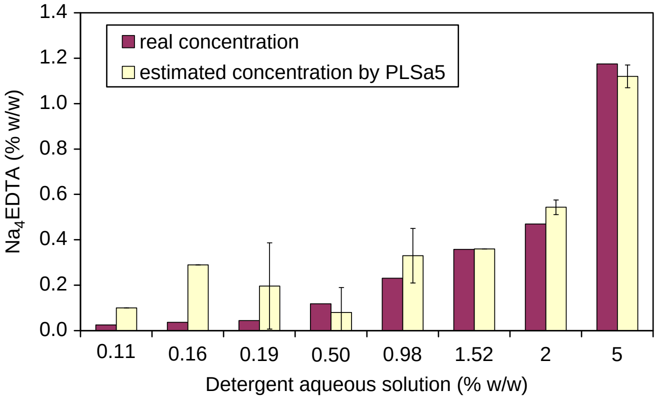

Fig. 6. Real and estimated amounts of Na_4EDTA in detergent aqueous solutions in the 0.11–5.00% w/w range.

prepared and evaluated using the developed PLS models. Fig. 5 shows the predictive ability of each PLS models. A good linearity can be observed between the amount of detergent and that of Na_4EDTA in the complex aqueous mixture employed. This indicates that matrix effects did not distort the spectral region of the carboxylate groups, especially at the highest detergent dilutions where both acquisition spectra modes (air and water background) are employed. In the diluted detergent solutions below 5% w/w, significant differences between the real and estimated Na_4EDTA concentrations by the PLS_{a5} can be observed (Fig. 6), showing that the model is only valid for Na_4EDTA concentrations higher than 0.3% w/w. This detection limit corresponds to a detergent aqueous solution of nearly 1.5% w/w.

4. Conclusions

In combination with PLS algorithm modeling, ATR-FTIR spectroscopy has been shown to be a simple, rapid and accurate technique for determining the quantity of Na_4EDTA in aqueous solutions, even when the asymmetric stretching vibration of the carboxylate groups at 1575 cm^{-1} overlaps or becomes indistinguishable among the spectra of low concentration solutions due to the strong water absorption band at 1635 cm^{-1}. In a Na_4EDTA concentration range from 0.3 to 28% w/w, the PLS models developed are simple —only one factor is used—, robust and as precise as the HPLC-UV method in evaluating the NaFeEDTA complex. Very effective calibration models that showed good correlations with the real Na_4EDTA concentrations were constructed. The proposed methodology is highly satisfactory for estimating the Na_4EDTA concentration present in complex matrices like industrial detergents and their aqueous solutions where several levels of dilution are involved, in order to tailor them for specific applications. In addition, this methodology can be extended to formulations of detergents containing other members of the aminopolycarboxylate family such as chelators.

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