JOURNAL OF CHEMOMETRICS
J. Chemometrics 2007; **21**: 263–269
Published online 27 July 2007 in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/cem.1068

Near infrared spectroscopy and multivariate curve resolution-alternating least squares incorporating ^{13}C-NMR information for monitoring epoxy resins reactions

M. Garrido, M. S. Larrechi* and F. X. Rius

Department of Analytical and Organic Chemistry, Faculty of Chemistry, Rovira i Virgili University, Marcel·lí Domingo s/n 43007, Tarragona, Spain

Received 28 September 2006; Revised 22 May 2007; Accepted 31 May 2007

This paper describes how data from two instrumental techniques—near infrared spectroscopy (NIR) and ^{13}C nuclear magnetic resonance (^{13}C-NMR)—are combined by means of multivariate curve resolution-alternating least squares (MCR-ALS) to obtain concentration and spectral profiles for the reaction between phenylglycidylether and aniline. The reaction, in stoichiometric proportions, was monitored by both spectroscopic techniques at 95°C. The concentration values obtained by ^{13}C-NMR were used as an equality constraint during the multivariate curve resolution of the near infrared data. The results obtained were recovered without ambiguities: that is to say, there was a unique solution. The goodness of the results was tested by comparing the recovered concentration profiles with the values obtained by high performance liquid chromatography (HPLC) as a reference technique. The statistical tests showed that there were no significant differences between the results of both methods ($\alpha = 5\%$). Also, the recovered spectra were compared with the experimentally recorded spectra for the reagents (i.e. phenylglycidylether and aniline) and the final product and the correlation coefficients were, in all cases, higher than 0.998. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: multivariate curve resolution; alternating least squares; nuclear magnetic resonance; near infrared; epoxy resins

1. INTRODUCTION

Near infrared spectroscopy (NIR) in combination with multivariate curve resolution methods has demonstrated to be a useful technique in many analytical applications due to the combination of an instrumental technique that incorporates an easy-to-obtain analytical signal with a powerful chemometric technique that can achieve the necessary spectral resolution [1–4]. Soft-modeling methods, in particular the multivariate curve resolution-alternating least squares method (MCR-ALS), have great potential when applied to spectroscopic data obtained from monitoring a chemical reaction, so the concentration profiles of each species involved in the reaction and the corresponding pure spectra can be estimated [5–7]. However, the presence of rotational and intensity ambiguities [8] is a characteristic problem in factor analysis decompositions of some bilinear data matrices and makes it difficult to obtain unique solutions. Instead of unique solutions, a band of feasible solutions are obtained that fit the experimental data equally well. The number of feasible solutions can be drastically reduced when constraints, which are inherent to and characteristic of the chemical system being studied, are applied to estimate concentration and spectra profiles (e.g. non-negativity, closure and unimodality constraints) [9,10]. Other constraints related to selectivity in concentration or spectral regions [8] and knowledge of local rank conditions [11] make it possible to obtain solutions that are nearly unique or totally eliminate the ambiguities. In addition, when the concentration and/or spectral profiles (totally or partially) are known for some of the species, they can be used as an equality constraint (i.e. the known values are set to be invariant during the iterative process) [12].

Unfortunately, in data matrices obtained from the spectroscopic monitoring of chemical reactions, knowledge of local rank conditions and selectivity regions are not usually expected. Furthermore, the spectral profiles of the reactants may usually be available for use as an equality constraint, but

*Correspondence to: M. S. Larrechi, Department of Analytical and Organic Chemistry, Faculty of Chemistry, Rovira i Virgili University, Marcel·lí Domingo s/n 43007, Tarragona, Spain.
E-mail: mariasoledad.larrechi@urv.cat

it is not always possible to have the spectra of the intermediate or final products. It is also uncommon to know how the concentration of some of the species evolves over time.

In some circumstances, a complementary technique of analysis can provide supplementary information that helps to resolve the system being studied successfully. Multivariate curve resolution has been used to combine such spectroscopic techniques as fluorescence and circular dichroism [13], near infrared and mid infrared [4] and mass spectrometry and circular dichroism [14]. It also makes it possible to combine UV-Vis and near infrared with calorimetric techniques [15,16].

This study uses multivariate curve resolution methods to combine the information supplied by two spectroscopic techniques—NIR and ^{13}C nuclear magnetic resonance (^{13}C-NMR)—when they are used to monitor an epoxy resin reaction. NMR has several advantages that make it suitable for monitoring reactions involving organic compounds: it is rapid, requires small amounts of sample and provides structural information of the investigated compounds because of the high selectivity of the signals. NMR spectroscopy has been used to characterize epoxy resins [17–20], usually to analyze either the final product structure or the influence of the molecular structure on the physical relaxations of the epoxy resin systems. However, to our knowledge, it has never been used to study the changes in the concentration of the species throughout the reaction process. Specially, ^{13}C-NMR presents a relatively simple pattern of signals that are hardly affected by the solvents used [20]. However, quantitative analysis may be unreliable due to the fact that the relaxation time for some atoms is long. Therefore, it is not always possible to obtain quantitative information about all the species.

Other techniques, such as high performance liquid chromatography (HPLC), have been used to obtain quantitative individual information about the evolution of each species in epoxy resins, but these procedures are usually laborious and time-consuming [21,22].

In the present paper, MCR-ALS has been applied to the near infrared data obtained from the on-line monitoring of the reaction between phenylglycidylether and aniline at 95°C, in order to obtain the corresponding spectral and concentration profiles. The resolution was improved by imposing an equality constraint, which consisted of the concentration values for some of the species involved in the reaction, obtained by at-line monitoring of the reaction using ^{13}C-NMR. To the best of our knowledge, no studies have been published on the use of ^{13}C-NMR for the quantitative monitoring of epoxy resins reactions.

In order to verify the validity of the concentration profiles obtained, the recovered spectra were compared with the recorded near infrared spectra of both the reactants (phenylglycidylether and aniline) and the final product of the reaction, in terms of correlation coefficient. The reaction was also monitored by HPLC and the results obtained were compared to those obtained by the NIR/NMR and MCR-ALS procedure.

2. EXPERIMENTAL

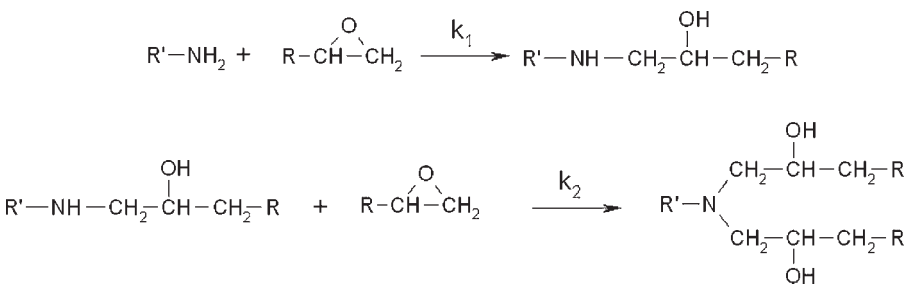
The reactions that take place between PGE and aniline are depicted in Scheme 1. Primary amine reacts with the epoxide to form a secondary amine and, in a further reaction, the secondary amine reacts with epoxide to form a tertiary amine. The experimental procedure for the reaction involved mixing the necessary amounts of aniline (Aldrich, distilled before using it) and PGE (Aldrich) at room temperature to obtain a molar ratio of 2.1. The reaction was carried out at 95°C and the epoxide concentration was not in excess to ensure that the reactions being studied were the only ones taking place and that there was no collateral etherification or homopolymerization reaction [21,23].

2.1. NIR monitoring

Typically, 1 ml of the reacting mixture was injected into the cell for liquids of the NIR spectrophotometer. The cell temperature was set at 95°C. The NIR spectra were recorded throughout the reaction every 4 nm, between 1100 and 2500 nm with an InfraAlizer 500 spectrophotometer from Bran-Luebbe. For each experiment, we automatically acquired data at intervals of 5 min until the end of the reaction. The reaction was considered to be complete when no change was observed in the spectra throughout the time. NIR spectra of the pure reactants (aniline and PGE) were also recorded in the same experimental conditions. The recorded spectra were exported and converted into MATLAB binary files [24].

2.2. ^{13}C-NMR analysis

The reaction times at which the ^{13}C-NMR experiments were carried out were selected by applying the evolving factor analysis algorithm (EFA) [25] to the NIR data obtained as in Section 2.1. The times at which the factors became significant,



Scheme 1. Chemical reaction between phenylglycidylether (PGE) and aniline.

DOI: 10.1002/cem

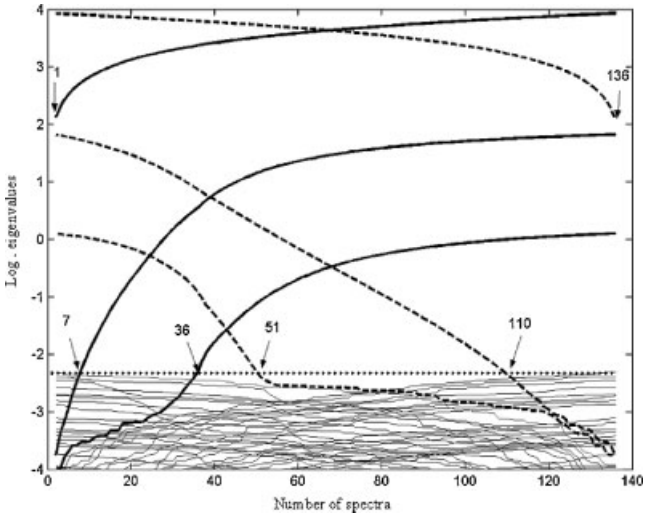


Figure 1. Evolving factor analysis plot of the NIR data recorded throughout the reaction with a PGE/aniline molar ratio of 2:1. The dotted line corresponds to the logarithm of the fourth eigenvalue, used as a threshold to select the number of significant components. Solid line: forward analysis, dashed line: backward analysis.

both in the forward and backward analysis, were selected for the NMR experiments (see Figure 1).

The reaction was carried out under stoichiometric proportions (i.e. PGE/aniline molar ratio of 2:1) in a thermostatic bath (PolyScience, USA) at $95 \pm 0.2^{\circ}C$, and the temperature of the reacting mixture was controlled with an immersion probe thermometer (Crison). Six samples of the reacting mixture (about 150 mg) were withdrawn at different reaction times, in accordance with the EFA analysis, and immediately dissolved with $CDCl_3$. They were then kept at $20^{\circ}C$. In this way, the reaction can be considered to have stopped. A chronometer was used to synchronize the sampling in the ^{13}C-NMR experiment with the NIR measurements. ^{13}C-NMR spectra of the samples were recorded at room temperature at 75.4 M Hz in a Varian Gemini 300 NMR spectrometer with proton noise decoupling.

In order to quantitatively integrate the signals, the NMR spectra were acquired using inverse-gated decoupling and a relaxation time delay of about $5T_1$. This value (T_1) was the relaxation time of the carbons located in the *para* position with respect to the ether group of the PGE, which was used as the reference signal (see Figure 2, signal 7). It was the slowest relaxing nucleus of all the signals used in the quantification.

Relative quantification was carried out using the invariable signal of the reference carbon and assuming that, in all spectra, this signal had a concentration of $5.09\ mol\ kg^{-1}$ (of the amount of PGE that was initially present in the 2:1 PGE/aniline reacting mixture).

2.3. High performance liquid chromatography

For monitoring by HPLC, the reaction was carried out under stoichiometric proportions (i.e. PGE/aniline molar ratio of 2:1) in a thermostatic bath (PolyScience, USA) at $95 \pm 0.2^{\circ}C$. The temperature of the reacting mixture was controlled with an immersion probe thermometer (Crison).

The chromatographic separation was performed by reversed-phase HPLC using a Hewlett Packard series 1100 chromatographic system with a UV detector set at 254 nm to monitor the eluted species. The samples (19 samples withdrawn from the reacting mixture at different times, analyzed in triplicate) were prepared by weighing 10–25 mg of reacting mixture and dissolving them with methanol to 10 ml. Aliquots of this solution (20 μl) were injected into an analytical Hypersil ODS reverse-phase column (5 μm particle size), 200 mm × 4.6 mm i.d. (Agilent Technologies). The temperature of the column was kept at $20^{\circ}C$. HPLC analyses were carried out by gradient elution of the methanol-water system (both HPLC grade solvents from SDS) with a flow rate of $1.75\ ml\ min^{-1}$. The gradient ranged from 20% to 100% of methanol within 10 min.

The concentration of the species under study was calculated from the peak areas using the calibration curves of pure compounds. PGE and aniline were commercially available. The secondary amine product was prepared by reacting PGE with excess aniline (1:10 molar ratio) at $80^{\circ}C$ for 12 h. The excess aniline was distilled off under reduced pressure. Tertiary amine was obtained from the stoichiometric mixture (i.e. PGE/aniline 2:1) reacted at $120^{\circ}C$ for 20 h. The standard solutions for the calibration curves were made in triplicate and took into account the range of concentration of each species throughout the process. The areas of the chromatographic peaks had a linear relationship with respect to the concentration of the species in the mobile phase.

2.4. MCR-ALS optimization

In order to eliminate the vertical shift caused by using a NIR spectrophotometer with only one light beam, all the spectra were pretreated with an *off-set* correction [26]. The wavelengths of interest were selected and those in which no variation over time was observed were ignored because they provided no information about the reaction under study. The regions of the spectrum in which only noise was detected were also eliminated. The pretreated spectra were arranged in an experimental data matrix **D**.

Rank analysis was performed by singular value decomposition (SVD) [27] and confirmed by evolving factor analysis [25].

In order to overcome the rank deficiency of matrix **D**, a column-wise augmented matrix **M** was built with experimental data matrix **D** and the NIR spectra recorded for PGE and aniline (i.e. the reactants).

The initial estimate for the ALS algorithm was constructed using SIMPLISMA [28] as mentioned elsewhere [29].

The MCR-ALS optimization was carried out under the following constraints: non-negativity for both the spectral and the concentration profiles, unimodality for the concentration profiles and closure constraints for the concentration profiles. Likewise, an equality constraint was applied for the concentration profiles, by imposing that some concentration values, known by ^{13}C-NMR for certain reaction times, were fixed at each step of the optimization process.

DOI: 10.1002/cem

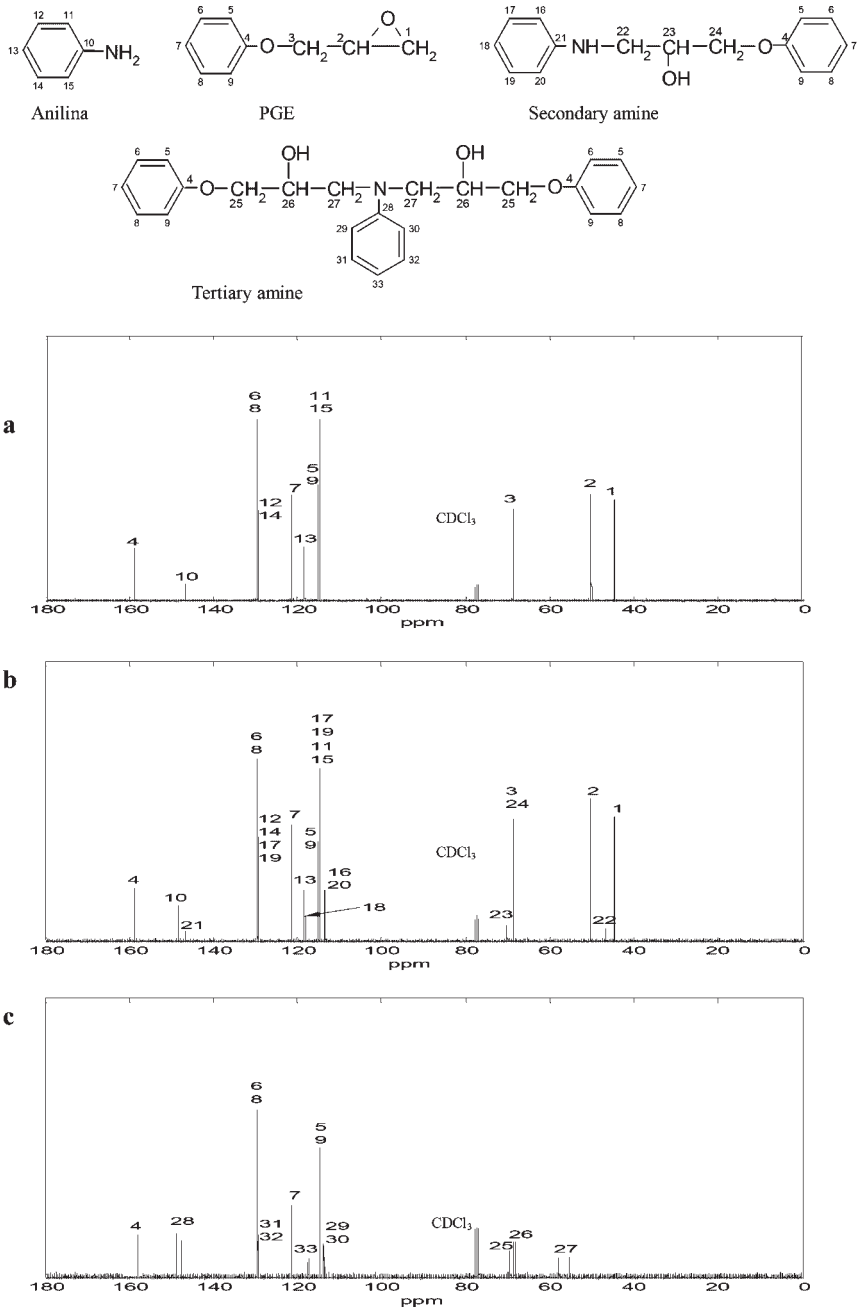


Figure 2. ^{13}C-NMR spectra of the reacting mixture at different reaction times (a) 0 min, (b) 45 min and (c) 675 min. The numbers corresponding to the signals have been assigned to the different carbon atoms in the upper part of the figure.

3. RESULTS AND DISCUSSION

As can be seen in Scheme 1, four sources of variability were expected, one for each of the four species involved in the reaction: PGE, aniline, the secondary amine and the tertiary amine. Rank analysis of matrix **D** showed that only three significant contributions were present (see Figure 1). In order to eliminate this rank deficiency, the column-wise augmented matrix **M** was built by adding the row vectors corresponding to the spectra of the reactants (i.e. PGE and aniline) to the experimental data matrix **D**. In this way, the rank deficiency was broken because the rank of the new matrix matched the number of absorbing species.

After the rank deficiency had been overcome, MCR-ALS was applied to augmented matrix **M**. When only non-negativity, unimodality and closure constraints were implemented, the results obtained were strongly affected by the intensity and rotational ambiguities. Therefore, a set of feasible solutions was obtained, as has been discussed in a previous article [7]. In order to minimize or totally eliminate the ambiguities, more forceful constraints are needed. External knowledge, consisting of the spectra of the reactants, was fixed throughout the iteration process, but it was not effective at diminishing the ambiguities and the results were approximately the same when this constraint was not applied.

DOI: 10.1002/cem

Figure 2 shows, as an example, the ^{13}C-NMR spectra for the reaction between PGE and aniline at three different times. The signals were assigned in accordance with the spectra reported in the literature for the same reaction [17,20]. Figure 2a shows the spectrum obtained at the beginning of the reaction, when PGE and aniline have still not significantly reacted. When the secondary amine starts to form, new signals are detected (Figure 2b) but by the end of the reaction they had totally disappeared (Figure 2c), and the tertiary amine had formed almost completely.

The evolution of PGE was monitored by two signals, 1 and 2. The secondary amine was monitored through the signals 22 and 23 and the tertiary amine was monitored through signals 25, 26 and 27 (see Figure 2). The 25, 26 and 27 carbons led to double peaks because of the different stereoisomeric forms of the tertiary amine. The tertiary amine consists of a mixture of RR, RS and SS stereoisomers at a molar ratio of 1:2:1. The RR and SS isomers produce the same NMR spectra, which are different from those produced by the RS isomer. Therefore, Fig. 2c shows two signals of similar intensities in several carbons of the tertiary amine [20]. This indicates that the reaction is not steroeselective. So, to calculate the concentration vales of the tertiary amine, the signals of the 25, 26 and 27 carbons were added together.

Signals 10–15 could be useful for monitoring aniline, but their relaxation times are so long that the quantitative results would not be trustworthy (relaxation times >5 sec). Therefore, ^{13}C-NMR can reliably monitor only the profiles for PGE, the secondary amine and the tertiary amine.

The times at which the NMR spectra were recorded were selected using EFA, as explained in section 2.2. Six spectra were selected: 1, 7, 36, 51, 110 and 136 (see Figure 1), at the following time points 0, 30, 175, 250, 545 and 675 min, respectively. So, samples of the reacting mixture were withdrawn at these reaction times and their ^{13}C-NMR spectra were recorded.

The new external information provided by ^{13}C-NMR consisted of the six concentration values corresponding to the quantified species (i.e. PGE, the secondary amine and the tertiary amine) at the selected reaction times. These values were fixed and imposed as an equality constraint during the MCR-ALS optimization. After the optimization process, the values of % of lack of fit and % of explained variance obtained were 0.57 and 99.997, respectively.

The spectra of the four species after MCR-ALS had been applied are shown in Figure 3. The goodness of the spectral profiles was evaluated by calculating the similarity coefficients [29] between the recovered spectra and the spectra recorded for the reactants (i.e. PGE and aniline), respectively. The values were 0.9986 for the PGE and 0.9999 for the aniline. In the same way, the recovered spectrum for the tertiary amine was compared with the last spectrum recorded for the reacting system, assuming that the conversion was almost 100%. The similarity coefficient for the tertiary amine was 0.9999. The similarity coefficient was high in all cases, which suggests that the recovered spectrum of the secondary amine was similar to its real spectrum. When the equality constraint (based on the NMR known concentration values) was not used, the correlation coefficients were worse.

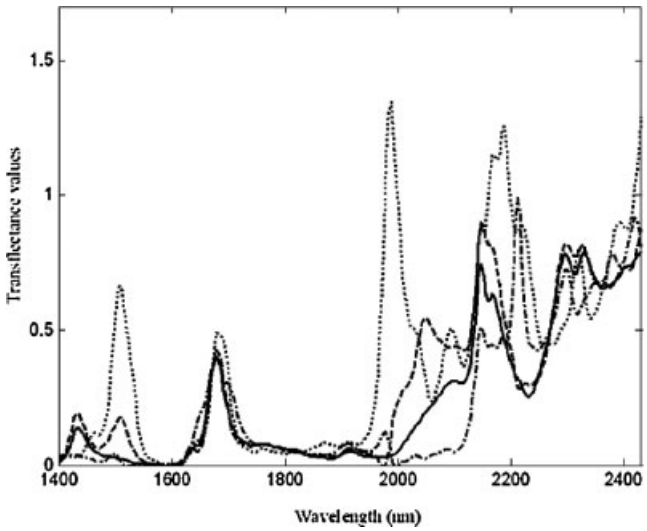


Figure 3. Spectra recovered by MCR-ALS: aniline (dotted line), PGE (dash-dot line), secondary amine (dashed line) and tertiary amine (solid line).

The concentration profile of each species, recovered in % w/w, was divided by the corresponding molecular weight in order to express the concentrations in mol kg^{-1} (see Figure 4). The initial concentration values corresponded well to the molar ratio used in the reaction (PGE/aniline molar ratio of 2:1). Likewise, the concentration of the tertiary amine at the end of the reaction reached the value predicted by the stoichiometry.

Figure 4 shows that PGE was not totally consumed, contrary to what was expected at the end of the experiment. One possible explanation for this is that the NIR spectra for

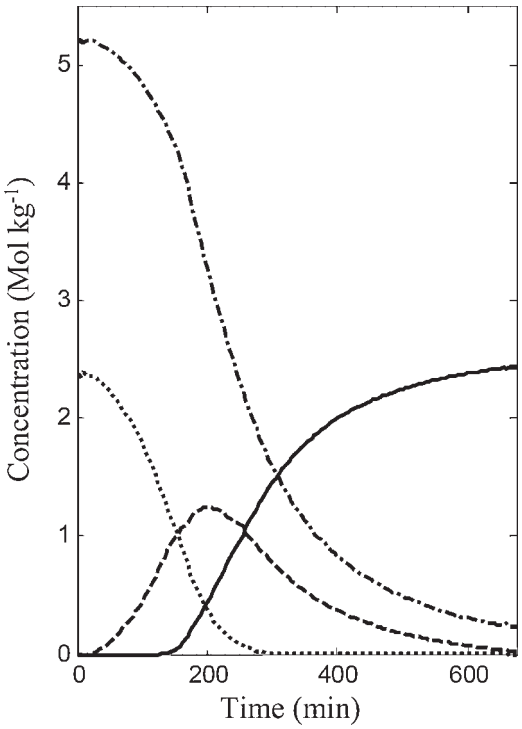


Figure 4. Concentration profiles recovered by MCR-ALS: aniline (dotted line), PGE (dash-dot line), secondary amine (dashed line) and tertiary amine (solid line).

DOI: 10.1002/cem

each experiment were recorded until the band corresponding to the oxirane group (2208 nm) disappeared. At this point, the reaction is considered to have finished. The NIR spectra may show that the band disappears at 2208 nm, but the reaction has not really stopped, and a small quantity of epoxide has still not reacted.

This clearly indicates the disadvantages of using a univariate approach for the near infrared monitoring of this kind of reaction since, in the last stages of the reaction it is difficult to say when a band has totally disappeared. Likewise, when a band has nearly disappeared, it is not easy to integrate its area to quantify the extent of the reaction.

Known concentration values were used as a constraint during the ALS optimization process and, even though only a few of them were available and they corresponded to only three of the four species involved, unique solutions were obtained both for the concentration and the spectral profiles. This was corroborated by calculating the band boundaries of feasible solutions [30], under non-negativity and closure constraints, which matched the ALS solutions.

Combining NMR supplementary information and NIR spectra, in the way of row-wise augmented matrices, also could be an interesting strategy to analyze this set of kinetic data. However, due to instrumental limitations, this approach could not be applied in our study. The procedure used for the ^{13}C-NMR measurements involved withdrawing aliquots of the reacting mixture at certain reaction times and, then, dissolving them in individual NMR tubes with $CDCl_3$. Unfortunately, because of the differences between tubes, amounts of solvent used and variations in the magnetic field there were differences between measurements. The observed effect was that the signals in the different spectra could not be perfectly overlapped. These differences do not affect the univariate analysis of the spectra, but the multivariate analysis since more components than the expected appear when factor analysis is carried out. A solution for this trouble may be to perform the reaction directly in a single NMR tube, setting the appropriate temperature and recording the NMR spectra at the desired times. In this case, the effect of the temperature in the relaxation times should be carefully studied in order to obtain quantitative results.

In order to further assess the validity of the results obtained by MCR-ALS, the recovered concentration profiles were compared with the concentration values obtained by HPLC (see Figure 5). A preliminary visual inspection made it possible to conclude that there is a good correspondence between the MCR-ALS concentration profiles and those obtained by liquid chromatography. However, the equivalence between data needs to be quantified. Since the evolution of the species are related to one another by the underlying mass balance, the concentration profiles were jointly analyzed for the four species. When the concentrations recovered by MCR-ALS were plotted versus the concentrations recovered by HPLC, a straight regression line was obtained, with a slope near to 1 and an intercept near to 0 ($y = 0.93x - 0.00$). The qualitative similarity between the profiles obtained by both methods was evaluated in terms of the correlation coefficient of this straight line. The value obtained was 0.996.

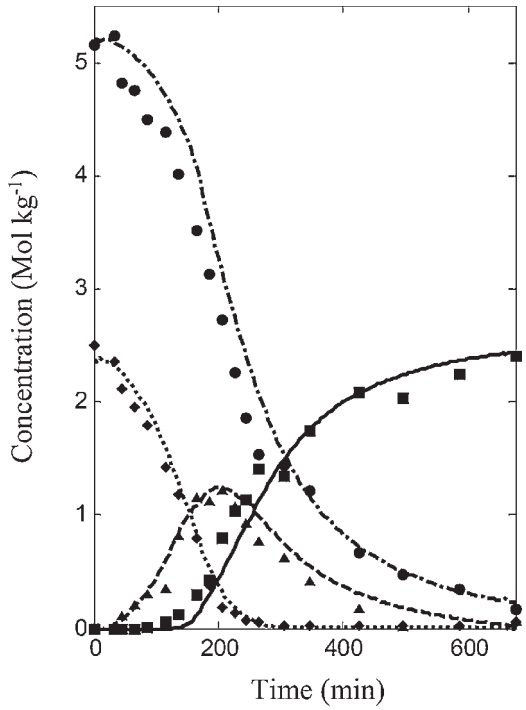


Figure 5. Superposition of the concentration profiles recovered by MCR-ALS and the experimental values obtained by HPLC for the reaction between PGE and aniline (molar ratio of 2:1). For the MCR-ALS concentration profiles: aniline (dotted line), PGE (dash-dot line), secondary amine (dashed line) and tertiary amine (solid line). HPLC experimentally determined results: (◆) aniline, (●) PGE, (▲) secondary amine and (■) tertiary amine.

The statistical joint interval test of slope and intercept was used to test for the presence of bias [31]. The results show that there are no significant differences between the concentration profiles obtained by the two techniques ($\alpha = 5\%$).

4. CONCLUSIONS

Combining the results obtained from two spectroscopic techniques—near infrared and ^{13}C-NMR—by means of MCR-ALS led to spectral and concentration profiles that adequately described the species studied and their evolution over time. Furthermore, the concentrations obtained by ^{13}C-NMR for some of the species involved in the reaction at a given reaction time were used as equality constraint, which made it possible to obtain unique solutions for both concentration and spectral profiles.

The validation process showed that the recovered concentration profiles were not significantly different from the values of concentration obtained by HPLC used as a reference technique ($\alpha = 5\%$). On the other hand, the recovered spectra showed high similarity coefficients (>0.998) when they were compared with the spectra of the experimentally recorded pure compounds.

Although the proposed strategy involves using a complementary spectroscopic technique to achieve results free of ambiguities, the concentrations obtained by ^{13}C-NMR are easily determined and effortlessly incorporated as an

DOI: 10.1002/cem

equality constraint into the MCR-ALS algorithm, which mean that this method is a satisfactory tool for monitoring epoxy resins reactions.

Acknowledgements

The authors acknowledge economic support from the MCyT (project no. BQU2003-1142).

REFERENCES

1. Puxty G, Maeder M, Radack HP, Gemperline PJ. Equilibrium modeling of mixtures of methanol and water. *Appl. Spectrosc.* 2005; **59**: 329–334.
2. Czarnik-Matusewics B, Pilorz S, Hawranek JP. Temperature-dependent water structural transitions examined by near-IR and mid-IR spectra analyzed by multivariate curve resolution and two-dimensional correlation spectroscopy. *Anal. Chim. Acta* 2005; **544**: 15–25.
3. Blanco M, Alcala M, González JM, Torras E. Near infrared spectroscopy in the study of polymorphic transformations. *Anal. Chim. Acta* 2006; **567**: 262–268.
4. Navea S, de Juan A, Tauler R. Modeling temperature-dependent protein structural transitions by combined near-IR and mid-IR spectroscopies and multivariate curve resolution. *Anal. Chem.* 2006; **75**: 5592–5601.
5. Tauler R, Izquierdo-Ridorsa A, Casassas E. Simultaneous analysis of several spectroscopic titrations with self-modeling curve resolution. *Chemom. Intell. Lab. Syst.* 1993; **18**: 293–300.
6. Izquierdo-Ridorsa A, Saurina J, Hernandez-Cassou S, Tauler R. Second-order multivariate curve resolution applied to rank-deficient data obtained from acid-base spectrophotometric titrations of mixtures of nucleic bases. *Chemom. Intell. Lab. Syst.* 1997; **38**: 183–196.
7. Larrechi MS, Rius FX. Spectra and concentration profiles throughout the reaction of curing epoxy resins from near-infrared spectroscopy and multivariate curve resolution methods. *Appl. Spectrosc.* 2004; **58**: 47–53.
8. Tauler R, Smilde A, Kowalski B. Selectivity, local rank, 3-way data-analysis and ambiguity in multivariate curve resolution. *J. Chemometrics* 1995; **9**: 31–58.
9. Gargallo R, Tauler R, Cuesta-Sanchez F, Massart DL. Validation of alternating least-squares multivariate curve resolution for chromatographic resolution and quantitation. *Trends Anal. Chem.* 1996; **15**: 279–286.
10. de Juan A, Vander Heyden Y, Tauler R, Massart DL. Assessment of new constraints applied to the alternating least squares method. *Anal. Chim. Acta* 1997; **346**: 307–318.
11. Manne R. On the resolution problem in hyphenated chromatography. *Chemom. Intell. Lab. Syst.* 1995; **27**: 89–94.
12. de Juan A, Tauler R. Chemometrics applied to unravel multicomponent processes and mixtures—revisiting latest trends in multivariate resolution. *Anal. Chim. Acta* 2003; **500**: 195–210.
13. Navea S, de Juan A, Tauler R. Detection and resolution of intermediate species in protein folding processes using fluorescence and circular dichroism spectroscopies and multivariate curve resolution. *Anal. Chem.* 2002; **74**: 6031–6039.
14. Navea S, Tauler R, de Juan A. Monitoring and modeling of protein processes using mass spectrometry, circular dichroism, and multivariate curve resolution methods. *Anal. Chem.* 2006; **78**: 4768–4778.
15. Zogg A, Fischer U, Hungerbühler K. A new approach for a combined evaluation of calorimetric and online infrared data to identify kinetic and thermodynamic parameters of a chemical reaction. *Chemom. Intell. Lab. Syst.* 2004; **71**: 165–176.
16. Ma B, Gemperline PJ, Cash E, Bosserman M, Comas E. Characterizing batch reactions with in situ spectroscopic measurements, calorimetry and dynamic modeling. *J. Chemometrics* 2003; **17**: 470–479.
17. Jullien H, Petit A, Merienne C. The microwave reaction of phenyl glycidyl ether with aniline on inorganic supports: a model for the microwave crosslinking of epoxy resins. *Polymer* 1996; **37**: 3319–3330.
18. Oommen C, Amanulla S, Jain SR. Characterization of diglycidylamine epoxy resins based on bis-hydrazones. *Eur. Polym. J.* 2000; **36**: 779–782.
19. Xu K, Chen MC, Zhang K, Hu JW. Synthesis and characterization of novel epoxy resin bearing naphthyl and limonene moieties, and its cured polymer. *Polymer* 2004; **45**: 1133–1140.
20. Dyakonov T, Chen Y, Holland K, Drbohlav J, Burns D, Vander Velde D, Seib L, Soloski EJ, Kuhn J, Mann PJ, Stevenson WTK. Thermal analysis of some aromatic amine cured model epoxy resin systems—I: materials synthesis and characterization, cure and post-cure. *Polym. Degrad. Stabil.* 1996; **53**: 217–242.
21. Mijovic J, Fishbain A, Wijaya J. Mechanistic modeling of epoxy amine kinetics.1. Model-compound study. *Macromolecules* 1992; **25**: 979–985.
22. Swier S, Van Mele B. Mechanistic modeling of the reaction kinetics of phenyl glycidyl ether (PGE) plus aniline using heat flow and heat capacity profiles from modulated temperature DSC. *Termochim. Acta* 2004; **411**: 149–169.
23. May CA. *Epoxy Resins*. Marcel Dekker: New York, 1988.
24. The Mathworks, MATLAB Version 6.5, Natick, MA, 2002.
25. Keller HR, Massart DL. Evolving factor analysis. *Chemom. Intell. Lab. Syst.* 1992; **12**: 209–224.
26. Kelly JJ, Barlow CH, Jinguji TM, Callis JB. Prediction of gasoline octane numbers from near-infrared spectral features in the range 660–1215 nm. *Anal. Chem.* 1989; **61**: 313–320.
27. Massart DL, Vandeginste BGM, Buydens LMC, de Jong S, Lewi PJ, Smeyers-Verbeke J. *Handbook of Chemometrics and Qualimetrics: Part A*. Elsevier: Amsterdam, 1997.
28. Windig W, Guilment J. Interactive self-modeling mixture analysis. *Anal. Chem.* 1991; **63**: 1425–1432.
29. Garrido M, Lazaro I, Larrechi MS, Rius FX. Multivariate resolution of rank-deficient near-infrared spectroscopy data from the reaction of curing epoxy resins using the rank augmentation strategy and multivariate curve resolution alternating least squares approach. *Anal. Chim. Acta* 2004; **515**: 65–73.
30. Tauler R. Calculation of maximum and minimum band boundaries of feasible solutions for species profiles obtained by multivariate curve resolution. *J. Chemometrics* 2001; **15**: 627–646.
31. Riu J, Rius FX. Assessing the accuracy of analytical methods using linear regression with errors in both axes. *Anal. Chem.* 1996; **68**: 1851–1857.

DOI: 10.1002/cem