INTRODUCTION

Second-order calibrations where a spectral data matrix per sample is used are of great interest in analytical chemistry as they allow the quantification of analytes in the presence of unknown and uncalibrated interferents and do not require large calibration data sets as e.g. in PLS calibration. In a previous work [1] we presented automatic FT-IR flow titrations of aqueous mixture samples of diprotic organic acid analytes with and without a sugar interferent. Accurate qualitative determination of the acid contents in the mixtures by second order calibration was achieved by simultaneous analysis of mixture and acid standard titrations with multivariate curve resolution – alternating least squares (MCR-ALS).[2]

However, second order calibrations could not be established if only one diprotic acid was regarded as analyte and the other as an unknown interferent. This is a result of the complexity of the data sets. The pKa values of the two diprotic acids studied (malic and tartaric acid) are very similar and thus the concentration profiles of the different acid species are too correlated for successful resolution of the mixture systems.

In this contribution we describe how the difficulties in data analysis have been overcome. The pH was measured during the titration of the samples and included in a novel data analysis routine that combines soft- and hard-modeling features. A "hard" pH equilibrium model was implemented as an additional constraint in the "soft" MCR-ALS program. This approach allows the successful resolution of the mixture systems.

WHAT HAPPENS TO A MIXTURE OF ACIDS IN THE PRESENCE OF INTERFERENTS?

In this work the equilibrium constraint was only applied to the analyte diprotic acid in the mixture and the standard sample. The interferent diprotic acid was only constrained to positive concentration profiles.

CHEMICAL PROBLEM

Quantitation of a diprotic acid (malic or tartaric acid) in an aqueous mixture sample in the presence of an interferent diprotic acid.

• Unknown interferents: diprotic acid (malic or tartaric acid), monoprotic acid (lactic acid) or sugar (sucrose).

• Samples are titrated, FT-IR spectra and pH are recorded simultaneously.

• Second derivative spectra are used for elimination of major baseline contributions.

DATA EVALUATION

MCR-ALS (Soft Modeling)

The spectral matrix D is decomposed into concentration profiles and pure spectra for each modeled component:

\[
D = CS^T + E
\]

1. Determine number of components contributing to D.
2. Find initial estimates for C or S^T.
3. Constrained alternating least squares calculation of C and S^T until convergence is achieved.
4. Extract quantitative information

Simultaneous analysis of mixture and standard sample for quantification

Quantitation results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acid</th>
<th>Titration</th>
<th>pH</th>
<th>fit [%]</th>
<th>conc.</th>
<th>error [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MT1;M]</td>
<td>-</td>
<td>0.15</td>
<td>9.1</td>
<td>3.20</td>
<td>3.17</td>
<td></td>
</tr>
<tr>
<td>[MT2;M]</td>
<td>-</td>
<td>0.49</td>
<td>6.9</td>
<td>3.20</td>
<td>3.17</td>
<td></td>
</tr>
<tr>
<td>[MT3;M]</td>
<td>-</td>
<td>0.74</td>
<td>4.8</td>
<td>3.48</td>
<td>3.48</td>
<td></td>
</tr>
<tr>
<td>[MT4;M]</td>
<td>-</td>
<td>1.26</td>
<td>3.0</td>
<td>3.42</td>
<td>3.42</td>
<td></td>
</tr>
<tr>
<td>[MT5;M]</td>
<td>-</td>
<td>2.06</td>
<td>1.0</td>
<td>3.42</td>
<td>3.42</td>
<td></td>
</tr>
<tr>
<td>[MT6;M]</td>
<td>-</td>
<td>1.46</td>
<td>7.4</td>
<td>3.42</td>
<td>3.42</td>
<td></td>
</tr>
<tr>
<td>[MT2;T]</td>
<td>-</td>
<td>2.06</td>
<td>4.8</td>
<td>3.42</td>
<td>3.42</td>
<td></td>
</tr>
<tr>
<td>[MT3;T]</td>
<td>-</td>
<td>1.46</td>
<td>7.4</td>
<td>3.42</td>
<td>3.42</td>
<td></td>
</tr>
<tr>
<td>[MT4;T]</td>
<td>-</td>
<td>2.06</td>
<td>4.8</td>
<td>3.42</td>
<td>3.42</td>
<td></td>
</tr>
<tr>
<td>[MT5;T]</td>
<td>-</td>
<td>1.46</td>
<td>7.4</td>
<td>3.42</td>
<td>3.42</td>
<td></td>
</tr>
</tbody>
</table>

Equilibrium constraint (Hard model) for MCR-ALS

In step 3 of the MCR-ALS algorithm a new constraint is implemented:

• In each iteration the soft-modeled concentration profiles C are passed to a non-linear least squares (NLLS) routine [3] that fits an equilibrium model to C. After the NLLS fit the optimised C is passed back to the MCR-ALS algorithm.

• The equilibrium model is based on the Mass-Action-Law:

\[
C_{eq} = \frac{[H^+]^a [C]^b}{[H]^c [C]^d}
\]

• The equilibrium parameters \( a, b, c, d \) can be optionally fitted or fixed for each matrix.

In this work the equilibrium constraint was only applied to the analyte diprotic acid in the mixture and the standard sample. The interferent diprotic acid was only constrained to positive concentration profiles.

CONCLUSION

• Novel combination of MCR-ALS with equilibrium constraint.

• Correct modeling of analyte in highly correlated FT-IR mixture titration data.

• Equilibrium constraint yields:

• correct concentration profiles for the analyte diprotic acid.

• Analyte concentration in the mixture (as a fitted parameter of the hard model)

• Flexible and general implementation of the equilibrium constraint.

• Useful for other equilibrium based systems.

REFERENCES

