Determination of Organic Acids by Flow Injection FT-IR Spectroscopy Using pH Gradients and Advanced Chemometric Data Evaluation

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Introduction

Organic acids like acetic, citric, lactic, malic or tartaric acid among others are analytes of interest due to their widespread occurrence as e.g., constituents in food and beverage samples and their key role in atmospheric chemistry such as ozone degradation. The standard methods for their determination in both cases are ion-exchange chromatography or HPLC, which have already been well developed for routine applications. In our contribution we show a new rapid approach for the quantitative determination of organic acids (malic, citric, tartaric acid) as minor components in complex aqueous matrices like e.g., fruit juices by FT-IR spectroscopy without prior separation step. The matrix absorption due to sugars as major components is pH-independent below pH 10 and can thus be eliminated by online modulation of the pH-value of the samples. Therefore it is possible to calibrate the system only with the pH-dependent analytes. The matrix components (sugars) do not have to be taken into account thus facilitating the calibration procedure. The use of buffer substances for pH-modulation is not possible as these can thus be eliminated by online modulation of the pH-value of the samples. Therefore it is possible to calibrate the system only with the pH-dependent analytes. The matrix components (sugars) do not have to be taken into account thus facilitating the calibration procedure.

Data Treatment

1. Determining the endpoint of the titration by calculating the first derivative of selected wavelengths versus time
2. Calculating the difference spectrum acidic - basic
3. Calculating the first derivative of the difference spectrum for PLS-calibration

Method

Our method consists of preparing the calibration solutions in a SIA-system equipped with a mixing chamber. An HPLC pump is used to prepare a constant titrant flow by mixing a constant flow of HNO3 and NaOH. The calibration sample flow and the titrant flow are combined in a T-piece and FT-IR-spectra are recorded during the titration of the samples. The resulting 3D data arrays are evaluated as described below.

SIA-FT-IR Manifold

Figure 1: SIA-FT-IR Manifold
MC: mixing chamber. HC: holding coil.
HPLC-pump

Figure 2: 3D Data Array
The titration is proceeding from acidic to basic.

Figure 3: Determination of the endpoint of titration, malic acid
Figure 4: Calculating the difference spectrum and the first derivative for PLS-calibration

Results

Calibration set:
Full 3-level experimental design with malic, citric and tartaric acid (0-6 g/l) without sugars
Test set:
Samples containing organic acids and sugars
PLS Results:
3 latent variables, R2 > 99.6%

Table: PLS Results
<table>
<thead>
<tr>
<th>Component</th>
<th>R2 train</th>
<th>R2 test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malic acid</td>
<td>0.99</td>
<td>0.98</td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.98</td>
<td>0.96</td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>0.99</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Conclusion

In this work we show a new application of SIA - FT-IR for the determination of organic acids in aqueous samples by means of online pH modulation. By properly determining the endpoint of the titration, the recorded 3D data arrays and calculation of difference spectra and their first derivatives it is possible to eliminate the pH-independent matrix absorption and baseline changes within pH in the water background. This method greatly reduces the complexity of the calibration samples by only modeling the analytes of interest. PLS-calibration gives very good predictions for sugar containing samples.

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Figure 5: 3D Data Arrays
Samples with/without sugar
Figure 6: matic acid with / without sugar, first derivatives of difference spectra
Figure 7: matic acid with / without sugar, first derivatives of difference spectra