Application Note AN M75

Classification of Essential Oils with FT-IR Spectroscopy in Quality- and Process Control

Introduction

Until recently, mid-infrared spectroscopy was primarily used in agricultural research as a qualitative technique for identification and verification of unknown pure substances isolated from extracts or distillates. Usually infrared spectra obtained from plant samples are very complex because each functional group in a molecule contributes more or less to the spectral output. The net result is a spectrum in which band assignments may be difficult due to the fact that overlapping and mixing of various vibrational modes occur.
The comparatively new approach to utilize MIR spectra for analysis of plant samples in the same fashion as near infrared spectra provides an additional advantage of spectral interpretability.

Experimental

Mid IR spectra of essential oils were recorded using an ALPHA FT-IR spectrometer equipped with a single reflection ATR-module.

For the measurement approx. 2µl of the essential oil were placed on the surface of the diamond ATR crystal. The sample spectra were measured by accumulation of 32 scans at a spectral resolution of 4 cm^{-1}, resulting in a measurement time of about 30 seconds per sample.

To differentiate the oil chemotypes a hierarchical cluster analysis of the spectra was carried out using the OPUS/IDENT software. The spectral distances were calculated applying the standard algorithm (Euclidian distance) on the first derivative spectra of the samples.

To quantify specific oil components a multivariate evaluation approach was chosen applying the partial least square (PLS) algorithm (OPUS/QUANT software). For calibration the spectral range from 375 to 1900 cm^{-1} was selected. As reference method for the calibration of the IR-data gas chromatography (GC) was used. The accuracy of each calibration model was characterised by the root mean square error of cross validation (RMSECV) between the analysis result based on the IR-spectra and the reference GC value.

Results and Discussions

Whereas NIR spectroscopic data can be interpreted only by application of chemometric algorithms MIR spectra obtained from the isolated essential oils present characteristic spectral patterns which can be used to discriminate different plant species and chemotypes. Generally, those compounds of essential oils occurring only in low concentration (< 1 %) do not influence the ATR-IR spectrum significantly.

As an example all spectra obtained from different basil (Ocimum sp.) oil chemotypes show individual fingerprints and can even be discriminated by visual inspection (Figure 1).

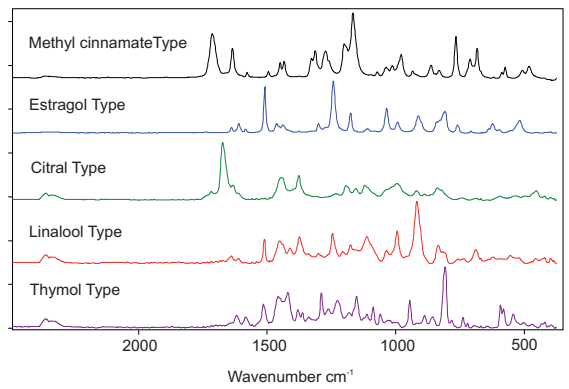

Fig. 1 ATR-FT-IR spectra of different basil oil chemotypes

Nevertheless, a chemometric evaluation like hierarchical cluster analysis is an objective method to perform a qualitative discrimination of different oil chemotypes. It has been proved that the cluster analysis method applied on ATR-IR spectra allows a rapid and reliable discrimination of various basil chemotypes (Figure 2).

Also classification of various citrus oils and quantification of important components can be successfully performed with ATR-IR spectroscopy.

Limonene is the main component (content >90 %) in grapefruit, orange and bitter orange oils and also occurs in other citrus oils in high amounts of 50-78 %. Therefore the MIR spectra of these oils are dominated by bands of this monoterpene, e.g. at 886, 1436 and 1644 cm^{-1} (Figure 3).

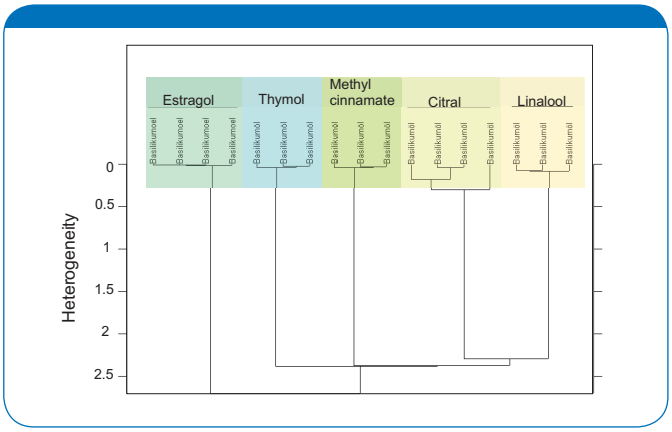

Fig. 2 Discrimination analysis of different basil oil chemotypes

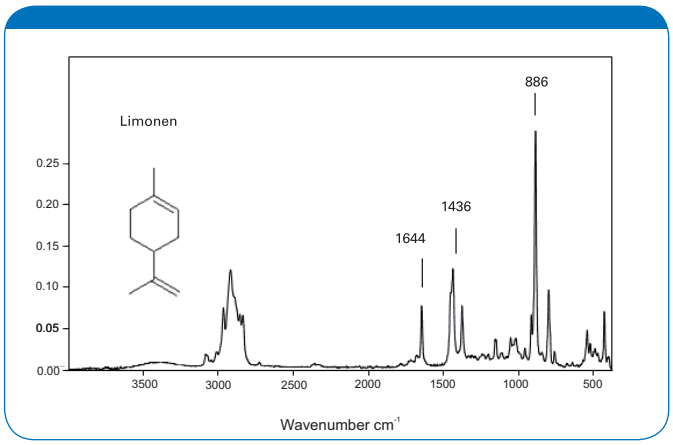

Fig. 3 ATR-FT-IR spectrum of limonene

Using the PLS algorithm on oil spectra with varying limonene content a quantitative calibration can be set up that provides a very good prediction quality over the complete concentration range (Figure 4). The RMSECV of the PLS method is in the same order of magnitude like the standard error of the GC reference method.

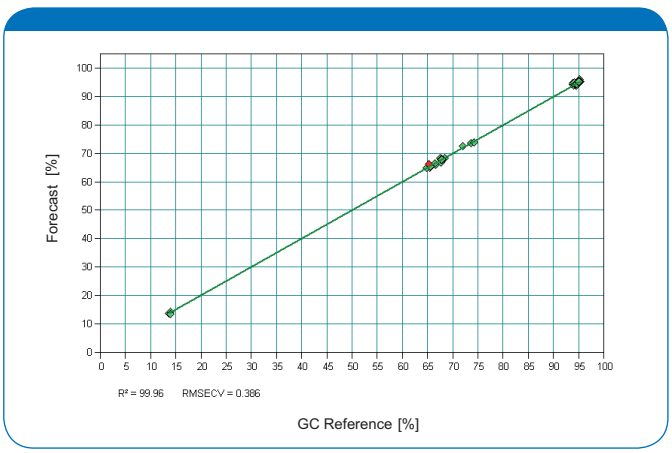

Fig 4 GC percentages vs. ATR-FT-IR prediction of limonene in various citrus oils

The IR-method can also be used to determine the linalyl acetate content in lavender oil (Lavandula angustifolia), spike lavender oil (Lavandula latifolia) and lavandin oil (L. angustifolia x L. latifolia). Furthermore, the individual content of other main components (e.g. linalool, 1,8-cineole, camphor) can be reliably determined in parallel.

Conclusion

The ATR-FT-IR spectrometer ALPHA presented here can be used for rapid classification of different essential oils used in the flavour and fragrance industry. Furthermore, the ATR-FT-IR method allows the quantification of essential oil components in a very quick and easy way. Therefore this technique has the potential to partly replace gas chromatography methods in industry for control of purifying, blending and re-distillation processes.
Due to the small size and portability of the ALPHA system it can be used in combination with micro-hydrodistillation to perform on-site measurements of essential oil plants collected from natural habitats.

References

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