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Fourier Transform Infrared Spectroscopy with Multivariate Analysis as a Novel Method for Characterizing Alcoholic Strength, Density, and Total Dry Extract in Spirits and Liqueurs

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Abstract Fourier transform infrared (FTIR) spectroscopy allows fast throughput screening of beverages (less than 2 min per sample). Using partial least squares (PLS) regression, it was demonstrated that relative density and alcohol content, which have previously been calibrated only for extract-free spirits, can also be determined in highly viscous liqueur samples. In addition, total dry extract (TDE) was successfully calibrated for the first time for both spirit and liqueur screening. An inter-laboratory validation showed that the standard errors of prediction, ranging between 0.0006 and 0.0078 (relative density), 0.23 and 0.74 % vol (alcoholic strength), and 0.55 and 7.53 g/l (TDE), were satisfactory for use of the FTIR-PLS method in the context of screening analysis in official food control of alcoholic beverages.

Keywords Spirit Drinks · Liqueur · FTIR · Chemometrics · Multivariate Data Analysis · PLS · Total Dry Extract

Introduction

In the context of quality control of alcoholic beverages, a range of different analytical methods had to be used in the past. For example, the alcoholic strength was usually determined by reference methods like distillation and pycnometry or by more advanced analytical instruments using steam distillation and oscillation-type densimetry (Lachenmeier et al. 2003, 2005a, 2006a). In addition, higher alcohols and other volatile compounds were determined using gas chromatography (Lachenmeier et al. 2006b; European Commission 2000). Therefore, by means of these traditional techniques, beverage analysis is time consuming and expensive. Increasing requirements and cost pressures nowadays force both government and commercial food testing laboratories to replace these traditional reference methods with faster and more economical systems.

The most promising approach to overcome these problems is the use of multivariate data analysis with different analytical techniques (Arvanitoyannis et al. 1999). Such techniques were used, for example, to classify vinegar samples using near-infrared spectroscopy (Saiz-Abajo et al. 2004a, b). Fourier transform infrared (FTIR) spectroscopy in the mid-infrared range was introduced into wine analysis (Patz et al. 1999, 2004; Nieuwoudt et al. 2004; Gishen and Holdstock 2000; Kupina and Shrikhande 2003; Coimbra et al. 2002), as well as into the analysis of other alcoholic beverages like spirits and beer (Palma and Barroso 2002; Lachenmeier 2007).

As a multi-component screening method, FTIR in combination with multivariate data analysis is able to simultaneously determine the alcoholic strength as well as a number of volatile compounds in less than 1 min per sample (Lachenmeier 2005, 2007; Lachenmeier et al. 2005b; Lachenmeier and Nerlich 2006; Triebel et al. 2007).

In this study, we have expanded the FTIR method to characterize not only the volatile part of spirits and liqueurs but also the nonvolatile content that is commonly referred to as total dry extract (TDE). For validation purposes, we transferred the FTIR calibrations between different instruments in different laboratories and report, for the first time, inter-laboratory method performance data.

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Materials and Methods

Fourier Transform Infrared Spectroscopy

The WineScan FT 120 instrument (Foss Deutschland, Hamburg, Germany) was used to generate the FTIR spectra. The Wine Scan is a task-specific Fourier Transform Infrared Interferometer for alcoholic beverages. It scans the full infrared spectrum. The instrument has been approved for wine analysis since 1996 with ready-to-use must and wine calibrations provided by the manufacturer (Patz et al. 2004). The conventional and part of the near-infrared range is scanned between 10.8 and 2 μm, which corresponds to the wavenumbers of 926 to 5,012 cm^{-1}. It acquires 1,060 data points for data analysis. The spectral regions of water absorption between 1,447 and 1,887 cm^{-1} and 2,971 and 3,696 cm^{-1} were eliminated to prevent noise being included in the calculation.

No prior preparation of the samples is required for spirit drinks and liqueurs. For sampling, the injection nozzle of the spectrometer is plunged directly into the sample. The sample is then sucked into the analyzer and thermostated at 40 °C, so that no external thermostating is necessary. After measurement in the sample cuvette, the whole system and tubes are automatically cleaned by a built-in cleaning system. The duration of the whole procedure including measurement and data analysis is less than 2 min.

Multivariate Data Analysis and Validation

As usual, the sample interferogram is Fourier transformed in the first step. Next, the water spectrum is divided from the sample spectrum to eliminate the background absorbance of water. In the third step, the sample spectrum is standardized using an equalizer sample, so that a transfer of calibrations between instruments is possible (e.g., the calibrations may be used in other laboratories that do not have the capabilities for reference analytics). The absorbance is calculated, and the multivariate data analysis is performed.

For quantitative determination from the FTIR spectra (applying partial least squares (PLS) regression), the standard software FT 120 v2.2.2 was used (Foss Deutschland, Hamburg, Germany). Before PLS regression, the appropriate wavelength ranges for the analytes were selected using the automatic filter selection tool of the FT 120 software, which applies multivariate data analysis. The optimal number of PLS factors was selected based on the first minimum of the standard error of cross-validation (SECV) to avoid overfitting. The statistical parameters were calculated using standard formulas (e.g., Esbensen 2001; Kessler 2006).

As we had two instruments available at our sites in Stuttgart and Karlsruhe, each calibration was exported to the other instrument; then, slope/intercept corrections were applied to adapt the calibration to the specific instrument and, finally, the calibrations were validated using independent samples (inter-laboratory validation).

Reference Procedures

For the determination of the total dry extract according to Commission Regulation (EEC) No. 2676/90 (European Commission 1990), the density of the original sample (ρ_S) and of the alcoholic distillate (ρ_A) have to be determined. The specific gravity d_r of the distillation residue has to be calculated by the following formula: $d_r = 1.00180(\rho_S - \rho_A) + 1.00000$. The total dry extract expressed in grams per liter

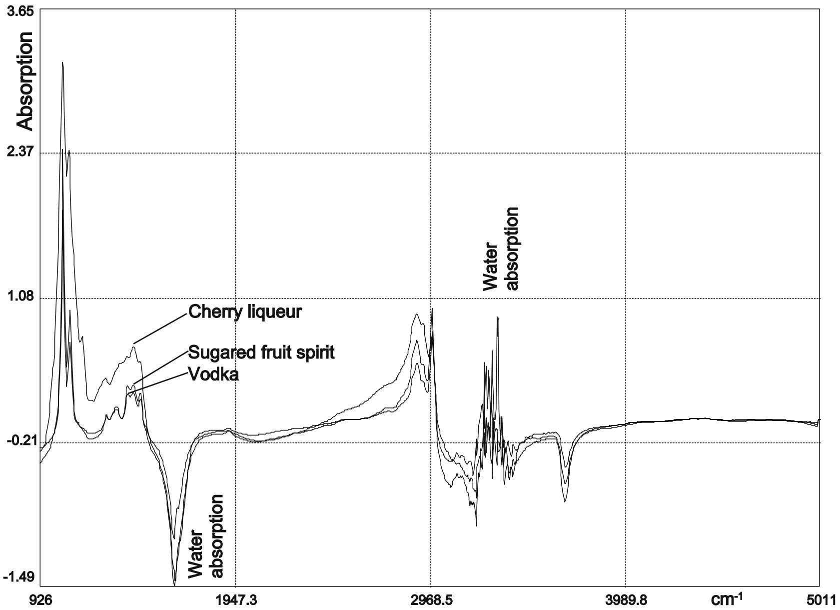

Fig. 1 FTIR spectra of three alcoholic beverages with different contents of total dry extract. The vodka was extract-free, the fruit spirit contained 10 g/l, and the cherry liqueur contained 410 g/l of total dry extract

Table 1 Spirits: reference data

	Calibration set			Validation set		
	n	Range	Mean, SD	*n*	Range	Mean, SD
Relative density	180	0.939–0.979	0.950±0.004	118	0.938–0.959	0.950±0.004
Alcohol (% vol)	180	30.26–53.03	40.37±2.34	118	36.01–46.86	40.29±1.95
Total dry extract (g/l)	180	0–39.7	1.81±5.77	118	0–35.7	8.06±8.18

was then looked up in the table for the calculation of the content total dry extract. The densities were determined using either oscillation-type density meters (Karlsruhe) or pycnometry (Stuttgart).

Results and Discussion

Calibration and Validation of the PLS Procedure

Water, ethanol, and many other compounds of alcoholic beverages contain absorptions of various functional groups in the infrared spectra. However, the constituents of spirit drinks are chemically very similar and therefore display similar and overlapped absorptions, which cannot be assigned to individual compounds; i.e., the spectra look very homogenous and cannot be interpreted conventionally (Fig. 1). Therefore, chemometric techniques have to be used to calibrate the instrument against the chemical reference method, which makes FTIR a secondary analytical technique.

The content of total dry extract leads to relatively large differences in the spectra, e.g., if the vodka is compared to the liqueur in Fig. 1. Therefore, we have decided at the beginning of our investigation to establish two different PLS calibrations: one for extract-free spirits or spirits with only low contents of TDE (<10 g/l; spirit calibration). This group comprises all kinds of spirits, like rum, vodka, brandy, whisky, fruit spirits, and tequila, which are—if at all—sugared only to round off the final taste of the product. The other calibration comprises highly sugared spirits and liqueurs with a TDE usually higher than 100 g/l (liqueur calibration). There are not many products in the market with a TDE between 20 and 100 g/l as they do not fit into one of the established product categories laid down in European Union Regulation (European Council 1989). Therefore, this range is not well described by our calibrations, and the analyst should decide in each individual case which calibration to use for such samples. In general, FTIR results in such cases with concentrations outside the calibration range should be verified by reference analytics.

Tables 1 and 2 illustrate information concerning the reference data. The used calibration sets had a higher bandwidth for every parameter than the validation sets. The results obtained through calibration and validation are shown in Tables 3 and 4. Clearly, the range of reference values encompasses the characteristic appraisal of a broad range of spirit drinks and beer. The values of coefficient of correlation (R^2), standard error of cross-validation, and standard error of prediction (SEP) indicate the precision achieved in calibration and validation. According to the criteria proposed by Shenk and Westerhaus (1996), an R^2 value greater than 0.90 indicates ‘excellent’ quantitative information, while a value between 0.7 and 0.9 is described as ‘good’. An R^2 value between 0.5 and 0.7 demonstrates good separation of samples into high, medium, and low groups, indicating that the calibration can only be used for screening purposes.

Statistical data for calibration of relative density and alcohol content were within expectations for the investigated products (Tables 3 and 4). The values of the intra-laboratory cross-validation could almost be reached with the inter-laboratory test set. For relative density, no repeatability is given in the official method, but the value of 0.0004 for spirits was well in line with the precision that can be reached with FTIR calibration of wine, according to the manufacturer. The standard error of cross-validation and the standard error of prediction did not differ much for spirits. However, for liqueurs, SEP was tenfold higher than the SECV for relative

Table 2 Liqueurs: reference data

	Calibration set			Validation set		
	n	Range	Mean, SD	*n*	Range	Mean, SD
Relative density	91	0.911–1.132	1.042±0.041	72	0.994–1.100	1.051±0.030
Alcohol (% vol)	91	14.33–60.04	26.96±9.11	72	13.17–36.51	24.48±6.91
Total dry extract (g/l)	91	69.4–409.6	211.1±74.2	72	99.7–339.8	211.3±67.8

Table 3 Spirits: validation results of the calibration set and the independent validation set

	Cross-validation (intra-laboratory)				Validation (inter-laboratory)	
	PLS factors	SECV	Repeatability	R^2	SEP	R^2
Relative density	5	0.0004	0.0001	0.9380	0.0006	0.9731
Alcohol (% vol)	5	0.1996	0.0927	0.9937	0.23	0.9859
Total dry extract (g/l)	8	0.4630	0.1207	0.9934	0.55	0.9954

The validation measurements were done on a second instrument in another laboratory.

density and threefold higher for alcohol. As liqueurs consist of many components, compared to spirits, the variety of the calibration set might not have covered all matrices in the validation set. Nevertheless, the results obtained are suitable for screening purposes.

Total dry extract, which was calibrated for the first time, showed a very good SECV of 0.46 g/l for spirits and 4.2 g/l for liqueurs. These values are equivalent to a relative error of 25% for spirits and 2.0% for liqueur when compared to the mean value of the calibration set. As to be expected, the results for liqueur are much more accurate due to higher contents of TDE in the samples. Contrary to the parameters relative density and alcohol, SEP did not differ much from SECV. Thus, transferring extract calibrations to other machines is easily possible by just performing a slope/intercept correction with about 10–15 samples.

Verified using inter-laboratory validation, it was found that excellent quantitative information is available for all parameters evaluated in this study. As expected, the standard errors of cross-validation are a bit lower than the standard error of prediction in the inter-laboratory validation. It is remarkable that the calibrations can be very simply transferred from one instrument to another.

Application to Spirit and Liqueur Analysis

The law for spirits is harmonized in the European Union (European Council 1989). Most spirits are allowed to be sweetened to round off the final taste of the product (usually up to a maximum of 10–20 g/l of sugar). Exemptions are German fruit spirits with protected geographical indications (e.g., Black Forest cherry spirit) that are not allowed to be sweetened. As the TDE is a very good indicator for illegal sweetening, the FTIR methods allow, for the first time, an efficient and economic control of this parameter. By the use of FTIR, we were able to more than double the number of analyzed samples per year. The time-consuming densimetric reference methods had to be applied only in conspicuous cases. FTIR screening can also cut sample preparation costs for conventional methods, as distillation is not needed for quantification of higher alcohols by gas chromatography if the TDE is lesser than 2 g/l.

For liqueur analysis, the advantage is even more evident as all samples must comply by law with the minimum sugar content of 100 g/l in the European Union (European Council 1989). In our experience, accurate reference results in liqueur analyses were only possible by experienced laboratory technicians (Lachenmeier et al. 2005a). However, using FTIR spectroscopy, untrained personnel could easily achieve accurate results, which were included in the inter-laboratory validation studies. Furthermore, handling of the often highly viscous liqueur samples requires a trained staff with lots of experience. In contrast, FTIR screening can be conducted even by inexperienced workers.

Besides TDE, the FTIR method is able to check the tolerance for labeling of alcoholic strength as well as density, which is a parameter for identity checks.

Conclusions

FTIR spectroscopy in the mid-infrared range in combination with PLS regression is nowadays an established procedure for the multicomponent screening in wine analysis (Patz et al. 1999, 2004; Nieuwoudt et al. 2004; Gishen and Holdstock 2000; Kupina and Shrikhande 2003).

Table 4 Liqueurs: validation results of the calibration set and the independent validation set

	Cross-validation (intra-laboratory)				Validation (inter-laboratory)	
	PLS factors	SECV	Repeatability	R^2	SEP	R^2
Relative density	5	0.0007	0.0001	0.9996	0.0078	0.9282
Alcohol (% vol)	7	0.1995	0.0552	0.9993	0.7472	0.9855
Total dry extract (g/l)	4	4.2100	0.5971	0.9975	7.5303	0.9864

The validation measurements were done on a second instrument in another laboratory.

We have shown that it is equally well suited for the analysis of relative density, alcohol, and total dry extract in spirits and liqueurs and offers considerable advantages when measured against conventional methods of analysis. Even high contents of total dry extract, leading to a viscosity that is demanding for official reference methods, is no handicap for FTIR sampling. As an efficient high-throughput tool (30–60 samples per hour), FTIR supplies simple and cost-effective screening of alcoholic beverages to check the legal requirements in the European Union. If the need arises, further quality classifications are possible from the FTIR spectra by use of principal component analysis (Lanchenmeier 2007).

References

Arvanitoyannis IS, Katsota MN, Psarra EP, Soufleros EH, Kallithraka S (1999) Trends Food Sci Technol10:321

Coimbra MA, Goncalves F, Barros AS, Delgadillo I 2002 J Agric Food Chem 50:3405

Esbensen K 2001 Multivariate data analysis in practice. CAMO Process AS Oslo, Norway

European Council (1989) Off J Europ Comm L160:1

European Commission (1990) Off J Europ Comm L272:1

European Commission (2000) Off J Europ Comm L333:20

Gishen M, Holdstock M (2000) Austr Grapegrow Winemak Ann Technol Issue 75

Kessler W (2006) Multivariate Datenanalyse. Wiley, Weinheim, Germany

Kupina SA, Shrikhande AJ 2003 Am J Enol Vitic 54:131

Lachenmeier DW (2005) Anal Bioanal Chem 382:1407

Lachenmeier DW (2007) Food Chem 101:825

Lachenmeier DW, Nerlich U (2006) Monatsschr Brauwissensch 59:114

Lachenmeier DW, Sviridov O, Frank W, Athanasakis C (2003) Deut Lebensm Rundsch 99:439

Lachenmeier DW, Burri PA, Fauser T, Frank W, Walch SG (2005a) Anal Chim Acta 537:377

Lachenmeier DW, Richling E, López MG, Frank W, Schreier P (2005b) J Agric Food Chem 53:2151

Lachenmeier DW, Walch SG, Kessler W (2006a) Eur Food Res Technol 223:261

Lachenmeier DW, Sohnius E-M, Attig R, López MG (2006b) J Agric Food Chem 54:3911

Nieuwoudt HH, Prior BA, Pretorius IS, Manley M, Bauer FF (2004) J Agric Food Chem 52:3726

Palma M, Barroso CG 2002 Talanta 58:265

Patz CD, David A, Thente K, Kürbel P, Dietrich H (1999) Vitic Enol Sci 54:80

Patz CD, Blieke A, Ristow R Dietrich H (2004) Anal Chim Acta 513:81

Shenk JS, Westerhaus MO (1996) Davies AMC, Williams P Near infrared spectroscopy: the future waves NIR Chichester, UK, p 198

Saiz-Abajo MJ, Gonzalez-Saiz JM, Pizarro C (2004a) J Agric Food Chem 52:7711

Saiz-Abajo MJ, Gonzalez-Saiz JM, Pizarro C (2004b) J Near Infrared Spectrosc 12:207

Triebel S, Sproll C, Reusch H, Godelmann R, Lachenmeier DW (2007) Amino Acids 33:451