

Analytical, Nutritional and Clinical Methods

Rapid quality control of spirit drinks and beer using multivariate data analysis of Fourier transform infrared spectra

Dirk W. Lachenmeier *

Chemisches und Veterinäruntersuchungsamt (CVUA) Karlsruhe, Weißenburger Str. 3, D-76187 Karlsruhe, Germany

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Abstract

Fourier Transform Infrared (FTIR) spectroscopy in combination with multivariate data analysis is introduced for the quality control and authenticity assessment of spirit drinks and beer in official food control. The spectra were measured using a FTIR interferometer, which is purpose-built for the analysis of alcoholic beverages and includes an injection unit for liquids with automatic thermostating of the sample. Only 2 min are required for FTIR measurement. For spirit drinks, no sample preparation is required at all. Carbon dioxide containing samples, such as beer were prepared by degassing.

Using the partial least squares (PLS) method, FTIR spectra were correlated with results from reference methods. During validation with an independent set of samples, strong correlation with the reference values and great accuracy were demonstrated for the spirit parameters density, ethanol, methanol, ethyl acetate, propanol-1, isobutanol and 2-/3-methyl-1-butanol ($R^2 = 0.90\text{--}0.98$), as well as for the beer parameters ethanol, density, original gravity and lactic acid ($R^2 = 0.97\text{--}0.98$). Further beer parameters like pH, bitterness unit, and EBC colour ($R^2 = 0.63\text{--}0.75$) showed lower correlation and accuracy, but can be determined semi-quantitatively in the context of a screening analysis.

In addition, principal component analysis (PCA) was applied to the analysis results. A differentiation of deteriorated fruit spirits distilled from microbiologically spoiled mashes was possible.

The results obtained suggest that FTIR is a useful tool in the quality control of alcoholic beverages, since quantitative determination of essential compounds as well as chemometric classification are simultaneously possible. Through use of FTIR screening, the majority of all samples were classified as being in conformance with legal and quality requirements. Only conspicuous analysis results (approx. 12% of all samples), which exceeded the predefined limits, must be confirmed by complex and labour-intensive reference analyses. In comparison to conventional methods, FTIR spectroscopy is faster and only requires a simple sample preparation.

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1. Introduction

In the context of quality control of alcoholic beverages in distilleries and breweries or in official food control, a range of different analytical methods has to be used. The alcoholic strength is usually determined by reference methods like distillation and pycnometry or by analytical instruments, which combine oscillation-type densimetry and

refractometry (Lachenmeier, Burri, Fauser, Frank, & Walch, 2005a; Lachenmeier, Sviridov, Frank, & Athanasakis, 2003). In addition to organoleptical and microbiological examination for a standard beer analysis, EBC colour and bitterness unit are assessed by photometry. Organic acids are determined using enzymatic analyses or liquid chromatography. For a standard spirit drink analysis, higher alcohols and other volatile compounds are determined using gas chromatography. Therefore, by means of these traditional techniques, beverage analysis is time-consuming and expensive. Increasing requirements and cost-pressures nowadays force both government and

* Tel.: +49 721 926 5434; fax: +49 721 926 5539.

E-mail address: lachenmeier@web.de.

commercial food-testing laboratories to replace these traditional reference methods with faster and more economical systems.

A first possibility to optimise beer analysis was the use of high-resolution nuclear magnetic resonance (NMR) spectroscopy and multivariate analysis (Duarte, Barros, Almeida, Spraul, & Gil, 2004; Lachenmeier et al., 2005b), which is currently restricted by the extremely high cost of instruments. The less expensive Fourier transform infrared (FTIR) spectroscopy has shown some potential for specific tasks like the classification of brandy or tequila (Palma & Barroso, 2002; Lachenmeier, Richling, López, Frank, & Schreier, 2005c). In this study, FTIR in combination with Partial Least Squares (PLS) regression is evaluated for the first time as a complete multi-component screening method for spirit drinks and beer in the context of official food control.

2. Materials and methods

2.1. Sample collective

A total of 535 spirit drinks and 461 beers submitted to the Chemical and Veterinary Investigation Laboratory of Karlsruhe were analysed. This institute covers the German districts of Karlsruhe in North Baden (spirits and beer) and Freiburg in South Baden (beer) and participates in official food and animal health control in the German Federal State of Baden-Württemberg, an area with approximately 22,500 distilleries (80% of all German distilleries) and 169 breweries. The sampling was conducted by local authorities, either directly from the distilleries and breweries, or from retail trade.

The beer sample collective comprised a wide range of different beer styles including 322 bottom-fermented (e.g. Pilsener, Lager and Export type) and 139 top-fermented (e.g. wheat, Alt, ale type) beers. Three hundred and fifty-four beer samples were of light colour, 107 were dark or black. Three hundred and eighty samples were standard “Voll beers” (original gravity 11–16%), 81 samples were “Stark beer” or “Bock beer” type (original gravity >16%).

The spirit drink collective included 273 fruit spirits, 73 vodkas, 25 rums, 23 brandies, 86 tequilas, 18 whiskeys, and 19 absinthes with alcoholic strengths varying between 25 and 73%vol.

2.2. Fourier transform infrared (FTIR) spectroscopy

The WineScan FT 120 instrument (Foss Deutschland, Hamburg, Germany) was used to generate the FTIR spectra. The WineScan 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, Blicke, Ristow, & Dietrich, 2004). The conventional and part of the near-infrared range is scanned between 10.8

and 2 μm , which corresponds to the wavenumbers of 926–5012 cm^{-1} . It acquires 1060 data points for data analysis. The spectral regions of water absorption between 1447–1887 cm^{-1} and 2971–3696 cm^{-1} were eliminated to prevent noise being included in the calculation.

No prior preparation of the samples is required for spirit drinks. The beer samples were degassed by filtration through fluted filter paper and subsequent ultrasonication for 10 min. For sampling, the injection nozzle of the spectrometer is plunged directly into the sample. The sample is then thermostated at 40 °C in the analyser, 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.

2.3. Multivariate data analysis

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 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 PLS regression), the standard software FT 120 v2.2.2 was used (Foss Deutschland, Hamburg, Germany). Prior to 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 ranges were selected based on the correlation between the reference results for the component in question, and the sample variation in each wavenumber in the spectra by a non-disclosed algorithm of Foss. Initial calibrations for each analyte provided by the manufacturer were used and adapted to the sample collective. The optimal number of PLS factors was selected based on the lowest standard error of cross-validation (SECV). The statistical parameters were calculated using standard formulas (e.g. Ref. (Esbensen, 2001)).

2.4. Validation

Because the Foss FT 120 software only allows cross-validation, the spectra were exported to the software Unscrambler v9.2 (CAMO Process AS, Oslo, Norway) for test-set validation to verify and validate the results. The selection of sub-groups as test-sets was uncritical because of the high number of samples. One third of the samples was selected randomly. Of course, it was assured that the total variance was covered in both sets. In this case, the optimal number of PLS factors was selected based on the lowest standard error of prediction (SEP). Besides for PLS regression, the Unscrambler software was used

for principal component analysis (PCA) to spot outliers and to classify samples.

2.5. Reference procedures

In all cases, there was a full organoleptical and chemical examination. The beer analysis included the determination of relative density, ethanol and original gravity using refractometry and oscillation-type densimetry, the determination of lactic acid using enzymatic analysis (R-Biopharm, Darmstadt, Germany), as well as the determination of pH, bitterness unit and EBC colour using standard procedures. The classic method of Weber was used to assess the addition of roasted malt beer concentrate (so-called “colouring beer”), which may be used for colouration of dark beer (Weber, 1973). For spirit drinks, alcoholic strength and density were determined using steam-distillation and oscillation-type densimetry (Lachenmeier et al., 2003; Lachenmeier et al., 2005a). The volatile compounds methanol, ethyl acetate, propanol-1, isobutanol and 2-/3-methyl-1-butanol were determined using gas chromatography with flame ionisation detection (European Commission, 2000).

3. Results and discussion

3.1. Detection and removal of outliers

Before the actual data analysis, the sample collective was checked for outliers to obtain robust models. First, the FTIR spectra were checked visually for abnormal spectra, which may result from incorrect sampling with air bubbles. Fig. 1 shows an example of this approach. Two

spectra diverged from the main collective spectra of the beer samples. The divergence could be explained easily: The first spectrum was a beer mixed with lemonade, which was integrated in the sample set by mistake. The second abnormal spectrum was an alcohol-free beer. Second, PCA was applied to the spectra. Fig. 2 shows that some further outliers can be detected by this approach. These samples were also conspicuous by their high residual variance, which could be attributed to the fact that these samples were microbiologically spoiled with large bacteria counts. Only such obvious erroneous samples or samples

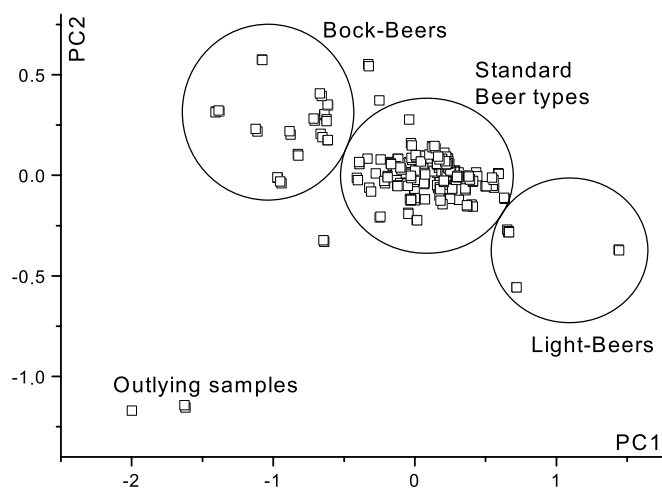


Fig. 2. PCA approach for outlier detection. Further outliers can be eliminated by using PCA on the whole spectral range, e.g. samples with incorrect sampling (air bubbles in the measuring cell). Besides, a clustering according to the original gravity content can be noted.

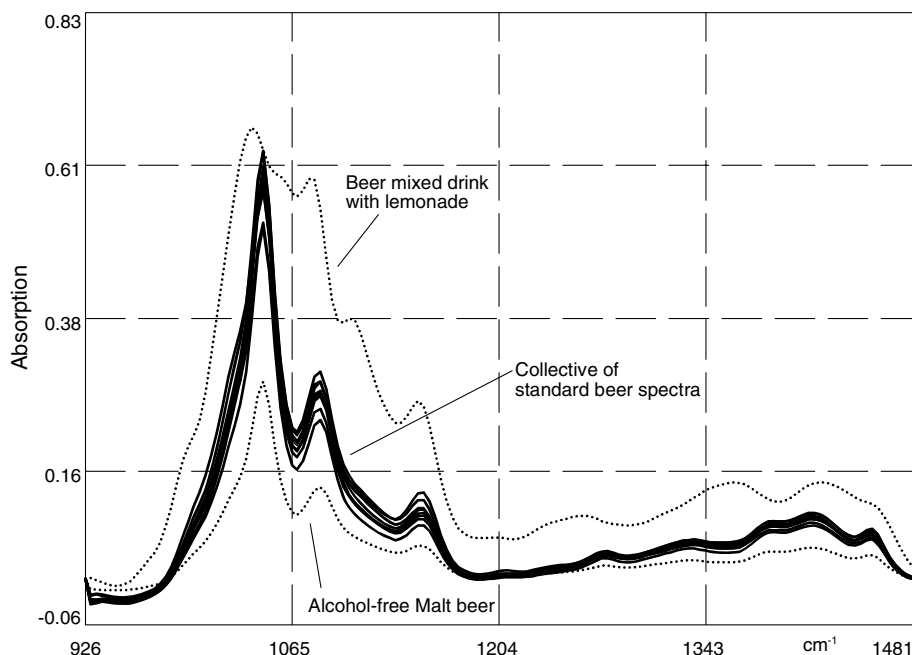


Fig. 1. Spectral approach for outlier detection. The FTIR spectra of beer samples in the characteristic range between 926 and 1481 cm^{-1} clearly include two abnormal spectra, which could be identified as a beer mixed with lemonade and an alcohol-free beer erroneously integrated into the sample set.

with measurement errors were removed in order to gain robust models, which span a high variation and can handle the complete sample collective.

3.2. 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 or beer are chemically very similar and therefore display similar and overlapped absorptions, which cannot be assigned to individual compounds, i.e. the collective of beer and spirit drink spectra looks very homogenous and cannot be interpreted conventionally (Fig. 3). Therefore, chemometric techniques have to be used to calibrate the instrument against the chemical reference method, which makes FTIR a secondary analytical technique. Tables 1 and 2 illustrate information concerning the reference data and the results obtained through calibration and valida-

tion. 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 (SECV) and standard error of prediction (SEP) indicate the precision achieved in calibration and validation. According to the criteria proposed by Shenk and Westerhaus (Shenk & 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.

Verified using test-set validation, it was found that excellent quantitative information is available for all parameters in the spirit drink analysis. As expected, the standard errors of cross validation are a bit lower than the standard error of prediction in the test-set validation. In general, the cross validation approach also showed a higher number of PLS

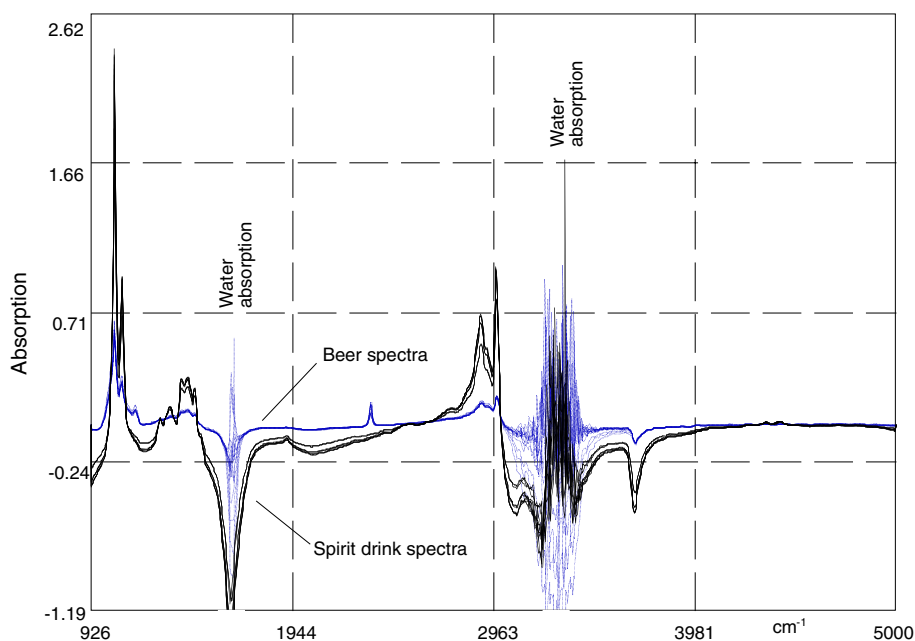


Fig. 3. FTIR spectra of 10 typical beer samples (dotted lines) and 10 typical spirit drinks (black lines).

Table 1
Reference data and validation results for spirit drinks

	Reference data		Cross validation (Foss FT 120) using selected wavenumber ranges				Test-set validation (Unscrambler) using full spectrum			
	Range	Mean, SD	PLS factors	SECV	Repeatability	R^2	PLS factors	SEP	Mean Bias	R^2
Relative density	0.875–1.037	0.951 ± 0.015	6	0.0007	0.0001	0.999	5	0.0013	0.0001	0.955
Alcohol [%vol]	25.0–78.1	41.2 ± 6.3	5	0.17	0.02	0.998	5	0.21	−0.03	0.940
Methanol [g/hl alc.]	0–1272	313 ± 308	13	23.5	17.2	0.997	5	36.9	−15.5	0.981
Ethyl acetate [g/hl alc.]	0–710	122 ± 141	8	29.9	18.3	0.994	6	40.7	7.2	0.954
Propanol-1 [g/hl alc.]	0–3184	205 ± 378	8	40.8	16.6	0.989	6	47.3	0.4	0.953
Isobutanol [g/hl alc.]	0–216	43 ± 34	10	22.4	15.8	0.975	8	24.7	1.9	0.943
2-/3-Methyl-1-butanol [g/hl alc.]	0–454	130 ± 93	6	36.0	3.08	0.940	9	35.8	0.1	0.901

Table 2
Reference data and validation results for beer

	Reference data		Cross validation (Foss FT 120) using selected wavenumber ranges				Test-set validation (Unscrambler) using full spectrum			
	Range	Mean, SD	PLS factors	SECV	Repeatability	R ²	PLS factors	SEP	Mean Bias	R ²
Relative density	1.001–1.046	1.011 ± 0.005	5	0.0004	0.0001	0.995	4	0.0006	–0.0001	0.983
Alcohol [%vol]	0.2–9.5	5.3 ± 1.5	5	0.10	0.02	0.972	3	0.21	–0.06	0.973
Original gravity [%mas]	4.61–20.65	12.67 ± 2.71	5	0.29	0.09	0.977	2	0.44	–0.10	0.976
pH	3.96–4.74	4.39 ± 0.18	4	0.03	0.005	0.971	5	0.11	–0.001	0.705
Lactic acid [mg/l]	28–3454	216 ± 356	9	19.08	9.80	0.956	6	78.52	3.91	0.979
Bitterness unit	5.1–36.2	19.2 ± 7.1	9	4.37	0.44	0.709	6	5.18	–0.11	0.625
EBC colour	5–114	38 ± 28	11	19.80	4.15	0.790	7	19.10	2.19	0.747
Quotient after Weber	0.09–1.78	0.64 ± 0.38	9	0.14	0.06	0.825	11	0.25	0.05	0.669
Extinction after Weber	0.02–0.27	0.09 ± 0.06	10	0.02	0.006	0.824	11	0.027	0.004	0.862

factors than the test-set validation. In this case, cross validation appeared to give slightly over-optimistic estimates of the prediction errors, and the results of test-set validation were, therefore, used for further evaluation of the models.

For beer analysis, excellent quantitative information was only available for the parameters density, alcohol, original gravity and lactic acid, whereas the other parameters showed inferior correlation and higher prediction errors. The reason for the lower performance of the method for beer compared to spirit drinks is the fact that the beer matrix is more complicated (e.g. influenced by residual contents of carbon dioxide or yeast particles).

The fact that calibration methods will never perform better than the reference method must also be considered. It was our aim to include all classes of spirit drinks and beer into one calibration, which leads to higher prediction errors compared with calibrations for sub-groups (e.g. only for fruit spirits). The advantage of this approach is that the PLS models proved to be very robust and can be used universally for all alcoholic beverages, which are submitted for analysis. There is also no decision-step prior to analysis, which PLS model has to be used, so that the FTIR screening analysis can be accomplished even by untrained technical personnel.

FTIR should be treated as a fast, reliable screening method. Due to the calibration sets and not to the FTIR technique itself, the quantitative results have not enough confidence for official complaints against manufacturers. In this regard, the results should be confirmed using reference methods.

3.3. Application to beer analysis

The oldest food regulation in the world is the German beer purity law of 1516, which is still in-force today. It states that only barley malt, hops, yeast and water are allowed to be used for beer production. Furthermore, beer categories depending on the content of original gravity are defined. Original gravity describes the concentration of solids in the unfermented wort, which the beer is made from. Standard beers have an original gravity of at least 11%.

Beer with original gravity below 11% has to be labelled. Beers named Starkbier or Bockbier are required to have an original gravity of 16% or more. In addition, beer is taxed upon its original gravity, therefore the determination of this parameter is very important in food control. Traditionally it is calculated from real extract and alcohol content of the beer. The second parameter to be quantified in the context of the official food monitoring is the ethanol concentration. By directive in the European Union, maximum tolerances of the indication of the alcoholic strength in the labelling are specified. For beers having an alcoholic strength not exceeding 5.5%vol the tolerance is 0.5%vol, whereas for beers above 5.5%vol the tolerance is 1%vol (European Commission, 1987).

The FTIR-PLS models allow the efficient control of the legal tolerances for alcohol and original gravity with sufficient accuracy. The SEP for alcohol (0.2%vol) is below the specified labelling tolerances. The SEP of original gravity (0.4%mas) is comparable to the standard error of the reference procedure (0.2%mas). None of the beers was false-positive out of the tolerance either for alcohol or original gravity.

Lactic acid, which is produced by beer spoilage bacteria, can be used as an indicator for production hygiene. Beer normally contains up to 200 mg/l of lactic acid (Uhlig & Gerstenberg, 1993), higher concentrations provide an indication for the presence of lactic acid bacteria as *Lactobacillus* or *Pediococcus*. The FTIR procedure allows to select conspicuous samples which may be analysed selectively for beer spoilage by microbiological analysis.

The correlation between the FTIR spectra and the pH value is relatively low, but the SEP of 0.1 pH units is adequate to check ample deviations of the normal pH range, which may occur if residues of alkaline or acid disinfectants contaminate the beer.

Lower correlation was also gained for the parameters, which characterize the bitter hop flavour or the colour of beer. In the case of the bitterness unit with an SEP of 5.2 units, however, a classification of the beers into groups with high and low values is possible, so that it can be checked if Pilsener beers have the required hop dosage for the distinct hop flavour and pronounced bitter taste. Such a classification is also possible for the colour

parameters. The FTIR method allows at least to classify the samples according to their EBC colour (e.g. light- and dark-coloured beers). The indices of the method after Weber allow to assess if roasted malt beer concentrate was used in the production process. This method is rather popular in Germany as it allows to convert light beer types to dark beer types, without the need to establish a separate brewing process using coloured malts (Riese, 1997). Often, the addition of roasted malt beer concentrate is not labelled in the ingredients list. The FTIR method allows to select conspicuous samples, for confirmation by size-exclusion chromatography (Schöne, 1973; Coghe, Adriaenssens, Leonard, & Delvaux, 2004).

3.4. Application to spirit drink analysis

The law for sprits is harmonized in the European Union. Minimum requirements for alcoholic strength and volatile congeners must be checked. Maximum contents for methanol or hydrocyanic acid are given (European Council, 1989). The tolerance for labelling of alcoholic strength is very strict with 0.3%vol (European Commission, 1987). The density and alcoholic strength measurements were highly accurate. The SEP for alcohol was 0.2%vol, which is below the labelling tolerance of 0.3%vol. The volatile compounds show higher SEP values between 25 and 47 g/hl alc. because the calibration encompasses a very wide range, e.g. up to 3184 g/hl alc. for propanol-1. In practice, the calibration allows the efficient control of all legal requirements. As with every screening procedure, the cut-off levels for confirmatory analyses should be adjusted under consideration of the SEP values to avoid false negative results. For example, a cut-off level of 900 g/hl alc. to check the maximum methanol content of 1000 g/hl alc. in fruit spirits would avoid false-negative results on the 5% significance level.

The quantitative results of the PLS regression (i.e. the concentration of the volatile congeners methanol, ethyl acetate, propanol-1, isobutanol and 2-/3-methyl-1-butanol) can be further interpreted using PCA. As example, a sub-collective comprising stone-fruit spirits was analysed (Fig. 4). The first two PCs describe 95% of the total variability of the data. The variance in PC1 discriminates the main collective of samples from four anomalous samples. From the loadings, it can be seen that propanol-1 is the main influence factor for this discrimination. This deviation with high contents of propanol-1 over 600 g/hl alc. could be confirmed using gas chromatography and the samples were judged to be distilled from micro-biologically spoiled mashes according to the criteria of Frank (1983).

A second discrimination can be seen on PC2, which is attributable to the methanol content. Spirits distilled from *Prunus avium* L. (cherry) can be distinguished from spirit distilled from *Prunus domestica* L., however, a differentiation between the sub-species *domestica* (plum) and *syriaca* (mirabelle) was not possible.

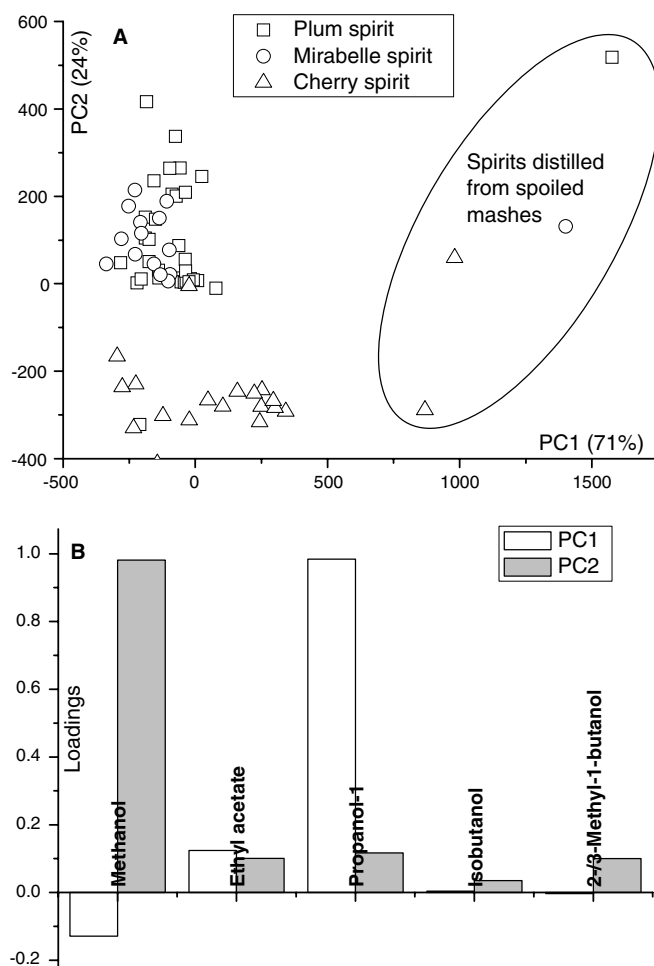


Fig. 4. Principal component analysis of the quantitative results of fruit spirits. The PCA scores plot (A) and the corresponding loadings (B) are shown.

3.5. Comparison with other screening methods

During the past 10 years, near-infrared (NIR) spectroscopy was the only spectroscopic technique available for the screening analysis of alcoholic beverages (Teass, Byrnes, & Valentine, 1995; Maudoux, Yan, & Collin, 1998; Cejka et al., 2000; Damberg, Kambouris, Francis, & Gishen, 2002; Barboza & Poppi, 2003). Due to the low sensitivity, the application range was limited to the principal constituents (e.g. alcoholic strength, original gravity), so that NIR did not find a wide application in food testing laboratories. The determination of minor constituents (e.g. bitterness) was only possible after evaporation of water (dry extract spectroscopy) (Chandley, 1993). Only in the last years, FTIR spectroscopy in the mid-infrared range did arise interest because the spectra are more specific and clear response peaks can be observed in comparison to NIR. FTIR/PLS is nowadays an established procedure for the multicomponent screening in wine analysis (Patz, David, Thente, Kürbel, & Dietrich, 1999; Gishen & Holdstock, 2000; Kupina & Shrikhande, 2003; Patz et al., 2004; Nieuwoudt, Prior, Pretorius, Manley,

Table 3
Comparison between traditional reference procedures, NMR and FTIR screening

	Reference procedures	NMR	FTIR
Sample preparation	Degassing (beer) Distillation	Degassing (beer) Buffer addition	Degassing (beer)
Analysis	Oscillation-type densimetry, refractometry, gas chromatography, enzymatic analysis, photometry	NMR/PLS (12 min)	FTIR/PLS (2 min)
Total time	Days until final result	12 min	2 min
Costs	High	High	Low
Applicability	Accurate quantitative determination	Selective and sensitive qualitative and quantitative analysis	Fast semi-quantitative determination to select conspicuous samples for confirmatory analysis

& Bauer, 2004). In contrast to NIR, the analysis of minor components like higher alcohols in spirit drinks or bitterness unit and lactic acid in beer is possible using FTIR with satisfactory accuracy.

Much richer information is provided using ^1H NMR in comparison to NIR or FTIR. The NMR spectra of beer samples showed distinct signals for more than 30 components including water, ethanol, higher alcohols, organic acids, amino acids and fatty acids (Duarte, Barros, Belton, Righelato, Spraul, Humpfer & Gil, 2002; Duarte et al., 2003; Gil et al., 2003; Gil et al., 2004; Lachenmeier, Frank, Humpfer, Schäfer, Keller, Mörtter & Spraul, 2005). NMR showed, therefore, lower SEP values than the corresponding FTIR procedure. A comparison between the FTIR and NMR screening procedures and the reference methods is given in Table 3. In a cost-benefit calculation, FTIR appears so far as the most advantageous screening method because of the lower investment and operational costs. After the establishment of the FTIR calibrations, the procedure was used for real screening of all submitted samples. Only 12% of the samples with conspicuous results had to be confirmed using reference analytics, which led to a total cost reduction of 58%.

4. Conclusion

FTIR/PLS offers considerable advantages when measured against conventional methods of analysis and will acquire increasing importance as an efficient high-throughput tool for screening alcoholic beverages (30 samples/hour). It supplies simple and cost-effective control of the legal parameters like ethanol, volatile congeners, and original gravity. In addition to quantitative PLS analysis, PCA classification for authenticity control is possible. With information gained by FTIR screening, decisions can be made as to whether additional analyses (with more time-consuming and expensive, but more accurate, standard procedures) are required.

In the future, further quality-relevant parameters can be calibrated (e.g. sulphurous acid for new EU allergen labelling rules, or microbial counts for beer).

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References

- Barboza, F. D., & Poppi, R. J. (2003). Determination of alcohol content in beverages using short-wave near-infrared spectroscopy and temperature correction by transfer calibration procedures. *Analytical and Bioanalytical Chemistry*, 377(4), 695–701.
- Cejka, P., Kellner, V., Culík, J., Jurková, M., Horák, T., & Poledníková, M. (2000). Determining the original gravity using near-infrared spectrometry and cryoscopy. *Monatsschrift für Brauwissenschaft*, 53(11–12), 223–228.
- Chandley, P. (1993). The application of the DESIR technique to the analysis of beer. *Journal of Near Infrared Spectroscopy*, 1(3), 133–139.
- Coghe, S., Adriaenssens, B., Leonard, S., & Delvaux, F. R. (2004). Fractionation of colored maillard reaction products from dark specialty malts. *Journal of the American Society of Brewing Chemists*, 62(2), 79–86.
- Damberg, R. G., Kambouris, A., Francis, I., & Gishen, M. (2002). Rapid analysis of methanol in grape-derived distillation products using near-infrared transmission spectroscopy. *Journal of Agricultural and Food Chemistry*, 50(11), 3079–3084.
- Duarte, I., Barros, A., Belton, P. S., Righelato, R., Spraul, M., & Humpfer, E. (2002). High-resolution nuclear magnetic resonance spectroscopy and multivariate analysis for the characterization of beer. *Journal of Agricultural and Food Chemistry*, 50(9), 2475–2481.
- Duarte, I. F., Barros, A., Almeida, C., Spraul, M., & Gil, A. M. (2004). Multivariate analysis of NMR and FTIR data as a potential tool for the quality control of beer. *Journal of Agricultural and Food Chemistry*, 52(5), 1031–1038.
- Duarte, I. F., Godejohann, M., Braumann, U., Spraul, M., & Gil, A. M. (2003). Application of NMR spectroscopy and LC-NMR/MS to the identification of carbohydrates in beer. *Journal of Agricultural and Food Chemistry*, 51(17), 4847–4852.
- Esbensen, K. (2001). *Multivariate data analysis in practice* (5th ed.). Oslo, Norway: CAMO Process AS.
- European Commission (1987). Commission Directive (87/250/EEC) on the indication of alcoholic strength by volume in the labelling of alcoholic beverages for sale to the ultimate consumer. *Official Journal of the European Communities*, L113, 57–58.

- European Commission (2000). Commission Regulation (EC) No 2870/2000 laying down Community reference methods for the analysis of spirits drinks. *Official Journal of the European Communities*, L333, 20–46.
- European Council (1989). Council Regulation (EEC) No 1576/89 laying down general rules on the definition, description and presentation of spirit drinks. *Official Journal of the European Communities*, L160, 1–17.
- Frank, W. (1983). Composition of commercial Cherry brandy. *Branntweinwirtschaft*, 123, 278–282.
- Gil, A. M., Duarte, I., Cabrita, E., Goodfellow, B. J., Spraul, M., & Kerssebaum, R. (2004). Exploratory applications of diffusion ordered spectroscopy to liquid foods: an aid towards spectral assignment. *Analytica Chimica Acta*, 506(2), 215–223.
- Gil, A. M., Duarte, I. F., Godejohann, M., Braumann, U., Maraschin, M., & Spraul, M. (2003). Characterization of the aromatic composition of some liquid foods by nuclear magnetic resonance spectrometry and liquid chromatography with nuclear magnetic resonance and mass spectrometric detection. *Analytica Chimica Acta*, 488(1), 35–51.
- Gishen, M., & Holdstock, M. (2000). Preliminary evaluation of the performance of the Foss WineScan FT120 instrument for the simultaneous determination of several wine analyses. *The Australian Grapegrower and Winemaker*, Ann. Technol. Issue, 75–81.
- Kupina, S. A., & Shrikhande, A. J. (2003). Evaluation of a Fourier transform infrared instrument for rapid quality-control wine analyses. *American Journal of Enology and Viticulture*, 54(2), 131–134.
- Lachenmeier, D. W., Burri, P. A., Fauser, T., Frank, W., & Walch, S. A. (2005a). Rapid determination of alcoholic strength of egg liqueur using steam distillation and oscillation-type densimetry with peristaltic pumping. *Analytica Chimica Acta*, 537(1–2), 377–384.
- Lachenmeier, D. W., Frank, W., Humpfer, E., Schäfer, H., Keller, S., & Mörtter, M. (2005b). Quality control of beer using high-resolution nuclear magnetic resonance spectroscopy and multivariate analysis. *European Food Research and Technology*, 220(2), 215–221.
- Lachenmeier, D. W., Richling, E., López, M. G., Frank, W., & Schreiber, P. (2005c). Multivariate analysis of FTIR and ion chromatographic data for the quality control of tequila. *Journal of Agricultural and Food Chemistry*, 53(6), 2151–2157.
- Lachenmeier, D. W., Sviridov, O., Frank, W., & Athanasakis, C. (2003). Schnellbestimmung des Alkoholgehaltes in Emulsionslikören und anderen Spirituosen mittels Wasserdampfdestillation und Biegeschwinger. *Deutsche Lebensmittel-Rundschau*, 99(11), 439–444.
- Maudoux, M., Yan, S. H., & Collin, S. (1998). Quantitative analysis of alcohol, real extract, original gravity, nitrogen and polyphenols in beer using NIR spectroscopy. *Journal of Near Infrared Spectroscopy*, 6(A), 363–366.
- Nieuwoudt, H. H., Prior, B. A., Pretorius, I. S., Manley, M., & Bauer, F. F. (2004). Principal component analysis applied to Fourier transform infrared spectroscopy for the design of calibration sets for glycerol prediction models in wine and for the detection and classification of outlier samples. *Journal of Agricultural and Food Chemistry*, 52(12), 3726–3735.
- Palma, M., & Barroso, C. G. (2002). Application of FT-IR spectroscopy to the characterisation and classification of wines, brandies and other distilled drinks. *Talanta*, 58(2), 265–271.
- Patz, C. D., Blicke, A., Ristow, R., & Dietrich, H. (2004). Application of FT-MIR spectrometry in wine analysis. *Analytica Chimica Acta*, 513(1), 81–89.
- Patz, C. D., David, A., Thente, K., Kürbel, P., & Dietrich, H. (1999). Wine analysis with FTIR spectrometry. *Viticultural and Enological Sciences*, 54(2–3), 80–87.
- Riese, J. C. (1997). Colored beer as color and flavor. *MBBA Technical Quarterly*, 34(2), 91–95.
- Schöne, H. J. (1973). Detection of colouring in beer. *Brauwissenschaft*, 26(11), 344–351.
- Shenk, J. S., & Westerhaus, M. O. (1996). Calibration the ISI way. In A. M. C. Davies & P. Williams (Eds.), *Near Infrared Spectroscopy: The future waves*. Chichester, UK: NIR Publications.
- Teass, H. A., Byrnes, J., & Valentine, A. (1995). Full diameter near-infrared analyzer measuring ethyl alcohol in breweries. *Brauwelt International*, 184–186.
- Uhlig, R., & Gerstenberg, H. (1993). Über den Milchsäuregehalt infizierter Biere. *Brauwelt*, 133(7–8), 280–286.
- Weber, O. (1973). Analytische Anhaltspunkte zur Erkennung umgefärbter Biere. *Lebensmittelchemie und gerichtliche Chemie*, 27, 190–197.