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Comparison of Different Approaches to Rapid Screening of Headspace Samples: Pros and Cons of Using MS-Based Electronic Noses versus Fast Chromatography

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ABSTRACT

In recent years there has been a growing demand on fast screening systems for classification of samples using their volatile composition. Typically, these samples can be analyzed by either static headspace or thermal desorption analysis. Several different approaches are possible, but common to many of the systems is that a chemometrics software package is used to explore and classify the data. The present paper compares three instrument configurations: a “Fast” GC system, an “e-nose” headspace mass spectrometer, and a conventional headspace GC-MS, which can also be used as an e-nose or Fast GC. This paper will discuss these three approaches to rapid sample classification, illustrating the differences using typical commercial examples.

The three different approaches all have pros and cons that make them more or less suitable for any given application. The Fast GC and the conventional GC-MS have the advantage of providing complete chromatograms with separation of compounds. The GC-MS is the most versatile system because it can be used for both liquid and headspace measurements. In addition the headspace GC-MS configuration can also be used as an e-nose or in a Fast GC mode. As long as no separation is done, the e-nose and the headspace GC-MS in the e-nose mode have similar throughput (2 to 4 minutes per sample) and the Fast GC has the longest analysis time (approximately 11 minutes from sample to sample). When cost is a factor, Fast GC is the least expensive, while the headspace GC-MS with e-nose capabilities is the most expensive system.

INTRODUCTION

In quality control applications throughput is a key property for instrumental analysis. In food and flavor applications headspace analysis is the most commonly used technique to analyze the volatile composition of samples. This study compares three different approaches to rapid headspace screening. The Gerstel ChemSensor is a mass spectrometer based electronic nose that appears ideal for such applications. However, the approach of avoiding separation and subsequent analysis of the fingerprint mass spectrum may be a compromise in accuracy and sensitivity. Therefore this approach has to be compared to the analysis of the complete chromatographic trace. In order to increase the throughput the chromatography has to be performed using short columns with small inner diameters in conjunction with high column head pressures and fast oven heating rates. This technique is called Fast or Flash Chromatography. For automation of data evaluation for all techniques, we used the same chemometrics package with minor modifications when needed.

In order to compare the power of the different techniques three different instrument configurations were chosen and two different analysis rounds were performed. The first round compared the discrimination power between different samples while the second round was performed to test accuracy by evaluating the ability to detect known false samples.

EXPERIMENTAL

Samples. To evaluate the different approaches mainly fruit flavor samples were used in this study. This sample type was chosen because of the high alcohol content in the matrix that is known to cause chromatographic problems. The flavors typically contained ethanol (EtOH) or propylene glycol (PPG) as carrier alcohols. The experiment was divided into two rounds. In round 1, 19 different flavor types were analyzed (mainly one lot per sample type) to evaluate the discrimination efficiency of the different approaches (Table 1). In round 2 four different flavor types were used (Table 2). In this case we had samples from different good lots plus known false samples that were used for predictions.

Table 1. Samples used in the discrimination efficiency experiment (training set).

No.	Flavor	Supplier	Solvent
3	Strawberry	Q	EtOH
4	Strawberry	S	PPG
5	Strawberry	Z	PPG
6	Strawberry	Q	EtOH
7	Strawberry	Q	PPG
8	Strawberry	Q	PPG
9	Strawberry	Q	EtOH
10	Strawberry	X	EtOH
11	Strawberry	Q	PPG
12	Strawberry	Q	EtOH
13	Strawberry	Q	EtOH
14	Strawberry	Q	EtOH
15	Strawberry	G	EtOH
16	Blueberry	Q	PPG
17	Forest Fruit	Q	EtOH
18	Blackberry	Q	EtOH
19	Raspberry	Q	PPG
20	Forest Berry	Q	PPG
21	Tutti Frutti	Q	EtOH

Table 2. Samples used in the prediction experiment (testing set).

Flavor	Good lots	Bad lots
Apple	2	2
Apricot	4	2
Cream	1	1
Citrus	3	3

Instrumentation. Three different instrument configurations were used in this study. These were a GC, a GC-MS and an electronic nose.

GC. The GC (6890, Agilent Technologies) was equipped with a headspace unit (MPS 2, Gerstel) and FID. A DB-Wax Column (10 m x 0.10 mm x 0.20 µm) was used for separation. The inlet (CIS 4, Gerstel) was set to the hot split mode (250°C, 30:1) and the EPC pneumatics was set to the constant flow mode (0.7 mL/min He). The GC oven had an initial temperature of 50°C and was ramped at 55°C/min to a final temperature of 230 °C (1 min). Headspace injections were performed every 10.5 min due to a 5 min oven cool down.

GC-MS. The GC-MS was a Headspace ChemSensor System consisting of a headspace unit (MPS 2, Gerstel) and a GC-MS (6890-5973N, Agilent Technologies). This instrument was used for conventional headspace GC-MS analysis as well as Fast GC-MS and Headspace ChemSensor mode. Conventional GC-MS measurements were performed using a DB-Wax column (30 m x 0.25 mm x 0.25 µm) while later a column for Fast GC use was installed (DB-Wax, 10 m x 0.10 mm x 0.20 µm). The MSD was used in scan mode (35 – 200 amu). The scan rate was at 6 scans/sec for conventional GC-MS and at 11 scans/sec for Fast GC use. The inlet (CIS 4, Gerstel) was set to the hot split mode (250°C, 30:1) and the EPC pneumatics was set to the constant flow mode (1 mL/min He conventional; 0.7 mL/min He Fast GC). The GC oven had an initial temperature of 50°C and was ramped with 10°C/min (conventional)/ 50°C/min (Fast GC) to a final temperature of 230 °C (1 min). Headspace injections were performed every 40 min (conventional) or 10.5 min due to a 5 min oven cool down (Fast GC). The runs under Fast GC conditions were used to evaluate both the Fast GC-MS (chromatographic trace) and Headspace ChemSensor System performance (fingerprint mass spectrum).

Electronic Nose. The electronic-nose used was a ChemSensor 4440 consisting of a headspace unit (7694, Agilent Technologies) directly coupled to a mass selective detector (5973, Agilent Technologies). The MSD was used in scan mode (35 – 200 amu, 11 scans/sec). Headspace injections were performed every 3 minutes.

Chemometrics Software. For all approaches chemometrics software (Pirouette 3.04, Infometrix, Inc.) was used to evaluate the data. Pirouette was used to automatically create ASCII files from Agilent GC ChemStation data by using a post-run macro. We choose to import the complete chromatographic trace vs. exporting the peak table. This has the advantage that not only calibrated compounds but every peak that might appear will be taken into account by the pattern recognition software. Chromatographic data from MSD ChemStation had to be formatted manually in order to be compatible with Pirouette. An alignment algorithm to account for retention time shifting is available in Pirouette. Predictions can potentially be automated by using the InStep 2.1 (Infometrix, Inc.) client.

The ChemSensor and Headspace ChemSensor System were equipped with ChemSensor Software (Agilent Technologies). This software creates a single fingerprint mass spectrum regardless of retention time.

Headspace sampling. 1 mL aliquots of the flavors were placed into 10 mL vials, which were sealed with crimp caps and equilibrated for 15 minutes at 70°C before headspace sampling. The headspace is transferred either through a heated transfer line (95 °C) or gastight, heated syringe (85 °C) to the GC inlet or to the mass selective detector directly in the case of the ChemSensor 4440. For all instruments except the ChemSensor 4440 that was equipped with a 3 mL sample loop, 1 mL of headspace was injected. In round 1 five samples of each flavor type were analyzed. In round 2 we used 8 to 10 samples from all good lots and predicted 2 samples from each false lot vs. the chemometric models.

RESULTS AND DISCUSSION

A comparison of the analysis time of conventional headspace GC-MS with the fast screening approaches can be seen in Figure 1.

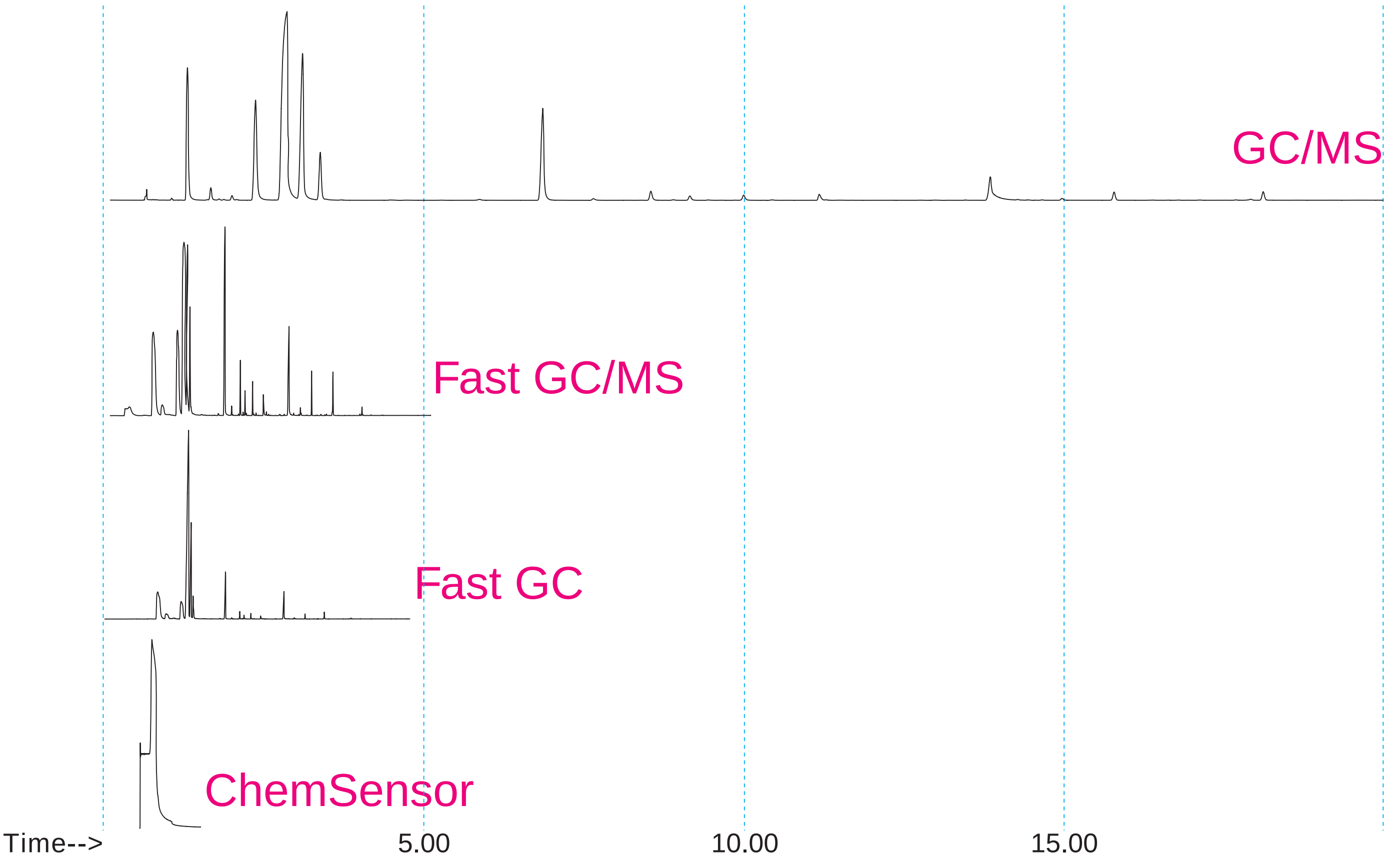
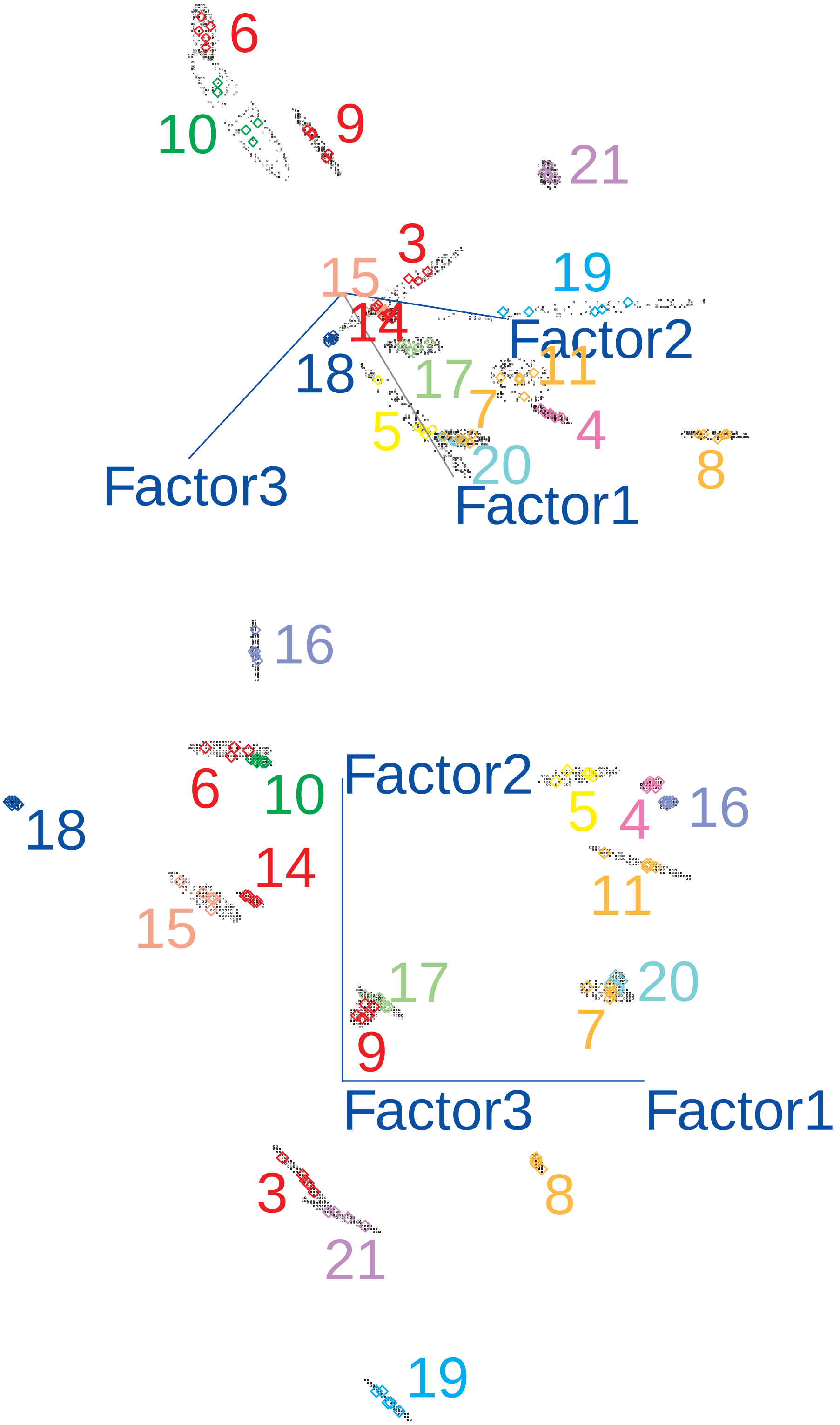


Figure 1. Comparison of the analysis time of conventional headspace GC-MS with Fast GC-MS, Fast GC and ChemSensor.

Figure 1 shows the typical output of the different approaches. Comparing conventional headspace GC-MS with the Fast GC approaches it can be seen that using the Fast GC approaches does not lead to a loss in sensitivity. This is obvious by looking at the sharp peaks following the solvent at about 1 min. The FID signal in the Fast GC chromatogram shows an overwhelming ethanol peak but when scaled to highlight the peaks after ethanol, the same pattern was found as seen in the Fast GC-MS trace. The ChemSensor that does not use any separation of compounds just gives rise to one large signal. Comparing the run times of the different approaches visualizes that the cycle times from injection to injection are very different. Conventional GC-MS is the slowest approach with cycle times of about 40 min while the Fast GC approaches need about 11 min and the ChemSensor allows injection of samples every 3 min.

In the first analysis round the different approaches were compared regarding the discrimination efficiency. The projection of the 17 different flavor types into the 3-dimensional space of the first 3 factors of a Soft Independent Modeling of Class Analogy (SIMCA) classification model is shown in Figure 2.



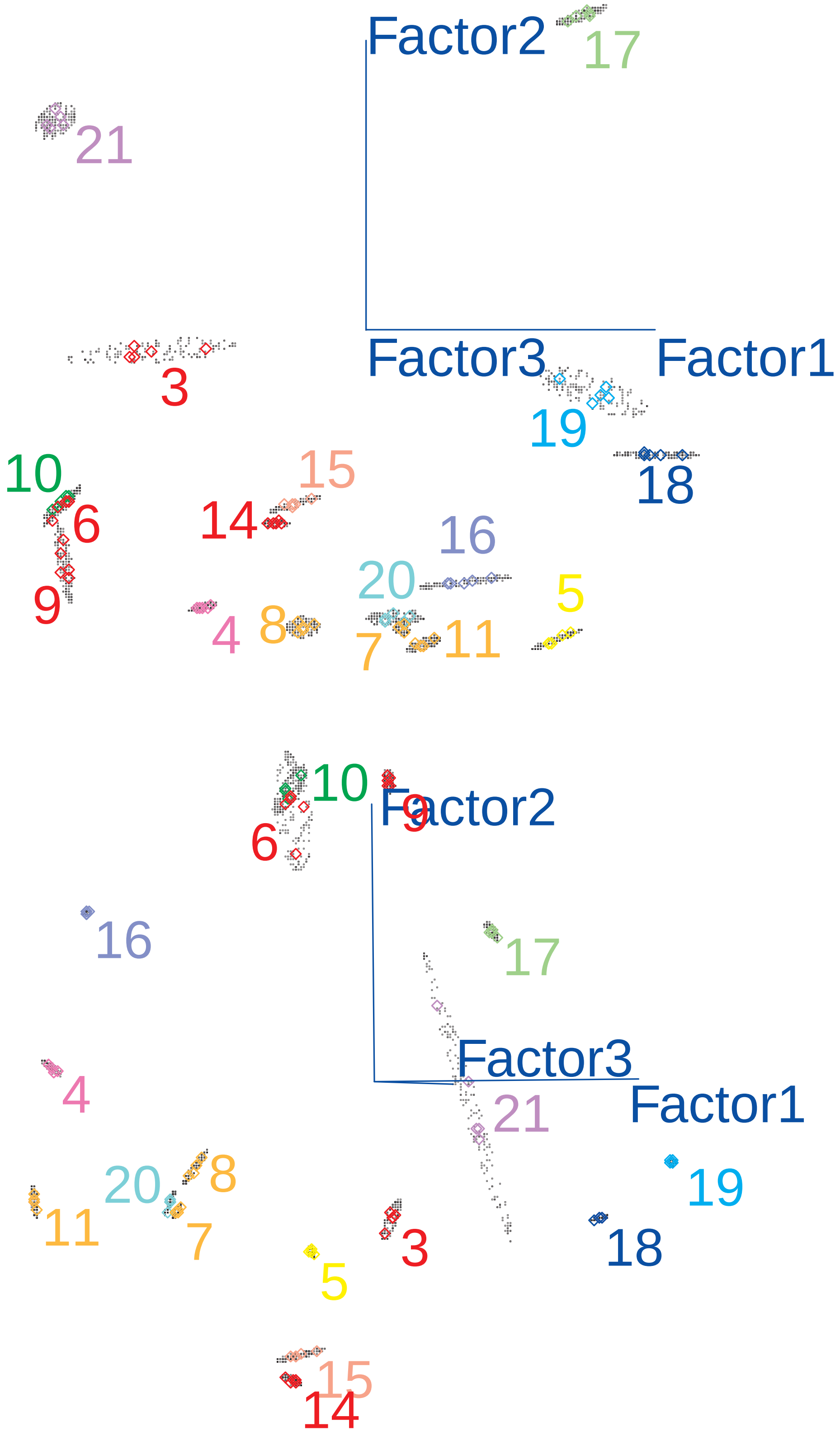


Figure 2. SIMCA class projection plots of 17 different fruit flavors for the mass spectral approaches of the ChemSensor (A) and the Headspace ChemSensor System (B) and the chromatographic approaches Fast GC (C) and Fast GC-MS (D). For all models except Fast GC mean-center preprocessing was chosen. Due to the large solvent peak autoscaling has to be performed for Fast GC.

Nearly all of the flavors can be discriminated by the different approaches. One group of sample types 20 and 7 always cluster together. Analysis of these samples by conventional headspace GC-MS analysis shows that the chromatograms are virtually identical although samples were labeled as strawberry and the other as forest berry flavor (see Table 1).

In round 2, the different approaches were compared on the basis of the prediction of known false samples. From all good lots of each flavor SIMCA models were built and the known false samples were predicted using these models. Table 3 shows the results of these predictions.

Table 3. Results of the predictions of false samples using SIMCA models built from good lots. PP names the chosen preprocessing type (AS = autoscale, MC = mean center). Zero = identified as false; 1 = false positives (not identified as false).

Flavor:		Apple				Apricot								Cream		Citrus											
	PP	1.1	1.2	2.1	2.2	1.1	1.2	1.3	1.4	2.1	2.2	2.3	2.4	1.1	1.2	1.1	1.2	1.3	1.4	2.1	2.2	2.3	2.4	3.1	3.2	3.3	3.4
Fast GC	AS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	0	1	1	1	1	1	0	1
Fast GC-MS	MC	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
HSSensor System	MC	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Chem-Sensor	MC	1	1	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	0	0	1	0

As can be seen from Table 3 all apricot and cream samples were correctly classified as false samples by all techniques. For the apple samples the Fast GC-MS and ChemSensor were not able to identify all samples of type 1 correctly. For the citrus samples the most false positives were found. The Fast GC and the ChemSensor were not able to identify the false samples at all, while the other two techniques identified all samples correctly. The different result for the ChemSensor 4440 and the Headspace ChemSensor System is probably due to the different scan rates. Keep in mind that the Headspace ChemSensor System was always set to Fast GC conditions and the ion information (fingerprint mass spectrum) is calculated from GC-MS runs with separation.

CONCLUSIONS

Regarding throughput all configurations, except the GC-MS (40 min runs) are adequate for fast screening (3 to 11 min) of volatiles and classification of most flavor types. An advantage of all approaches is that chemometrics knowledge is only necessary for model development (unlike interpretation of chromatography data). During model development proper selection of pre-processing (mean-centering or autoscaling) increases discrimination power. One should keep in mind that the Fast GC approach gives you more options of data evaluation because it offers the complete chromatographic trace while the ChemSensor offers ion ratio information.

Possible limitations that were not investigated in this study are the unknown long-term model stability. For the chromatographic approaches this can be influenced by column aging and column to column reproducibility. There are two approaches to overcome these problems, Retention Time Locking (RTL, Agilent Technologies) or the alignment algorithm of Pirouette. However, our results indicate that the high amount of solvents in flavor samples will only affect those compounds following the solvent. This will make RTL and alignment nearly impossible. For the mass spectral approaches one has to deal with retuning or even filament failures.

Again there is a workaround in Pirouette that is called calibration transfer. The feasibility of this procedure has still to be proven for these types of applications. Large amounts of time are required to build these chemometric models when many products are present with either chromatographic or mass spectral techniques. Since the chemical sensor runs are much shorter model building is much less burdensome.

Summarizing the Pros and Cons of the chromatographic and mass spectral approaches leads to the following.

Chromatographic Pros and Cons

- Pros
  - Complete chromatographic trace available for further data analysis
  - Simple and inexpensive instrumentation
- Cons
  - Fast GC approach is problematic for samples containing high amounts of solvents like EtOH
  - Fast GC needs more method development than mass spectral approaches
  - Analyte variety is limited by the selected detector

Mass Spectral Pros and Cons

- Pros
  - No further method development besides chemometric models necessary
  - All sample types that contain volatiles can be analyzed without sample preparation
  - ChemSensor System Setup is most flexible and allows use of the instrumentation as conventional GC-MS, Fast GC-MS, and ChemSensor (the latter two simultaneously)
- Cons
  - Relatively expensive
  - Qualified personnel for maintenance necessary

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