GLOBAL ANALYTICAL SOLUTIONS

GERSTEL

AppNote 5/2002

Characterization of a Mass Spectrometer based Electronic Nose for Routine Quality Control Measurements of Flavors

Arnd C. Heiden
Gerstel GmbH & Co. KG, Eberhard-Gerstel-Platz 1, D-45473 Mülheim an der Ruhr, Germany

Carsten Müller, Hans Steber
Franz Zentis GmbH & Co., Jülicher Straße 177, D-52070 Aachen, Germany

Keywords

Chemometrics, ChemSensor, electronic nose, mass spectrometer (MS), fruit flavor, discrimination, headspace, quality control, off-flavor, fingerprint mass spectra

Abstract

The Gerstel ChemSensor 4440A consists of a headspace autosampler that is directly coupled to a quadrupole mass spectrometer. The analysis time per sample is only 3 to 4 min. For multivariate data analysis the Infometrix' Pirouette pattern recognition software package is used to classify the data.

This instrument was applied to the classification of several different fruit flavors. These flavors typically contain large amounts of Propanediol and Ethanol as carrier.

Introducing this chemical sensor into the routine analysis means, investigating both the qualitative (classification) and quantitative (regression) chemical composition of different flavors. In qualitative analysis, Soft Independent Modeling

of Class Analogy (SIMCA), one of the multivariate analysis routines, was used. SIMCA shows the composite spectrum of a flavor sample as a point on a three-dimensional plot. The projections from similar flavors cluster together on the plot, those that differ in their volatile composition cluster in different locations.

For quantitative analysis the Partial Least Squares (PLS) algorithm was used. In prediction mode these algorithms compare mass spectral fingerprints of unknown flavor samples to those of known good flavor samples. The ChemSensor was capable of discriminating differences in the composition based on the fingerprint mass spectra of the flavors in a pass/fail context. The results of this flavor analysis can serve as an objective guide in food-processing, e.g. for assessing the quality of raw material, intermediate- and end products.

One main concern of this study was to evaluate the long term stability of the chemometric models regarding instrument drift or necessary maintenance of the instrument.

Introduction

Nowadays life without flavors is practically unthinkable. Artificial, nature identical and natural flavors are ingredients for nearly all varieties of modern foods. Regarding fruit flavors, the processing industry uses several slightly different flavors from various suppliers for products like fruit preparations, yogurt, and beverages. Due to the relatively high number of different types or lots of flavors that are delivered daily, it is not possible to qualify the flavors by sensory analysis like olfaction and tasting alone.

A common but time consuming technique to analyze flavors is Headspace Gas Chromatography (/Mass Spectrometry). It is therefore of high interest to provide a rapid screening technique in order to qualify the incoming flavors.

Electronic noses are such systems for the rapid screening of samples with subsequent data analysis using pattern recognition software packages. The term includes systems based on solid state sensors (metal oxides, quartz microbalances or conducting polymers) as well as mass spectrometers.

The classical electronic noses may be less specific or are often affected by sample or environmental factors. The quadrupole technology of the Gerstel ChemSensor 4440A (Figure 1) is a stable and reliable technology, which is not affected by environmental factors such as humidity, temperature fluctuations or sensor poisoning.

The MSD operates over a wide user-selectable mass range, that can be adapted to the analyte. In a mass spectrometer, the various compounds of the sample vapor phase (flavor molecules) are ionized and fragmented, with each compound producing a characteristic fragmentation pattern. The chemical sensor avoids time consuming chromatographic separation by simultaneous introduction of all compounds into the MSD. The output vector is a characteristic fingerprint mass spectrum. This final spectrum is a composite of a hundred or more scans. Because only volatile samples are introduced, the mass sensor`s source rarely, if ever, needs cleaning.

Figure 1. Gerstel ChemSensor 4440.

Experimental

Analyzed flavor samples are commercial flavors used by Zentis for further processing. 1 mL of the liquid flavor sample is loaded in 10 mL vials and sealed with a crimp cap. Each flavor type is prepared in 8 replicate vials. After the vials are loaded in the autosampler and heated for 15 minutes at 60°C, 1mL of the headspace from the vial is sent to the MSD, where the fingerprint mass spectrum of each sample is acquired in 1.5 minute runs in the scan mode (35-150 amu). With the six-sample overlap-heating feature of the autosampler oven, samples can be analyzed every 3 to 4 min. Therefore a tray of 44 samples can be analyzed in about 3 hours.

Results and Discussion

The Gerstel ChemSensor can rapidly distinguish among similar products with volatile constituents.

It was successfully applied to the classification of several different fruit flavors (strawberry, raspberry, pear, passion fruit) from different suppliers that are of high importance to Zentis.

Figure 2 shows a SIMCA model of several different lots of a strawberry flavor. The smaller dots in the background represent a 95% significance level ellipse. This model can be used to predict unknown samples (new flavor lots). Figure 3 shows a prediction of unknown strawberry flavor samples against the model of known good strawberry flavor samples. In the three dimensional SIMCA class projections the blue colored samples differ significantly from the model (see confidence level). These differences in the flavor composition can also be seen in the line plot of the normalized data set (Figure 4).

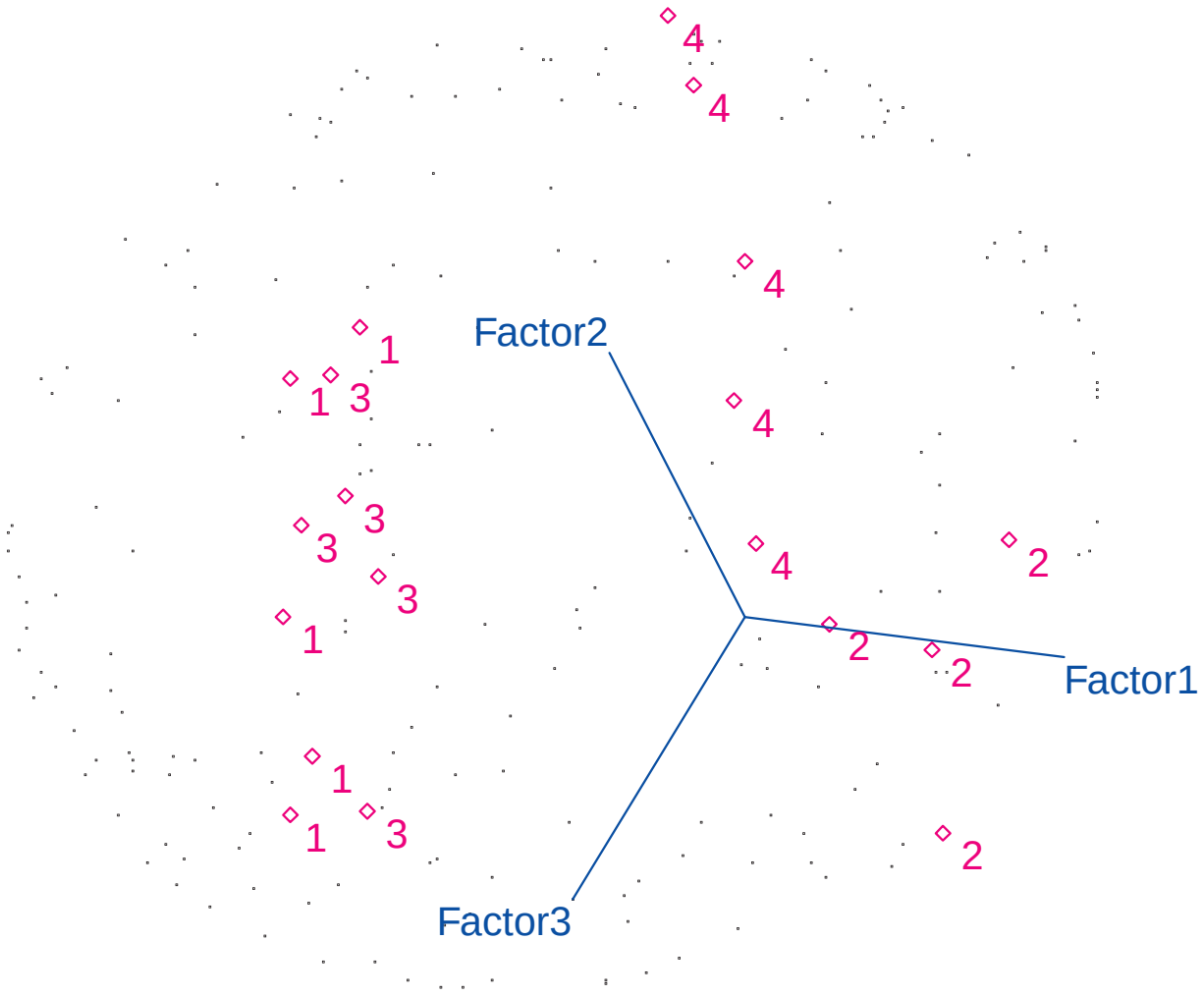

Figure 2. SIMCA model for a strawberry flavor.

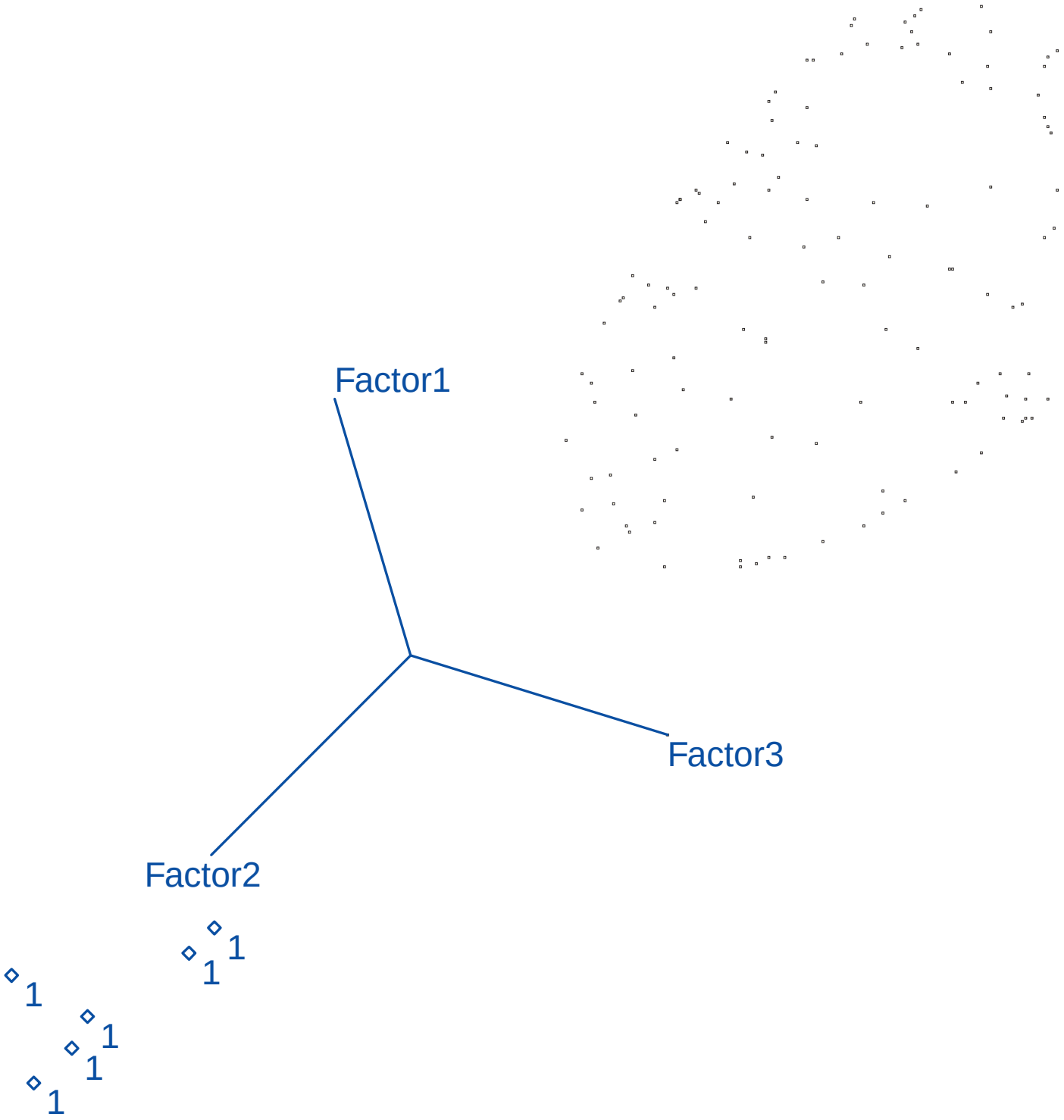

Figure 3. Prediction of a new flavor lot against the strawberry SIMCA model.

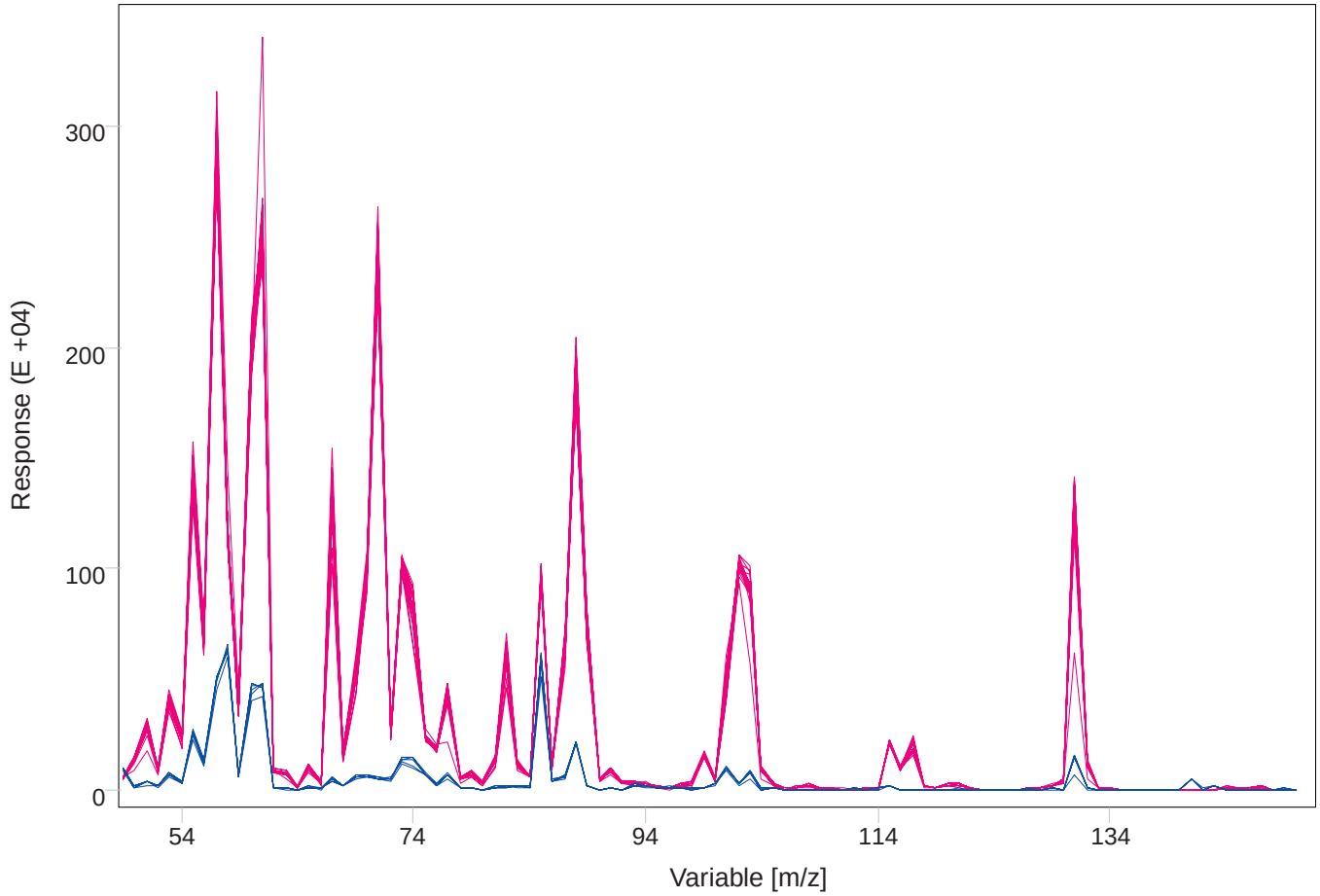

Figure 4. Normalized data of the Strawberry model (red) and the new flavor lot (blue).

However, identification of the wrongly declared flavor as a coconut flavor was only possible by subsequent sensory evaluation. This is partly due to the fact that coconut flavor was not included in the flavor model construction.

Tables 1 and 2 present the ratio of strawberry and raspberry flavor mixtures. Table 1 shows the ratios used to create a PLS model and Table 2 describes the ratios that were used for predictions.

Table 1. Ratio of strawberry and raspberry flavors used to create a PLS model.

Raspberry [µL]	Strawberry [µL]
0	1000
100	900
190	810
250	750
275	725
500	500
700	300
900	100
1000	0

Table 2. Ratio of strawberry and raspberry flavors used to predict against the PLS model.

Raspberry [µL]	Strawberry [µL]
82	918
170	830
210	790
350	0
600	400
800	200
950	50

Figure 5 shows the prediction vs. the PLS regression model. Zero stands for pure strawberry and 1000 for pure raspberry flavor. The two samples annotated 350 are classified as pure raspberry flavors (see Table 2). For these samples addition of strawberry flavor (650 µL) was accidentally forgotten. Slight discrepancies in the prediction of the 210 samples suggest slight error in their preparation.

For routine measurements long term stability is of major importance. Models are valid as long as the instrument is not retuned. In case of retuning the system, remodeling is normally necessary. However, Pirouette offers a tool to avoid the necessity to rebuild all models. This technique is called calibration transfer. It requests to run a few repeat samples of the type that was used to create the model.

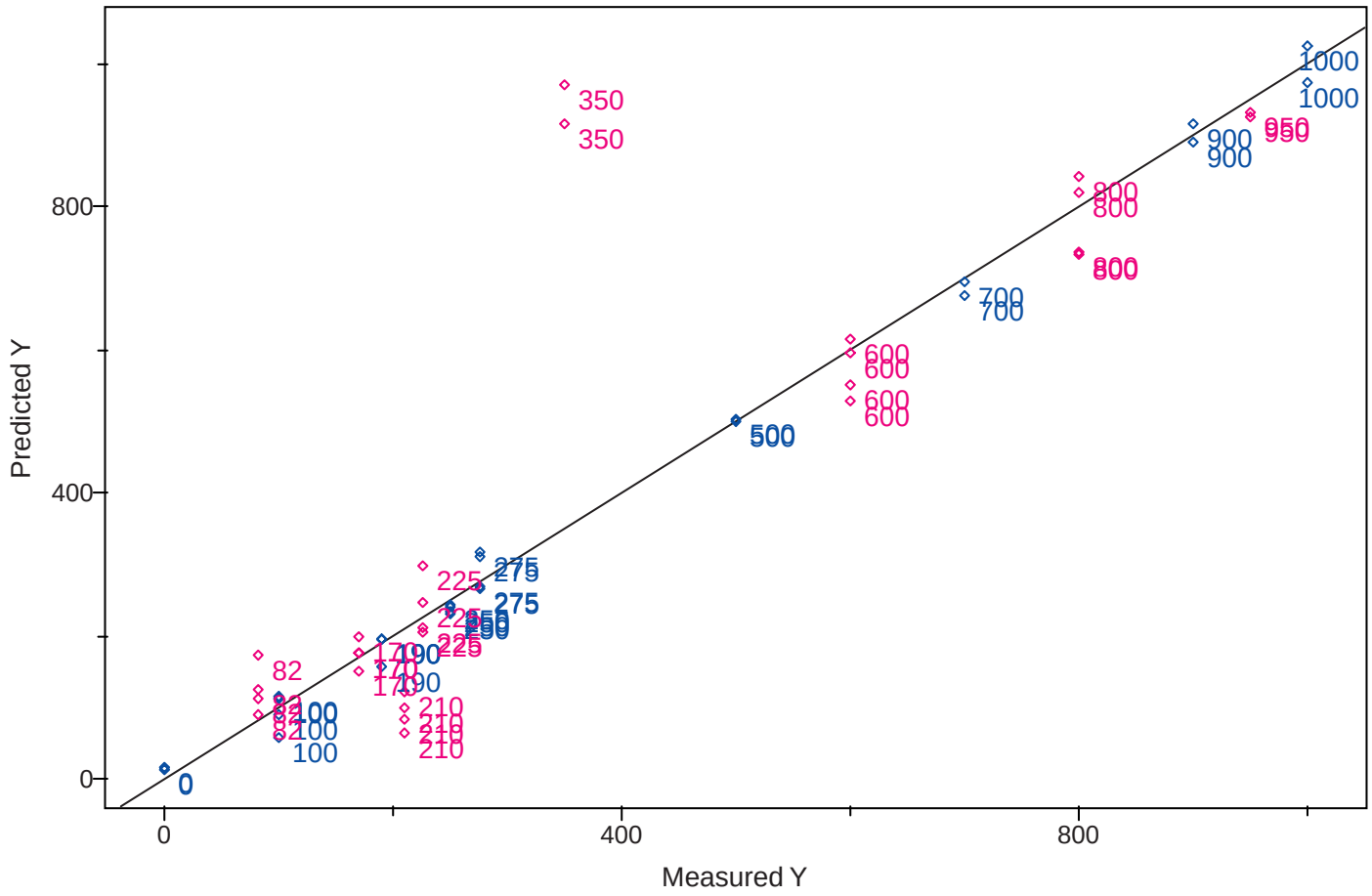

Figure 5. Prediction (red) of strawberry/raspberry flavor mixtures vs. a PLS model (blue).

Figure 6A shows a SIMCA prediction for data after retuning the instrument using calibration transfer but only repeat samples of type 1 & 2 (yellow) were used. This leads to the result that only sample type 1 & 2 fit into their significance level while all others (red, green and blue) do not match . It is therefore necessary to run repeat samples of all sample types. Now all sample types match within their significance level (Figure 6B).

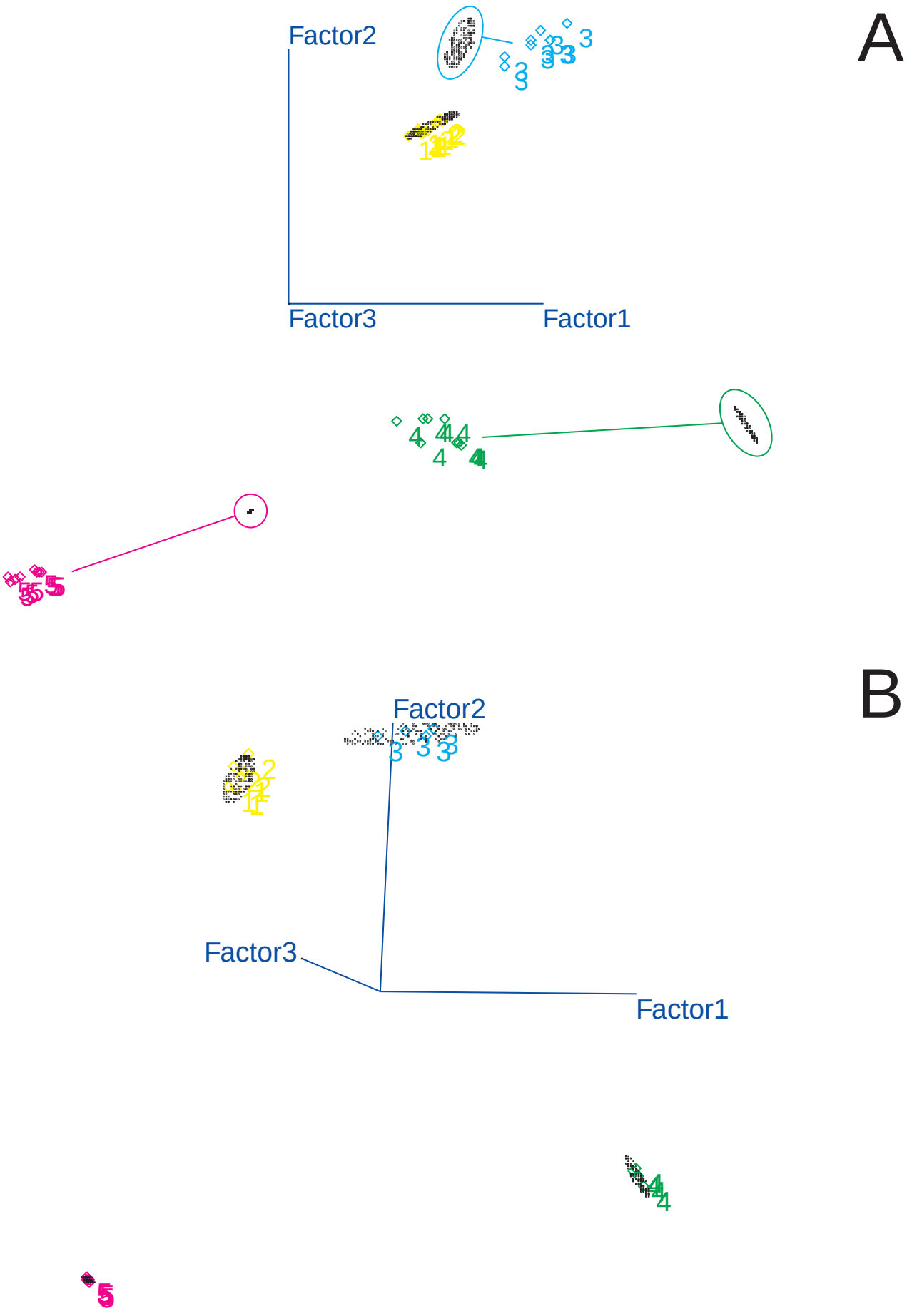

Figure 6. Use of calibration transfer to avoid remodeling. Running repeat samples of one type only (A) and all types (B).

Another concern of Zentis was the classification of fruit preparations that are going to be shipped to customers. First experiments showed that fruit preparations cannot be discriminated easily. This is due to the fact that fruit preparations are not homogenous and therefore the reproducibility of samples from one class is very poor. In order to analyze fruit preparations more experiments are necessary and probably a short sample preparation like homogenization is necessary.

Conclusions

The GERSTEL ChemSensor 4440A has proven to be capable of detecting differences in the quality of incoming flavors. By comparing new flavor lots receipts to models classification of unknown samples is possible. An algorithm called calibration transfer succesfully corrected model drift after instrument retuning.

Further experiments to prove the feasibility of calibration transfer in routine analysis for extended time periods are necessary.

GERSTEL GmbH & Co. KG
Eberhard-Gerstel-Platz 1
45473 Mülheim an der Ruhr
Germany
+49 (0) 208 - 7 65 03-0
+49 (0) 208 - 7 65 03 33
gerstel@gerstel.com
www.gerstel.com

GERSTEL Worldwide

GERSTEL, Inc.
701 Digital Drive, Suite J
Linthicum, MD 21090
USA
+1 (410) 247 5885
+1 (410) 247 5887
sales@gerstelus.com
www.gerstelus.com

GERSTEL AG
Wassergrabe 27
CH-6210 Sursee
Switzerland
+41 (41) 9 21 97 23
+41 (41) 9 21 97 25
swiss@ch.gerstel.com
www.gerstel.ch

GERSTEL K.K.
1-3-1 Nakane, Meguro-ku
Tokyo 152-0031
SMBC Toritsudai Ekimae Bldg 4F
Japan
+81 3 5731 5321
+81 3 5731 5322
info@gerstel.co.jp
www.gerstel.co.jp

GERSTEL LLP
10 Science Park Road
#02-18 The Alpha
Singapore 117684
+65 6779 0933
+65 6779 0938
SEA@gerstel.com
www.gerstel.com

GERSTEL (Shanghai) Co. Ltd
Room 206, 2F, Bldg.56
No.1000, Jinhai Road,
Pudong District
Shanghai 201206
+86 21 50 93 30 57
china@gerstel.com
www.gerstel.cn

GERSTEL Brasil
Av. Pascoal da Rocha Falcão, 367
04785-000 São Paulo - SP Brasil
+55 (11)5665-8931
+55 (11)5666-9084
gerstel-brasil@gerstel.com
www.gerstel.com.br

Awarded for the active pursuit of environmental sustainability