

GLOBAL ANALYTICAL SOLUTIONS



**GERSTEL**

AppNote 2/2004

## Analysis of Packaging Materials using a Mass Spectral Based Chemical Sensor

Vanessa R. Kinton

*Gerstel, Inc., Caton Research Center, 1510 Caton Center Drive, Suite H, Baltimore, MD 21227, USA*

Arnd C. Heiden, Carlos Gil

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

### **KEYWORDS**

Paper/Pulp, Polymers & Plastics, Pattern Recognition, Mass Spectrometry.

### **ABSTRACT**

Packaging materials for foodstuffs or consumer usage must not alter the flavor or odor of the substance being packaged. Examples of packaging materials include the paper used to wrap cigarettes, the paper cartons used in orange juice or milk and the Polyethylene (PE) often used for caps to seal soft drink bottles. Sometimes, due to differences in the raw materials or changes in the production processes, chemical inconsistencies can be found in these packaging materials. For example, a common issue with packaging materials is encountered when they emit off-odors.

Traditionally acceptance of batches is often based on sensory panels. However this is very subjective and time consuming. Ideally an objective and fast screening system should be located directly at the production floor. This is a typical application for chemical sensors.

In this study, paper and PE samples classified as acceptable (no-odor) and unacceptable (off-odor) were used to train a mass spectral based chemical sensor. This sensor incorporates well-known mass spectrometry technology with multivariate data analysis. The mass spectral fingerprint obtained with the sensor was used to create multivariate classification models that were later used to classify unknown samples as acceptable or unacceptable.

Unknown samples for these two applications were successfully classified using KNN classification models. In addition the results of the PE samples were compared to those obtained by the sensory panel. These results are encouraging, due to the level of accuracy and shorter analysis times compared to traditional (e.g. GC/MS) techniques.

In a third application we analyzed ppb amounts of TPGDA in milk and orange juice cartons with the Headspace ChemSensor. This was possible using the MSD in selected ion monitoring mode.

## INTRODUCTION

The use of static headspace (HS) coupled to a gas chromatograph (GC) or a GC-mass spectrometer (GC/MS) is widely used to detect contaminants in food packaging. For example, in 1979 the Ministry of Health in Germany indicated HS-GC as the official method to detect trace monomeric vinyl chloride in products made of PVC and in the foodstuff that is in direct contact with them [1]. Although GC/MS has proven to be a reliable analytical technique, its drawbacks include long analysis times and difficult interpretation of results by inexperienced personnel.

The use of a headspace-mass spectrometry based chemical sensor retains the benefits of using mass spectrometry but speed the analysis substantially when compared to GC/MS. Faster analysis times are a result of not having a long chromatography column and easy customized reports are displayed instead of total ion chromatograms.

In this study we examine three different packaging applications of a MS based ChemSensor. The first application deals with specialty papers. The papers used in food and cigarettes packaging require materials with minimum odor. Up to now, these papers are frequently evaluated by a sensory panel (Robinson test). We investigated using the ChemSensor to obtain faster and more objective responses than the ones obtained with the sensory panel.

The objective was to classify the paper samples into "low odor" and "high odor" lots.

The second application deals with the differentiation of good and bad lots of PE granulate. PE is used in the manufacturing of packaging material for the food industry. These packaging materials are not allowed to have any own odor in order to avoid contamination of the food. Our goal was to use the ChemSensor and provide a fast and objective device to classify samples into "no odor" and "odor" lots.

The last application deals with the detection of tri (propylene glycol) diacrylate (TPGDA) in milk and orange juice cartons. The current method used to detect this compound is time-consuming [2]; therefore, a replacement method should be faster and able to detect TPGDA in the ppb range.

## EXPERIMENTAL

*A. Specialty packaging papers.* 4 different paper types were analyzed. Prior Robinson test results performed by a customer showed that sample type # 1 had the lowest odor and sample # 3 the highest odor.

One paper strip (3.5 cm x 23 cm) of each sample was coiled up and transferred into a 10 mL vial. The vial was immediately sealed with a crimp cap.

### *Analysis conditions.*

Incubation	120°C (30 min)
Injection	2.5 mL, split 20:1, at 180°C
MSD	scan mode, 35-200 amu, 1.0 min runs

*B. PE samples.* 18 PE granulate samples were provided by a customer. Eight were reference samples and 10 unknown samples. The reference samples were four samples with acceptable odor and four with reject off-odor.

3 g of each sample was weight into 10 mL vials which were immediately sealed with crimp caps. The analysis consisted of 5 replicas of each reference sample and 3 replicas of each unknown sample.

### *Analysis conditions.*

Incubation	80°C (20 min)
Injection	2 mL, split 5:1, at 180°C
MSD	scan mode, 35-150 amu, 1.0 min runs

One sample of each type was also analyzed with chromatographic separation by static HS using a GC-MS instrument equipped with a MultiPurpose Sampler MPS 2 (GERSTEL Headspace ChemSensor System).

*C. Milk and orange juice cartons.* Four paper samples were analyzed: samples A and B with low TPGDA

level; sample C in the 75 ppb range level and sample D, a 100 ppb standard. Approximately 2.0 g of each of the inside of each carton were weighed into 20 mL vials. The analysis consisted of at least 8 replicas of each carton (Note: because of the difficulty of manually peeling the inside of the cartons, the true amount of TPGDA was not consistent in the 2.0 g samples).

*Analysis conditions.*

Incubation 85°C (25 min)  
Injection 2 mL, split 10:1, at 180°C  
MSD SIM mode, Ions 41, 55, 71, 85, 113, 135, 157, 171, 215, 225

Also, the pure TPGDA standard was analyzed and a mass fingerprint was obtained for this compound.

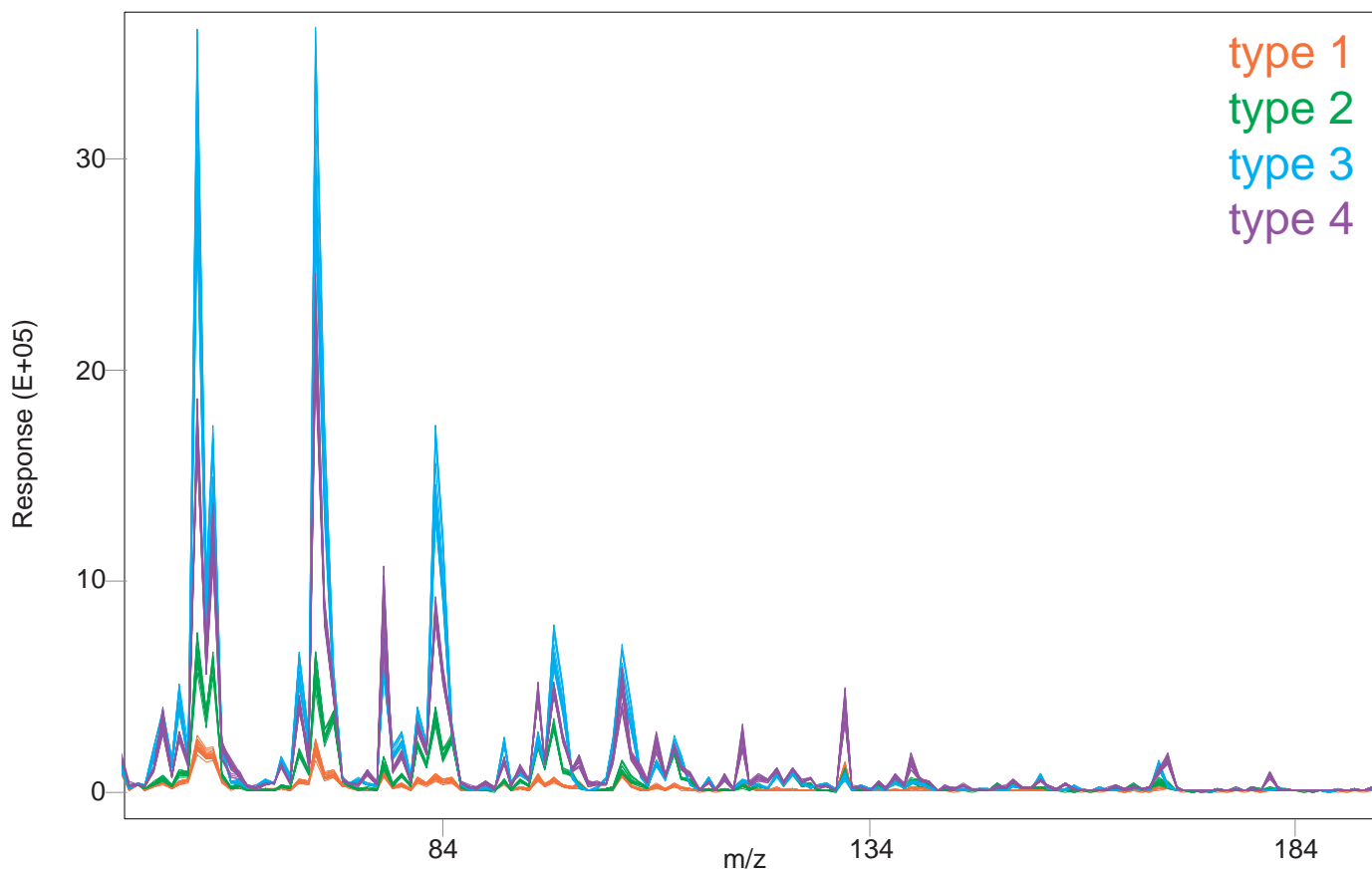
## RESULTS AND DISCUSSION

*A. Specialty packaging papers.* The entire HS volatiles of each paper were analyzed using static HS coupled to a MS (Figure 1).



**Figure 1.** GERSTEL Headspace ChemSensor.

Using a special set of GERSTEL ChemSensor macros for the Agilent MSD ChemStation an ASCII file is automatically created after each run. The ASCII file contains a characteristic mass spectral fingerprint that can be used to train the ChemSensor. These fingerprints for each type of paper are displayed using lineplots in Figure 2.



**Figure 2.** Mass spectral lineplots of specialty packaging paper obtained after sampling with static HS ChemSensor. Samples were equilibrated at 120 °C.

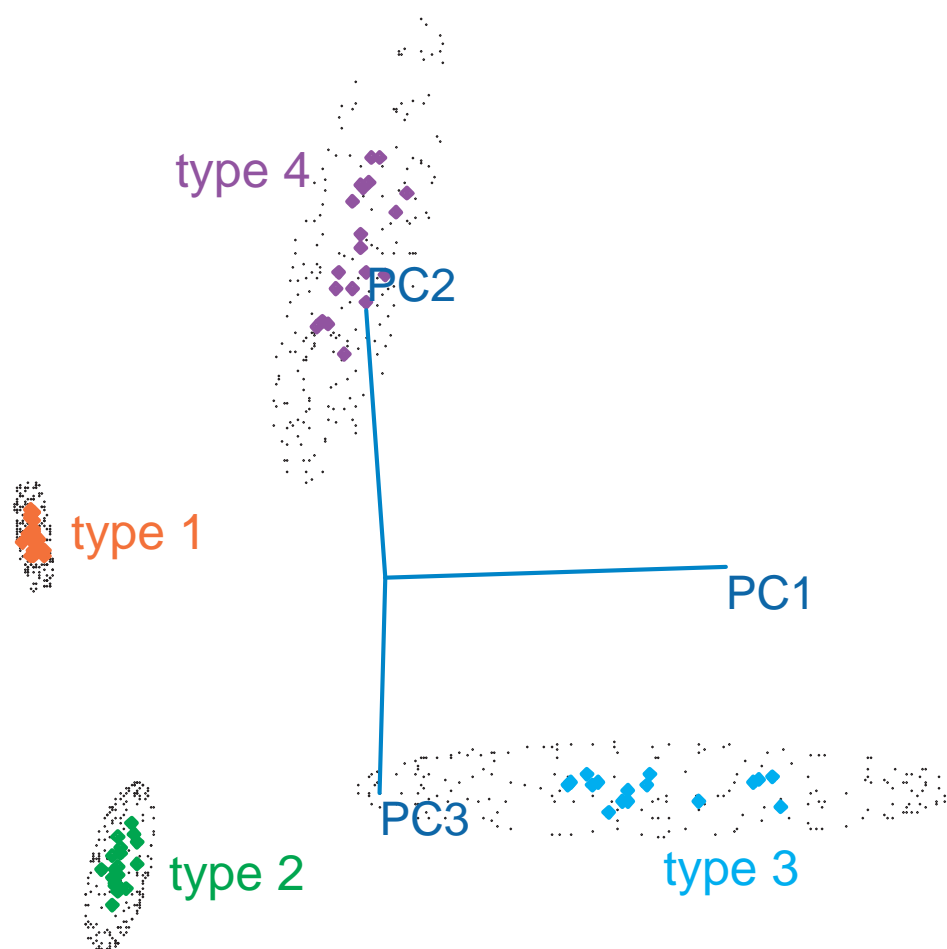
The x-axis in Figure 2 represents the ions (m/z) and the y-axis their abundance. Note that the first ions (m/z 35-45) are not displayed in Figure 2 because their abundances are too high. Inspection of this plot reveals enough differences in the ion abundance ratios of different sample types as expected. Only the orange traces (sample type # 1) show very little abundance, this is in accordance to its low odor (Robinson test).

Two chemometric classification models were created with the above data. SIMCA uses principal component analysis (PCA) to model the shape and position of the samples. An acceptance region (confidence interval) is then created for each different type of class. The interclass distance between sample types is reported in Table 1.

**Table 1.** Interclass distances between classes.

	CS1	CS2	CS3
CS2	8.9		
CS3	54.8	42.5	
CS4	33.1	16.1	27.5

As a rule of thumb an interclass distance of higher than 3 indicates that the samples are separable. For this analysis, it can be seen that there is sufficient separation for almost all sample types. The SIMCA 3D-plot as seen in Figure 3 visualizes this finding.



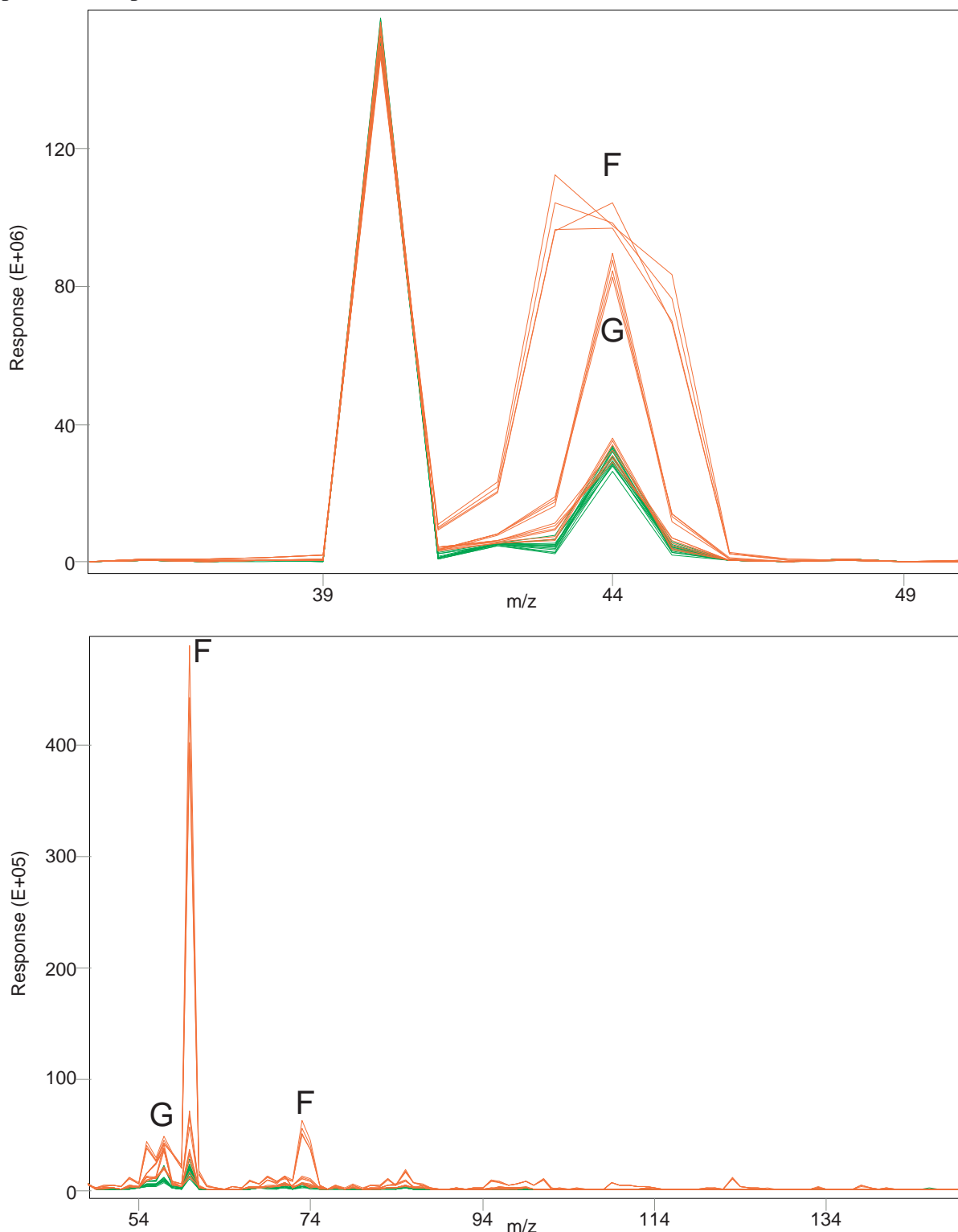
**Figure 3.** SIMCA model for specialty packaging paper obtained after sampling with static HS ChemSensor. Samples were equilibrated at 120 °C.

The second classification model used was K-Nearest Neighbors (KNN). KNN is a model that classifies unknowns based on their proximity to samples already placed in categories. For the model building only sample types # 1 and # 3 were used. Sample type # 1 represents the “low-odor” category and type # 3 the “high-odor” category. The distance between

an unknown (sample types # 2 and # 4) and a set of samples with known class is calculated. The unknown is then classified according to its closest K samples. Using KNN all samples of type # 2 were predicted into the “low-odor” category (type # 1) and all samples of type # 4 into the “high-odor” category (type # 3).

B. PE samples. After close examination of the PE reference samples using their mass fingerprints, it was found that two reference samples had extremely high responses. Samples labeled F and G show much

higher signals. Figure 4 shows the low odor samples with green traces and the samples with off-odor with orange traces.



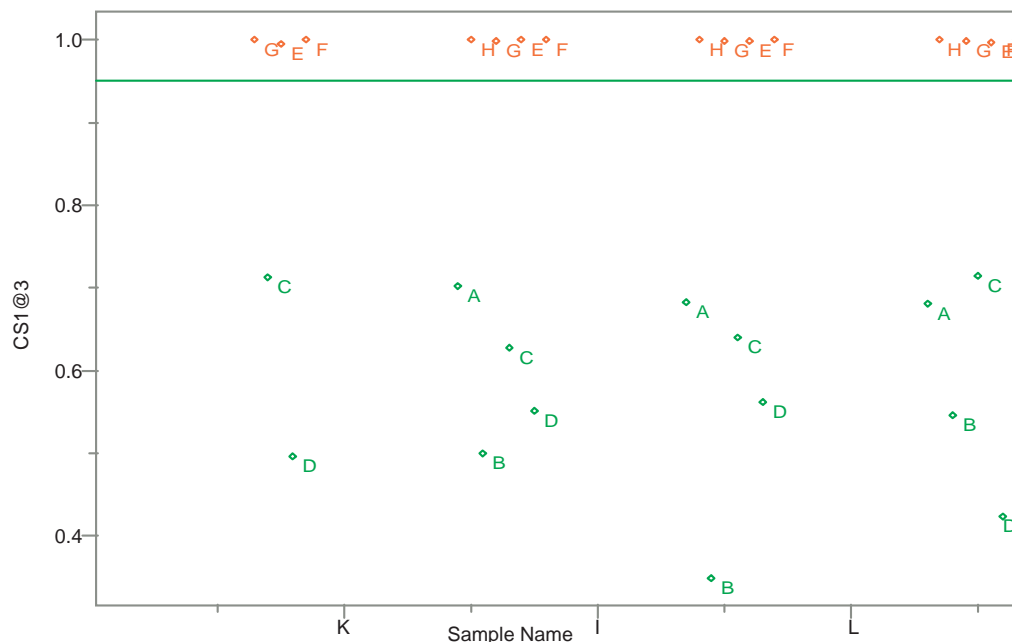
**Figure 4.** Mass spectral lineplots (upper plots: m/z 35-50, lower plots: m/z 51-150) of PE samples with static HS ChemSensor. The high odor samples are orange traces and the low odor samples are green traces.

It is obvious that samples F and G have very high levels of ions 44 and 74 when compared to the rest of the reference samples. To obtain a better visual clas-

sification these extreme bad samples were excluded from the data set.

Two chemometric models were created with the above data: SIMCA and KNN. For SIMCA only the good sample types were used to create the model. All bad samples should then be predicted as unknown.

Figure 5 shows the class probability plot of the reference samples. The green line represents a 95 % confident interval (y-axis) which seems to be reasonable for these samples.

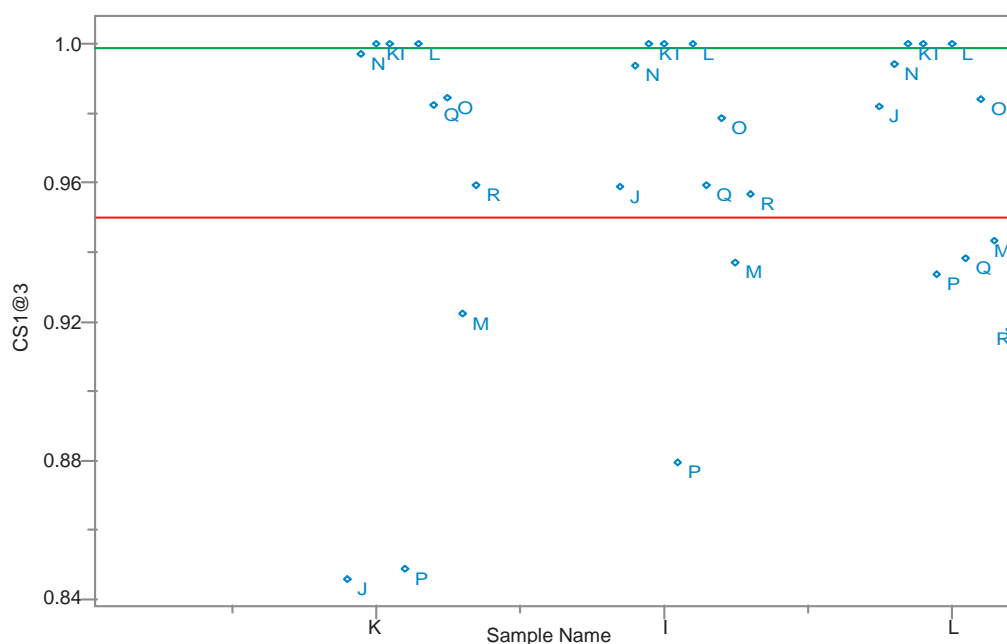


**Figure 5.** SIMCA class probability plot for PE good reference samples (green projections) and bad samples (orange projections). A probability of 1 means no correlation between the sample and the model.

We created a K-Nearest Neighbors (KNN) model with two categories (bad and good) and set K to 4. Using KNN, sample types I, K and L predicted into the “bad” category.

higher probability, e.g. 99.9 % similar results to KNN were achieved. Figure 6 shows the class probability plot. Depending on the prediction probability samples like N, O or Q could be classified as good (below the probability line) or not. The final decision which probability is correct should be based on results taken from representative reference methods.

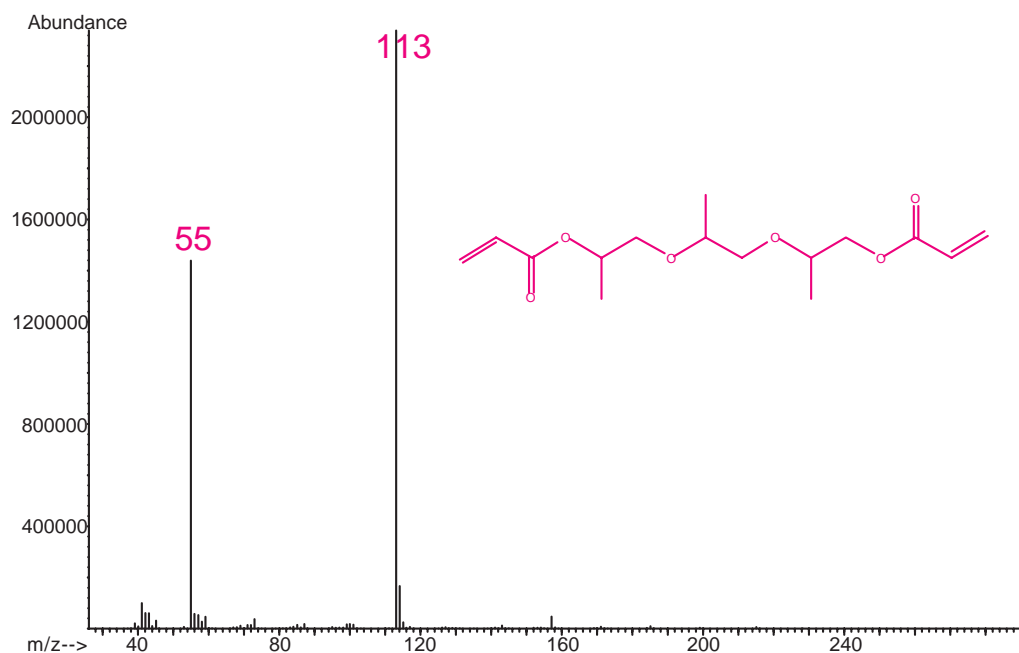
SIMCA results depended highly on the prediction probability. Setting the probability to 95 % only a few samples were predicted into the good category. At a



**Figure 6.** SIMCA prediction Class Probability plot for PE unknown samples. Green line 99.9 % confidence interval, red line 95 %.

C. Milk and orange juice cartons. The structure of TPGDA is shown in Figure 7. A mass spectral fingerprint of TPGDA was obtained using the neat standard. Figure 7 shows that the main ions for this compound

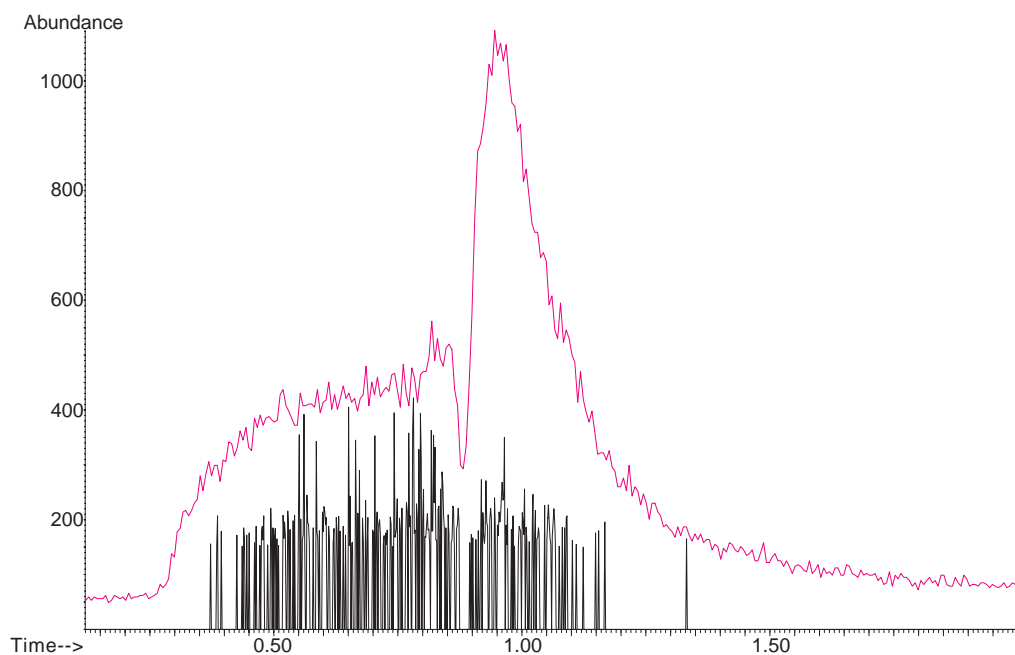
are 55 and 113, which can be attributed to the acryloyl ion (55,  $[\text{CH}_2=\text{CH}-\text{C}=\text{O}]^+$ ) and to an acryloyl group in which a propyloxy unit is attached (113,  $[\text{CH}_2=\text{CH}-\text{CO}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2]^+$ ).



**Figure 7.** Mass spectrum of tri (propylene glycol) diacrylate (TPGDA).

Initially, all four samples were analyzed in the SCAN and SIM mode. Figure 8 shows an extracted ion chromatogram overlay of ion 113 for sample C using SCAN and SIM mode. Because of the higher response using SIM; we decided to continue all ChemSensor analysis in the SIM mode.

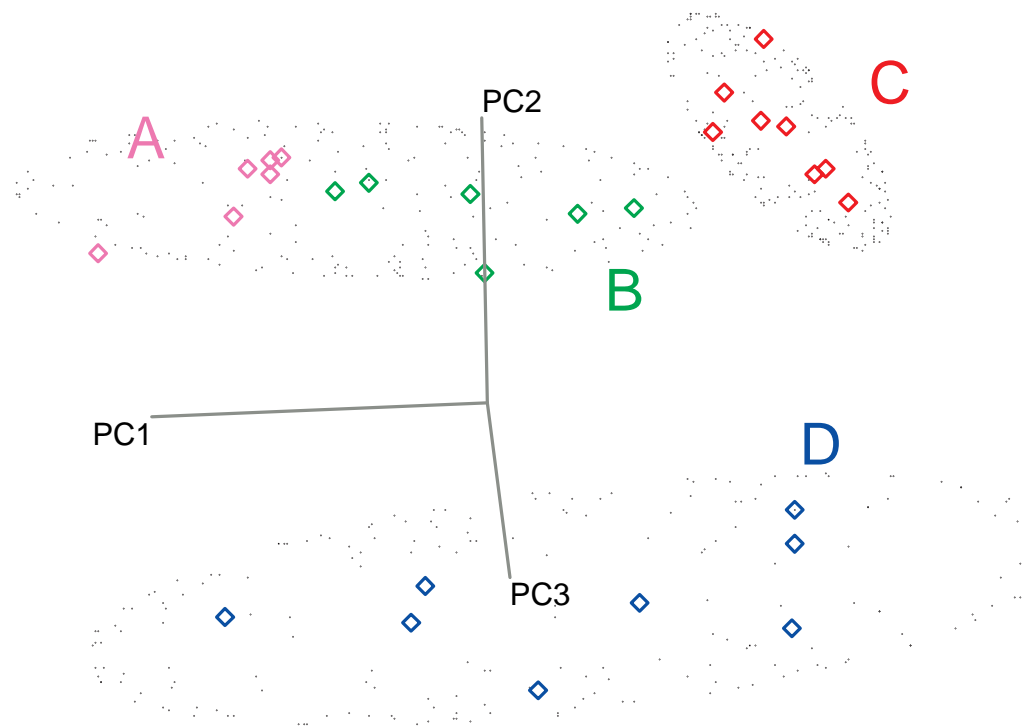
[Note: recent experiments using the ChemSensor in the SIM and SCAN mode indicate that higher sensitivity depends on several parameters like scan rate, number of SIM ions, dwell time, etc. In some cases higher sensitivity is not always achieved when the ChemSensor is run in the SIM mode].



**Figure 8.** Extracted ion chromatogram overlay for mass 113 obtained by sampling the HS of sample C. The yellow trace was obtained using a scan range of 50-160 amu and the white trace using the MSD in the SIM mode, 10 masses.

Figure 9 shows a class projections plot for the SIMCA model obtained while sampling the static HS. For this model, 3 classes were used: samples A and B were grouped together into one class (low level of TPGDA),

sample C (75 ppb) and D (100 ppb). It can be seen from this plot that there are three different, well-separated clusters. The interclass distances between these samples ranged from 6.2 to 7.5.



**Figure 9.** Class Projections plot for a SIMCA model with three classes (samples A and B were grouped together). Samples were analyzed using the GERSTEL Headspace ChemSensor in the SIM mode.

In a separate experiment, we analyzed the four samples using an enrichment technique. Using Stir Bar Sorptive Extraction (SBSE), we found differences in the samples that were not related to their levels of TPGDA. These results indicate that there could be sample variability in the cartons themselves. The level of TPGDA in the cartons is determined by migration from the printed carton to the unprinted side of the next stacked carton, this migration may change from carton to carton. It is recommended that the standard sample has the same composition as the other samples and only differ in the level of TPGDA.

## CONCLUSIONS

Using a MS based ChemSensor we were able to train the instrument to detect packaging materials that had unacceptable odors. The analysis times were fast and prediction of unknown samples was accurate.

Using the ChemSensor in the headspace (HS)-SIM mode we were able to detect fragments of TPGDA in samples C and D. We will expand this application to test the ChemSensor in the SPME mode which we expect to provide higher sensitivity.

## REFERENCES

- [1] Kolb, B. & Ettre, L. S. Static Headspace-Gas Chromatography Theory and Practice, Wiley-VCH, New York 1997.
- [2] Marek, T. & Grollmann, U., DIC Technical Review, 1999, 5, 93.







**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 Toritsuudai Ekimae Bldg 4F  
Japan

☎ +81 3 5731 5321  
☎ +81 3 5731 5322  
@ info@gerstel.co.jp  
🌐 www.gerstel.co.jp

**GERSTEL LLP**

Level 25, North Tower  
One Raffles Quay  
Singapore 048583

☎ +65 6622 5486  
☎ +65 6622 5999  
@ SEA@gerstel.com  
🌐 www.gerstel.com

**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

Information, descriptions and specifications in this  
Publication are subject to change without notice.  
GERSTEL, GRAPHPACK and TWISTER are registered  
trademarks of GERSTEL GmbH & Co. KG.

© Copyright by GERSTEL GmbH & Co. KG



Awarded for the  
active pursuit of  
environmental sustainability