GERSTEL

AppNote 7/2005

Detection of Packaging Emissions using a Flexible Headspace Sampler Combined with a Multi Sensor System and a Separation Unit

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

Frank Röck, Alexander Gurlo, Udo Weimar
*Inst. f. Physical Chemistry, University of Tübingen,
Auf der Morgenstelle 8, D-72076 Tübingen, Germany*

Michael Blaschke
*AppliedSensor GmbH, Gerhard Kindler Str. 8,
D-72770 Reutlingen, Germany*

KEYWORDS

Packaging Emissions, Headspace Sampler, MOS-Sensor, FID

ABSTRACT

The quality of packaging material used in the food industry is regularly controlled in order to avoid negative effects on product quality caused by emissions. In this publication, a fast and economical system based on a sensor array is presented. To eliminate interferences, a separation unit in the sampling system was added. As demonstrated for paperboard samples, it is possible to separate the main interfering compound, water vapor, and organic solvents into two peaks using a short packed polar column. The same approach can be used to analyze other packaging materials. For example, the emission of acetaldehyde from PET (polyethylene terephthalate) bottles, which causes an undesirable off-flavor, is easily detectable.

With a slight modification of the headspace sampler it is possible to measure emissions from the inner varnish of sealed beverage cans as a production control.

INTRODUCTION

Nowadays, nearly every foodstuff available for consumers is packaged. A large variety of materials is used for food packaging. The most important aspect of packaging is to protect the product from a variety of environmental factors to maintain product quality and freshness during storage. However, the packaging material itself can have a negative impact on the content; for example, it can release solvents and various off-odor compounds. In the case of paperboard samples, sources of these undesirable substances (i.e. off-odours or off-tastes) are usually residual solvents from printing inks, lacquers, adhesives or varnishes used in manufacturing processes (i.e. rotary print, offset, hot foil stamping).

To ensure consumer safety and customer satisfaction, off odors and residual solvents must be monitored at an early stage during production of packaging materials.

Currently, the amount of residual solvent is determined quantitatively using instrumental analysis techniques like HS-GC-MS (headspace - gas chromatography - mass spectrometry) to ensure that threshold values are not exceeded [1-2]. The total amount of volatile compounds is usually expressed as mass of the odorous compound per unit surface area of packaging (in mg/m^2) [3]

The most significant drawbacks of this approach are the time required and the cost of analysis. HS-GC-MS requires expensive instrumentation and skilled employees in order to provide reliable interpretation of the data obtained.

For these reasons it is desirable to develop a fast and simple quality control technique. A rapid monitoring system based on a sensor array is able to meet most of the described requirements. Adding a small separation column to eliminate interfering compounds resulted in a robust and easy-to-handle system.

EXPERIMENTAL

The aim was to develop a dedicated system that is so simple to handle that it can be used by unskilled personnel at the production line. The design is based on a valve-less single-shot headspace sampling unit together with a Metal Oxide Sensor (MOS) array (Figure 1).
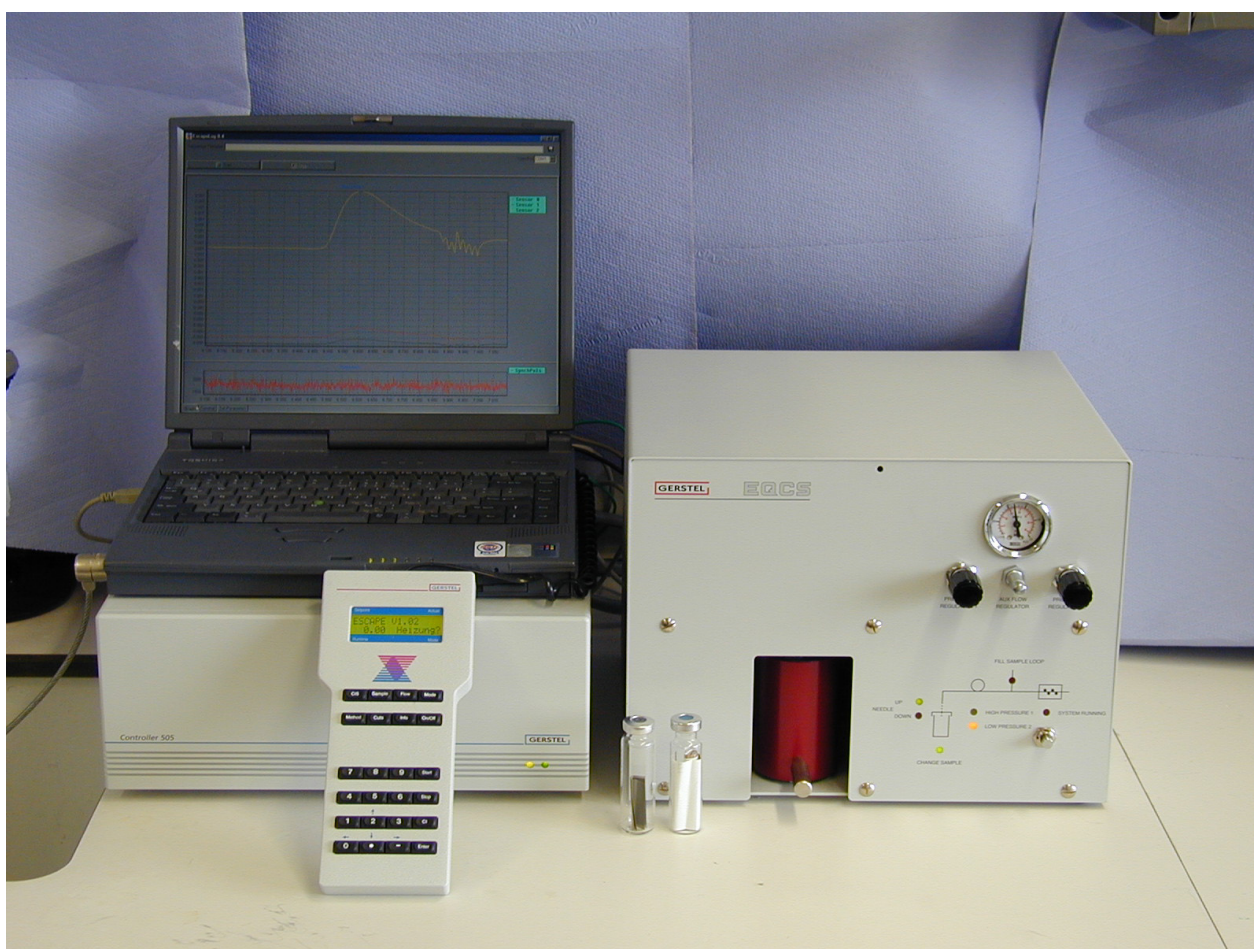

Figure 1. System base for paperboard samples.

The headspace sampling system can be supplied with a chromatographic column to eliminate interferences. Without the column, the system is similar to laboratory set-ups with commercial headspace samplers used as sample introduction system for electronic sensor systems. Figure 2 shows the flow scheme of the valve-less headspace system with all active parts.

The heart of the system is its sample flow path from headspace vial to detection via the chromatographic column. Pressure regulator PR1 in combination with solenoid valve SV2 as well as pressure regulator PR 2 in combination with solenoid valve SV3 are used to regulate the pressure in the whole system. Two pressure regulators are needed in order to switch between two pressure levels without using expensive electronic pressure regulators. Instead of valves two restrictions are installed in the flow path. One is installed directly before the headspace vial. Its function is twofold: To prevent loss of analytes by diffusion, and to restrict flow from the system when the headspace vial is removed, preventing a pressure drop. The second restriction is installed between the sample loop and the sensor chamber. This restriction is needed when the sample loop is filled. The second restriction can be replaced by a chromatographic column which can help to eliminate interferences. For this work, a packed column (6 ft, OD 1/8", Phase 25% Sorbitol; Solid Support Chromosorb WHP 80/100 MESH) was chosen because paper board often has a high water content (up to 10%). Organic compounds must be separated from water in order to be determined using MOS sensors.
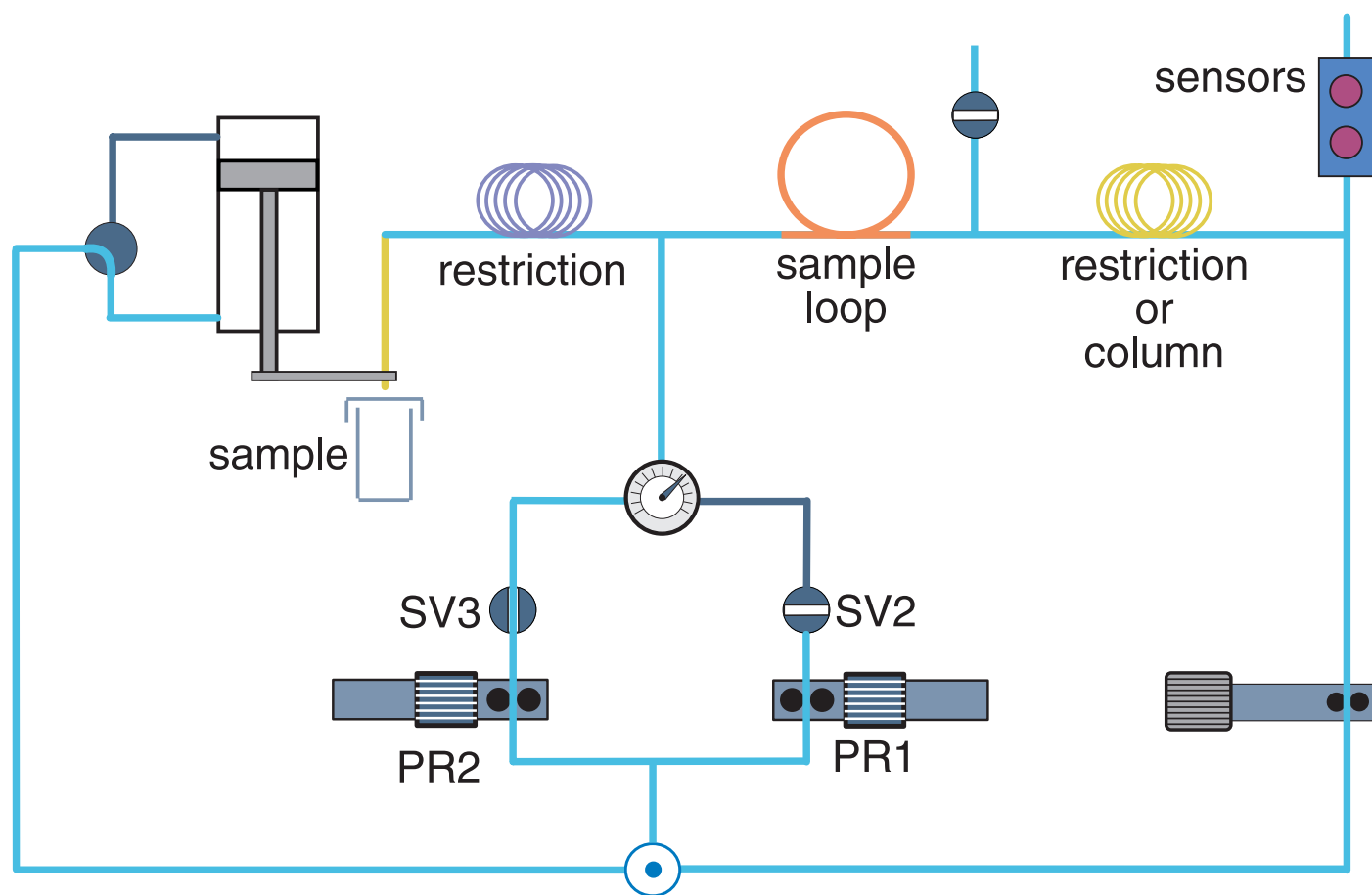

Figure 2. Flow scheme of the headspace sampling system.

Sensor array. Micromachined gas sensors [4] based on semiconducting metal oxides (µ-MOS sensors) were used as detectors (sensing elements) in sensor arrays due to their high sensitivity and long-term stability [5]. In a MOS sensor, conductance varies as a function of the vapor composition and analyte concentration [6]. The preferential reaction with certain gases (selectivity of the sensors) was tuned using surface additives such as platinum and palladium in different concentrations and / or by varying the operating temperature (Table 1).

	Additive	Operating temperature
Sensor 1	Pd 3%	280°C
Sensor 2	Pd 3%	350°C
Sensor 3	Pd 0.2%	310°C

Table 1. Composition and operating temperatures of the µ-MOS sensors [11].

FID. The reference standard solvent amount was determined using a Hewlett-Packard headspace auto-sampler (HP 7694 HSS), combined with a packed polar column and a Flame Ionization Detector (FID).

Data evaluation. The correlation between sensor (µ-MOS) signals and instrumental data (FID, GC-MS) was performed with the software package "Unscrambler" (version 7.6) using Multivariate calibration and classification. Principal Component Analysis (PCA) and Principal Component Regression (PCR) were used [7]. Multiple Linear Regression (MLR) was used to correlate sensor signals and sensory panel data.

Packaging samples. All measurements were performed on real paper and paper board packaging materials. A controlled selection of samples was not possible, these had been randomly taken by production (manufacturing). To determine the total solvent amount, four different types of samples were chosen. All samples were produced using a rotary printing process, since compared with offset printing the solvent amount is quite high and compliance with threshold values more critical. For each sample type several batches were available, altogether 20 samples with different amounts of solvent and different composition.

Procedures. The packaging materials were cut in pieces of 100 cm², introduced in 20 mL headspace vials and immediately sealed gas-tight with a silicone/PTFE- (polytetrafluoroethylene) septum. The vials and samples were equilibrated in the oven of the headspace

sampler for 60 min at 85°C. The sample loop (1 mL) and the polar column were kept at 120°C. As carrier gas, air was used.

Set-up. To detect the total amount of residual solvent, water and organic solvents are separated using a packed polar column (flow rate 20 mL/min, temperature 120°C). Detection is performed by 3 metal oxide sensors (Figure 3).

RESULTS

The objective of this study was to develop a rapid procedure to determine the total amount of residual solvent in packaging materials. It is well known, that paper and board packaging is hydrophilic, taking up significant amounts of moisture from ambient air during production and storage. It is also known that water vapor interferes with solvent detection by gas sensors that are based on semiconducting metal oxides [6]. To achieve results that are less sensitive to variations in humidity, a packed column was used to separate water from the solvent peak (all solvents in one peak).

With the packed polar column used in this work, separation of water from the organic solvents is easily achieved under isothermal conditions. Separation is fast, it takes just 4 minutes to get the integral solvent related signal (Figure 3). One can clearly see that the organic solvent peak and the water peak are completely separated. This means it is possible to obtain results without interference from water.
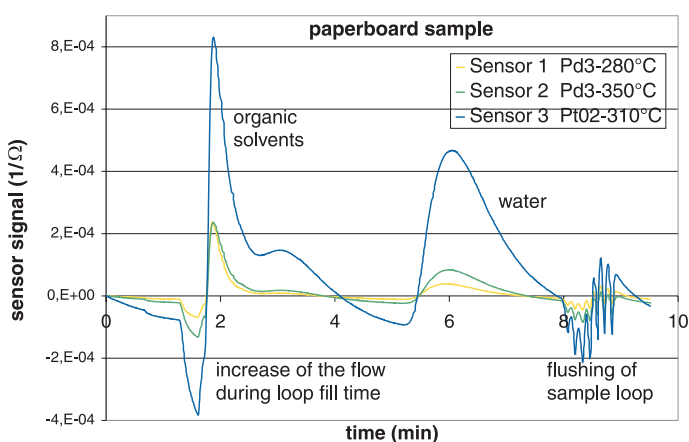

Figure 3. Typical example: Chromatograms of a sample produced with rotary press printing.

After selecting optimal parameters, peak areas of the resulting sensor signals were used for the evaluation. Prediction of the total amount of organic solvent in a sample was approached in two different ways. The first approach was to correlate the area of sensor signals ("predicted solvent amount") with the "true solvent

amount" obtained from an FID-based headspace system that was used to determine residual solvent in the packaging material without chromatographic separation. The correlation was obtained using a Principal Component Regression (PCR) model in which the inputs were the signals of the 3 sensors in the array. The FID was calibrated using an ethanol standard and the FID signals (i.e. "true solvent amount") from the packaging samples were expressed in ethanol equivalents. This approach is based on the assumption that ethanol is representative of the residual solvent.

A calibration of the system for all 20 paper /board samples (Figure 4) shows good correlation between predicted and true solvent amount. The good correlation is probably partly due to the way in which the data was obtained, meaning that the set-up is similar and the samples were measured with both methods over a time period of only a few days.
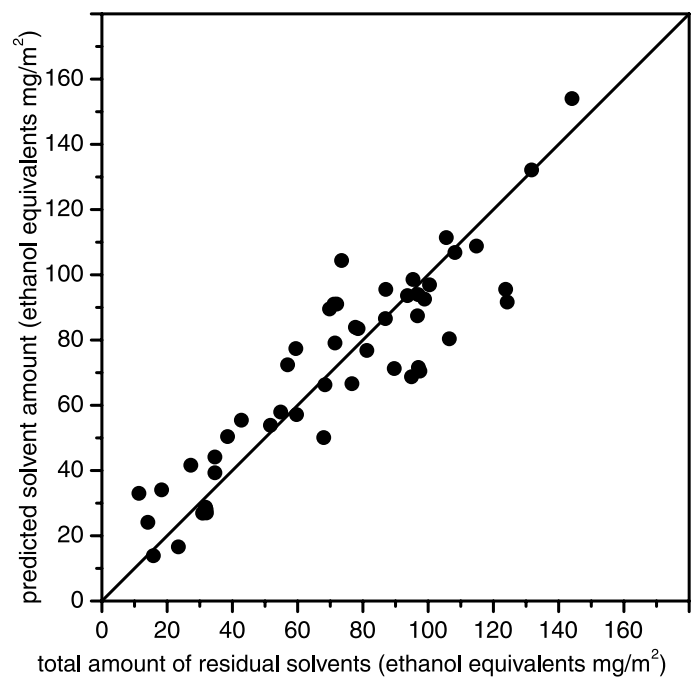

Figure 4. Prediction of the ethanol equivalents of residual solvents. The FID reference is the average of three measurements and every measurement was repeated after putting the raw samples in storage for a few months.

It is important to point out that expressing concentrations in terms of ethanol equivalents does have some limitations: The approximation does not take into account the different sensitivity of the FID to different solvents and the fact that quite different compositions of the gas phase could result in identical FID signals. The main important limitation is a possible mismatch

between the FID area and the total solvent concentration. Consequently, the potential of the sensor array/ polar column approach was explored using calibration data that accurately describes the total solvent content. For exact quantification, GC-MS measurements were performed. In the samples, ethanol, 2-propanol, isopropyl acetate, ethyl acetate, acetone, 1-ethoxy-2-propanol, and methanol were found. A prediction of this data (Figure 5) is not as good as in the previous case. A possible explanation may be, that the solvent amount varies during the period of time between the measurements with the GC-MS and the sensor system (several weeks). For a rapid screening of samples, the accuracy is still satisfactory.
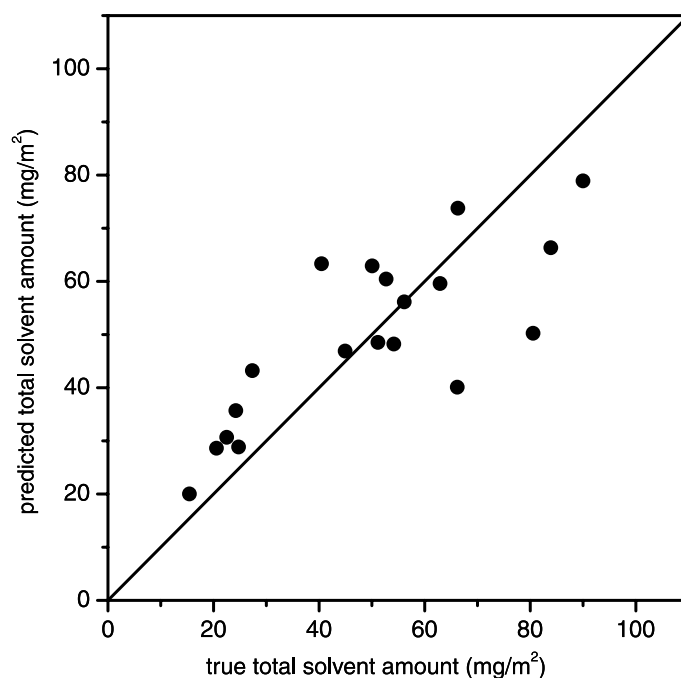

Figure 5. Prediction of the total amount of residual solvents determined by GC-MS.

In addition to paperboard packaging, beverage containers such as PET-bottles and metal cans were tested for volatile organic compound emissions. PET bottles are easier to analyze because PET normally emits only acetaldehyde. On the other hand, the acetaldehyde concentration is much lower than emissions experienced from paperboard samples. High sensitivity and fast sensor response are necessary. First measurements (Figure 6) are very encouraging and promise a good prediction of the emission even in this concentration range.
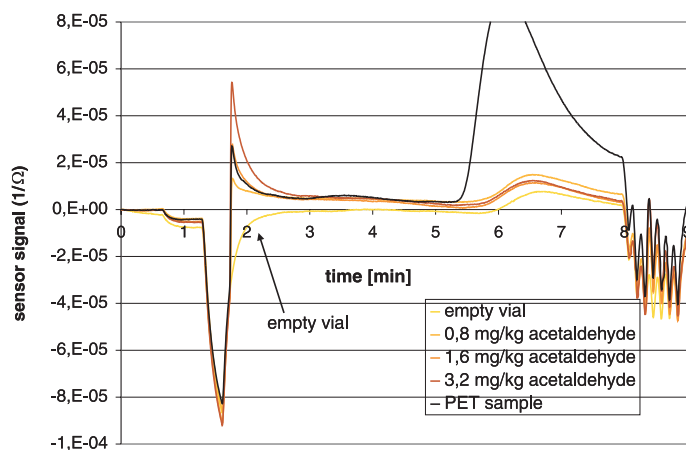
Figure 6. Response of the Pd 3% sensor (280°C) for different concentrations of acetaldehyde. The acetaldehyde concentration of the PET-sample is in the range of 1,6 mg/kg.

Metal beverage cans exhibit emission of volatile organic compounds from the varnish used to coat the inside. This can of course affect the quality of packaged products. By simply exchanging the sample oven the headspace system can be adapted to handle beverage cans directly for analysis (Figure 7). The whole system is based on the described sampling unit. For a first test, an FID was installed instead of the sensors since it was important to evaluate the sampling technique in a comparison with existing analytical data based on FID results. Initial results obtained with this system are very promising and a further study is planned to compare FID data with sensor data.
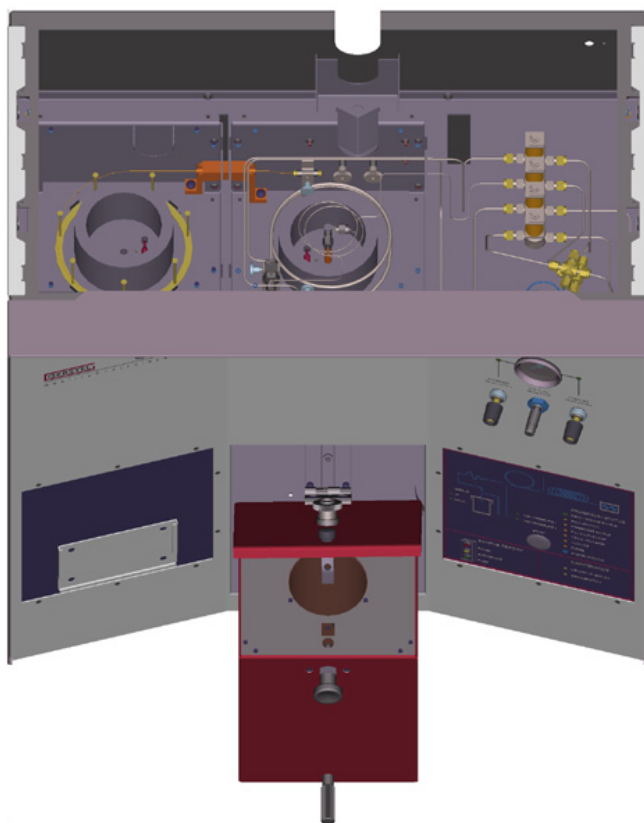

Figure 7. Instrument for sampling beverage cans; sampling unit (1) with sample heater (2); FID (3).

Figure 8. Design study of the instrumentation for beverage packaging analysis (sampling unit with sensor panel); by exchanging the sample oven also other sample types are possible.
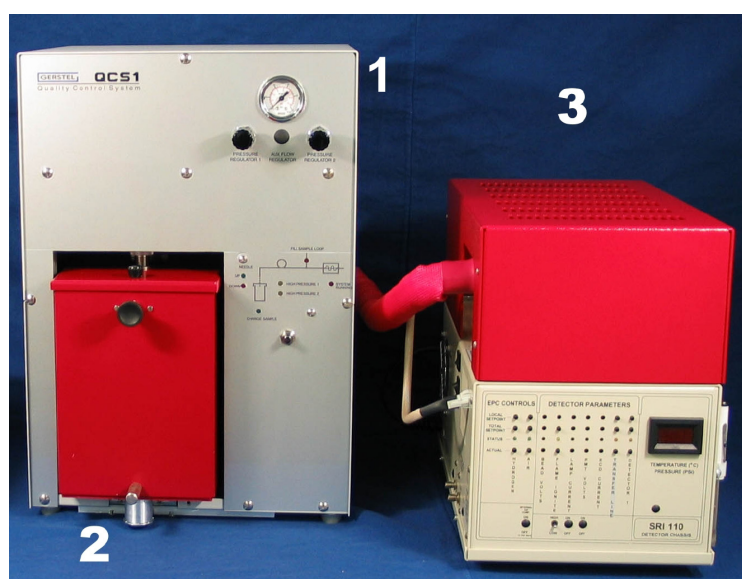
CONCLUSION

The combination of a simple headspace sampler with a small separation column and a sensor array with 3 micromachined metal oxide sensors provides an efficient tool for rapid quantitative determination of total residual solvent in packaging material. Using a packed polar column, the organic solvent peak and the water peak are fully separated. Good data can be obtained very quickly without interference fram water adsorbed in the packaging material. The next step will be to devise an application specific calibration method that will work without direct reference to analytical instrumentation results, enabling the use of the instrumentation for independent process quality control.

When equipped with a detector such as an FID instead of the sensors, the developed sampling unit is suitable for measuring volatile organic emissions from bulky packaging material such as metal cans or PET-bottles. The system is designed to be used in production facilities directly at the production line for quality control.

REFERENCES

[1] DIN EN 13628-1 and -2. Packaging; Flexible packaging material - Determination of residual solvents by static headspace gas chromatography. Part 1: Absolute methods; German version EN 13628-1:2002; and Part 2: Industrial methods; German version EN 13628-2:2002. DIN Deutsche Institut für Normung e.V. (German Institute for Standardization): Berlin, 2003

[2] DIN EN 14479. Packaging, Flexible packaging material - Determination of residual solvents by dynamic headspace gas chromatography – Absolute method; German version EN 14479:2004. DIN Deutsche Institut für Normung e.V. (German Institute for Standardization): Berlin, 2004

[3] Piringer, O.-G.; Rüter, M. in Plastic Packaging Materials for Food: Barrier Function, Mass Transport, Quality Assurance, and Legislation; Piringer, O.-G.; Baner, A. L., Eds.; Wiley-VCH: Weinheim, 2000; pp. 407-426

[4] Graf, M.; Barrettino, D.; Taschini, S.; Hagleitner, Ch.; Hierlemann, A.: Baltes, H. Anal. Chem. 2004, 76, 4437-4445

[5] Barsan, N.; Stetter, J.R.; Findlay, M.; Göpel, W. Anal. Chem. 1999, 71, 2512-2517

[6] Barsan, N.; Weimar, U. J. Electroceramics 2001, 7, 143-167

[7] Naes, T.; Isaksson, T.; Fearn, T.; Davies, T. Multivariate Calibration and Classification, NIR Publications: Chichister, 2002

[8] www.escape-project.org

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
@ gerstelag@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

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

ISO 9001
CERTIFIED QM-SYSTEM
ISO 9001:2008
CERTIFICATE NO. 0086 D

ECOPROFIT®

Awarded for the
active pursuit of
environmental sustainability