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Journal of Chromatography A, 845 (1999) 85–92

JOURNAL OF
CHROMATOGRAPHY A

Chemosensory system for rapid automated quality control

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Abstract

For determination of out-gassings from plastic materials gas chromatographic methods coupled with headspace or thermal desorption sampling techniques are very well established. Nowadays, as a new analytical method, gaseous samples can also be classified by use of a chemosensory system ('electronic nose'). Sensor measurements can be carried out quickly and enable reproducible detection of out-gassings in terms of a reliable finger print characterisation. The quartz microbalance chemosensory system under investigation uses the same sampling devices as headspace-GC and, moreover, an array of sensor elements which are coated with stationary phases of selected polarity, known from gas chromatography, as gas-sensitive layers for interaction with the analytes. This allows sensor method development to be complemented and verified by headspace gas chromatographic determinations. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Chemosensors; Headspace analysis; Polymers

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1. Introduction

As a result of the polymerisation procedure polymer material shows different properties related to, e.g., its amount of remaining monomers and other accompanying components. Acrylonitrile–butadiene–styrene (ABS) co-polymers are significantly different in their thermal stability if manufactured according to a bulk or to an emulsion polymerisation process, respectively. In order to get emulsion polymerisate thermally more stable polymers are treated with additives. These various procedures, but also minor differences in the production processes, influence the out-gassing characteristics, particularly if the polymer is exposed to elevated temperatures. On the other hand, this effect can be used as a quality indicator for the respective product.

This report describes a successful differentiation of the same type of polymer material from different polymerisation processes, due to their different out-gassing characteristics which can be determined by use of headspace-gas chromatography as well as by use of a sensor system. The latter does not require any separation step. Instead of a separation procedure, modern methods of pattern recognition routines are applied to the different signals coming from the array of differently responding sensor elements.

2. Sensor technologies for headspace determinations

A standardised and reproducible sampling technique is a precondition for reliable sensor measurements. Equilibrium headspace sampling has become a well-established procedure in analytical chemistry,

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PII: S0021-9673(99)00376-3

particularly in gas chromatography, for examining volatile compounds in almost any liquid and solid sample matrix. On the other hand, static headspace sampling offers a limited volume of headspace gas to be transferred to an analyser. Therefore, the sample path and the sensor cell should be of small volume which in addition guarantees a minimum of surface where un-wanted adsorption can take place.

General criteria for the selection of sensor elements are their sensitivity and, even more important, their reproducibility for the respective application. Nonetheless, different sample humidity should not affect the sensor response. Array dimension, i.e., number of sensor elements, influence the discrimination ability of a sensor system. A large sensor array, however, will increase the calibration effort considerably. Therefore, preferably less sensor elements with different but well-graded response characteristics are used rather than having a large array of sensor elements with very similar sensitivities.

If the sensors respond with a linear characteristic to the concentration of the volatile compounds, the signal pattern can be normalised in order to be concentration independent. This is necessary, if the quality and not the quantity of the volatile compound is in question. Furthermore, for quantitative analysis a linear sensor characteristic reduces the calibration and training effort considerably.

Different sensor technologies are used in today's commercially available sensor systems. The most important types of chemosensors used for this applicational field are inorganic metal oxide semiconductors, organic conducting polymers and mass-sensitive piezoelectric sensors. The latter can be splitted up into bulk acoustic wave and surface acoustic wave sensors, coated with stationary phases from gas chromatography or supramolecular host molecules.

Metal oxide semiconductor sensors (MOX) oxidise or reduce the analyte at elevated temperatures (250–450°C). As a result of this the electrical resistance of the sensor will change. The sensors show a non-linear characteristic. During the measurement the composition of the headspace gas changes due to the reaction, the signal pattern of the sensors will, therefore, change gradually as well. Below 30% of relative humidity the sensor response is remarkably affected by humidity variations. Therefore a humidity management is required to keep relative humidity well above 30%.

Due to their polar structure conducting organic polymers (CP), e.g. polymers of pyrrole and aniline, show response to polar compounds especially. By incorporating different metal ions in the polymer the interaction with polar analytes can be modified within a certain polarity range. A general characteristic of this type of sensor technology is its high sensitivity to humidity up to very high water vapour concentrations, which usually is a draw-back for samples with varying humidity.

Sensors based on mass-sensitive devices, such as quartz crystal microbalance (QMB) or surface acoustic wave (SAW) oscillators, respond on changes of mass very accurately via resonance frequency shifts. Coated with a gas-sensitive layer material, e.g., with stationary phases as known from gas chromatography, these devices can be used as gas sensors with a highly linear characteristic to a large variety of analytes. The interaction between volatile substances and the layer material, consisting of distribution and adsorption effects, results in a mass increase and changes the oscillation to lower frequencies.

In a typical SAW oscillator an acoustic wave propagates along the surface, whereas in a QMB crystal the acoustic wave propagates in the bulk. SAW sensors are coated with ultrathin gas-sensitive layers to avoid damping of the oscillation and are theoretically of higher sensitivity because of their higher resonance frequency. In practice this advantage is compensated by using thicker coatings on the QMB devices which results in a higher loading capacity of these sensors. The resonance frequency is one-order of magnitude lower compared with SAW oscillators, allowing a wider tolerance for temperature control of the oscillator electronics.

3. The quartz microbalance system

A large variety of chemical-sensitive coatings can be deposited onto quartz crystal microbalances. The long-term characteristics of these sensor types are mainly dependent on the ageing and bleeding of the coating material. Stationary phases used in gas chromatography have been optimised in respect to these features in the past. Also, a QMB sensor, coated with these polymers, is reasonably well understood in its physical and chemical properties and shows reproducible and stable behaviour for a wide range of chemical substances.

The sensor system QMB 6 uses a total of six different quartz microbalance sensors, coated with stationary GC phases. Three of each sensors are integrated on a common quartz substrate and all sensors are built in a small measuring cell of only 1.5 ml volume and are connected directly to the headspace injection needle head (Fig. 1). Sensor cell and all sample paths are temperature controlled.

The sensor system discriminates between complex headspace gas compositions without any separation step. In order to analyse the gas composition in detail and to complement the sensor method development a GC separation was run. This can be done separately or by splitting the headspace sample to the sensor and to GC instrumentation.

In contrast to other sensor technologies, piezoelectric resonators generate a fully digital electrical output signal with all advantages to further signal processing, e.g., no A/D conversion is required. The multivariate, six-dimensional data from the QMB 6 system are evaluated by principal component analysis for visualisation and multivariate discriminant analysis or artificial neural networks for classification of the samples [1,2]. A training set of data is collected for each sample class. Data from the same class should cluster in the multidimensional signal space. The classification routines evaluate the distance of the six-dimensional sensor vector to the respective cluster of sample classes, taking into account the distribution of the sample classes.

4. Experimental

An Automatic Headspace Sampler HS 40 XL (Perkin-Elmer, Norwalk, CT, USA) has been equipped with the Sensor System QMB 6 (HKR Sensorsysteme, D-81371 Munich, Germany). The interface was accomplished by coupling the sensor cell directly to the dosing head of the headspace sampler with a heatable transfer capillary of approximately 10 cm in length (Fig. 1). The sensor measuring chamber and the oscillators are included in a compact module, which is also temperature controlled. For each sensor element a special oscillator circuit is built up. The oscillators have a basic frequency in the range of 10 MHz with a resolution of ±1 Hz. Sensor data evaluation and management as well as complete control of the headspace sampler and the measuring process is performed by a personal computer with the help of QMBSOFT (HKR

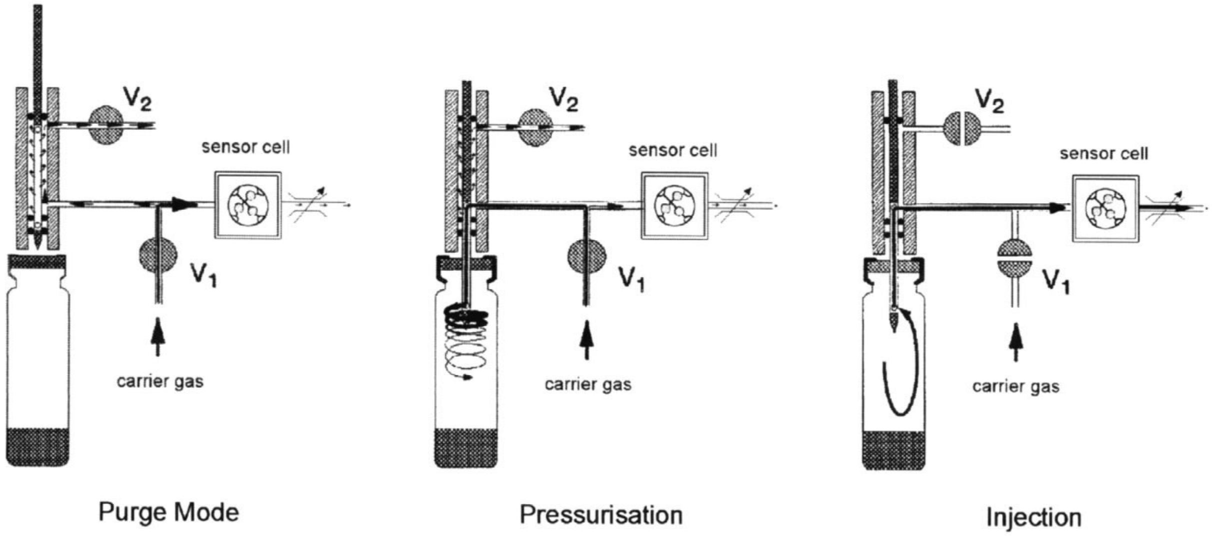


Fig. 1. Connection of the QMB6 measuring chamber to the headspace sampler and HS dosing principle.

Sensorsysteme) 32-bit software based on Windows NT (Microsoft, Redmond, WA, USA).

The chromatographic runs were carried out on a HS 40 XL Automatic Headspace Sampler connected with an AutoSystem XL GC, FID. For separation a 50 m×0.32 mm, 1 μm PE-5 capillary column and for data evaluation TurboChrom software (all equipment from Perkin-Elmer) was used.

Two grams of ABS polymer sample existing of small plastic chips of approximately 4×5×0.5 mm in size was weighed in each of the headspace vials and was thermostatted for 150 min at 90°C. After equilibration followed by pressurisation of the headspace vial to a predefined pressure the headspace gas was transferred to the sensor cell or to the gas chromatograph, respectively.

5. Results and discussion

Static headspace-gas chromatography (HS-GC) is a standard procedure for determination of volatile compounds in polymers. Quantitative analysis for this type of sample often is carried out by multiple headspace extraction (MHE) procedures. MHE compensates for the matrix influence on the headspace equilibrium. Theoretical background and principles of MHE techniques as well as their use for quantification are outlined in detail elsewhere [3]. The analysis presented here was done by applying a simplified procedure, which is commonly in use when quantitative data is in question on the basis of an average response [4]. This procedure directly corresponds with a HS-GC method for the determi-

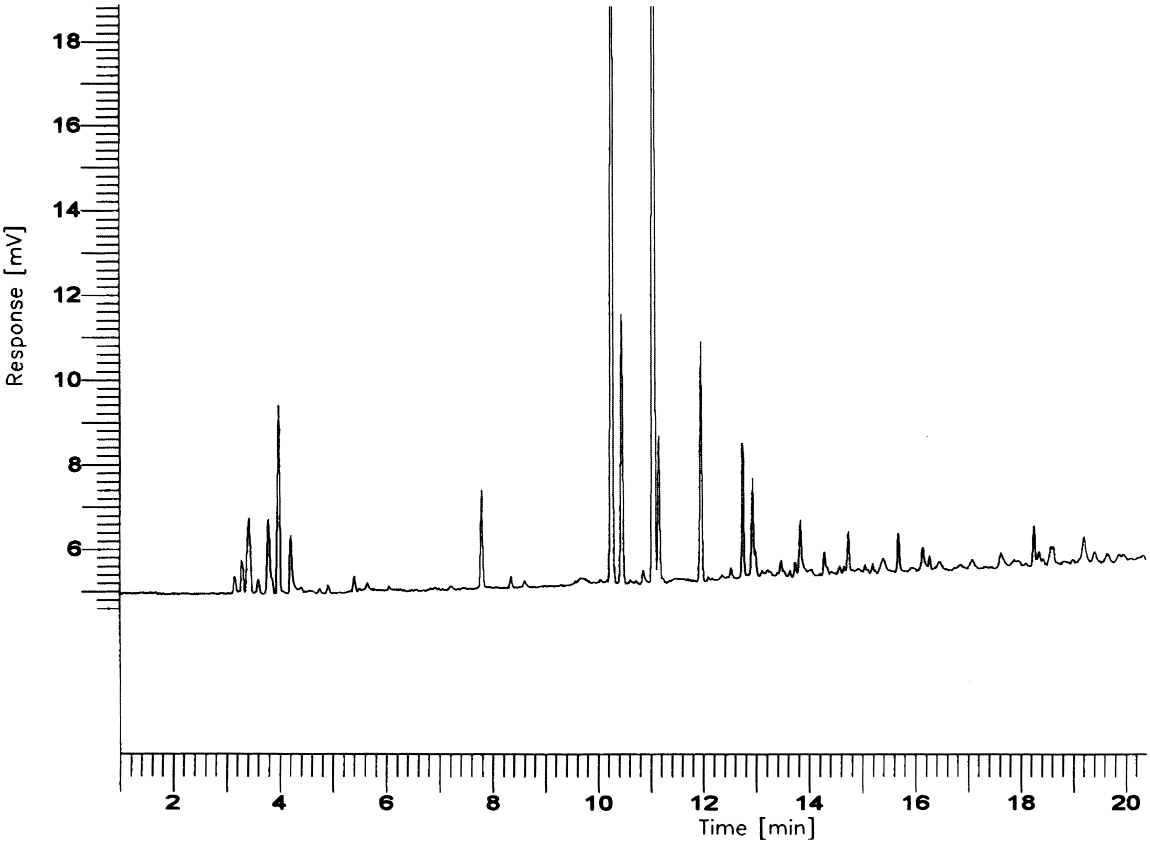


Fig. 2. HS-GC chromatogram of out-gassings from a ABS polymer manufactured according to a mass polymerisation process (sample ABS K).

nation of organic emissions from non-metal materials used in automobiles [5].

Six polymer samples were analysed coming from three generally different production processes, each pair from identical production process was of different manufacturing charges.

The HS-GC chromatograms varied regarding the number and also the intensities of the peaks as expected. With the bulk polymers (Fig. 2) the lowest flame ionization detection (FID) signals are observed, followed by the emulsion polymers (Fig. 3) and finally by those treated with additives. As already mentioned, data were not evaluated as a single peak identification but a peak area total was calculated in the retention time range between 3.1 and 18.5 min. These area total values were in addition normalised in order to get results which are comparable with those received from the QMB6 sensor system.

The first phase of the sensor analysis includes pressurisation of the sample to a predefined pressure and equilibration of the sample headspace for a pre-set time interval. The sample temperature is kept constant during the whole analysis. In the second phase the headspace is injected into the sensor cell by switching a solenoid valve (see Fig. 1). Within seconds the sensors reach a steady-state sensor signal. Due to the linear response the sensor signals can be normalised to form a concentration-independent pattern within 2–3 decades of the analyte concentration.

The multivariate data (six-dimensional) from the QMB 6 system is evaluated by principal component analysis for visualisation and mulitvariate discrimin-

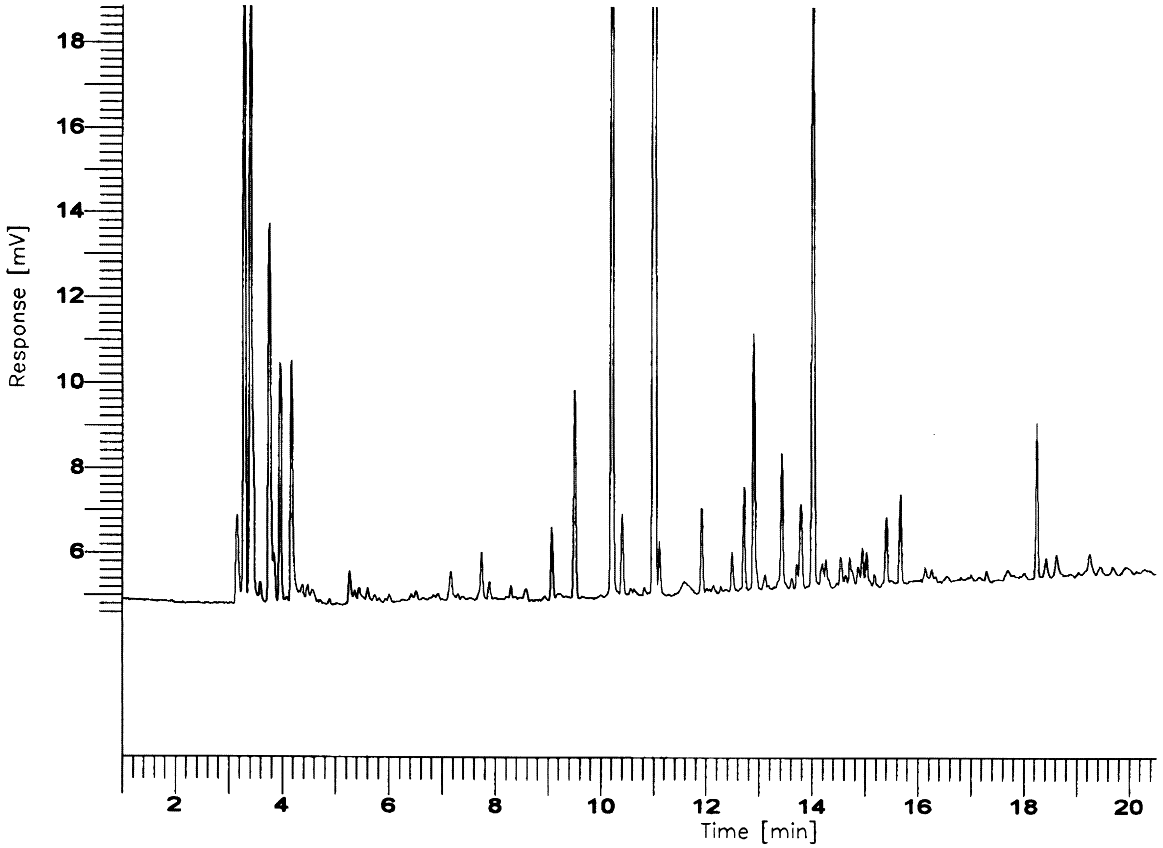


Fig. 3. HS-GC chromatogram of out-gassings from a ABS polymer manufactured according to an emulsion process (sample ABS Z D).

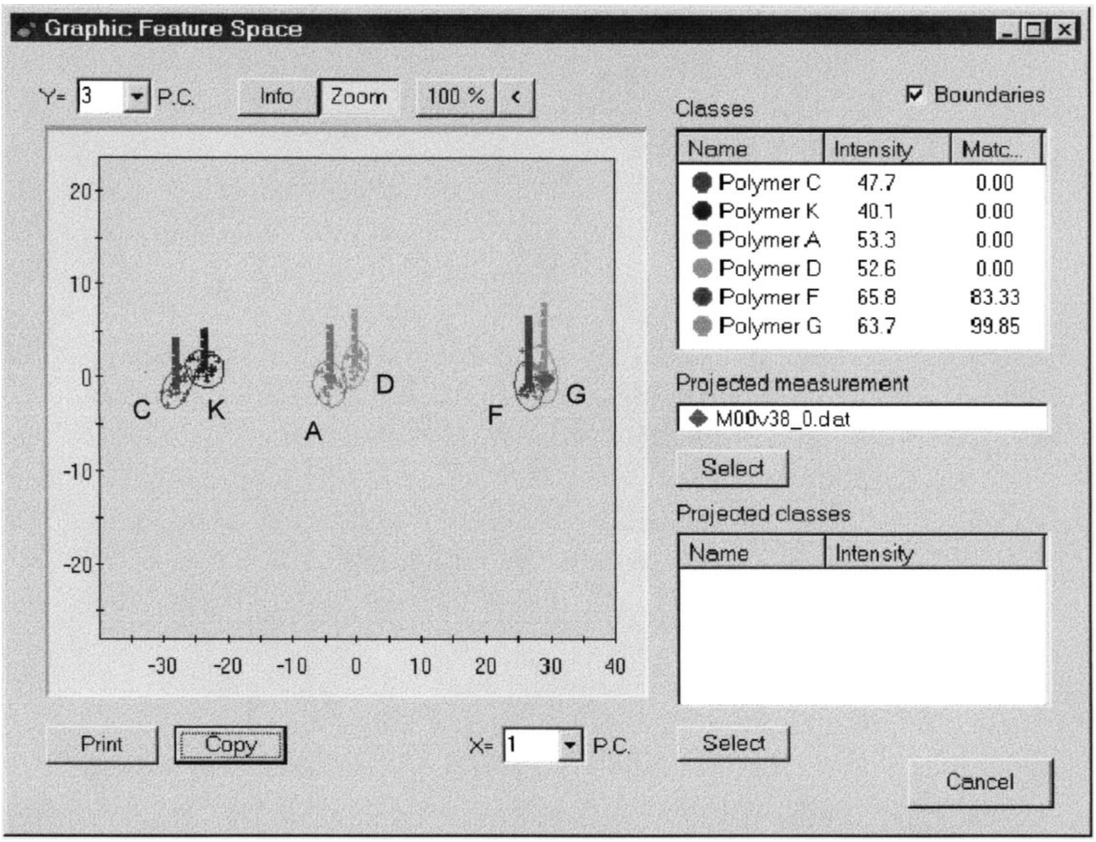
ant analysis or artificial neural networks for classification of the samples. As a first step, a training set of data is collected for each sample type generating a sample class. After that data (i.e., the data vector) from actual measurements are compared with the training data. The actual data vector should be close to one of these clusters, if identical composition of the headspace gas is detected.

The analysed polymer samples show six clusters of sample types on the discriminant plane (Fig. 4). The ellipses which represent a 95% confidential interval are well separated for the materials from the different polymerisation processes, while the samples from identical production processes, but from different batches, build data clusters closely overlapping on the discriminant plane, indicating a high degree of similarity.

A more detailed look on the response characteristics of the sensor shows the single element pattern plot (Fig. 5). The more non-polar coatings on the elements 1, 2 and 3 of the sensor array contribute most to the discrimination of the samples. This is in correspondence with the HS-GC analyses where non-polar and lower polar compounds (esters) were found (Fig. 6).

6. Conclusion

The quality of polymer material can be determined according to its out-gassing characteristics by use of a quartz microbalance sensor system. The sensor detects the composition of the volatiles in the gas phase very reproducible. The elements of the sensor



Y= 3 P.C.

X= 1 P.C.

☑ Boundaries

Classes

Name	Intensity	Matc...
● Polymer C	47.7	0.00
● Polymer K	40.1	0.00
● Polymer A	53.3	0.00
● Polymer D	52.6	0.00
● Polymer F	65.8	83.33
● Polymer G	63.7	99.85

Projected measurement

◆ M00v38_0.dat

Fig. 4. Analysis of ABS polymers by QMB6 sensor measurements. Polymers are classified according to their manufacturing processes. Ellipses show the 95% confidence interval of the respective material on the discriminant plane.

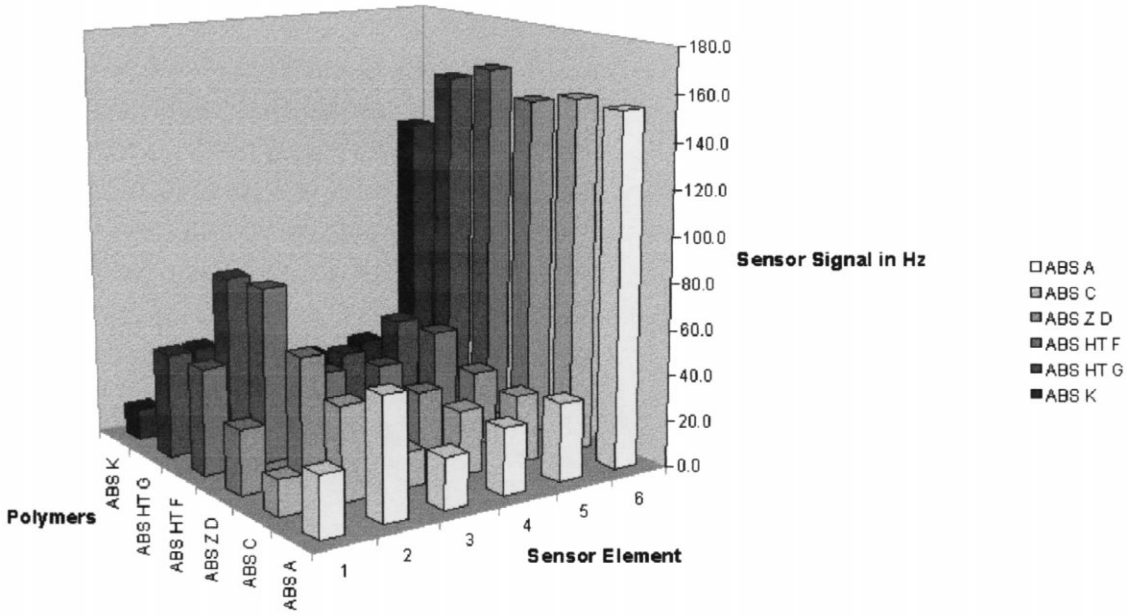


Fig. 5. Signal patterns of sensor array responses on different ABS polymers.

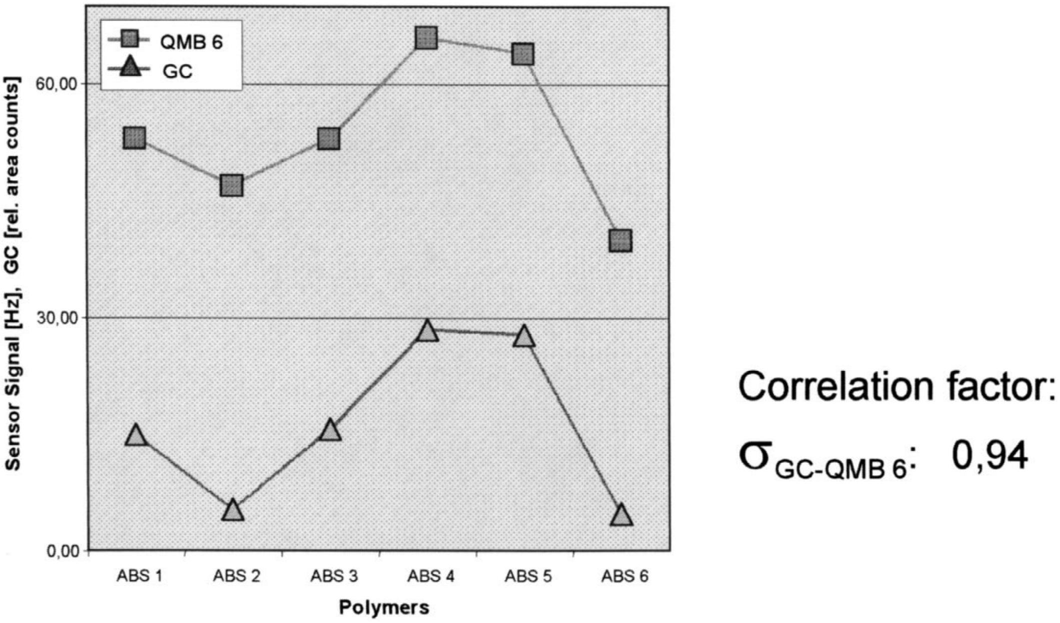


Fig. 6. Correlation between average sensor signals of QMB 6 and GC total area counts (normalized).

array are coated with selected stationary phases known from gas chromatography. They interact specifically according to their polar behaviour with the compounds of a gas mixture generating a typical signal pattern. The signal is evaluated by use of modern pattern recognition routines. The results achieved with the chemosensor correspond well with determinations performed by headspace gas chromatography.

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