

Fast Gas Chromatography Setup for Online Contaminant Monitoring in Plastics Recycling

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Summary:

This article presents a gas chromatography (GC) based solution for the online detection of contaminants in plastics recycling. The goal is to continuously assess post-consumer recycled plastics for adaptive treatment by stripping odorous substances and other contaminants in a compounding step. Based on earlier work, an automated sample transfer to a purpose-built GC setup has been devised. Steep heating rates and cooling rates exceeding -100 Kmin^{-1} allow for fast repetition of measurements and the integrated GC detector enables accurate peak reconstruction for dense short-column chromatograms.

Keywords: Gas chromatography, sampling, metal oxide sensor, plastics recycling, online monitoring

Introduction

Plastics recycling makes a significant contribution to sustainability as it helps to conserve finite fossil resources and reduce pollution. Therefore, legislation and commercial interests have led to recent developments in many aspects of the recycling loop. In order to reach the ambitious goals set by e.g. Directive (EU) 2018/852 [1], the recycling quota must be significantly increased. For post-consumer recycling (PCR), a major issue is the contamination of the collected material due to content residues and cross-contamination from other waste. One way to leverage PCR usage is to closely scrutinize the material at hand, ideally with continuous monitoring methods.

In prior work it has been found that a great variety of substances is present in PCR plastics processing [2], [3]. An interesting measuring location is the vacuum degassing of an extrusion process, such as the initial compounding or the recompounding steps; here, the overall conditions of molten material, high temperature and low ambient pressure force the phase change of contaminants to the headspace atmosphere [2]. However, this complicates the transfer of samples to the measurement system, especially when it needs a pressure gradient or temperature variation as it is the case with gas chromatography (GC) setups. The occurring phase transitions have been investigated [2] and a concept has been devised [3] and realized [4] to enable an online monitoring of relevant contaminants.

Materials and Methods

One main aspect of the sampling and measurement setup presented [4] is the need for fast temperature modulation of the system components. This includes the condensation/evaporation, adsorption/desorption parts as well as the GC oven and the detector; others can be stationarily tempered, e.g. valve blocks and connections. Heating can be accelerated by adding heating power when homogenous temperature spreading can be ensured [5]; however, temperature descents must be similarly enforced. This is realized by the integration of internal liquid cooling for all relevant parts. The cooling fluid is pre-cooled at $-15 \text{ }^\circ\text{C}$ to reset starting conditions within 60 s from the components' maximum temperature, requiring cooling rates beyond -100 Kmin^{-1} . The complexity of the automated setup requires that an industrial PLC (*programmable logic control*) replaces the self-made control from the setup [2], which also enables future integration into the automation context of the processing machine.

At the heart of the GC setup, a radiation heated oven accommodates a capillary column of 0.5 m to 5 m length and is equipped with twofold cooling capabilities (air exchange and fluid cooling) and an integrated detector to prevent cold zones on the column. Low thermal mass and adjustable insulation allow for fast thermal ramps [4]. The use of a self-heating [6] or micromachined column [7] known from other fast and sensor GC applications was dismissed: Using the same FFAP as in the laboratory analyses allows to

maintain comparability with those analyses. Also, the focus in the current application is robust operation, rather than miniaturization.

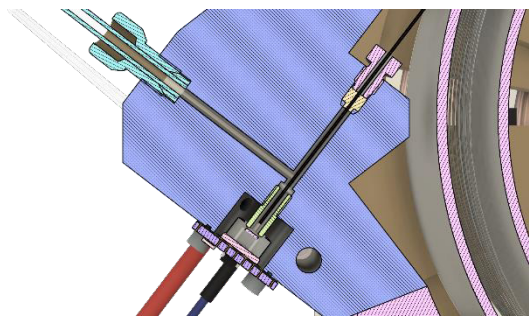


Fig. 1. Cross-section of the integrated detector in the GC oven. Makeup gas (top left) and eluents from the capillary column (top right) are applied directly to the gas sensor (bottom left).

Regarding the detector, metal oxide semiconductor (MOS) gas sensors have been found suitable as GC detectors, especially for fast GC setups with short gas peaks [8]. Certain aspects are crucial for effective detection, such as the gas transfer from the column to the sensing layer. Based on the approach shown in [9], the oven-integrated detector of Fig. 1 has a tailored nozzle that brings eluents and makeup gas directly to the sensing layer. As illustrated in Fig. 2 for a GGS 1330 (*Umweltsensortechnik GmbH, Geratal, Germany*), the resulting concentration profile at the sensor enables accurate peak reconstruction. Adding dead volume between column and sensor results in a significantly poorer gas profile as shown for the outlet of the sensor chamber.

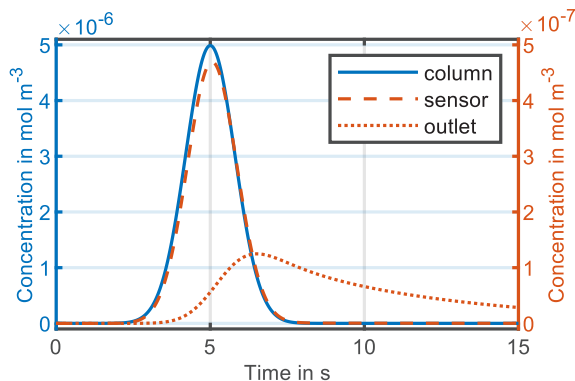


Fig. 2. COMSOL simulated peak concentrations in the column (left y-axis), on the sensing layer and at the sensor chamber exhaust (both right axis). Right y-axis scaled 10-fold to consider dilution by make-up gas.

The nozzle is exchangeable to adapt to various sensors. Fitting sensor boards have been made for analog thick-film and thin-film sensors as well as recent types with integrated digital interface.

Results and Outlook

The novel setup presented combines a complex process sampling method exploiting phase transition processes and an integrated GC oven with

MOS sensor detector. This provides a fast and cost-efficient solution for the current task of contaminant monitoring in PCR plastics and will be demonstrated in on-site experiments at the compounding extruder. The setup also allows for extensive research on implementation details and adaptation to emerging applications.

Acknowledgements

This work has been funded by the German Federal Ministry of Education and Research (BMBF) under grant number 033K1116 as part of the innovation lab KIOptiPack.

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