Polymers in the Microwave

Fast Ways to Extract Additives

Polymers are usually stabilized with additives in order to maintain the desired properties despite environmental stress and aging. The adequate determination of such compounds is of great importance for polymer research, process control and quality assurance. The most error-prone and critical process step in these cases – as in many other analytical processes – is the sample preparation, the extraction of the analytes prior to the detection step.

Plastics and Additives

There are a great number of polymers, co-polymers, blends and additives to control the properties of plastic products. These additives can be UV-stabilizers, antioxidants, antistatic agents, plasticizers, lubricants, acid scavengers, nucleating and clarifying agents, optical brighteners, cross linkers and several others, which are introduced to accurately control material behavior. The physical and chemical properties are manifold, as are the demands on the analytical workflows for the determination of such additives from different polymer matrices.

Standard Workflow

There are different approaches for the determination of polymer additives. The most common way is to extract the additives after a homogenization step with organic solvents and detect the molecules of interest with HPLC (high-performance liquid chromatography). Figure 1 shows the typical workflow for the analysis of stabilizers in plastic materials. Each of those steps carries certain error risks; the biggest challenge for the analytical chemist is to develop methods with minimized error.

Nowadays there are several commonly used methods to extract additives from the polymer matrix, including ASE (Accelerated Solvent Extraction), SFE (Supercritical Fluid Extraction) and MAE (Microwave-assisted Solvent Extraction), which have displaced classical extraction techniques like Soxhlet extraction or simple heating under reflux conditions. These methods are faster, more convenient, consume much less reagents and are also more reliable in terms of repeatability and error rate.

Though MAE has gained an increased market share in the recent past, the potential of microwave chemistry for sample preparation in polymer analytics is far from exhausted.

Challenges in the Method Development

To ensure that a HPLC system can be applied for the detection of the analytes, one important point has to be considered: dissolved polymer residues in the extract hinder the adequate detection of the analytes because of the fact that commonly used eluent mixtures (e.g. acetonitrile, methanol and water) cause precipitation of the polymer which may damage the whole chromatographic system.

The analyst has to find a selective solvent – this demands a systematic and complex method development procedure – or has to introduce an additional precipitation step prior to the detection, resulting in higher measurement uncertainty.

A further point which has to be investigated during method development and validation processes is the stability of the additives of interest.

In order to receive robust and reliable methods for the routine analysis of several analytes and polymer matrices, a lot of extraction parameters must be varied and tested systematically. Besides the earlier mentioned compatibility between extraction agent, polymer and additive,

Fig. 1: General workflow for the determination of additives in plastics

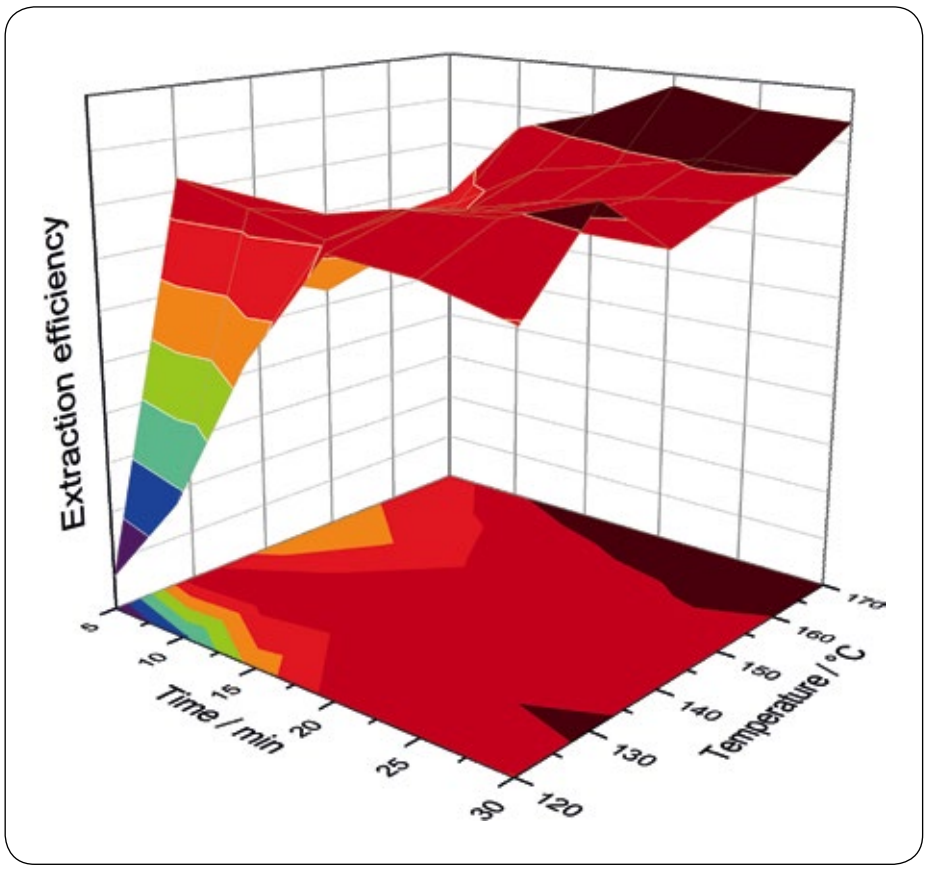

Fig. 2: Optimization of the extraction procedure for Irganox 1330 in polypropylene extracted with ethyl acetate

the right extraction temperature and time are equally crucial to the success of an analytical method. A systematic method development is therefore clearly essential to match the according polymer type, additive and solvent. In such cases the high throughput capabilities offered by microwave systems are certainly advantageous when performing screening experiments for comprehensive method development tasks.

Influence of Temperature Measurement

Figure 2 shows the results of an experiment series showing the extractability of a typical stabilizer for polypropylene (Irganox 1330) with ethyl acetate under different conditions, resulting in 36 experiments performed to determine the optimum extraction parameters [1]. The best overall parameters led to analyte recoveries of 95 % of the declared values and a method reproducibility better than 2 %. In this context the importance of the temperature measurement should also be mentioned. Temperature deviations during the extraction can lead to reduced reproducibility and recovery or undesired dissolution of the polymer matrix itself. Therefore it is advantageous to work with a system which allows the measurement of the temperature directly in the vessel instead of an IR measurement on the vessel surface outside. Modern microwave systems offer such a temperature measurement option. For example, the Ruby Thermometer used in Monowave 300 (Anton Paar, Graz, Austria) ensures an exact temperature measurement in the vessel during the whole extraction process.

Summary

The sample pretreatment procedure for the analysis of additives in plastics can be significantly simplified and accelerated by means of modern extraction techniques such as microwave-assisted extraction.

MAE (Microwave-assisted Solvent Extraction) is a fast, robust and efficient method supporting modern analytical chemistry. Monowave 300 with MAS 24 and the Ruby Thermometer offers features like stirring, internal temperature measurement and automation – all prerequisites for effective and efficient method development tasks.

References

[1] Sternbauer L. *et al.:* Polymer Testing 32, 901-906 (2013)

Contact
Edit Marosits
Anton Paar GmbH
Graz, Austria
edit.marosits@anton-paar.com
www.anton-paar.com