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Determination of nucleating agents in plastic materials by GC/MS after microwave-assisted extraction with *in situ* microwave-assisted derivatization

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ABSTRACT

This work demonstrates the analysis of sorbitol-based nucleating and clarifying agents (NCAs) used as additives for polyolefin-based materials by gas chromatography/mass spectrometry (GC/MS), employing a highly reliable and efficient sample preparation methodology applying microwave irradiation. A derivatization by silylation of the analytes was done to improve the GC-suitability of the analytes. After successful optimization of the conditions for a microwave-assisted derivatization (MAD), the microwave-assisted extraction (MAE) of the analytes from polymer samples was investigated. Tetrahydrofuran (THF) turned out to be the best extraction solvent, as poorly soluble analytes show the highest solubility in this solvent and THF supports the silylation after extraction. This two-step approach and subsequent chromatographic determination resulted in reproducibilities from approximately 2% up to 6% and recoveries from 95.8% up to 104.2% in real samples. In order to reduce the number of sample preparation steps a one-step approach was investigated and optimized, in which MAE and MAD were carried out simultaneously. The developed procedure resulted in remarkably better repeatabilities ranging from 0.05% up to 4% and reproducibilities of up to 10%. The recoveries matched those obtained with the two-step process. Linearities could be achieved in both approaches with R^2 better than 0.99 for all selected analytes over two orders of magnitude. All data indicate the suitability of both presented methods for the reliable determination of sorbitol-based NCAs in polyolefin materials.

1. Introduction

Nowadays, plastic materials have a decisive influence on our everyday lives. Especially polyolefins have become a major player in plastic applications as they can be used in a lot of different areas as for example in automotive or packaging industries. In order to improve the properties of polyolefins, various different substances can be added during their manufacturing process such as antioxidants, UV-stabilizers, antistatic agents, plasticizers, slip agents, processing aids, acid scavengers, nucleating and clarifying agents, optical brighteners, crosslinking agents and a lot more, typically present at levels from 0.01% to 0.5% in the polymer.

Polyolefins are semi-crystalline polymers. The degree of crystallinity influences the mechanical, thermal and chemical properties of the materials. Polypropylene crystallizes rather slowly by formation of relatively big spherulites. The size of the spherulites is larger than the wavelength of visible light. Consequently the light is scattered at the spherulites, which causes the material to appear opaque. This is highly undesired for the production of clear plastic materials. The nucleation process can be influenced by addition of so-called nucleating agents. Ordinary nucleating agents simply initiate the formation of spherulites, but they do not improve the optical properties of the material. In the last years several different types of new nucleating agents having a clarifying effect on the material were developed [1–4]. By the use of such nucleating and clarifying agents (NCAs) the formed spherulites are smaller than the wavelength of light, which results in a reduction of haze. By the use of such NCAs, polyolefin materials can be used for applications where the material should be clear and transparent like household storage containers, various product packaging improving the esthetics or laboratory equipment. This fact offers new application possibilities of polyolefins as they now can compete with other transparent thermoplastics like polyethylene terephthalate and amorphous plastic materials such as polystyrene or polycarbonate [5], especially considering the controversial application of the latter two polymers because of their rather toxic monomers styrene and bisphenol A in food packaging industry. Additionally, the use of highly effective nucleating and clarifying

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agents also leads to reduced odor of plastic materials, to an enhancement of productivity, as well as to a reduction of energy, CO_2-emissions and costs by lowering processing temperatures and cycle times [5].

For the successful development and design of new plastic materials with desired properties as well as to assure the materials' quality, analytical techniques are demanded to determine the level of additives such as NCAs in polyolefin samples.

Differently to studies about the physical properties and effects of NCAs as well as resulting material properties [1–4,6–9], hardly any analytical studies were published dealing with the analysis of NCAs.

This paper in particular deals with sorbitol-based NCAs, which have been widely used since their introduction. Even though these NCAs are so popular, analytical studies have been carried out to a low extent. Most probably this is because of the very poor solubility of these substances in various solvents, which complicates the preparation of stock solutions [10] and also the choice of a proper extraction solvent.

First analytical studies were carried out in 1998, presenting the matrix-assisted laser desorption/ionization mass spectrum of one selected sorbitol-based NCA in the context of thermal vapor deposition, already mentioning the solubility problems occurring with these types of sorbitol derivatives [11]. Most of the rare work on sorbitol-based NCAs was conducted in the field of studies on extractables and leachables. In 2002, strategies for performing migration studies were discussed by Feigenbaum et al. [12], in which the extraction of one sorbitol-based NCA and gas chromatographic data were mentioned. In 2006, sorbitol-based NCAs were noticed in the context of suitability of packaging for pharmaceuticals as a conference proceeding, which was published by Jenke in 2008 [13]. A sorbitol-based NCA could be detected after refluxing samples in *iso*-propanol and subsequent liquid chromatography with UV-detection (LC/UV). The most recent work notes NCAs as possible contaminations and interferences in everyday lab-work-flow when using plastic articles such as pipette tips, vials or other containers made of plastic [10], and chromatographic as well as mass spectrometric data of selected NCAs and their trimethylsilyl (TMS)-derivatives were provided. LC/MS has also been investigated within this work [10]. Because of the low dissolution propensities, liquid chromatography needs tailored mobile phase compositions and gradients in order to elute the substances from the column and to provide a good separation from other sample components. Especially in real samples, known and unknown matrix components can cause interference. Poor separation in liquid chromatography can lead to suppression effects when mass spectrometric detection is applied. For routine applications in industries, GC/MS is favored because it is easy to use and robust. Additionally to the high separation efficiency, GC/MS (similar to LC/MS) is well known for its excellence in quantitation. Even though very often derivatization is an undesired but necessary sample preparation step, it can enhance the volatility and stability of the analytes and it may lead to better separation and to unique mass spectral features facilitating identification and quantitation. By means of modern autosamplers and state-of-the art sample preparation equipment such as microwave reaction systems, derivatization reactions can be done reliably and fast.

Until now, no proper and complete analytical methodology for the extraction and determination of sorbitol-based NCAs has been developed to our knowledge. On the other hand, the need for reliable analytical methods for the identification and determination of sorbitol-based NCAs was clearly illustrated recently in August 2013, when holders of the patents for NCAs claimed other Asian companies of infringing their patents by selling competitive NCAs [14].

This work presents a microwave-assisted extraction of these types of NCAs together with a microwave-assisted silylation using *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) without any prior sample pre-treatment such as cryogenic milling *etc.* Furthermore, the two-step sample preparation could be translated to a single step without losing analytical performance. Additionally, we present a mechanism of ion formation, clarifying the fragmentation pattern of the electron ionization (EI)-spectra of the TMS-derivatives, which could not be explained until so far [10]. The postulated mechanism could be applied to all selected analytes and also lead to successful identification of other derivatives of sorbitol-based NCAs occurring in real samples which were not scope of this work in the beginning.

2. Experimental

2.1. Chemicals

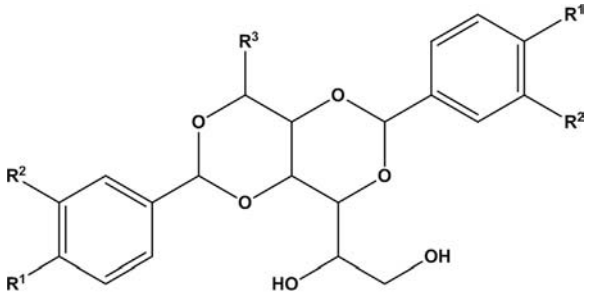
The sorbitol-based NCAs Irgaclear D and Irgaclear DM were obtained from BASF (Ludwigshafen, Germany), Millad 3988 and Millad NX 8000 were both obtained from Milliken (Spartanburg, SC, USA) and NC-4 from Mitsui Chemicals (Tokyo, Japan).

The structures and further information of the five selected analytes are shown in Fig. 1. Triphenylbenzene (Merck, Darmstadt, Germany) served as internal standard for GC. All substances were dissolved in tetrahydrofuran (THF) for chromatography (LiChrosolv®, Merck, Darmstadt, Germany). For the derivatization of the target analytes, *N*,*O*-bis(trimethylsilyl)trifluoroacetamide containing 1% of trimethylchlorosilane (TMCS) from Aldrich (St. Louis, MO, USA) was used. Pyridine obtained from Aldrich (St. Louis, MO, USA) was used as supporting solvent for the silylation reaction as it acts as proton scavenger.

Stock solutions of each of the chosen NCAs were prepared in THF at a concentration of 200 mg L^{-1} as this was the maximum concentration that could be achieved for all analytes. Other solvents failed in providing higher dissolution propensities. The internal standard was dissolved at 500 mg L^{-1} in THF. Further dissolutions if necessary were all done in THF.

2.2. Samples

Two real polypropylene (PP) samples served for the development of the two-step and the one-step procedure. The NCAs



Tradename	R^1	R^2	R^3	CAS-no.
Irgaclear D	H	H	H	19046-64-1
Irgaclear DM	Me	H	H	81541-12-0
NC-4	Et	H	H	79072-96-1
Millad 3988	Me	Me	H	135861-56-2
Millad NX 8000	*n*-Pr	H	*n*-Pr	882073-43-0

Fig. 1. Basic structure of sorbitol-based NCAs and an overview of different side chains giving the substances discussed in this work, their systematic names and CAS-numbers.

present in the two materials were Millad 3988 and Millad NX 8000, respectively.

For the validation of the two-step and one-step method, commercial technical-grade polypropylene containing various additives like antioxidants and others was used to investigate matrix interferences.

2.3. Instrumentation and parameters

All microwave-related experiments (extractions and derivatizations) were conducted in a Multiwave PRO from Anton Paar (Graz, Austria). Depending on the size of the used analytical vials, two different rotors for the Multiwave PRO were used. Each rotor offered place for four silicon carbide (SiC)-plates. Different SiC-plates were used for different vial sizes. A SiC-plate for 2 mL vials could accommodate 20 glass vials, whereas SiC-plates for 5 mL vials could offer 24 positions each. The system was run at the maximum power recommended, depending on the number of SiC-plates being used during operation (700 W for 2 plates, 1500 W for 4 plates). The power input was controlled via an infrared (IR)-temperature sensor. As the IR-temperature sensor is located underneath the SiC-plates, the effective temperature in the vials differs from the IR-temperature by a factor of 1.15. This conversion factor is provided by the manufacturer of the instrument. An IR-temperature of 100 °C refers to an actual temperature of 115 °C in the vials.

The tightly capped vials could be operated with sample solution volumes between 0.1 and 1.5 mL in case of 2 mL vials, and between 0.3 and 3 mL in case of 5 mL vials. Both types of glass vials can withstand a maximum pressure of 20 bar according to the specification of the manufacturer.

Separation and detection of derivatized NCA-species was carried out on an Agilent 6890N/5973N gas chromatography/mass spectrometry (GC/MS) system (Palo Alto, CA, USA) utilizing helium as carrier gas at a constant flow rate of 1.5 mL min^{-1}. The GC was equipped with a programmed temperature vaporization inlet (Cooled Injection System 4, CIS 4) from Gerstel (Mülheim an der Ruhr, Germany). The analytical column was a ZB-35HT (15 m × 250 μm × 0.10 μm) from Phenomenex (Aschaffenburg, Germany). Sample introduction was performed by injecting 1 μL in splitless mode into a 2 mm ID single-baffle liner containing deactivated quartz wool (Sky®-deactivation) from Restek (Bellefonte, PA, USA) at 40 °C (0.08 min) which then was heated at 12 °C s^{-1} to 275 °C (2 min). Separation of the analytes was achieved by a linear temperature gradient of the GC oven starting at 40 °C (0 min) and ending at 370 °C (2 min) at a rate of 30 °C min^{-1}. The MS transfer line was held at 300 °C throughout the whole run. Detection was carried out in electron ionization (EI) mode at 70 eV after a solvent delay of 3 min with source and quadrupole temperatures of 230 °C and 150 °C, respectively. Mass spectra were recorded in scan mode in the 50–800 m/z range.

2.4. Sample preparation

2.4.1. Two-step approach

2.4.1.1. Derivatization of NCAs within the two-step approach. The derivatization was optimized regarding time and temperature. The time was varied between 10 min and 30 min and the temperature between 100 °C and 150 °C. For this purpose a standard solution of NCAs was prepared containing approximately 40 mg L^{-1} each and the internal standard at 50 mg L^{-1}. 50 μL of this standard solution were transferred into a 2 mL-vial, 50 μL pyridine and 50 μL silylation reagent (BSTFA: TMCS 99: 1) were added. Using THF the final volume was adjusted to 500 μL. The vial was closed with an appropriate teflon-sealed screw cap and put into the SiC-plate. A metal plate was placed right on top of the vials within the SiC-plate and fixed with screws in order to prevent the vial's septum from rupturing. After MAD, the samples were allowed to cool down before they were subjected to direct GC/MS analysis.

It turned out, that the temperature is the most important factor in silylation of the compounds. A time of 10 min and a reaction temperature of 150 °C gave the most complete reaction yielding in the highest peak areas of TMS-derivatives. Extending the time to 30 min at 150 °C did not give higher yields. Reducing the temperature and extending the time did not transfer the NCAs into their TMS-ethers quantitatively. Consequently, 10 min at 150 °C IR were chosen to be the MAD conditions for the two-step process.

2.4.1.2. Extraction of NCAs within the two-step approach. The microwave-assisted extraction (MAE) was adapted from our previous work in the field of polymer extraction [15]. The main difference of the mentioned reference to this work is the use of SiC-plates in which the glass vials were placed. Without employing SiC-plates the heating of the solvent assisted by microwaves takes place by mainly dipole rotation (and ionic conduction) of the solvent itself, generating an in-core heating. Especially for solvents that are less susceptible to microwaves, SiC supports the heating process. SiC is heated by the microwaves very efficiently so that an additional “conventional” heating by means of conduction facilitates the in-core heating. The choice of THF instead of ethylacetate (EtOAc) as in [15] was not expected to lead to dramatical changes in microwave interaction and extraction behavior, as THF and EtOAc have quite similar properties such as boiling point, dissolution propensities and dissipation factors [16].

For MAE of the NCAs approximately 50.0 mg polymer sample pellets of known NCA content were weighed accurately into a 5 mL-vial. After addition of 250 μL of internal standard (500 mg L^{-1} triphenylbenzene in THF) and 2250 μL THF the vial was closed with a lip-type teflon seal and a PEEK screw cap and put into a SiC-plate of the microwave system. The extraction was performed for 25 min at 135 °C IR. After cooling down to room temperature, the sample was passed through a 0.45 μm nylon syringe filter (Machery-Nagel, Düren, Germany). 50 μL of the clear solution were subjected to MAD as described in Section 2.4.1.1.

2.4.2. MAE with in situ MAD of NCAs as one-step approach

For the development of a one-step method for both the MAE and MAD a Box–Behnken-design of experiment (DOE) with three center points was conducted using the DOE-software Design Expert 8 (Stat-Ease, Inc., Minneapolis, MN, USA). The basic conditions of 50.0 mg of sample weight and a total volume during the experiments of 2.5 mL were kept constant during all experiments. The parameters that should be optimized were the amount of pyridine, the amount of silylation reagent, time and temperature. The amounts of pyridine and silylation reagent were varied between 50 and 250 μL. The time was optimized between 10 and 30 min and the temperature ranged between 120 and 150 °C. The low and high values are coded by the software with −1 (lowest level) and +1 (highest level). An overview of the parameters and coding factors is given in Table 1. Response variables measured were the ratio of the peak areas of the target analytes

Table 1
Coding factor levels of the Box–Behnken design.

Parameters	−1	+1
V(Pyridine) (μL)	50	250
V(Silylation reagent) (μL)	50	250
Time (min)	10	30
Temperature (°C)	120	150

(Millad 3988 and Millad NX 8000) and the internal standard related to the mass of sample. The concentration of the internal standard (50 mg L^{-1}) was kept constant throughout all experiments.

The further procedure for the operation of the Multiwave PRO is given in Section 2.4.1.2. After cooling down and filtration as described in Section 2.4.1.2, the filtrate was diluted 10-fold with THF prior to GC/MS analysis.

3. Results and discussion

3.1. GC performance and mass spectral features

A silylation of the target analytes was indispensable, as the underivatized species gave unacceptable peaks shapes and responses.

Fig. 2 shows a chromatogram of the separation of TMS-derivatives of the selected sorbitol-based NCAs. A good separation could be achieved with the chromatographic conditions given in Section 2.3. Especially the TMS-derivatives of NC-4 and Millad 3988 were nicely separated even though they possess the same molecular masses and their structures only differ in the alkyl-residues of the aromatic domain. NC-4 shows one ethyl side chain, whereas Millad 3988 has two vicinal methyl groups. The EI mass spectra of the TMS-ethers of Irgaclear D, Irgaclear DM and Millad 3988 were already discussed in previous work [10]. TMS-NC-4 exhibits the same mass spectral features as TMS-Millad 3988. Although mass spectrometric detection was used, confidence in identification of these two analytes could only be achieved by a chromatographic separation. The EI mass spectrum of the TMS-derivative of Millad NX 8000 is shown in Fig. 3A, which was not available in literature until so far. Although the mass spectra of common NCAs have been already investigated, the authors claimed that the formation of the base peak of TMS-Irgaclear D at m/z 179 was not fully understood [10]. Differently to Irgaclear D, the NCAs Irgaclear DM, NC-4 and Millad 3988 feature alkyl side chains on their aromatic rings (two additional methyl groups for Irgaclear DM, two additional ethyl groups for NC-4 and four additional methyl groups for Millad 3988). The mass spectra of TMS-Irgaclear DM and TMS-Millad 3988 (and consequently also TMS-NC-4) show signals occurring at m/z 193 and m/z 207, respectively. Even though these features are not the base peaks in the corresponding spectra as in the mass spectrum of TMS-Irgaclear D, the assumption of a correlation between the structural features and the mass spectral signals is quite obvious as the difference is always m/z +14. However, conventional fragmentation mechanisms as already discussed [10] did not lead to a clear

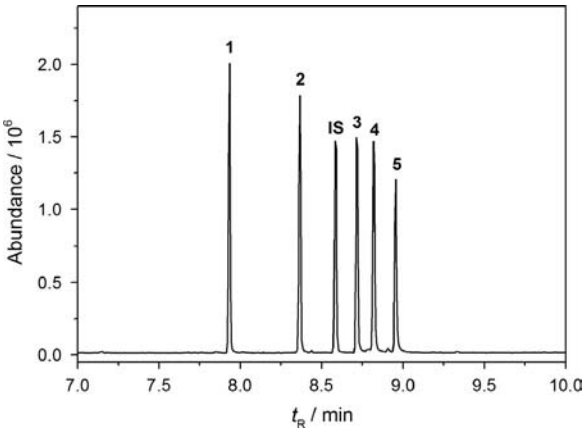


Fig. 2. Chromatogram of a standard solution of the TMS-derivatives of the NCAs Irgaclear D (1), Irgaclear DM (2), NC-4 (3), Millad 3988 (4), Millad NX 8000 (5), all at a level of 6 mg L^{-1} and the internal standard (IS) at 5 mg L^{-1}.

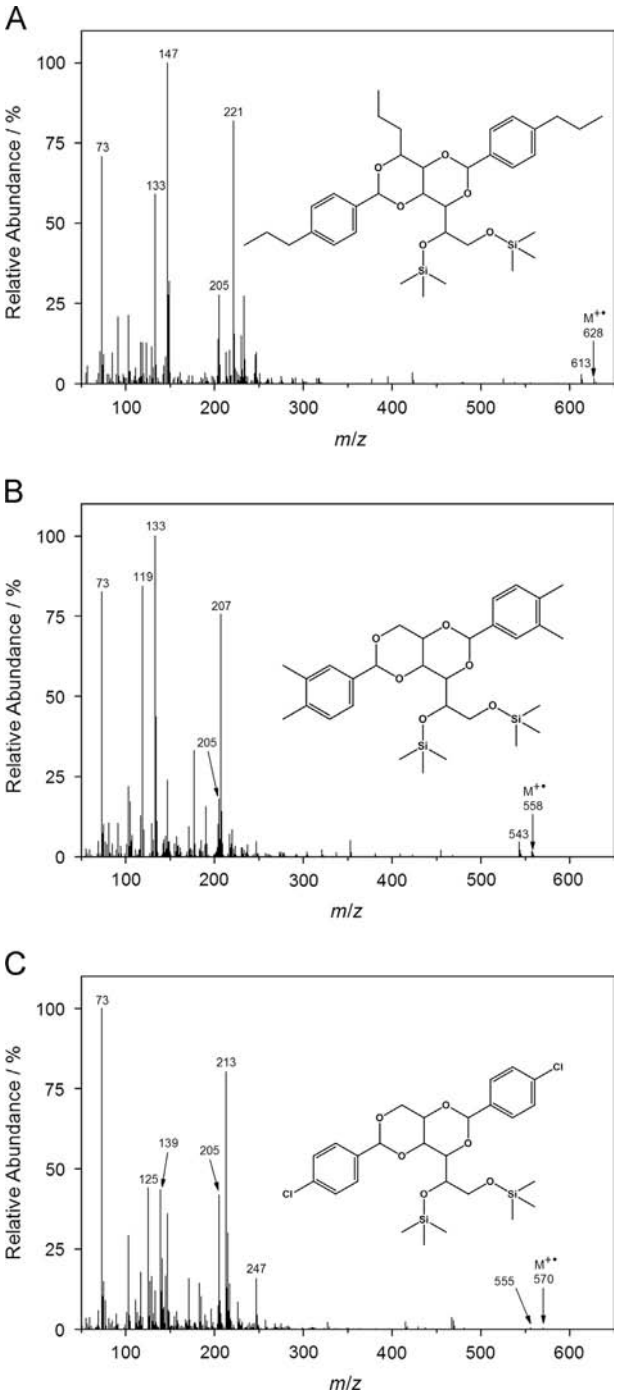


Fig. 3. EI-mass spectra and structures of TMS-derivatives of Millad NX 8000 (A), Millad 3988 (B) and the chlorinated species (C), which was identified in a real sample.

understanding of the formation of these species. In Fig. 4 we postulate a mechanism of ion formation, which successfully explains all signals (m/z 179, 193, 207 and 221 for Millad NX 8000). The first step in the mechanism is the homolytic cleavage of the acetal bonds leading to a positively charged substituted benzaldehyde radical (I) which can recombine with a previously formed trimethylsilyl radical (II) which leads to the final substituted benzylidene(trimethylsilyl)oxonium ion (III). This approach enables to clarify the formation of major signals in all mass spectra of selected sorbitol-based NCAs.

During analysis of real samples, one sample showed a peak occurring at the same retention time as TMS-Millad 3988, however

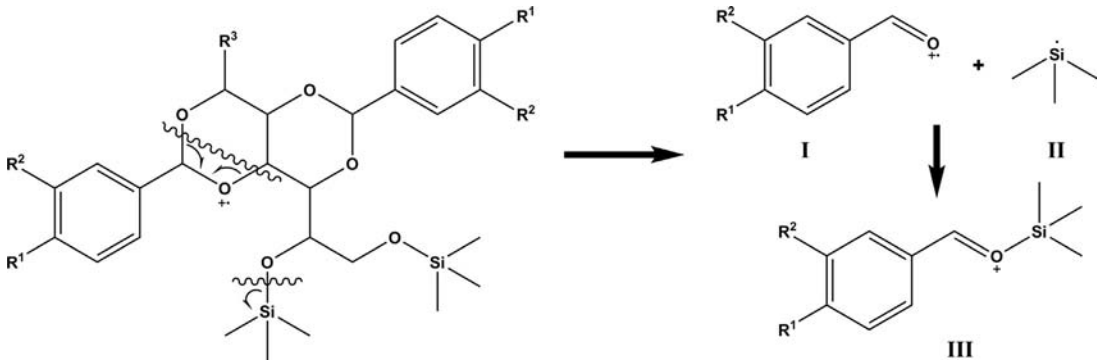


Fig. 4. Proposed mechanism of ion formation giving characteristic signals in the EI-mass spectra of TMS-derivatives. For a detailed description refer to text.

the mass spectrum observed in scan-mode did not correspond to TMS-Millad 3988 (Fig. 3B and C). By applying the postulated mechanism of ion formation and due to the observation of highly significant isotopic patterns, the structure elucidation revealed the presence of 1,3:2,4-bis-*O*-[(4-chlorophenyl)methylene]-D-glucitol, which is the chlorinated analog of Irgaclear D (Fig. 3C). The absolute position of the two chlorine atoms was expected to be at the mentioned position. A concrete confirmation about the position of the chlorine on the aromatic rings could not be made by employing GC/EI-MS.

3.2. Optimization of the one-step approach

The chosen Box–Behnken design model significantly fitted the collected data. An optimization was conducted by considering different aspects. Highest priority was given to the maximization of response variables, which was elementary for a quantitative transformation of sorbitol-based NCAs into their TMS-derivatives. Temperature was chosen to be of rather low priority, so it was allowed to possess any values within the given limits of 120 °C and 150 °C. It was tried to minimize the duration of the procedure without losing yield of the silylation reaction. The amounts of pyridine and silylation reagent were optimized towards low values in order to reduce the consumption of rather harmful and expensive reagents. However, trying to meet the desired requirements was not accomplished. It turned out that the amounts of reagents – which should be minimized – had a tremendous influence on the response variables. This fact could be confirmed statistically by the *p*-values obtained from ANOVA calculations (time: 0.0137, temperature: 0.5040, pyridine and silylation reagent: both < 0.0001). The volumes of pyridine and of the silylation reagent had to reach the highest values given (250 μL) in order to complete the reaction. In terms of pyridine and silylation reagent, any lowering of the values leads to an insufficient silylation. However, keeping the reagents at high values, the other parameters time and temperature could be varied almost independently in a very large area illustrated by the software. Setting the volumes of the reagents for derivatization to 250 μL each, several different possibilities were suggested by the software. According to the design model, 10 min of duration should be sufficient when the temperature is kept between 120 °C and 140 °C. However, examination of these proposed parameters did not lead to full recoveries. An increase of time to 25 min and a temperature of 135 °C – which was another suggested solution – gave high efficiencies and good repeatabilities. Interestingly, the finally selected parameters matched those of the simple extraction in THF as described in Section 2.4.2. This concludes the silylation reaction to work at lower temperatures when given a bit more time, even when the sample is still being extracted.

3.3. Analytical performance and robustness

Calibration curves and analytical parameters were obtained by external calibration using an internal standard in the presence of a commercial technical-grade polymer without any target analytes. To determine the robustness of the methods, linear ranges, limits of detection (LODs) and limits of quantification (LOQs), commercial technical-grade PP containing Irganox 1010, Irganox 1330, Irgafos 168 and calcium stearate was used as surrogate for simulating matrix effects. Both previously mentioned methods (two-step and one-step) were validated by weighing approximately 50.0 mg of the PP which did not contain any NCAs. The extraction solvent was spiked with the NCA-solutions in THF between 1 mg L^{-1} and 200 mg L^{-1}. The internal standard's concentration was kept at 50 mg L^{-1}, resulting in injected solutions containing each NCA from 0.1 mg L^{-1}–20 mg L^{-1}. Considering the amount of 50.0 mg sample pellets used, the calibration obtained would correspond to a (linear) measuring range of 50–10,000 ppm in the polymer. Table 2 gives the summary of the data obtained for the validation procedure for the two-step and the one-step approach.

At this point it should be mentioned that spiking the extraction solvent in the presence of the polymer is not representative with respect to a true extraction procedure. Unfortunately, spiking the solid polymer directly with the analyte was less feasible because this hardly results in a homogeneously spiked polymer.

Both procedures showed very good linearities and R^2 of at least 0.99 for all NCAs (in most cases correlation coefficients were greater than 0.999) over almost two orders of magnitude. LODs and LOQs were obtained by determining the concentrations giving a signal to noise (S/N)-ratio of 3 and 10, respectively. Repeatabilities ($n=3$, on the same day) and reproducibilities ($n=6$, on consecutive days) were measured at an NCA-spiking level of 20 mg L^{-1} (injection of 2 mg L^{-1}, approx. 1000 ppm in polymer).

The two-step process was satisfactory by delivering very good repeatabilities ranging from 0.19% to 6.05% and reproducibilities from 2.02% up to 6.73%. Similar good performance was achieved by the one-step procedure with remarkably good values of a maximum of 3.23% down to 0.05% for repeatability. However, it seems that the presence of the polymer matrix during the *in situ* process caused the reproducibilities to decrease to values of around 6–10%, which is still fully sufficient for routine applications.

Real samples with known NCA content were subjected to analyses in triplicate for each sample preparation methodology in order to evaluate the suitability under real conditions. The two-step process gave recoveries of 104.2% of the declared values (1.87% RSD) for Millad 3988 and 95.8% (1.39% RSD) for Millad NX 8000. Results of the *in situ* process were totally comparable, giving 102.8% recovery (2.62% RSD) and 93.4% recovery (3.11% RSD) for Millad 3988 and Millad NX 8000, respectively.

Table 2
Comparison of the validated sample preparation procedures.

Analyte	LOD[a] (mg L^{-1})	LOQ[b] (mg L^{-1})	Linear range (mg L^{-1})	R^2	Repeat. ($n=3$) (%)	Reprod. ($n=6$) (%)
Two-step procedure						
Irgaclear D	0.08	0.27	0.27–16.0	0.9996	0.19	2.02
Irgaclear DM	0.05	0.17	0.17–18.7	0.9960	0.71	6.54
NC-4	0.10	0.33	0.33–17.0	0.9994	6.05	4.94
Millad 3988	0.07	0.24	0.24–17.1	0.9995	3.47	3.87
Millad NX 8000	0.03	0.11	0.11–17.6	0.9957	4.65	6.73
One-step procedure						
Irgaclear D	0.08	0.27	0.27–16.0	0.9997	2.61	6.53
Irgaclear DM	0.05	0.17	0.17–18.7	0.9999	3.23	7.89
NC-4	0.10	0.33	0.33–17.0	0.9998	0.44	7.43
Millad 3988	0.07	0.24	0.24–17.1	0.9997	1.74	9.89
Millad NX 8000	0.03	0.11	0.11–17.6	0.9999	0.05	5.88

[a] Based on $S/N=3$.
[b] Based on $S/N=10$.

4. Conclusion

The results presented in this paper could demonstrate that difficulties in extracting additives like sorbitol-based nucleating- and clarifying agents from polyolefines can be overcome by the employment of microwave irradiation. To make them compatible to GC/MS, the sorbitol-based NCAs were derivatized using a highly efficient silylation reagent and applying microwaves again. Initially, the extraction and derivatization of the analytes were carried out as two-step procedure. The investigation of a possible single-step *in situ* method was subsequently carried out on the basis of the two-step parameters supported by a design of experiment approach. The *in situ* procedure comprising of the simultaneous extraction and derivatization lead to reduction and acceleration of sample preparation steps without forfeiting the analytical performance. The trimethylsilyl-derivatives of sorbitol-based NCAs showed several characteristic mass spectral features of which the mechanism could be clarified and completed. This mechanism enabled to understand the formation of ions during electron ionization providing support in structural elucidation of unknown and new sorbitol-based NCAs. This could be demonstrated by analyzing real samples.

The presented tools can be applied very effectively in polymer analysis in polymer industries. This can be of high interest for manufacturers in order to control the properties of polymers, to design new plastic materials, to maintain the quality of the plastic products and to deal with claims of customers. The work presented describes procedures for the reliable determination of sorbitol-based NCAs. However, the methodology may in all likelihood be also applicable to other NCAs or different polymer additives such as slip agents, acid scavengers and antistatic agents for which a proper extraction and derivatization may be necessary. This task will be the scope of further investigations.

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