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In cooperation with Volvo Car Corporation

Identify and quantify additives in polypropylene, polyethylene and polyamide

Using an High Performance Liquid Chromatography

Thesis for Bachelor of Science in Chemical Engineering

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Abstract

Plastic materials such as polyethylene, polypropylene and polyamide contain different additives that can be divided in for instance antioxidants, heat and photo stabilizers to prevent rapid degradation of the material from UV-light, heat and oxygen. Ten different additives, which are common in these plastics, are the basis of this assay and an analysis will be formed to identify these compounds in plastics. The additives are either antioxidants or hindered amine light stabilizers which will decrease in concentration due to reaction occurring during the time. It is important to study the degradation process during time to control the quality of the material.

For this analysis there is a high pressure liquid chromatography (HPLC) available, which is equipped with a reversed phase column and a UV-detector. This is a proven method for analyzing additives in plastics but so many as ten compounds are not usually analyzed simultaneous. To develop method parameters as mobile phase, wavelength, injection volume and flow are optimized in order to benefit as many additives as possible. For preparation of the plastics a Soxhlet extractor is chosen for extraction.

The goal of this work is to find a method suitable for as many of the compound as possible in an appropriate time, analyze the plastic material and find the degradation of it regarding the additives. Multiple factors can be tested and adjusted to receive the best method. The sample mass for extraction, solvent for extraction, extraction technique influences the outlet of additives from plastics. The extracted compounds will then be dissolved in a solvent before injection. The volume for injection should contain a high concentration of the additives for a good signal on the chromatograph, which requires a lot of time for preconcentration. To see how well the HPLC is regarding analysis of the selected additives a comparison of mass spectrometry could be made. The HPLC used for this analysis are equipped with a ultraviolet detector and different columns could be tested to obtain more additives and receive better results. Since the time of this work is limited a choice of parameters are made to find out the degradation of compounds in plastics

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Introduction

Plastic is the material used to a very great extent and you encounter it daily. It is often used as a structural material and when it is used outside it is affected by UV-light, heat and oxygen. The influents of these factors lead to a photo-oxidation that creates free radicals decomposing the long polymer molecule in plastics to shorter chains or form crosslinks between chains in the polymer.[1] This leads to changes in properties of the material. Today´s commercially available plastic contains besides the base polymer numerous other ingredients, among other different kind of additives. Additives such as antioxidants, heat and photo stabilizers are added to prevent undesirable reactions. Additives are not able to prevent degradation and aging of the polymer but may slow it down.[2] Some of these additives also undergo many chemical transformations that could provide byproducts as a consequence to protect the plastic material. The additives are consumed over time and a reduction of these additives could accelerates the aging of polymers even more than photo- and thermal oxidation.[18] Identification and quantification of these additives are important for quality control and to study the degradation process.[3] It is also important to study the degradation to prevent for instance the damaging and discoloration of the material that this process provides. Some of the additives are bio-accumulated and toxic for humans and environment, which makes analysis of the compounds very important from this point of view as well.[19] This analysis will also include a determination of degradation of the additives that occur with time.

Polyethylene, polypropylene and polyamide are the plastic materials studied regarding antioxidants and light stabilizers. The antioxidant protects the plastic material from thermo-oxidative degradation. Irganox 1010, Irganox 1076 and Irganox 1098 are sterically hindered phenolic antioxidants used for this study that ensure processing stability and long term thermal stability of polymers.[4] Tinuvin 770, Tinuvin 622 Chimassorb 944 and Chimassorb 119 FL are hindered amine light stabilizers (HALS), which are the most effective of the light stabilizers for polyolefins and studied.[5] HALS consists of a wide variety of compounds whose functions are to absorb light, increase mechanical strength or improve thermal stability.[6] HALS are not easily separated from other additives with liquid chromatography because of the numerous basic amino groups.[19] Tinuvin 123 is an hindered amine light stabilizer based on an amino-ether functionality that is used as heat and light stabilizers, oxidants and radical scavengers.[8] Irgafos 168 is a trisarylphosphite, a secondary antioxidant, which protect the material from discoloration and change of physical properties caused by excessive heat exposure and will also be analyzed.[9] [18] Information about the studied additives by molecular weight and structure are shown in table 1.

The concentration of stabilizers and antioxidants in plastic material are low so a sensitive analytical procedure is needed to measure it. A high performance liquid chromatography (HPLC) is used for the analysis of additives in plastics due to its advantage which includes speed, sensitivity and high resolution.[7] The equipment uses a reversed phase column and is equipped with an UV-detector. The analyzed additives, which are mainly antioxidants and stabilizers, can be quantitatively and qualitatively analyzed by HPLC once the method is established.[7]

Theory

Preparation

The preparations of the different plastics are important and will facilitate the extraction of the additives in plastic material. Preparation is performed by filing, powdering by pestle and mortar, rasping or cutting the material to pieces before extraction. The choice of size of the prepared material is important because a larger piece prevents the extraction while a too small piece may give unextracted material. The choice of size and preparatory method is therefore important and different methods are tested to receive the most suitable for the materials.

Extraction

Extraction of the material with an appropriate solvent separates the desired constituents from its main material. Various solvents are tested to obtain the one with the best ability to dissolve the compounds of interest. Extraction takes place in a Soxhlet extractor for 16 hours with different solvents depending on the material. This method is chosen for extraction because it is simple, inexpensive and demands no supervision. The sample is placed in a thimble holder, which gradually fills with condensed solvent from a distillation flask until the liquid reaches the overflow level. A siphon aspirates then the extract from the thimble holder and unloads it back into the distillation flask which increases the amount of extract in solvent. This process is repeated until extraction is complete, which for this extraction assumes to be after 16 hours. Figure 1 shows the components of a Soxhlet extractor.

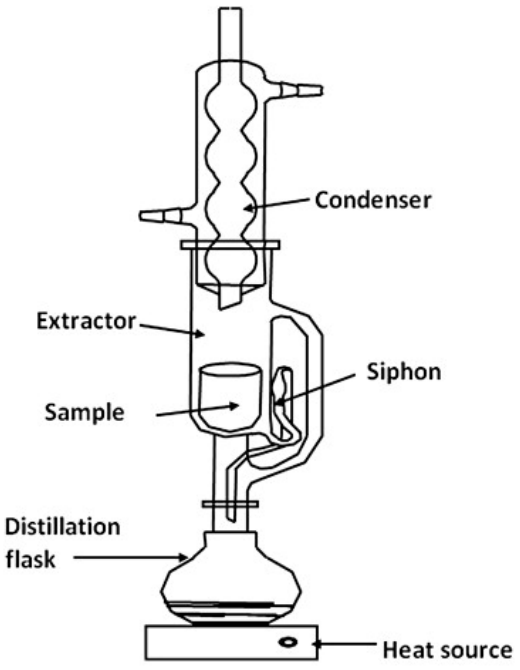


Figure 1-Components of a Soxhlet extractor

Evaporation

Once the extraction is complete, the additives are dissolved in the chosen solvent. Evaporation must now take place to separate the desired compounds from its solvent and obtain a solid sample. The issue regarding evaporation is how much of the liquid phase should be vaporized. If there is only solid phase left in the E-flask it may be difficult to remove it then it is stuck to the glass. If there is some solvent left the solute may be unable to resolve it in a new solvent. The remaining solid residue from extraction is dissolved in chloroform, which should dissolve all the studied additives and is used as a blank for this analysis, before an injection to the HPLC takes place. Rotational and hot bath evaporation are used and tested to obtain the best evaporation method.

The rotational evaporation contains a pump to produce vacuum, which decreases the boiling point of the bulk liquid and thus speeds up the evaporation of the solvent. The solvent is placed in an E-flask in 40 degree water and the pressure can be adjusted to the choice of solvent. The flask is spinning during the procedure and the process is finished then enough solvent is evaporated.

The E-flasks containing additives dissolved in solvent is placed above heated water in the hot bath evaporator. The equipment has capacity of evaporate eight flasks at a time and one place could be exposed to air, which speeds up the process. Since there is no vacuum used this method takes longer time. Both evaporation methods are tested and the rotational is faster but since the flask spins sidelong solid phase could be stuck higher up on the glass, which is harder to dissolve. The hot bath takes longer time but the solid residue is placed on the bottom of the flask. The location of the solid residue is important and placement on the ground of the flask facilitates the dissolution which makes the hot bath evaporation more suitable for this analysis.

HPLC

High performance liquid chromatography uses high pressure to force solvent through a closed column containing fine particles. It is used for this analysis due to its advantage of high resolution, high speed and sensitivity. The HPLC system consists of an autosampler, a solvent delivery system, a sample injection valve, a high-pressure chromatography column and a detector, a UV-detector for this analysis.[21]

This analysis uses adsorption chromatography and it is called a reversed-phase chromatography. The stationary phase is nonpolar or weakly polar and the solvent is more polar. The molecules of the solvent are competing with solute molecules for sites on the stationary phase. A separation of the compounds occurs by the differences of being absorbed to the stationary phase and elution occurs when solvent displaces solute from the stationary phase. [21]

Two types of elution were tested, isocratic and gradient elution. The gradient elution was performed with a continuously change of solvent composition to increase eluent strength which is required to elute more strongly retained solutes. The isocratic elution used a single solvent or a constant solvent mixture to separate the compounds. [21]

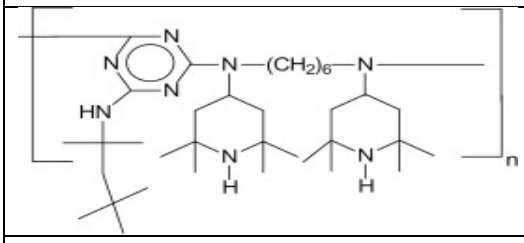
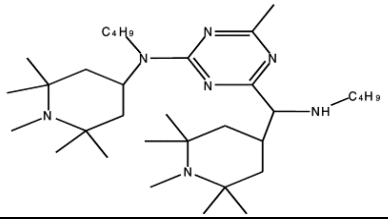
Analysis

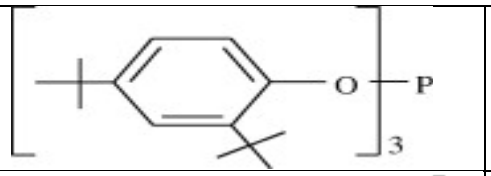
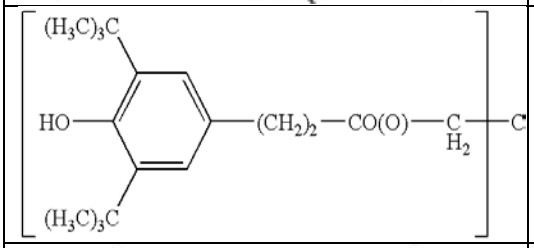
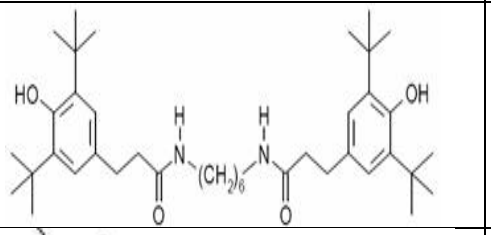
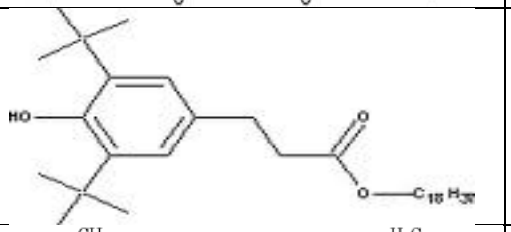
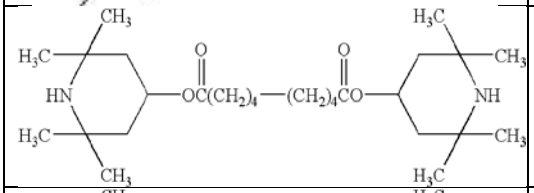
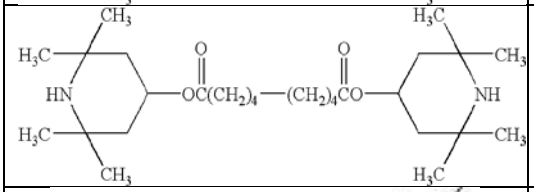
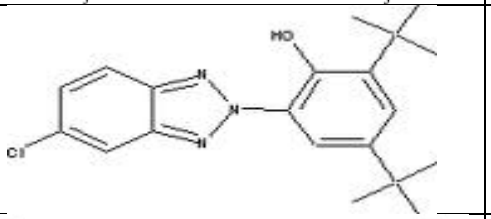
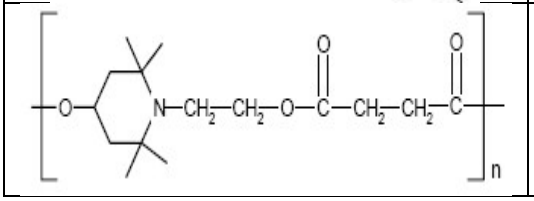
The chromatograph will show different peaks that symbolizes compounds present in the material. To see what peak belongs to a compound standard samples are made containing pure additive dissolved in chloroform. By analyzing it information about retention time and peak form are obtained. The solvent will be injected to obtain retention time for the blank. Standards containing numerous additives are also made with different samples of linearly increasing concentrations in order to construct a calibration curve. Values for the different concentrations are plotted and a slope is formed between the values. This curve is later used to determine the concentration of the different substances in plastics.

The ideal conditions would be to find a method capable of analyzing the plastics regarding all additives. Different parameters are adjusted such as mobile phase composition, flow, injection volume, column temperature and type, wavelength of the detector and gradient and isocratic elution will be tested to optimize the method. The chromatography will show narrow and distinct peaks for the method to be approved for the compound. The retention time for the compounds should ideally be as short as possible in order to reduce the analysis time but not similar so that they collide. The peaks should be separated for a better analysis and to avoid overlap of peaks. Overlapping of peaks would imply that it becomes difficult to distinguish the additives in plastics. Two factors contribute to a good separation. One is the difference in elution time between peaks and further apart peaks will give a better separation. The other factor is how broad the peaks are and the wider peaks, the poorer separation. These two factors contribute to the measurement resolution which can be calculated from the formula: □□□□□□□□□□ = $\frac{\nabla□}{□(□□)}$. ∇□ is the difference in elution time and □(□□) is the average width of the two peaks in corresponding units. A larger resolution indicates a better separation of peaks. [22]

Some additives will probably not be visible in the chosen wavelength range, suitable in the mobile phase or for the analytical equipment. More than one method will almost certainly be needed to analyze the selected compounds. It facilitates however to adjust the parameters so that as many as possible of the compounds are able to be analyzed by one method.

Table 1- Structure and molecule weight of the additives

Structure	Trade and Chemical names, molecule weight
	Chimassorb 944-Poly-{[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl] [(2,2,6,6-tetramethyl-4-piperidyl)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidyl)imino]}, 2500 g/mol[10]
	Chimassorb 119 FL-135TRIAZINE246TRIAMINENN12ETHANEDIYLBIS;TETRAKIS(4,6-BIS(N-BU-N-PENTAME-4-PIPERI;n''-dibutyl-n',n''-bis(1,2,2,6,6-pentamethyl-4-piperidinyl , 2285.61 g/mol [11]

	Irgafos 168- Tris(2,4-di-tert-butylphenyl) phosphite, 646,9 g/mol[12]
	Irganox 1010- Pentaerythritol Tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), 1178 g/mol [11]
	Irganox 1098- N,N'-Hexamethylene bis[3-(3,5-di-t-butyl-4 -hydroxyphenyl)propionamide], 637 g/mol [13]
	Irganox 1076- Octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate, 531 g/mol [14]
	Tinuvin 770- Bis(2,2,6,6,-tetramethyl-4-piperidyl)sebaceate, 481 g/mol [11]
	Tinuvin 123- bis-(1-octyloxy-2,2,6,6-tetramethyl-4-piperidinyl) sebacate, 737,15 g/mol [15]
	Tinuvin 327- 2-(2'-Hydroxy-3',5'-di-tert-butylphenyl) -5-chlorobenzotriazole, 357,9 g/mol [16]
	Tinuvin 622- Butanedioic acid, dimethylester, polymer with 4-hydroxi-2,2,6,6-tetramethyl-1-piperidine ethanol, 3100-4000 g/mol. [17]

Experiment

The experimental part will mainly describe the procedure which includes parameters used for different runs. Only changes that are forcing a new run are described. There has been small adjustment during the runs, which are described in results and discussion part. The chemicals and were it was purchased from, equipment, column type and materials will also be examined.

Chemicals

There were ten additives chosen for this analysis: Irgafos 168, Irganox 1010, Irganox 1098, Irganox 1076, Chimassorb 944, Chimassorb 119 FL, Tinuvin 770, Tinuvin 327, Tinuvin 622 and Tinuvin 123. All the additives are purchased from Ciba. The first nine were solid at room temperature while the last one was a liquid. Chloroform, acetone, toluene, tetrahydrofuran, methanol and acetonitrile were used as solvent and mobile phases and they were all of analytical grade. The solvents are purchased from VWR.

Equipment

The high performance liquid chromatography used consisted of a Varian 9012 Solvent Delivery System, a Varian 9100 Autosampler and a Varian 9050 UV-VIS detector.

Column type

A reversed phase column was used and three different types tested. An old and a new Purospher ® STAR, RP-18 endcapped (5µm), Hibar ® RT 150-4,6(mm) and one Purospher ® STAR, RP-18 endcapped (5µm), Hibar ® RT 250-4,6 (mm). The three columns were purchased from Merch Millipore and the length was either 150 mm or 250 mm. The column consisted of particulate silica which was delivered in stainless steel column to keep the stationary phase particles in place. The columns were pressure stable up to 400 bar and was connected to the HPLC system without any additional column holder.

Materials

The plastic materials analyzed were polyamide, polypropylene and polyethylene. Six different materials of polyamide were tested, one new material and five exposed to 80°C, 100°C, 120°C, 140°C and 160°C for 168 hours. They were all purchased from Lanxess. Two materials of polypropylene was tested, one new and one degraded in 100°C for 1900 hours and they were brought from LyondellBasell. Two materials of polyethylene were examined, one new and one degraded in 50°C for 2000 hours and they were purchased from BASF.

Procedure

Nine of the additives (excluded Tinuvin 622) were weight and dissolved in chloroform up to 100 ml in an E-flask. The weight and concentration are shown in table 2.The prepared additive standards were shaken and small amounts transferred to a vial and then placed into the autosampler of the high pressure liquid chromatography. HPLC analysis were run with different parameters testing such as flow from 1.0 to 1.5 ml/min, injection volume from 5 to 60 µL, mobile phase consisting of different ratios of acetonitrile, methanol and water with isocratic or gradient elution. The column was either aged or new of the type Purospher ® STAR, RP-18 endcapped (5µm), Hibar ® RT 150-4,6(mm) with a length of either 150 or 250 mm. The column temperature ranging from room temperature to 50 degrees. The wavelength for UV-detector varies from 190 to 340 nm.

Table 2- Weight and concentration for standards

Standard	Weight (g)	Concentration (mg/ml)
Irgafos 168	3,9963	39,96
Irganox 1010	4,03246	40,32
Irganox 1076	3,9413	39,45
Irganox 1098	4,01945	40,19
Tinuvin 123	3,9154	39,15
Tinuvin 327	4,03064	40,31
Tinuvin 770	3,9863	39,86
Chimassorb 119 FL	4,15027	41,5
Chimassorb 944	4,07513	40,75

The first experiment was performed to start with testing a mobile phase and wavelength to see if it is suitable for the additives. Nine additives and one blank as chloroform were injected with following conditions: wavelength of 280 nm, mobile phase consisted of H_2O:ACN 90:10 and changed to 10:90 in 15 minutes, flow of 1.50 ml/min, injection volume of 60 µL. The old column was of types Purospher ® STAR, RP-18 endcapped (5µm) with a length of 150 mm was used at room temperature and the analysis lasted for 20 minutes.

For the second run a change in composition of mobile phase and prolongation of time were performed to obtain more peaks and better separation of peaks. The nine additives plus one blank with the same column as the previous run was placed in an oven at 27 degrees. A wavelength of 210 nm was used and an isocratic elution with H_2O:ACN 20:80 for 20 minutes. The flow was set to 1.5 ml/min and one injection per sample with 30 µL was established.

Additional and clearer peaks were the goal for the third experiment. It used following conditions for all the additives: A flow of 1.5 ml/min, gradient elution of H_2O:ACN 25:75 changed to 0:100 for five minutes and held constant until the end, when 20 minutes has passed. The old column as Purospher ® STAR, RP-18 endcapped (5µm) with a length of 150 mm at 50 degrees was used. Two injections per sample with a volume of 20 µL and a wavelength of 210 nm were proven.

The fourth run took place only for Chimassorb 944 and 119 FL, Tinuvin 123 and blanks because they did not receive fine peaks in the previous runs. A wavelength of 250 nm and a mobile phase of MeOH:ACN changed from 40:60 to 0:100 in 10 minutes and held constant to 20 minutes. The same column as before was used at 50 degrees was applied. Two injections of each sample were proven with an injection volume of 30 µL.

A division of the additives occurs and the fifth experiment was run with the old column as Purospher ® STAR, RP-18 endcapped (5µm) with a length of 150 mm at 50 degrees. It was performed for Irgafos 168, Irganox 1010, 1098 and 1076, Tinuvin 327 and 770 and one blank with an injection volume of 20 µL. The wavelength was set to 210 nm and gradient elution of MeOH:ACN 40:60 altered to 0:100 during the entire run of 20 minutes.

Ten milliliters of each of the six additives Irgafos 168, Irganox 1010, 1076 and 1098, and Tinuvin 327 and 770 were poured in a 100-ml E-flask and filled with chloroform up to 100 ml. This mix of additives resulted in a dilution of factor ten. Mixes were also done by a dilution of 100, 1000 and 1000 from the initial concentration. The four E-flasks were marked Std 1, Std 2, Std 3 and Std 4 regarding the number of times they have been diluted and Std 1 was the highest concentration.

The sixth run was performed to create a calibration curve, since the parameters were established by running samples with different concentration of a mix of additives. This run used the same column as before at 50 degrees for Std 1-4 and blanks between each Std. Two injection of each sample with a volume of 20 µL and a flow of 1.5 ml/min occurred. The mobile phase used consisted of MeOH:ACN 20:80 which changed to 0:100 for 10 minutes and held constant until 20 minutes was passed.

A seventh run with just a change in mobile phase to isocratic MeOH:ACN 30:70 from the previous one was performed to receive nicer peaks and some peaks to elute earlier. The four standards plus Irgafos 168, Irganox 1010, 1076 and 1098, and Tinuvin 123 and 770 were run.

The equipment was serviced before the eight run and the tubing between the column and the delivery system was replaced to a smaller one. The mobile phase consisted of MeOH:ACN 20:80 and run constant in ten minutes and then altered to 35:65 until 35 minutes has passed. A flow of 1.3 ml/min, wavelength of 210 nm and two injections per sample was used. Four Std and the six additives plus Tinuvin 622 were tested.

The samples of plastic material were extracted and polyamide were first filed and then pulverized by pestle and mortar. Polyethylene and polypropylene were prepared by using a rasp. Two samples of every test were weighed and put in a container placed in an extraction tube. Various solvents as toluene, chloroform and acetone were tested to dissolve the various plastics, and the E-flasks were put in the Soxhlet extraction for 16 hours. The plastic samples were then evaporated by a hot bath or a rotation evaporator to obtain total dryness and weighted again.

The E-flasks contained no more than the solid additives were filled with about 80 milliliter of chloroform and shaken. A few milliliter of each sample were transferred to a vial and put in the autosampler of HPLC for analyze.

The ninth run was operating to analyzing the plastic material on following parameters: wavelength of 220 nm, a flow of 1.0 ml/min, the mobile consisted of Methanol:Acetonitrile 20:80 and run constant for ten minutes and then changed to 35:65 until 35 minutes has passed. This was the same parameters as the eight run, the definite run, except the wavelength was set to 220 nm due to problems with the detector. Two injections per sample and a volume of 10 µL were used and injected in the old column of Purospher ® STAR, RP-18 endcapped (5µm) of length 250 mm. Different weight and solvent are used for the preparation of polyamides, polypropylene and polyethylene and new and aged plastic samples were injected. The six additives and mixed standards were also analyzed to create a calibration curve.

A tenth analyze was run to found a method for Chimassorb 119 FL, Chimassorb 944, Tinuvin 123 and Tinuvin 622. The four compounds were dissolved in either chloroform or toluene and this analyze should

also find the most suitable solvent. The samples were injected two times of 20 µL per sample and dissolved in each solvent plus blanks of chloroform and toluene. The mobile phase consisted of n-Hexane:Ethanol:Toluene 88:11:1 and run isocratic with a flow of 1,5 ml/min and an analysis time of 30 minutes. The old column of Purospher ® STAR, RP-18 endcapped (5µm) with a length of 250 mm was used and a wavelength of 225 nm.

Results and discussion

Optimizing an analyze method for high pressure liquid chromatography regarding different additives required great accuracy and took very long time to perform. There has been much small adjustment during the runs but the experiments described at the experiment part were the major change that required the entire method to be restarted. The optimization can be constantly improved and since the time of this bachelor thesis were limited, it was important to obtain a method that worked for so many additives as possible. It was also of paramount importance that the showed peaks were separated and preferably as narrow as possible with a short retention time and good baseline.

The first experiment showed that Irgafos 168 eluted at the end of the run and that the peak was too wide so the next run should be performed in 30 minutes at an injection volume of 30 µL. An identification of two unseparated peaks for Irganox 1098 occurred and to separate it and receive a lower pressure the mobile phase should be changed to a lower content of water. The separation should be done by making the solvent more unpolar and the pressure should be decreased due to a lower content of water, which has a high compressibility. The chromatography also showed a synchronous noise at the baseline and to reduce it to an acceptable level the mobile phase was pumped extra-long time to remove air at the apparatus. The mobile phase change was first set to H_2O:ACN 60:40 and changed to 20:80 due to a reduction of the expensive acetonitrile but to receive a faster elution the next run were performed with an isocratic elution of 20:80. To improve the resolution of the run the column was placed at an oven for 27 degrees and a new column of Purospher ® STAR, RP-18 endcapped (5µm) with a length of 150 mm was tested but without significant improvement. The light above the equipment should also be switched off to possible reduce noise from the UV-detector.

The observation of the second run was that both Irgafos 168 and Irganox 1098 exhibited wide peaks with poor separation of Irgafos 168 so a new analysis with another wavelength was tested. A wavelength of 250 nm received a good peak for Chimassorb 119 FL that eluted early but Irganox 1010, Tinuvin 123, 327 and 770 were barely visible. Irganox 1076 and 1098 were not detected at all.

The third run detected all the additives beside Chimassorb 119 FL and 944 and Tinuvin 123. A conclusion that all the additives cannot be analyzed simultaneously regarding wavelength was made. Further analysis will be done by optimizing other parameters than wavelength for the six detected additive, since they were visible at 210 nm. Irgafos 168 showed a poor separation on the first peak and three different peaks. Irganox 1010 exhibited a third peak for the first injection but not for the second one. For Irganox 1076 one large and one small peak were obtained for the two runs with different retention times. Irganox 1098 showed poor separation on the first peak and one run did not detect a second peak. One run for Tinuvin 327 showed a good peak but not the other run. Tinuvin 770 exhibited a large and a small peak for two runs. Since the peaks were missing or they differ in size between runs it might be due

to a stronger solvent than the mobile phase so the water of the mobile phase should be changed to the more unpolar methanol.

The fourth run did not produce good results and will cause difficulties for later analysis because the three compounds showed different visibility on the tested wavelength. Chimassorb 119 FL was clearly visible in this wavelength, Tinuvin 123 was slightly visual and Chimassorb 944 was not visible at all. The problem now was how to analyze the three additives together when they do not seem to appear on the same wavelength.

For the fifth run the mobile phase was changed intensively to improve the first peak, Irganox 1010. A change of the mobile phase from 30:70 to 0:100 during the entire run received a better peak that was better separated from the blank. The mobile phase was then changed to a gradient elution from 25:75 to 0:100 and a narrower peak was obtained. A better peak for Irganox 1010 was received then a gradient elution from 20:80 to 0:100 in ten minutes and held constant the rest of the run were used. A volume of 5 µL was injected and this change of parameters was applied for the other additives. The baseline was negative for Irgafos 168 and Irganox 1076, which both were analyzed three runs after blanks. This could be due to impurities in the column so an additional experiment was run with a blank between every new sample running to clean the column. The runs with blank between every new sample did not obtained negative baselines so for further analysis a blank will be used every second run. The peak of Irgafos 168 differed in size between the two runs, but had same retention time and Irganox 1076 varied slightly in peak area. Irganox 1098 and Tinuvin 327 and 770 provided accepted peaks so this run should be tested for next analysis with mixed standards.

Since the method was approved it was time for analyzing several standards with different concentration to create a calibration curve. The sixth run obtained many early peaks and one missing or combined with another one so the mobile phase was changes to a gradient one during 20 minutes instead of ten which resulted in a separation of the two peaks. The pressure was also considered high so the column was changed to the new column of Purospher ® STAR, RP-18 endcapped (5µm) with a length of 150 mm and a decrease in pressure was obtained. An isocratic elution with MeOH:ACN 30:70 was tested with just small improvements in the chromatography, but above all more economical mobile phase was obtained so this phase should be used for further runs.

The seventh run adjusted much in order to get well separated peaks to elute early for standards. After the initial parameters were used the following notation were made: Irganox 168 showed three good peaks but the last one eluted late, Irganox 1010 has one clear peak and one small, Irganox 1076 has one late and clear peak that was wide, Irganox 1098 received one clear and high peak that was weakly separated from the blank, Tinuvin 327 has one good peak and Tinuvin 770 an early and clear peak. Std 1 showed seven clear peaks plus one blank, Std 2 has seven peaks that were less clear, Std 3 received two clear peaks and two semi-clear peaks and Std 3 displayed no clear peaks. Since a weakly separation of Irganox 1010 and the blank was obtained and the two peaks eluted late the mobile phase was optimized and a gradient elution of MeOH:ACN 20:80 held constant for ten minutes and then increased to the final content of 35:65 in 35 minutes was determined. Although this method was the best one obtained Irganox 1010 was barely separated from the blank, Tinuvin 770 collided with the second peak of Irganox

1010 and Irganox 1098 clashed with Irgafos 168. The last collide was very problematic but by looking if some of the other two peak of Irgafos 168 was showed an identification of this compound or Irganox 1098 could be done.

The eight run were the definite since it was improved by small adjustment of the approved version for analyzing the six additives. Std 1 was clearly visible with good peaks as well as Std 2 but with smaller peaks and both feature eight peaks, included blank. Std 3 showed two small peaks plus one for blank and for Std 4 only the blank are visible. Considering the last two standards with barely visible peaks it was concluded that the concentration was too low. Two new standards were made, one with five times dilution of Std 1 and one with five times dilution of Std 2.

Table 3- Retention time for each standard and concentration for mixed standards

Standard	Retention time (min)	Mixed Standard 1 (mg/ml)	Mixed Standard 2 (mg/ml)	Mixed Standard 3 (mg/ml)	Mixed Standard 4 (mg/ml)
Irganox 1098	3,94	40,19	8,04	4,02	0,8
Tinuvin 770	5,43	39,86	7,97	3,98	0,8
Irgafos 168	6,48	39,96	7,99	4	0,8
Irganox 1010	7,62	40,32	8,07	4,03	0,81
Tinuvin 327	10,5	40,31	8,06	4,03	0,81
Irganox 1076	24,04	39,45	7,88	3,94	0,79
Irganox 1076	6,01	39,45	7,88	3,94	0,79
Irgafos 168	27,65	39,96	7,99	4	0,8
Irgafos 168	29,74	39,96	7,99	4	0,8

The preparation of the plastic sample was of paramount importance to receive as much of the additives from the material as possible. The size of the extracted pieces was important. Smaller pieces improve the mass transfer from the material to the solvent but to small could result in unextracted solids. The time of extraction was important as the rate of extraction increases with time but at sufficient length of time the extraction was no further preceding so 16 hour was set for all the solvents.

The plastic materials were prepared for a new run with the same parameters as the one before. The samples showed no peaks that indicated on any additives which aim to low concentrations of additives. Some possible reasons are a too small amount of plastic material extracted, extraction errors, wrong solvent or that the vial consisted of too much solvent. The first parameter that changed was a larger amount of material prepared for extraction. The plastic samples with an increased weight were analyzed but there were still no clear peaks. The concentration of the vial regarding the additives should now be increased to receive peaks.

The concentration of the extracted compounds in the vial that were injected in the HPLC should increase much and this was accomplished by placing the vial over the hot bath. The solvent evaporated and the vial was continuously refilled with new sample. The process was run until the E-flasks were empty which means that all the desirable compounds was transferred to the vial and the concentration improved. By

looking for precipitation remained in the flask additional solvent could be poured in the flask to continue the process further.

For the ninth analyze there were problems with the detector at the wavelength 210 nm so a change to 220 nm occurred. The sample has a high concentration so a good signal at the chromatography would hopefully be obtained. The six additives, four mixed standards and plastic samples of polypropylene, polyethylene or polyamide were injected. The concentration of the mixed standards and retention times for additives can be seen in table 3. The chromatography for the standards at the highest concentration was found in figure 1. A calibration curve was made by the different concentrations and signals from the four mixed standards. This curve was the basis for obtaining a concentration of the additives in plastics.

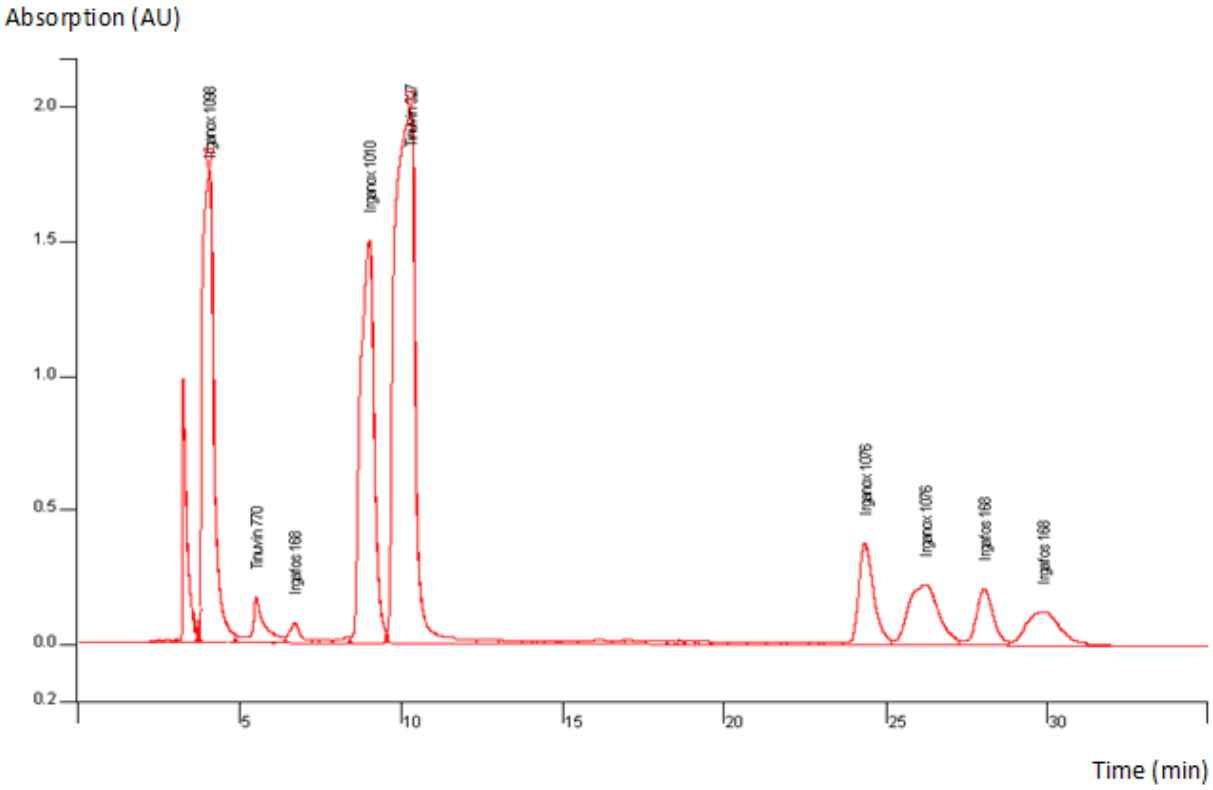


Figure 1-Chromatography of peaks for the six additives

The chromatography showed clear peaks that were well separated. The first peak was the blank which consisted of chloroform. Irganox 1098, Irganox 1010 and Tinuvin 327 have high peaks and Tinuvin 770 a short peak. Irganox 1076 exhibited two peaks successive and Irgafos 168 showed three peaks. The third peak of Irgafos 168 were covered with the larger peak of Irganox 1098 but by watching at the other two an identification of the compound was made.

The chromatography showed compounds with multiple peaks, either two or three peaks. This problem could be solved by using a solvent, which the sample was dissolved in, with lower elution strength. By injecting a solvent stronger than the mobile phase could also cause peaks shape problems. The shape issue could also be caused by contamination of the column. Washing the column by pumping of 100

percent methanol or acetonitrile could remove strongly attached materials bounded to the column. The contamination could also be prevented by using a well functional guard column.

Some of the peaks showed a tendency of tailing. It was a fairly common problem and the reason to this was mainly secondary chemical interactions between the sample and the silica-based column-packing material. To avoid this interaction the operation should be run in a lower pH since the silanol groups were acidic. Tailing could also occur by contamination or aging of the column, which required that the column was kept clean.

Peaks were obtained for the new and old sample of polyethylene and polypropylene. Weight, solvent and amount of additives for plastics are shown in table 4. These samples were injected and the peaks obtained from chromatography are shown in figure 2 and 3.

Table 4- Weight, solvent and amount extracted from plastic materials.

Plastic material	Solvent	Mass Sample (g)	Mass Residue (g)	Percentage of additive (%)
PE new	Toluene	4,75778	0,05536	1,2
PE aged	Toluene	4,80084	0,08754	1,8
PP new	Chloroform	5,7105	0,10579	1,9
PP aged	Chloroform	4,90232	0,06187	1,3

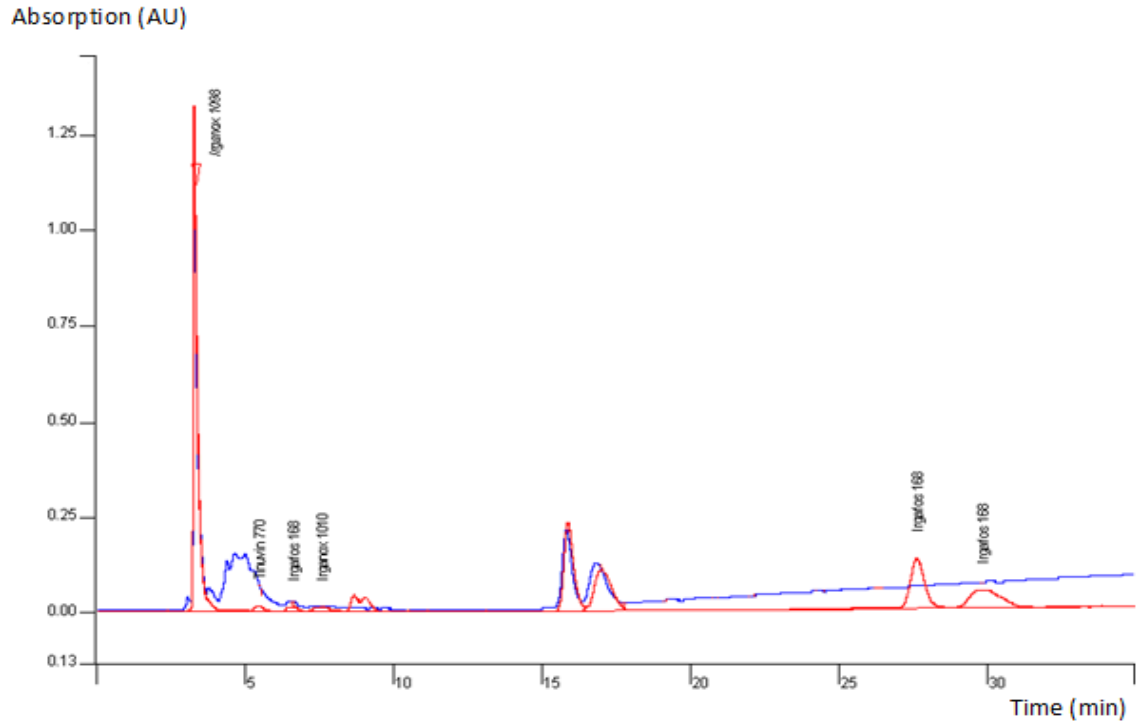


Figure 2-Chromatography for new and aged polypethylene

The red line symbolized a new material and the blue line an degraded material of polyethylene. The new material contained Irgafos 168 but it was consumed by time and a new compound was detected in the

degraded material and thus has been formed with time. There were also three peaks detected which unfortunately did not belong to any of the additive examined so they could not be identified. Tinuvin 770 and Irganox 1010 were also found in the new material but since the new top in the old sample was so wide which covered the peaks, they could not be detected.

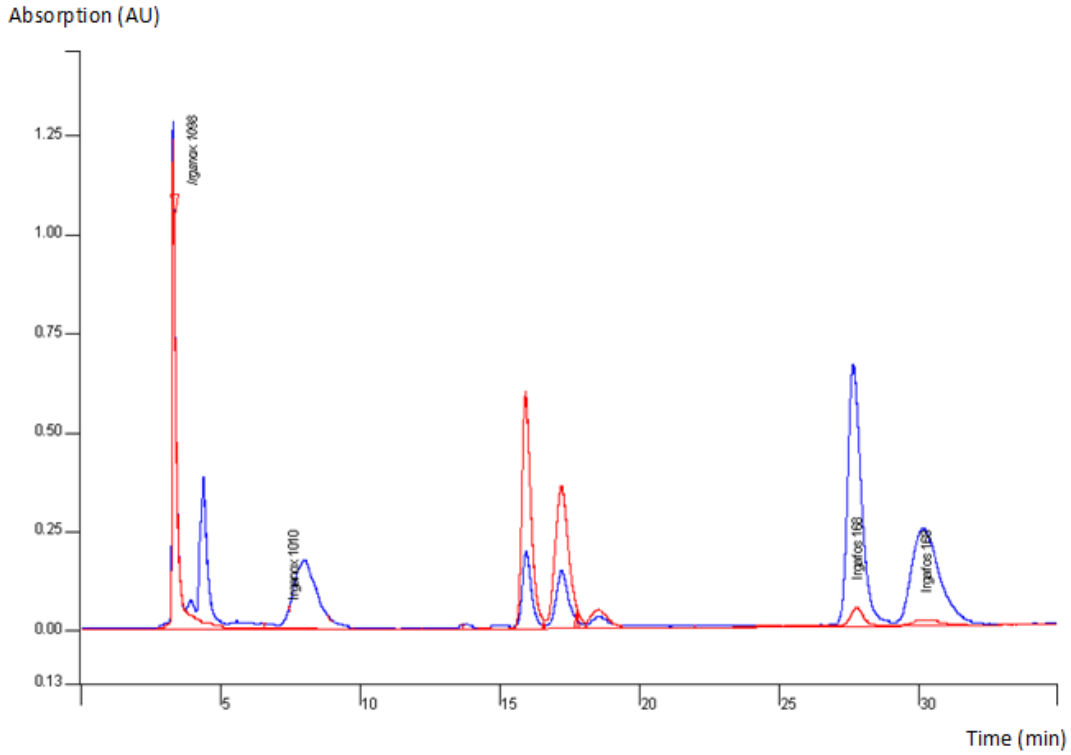


Figure 3- Chromatography for new and aged polypropylene

The blue line symbolized the new material and the red one the degraded material. Irgafos 168, Irganox 1010 and Irganox 1098 were found in the new material. Irganox 1098 and Irganox 1010 were completely consumed and Irgafos 168 was almost completely consumed. Two of the unidentified peaks obtained in polyethylene were also found in polyethylene and the concentration has increased with time.

Unidentified peaks found in polyethylene and polypropylene could belong to additives that were common in these plastics. Chimassorb 2020, Chimassorb 81, Irganox B 215, Irganox B 225 and Tinuvin 326 were five additives commonly added to polypropylene and polyethylene but none of them were available for this work so they could not be analyzed.

Irgafos 168 were consumed over time for both polyethylene and polypropylene while concentration was increased for other compounds. Irgafos 168 decomposes by oxidation and occasionally via hydrolysis to give 2,4-di-tert-butylphenol, also known as oxidized Irgafos 168. Oxidized Irgafos 168 can be formed during the polyolefin processing or as a by-product. [(18)] This fits with the peak appearing in new polyolefin material and then increased in concentration due to a reduction of Irgafos 168 as in polypropylene. By comparing this chromatography with one from a finished report oxidized Irgafos 168

are eluted before Irgafos 168 and has a smaller retention time than irganox 1076, which agrees with figure 1 and 3. [18]

Polyamide were also analyzed but without good results. The material was prepared by cutting, filed and pulverized by a pestle and mortar with different weights and dissolved in toluene and acetone. The problem was to find a suitable solvent extracting sufficiently much of the additives. The sample was preconcentrated to obtain a higher content of additives but without receiving any peaks on the chromatography.

The tenth analysis received peaks for the four additives which mean that the wavelength chosen was acceptable. The peaks were all eluted early, which resulted in a collision. The peaks for Chimassorb 119 FL and 944 were very wide which covered other peaks. The flow was changed to 1.0 ml/min which caused Chimassorb 119 FL and 944 to be slightly separated from the blank and a little improvement occurred when toluene was used as the solvent. Tinuvin 123 was separated from the blank and a small enhancement obtained with dissolution in toluene. Tinuvin 622 was separated from the blank but with a width peak. Overall the peaks were eluted at similar times which caused a bad separation. Analyzing the plastics with these parameters will not provide a convincing result because it would be difficult to distinguish the compounds. A better optimization regarding the parameters should be done do receive a good method. Since the two Chimassorb compounds showed large peaks it might be better to divide the four compounds and optimize two methods. A better method could be found by analyzing the four additives with alternative equipment. Chimassorb 119 FL, Chimassorb 944, Tinuvin 123 and Tinuvin 622 are all hindered amine light stabilizers which was not found to be easily detected by hplc-uv. The HALS could be analyzed with hplc, but coupled to another detector, for example evaporate light scattering or by using a mass spectrometer. By testing different equipment a comparison can be performed to obtain the best method.

A division of the four additives were made to receive a chromatography and an additional method. Since Chimassorb 119 FL and 944 were the two disturbing the chromatography the most, Tinuvin 123 and 622 were chosen to be analyzed. The parameters used were the same as the tenth experiment except an analysis time of 20 minutes. The chromatography of Tinuvin 123 and 622 dissolved was shown in figure 4.

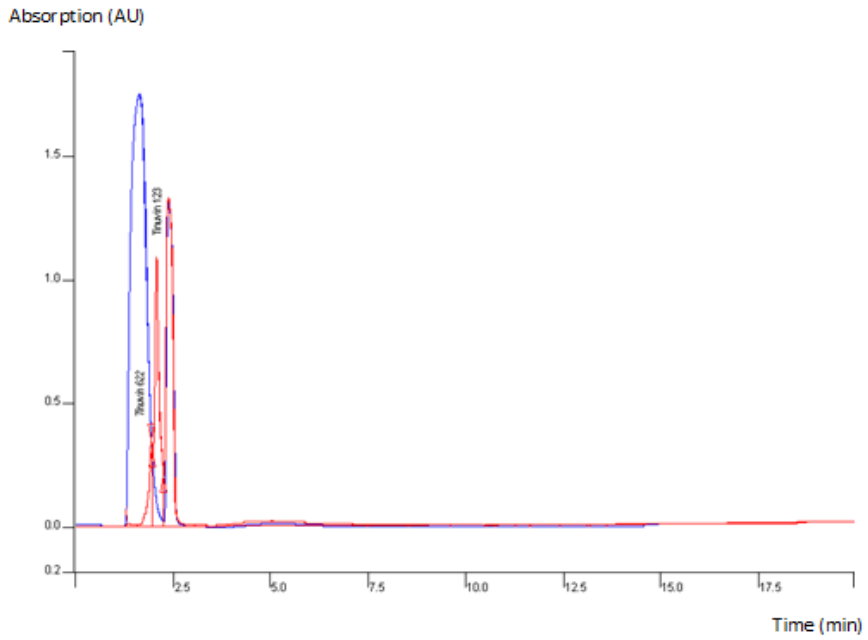


Figure 4-Chromatography for Tinuvin 123 and Tinuvin 622

The separation of the peaks for Tinuvin 123 and Tinuvin 622 was not completed. More work should be done for further optimization and to separate the peaks for better analysis. A major change of the mobile phase composition is a possible reason to separate the peaks. Another reason is to change the liquids of the mobile phase to receive a larger difference in retention time of the two peaks. If an analysis of these two Tinuvins were made for plastics it would be hard to identify them since Chimassorb has similar retention time.

A better method could be found by analyzing the four additives with alternative equipment. Chimassorb 119 FL, Chimassorb 944 and Tinuvin 622 are all hindered amine light stabilizers which was not found to be easily detected by hplc-uv. Mass spectrometry was tested for Chimassorb but without good result since the temperature was too low for splitting the large molecules. The three HALS and Tinuvin 123 could be analyzed with hplc, but coupled to another detector, for example evaporate light scattering. Tinuvin 123, 622 and the other six additives from the first method could be analyzed with mass spectrometer. The mass spectrometer is also a good alternative method to examine the plastic material and to found the unidentified peaks obtained in the two chromatography of the plastic materials.

Conclusion

A method for analyzing six additives has been established and optimized so good peaks regarding retention times, separation and widths were obtained. The other four additives, Chimassorb 119 FL, Chimassorb 944, Tinuvin 123 and Tinuvin 622 were all HALS and not easily detected with HPLC-UV. For analyzing all ten compounds it required at least two methods. Analysis with the six additives received best results when methanol and acetonitrile were used as mobile phase. Other liquids were tested as mobile phase but peaks were missing or differed in size between runs. The baseline was negative for some runs which could be caused by impurities of column. To clean the column a blank was run between every new sample which resulted in straighter baseline.

The plastic samples were dissolved in different solvent to receive as much additives from the plastic matrix as possible. Polyethylene dissolved in toluene resulted in unextracted material which made the solvent inappropriate for this plastic. Polyethylene was otherwise well dissolved in chloroform. Polyamide was dissolved in acetone and toluene without receiving good extraction. A preconcentration of the extracted material from polyamide dissolved in solvent was made before injection and different preparation size and weight were tested but no significant signal was found on the chromatography. These factors led to a conclusion that the solvent was not appropriate to extract polyamide. Polypropylene was extracted using chloroform and toluene. Chloroform was considered the best solvent and also used mainly for the samples. Different weight was tested for plastic samples and a too low weight did not give any peak on the chromatography. A weight of at least 3 gram was preferred and a preconcentration of the sample before injection to receive good peaks. The preconcentration is necessary due to the low concentration of additives in plastic material. In this analysis an increased concentration was accomplished by evaporate the vial and refill with more sample until a sufficiently high concentration assumed to be achieved before injection.

The first obtained chromatography showed clear peaks with good separation. To improve the chromatography other solvents should be tested, for instance more unpolar liquids to eliminate double peaks and tailing. Narrower peaks may also be achieved by a better optimization. The two chromatography of the plastic material exhibited two interesting peaks that did not belong to any of the standard compounds. A theory is that one of the peaks or both could belong to oxidized Irgafos 168 and to determine it, the compound should be run as a standard. The best way to identify the peaks is to analyze plastic material with another device, for instance a mass spectrometer.

The four HALS were analyzed by the second method needs to be improved significantly. If a division occurs as in figure 4, a better separation must be accomplished. Analyzing a plastic material with these parameters can also give peaks at similar retention time as Tinuvin 123 or 622, which just as well could belong to one of the two Chimassorb. An hplc analysis of these four compounds should be tested with another detector for possible obtain a good chromatography.

The first method was to analyze the six additives and I find it to be a good start to find a standard method. Distinct peaks were obtained but adjustments need to be made to get better shapes and avoid double peaks. The method should also be examined by adding more additives that were commonly used in plastics for a better analysis and to produce more results. This requires then a further optimization.

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