Quantitation of Hindered Amine Light Stabilizers (HALS) by Liquid Chromatography and Charged Aerosol Detection

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Overview

Purpose: To provide an analytical method for the identification and quantification of hindered amine light stabilizing (HALS) compounds, using the universal Corona charged aerosol detector.

Methods: A porous C18 and a solid-core C18 column with an alkaline mobile phase and post column acidification are used to characterize different HALS compounds by reversed-phase high pressure liquid chromatography (RP-HPLC) and charged aerosol detection.

Results: Two variants of a method were developed that can provide identification and quantitation of HALS.

Introduction

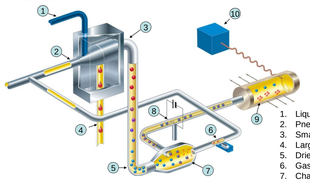
Plastics can be found in increasing number of products that are used today. Initially used in consumer appliances, plastics are often used as a material of choice in many products, due to their relative, low cost, ease of manufacturing, and light weight. When used as a structural material and especially for outside use, industrial plastics require additives to provide polymeric stability from the effects of temperature and light. Hindered amine light stabilizers (HALS) are added to impart these properties to plastics. HALS consist of a wide array of compounds, designed to absorb light, provide increased mechanical strength, and/or improve thermal stability. Over time, HALS have been designed for specific properties in individual resins and uses. HALS are often mixed in plastics depending on the environmental and use requirements of the plastic. This requires the production of a wide variety of HALS, ranging from simple molecules to complex polymeric structures.

Sixty thousand metric tons of stabilizers, both HALS and ultraviolet light absorbers (ULAs), were produced in approximately equal amounts, in 2007. The most produced stabilizers include Tinuvin®, Uvinul®, and Cyasorb®. Typical amounts used in polymers are between 0.2–0.5% for ULAs and 0.15–0.3% for HALS.[1]

Quantitation of HALS is not a simple task since many do not absorb ultraviolet light, many do not ionize, and some possess neither characteristic, making their detection difficult. Due to the variety of molecular size and forms, the chromatography of HALS can be equally challenging. Two HPLC methods that demonstrate the use of charged aerosol detection for the characterization and reproducible determination of nine different HALS are detailed.

The charged aerosol detector is a sensitive, mass-based detector, especially well-suited for the determination of HALS. As shown in Figure 1, the detector uses nebulization to create aerosol droplets. The mobile phase evaporates in the drying tube, leaving analyte particles, which become charged in the mixing chamber. The charge is then measured by a highly sensitive electrometer, providing reproducible, nanogram-level sensitivity. This technology has greater sensitivity and precision than evaporative light scattering (ELS), and it is simpler and less expensive to operate than a mass spectrometer (MS). Typical characteristics of chromatography with charged aerosol detection include: low-nanogram on-column (o.c.) sensitivity, over four orders of magnitude of dynamic range, and high precision results, typically less than two percent of peak area RSD. Analyte response is also largely independent of chemical structure, providing clear relationships among different analytes in a sample.

FIGURE 1: Schematic and functioning of charged aerosol detection.



1. Liquid eluent enters from HPLC system
2. Pneumatic nebulization occurs
3. Small droplets enter drying tube
4. Large droplets exit to drain
5. Dried particles enter mixing chamber
6. Gas stream passes over corona needle
7. Charged gas collides with particles and charge is transferred
8. High mobility species are removed
9. Charge is measured by a highly sensitive electrometer
10. Signal transferred to chromatographic software

Methods

Sample Preparation

Samples were dissolved in a variety of solvents, including acetone, acetonitrile/water (1:1), and methanol / chloroform (1:1).

Liquid Chromatography

HPLC System:	Thermo Scientific Dionex UltiMate 3000 RSLC, dual pump
HPLC Column (solid-core):	Imtakt Presto FF-C18, 2 µm, 250 × 3 mm
HPLC Column (porous):	Thermo Scientific Acclaim RSLC PA 2 C18, 2.2 µm, 100 × 2.1 mm
Column Temperature:	55 °C
Mobile Phase A:	50 mM Ammonium formate (pH 9.0)/acetonitrile (900:100)
Mobile Phase B:	Acetone/tetrahydrofuran/formic acid (500:250:0.3)
Acid Mobile Phase:	Acetone/water/formic acid (500:500:4)
Eluent Flow Rate:	0.3 mL/min
Acid Flow Rate:	0.2 mL/min, added post-column
Detector:	Thermo Scientific Dionex Corona ultra RS
Nebulizer Temperature:	20 °C Filter Setting: 5
Sample Temperature:	Ambient
Injection Volume:	5.0 µL

Gradient:

Solid-core Column

Time (min)	%A	%B
0.0	55	45
20.0	5	95
20.0	55	45
20.0	55	45

Porous Column

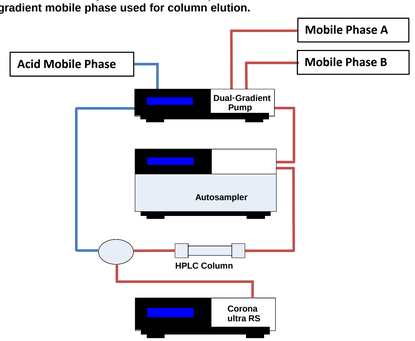
Time (min)	%A	%B
0.0	50	50
25.0	5	95
25.0	50	50
30.0	50	50

Data Analysis

All HPLC chromatograms were obtained and compiled using Thermo Scientific Dionex Chromeleon 6.8 Chromatography Data System.

The system was configured, as shown in Figure 2, so that the alkaline mobile phase gradient could be used for the chromatography, and the pH of this mobile phase could be acidified by adding and mixing acidified mobile phase, post-column.

FIGURE 2: HPLC system schematic for post-column acidification of alkaline, gradient mobile phase used for column elution.



Results

Solid-core C18 Column

Most of the HALS analyzed responded well to the solid-core HPLC column, including Hostavin® N30, Irgafos® 168, and Tinuvin 622 and 770. Triplicate injections of five concentrations are shown for a simple molecule, Irgafos 168, and a polymer, Tinuvin 622, in Figures 3 and 4, respectively. Calibration curves were generated and plotted as shown in Figures 5 and 6, respectively. All correlation coefficients were greater than 0.998.

FIGURE 3: Overlay of Irgafos 168 (in acetone) chromatograms, 1.6–12.5 µg on-column in triplicate.

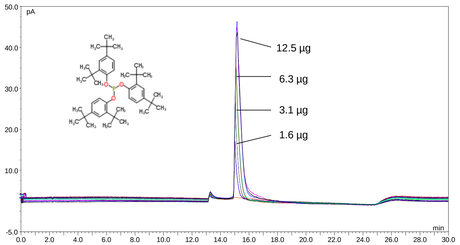


FIGURE 4: Overlay of Tinuvin 622 (in acetone) chromatograms, 3.1–50 µg on-column in triplicate.

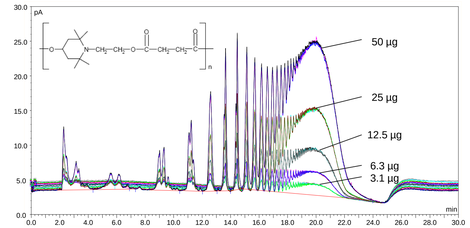


FIGURE 5: Calibration curve for Irgafos 168, from 1.6–12.5 µg o.c., triplicate injections.

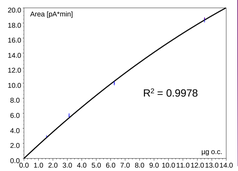
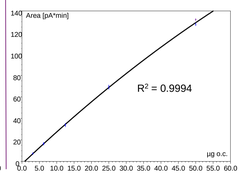


FIGURE 6. Calibration curve for Tinuvin 622 from 3–50 µg o.c., triplicate injections.



Replicate precision (n=3) %RSD calibration values and sensitivity values for the HALS on the solid-core column, are provided in Table 1. The limits of detection (LOD) and quantitation (LOQ) were calculated using signal-to-noise ratios (S/N) of the main peak for each analyte, where S/N = 10 was used for the LOQ, and a S/N =3.3 was used for LOD.

Table 1. Calibration precision and sensitivity values for HALS on solid-core column.

Analyte	%RSD	LOD (µg o.c.)	LOQ (µg o.c.)
Chimassorb 944	3.23	2.3	6.8
Chimassorb 2020	2.99	0.08	0.25
Hostavin N30	2.45	0.93	2.8
Irgafos 168	2.78	0.05	0.16
Tinuvin 622	2.34	0.65	1.95
Tinuvin 770	1.15	0.05	0.16

A porous C18 column was used for compounds that did not work well on the solid-core column.

Porous C18 Column

Three of the HALS appeared to retain/respond to a greater extent on the porous C18 column than with the solid-core column. Below are two HPLC chromatograms of two HALS, Cyasorb UV3529 and Sabo®stab UV119 (now known as Chimassorb® 119 FL), shown in Figures 7 and 8, respectively.

FIGURE 7: Chromatogram of Cyasorb UV3529 (in methanol/chloroform (1:1)) 50 µg on-column.

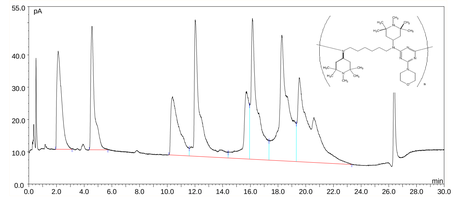
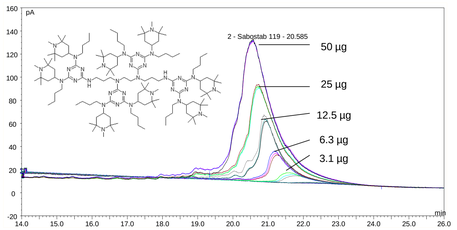


FIGURE 8: Overlay of Sabostab 119 (in methanol/chloroform (1:1)) chromatograms, 3.1–50 µg on-column in triplicate.



Calibration curves for the two HALS are shown in Figures 9 and 10, respectively. The method's sensitivity was derived from S/N ratios as previously described, and summarized in Table 2 for three HALS, including Cyasorb UV3346. All correlation coefficients were greater than 0.998, and %RSD of calibration values were below 5% for all three HALS.

FIGURE 9. Calibration curve for Cyasorb UV3529, from 3 to 50 µg o.c., triplicate injections.

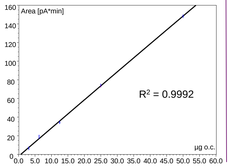


FIGURE 10. Calibration curve for Sabostab UV119, from 3–50 µg o.c., triplicate injections.

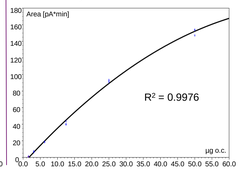


Table 2. Calibration precision and sensitivity values for HALS on the porous column.

Analyte	%RSD	LOD (µg o.c.)	LOQ (µg o.c.)
Cyasorb UV3346	2.72	2.3	6.8
Cyasorb UV3529	3.00	0.41	1.2
Chimassorb 119 FL	4.76	0.67	2.0

Conclusion

Two variants of a reversed-phase HPLC method were developed for the analysis of several species of HALS, using two different columns. Using the sensitivity of the charged aerosol detector, this method provided a means of characterizing and quantifying HALS, irrespective of whether they did or did not posses a chromophore or had the ability to ionize.

- Use of the Corona™ charged aerosol detector provided the necessary sensitivity to determine low levels of HALS that do not respond to UV or MS.
- The method enabled the routine quantitation of a variety of HALS.
- Method sensitivity was determined to be between 0.16–7 µg on-column.

References

1. Processing and Finishing of Polymeric Materials, Vol 2. Seidel, A, Parrish, K., Eds.; John Wiley & Sons:New Jersey, 2011. p 15.