

Identification of Components of Polymer Extracts by Gas Chromatography with EI and CI High Resolution Time-of-Flight Mass Spectrometry



LECO Corporation; Saint Joseph, Michigan USA

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1. Introduction

A GC-MS comprehensive profile of extracts of polymer extracts can provide valuable information for quality control or identification of adulterants. Samples can be analyzed for residual monomers, degradants, intermediates, additives or contaminants. Electron impact ionization (EI) mass spectrometry can provide valuable information through library comparisons provided that an adequate database is available. Often library hits can be misleading due to spectral similarity of homologous compounds. Matters are complicated further by the inability to confidently determine molecular formulas due to the absence of parent ions in mass spectra of labile compounds. A common mechanism for enhancing molecular ions is chemical ionization. The presence of molecular ions permits more effective utilization of the resolving power and mass accuracy inherent in high resolution TOF mass analyzers.

2. Results and Discussions

A polymer extract sample was previously analyzed (data not shown) using gas chromatography with detection by nominal mass EI mass spectrometry. Only seven of the greater than 20 components were confidently identified using this technique with library matching as the primary identification tool. Full characterization of the extract was achieved using a combination of ionization methods and high performance time-of-flight mass spectrometry. Methodology used in this application included high resolution, accurate mass electron impact ionization (EI) and chemical ionization time-of-flight mass spectrometry (HR-CI), 5% ammonia in methane reagent gas. The workflow consisted of acquiring EI data for library comparisons, followed by HR-CI data for secondary confirmation of formula and compound assignments. Robust formula determinations for molecular, adduct, and fragment ions were obtained through accurate mass measurements.

EI Data

An analytical ion chromatogram (AIC) trace showing compounds in the polymer extract is displayed in Figure 1. This extract was found to contain methylated cyclosiloxane homologs (**D4-DX**) with empirical formula C_2H_6OSi , butylated hydroxytoluene (BHT), a diisocyanate (1,1'-methylenebis[4-isocyanato]benzene, $C_{15}H_{10}N_2O_2$), a dilactone (1,6-dioxacyclododecane-7,12-dione, $C_{10}H_{16}O_4$) and a related tetralactone ($C_{20}H_{32}O_8$). Cyclosiloxanes **D4** to **D8** were easily identified using library match (LM) and accurate mass data for fragment ions. Molecular ions were

absent from the EI mass spectra of all these compounds; however, $[M-CH_3]^+$ fragment ions for **D4** – **D8** were produced with an average mass accuracy of 0.92 ppm. In these homologs, the relative abundance of $[M-CH_3]^+$ fragment ions decreased as the number of repeating units increased. In fact, **D9** and **D10** did not show $[M-CH_3]^+$ fragment ions in their mass spectra.

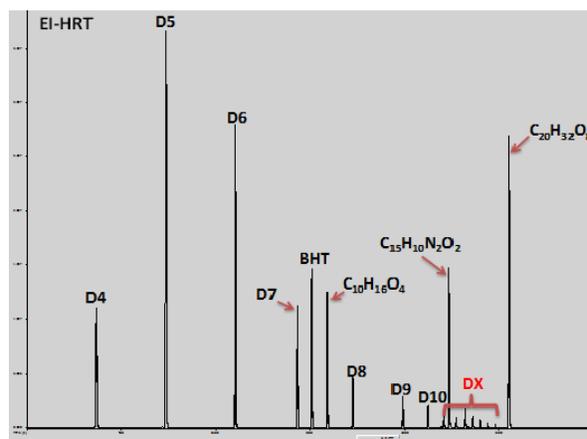


Figure 1. AIC of Polymer Extract Sample obtained using GC-EI.

An expansion of the AIC (Figure 2) shows the larger purported cyclosiloxanes **DX** and two additional compounds: a Diisocyanate (**A**) and (Z)-9-Octadecenamide (**B**). Cyclosiloxanes **D11** - **D17** could not be characterized by EI mass spectrometry. They produced similar mass spectra with the linear siloxane, hexadecamethyloctasiloxane ($C_{16}H_{50}O_7Si_8$), as their number one library hit. This is illustrated in Figure 3 which shows Peak True (Deconvoluted) mass spectra for **D14** and **D15** (LM values 828 and 839 for the incorrect hit).

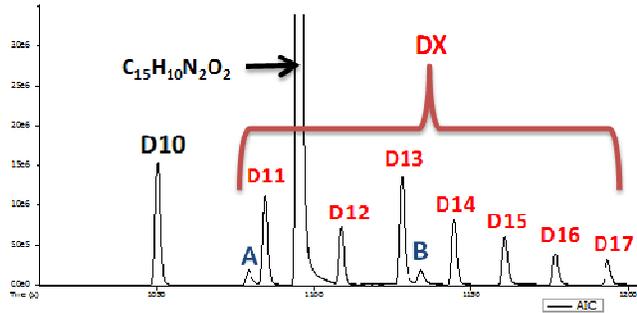


Figure 2. EI Data: AIC Expansion Showing Cyclosiloxanes (DX), a Diisocyanate (A) and (Z)-9-Octadecenamide (B).

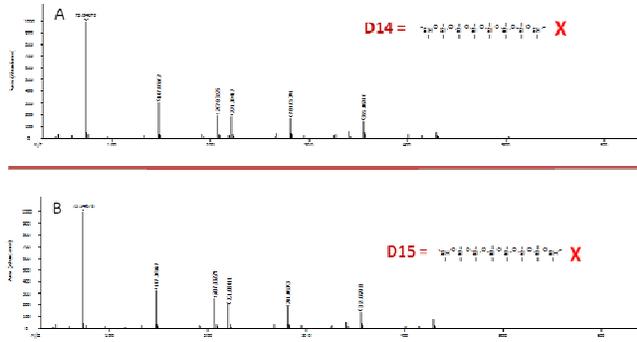


Figure 3. EI Peak True Mass Spectra for D14 (A) and D15 (B).

CI Data

A new HR-CI source was interfaced to the HRT and used to obtain pseudomolecular ion information and confirm the suspected identity of the expected larger cyclosiloxanes (DX) in the sample. HR-CI data was produced using 5% ammonia in methane as the reagent gas owing to its unique ionization properties. Retention times, areas and mass accuracy values for D4 – D17 cyclosiloxanes, BHT, diisocyanates, and the lactones are listed in Table 1. The average mass accuracy value for all compounds was 0.43 ppm. Protonated and ammoniated molecular ions for the dilactone (C₁₀H₁₆O₄) were found at m/z = 201.11214 (MA = 0.01 ppm) and m/z = 218.13863 (MA = -0.27 ppm). The protonated molecular ions for the diisocyanate and tetralactone were found at m/z = 251.08150 (MA = -0.31 ppm) and 401.21699 (MA = -0.24 ppm). An extracted ion chromatogram (XIC) for D11 to D17 is shown in Figure 4. Peak True mass spectral data and molecular ion region expansions for D14 and D15 are displayed in Figure 5.

Table 1. HR-CI Data: Compounds in Polymer Extract.

Compound	Formula	Species	Expected Ion m/z	Observed Ion m/z	Mass Delta (m/z)	Mass Accuracy (ppm)
D4	C8H24O4Si4	H Gain	297.08244	297.08219	-0.00026	-0.86
D5	C10H30O5Si5	H Gain	371.10123	371.10109	-0.00014	-0.37
D6	C12H36O6Si6	NH4 Gain	462.14657	462.14607	-0.00050	-1.08
D7	C14H42O7Si7	NH4 Gain	536.16536	536.16526	-0.00010	-0.19
BHT	C15H22O	H Gain	219.17434	219.17438	0.00003	0.15
Dilactone	C10H16O4	H Gain	201.11214	201.11214	0.00000	0.01
		NH4 Gain	218.13866	218.13863	-0.00006	-0.27
D8	C16H48O8Si8	NH4 Gain	610.18415	610.18423	0.00007	0.12
D9	C18H54O9Si9	NH4 Gain	684.20295	684.20295	-0.00002	-0.03
D10	C20H60O10Si10	NH4 Gain	758.22174	758.22170	-0.00004	-0.05
D11	C22H66O11Si11	NH4 Gain	832.24053	832.24025	-0.00028	-0.34
Diisocyanate	C15H10N2O2	H Gain	251.08150	251.08131	-0.00020	-0.78
C12	C24H72O12Si12	NH4 Gain	906.25932	906.25910	-0.00023	-0.25
C13	C26H78O13Si13	NH4 Gain	980.27811	980.27941	0.00129	1.32
C14	C28H84O14Si14	NH4 Gain	1054.29690	1054.29750	0.00059	0.56
C15	C30H90O15Si15	NH4 Gain	1128.31570	1128.31558	-0.00012	-0.11
C16	C32H96O16Si16	NH4 Gain	1202.33449	1202.33514	0.00066	0.55
C17	C34H102O17Si17	NH4 Gain	1276.35328	1276.35264	-0.00064	-0.50
Tetralactone	C20H32O8	H Gain	401.21699	401.21690	-0.00010	-0.24
		NH4 Gain	418.24354	418.24322	-0.00033	-0.78

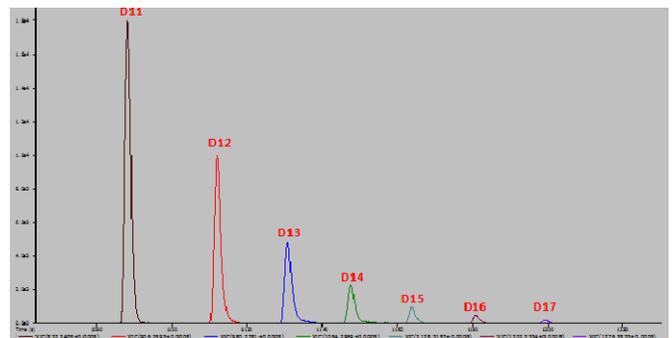


Figure 4. HR-CI: XIC for Cyclosiloxanes D11-D17 in Polymer Extract

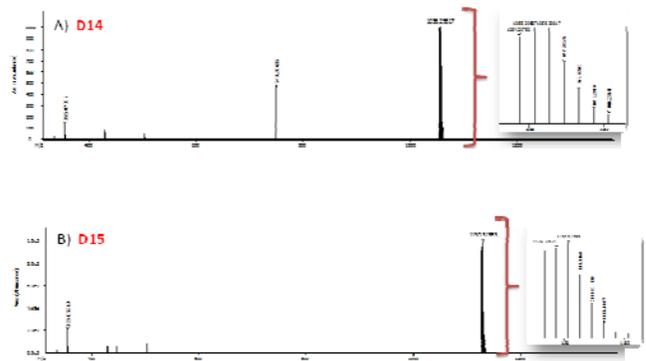


Figure 5. HR-CI: Peak True Mass Spectra for Cyclosiloxanes D14 (A) and D15 (B).

3. Conclusions

LECO's Pegasus GC-HRT mass spectrometer minimized matrix interferences and provided a comprehensive profile of a polymer extract. The combination of GC interfaced to high performance TOFMS with chemical ionization and electron impact ionization provided a platform for the confident characterization of extracts from a representative polymer. The complement of EI fragmentation for structural information and pseudomolecular ions for molecular formula facilitated the identification of several trace components in the extracts. This would not have been achieved without the information from chemical ionization and the superior mass accuracy of the GC-HRT. The Pegasus GC-HRT is ideally suited for the identification of unknowns and for obtaining valuable information for process and synthetic development, quality control of products and/or the identification of adulterants in materials.

4. Sample Preparations

Polymer beads (2.0 grams) and 15 mL of HPLC grade acetonitrile were placed in a 20 mL vial. The heterogeneous mixture was stirred and heated at a temperature of 37°C for 24 hours. This mixture was filtered through a 0.45 µm PTFE filter and a 1 mL aliquot of the solution was transferred to an MS vial for analysis.

5. Experimental Conditions

Chromatographic Parameters

Gas Chromatograph: Agilent Technologies 7890
with 7693 Auto Sampler
Column: Restek Rxi-5Sil MS
(30 m x 0.25 mm x 0.25 µm)
Carrier Gas/Flow: He; 1.0 mL/min constant flow
Injection Mode/Volume: Split 3:1, 0.5 µL
(CI-MS Splitless, 1 µL)
Temperature Program: 60°C (2 min hold) to 190°C
at 10°C/min (1 min hold) to
250°C at 50°C/min
(10 min hold)

Mass Spectrometry Parameters

Mass Spectrometer: LECO Pegasus® GC-HRT
Transfer Line Temp: 300°C
Ion Source Temp: 250°C (CI-MS 225°C)
Ionization: EI (70 eV); CI (140 eV);
positive ions
Mass Range (m/z): 50 to 650
(CI-HRT, 180 to 1400)
Acquisition Rate: 6 spec/s
Flight Path: High Resolution
($R_{FWHM} = 25,000$)
Mass Calibration: PFTBA (Internal)
CI Reagent Gas: 5% NH₃ in Methane

