Analysis of Polymer Extracts by Gas Chromatography-High Resolution Time-of-Flight Mass Spectrometry With Electron and Chemical Ionization

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Introduction

Comprehensive profiles of polymer extracts can provide valuable information for the quality control of products or identification of adulterated materials. Extractables and leachables may result from incomplete polymerization, surface residues, secondary packaging of components, or product degradation (Figure 1).

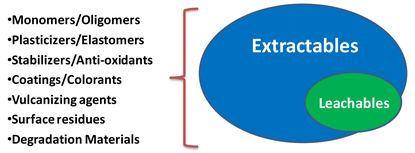


Figure 1: Potential Extractables and Leachables

Electron ionization mass spectrometry (EI-MS) can help characterize extract components through library comparisozns provided adequate databases are available. Often library hits are ambiguous due to mass spectral similarity of isomeric or homologous compounds. Matters are complicated further by the inability to determine molecular formulas because of the absence of parent ions in mass spectra of labile compounds. High quality spectral data and mass accuracy values (<1.0 ppm) facilitated confident characterization of residual monomers, oligomers, additives, and impurities in samples.

Characterization was facilitated through a combination of hard and soft ionization methods and high resolution time-of-flight mass spectrometry (HRT, Figure 2).

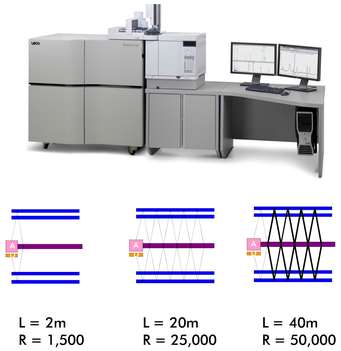


Figure 2: Pegasus® GC-HRT (top) and Operational Modes (bottom)

In this study, three samples (foam, rubber, and siloxane polymer) dispersed in thermoplastic polyurethane (TPU) polymer were analyzed using LECO's Pegasus GC-HRT. The combination of electron impact and chemical ionization high resolution time-of-flight mass spectrometry (EI and CI-HRT) was vital for unambiguous identification of polymer extractables.

Experimental

Sample Preparation

Polymers were extracted using common organic solvents (e.g., isopropanol, acetonitrile, etc.).

The procedure used for extraction of the Siloxane/TPU polymer is illustrated below (Figure 3).

Figure 3. Sample Preparation – Siloxane/TPU Polymer

Instrument Parameters

GC Parameters

GC:	Agilent 7890 and 7693 Auto Sampler
Column Type:	Restek Rxi-5Sil MS (30 m, 0.25 mm ID, 0.25 mm df)
Injection:	0.5 mL, Split 3:1 (CI Splitless); Inlet Temp. 250°C
Oven:	60°C (2 min) to 190°C at 10°C/min (1 min) to 250°C at 50°C/min (10 min)
Carrier Gas:	He, Constant Flow (1.00 mL/min)

MS Parameters

Spectrometer:	LECO Pegasus GC-HRT
Ion Sources:	LECO EI, CI
Source Temp.:	250°C (CI 225°C)
Transfer Line Temp.:	300°C
Spectral Acquisition:	6 spectra/second
Mass Range (m/z):	50–650 (CI 180–1400)
Calibration:	PFTBA (Internal)
CI Reagent Gas:	5% Ammonia in Methane
Folded Flight Path:	HR (R = 25,000 FWHM)

Analysis Workflow

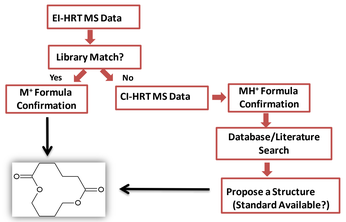
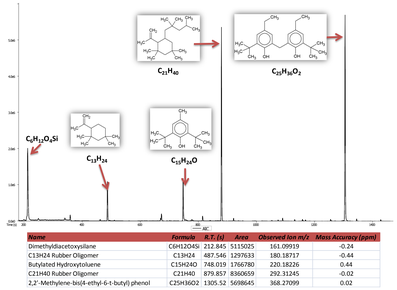


Figure 4: Polymer Analysis Workflow; EI and CI-HRT Analysis

Results (Rubber Extract)

The Analytical Ion Chromatogram (AIC) in Figure 5 shows a representative set of compounds in rubber extract: Radical inhibitors (e.g., butylated hydroxytoluene (BHT), 2,2′methylene-bis(4-ethyl-6-t-butyl)phenol), and oligomers such as 1-isopropenyl-2,2,4,4-tetramethylcyclohexane ($C_{13}H_{24}$) and 1,1,5,5-tetramethyl-2-(1-methylethenyl)-3-(2,2,4-trimethylpentyl) cyclohexane ($C_{21}H_{40}$). The mass accuracy values for these compounds ranged from -0.44 to 0.44 ppm. Peak true (Deconvoluted) mass spectra for BHT and the $C_{13}H_{24}$ oligomer are displayed in Figure 6.



Name	Formula	R.T. (s)	Area	Observed Ion m/z	Mass Accuracy (ppm)
Dimethyldiacetoxysilane	C6H12O4Si	212.845	5115025	161.09919	-0.24
C13H24 Rubber Oligomer	C13H24	487.546	1297633	180.18717	-0.44
Butylated Hydroxytoluene	C15H24O	748.019	1766780	220.18226	0.44
C21H40 Rubber Oligomer	C21H40	879.857	8360659	292.31245	-0.02
2,2'-Methylene-bis(4-ethyl-6-t-butyl) phenol	C25H36O2	1305.52	5698645	368.27099	0.02

Figure 5: AIC, Rubber Extract

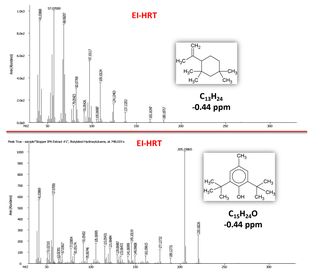
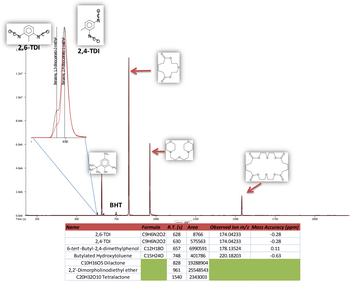


Figure 6: Peak True Mass Spectra for BHT and a $C_{13}H_{24}$ Oligomer in Rubber Extract

Results (Foam Extract)

An AIC of major components in foam extract are shown in Figure 7. Two monomers 2,4- and 2,6-toluene diisocyanate (2,4- and 2,6-TDI), and the radical inhibitors 6-*tert*-butyl-2,4-dimethylphenol and butylated hydroxytoluene were easily identified through spectral similarity and formula searches of their EI-HRT data. Mass accuracy values for these compounds ranged from -0.63 to 0.11 ppm. Identification of the lactones and catalytic foam agent, 2,2′-dimorpholinodiethyl ether, required a combination of EI-HRT and CI-HRT data analysis, as well as scientific database and literature searches. Peak True CI-HRT data for these compounds are displayed in Figure 8.



Name	Formula	R.T. (s)	Area	Observed Ion m/z	Mass Accuracy (ppm)
2,6-TDI	C9H6N2O2	628	8766	174.04233	-0.28
2,4-TDI	C9H6N2O2	630	575563	174.04233	-0.28
6-tert-Butyl-2,4-dimethylphenol	C12H18O	657	6990591	178.13524	0.11
Butylated Hydroxytoluene	C15H24O	748	401786	220.18203	-0.63
C19H16O5 Dilactone		828	19289954		
2,2'-Dimorpholinodiethyl ether		961	2554854S		
C28H32O10 Tetralactone		1540	2340303		

Figure 7: AIC and XIC Expansion Showing Diisocyanates 2,4- and 2,6-TDI in Foam Extract

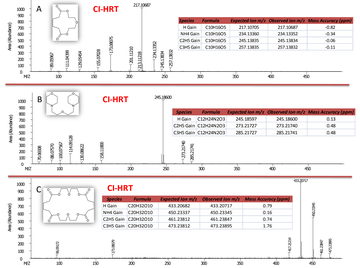


Figure 8: CI-HRT Data of a Dilactone (A), Dimorpholino Diethyl Ether (B), and Tetralactone (C) in Foam Extract

Results (Siloxane/TPU Extract)

EI-HRT analysis of the extract resulted in the AIC shown in Figure 9. The extract contained methylated cyclosiloxane homologs (D4-D10) with empirical formula C_2H_6OSi, BHT, diisocyante monomers and some lactones. Cyclosiloxanes D4-D8 were easily identified using spectral similarity matches and accurate mass data for fragment ions $[M\text{-}CH_3]^+$; however, D9, D10, and the series of compounds labeled **DX** (**D11–D17**) gave similar spectra as shown by two of the homologs later determined to be **D14** and **D15** (Figure 10) .

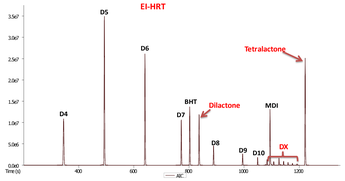


Figure 9: EI-HRT, AIC of Siloxane/TPU Extract

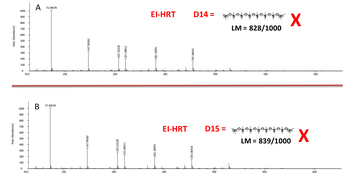


Figure 10: EI-HRT, Peak True Mass Spectra of D14 (A) and D15 (B)

CI-HRT data was critical for identification of the entire series of methylated cyclosiloxanes. An XIC of the CI-HRT data for **D11–D17** is shown in Figure 11. Peak True CI-HRT data for **D14** and **D15** confirms the formulas for these homologs (Figure 12). Table 1 lists the formulas and mass accuracy values (Ave. = 0.43 ppm) for the major components in the sample.

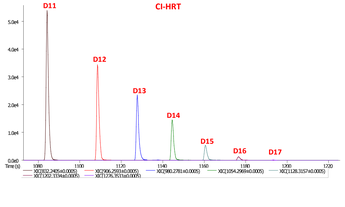


Figure 11: CI-HRT, XIC of D11-D17

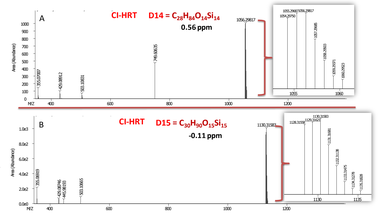


Figure 12: CI-HRT, Peak True Mass Spectra of D14 (A) and D15 (B)

Table 1: CI-HRT, Compounds in Siloxane/TPU Polymer

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	C19H16O4	H Gain	201.11214	201.11214	0.00000	0.01
		NH4 Gain	218.13868	218.13863	-0.00006	-0.27
D8	C16H48O8Si8	NH4 Gain	610.18416	610.18423	0.00007	0.12
D9	C18H54O9Si9	NH4 Gain	684.20295	684.20293	-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
MDI	C15H10N2O2	H Gain	251.08150	251.08131	-0.00020	-0.78
D12	C24H72O12Si12	NH4 Gain	906.25932	906.25910	-0.00023	-0.25
D13	C26H78O13Si13	NH4 Gain	980.27811	980.27941	0.00129	1.32
D14	C28H84O14Si14	NH4 Gain	1054.29690	1054.29750	0.00059	0.56
D15	C30H90O15Si15	NH4 Gain	1128.31570	1128.31558	-0.00012	-0.11
D16	C32H96O16Si16	NH4 Gain	1202.33449	1202.33514	0.00066	0.55
D17	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

Summary

The GC-HRT's high resolution, quality spectral data, and excellent mass accuracy values were very useful for the confident identification of monomers, oligomers, and additives in polymers. A combination of EI and CI-HRT was shown to facilitate confident identification of extractables and leachables from different types of polymer systems.