

PQRI

Product Quality Research Institute

Controlled Extraction Study “Unknown” Elastomer

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Chemistry: Phase 1 Studies

- Controlled Extraction Studies
- Multiple solvents with differing polarities:
 - Methylene chloride Polarity index = 3.1, 2-propanol Polarity index = 3.9, hexane Polarity index = 0
- Multiple extraction techniques
 - Sonication (1 hr), Soxhlet (up to 16 hr), reflux (4 hr)
- Multiple analytical techniques
 - LC/UV (DAD), LC/MS, GC/MS (results featured)

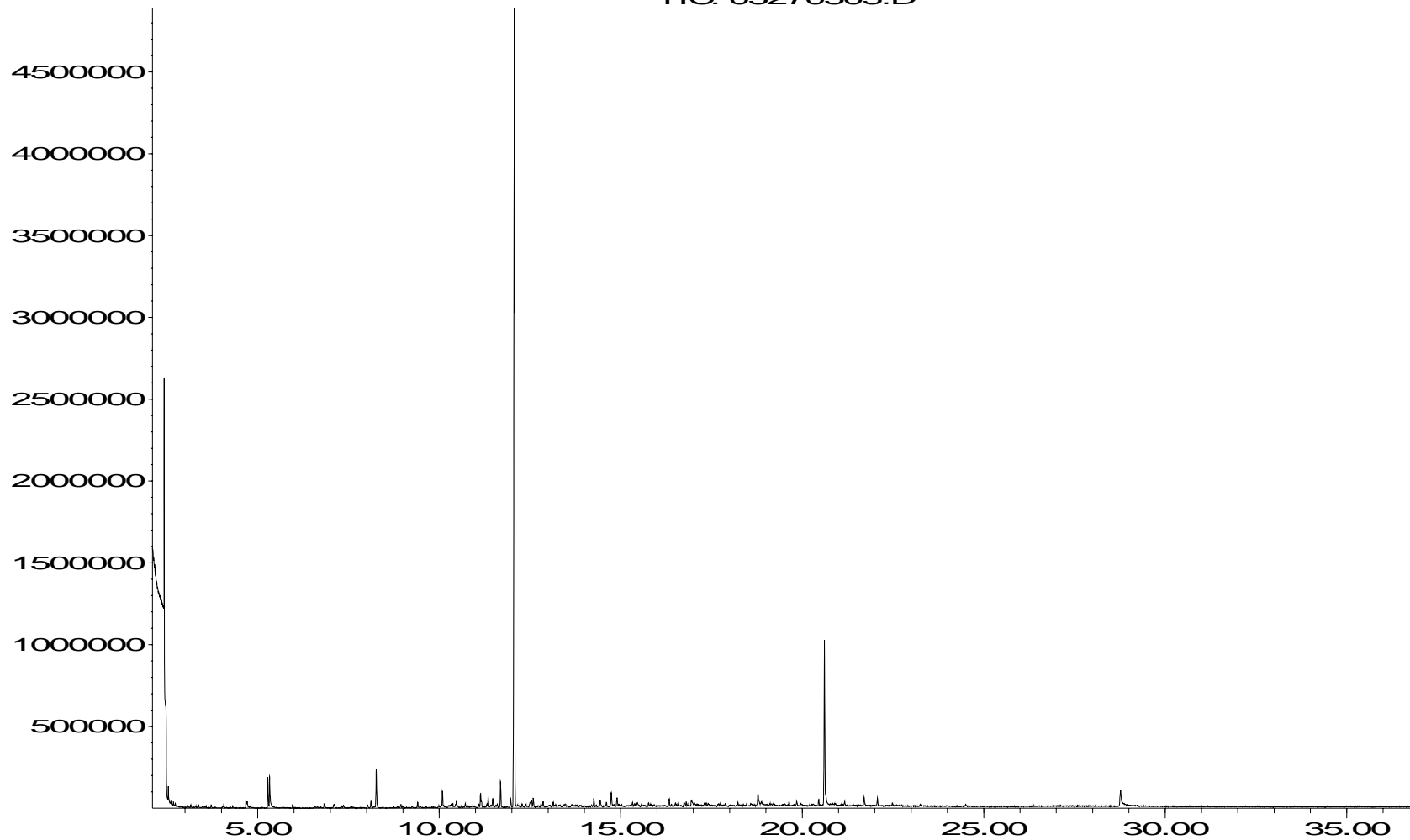
Chemistry: Phase 1 Studies

- For this particular test article, the only information available to the analytical chemists was that the elastomer was peroxide cured. The type of rubber, formulation ingredients (including curing agent and other additives and fillers), and manufacturing processes were not revealed.
- Question: Can our Controlled Extraction Study process effectively deformulate this elastomer?

GC/MS Total Ion Chromatogram (Soxhlet extraction in hexane for 16 hours)

Abundance

TIC: 03270303.D

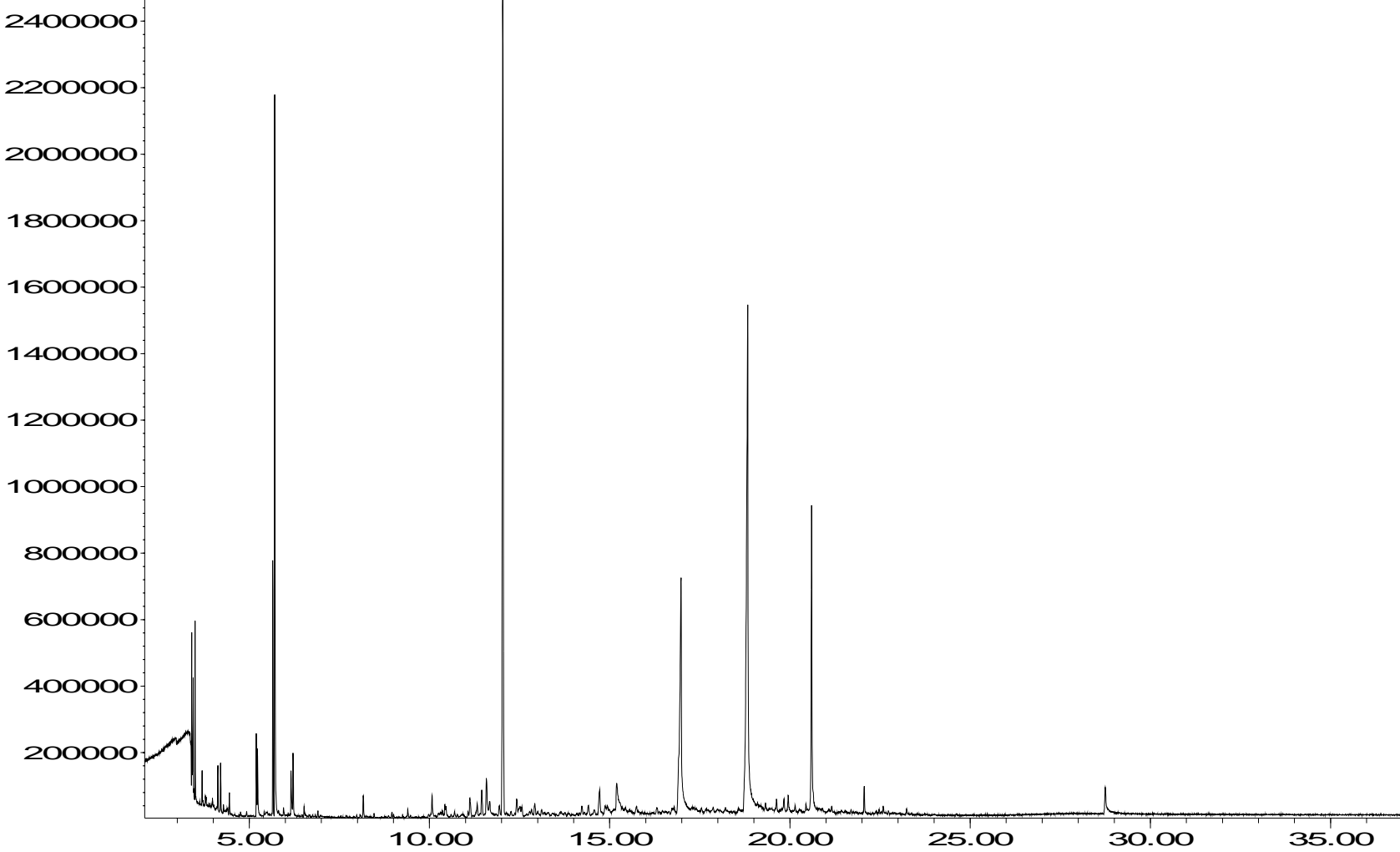


Time-->

GC/MS Total Ion Chromatogram (reflux extraction in 2-propanol for 4 hours)

Abundance

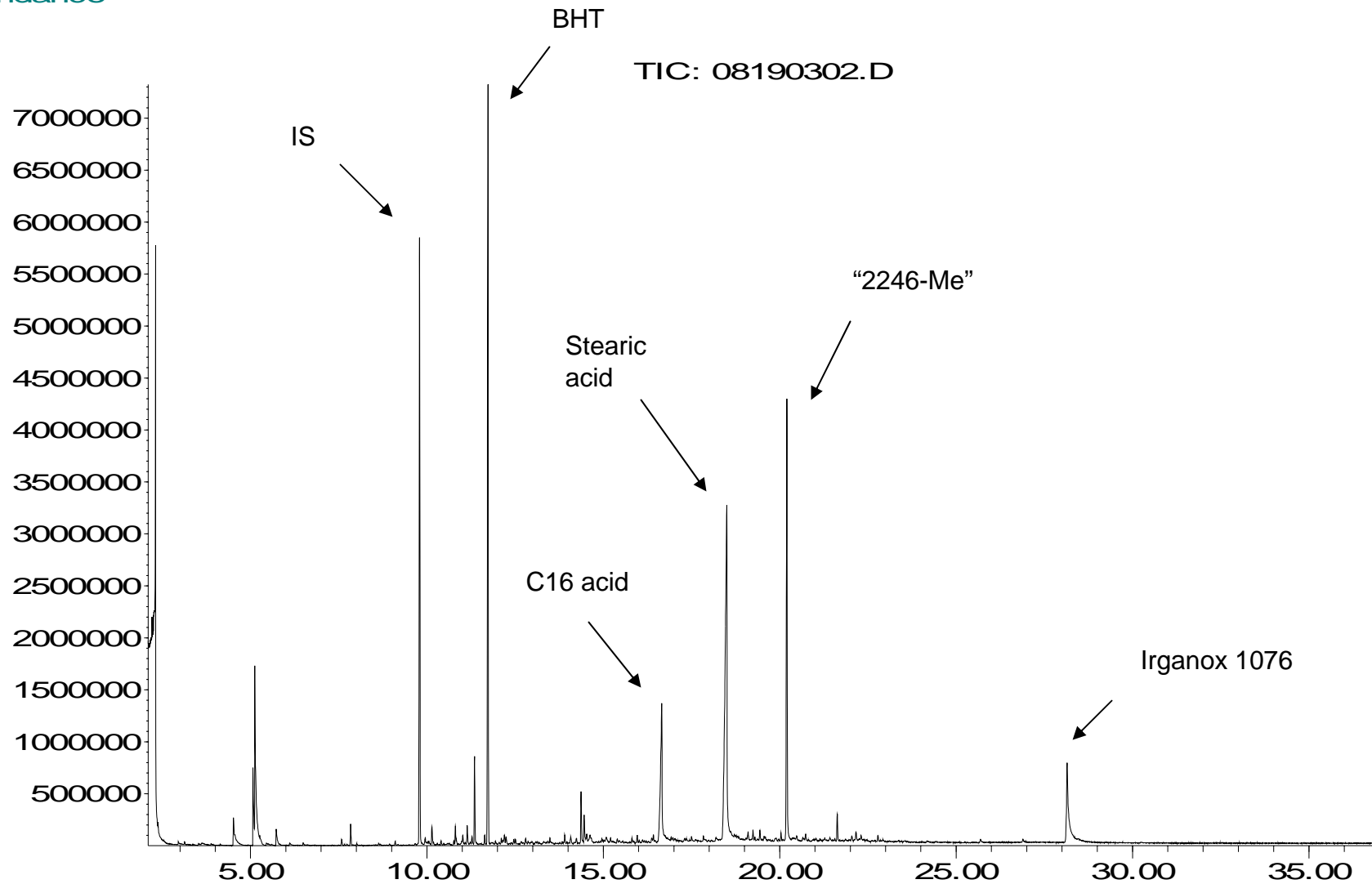
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Time-->

GC/MS Total Ion Chromatogram (Soxhlet extraction in methylene chloride for 16 hours)

Abundance



Time-->

Major Extractables Identified by GC/MS

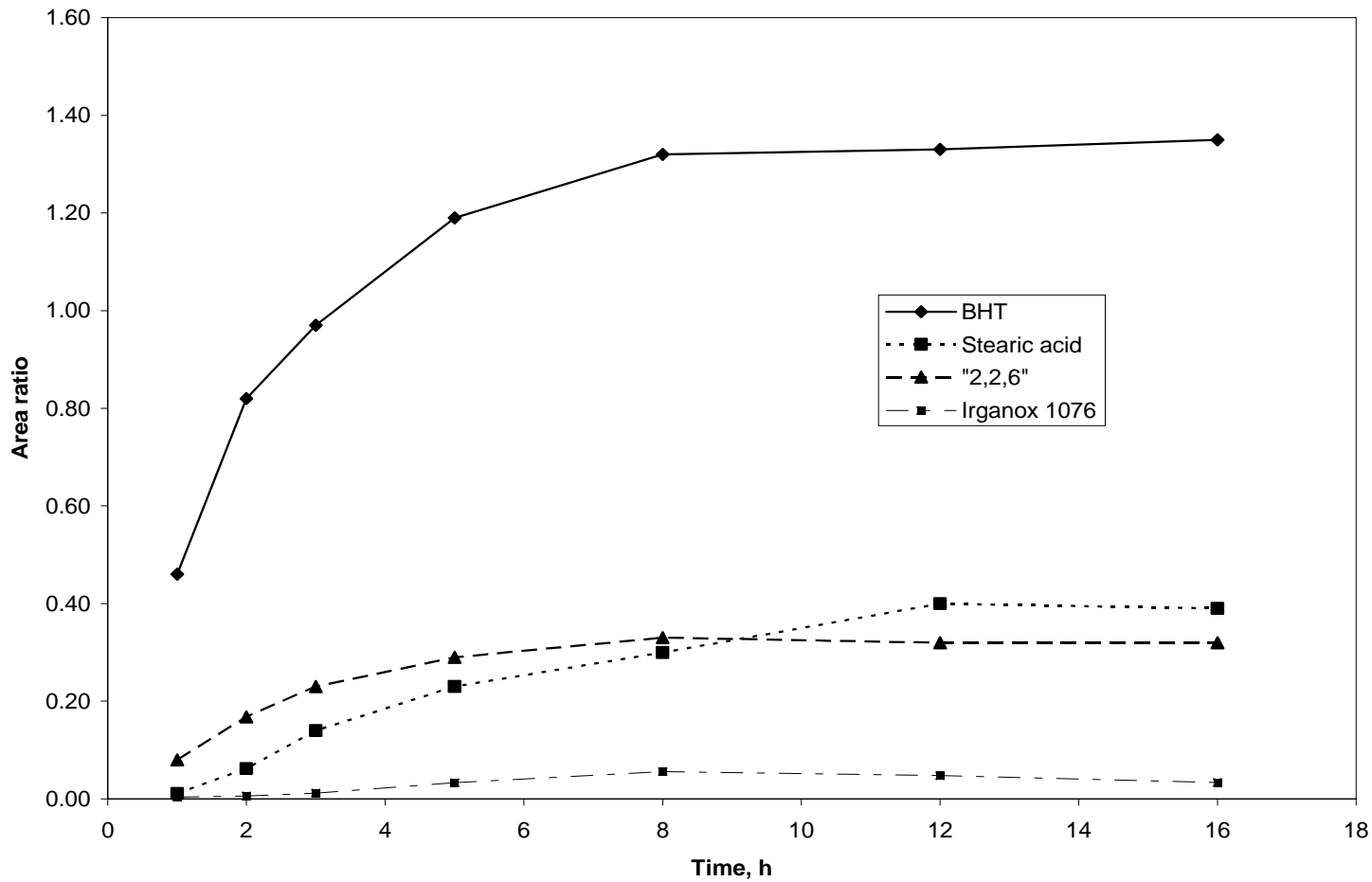
RETENTION TIME	IDENTIFICATION
MIN.	
9.53	2-fluorobiphenyl (internal standard)
11.48	Butylated hydroxytoluene
14.12	3,5-di-tert-butyl-1,4-hydroxybenzaldehyde
14.21	3,5-di-tert-butyl-4-hydroxy benzyl alcohol
14.37	Tetradecanoic acid
16.42	n-hexadecanoic acid
18.26	n-octadecanoic acid (stearic acid)
19.96	2,2'-methylene-bis-[6-(1,1-dimethylethyl)-4-methyl] phenol
27.86	Irganox 1076

Observations and Optimization of Extraction Conditions

- The GC/MS extractables profiles presented here show significant differences among extraction techniques
- Soxhlet extraction in Methylene Chloride was judged to provide the most complete profile
- An extraction optimization was accomplished with this system
- EXTRACTION OPTIMIZATION
 - Approx. 7 g of rubber was cut up into roughly uniform sized pieces, and loaded into a 33 x 90 mm cellulose extraction thimble
 - 200 mL of methylene chloride with 10 µg/mL 2-fluorobiphenyl internal standard was used to extract the rubber pieces
 - Aliquots were withdrawn from the extraction vessel at 1, 2, 3, 5, 8, 12 and 16 hours
 - These were analyzed by GC/MS

"UNKNOWN" ELASTOMER TEST ARTICLE EXTRACTABLES

Area Ratio vs IS for Valois Rubber



EXTRACTABLES PROFILE OF “UNKNOWN” TEST ARTICLE

- The previous plot shows that the extraction is satisfactory in 16 hours.
- The elastomer is likely to be peroxide cured based upon:
 - Detection of possible peroxide fragments
 - No sulfur-containing curing agents or fragments were detected
- The curing agent is likely to be aromatic based upon:
 - Identification of possible aromatic peroxide fragments
- The elastomer contains a combination phenolic antioxidant system
 - Confirmed compounds: 2,6-di-tert-butyl-4-methylphenol (BHT); 2,2-methylene-bis[4-methyl-6-tert-butyl]phenol (“2246-Me”) and Irganox 1076
- The presence of stearic acid and palmitic acid suggests a technical grade stearic acid and/or calcium stearate as a filler or flow modifier

EXTRACTABLES PROFILE OF “UNKNOWN” TEST ARTICLE

- The EPDM Formulation was disclosed to us after we completed the optimized extraction
 - 1. EPDM polymer: 64.0%
 - 2. Mineral Fillers: 34.4%
 - May include Stearic acid
 - 3. Antioxidant 1 (BHT): 0.3%
 - 4. Antioxidant 2 (“2246-Me”): 0.3%
 - 5. Peroxide: 1.0%

EXTRACTABLES PROFILE OF “UNKNOWN” TEST ARTICLE: CONCLUSIONS

- Qualitative controlled extraction studies are not sufficient to fully characterize this elastomer
- They are not sufficient to completely predict potential leachables or act as a basis for control of the elastomer composition
- Supplier information had significant limitations
 - Origin of the Irganox 1076
 - Technical grade additives (low purity)
- Best practice: use broad polarity range of solvents, and a variety of techniques, to best understand the composition of the test article
- BOTH detailed supplier information and detailed controlled extraction studies are needed for the test articles

Results

- The known elastomer formulation ingredients 2, 2'-methylene-bis(6-*tert*-butyl-4-ethyl phenol), Coumarone-Indene Resin, and Paraffin are accounted for in the extractables profiles.
- 2-mercaptobenzothiazole was not observed directly by GC/MS (it was observed by LC/MS, data not presented), but was observed indirectly through a reaction product with methylene chloride (see Peak 10).
- Tetramethylthiuram monosulfide was not observed either by GC/MS or LC/MS and was assumed to be totally consumed in the elastomer compounding process.

Best Practice Recommendations Supported by this Study

- Controlled Extraction Studies should employ vigorous extraction with multiple solvents of varying polarity.
- Controlled Extraction Studies should incorporate multiple extraction techniques.
- Controlled Extraction Studies should include careful sample preparation based on knowledge of analytical techniques to be used.
- Controlled Extraction Studies should employ multiple analytical techniques.
- Controlled Extraction Studies should include a defined and systematic process for identification of individual extractables.
- Controlled Extraction Study “definitive” extraction techniques/methods should be optimized.
- During the Controlled Extraction Study process, sponsors should revisit supplier information describing component formulation.