

# Controlled Extraction Study on Low Density Polyethylene (LDPE)

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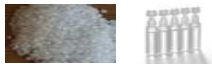
## Material

Polymer Structure:

Ethylene monomer  $\text{CH}_2=\text{CH}_2$



Polyethylene  $-(\text{CH}_2-\text{CH}_2)_n-$



Applications:

Overpouch, Blow Fill Seal Ampules, Flexible Bottles

## Composition

### Amounts/Functionality

- Dow 640-I LDPE resin: Base polymer
- Irganox B 215 (2:1 blend of Irganox 168 and Irganox 1010): Antioxidant, 1000 ppm
- BHT: Antioxidant, 200 ppm
- Calcium Stearate: Acid Scavenger and Slip agent 500 ppm
- Erucamide: Antistatic, 500 ppm
- Chimassorb 944: Hindered amine light stabilizer, 2000 ppm

## Inorganic Metals Detected

Element	Trace Elements and Metals Results, LDPE (Aqueous based extracts only)			
	pH 2.5 Extracts		pH 9.5 Extracts	
	Sonication	Sealed Vessel	Sonication	Sealed Vessel
Sodium (Na)	0.96	0.62	ME <sup>1</sup>	ME <sup>1</sup>
Bromine (Br)	0.40	0.01 <sup>2</sup>	0.08	0.04 <sup>2</sup>
Magnesium (Mg)	0.18	0.01	0.04 <sup>2</sup>	NP <sup>3</sup>
Iron (Fe)	0.12	0.03	NP <sup>3</sup>	NP <sup>3</sup>
Aluminum (Al)	0.09	0.04	NP <sup>3</sup>	NP <sup>3</sup>
Zinc (Zn)	0.08	0.01	NP <sup>3</sup>	NP <sup>3</sup>
Lanthanum (La)	0.01	0.01 <sup>2</sup>	0.02	0.02 <sup>2</sup>
Manganese (Mn)	0.01	NP <sup>3</sup>	NP <sup>3</sup>	NP <sup>3</sup>
Strontium (Sr)	0.01	NP <sup>3</sup>	NP <sup>3</sup>	NP <sup>3</sup>
Cobalt (Co)	0.01	NP <sup>3</sup>	NP <sup>3</sup>	NP <sup>3</sup>
Barium (Ba)	NP <sup>3</sup>	NP <sup>3</sup>	NP <sup>3</sup>	0.01 <sup>1</sup>

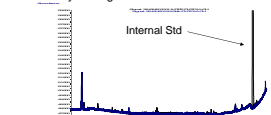
<sup>1</sup>ME = this element is a component of the extracting solution used and thus was not measurable as an extractable.  
<sup>2</sup>Detected in only one of the two replicate extracts.  
<sup>3</sup>NP = not present in this extract in measurable quantities.  
<sup>4</sup>Several elements, including Ni, Cu, Zn, Cr, As, Ba, and Hg were detected at very low levels in one replicate of one type of extracting solution.  
 Targets not detected using any extraction condition included: Li, Be, B, Si, Se, Ti, V, Ga, Sn, Y, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sb, Bi, Te, I, Cs, Pb, Hf, Ni, Sr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, La, Hf, Ta, W, Ra, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, and U.

## Solvent / Extraction Map

	Headpace	Reflux	Soxhlet	Sealed Vessel	Sonication
Hexane	x	x	x	x	x
n-Hexane	x	x	x	x	x
Isopropanol	x	x	x	x	x
Isopropanol/Water	x	x	x	x	x
Aqueous pH 2.5	x	x	x	x	x
Aqueous pH 9.5	x	x	x	x	x

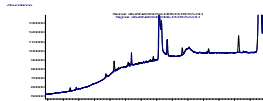
## Volatile Substances

Headspace GC-MS Profile:  
Part 1: Early eluting substances



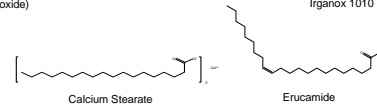
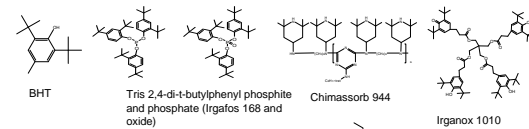
Overlays of PEG Blank (Blue) and LDPE Sample (Black)

Part 2: Late eluting substances



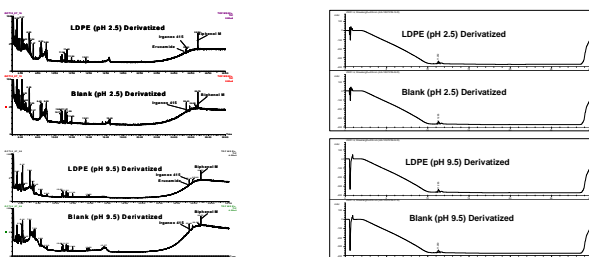
No volatile peaks were observed in the sample above 1 ppm which were not present in the blank.

## Structures



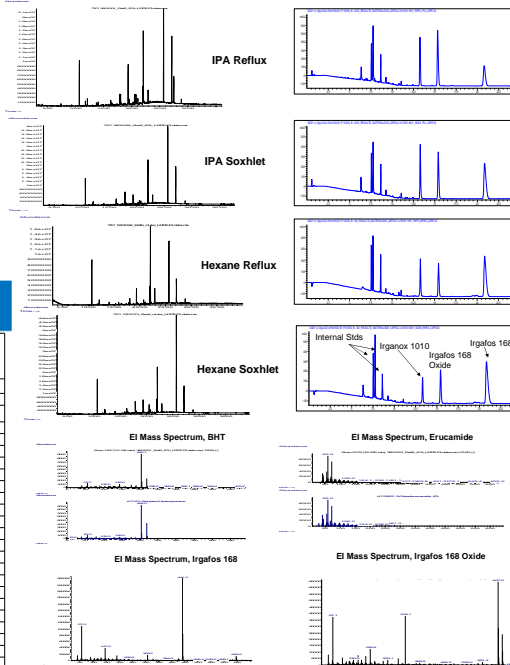
## Semivolatatile Substances

### Sonication Extractions



## Semivolatatile Extractables Amounts Detected Under Various Conditions and First Pass Identifications

Extractable	Retention Time (min)	Isopropanol Reflux µg/g	Isopropanol Soxhlet µg/g	Hexane Reflux µg/g	Hexane Soxhlet µg/g
2-Butanone	4.12	3.4	6.4	0.0	7.7
Nonanal	5.86	1.5	0.0	0.0	0.5
Octanal	7.42	7.7	1.2	2.8	1.7
Nonoic acid	9.17	3.6	2.6	0.0	0.7
Internal Std 2-Fluorobiphenyl	10.70	164.3	124.4	132.7	160.6
Unknown	12.01	14.6	19.5	16.4	26.6
BHT	12.13	26.2	24.9	16.5	24.5
Pentanamide	13.98	11.4	9.2	10.0	15.1
Cyclododecane	14.04	8.9	9.3	8.5	11.2
Unknown	14.06	13.3	9.0	8.5	11.2
Palmitic acid	16.29	18.9	31.0	0.0	18.5
Hexadecanamide	16.45	6.1	3.7	0.0	5.5
3,5-di-tert-Butyl-4-hydroxyphenylpropionic acid	16.48	5.3	3.9	0.0	5.8
Stearic acid	17.92	39.6	84.6	6.6	58.9
Aliphatic amide	18.04	41.4	10.4	8.4	10.3
Oleamide	19.37	193.1	64.5	57.9	75.6
Aliphatic amide	19.53	24.7	7.3	60.7	9.9
DEHP	20.51	30.3	21.2	35.4	35.4
Stearamide	20.76	46.5	16.1	0.0	11.7
Internal Std Irganox 415	21.99	56.4	56.4	56.4	56.4
Erucamide	22.07	291.3	273.5	271.9	234.1
Internal Std Bisphenol M	22.92	48.9	46.7	50.9	40.8
Irganox 168	25.67	482.2	616.9	286.0	638.1
Irganox 168 oxide	27.12	496.3	397.4	141.9	242.8
Dilauryl-3,3'-thiodipropionate (Irganox PS 800)	27.52	205.6	399.8	143.0	241.0



## Observations and Results

Metals testing yielded no significant species detected (all less than 1 ppm). Calcium (known additive) was not detected. Therefore the polymer appears resistant to dissolution in aqueous extract media. Volatiles testing showed no significant species. However, this was not surprising as LDPE was not expected to contain large amounts of residual solvents.

Aqueous sonication extraction also produced few extractables when analyzed by GC-MS and LC-UV-MS. However, reflux and soxhlet extraction in IPA and Hexane produced significant extractables, both related to known material composition, products/degradants of known additives and a few unexpected species (e.g. Dilauryl-3,3'-thiodipropionate and other antistatic amides). The Chimassorb 944 additive was not observed under any extraction condition or analytical technique. Peaks attributed to the other known additives (structures provided above) were detected under a number of conditions. Stearic acid was observed, which likely originates from the Calcium Stearate additive

Differences in the relative amounts of extractables detected between the IPA and Hexane solvents and the two extraction methods employed (reflux and Soxhlet) were noted. However, in many cases similar amounts were extracted. IPA appears more appropriate for polar species extraction and dissolution (e.g. fatty acids). Several species could not be assigned first pass identifications.

Expect to observe polyethylene oligomers, especially under aggressive extraction conditions. These will appear as various chained lengths branched saturated and unsaturated aliphatic hydrocarbons detected using GC-MS.

Overall LDPE appears to be very suitable for aqueous solvent and resistant to extraction. Profiles for organic solvent extraction are somewhat complex but manageable and provide relevant information about materials composition.