

### Summary

This application note describes a thermal gravimetric analysis coupled with Fourier transform infrared spectroscopy (TGA-FTIR) method for compositional analysis and component identification of an automobile tire. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) and gas chromatography-mass spectroscopy (GC-MS) are also used to assess the minor components in the tire.

### Background

The rubber used in automobile tires is a complex multi-component article which consists of several base polymers, plasticizers (oil), carbon black and inorganic fillers. The type and concentrations of the tire components have a major effect on the end-use properties of the material. Quality control and deformation of rubber tires is a challenging task due to the insolubility of the highly crosslinked polymers and the carbon black component that interferes with the analysis. One option is to use tedious solvent extraction methods combined with HPLC-MS or FTIR for identification of components. Here we describe an alternative direct TGA-FTIR method for compositional analysis and component identification of rubber tires that do not require multiple-step sample analysis and preparation.



TGA coupled with FTIR is a unique method for characterization of complex multi-component materials, combining the quantitative compositional analysis capabilities of TGA with the identification abilities of FTIR. The weight loss of the sample (heated at a controlled rate in an appropriate environment) due to evaporation of volatiles and/or degradation of constituents is measured by TGA and the evolved gases formed as a result of heating are analyzed by FTIR. The evolved gases are identified by comparing their spectra against FTIR database libraries. Highly volatile compounds evolve without decomposition and can be identified by using a standard FTIR database. Polymeric base materials will produce mono- and oligomeric materials upon thermal degradation that are best identified by comparison with FTIR polymer pyrolysis libraries.

Inorganic filler content was analyzed with EDS, and volatile additives were identified with GC-MS.

### Procedure

TGA-FTIR was run on a Michelin tire sample using a TA Instruments Q500 TGA coupled to a Biorad Excalibur FTS3000 FTIR bench. The TGA was fitted with the TA Instruments Evolved Gas Accessory (EGA) and the evolved gases were transported to the FTIR bench using a Pike Scientific TGA/FTIR accessory. The transport line and flow-cell on the FTIR bench were set to 260 °C.

The sample was loaded into the tared platinum pan of a TA Instruments Q500 TGA, weighed inside the closed furnace and heated at 10 °C/min under the following conditions:

- Start temperature: ambient
- Ramp rate: 10 °C/min from ambient to 600 °C
- Switch to air at 600 °C
- Ramp rate: 10 °C/min from 600 °C to 800 °C

The FTS3000 FTIR bench spectrometer acquired spectra in a “Collect-Kinetics” mode under the following conditions:

- Time resolution: 29.319 seconds
- Number of scans: 32
- Speed: 5 kHz
- Resolution: 4 cm<sup>-1</sup>

Sensitivity: 1

The spectra were extracted from FTIR absorbance of a Gram-Schmidt plot. The extracted spectra were compared against the FTIR database using Know-It-All Informatics System 9.5 software.

### **Results**

The weight loss and weight loss derivative curves (WLDC) for temperature ramp from ambient to 900 °C are shown in Figure 1, with the corresponding FTIR Gram-Schmidt plot in Figure 2 and an overlay of WLDC with the Gram-Schmidt plot in Figure 3. Three FTIR peaks match three main peaks in the WLDC plot and are detected with a slight delay because of the transit time of the evolved gases through the transfer line to the FTIR cell.

The amount of highly volatile compounds was determined in the temperature range from ambient to 340 °C (8.6 %). These constituents evaporated during the heating ramp and are composed of oil, plasticizers and small amounts of antioxidants, antiozonants and processing aids. As a mixture of compounds evaporated at a small concentration, FTIR sensitivity under the current setup was not sufficient to identify individual compounds. Further analysis with GC-MS would help to identify the species in the volatile components.

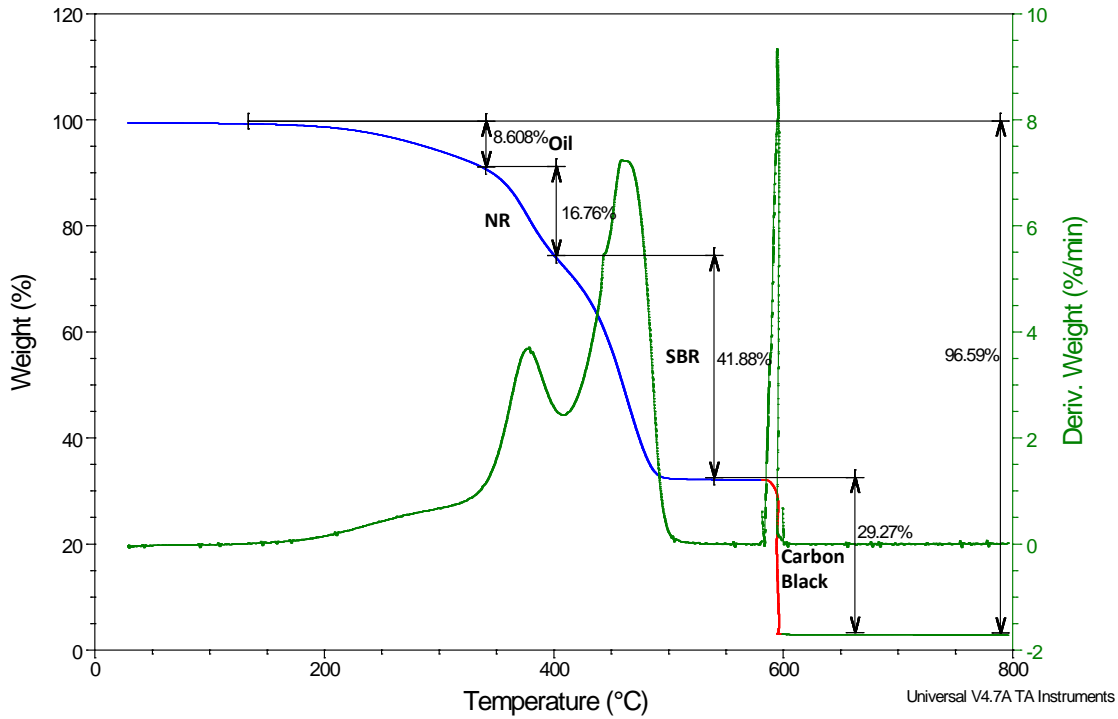
The temperature range from 340 °C to 550 °C corresponds to the thermal decomposition of polymers and was used for identification of base polymer constituents. Two base polymers were detected in this temperature range: one with maximum temperature degradation at 378 °C (WLDC plot) and elution time at 38 minutes (Gram-Schmidt plot) and second polymer with maximum temperature degradation at 463 °C (WLDC plot) and elution time at 48 minutes (Gram-Schmidt plot). The FTIR spectra extracted from Gram-Schmidt plot at 38 minutes (Extraction 1) and 48 minutes (Extraction 2) are shown in Figure 4. The best match of Extraction 1 was with the CROTUREZ B-100 (terpene resin), as shown in Figure 5. Terpenes are main components of natural resins with the isoprenoid repeat units and therefore the first base polymer was identified as a natural rubber (NR). This identification was confirmed by the strong absorbance at 890  $\text{cm}^{-1}$  present in Extraction peak 1, as shown in Figure 4. The absorbance at 890  $\text{cm}^{-1}$  is characteristic for a natural rubber (NR), or polyisoprene, degradation spectrum, as shown in Figure 8. Based on the TGA signal, the terpene content in the tire was 16.8%. The best match of Extraction 2 was with the KRATON D-2104 resin (butadiene-styrene-isoprene rubber), as shown in Figure 6. The absence of a strong absorbance at 890  $\text{cm}^{-1}$  for Extraction 2 indicated an absence of isoprene units, suggesting that the database match is not exact, and therefore the second polymer was identified as styrene-butadiene rubber (SBR). SBR and natural rubber are commonly used elastomers in automobile tires.<sup>1</sup> Based on the TGA signal, the SBR content in the tire was 41.9%.

The weight loss observed at 600 °C upon switching from nitrogen to oxygen was attributed to oxidation of carbon black. The gas evolved at 600 °C (Extraction 3) matches FTIR spectrum of carbon dioxide, which is an oxidation product of carbon black (Figure 7). Based on the TGA signal, the carbon black content in the tire was 29.3%. No more weight loss was observed at temperatures from 600 to 900 °C. The residue constituted 3.2 % and was identified as inorganic fillers.

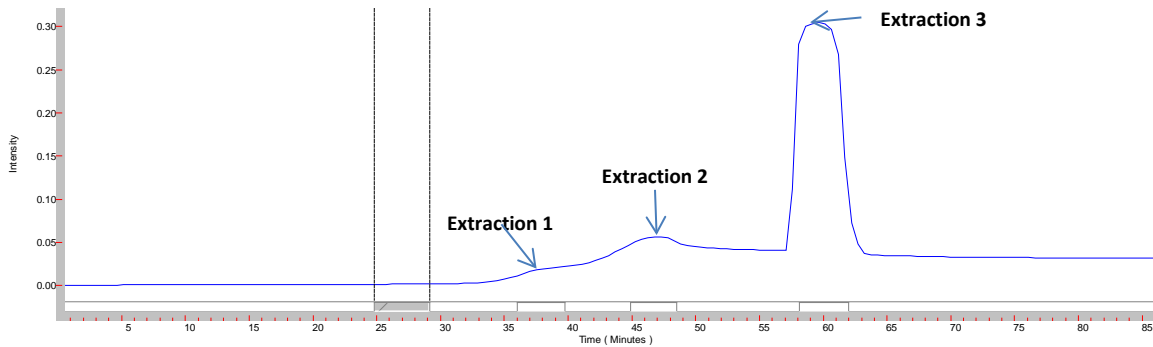
Net ash measurements showed the inorganic residue remaining after ashing was 0.3 wt.%. SEM-EDS analysis of the residue after ashing the rubber sample showed it was composed of zinc, iron, silica, and aluminum, with trace salts and sulfur (see Figure 9). The latter is likely the crosslinker.

The content and component identification of the tested rubber tire is summarized in Figure 1 and Table 1.

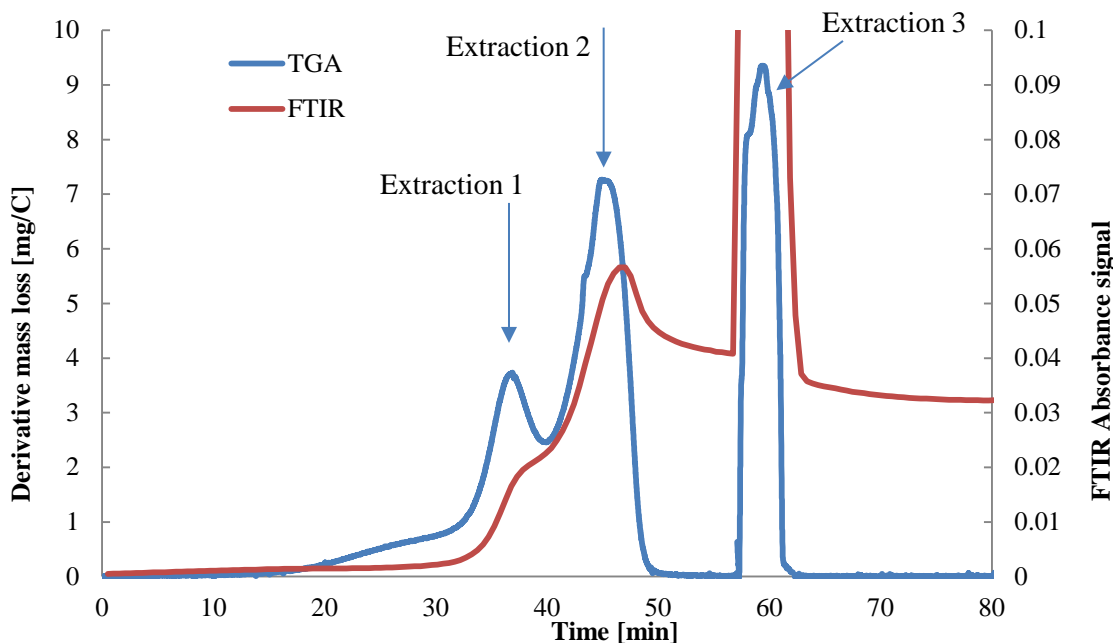
<sup>1</sup> Zabaniotou et al, J. Anal. App. Pyrolysis, vol 70, 711-922 (2003); Seidelt et al, J. Anal. App. Pyrolysis, vol 75, 11-18 (2006);



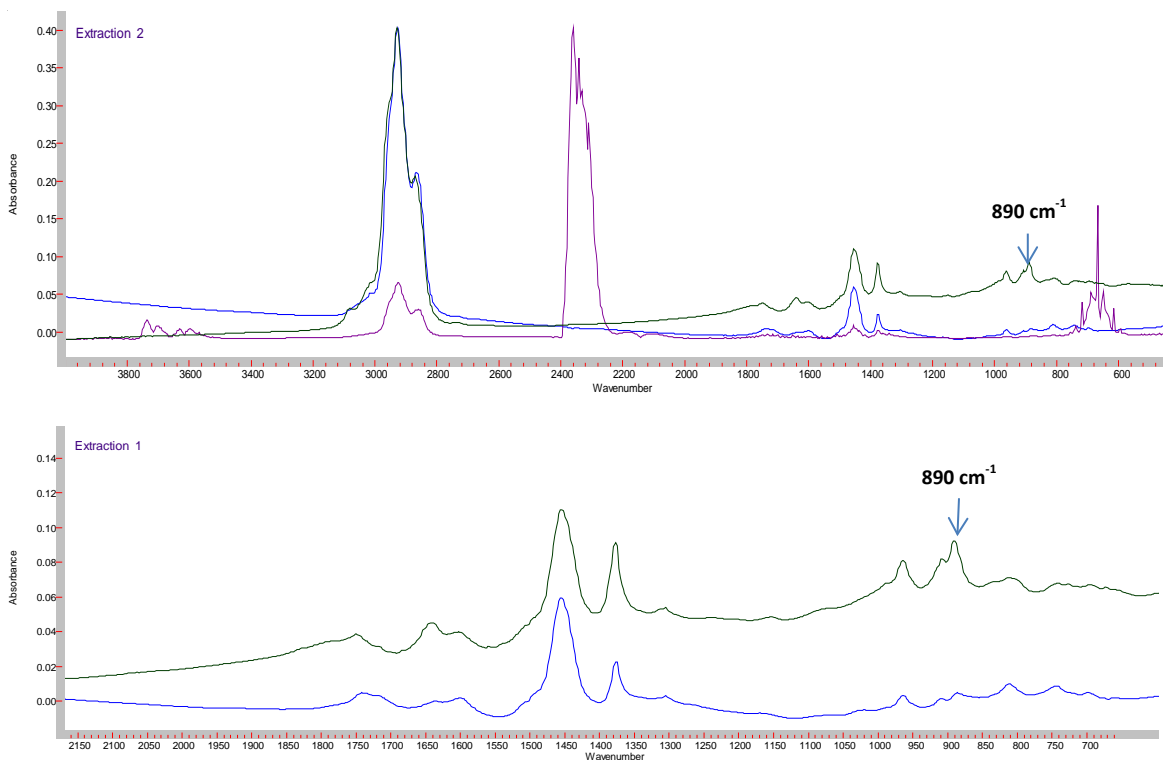
**Figure 1:** Weight loss curve (blue) and weight loss derivative curve (green) as a function of temperature for rubber tire. Switch from nitrogen to air at around 600 °C is labeled with red color.



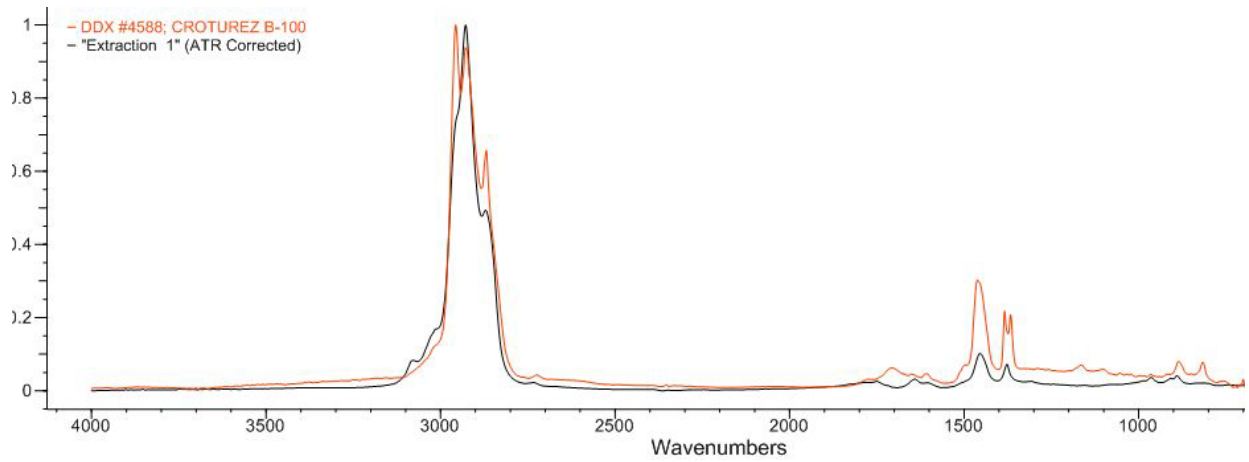
**Figure 2:** FTIR Gram-Schmidt plot for rubber tire as a function of time. Extraction regions for spectrum 1, 2 and 3 at 38, 48 and 60 minutes are denoted with arrows.



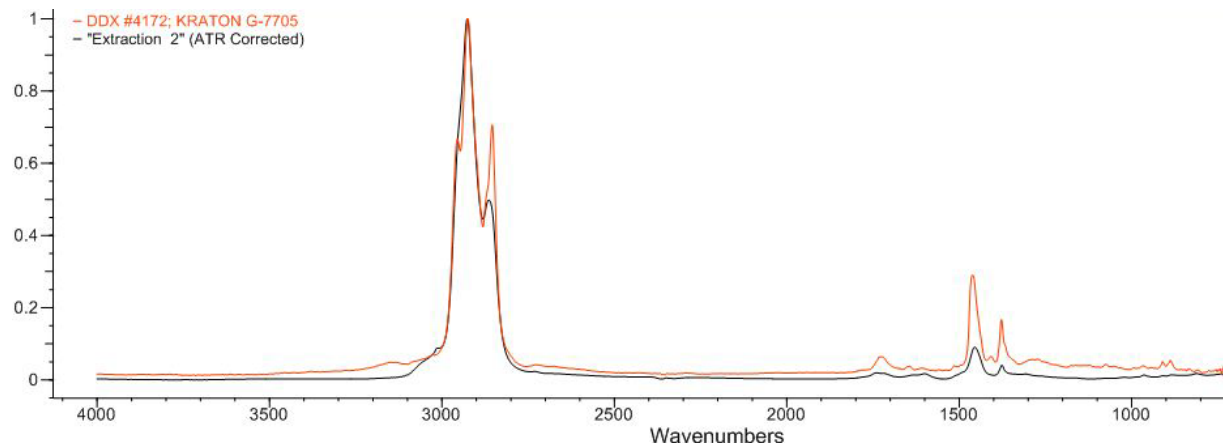
**Figure 3:** Derivative mass loss curve (blue) overlaid with FTIR Gram-Schmidt plot (red) for rubber tire as a function of time.



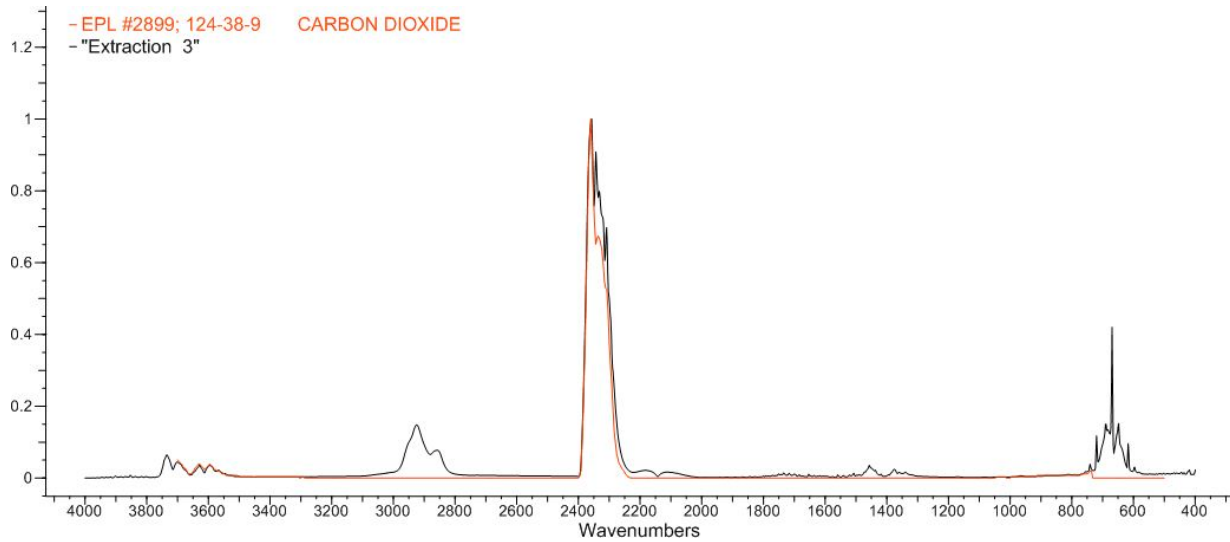
**Figure 4:** Spectra extraction from FTIR Gram-Schmidt plot (see **Figure 3**) at 38 minutes “Extraction 1” (green); at 48 minutes “Extraction 2” (blue) and at 60 minutes “Extraction 3” (pink). Top figure: three extractions spectra at full scale. Bottom figure: zoomed regions for “Extraction 1” and “Extraction 2”. The arrow denotes wavelength  $890\text{ cm}^{-1}$  characteristic of decomposed natural rubber (NR) polyisoprene.



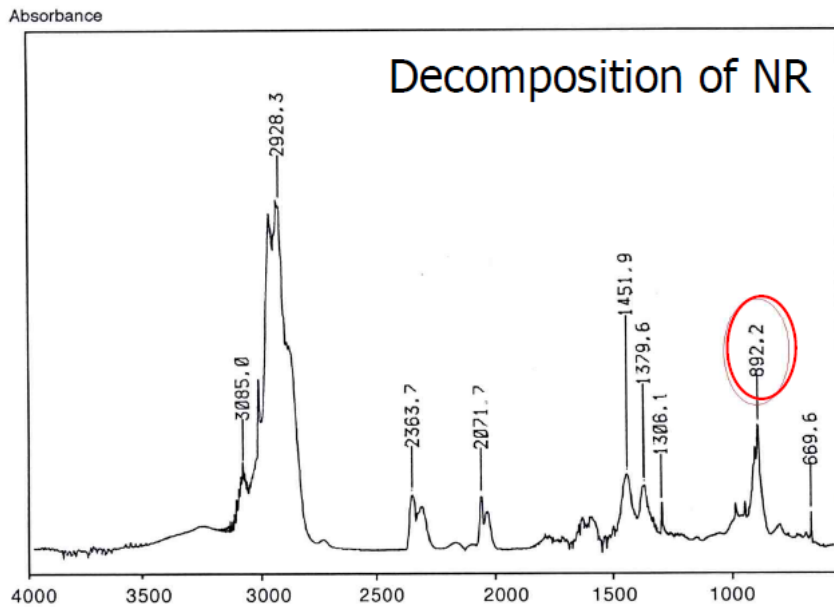
**Figure 5:** Comparison of FTIR extraction spectrum 1 at 38 minutes (black) with reference compound CROTUREZ B-100 (terpene resin) from FTIR database library (IR-Polymers, Controlled Pyrolyzates; code: DDX)



**Figure 6:** Comparison of FTIR extraction spectrum 2 at 48 minutes (black) with reference compound KRATON G-7705 (butadiene-styrene-isoprene rubber) from FTIR database library (IR-Polymers, Controlled Pyrolyzates; code: DDX)



**Figure 7:** Comparison of FTIR extraction spectrum 3 at 60 minutes (black) with reference spectrum for carbon dioxide from FTIR database library.

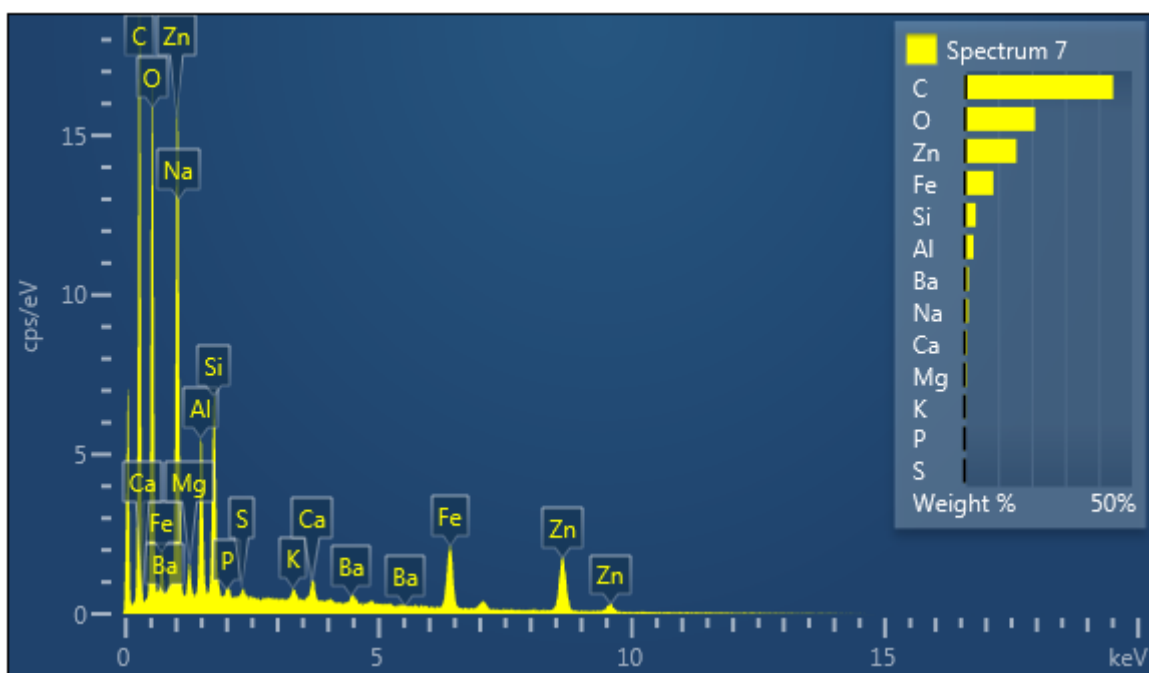


**Figure 8:** FTIR spectrum of temperature decomposed NR. Characteristic absorbance at 890  $\text{cm}^{-1}$  is denoted with red oval. The NR decomposition spectrum is from Rolf Schönherr, "TG-FTIR Atlas Elastomere", Verlag W.K. Schönherr, D-Burgdorf, 1996.

**Table 1: Composition and component identification of rubber tire.**

Weight [%]	Temperature max [°C]	Temperature range [°C]	Extraction time [min]	FTIR database match	Identity
8.6		30-340		not identified	oil
16.8	378	340-400	38	CROTUREZ B-100 (terpene resin)	NR
41.9	463	400-550	48	KRATON G-7705 (butadiene-styrene-isoprene rubber)*	SBR
29.3	595	550-600	60	carbon oxide	carbon black
3.2		600-900		not identified	inorganic fillers

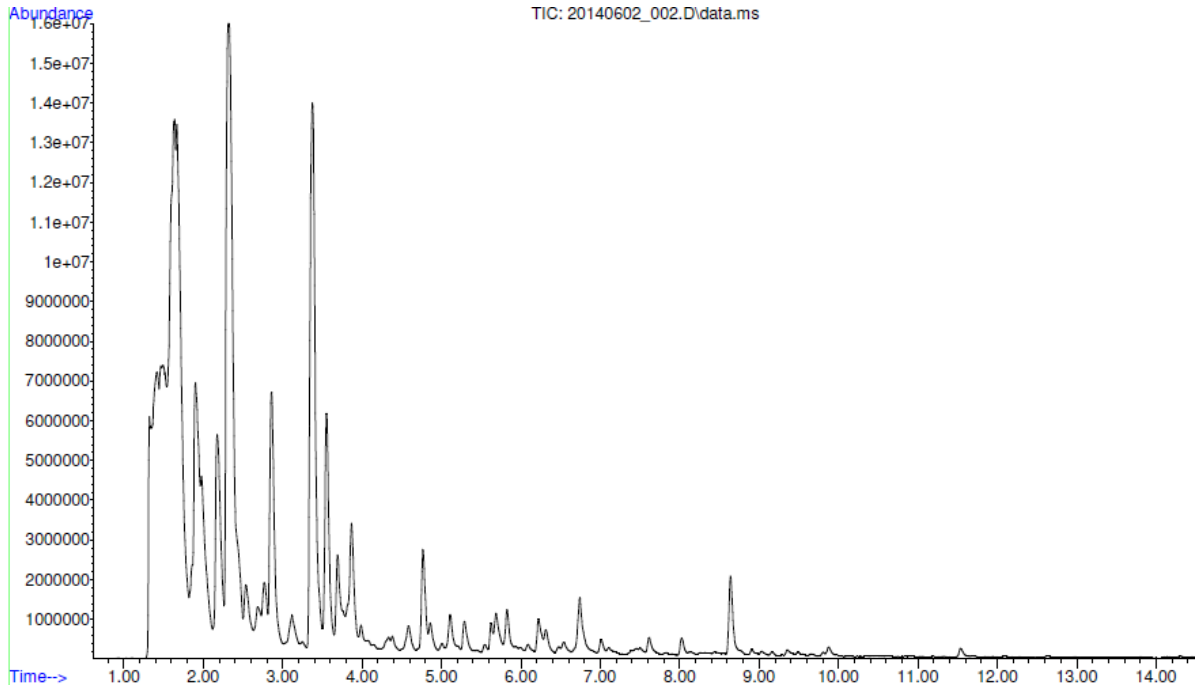
\*As the spectrum lacked the characteristic absorption peak for isoprene, it is better identified as a styrene-butadiene rubber.


**Figure 9: EDS elemental composition of residue remaining after ashing the tire sample.**

The volatile compounds present in the tire were identified using head space GC-MS. The sample was equilibrated in a headspace vial at 200 °C and gas phase was analyzed using an Agilent 6890 gas chromatograph equipped with an Agilent 5973 mass spectrometer.

The total ion chromatogram of the volatiles detected in the tire sample is shown in Figure 10. More than 40 compounds were detected by GC-MS. The compounds were identified by matching their mass spectra against the 2011 NIST/EPA/NIH mass spectral library. The identified compounds are tabulated in Table 2, sorted by the retention time. The best library match for the measured mass spectrum is shown with its CAS number, match factor, and chemical formula. A Match Factor greater than 900 is considered an excellent match; and 800-900 is considered as a good match. Most of the compounds identified in Table 2 have a Match Factor greater than 800. The compounds with Match Factor less than 800 are labeled with red. They have chemical structures similar to the reference compounds, but are not the exact match. The majority of the identified compounds are hydrocarbons that are constituents of mineral oil, used as a plasticizer for rubber tires. Also were identified rubber additives benzoxazole and benzothiazole (vulcanization accelerators), N-phenylformamide and quinoline.





**Figure 10: The total ion chromatogram of volatiles detected in the tire sample.**



**Table 2: Identification of volatiles in the tire sample. The compound with Match Factor less than 800 labeled with red.**

Retention Time [min]	% of total	Best Library Match	CAS#	Match Quality	Chemical Formula
1.92	8.93	Benzene	71-43-2	942	C <sub>6</sub> H <sub>6</sub>
2.18	4.07	2-Butenal, 2-ethenyl	20521-42-0	880	C <sub>6</sub> H <sub>8</sub> O
2.32	15.44	Methyl Isobutyl Ketone	108-10-1	895	C <sub>6</sub> H <sub>12</sub> O
2.54	1.39	Cyclobutene, 2-propenylidene-	52097-85-5	796	C <sub>7</sub> H <sub>8</sub>
2.69	0.87	Cyclohexane, 1,2-dimethyl-, cis	2207-01-04	787	C <sub>8</sub> H <sub>16</sub>
2.77	1.08	Cyclopropane, 1,1,2,3-tetramethyl-	74752-93-5	778	C <sub>7</sub> H <sub>14</sub>
3.38	9.92	2-hexanone, 5-methyl	110-12-3	922	C <sub>7</sub> H <sub>14</sub> O
3.56	3.42	Benzene, 1,3-dimethyl-	108-38-3	963	C <sub>8</sub> H <sub>10</sub>
3.70	1.67	Ethanone, 1-(1-cyclohexen-1-yl)-	932-66-1	874	C <sub>8</sub> H <sub>12</sub> O
3.87	2.31	Cyclohexanone	108-94-1	927	C <sub>6</sub> H <sub>10</sub> O
3.99	0.50	2-Hexen-1-ol, acetate	56922-75-9	818	C <sub>8</sub> H <sub>14</sub> O <sub>2</sub>
4.58	0.40	Hexanal, 2-ethyl-	123-05-7	752	C <sub>8</sub> H <sub>16</sub> O
4.77	1.34	Benzaldehyde	100-52-7	944	C <sub>7</sub> H <sub>6</sub> O
5.12	0.60	1,6-Octadiene, 2,6-dimethyl-	31222-43-2	775	C <sub>10</sub> H <sub>18</sub>
5.29	0.47	Octanal	124-13-0	939	C <sub>8</sub> H <sub>16</sub> O
5.55	0.09	Benzoxazole	000273-53-0	918	C <sub>7</sub> H <sub>5</sub> NO
5.63	0.28	1-Hexanol, 2-ethyl	104-76-7	909	C <sub>8</sub> H <sub>18</sub> O
5.69	0.66	1,4-Cyclohexanedione	637-88-7	686	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>
5.83	0.75	2(3H)-Furanone, 5-ethenyldihydro-5-methyl-	1073-11-6	929	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub>
6.23	0.48	1H-Pyrrole, 2,3-dimethyl-	600-28-2	697	C <sub>6</sub> H <sub>9</sub> N
6.32	0.33	Benzaldehyde, 2-methyl-	529-20-4	958	C <sub>8</sub> H <sub>8</sub> O
6.75	0.99	2-Pentanamine, N-ethyl-4-methyl-	42966-64-3	807	C <sub>8</sub> H <sub>19</sub> N
7.62	0.23	1-Butanamine, N-(2-furanylmethylene)-3-methyl-	52074-26-7	709	C <sub>10</sub> H <sub>15</sub> NO
8.03	0.23	Ethanone, 1-(3-methylphenyl)-	585-74-0	940	C <sub>9</sub> H <sub>10</sub> O
8.65	1.08	Benothiazole	95-16-9	952	C <sub>7</sub> H <sub>5</sub> NS
9.88	0.20	Formamide, N-phenyl-	103-70-8	850	C <sub>7</sub> H <sub>7</sub> NO
11.54	0.11	Quinoline, 2,4-dimethyl-	1198-37-4	839	C <sub>11</sub> H <sub>11</sub> N