DOUBLE THE SHOT, DOUBLE THE GAIN

Tracing chemical clues: Additive analysis of polymeric products using Double-Shot Pyrolysis Gas Chromatography/Mass Spectrometry (Py-GC/MS)

Chloe Ieong[a]
Supervised by Sally Coulson[b] and Mickayla Dustin[b]

a. School of Chemical Sciences, University of Auckland
b. The Institute of Environmental Science and Research Ltd

Common Polymeric Products found at Crime Scenes

Disposable gloves

Rubber smears from tyres

Road cone fragments

Wads from shotgun

Background

Rubber and plastic-like products are composed of polymeric materials.

Based on the prevalence of polymeric products they are frequently found at crime scenes.

Polymeric evidence found at a scene:

Scene — compare with — Suspect's possession — provide link between — Suspect / Crime scene

Current analytical methods focus on the detection of only the polymer.

A technique that detects both polymers and additives will provide better discrimination.

Aim: Increased Discrimination by Analysis of Additives

- Polymeric product = Polymer matrix + Additives
- Manufacturers' additive preferences drive chemical variation between brands

E.g., Two tyres from different brands
— 99% same polymer matrix
— 1% difference in additives
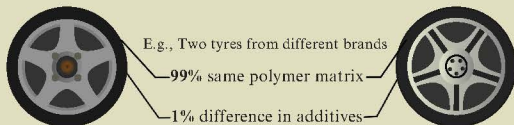
Analytical technique: Double-shot Pyrolysis-GC/MS

Thermal desorption of sample **1**

Compounds condensed **2** at the column using cryo-trap with $N_{2(liq.)}$ then released at the same time

GC **3** (compound separation)

MS **4** (compound identification)

Polymer detected

4 MS ← **3** GC ← Remaining sample pyrolysed **1**

Detects additives

Py-GC/MS components: Pyrolyser④ Cryo-trap② GC③ MS④

Results for tyre rubbers

- Single-shot (SS) Py-GC/MS involves pyrolysis at a set temperature
- Double-shot (DS) Py-GC/MS involves thermal desorption (TD) followed by pyrolysis (Py)
- The **DS-TD** allows the detection of **3 additional** additive compounds (**Bold** in Fig. 1)

  Isobutylamine: Rubber accelerator[1]

  Cyclohexanethiol: Chemical intermediate, stabiliser[2]

  1,2-dihydro-2,2,4-trimethyl-quinoline: rubber antioxidant[3]

Advantages for forensic analysis ⚠️

1 **Minimal** amount of sample needed

2 **Direct** analysis (no sample preparation required)

3 **Better** resolution of volatile compounds - including additives

Comparison of SS vs DS

DS-TD

DS-Py

SS-Py

Relative intensity

Elution time (min)

1: **Isobutylamine**
2: Benzene
3: Toluene
4: **Cyclohexanethiol**
5: D-Limonene
6: Benzothiazole
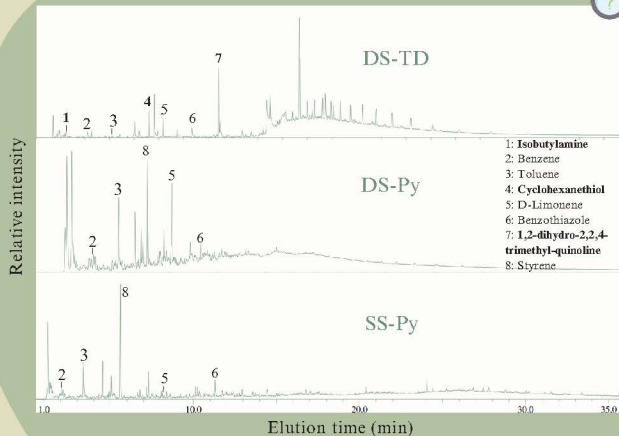7: **1,2-dihydro-2,2,4-trimethyl-quinoline**
8: Styrene

Figure 1. Total ion chromatograms of tyre rubber (tread). The numbered peaks are examples of the common compounds detected in tyres.

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