

Rapid Analysis of *p*-Phenylenediamine Antioxidants in Rubber

Introduction

p-Phenylenediamine (PPD) and derivative compounds are commonly used as antioxidants and antiozonants in black rubber. These compounds can cause sensitization leading to contact dermatitis in susceptible individuals. Detection of additives in polymers such as rubber can be important for clinical, forensic, and manufacturing applications. Here we show that DART can be used to identify the presence of these compounds within seconds without requiring

any solvents or sample preparation.

Experimental

Analysis was carried out by using the AccuTOF-DART. A piece of rubber from a mountain bike tire was placed in front of the DART ion source, which was operated with helium in positive-ion mode and a gas heater temperature of 250 degrees C. Signals appeared within seconds after placing the rubber in front of the DART source.

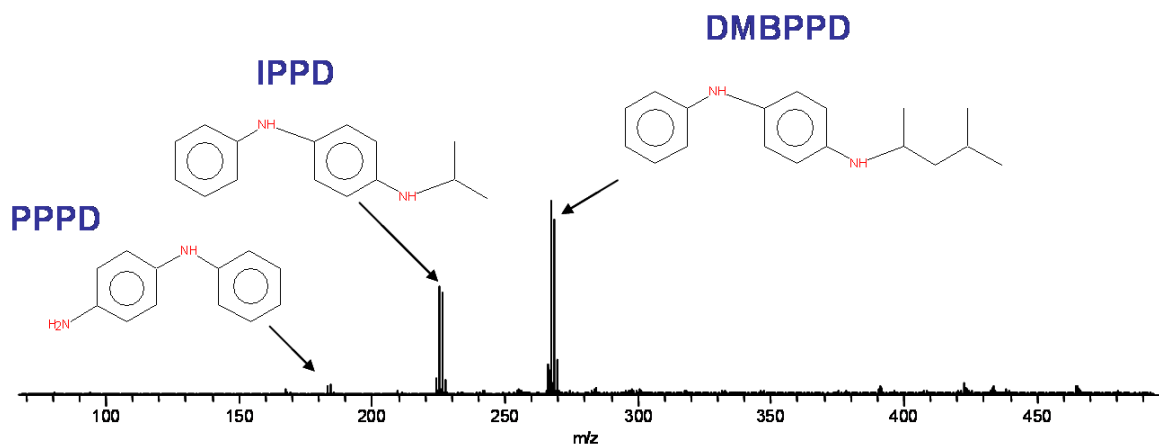


Figure 1. DART mass spectrum of a rubber particle from a mountain bike tire.

Meas. mass u	Abund. %	Diff. mmu	Unsat.	Compositions	
226.147202	0.00	0.20	8.0	C ₁₅ H ₁₈ N ₂	IPPD M ⁺
227.154297	0.00	-0.53	7.5	C ₁₅ H ₁₉ N ₂	IPPD [M+H] ⁺
268.194214	0.00	0.27	8.0	C ₁₈ H ₂₄ N ₂	DMBPPD M ⁺
269.201385	0.00	-0.40	7.5	C ₁₈ H ₂₅ N ₂	DMBPPD [M+H] ⁺

Table I. Elemental compositions for *p*-phenylenediamine antiozonants in a rubber tire.

Results

Exact mass measurements combined with accurate isotopic abundances provided elemental compositions (Table I) that were searched against the NIST mass spectral database. Three antiozonant compounds were recognized from their exact mass measurements

(see Table 1): N-Phenyl-*p*-phenylenediamine (PPD), N-Isopropyl-N'-phenyl-*p*-phenylenediamine (IPPD), and N-(1,3-Dimethyl butyl)-N'-phenyl-*p*-phenylene diamine (DMBPPD).