

SIMULTANEOUS DETERMINATION OF NATURAL AND STYRENE-BUTADIENE RUBBER TIRE TREAD PARTICLES IN ATMOSPHERIC DUSTS BY PYROLYSIS-GAS CHROMATOGRAPHY

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ABSTRACT

A method for simultaneous determination of natural rubber (NR) and styrene-butadiene rubber (SBR) tire tread particles in atmospheric dust is described. Particulate rubbers are pyrolyzed at 740°C for five seconds in a Curie-point pyrolyzer. The resulting pyrolyzates are separated and detected by a gas chromatograph equipped with dual flame ionization detectors. Among several pyrolysis products, isoprene and styrene are chosen as indicator compounds for NR and SBR, respectively. The method is applied to a suite of atmospheric dust samples collected in Seoul, Korea by an Andersen sampler and some analytical results are presented.

Atmospheric dust; gas chromatography; natural rubber; polymers; pyrolysis; styrene-butadiene rubber; tire tread.

INTRODUCTION

Pyrolysis-gas chromatography (Py-GC) has been successfully applied to the characterization of rubber components for many years [1-4]. Since Thompson et al. [5] reported evidence of tire-wear debris in the sweepings from tunnel and parking garages, several workers [6-8] have reported various analytical methods for determination of rubber particles in atmo-

spheric dusts. The amount of rubber loss from automobile tires has been also estimated from the number of registered vehicles and tire sales to be about 90 mg/km due to vehicle motion [9]. According to Pierson and Brachaczek [10] and Brown et al. [11], less than 5% of the total tire wear becomes airborne, but this amount is equivalent to 20% of the total airborne particulate matter exhausted from internal combustion engines burning regular gasoline.

Penetration and deposition of the airborne particulates in man's respiratory tract is a subject of aerodynamics [12]. The toxicity of a particulate pollutant is thus determined not only by its concentration and chemical composition, but also by the particle size of the pollutant.

This paper presents details of an analytical procedure for the simultaneous determination of natural rubber (NR) and styrene-butadiene rubber (SBR) tire tread particles in atmospheric dusts by Py-GC. The performance of the procedure and its application to a suite of urban atmospheric dust samples are discussed. In addition, the measured concentrations of total rubber particles and those particles which are small enough to penetrate into the alveoli are presented.

EXPERIMENTAL

Atmospheric dust sampling

Atmospheric dust samples were collected from the street in front of Yonsei University Campus, Seoul, Korea using an Andersen sampler (Kanomax, Model 3351) which was run for 10 days for each sample. We chose polyester filters (diameter: 80 mm; thickness: 0.075 mm) which enabled us to remove the dusts from the filter easily and thus reduce the relative error when weighing the samples. The collected airborne dust was kept in a desiccator for at least two days, where relative humidity was maintained at 50% using calcium chloride solution. In order to remove organic contaminants originating from asphalt particles or vehicle exhaust, the samples were rinsed with benzene-ethanol (4 : 1, v/v) in an ultrasonic bath for 30 seconds. After being dried at room temperature, the samples were weighed on a semi-microbalance (Mettler Model HK60).

Analytical standards of NR and SBR tire tread rubbers were prepared following the recipes which are given in Table 1.

Pyrolysis-gas chromatographic conditions

A Curie-point pyrolyzer (Japan Analytical Industries, Model JHP-2) was directly coupled to a gas chromatograph (Hitachi Model 163) equipped with dual flame ionization detectors. Atmospheric dust samples (0.5-1.0 mg)

TABLE 1

Chemical composition of standard tire tread rubber ^a

Passenger car		Truck and bus	
SBR (OE) ^b	60	NR	80
BR (OE)	40	BR	20
ZnO	3	ZnO	3
Stearic acid	2	Stearic acid	2
Carbon black	70	Carbon black	50
Process oil	10	Process oil	8
Antioxidant 3C ^d	1.5	Antioxidant 6C	1.7
Antioxidant RD ^f	1	Antioxidant RD ^f	0.8
Vulcanization		Vulcanization	
Accelerator CZ ^g	0.4	Accelerator MOR ^h	0.8
Accelerator TT	0.8		
Sulphur	2	Sulphur	2

^a Provided by Han Kook Tire Manufacturing Co. Seoul, Korea^b Oil extended^c Parts by weight^d N Isopropyl N phenyl *p* phenylenediamine
N (1,3 Dimethylbutyl) N *p* phenylenediamine^f Poly(2,2,4 trimethyl 1,2 dihydroquinoline)^g Cyclohexylbenzothiazolylsulphenamide^h N Oxydiethylene 2 benzothiazolylsulphenamide
Tetramethylthiuram disulphide

were pyrolyzed at 740 °C for five seconds. The temperatures of the pyrolyzer unit and the tube connecting pyrolyzer and gas chromatograph were maintained at 100°C and 200°C, respectively. The analytical column was a stainless steel tube (6 m X 3 mm I.D.) which was packed with 15% Apiezon grease L supported on 60-80 mesh Uniport B.

The column temperature was maintained at 55°C for the first seven minutes and programmed to increase at a ramp rate of 20°C/min up to 160°C. The nitrogen carrier gas flow-rate was 20 ml/min (Table 2).

TABLE 2

Pyrolysis-gas chromatographic conditions

Column	:	Stainless steel, 6 m X 3 mm I.D.
Packing	:	15% Apiezon grease L on Uniport B, 60-80 mesh
Column temperature	:	Initial: 55 °C Final: 160 °C Rate: 0 °C for 8 min; 20 °C/min
Carrier gas	:	Nitrogen, 20 ml/minute
Detector	:	Flame ionization
Pyrolysis	:	740 °C for 5 seconds

RESULT AND DISCUSSION

Column selection

The column was selected in such a way that simultaneous quantification of the isoprene and styrene peak could be achieved. A non-polar packing material is needed for good separation of isoprene, while a high-temperature packing material is necessary for good separation of styrene. The packing materials tested in this work were Apiezon grease L, TCP, SE-30, OV-1, OV-17, DC-200, DC-550, PEG-20M and FFAP. Among them, a 6-m-long column containing 15% Apiezon grease L showed the best separation performance.

Pyrolysis temperature

Seven kinds of pyro foils (358°C, 445°C, 590°C, 670°C, 740°C, 920°C and 1040°C) were tested to observe the effect of temperature on the pyrolysis characteristics of standard tire tread rubbers. The functional relationships between the production yields of isoprene, styrene and dipentene and pyrolysis temperature are summarized in Fig. 1. At 358°C, no pyrolyzates were produced. Yields of both isoprene and styrene were highest at 740°C, while the maximum dipentene production was observed at 445°C. Thus, only the 740°C pyrofoil was used for routine sample analysis.

Quantification of tire tread rubbers

For quantitative determination of tire tread rubbers, the pyrograms of samples were compared with those of standard tire tread rubbers. Typical

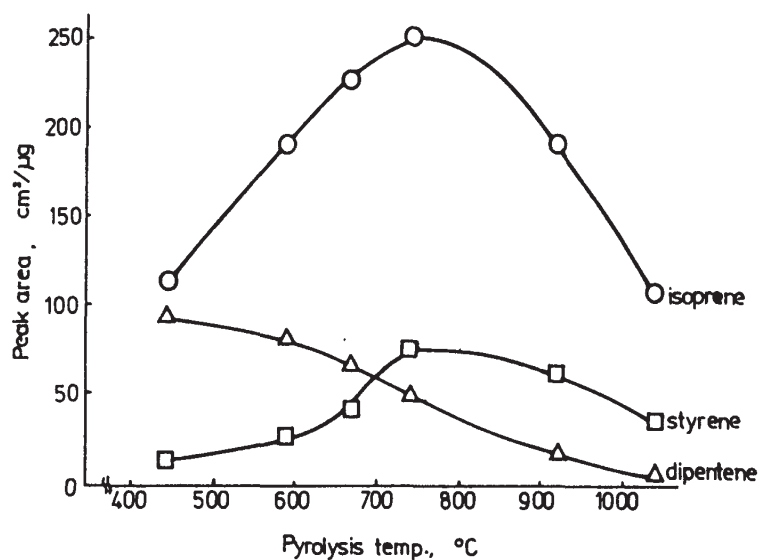


Fig. 1. Effect of pyrolysis temperature on pyrolysis products of the tire tread rubber.

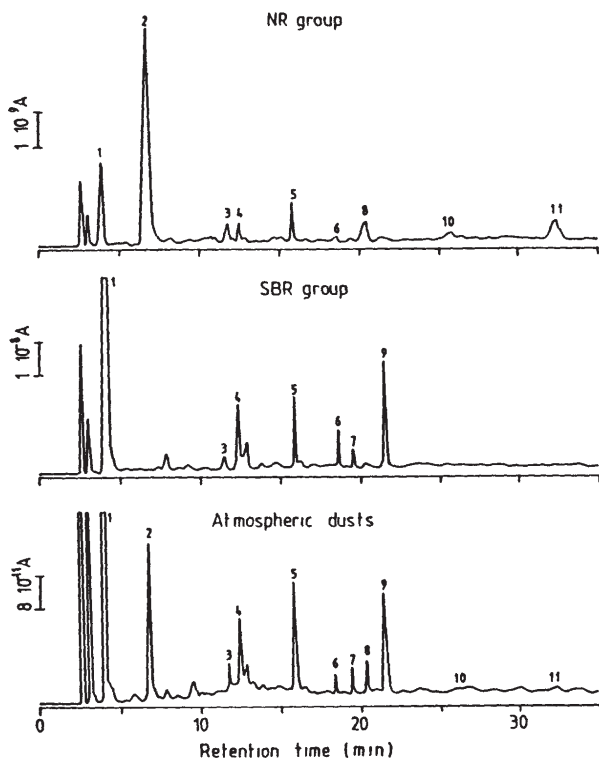


Fig 2 Pyrograms of tire tread rubbers and atmospheric dusts Peaks 1 = 1,3 butadiene
 2 = isoprene 3 = C_6H_{10} 4 = benzene 5 = toluene 6 = vinylcyclohexene 7 = ethylbenzene
 8 = xylene 9 = styrene 10 = $C_{10}H_{16}$ 11 = dipentene

pyrograms of the SBR group and NR group tire treads, and atmospheric dusts trapped in the fourth stage of the Andersen sampler, are shown in Fig. 2. The styrene peak was used for the determination of SBR group tire rubber and the isoprene peak for the determination of NR group tire rubber. Theoretically, dipentene can also be used for NR group determination but, in this work, the amounts of NR group rubber in the dust samples were too small to produce sufficient dipentene. The reproducibility of the pyrolyzate formation was investigated by varying the particle size from 14 to 100 mesh

TABLE 3

Reproducibility of the pyrolysis-gas chromatography *

Tire tread rubber	SBR (%)	NR (%)	RSD (%) <i>n</i> = 5
Passenger car	31.5	0	9.7
Bus and track	0	47.6	8.3

* Based upon peak area integration

TABLE 4

Size distributions of atmospheric dust and rubber components

Sampling period January 13-22 1987

Stage number	Particle size range (μm)	Sample weight (mg)	Sample conc ($\mu\text{g}/\text{m}^3$)	SBR ($\mu\text{g}/\text{m}^3$)	NR ($\mu\text{g}/\text{m}^3$)	Total rubber ($\mu\text{g}/\text{m}^3$)	Abundance ratio (%)
0	90-10	18.5	58.6	1.52	0.19	1.71	2.91
1	58-90	2.24	7.09	0.11	0.01	0.12	1.69
2	47-58	1.16	3.67	0.03	0.004	0.03	0.82
3	33-47	4.89	15.5	0.12	0.01	0.13	0.84
4	21-33	1.04	3.29	0.02	0.001	0.02	0.61
5	11-21	5.77	18.3	0.10	0.01	0.11	0.60
6	07-11	8.56	27.1	0.05	0.01	0.06	0.22
7	04-07	7.59	24.0	0.03	0.004	0.03	0.13
Total		49.8	157.5	1.98	0.23	2.21	1.40

It appeared that the reproducibility was strongly related to the particle size. The best reproducibility was obtained when 50-100 mesh particles were used (Table 3). In the pyrograms SBR group (styrene peak) and NR group (isoprene peak) were 74 ± 5.2 area unit / μg and 380 ± 20.8 area unit / μg , respectively.

Particle size distribution of rubber components

Atmospheric dust samples were collected using the Andersen sampler which was operated continuously for 10 days in March 1987. The samples were analyzed for NR and SBR rubbers and weighed at each stage. As summarized in Table 4, it can be seen that the mass size distribution of rubber components is not bimodal, but unimodal. This implies that almost all of the rubber particulates were produced from automobile tire tread by mechanical abrasion.

It is generally known that atmospheric dusts trapped below the sixth stage of an Andersen sampler can penetrate into alveoli [13]. It appeared that 32.4% of the total atmospheric dust could penetrate into alveoli, of which the rubber components formed 0.2%. The concentrations of NR group and SBR group tire tread were $0.23 \mu\text{g}/\text{m}^3$ and $1.98 \mu\text{g}/\text{m}^3$, respectively.

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