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Short Communication

High-performance liquid chromatography of rubber antidegradants with diode-array detection

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ABSTRACT

High-performance liquid chromatography (HPLC) using diode-array detection is described for the separation and determination of antioxidants applied in tyre production.

An octadecyl silica column was used with a methanol–0.05% ammonia solution as the mobile phase. The extraction recoveries were determined for the rubber samples with contents of the antioxidants N-phenyl-N′-isopropyl-*p*-phenylenediamine (CD), N-phenyl-*β*-naphthylamine (PBN) and 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ).

The influence of weather conditions on the contents of CD and PBN in tyre samples was evaluated and the stability changes were compared for rubber samples before and after vulcanization procedures.

The HPLC method has also been applied to the determination of the antioxidant PBN contents in rubber samples used as the raw materials. Detection limits were 0.26, 0.14 and 0.41 mg/kg for CD, PBN and TMQ, respectively.

INTRODUCTION

Antidegradants are commonly used in the rubber and plastics industry to improve the dynamic characteristics of rubber products and prevent their degradation. The analysis of different types of antioxidants has been described [1–4]. Thin-layer and gel permeation chromatography have been applied to the analysis of additives used for the stabilization and vulcanization for rubbers [5,6] after their extraction with polar solvents (acetone, diethyl ether, ethanol, isopropanol). Typical amine stabilizers used

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in rubber production have been determined [7] using a polystyrene gel chromatograph with tetrahydrofuran as the solvent.

The application of silica columns to the antidegradants separation has been described [8,9]. It was stated that adsorption chromatography is not suitable for this purpose as aromatic diamines (*e.g.*, *p*-phenylenediamine) are chemisorbed on active hydroxyl groups on the surfae of the adsorbent.

The high-performance liquid chromatographic (HPLC) separation of antioxidants from rubber and plastics with the macroporous gel Separon SE and methanol and acetonitrile as eluents has been reported [10]. The samples of rubber were Soxhlet extracted for 24 h in acetone and the extract was evaporated to dryness and the residue dissolved in methanol. Methanol–water, acetonitrile–water and tetrahydrofuran–water were tried as mobile phases but methanol–diethyl ether–water (80:10:10) was recommended. UV detection was applied at 254 nm. The determination of secondary aromatic amine antioxidants (*e.g.*, phenyl-1-naphthylamine) and the isolation and identification of their intermediate oxidation products (dimer, trimer, tetramer) after 24 h at 190°C have been described [11]. Liquid chromatography was used for separation, with identification of the intermediate products by mass spectrometry and determination using gas chromatography with a thermionic detector.

We described in previous papers [12–14] the application of HPLC for the control of the stability of dialkyldithiocarbamates (dimethyl and dibutyl derivatives, which have been used as antioxidants in the plastics and rubber industry), with their simultaneous separation together with the main degradation products (tetraalkylthiuram disulphides, monosulphides and dialkylthiourea).

The aim of this work was to develop a control method for the determination of antidegradants applied in tyre production. An HPLC method using diode-array detection was applied in the combination with extraction procedures. This method can be recommended for control analyses in rubber factories (control of standards purity, contents of antidegradants before and after the vulcanization process) and it has been applied in studies of stability changes under the influence of oxygen, temperature and time.

EXPERIMENTAL

Apparatus

All experiments were carried out on a Waters Assoc. modular HPLC system with a Model 990 a diode-array detector. A Separon C_{18} (5 μm) glass column (150 × 3.2 mm I.D.) with a short C_{18} (7 μm) precolumn (30 × 3.2 mm), both from Tessek (Prague, Czechoslovakia), were used with methanol–0.05% ammonia solution (pH 7.2) (85:15) as the mobile phase.

Chemicals

Antidegradants used for tyre production, CD (N-phenyl-N'-isopropyl-*p*-phenylenediamine), PBN (N-phenyl-β-naphthylamine) and TMQ (2,2,4-trimethyl-1,2-dihydroquinoline), were obtained as standards from the Institute of Rubber Technology (Gumárne Púchov, Czechoslovakia). Their purity was verified by elemental analysis using a Model 1108 Elemental Analyser (Carlo Erba, Milan, Italy). All solvents were of analytical-reagent grade from Lachema (Brno, Czechoslovakia).

Procedures

Extractions were made with acetone according to a published procedure [5,10] or directly on 0.1-g rubber samples by extraction with four 10-ml volumes of methanol. The extracts were filtered using Tessek cellulose filters and injected in volumes of 20 μl into the chromatographic column.

RESULTS AND DISCUSSION

The purities of the antidegradants CD, PBN and TMQ were checked by elemental analysis and the results are given in Table I. Three different standards of TMQ were analysed and compared [Matoflex (Czechoslovakia), Naogard (Hungary) and Flectol (Germany)]. For all three standards the chromatograms are shown in Fig. 1. The three chromatograms confirmed that TMQ is a mixture of different monomers eluted at about 4.5, 6.3 and 8.1 min.

TABLE I

RESULTS OF ELEMENTAL ANALYSIS OF THE ANTIDEGRADANTS

Antidegradant	Theoretical (%)			Found (%)		
	C	H	N	C	H	N
CD	79.26	8.37	12.34	79.37	7.99	12.49
PBN	87.27	6.36	6.35	87.05	5.95	6.52
TMQ (Matoflex)	83.24	8.67	8.09	82.82	8.50	7.93
TMQ (Naogard)	83.24	8.67	8.09	83.31	8.63	8.02
TMQ (Flectol)	83.24	8.67	8.09	82.99	8.59	7.77

The optimum mobile phase for the separation of CD, PBN and TMQ was methanol–0.05% ammonia solution (pH 7.2) (85:15). A flow rate of 0.3 ml/min resulted in a simultaneous separation with good resolution ($R_{ij} > 1.25$). The elution times for CD and PBN were 3.6 and 5.7 min, respectively. The resolution values for CD and PBN was $R_{ij} = 1.92$ and that for CD and TMQ was $R_{ij} = 2.86$. This means that combinations of the antidegradants CD–PBN and CD–TMQ can be evaluated quantitatively without problems.

The main reason for the use of TMQ instead of PBN in tyre production is the possible carcinogenicity of PBN. Rubber mixtures before vulcanization and vulcanized rubber products (different types of tyres produced in Gumarne Púchov) were extracted according to the procedures described under Experimental. The average extraction recoveries (for five parallel experiments) were for CD 95.4 ± 2.1%, for PBN 97.3 ± 1.9% and for TMQ 84.2 ± 3.1%.

Comparing the results of HPLC analysis of rubber samples before and after vulcanization procedures it was found that in many instances the antidegradant concentrations were lower after vulcanization. Using diode-array detection it was found that in some rubber samples after vulcanization CD was degraded and a new peak was observed in the chromatogram (retention time 4.4 min). The absorption maxima for CD and its degradation product were 206.4 and 288.0 nm, respectively.

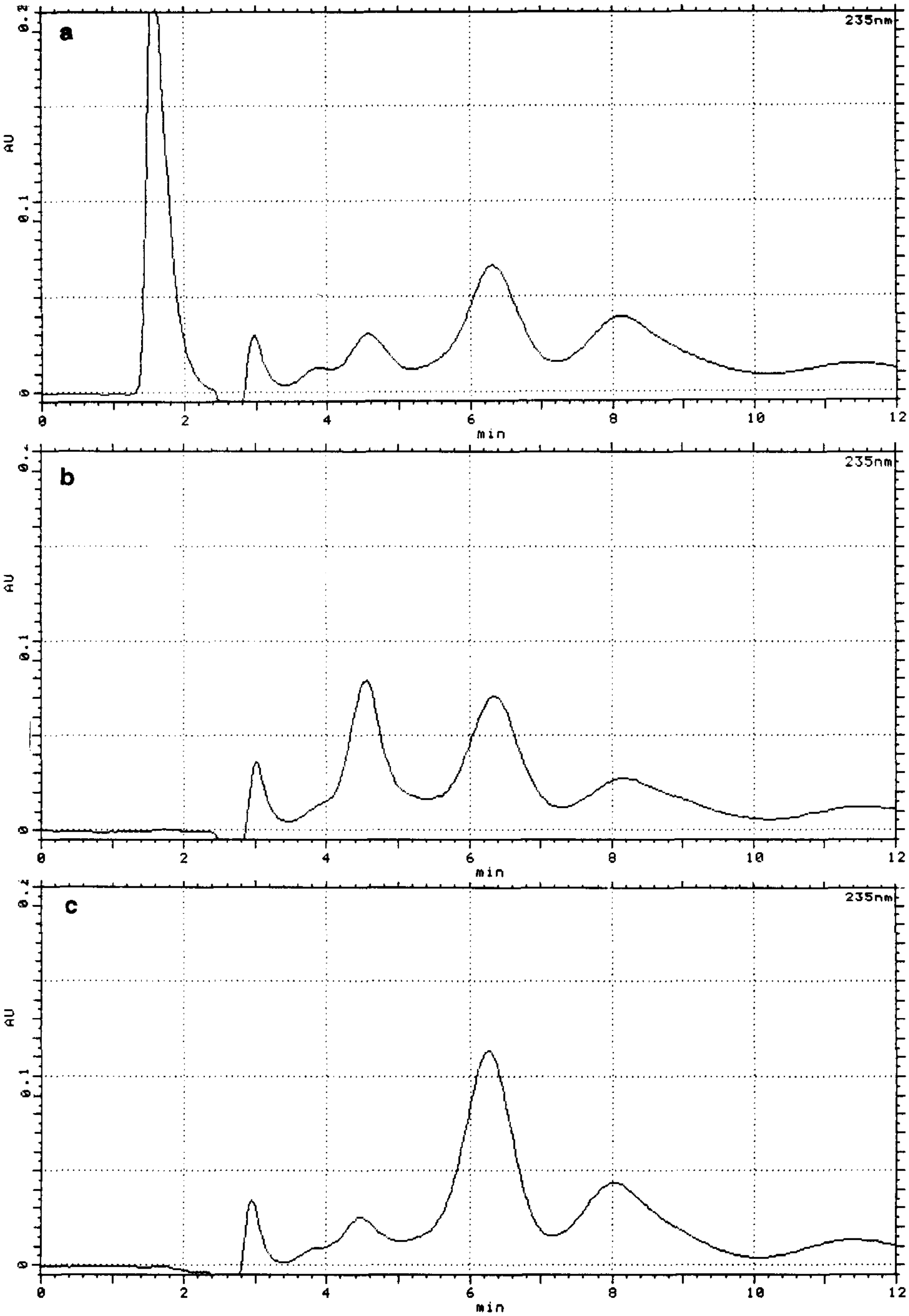

Fig. 1. HPLC of TMQ samples: (a) Matoflex; (b) Naogard; (c) Flectol. Column: Separon C_{18} (5 μm) (150 × 3.2 mm I.D.). Mobile phase: methanol–0.05% ammonia solution (85:15). Flow-rate: 0.3 ml/min.

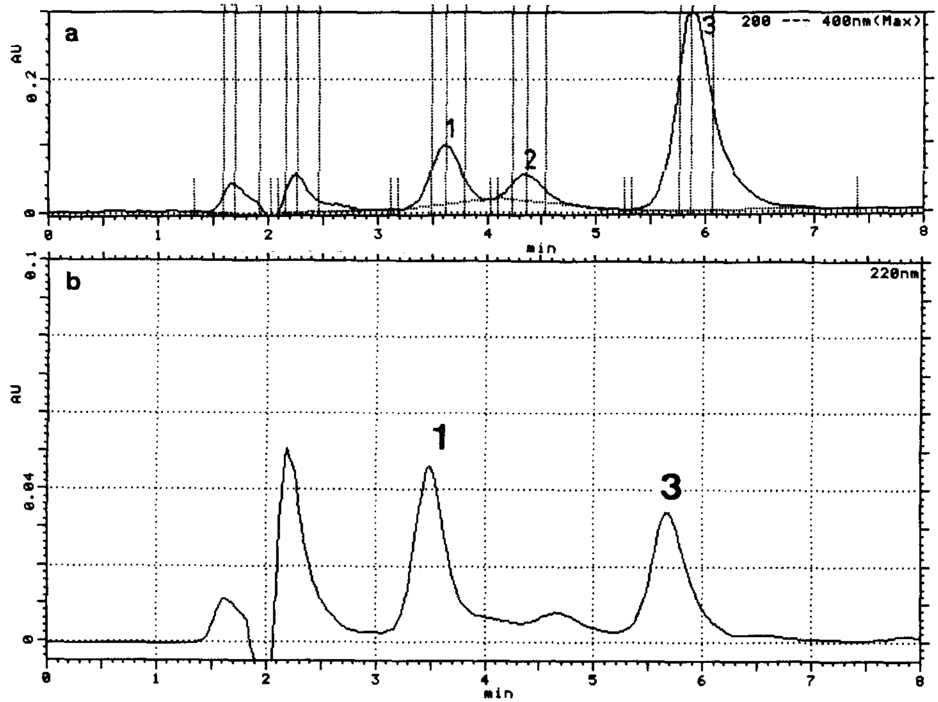

Fig. 2. HPLC of (a) a vulcanized rubber product extract and (b) a non-vulcanized rubber mixture. Peaks: 1 = CD; 2 = degradation product of CD; 3 = PBN.

The HPLC separations of the extract of the vulcanized rubber product and the rubber mixture before vulcanization are illustrated in Fig. 2. The contents of CD and PBN in rubber samples before and after vulcanization are given listed in Table II.

HPLC was also applied to the determination of the antidegradant contents in rubber used as the raw materials. It was found that some of rubber additives used contain small amounts of PBN (Fig. 3) and for this reason PBN was also identified using diode-array detection in the extracts of tyres prepared without the direct addition of PBN (Fig. 4).

The results of the determination of CD and PBN in tyres produced in Gumárne Púchov are given in Table III. Three samples with known amounts of both antidegradants were evaluated after subtraction of the concentrations of PBN found in

TABLE II

CONTENTS OF CD AND PBN IN RUBBER BEFORE AND AFTER VULCANIZATION

Antidegradant	Before vulcanization (%)	After vulcanization (%)
PBN	0.634	0.560
CD	0.890	0.814

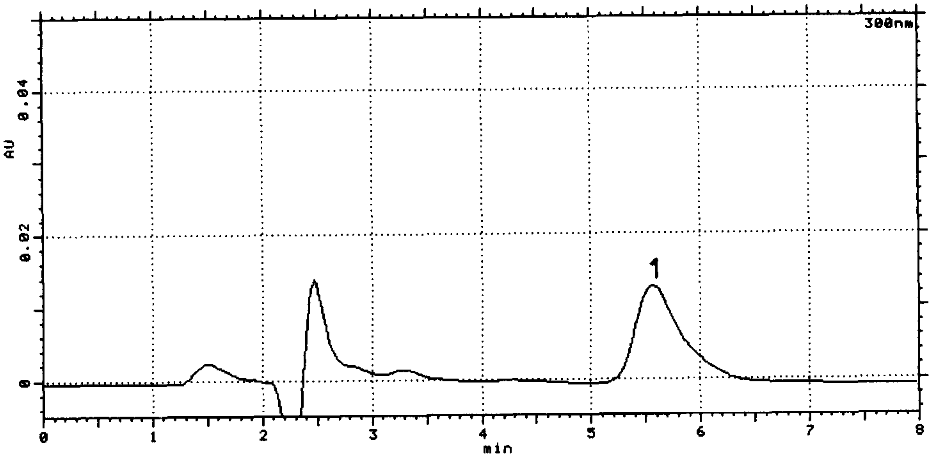

Fig. 3. HPLC separation of an extract of rubber (SKI-3). Conditions as in Fig. 1. Peak 1 = PBN.

the rubber samples without PBN (blank). The average value was also subtracted from the results obtained for unknown samples (Nos. 19 and 208). The content of PBN in rubber (SKI-3) was about 0.2%.

The data were evaluated using linear regression according to the calibration graph $y = 2.06 + 89.4x$, where y is the peak area (mm^2) and x the concentration (μg/g); the correlation coefficient was $r = 0.9962$. The response of the detector was linear for antidegradant concentrations in rubber samples in the range 0.1–10 μg/ml (five parallel experiments for one determination); relative standard deviations are given in Table III. The detection limits were CD 0.26, PBN 0.14 and TMQ 0.41 mg/kg.

The influence of weather conditions on the contents of CD and PBN in two samples (Nos. 05 and 12) was studied by analysing the samples immediately after

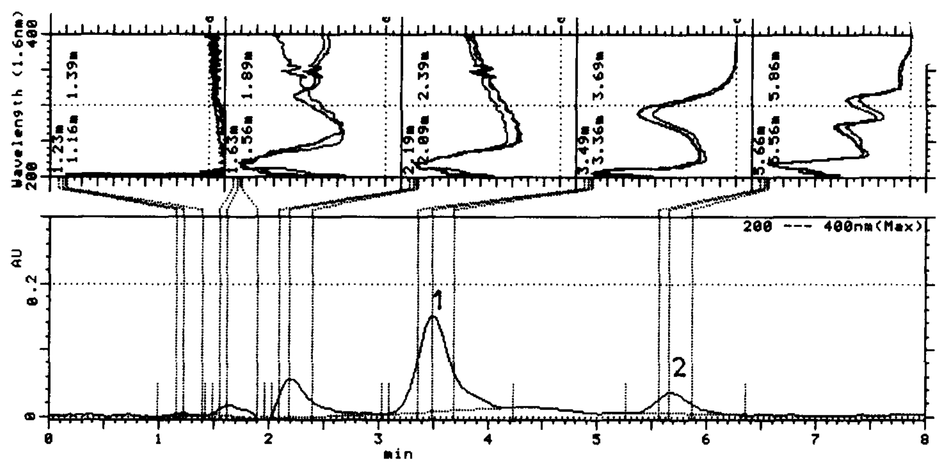

Fig. 4. HPLC separation of an extract of vulcanized rubber tyres prepared without PBN. Conditions as in Fig. 1. Peaks: 1 = CD; 2 = PBN.

TABLE III

CONTENTS OF CD AND PBN IN EXTRACTS OF TYRES

Sample No.	Antidegradant	Content (%)	Extraction recovery (%)	R.S.D.[a] ($n=5$) (%)
	PBN	0.582	96.52	2.2
05-20	CD	0.814	95.29	2.0
	PBN	0.506	97.27	1.8
15-07	CD	0.498	95.57	2.1
	PBN	0.516	98.01	1.7
90-15	CD	0.799	94.85	2.4
	PBN	0.498	–	–
19	CD	0.466		
	PBN	0.528	–	–
208	CD	0.501		

[a] Relative standard deviation.

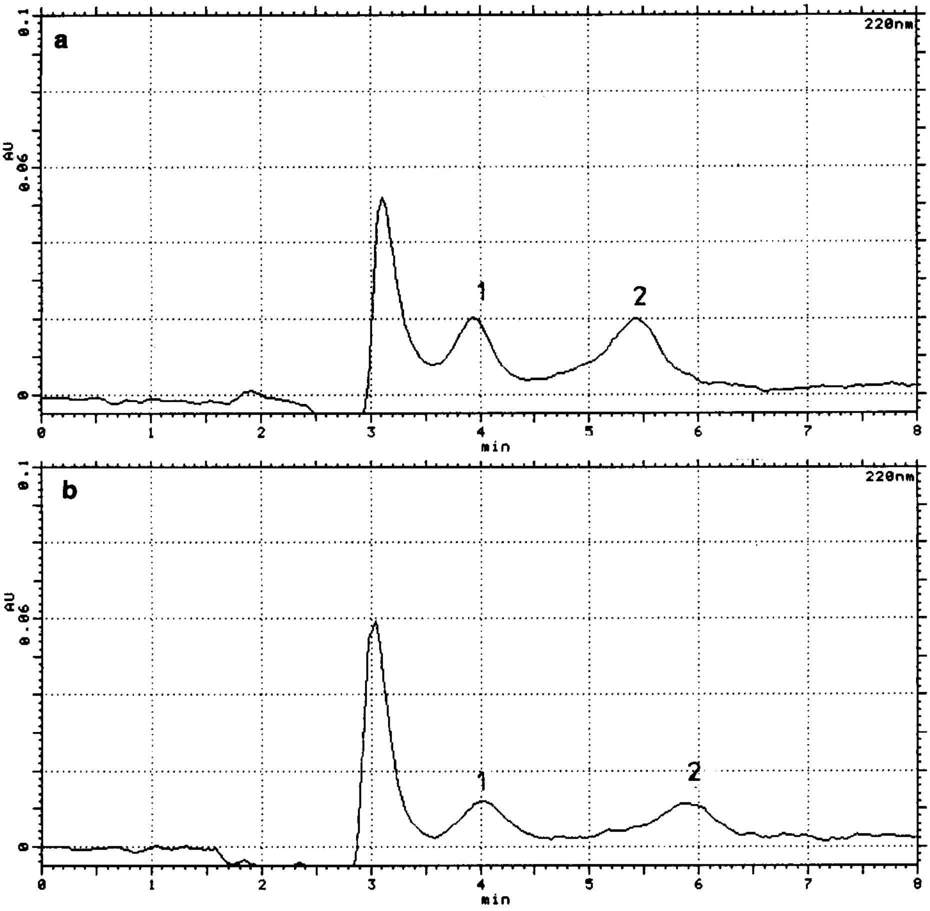

Fig. 5. HPLC of tyre sample 05 (a) before and (b) after exposure to weather for 4 months. Conditions as in Fig. 1. Peaks: 1 = CD; 2 = PBN.

TABLE IV

CONTENTS OF CD AND PBN (%) IN SAMPLES 05 AND 12 BEFORE AND AFTER THE EXPOSURE TO WEATHER CONDITIONS

Sample No.	Antidegradant	Time of exposure (months)		
		0	4	5
05	PBN	0.549	0.169	0.093
	CD	0.806	0.159	0.095
12	PBN	0.315	0.051	0.050
	CD	1.139	0.251	0.236

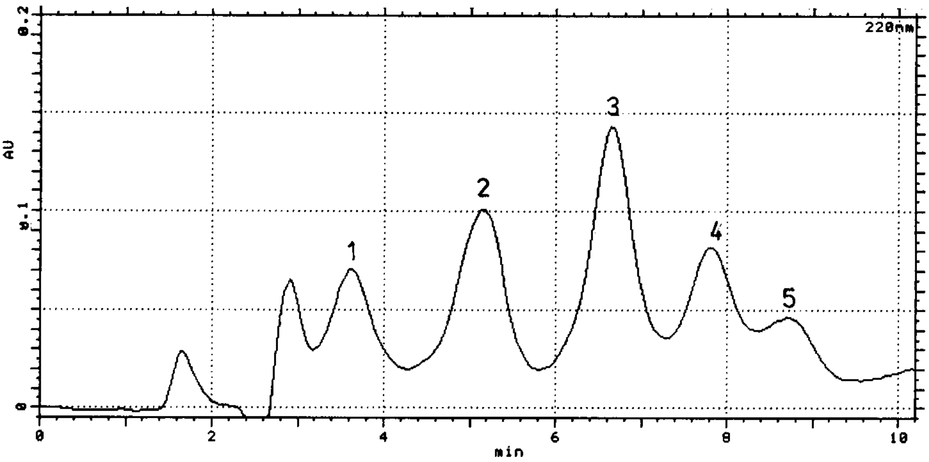

Fig. 6. HPLC of an extract of a rubber sample with CD and TMQ added. Conditions as in Fig. 1. Peaks: 1 = CD; 2 = PBN; 3 = TMQ; 4,5 = degradation products of TMQ.

production and after 4 and 5 months of exposure. The results are given in Table IV and chromatograms of sample 05 before and after exposure are shown in Fig. 5. It is obvious that the concentrations of both antidegradants decreased rapidly during exposure (June–October).

Fig. 6 is a chromatogram of the extract of a rubber sample (No. 276) with CD and TMQ added. This separation also illustrates the simultaneous determination of CD, PBN and TMQ, because PBN was originally used as an additive in the rubber.

In conclusion, this method achieves the rapid simultaneous separation (12 min) of antidegradant applied in tyre production (CD, PBN and TMQ) together with the degradation products before and after vulcanization.

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