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Note

Determination of antioxidants in gasoline by micro high-performance liquid chromatography

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Gasoline contains various kinds of additives in order to improve its performance, *e.g.*, antioxidants, metal deactivators, corrosion inhibitors, anti-pre-ignition agents, anti-icers, carburettor detergents, intake valve deposit control additives, dyes, antiknocks, etc.[1,2]. Anti-oxidants protect olefins and other components in gasoline from oxidation. The determination of such compounds is of practical importance in estimating the stability of gasoline and in controlling its quality. *p*-Phenylenediamines and phenols are usually employed in gasoline as well as in rubber. These substances have been determined by colorimetry[3–7] or other methods[8–15]. Although the colorimetric method is quantitative and sensitive, it involves oxidation of the antioxidants before the measurement. Thus, there have been problems with reproducibility or conveniency of the analysis.

We have developed a precolumn concentration method for the determination of dilute components in micro high-performance liquid chromatography (HPLC)[16] and have applied it to the analysis of corticosteroids[17,18], catecholamines[19,20] and bile acids[21,22] in biological fluids, or to organic compounds in water[18]. The micro precolumn comprises PTFE tubing packed with commercially available materials. The solutes of interest are collected on the precolumn by passing a sample solution through it. The packing materials are carefully selected by considering the nature both of the solutes and the matrix solution. This micro precolumn method can replace the conventional pretreatments such as extraction and evaporation which are generally adopted in HPLC.

This paper describes the applicability of the micro precolumn concentration method to the analysis of additives in gasoline.

EXPERIMENTAL

Apparatus

A micro liquid chromatograph comprised a Micro Feeder (Azumadenkikogyo, Tokyo, Japan) equipped with a gas-tight syringe MS-GAN 050 (Terumo, Tokyo,

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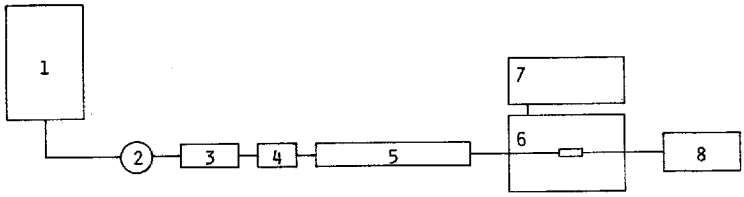

Fig. 1. Block diagram of the apparatus. 1 = Pump; 2 = micro valve injector; 3 = concentration column; 4 = guard column; 5 = separation column; 6 = UV detector; 7 = calculator; 8 = waste reservoir.

Japan) as a pump, a micro valve injector ML-422 (0.021 μl; JASCO, Japan Spectroscopic, Tokyo, Japan), a concentration column (PTFE tubing, 10 × 0.2 mm I.D.), a guard column (PTFE tubing, 5 × 0.2 mm I.D.), a separation column (fused-silica, 150 × 0.26 mm I.D.) and a UV spectrophotometer Uvidec-100III (JASCO, cell volume 0.04 μl), as shown in Fig. 1. Calculations were performed with Chromatopac C-R1A (Shimadzu, Kyoto, Japan). Develosil-60-10 (10 μm; Nomurachemical, Seto-shi, Japan) and Spherisorb 5A (5 μm, Phase Separation) were selected as packing materials for concentration columns. The former is a silica gel and the latter alumina. LiChrosorb RP-18 (5 μm; Merck, Darmstadt, F.R.G.) was selected as the packing material for both a guard column and a separation column. The packing procedures were nearly the same as in previous work[23].

Reagents

N,N′-Di-*sec.*-butyl-*p*-phenylenediamine (BPA), N-phenyl-N′-*sec.*-butyl-*p*-phenylenediamine (PBPA) and 2,6-di-*tert.*-butyl-*p*-cresol (DBPC) were obtained from Sumitomo Chemical (Tokyo, Japan), and N,N′-disalicylidene-1,2-propanediamine (DSPA) was obtained from Tokyo Chemical Industry (Tokyo, Japan). Gasoline samples were supplied from service stations. Other reagents were obtained from Wako Pure Chemical Industries (Osaka, Japan), unless otherwise noted.

Sample preparation and precolumn concentration

Standard solutes were dissolved in acetonitrile and stored in a refrigerator (stock solution). When collecting these substances on a silica gel or alumina concentration column, the stock solution was diluted 5000–30,000 times in *n*-hexane and an adequate volume (100–300 μl) of the sample solution was quickly passed through the concentration column. Prior to the concentration process, the concentration column was washed successively with acetonitrile, dichloromethane and *n*-hexane. In the case of gasoline samples, 20 μl of gasoline were diluted 300 times in *n*-hexane and 300 μl of the resulting solution were then introduced into the concentration column that had been washed as for standard samples. After collecting the samples, the concentration column was purged of *n*-hexane in a stream of nitrogen and then connected to the head of the separation column. The constituents injected on the column were contained in 1 μl of the sample gasoline.

RESULTS AND DISCUSSION

Addition of *n*-hexylamine to the mobile phase resulted in symmetrical peaks in reversed-phase chromatography. The mobile phase was consequently alkaline, and

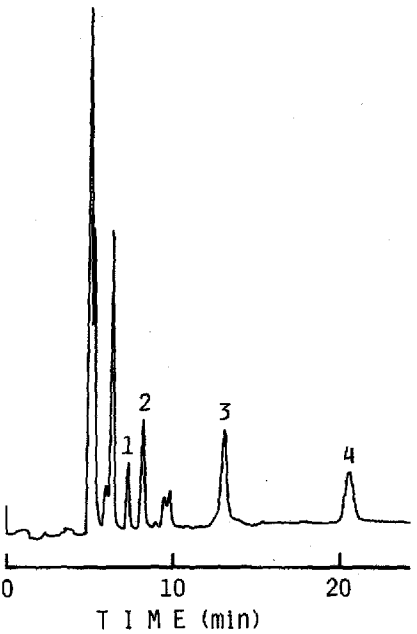

Fig. 2. Separation of antioxidants and a metal deactivator. Column: RP-18, 150 × 0.26 mm I.D. Mobile phase: acetonitrile–water–*n*-hexylamine (65:35:1). Flow-rate: 2.1 μl/min. Samples: 1 = BPA; 2 = PBPA; 3 = DSPA; 4 = DBPC. Injection volume: 0.021 μl. Wavelength of UV detection: 280 nm.

the guard column was frequently changed in order to prevent deterioration of the separation column. Fig. 2 demonstrates the separation of antioxidants (BPA, PBPA and DBPC) and a metal deactivator (DSPA) on an ODS column (150 × 0.26 mm I.D.). These substances are separated from impurities which may be included in the standard solutes or resulting from oxidation of them. The sample was loaded with the micro valve injector.

The recovery test was performed with standard solutes. Recoveries were calculated by comparing peak heights obtained with precolumn injection and valve injection. The results are shown in Table I. BPA and PBPA could be quantitatively collected on both silica and alumina concentration columns, while the recoveries of

TABLE I

RECOVERY OF ADDITIVES

Precolumn: 10 × 0.2 mm I.D. Operating conditions as in Fig. 2.

Additive	*Recovery (%)*	
	Develosil-60-10	*Spherisorb 5A*
BPA	99	87
PBPA	97	83
DSPA	33	23
DBPC	0	0

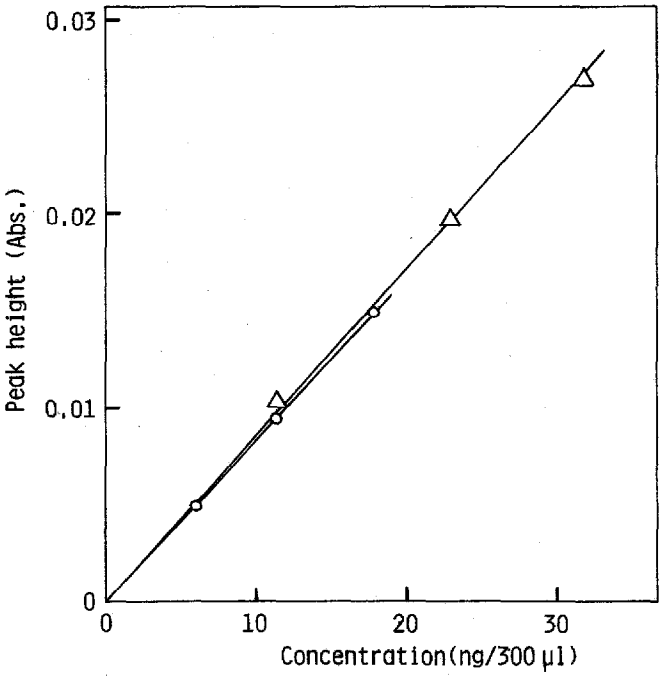

Fig. 3. Calibration curves for antioxidants. Concentration column: Develosil-60-10, 10 × 0.2 mm I.D. Samples: 300 μl of BPA (△) or PBPA (○). Other operating conditions as in Fig. 2.

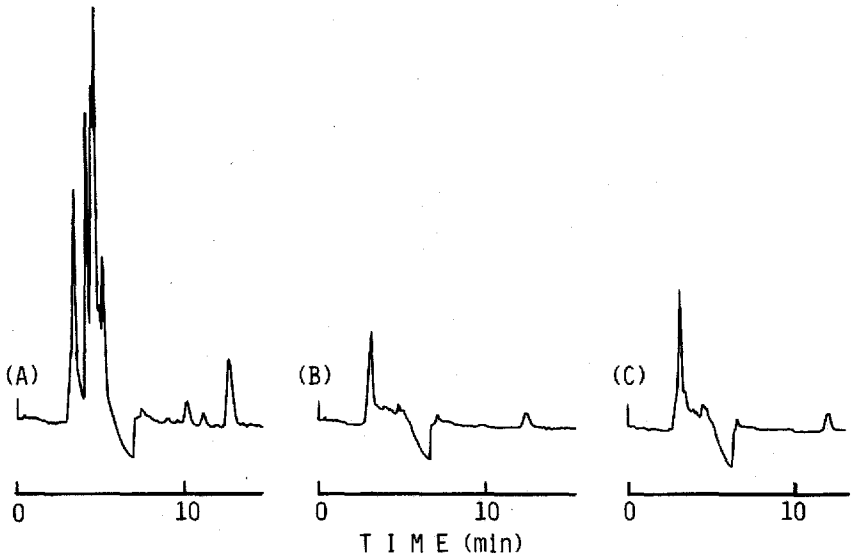

Fig. 4. Chromatograms of refinery stocks. Concentration column: Develosil-60-10, 10 × 0.2 mm I.D. Samples: A = catalytically cracked gasoline; B = light straight run gasoline; C = catalytic reformate gasoline. Other operating conditions as in Fig. 2.

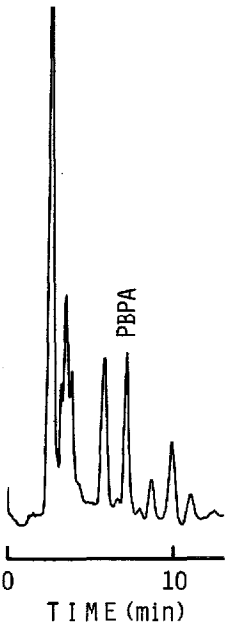

Fig. 5. Separation of PBPA in gasoline. Concentration column: Develosil-60-10, 10 × 0.2 mm I.D. Sample: commercial gasoline. Other operating conditions as in Fig. 2.

DBPC and DSPA were poor due to breakthrough. Develosil-60-10 gave better results than Spherisorb 5A. The recoveries of DBPC and DSPA from an aqueous solution could be improved by using ODS as the precolumn material, but was unsuitable for the analysis of real samples since a lot of interesting constituents are also collected and gasoline was difficult to dissolve in water. Thus, BPA and PBPA were determined by using Develosil-60-10 as the concentration column.

Fig. 3 shows calibration curves for BPA and PBPA. Linear relationships are observed up to *ca.* 30 ng/300 μl. The detection limit was *ca.* 0.3 ng/300 μl (corresponding to 0.3 ppm in gasoline) for a signal-to-noise ratio of 2. It can be improved by increasing the concentration volume. About 5 min were required to pass 300 μl of the sample solution.

Fig. 4 shows chromatograms of catalytically cracked gasoline, light straight run gasoline and catalytic reformate gasoline which do not contain antioxidants. The results suggest the possibility of determining BPA and PBPA since there is no interfering peak during their elution time.

Fig. 5 shows the separation of PBPA in gasoline. The concentration of PBPA in this gasoline was determined as 8.6 μg/ml with an error of *ca.* 2%. In the analysis of gasoline samples, the retention time of antioxidants was slightly decreased compared with that observed for standard samples. Thus, the solutes were identified by adding standard solutes to gasoline. This drawback can be overcome by using a multichannel photodiode array UV detector. BPA in gasoline could also be determined by this system.

CONCLUSIONS

Micro HPLC using off-line precolumn concentration permitted the rapid determination of antioxidants in gasoline. This system will be useful in routine work if on-line precolumn concentration and a multichannel photodiode array detector can be employed.

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