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Note

Group separation of petroleum using supercritical fluids

A comparison of supercritical nitrous oxide and carbon dioxide as mobile phases

ELSA LUNDANES*, BERIT IVERSEN and TYGE GREIBROKK
Department of Chemistry, University of Oslo, P.B. 1033, Blindern, 0315 Oslo 3 (Norway)

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Recently there has been an interest in using supercritical fluids for the group separation of petroleum samples. Supercritical carbon dioxide (CO_2)[1,2] and sulphur hexafluoride (SF_6)[3] have been used as mobile phases for the group separation of gasoline[1,3] and high-boiling petroleum fractions[2]. Gasolines were separated into saturates, olefins and aromatics, whereas high-boiling petroleum residues and crude oil were separated into saturates, aromatics and polar compounds. In contrast to liquid chromatographic (LC) group separations, the supercritical fluid chromatographic (SFC) group separations with the above-mentioned fluids can utilize conventional flame ionization detection (FID) for direct quantitation.

The objective of this investigation was to examine the possibility of using supercritical fluids other than CO_2 for the group separation of high-boiling petroleum fractions and crude oil. Other fluids suited to FID are nitrous oxide (N_2O) and ammonia. Ammonia, with its large dipole moment and high proton affinity, is an interesting mobile phase. However, difficulties due to chemical attack on polymeric components in the apparatus have been observed[4]. Nitrous oxide was thus chosen for this study. Supercritical N_2O has been reported to be a more effective extractant[5] and a stronger eluent[6] than supercritical CO_2. It has also been reported[7] that supercritical N_2O possesses a solvating power similar to that of supercritical CO_2.

This paper describes the difference between supercritical N_2O and supercritical CO_2 as mobile phases for group separation of petroleum samples. For both mobile phases the group separation into saturates, aromatics and polar compounds is obtained on a three-column system with column-switching and back-flushing.

EXPERIMENTAL

Materials

The liquid N_2O (medical grade) and liquid CO_2 (standard grade) were obtained from AGA Norgas, Oslo, Norway. Carbon disulphide was purchased from Rathburn Chemicals (Walkerburn, U.K.), and the standards were obtained from different commercial sources. Crude oil and high-boiling distillation fractions and residues were obtained from Statoil, Stavanger, Norway.

Instrumentation

The liquid CO_2 was transferred from the cylinder to the pump by an eductor tube, while the liquid N_2O was transferred from an upside-down cylinder through a stainless-steel transfer line to the pump. A 2-μm filter was inserted in the line to prevent particles in the cylinders from entering the pumping system. The pumping system consisted of a μLC-500 micro-pump from ISCO or a modified Model 6000 A pump from Waters[8]. In some experiments a purifier column (500 × 7 mm I.D.) filled with 28-mesh activated carbon (Alfa Products) or basic alumina (superactive 1 from Woelm) was inserted in front of the injector. Samples were injected with a Rheodyne 7520 micro-HPLC injector. A Hewlett-Packard 5790 A flame ionization detector with wide bore or capillary jet was used, with a hydrogen flow-rate of 40–60 ml/min and with the air supply replaced by oxygen (*ca.* 50 ml/min). The restrictor was made by crimping the end (1–2 mm) of a piece of 0.4 mm O.D. and 0.1 mm I.D. platinum tubing (Goodfellow Metals, Cambridge, U.K.). The restrictor outlet was located 5–7 mm below the jet tip of the detector. One six-port, two-position valve was obtained from Valco and one from Waters. Both were operated manually. The columns and the Valco valve were kept in the oven of the HP-5790 A gas chromatograph, while the Waters valve was connected through a hole in the inner wall of the oven where the outer wall was removed.

Columns

Two 250 × 1.3 mm I.D. CP-Spher silica (8 μm) columns were purchased from Chrompack (Middelburg, The Netherlands) and two 30 × 2.1 mm I.D. Spheri-5 cyano (5 μm) MPLC™ cartridge-type columns from Brownlee Labs (Santa Clara, CA, U.S.A.). One of the 250 × 1.3 mm I.D. silica columns was impregnated with silver nitrate as described elsewhere[2]. The two cyano columns were used in series for the group separation.

RESULTS AND DISCUSSION

Delivery of fluid

A reciprocal HPLC pump has been used[8] successfully for the delivery of CO_2. However, this pump did not give a long-term stable flow of N_2O. The reason for the different behaviour with these two fluids is not obvious. In the temperature range from −10°C to 0°C the viscosity of liquid N_2O is equal to that of CO_2[9]. One possible explanation is that the Kalrez O-rings in the extra check-valves of the pump behave differently with CO_2 and N_2O since differences in swelling has been observed in these two media[10]. A syringe pump was found to give a stable delivery of N_2O (and CO_2). This pump was modified by introducing a cooling coil (−15°C) around the cylinder to obtain an efficient filling.

Detection by FID

When N_2O was used as mobile phase, the flame in the detector (which is constructed for capillary columns) was pale yellow. It is known that the combustion with N_2O as oxidation agent forms nitrous oxides[9], and the smell of these was detected. The baseline level at the detector was much higher with N_2O as mobile phase than with CO_2. The baseline level was not reduced by using either activated carbon or alumina in the purifier column. When the reciprocal pump was used, pulsing of the detector signal was observed. By using lower flow-rates (less than 0.1 ml/min) the baseline level was reduced. The amount of N_2O used in capillary SFC has not been reported to be a problem during detection[11].

Less than 1 ng of the C_{20} *n*-alkane could be detected using supercritical CO_2 (190 bar, 40°C) at a flow-rate of 0.3 ml/min ($k' = 0.75$ on a 200 × 2.1 mm I.D. C_{18} column; $N_{h/2}$ *ca.* 10 000). The detection limit was increased by a factor of *ca.* 1000 replacing supercritical CO_2 with supercritical N_2O as mobile phase. However, when 0.5 μl of crude oil or slightly diluted high-boiling fractions was injected, the amount of each fraction was well within the limit of detection.

The high background level observed with supercritical N_2O as mobile phase was independent of the type of restrictor investigated (platinum, stainless steel and fused silica[10]). The platinum restrictor has been used successfully with supercritical CO_2 as mobile phase[2]. However, when supercritical N_2O was used as mobile phase, a gradual clogging of the platinum restrictor was observed. The same was observed when N_2O was delivered directly from the pump to the restrictor (with a 2-μm in-line filter), and this indicates that the clogging is caused by the N_2O itself. Clogging of fused-silica (10 μm) restrictors was not observed.

Group separation

When supercritical CO_2 was used as mobile phase a silver-impregnated silica column was needed to obtain complete separation between saturates and aromatics[2]. The separation between saturates and aromatics on silica alone was not improved when supercritical N_2O replaced the CO_2 as mobile phase. Therefore a silver-impregnated silica column was also included with supercritical N_2O to obtain separation between saturates and aromatics. The retention time of benzene was less with supercritical N_2O as mobile phase than with CO_2. Yet a complete separation of saturates and aromatics was obtained for high-boiling distillation fractions and crude oil. Fig. 1 shows the separation of saturates and aromatics on a dual silica plus silver-impregnated silica column with supercritical N_2O as mobile phase. The aromatics are back-flushed from the columns. In the same way as with supercritical CO_2 as mobile phase, the use of a dual-column system was necessary to reduce the tailing of the back-flushed aromatics.

The retention order of polycyclic aromatic hydrocarbons on a cyano column

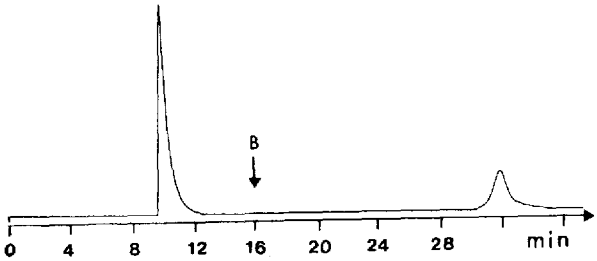

Fig. 1. Separation of 1 μl of distillation fraction C_{20} on a 25-cm silica column plus a 25-cm silver-impregnated silica column eluted with supercritical N_2O (0.14 ml/min, reciprocal pump) at 270 bar and 60°C. The platinum restrictor was used and the flame ionization detector was operated at 350°C. Back-flushing started at B.

was the same with supercritical N_2O and CO_2. The retention of chrysene was less with supercritical N_2O than with supercritical CO_2 at equal reduced pressures and temperatures.

Group separation into saturates, aromatics and polar compounds of high-boiling residues was obtained using the three-column system with column-switching and back-flushing described elsewhere[2]. Fig. 2 shows the group separation of a high-boiling residue into saturates, aromatics and polar compounds using supercritical CO_2 and supercritical N_2O as mobile phases at the same reduced pressure and temperature. The most noticeable difference in the chromatograms is the difference in peak shape of the back-flushed polar compounds. When supercritical N_2O was used as mobile phase, the polar compounds were back-flushed as a single peak with little tailing, whereas they were back-flushed as a double peak with supercritical CO_2. Less tailing of the aromatics was also observed when N_2O was used as eluent. Carbon disulphide, which was needed for injection of the high-boiling residues, gave a small but detectable FID response with both mobile phases and therefore the amount was kept at a minimum. The contribution from CS_2 to the FID signal of the saturates was less than 1–2% and can be corrected for.

Crude oil was also group-separated using the same column system. A complete separation between saturates and aromatics was obtained using both supercritical N_2O and supercritical CO_2 as mobile phases. As for high-boiling residues, supercritical N_2O gave less tailing of the back-flushed aromatics and polar compounds and the latter were eluted as a single peak using supercritical N_2O as mobile phase.

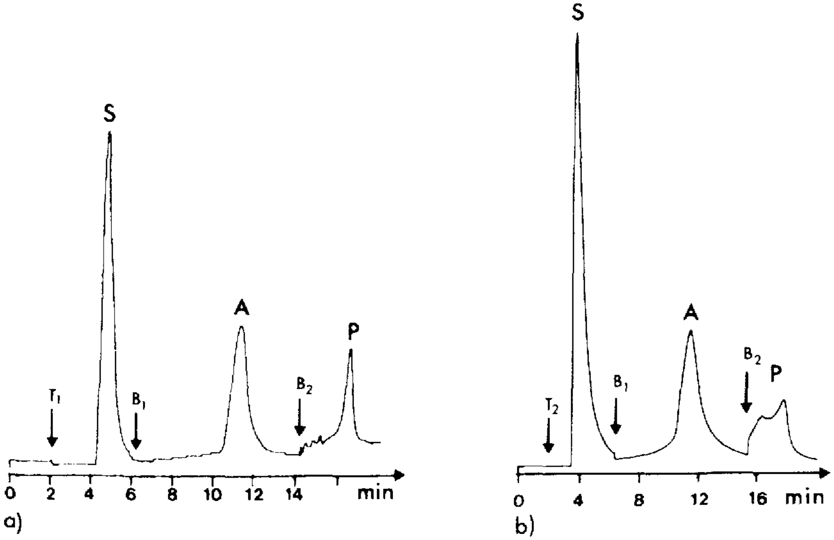

Fig. 2. Group separation into saturates (S), aromatics (A) and polar compounds (P) of a deasphalted high-boiling residue from North Sea oil using a three-column system[2]. The injection volume was 0.5 μl and one-quarter of this was CS_2. The platinum restrictor was used and the flame ionization detector was operated at 350°C. The aromatics left the cyano column at T_1 (N_2O) and T_2 (CO_2). Back-flushing of the aromatics started at B_1 and of the polar compounds at B_2. Both mobile phases were delivered by the syringe pump. (a) Supercritical N_2O (195 μl/min) at 280 bar and 55°C. (b) Supercritical CO_2 (250 μl/min) at 280 bar and 50°C.

CONCLUSION

Both supercritical N_2O and CO_2 can be used as mobile phase for group separation of high-boiling petroleum samples and crude oil into saturates, aromatics and polar compounds. The group separation is obtained using a three-column system consisting of cyano plus silica plus silver-impregnated silica columns with column-switching and back-flushing. Compared with supercritical CO_2, supercritical N_2O gives less tailing of the back-flushed aromatics and polar compounds.

A high background level of the FID signal is observed with supercritical N_2O as mobile phase in the 0.1–0.3 ml/min range, which is suitable for microbore columns. The detection limit is in the microgram range, which is three orders of magnitude higher than with supercritical CO_2 as mobile phase. The lack of a suitable restrictor for the flow-rates used for microbore columns makes the FID difficult with supercritical N_2O, and quantitation is much easier with CO_2. Supercritical CO_2 is therefore so far the mobile phase of choice for group separation of petroleum samples with direct quantitation by FID.

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