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# ANALYSIS OF NITROGEN HETEROCYCLES IN SHALE OIL BY A DUAL CAPILLARY COLUMN HEART CUTTING TECHNIQUE

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## SUMMARY

The analysis of nitrogen heterocycles in a shale oil matrix is described. A dual column gas chromatograph is used for the analysis after a simple sample preparation scheme is used. Details of the apparatus, especially the inter-column pneumatic microswitch, are given. Quantitation by the standard addition method using internal volume corrections is described. Future direction for further development of this technique is briefly discussed.

## INTRODUCTION

A most difficult analytical problem in gas chromatography (GC) is the quantification of closely eluting isomer pairs in very complex matrices. Such a problem is encountered in measuring nitrogen heterocyclic (NHET) compounds in a highly complex matrix such as shale oil.

Several separation schemes are available for isolation of N-heterocyclic fractions from complex matrices[1–7]. These methods utilize column chromatography, high-performance liquid chromatography (HPLC), and acid–base extraction, and have been used for quantitation of nitrogen heterocycles in particulate and soil matrices. For the analysis of shale oil, however, these methods could not remove all the analytical interferences necessary to allow quantification of 3-ring N-heterocycles by capillary gas chromatography. A dual-column, heart cutting, capillary gas chromatographic technique, however, was developed and found suitable for this quantification.

The heart cutting technique is multidimensional chromatography in which two columns are used in series to affect a desired separation[8–14]. A sample is injected onto the head of the first column and allowed to partition down the column. The end of the first column is connected to a pneumatic switch[15] which can direct that column's effluent either to a flame ionization detector or to the head of a second column. At a pre-selected time, a small portion of the effluent from the first column containing the specific analytes of interest is switched onto the head of the second column and further separation of the analytes occurs.

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## EXPERIMENTAL*

A shale oil Standard Reference Material (SRM 1580)[16] was analyzed for 5,6-benzoquinoline (BQ), and quantitative analysis was carried out using a standard addition method. Prior to sample preparation, weighed oil samples were enriched with a known amount of the BQ. A series of four samples was prepared, containing 0, 1, 2, and 3 ml of the enrichment solution, respectively. This solution, 10.0 $\mu$g/ml BQ in methylene chloride, was made such that each milliliter contained approximately the same amount of BQ that was present in the unenriched sample.

A volume fraction containing basic nitrogen heterocycles was extracted from the oil by a sample work-up procedure shown schematically in Fig. 1. The NHET fraction was dried over anhydrous sodium sulfate and then evaporatively concentrated to approximately 100 $\mu$l under a flow of purified nitrogen gas. The sample was then analyzed using GC.

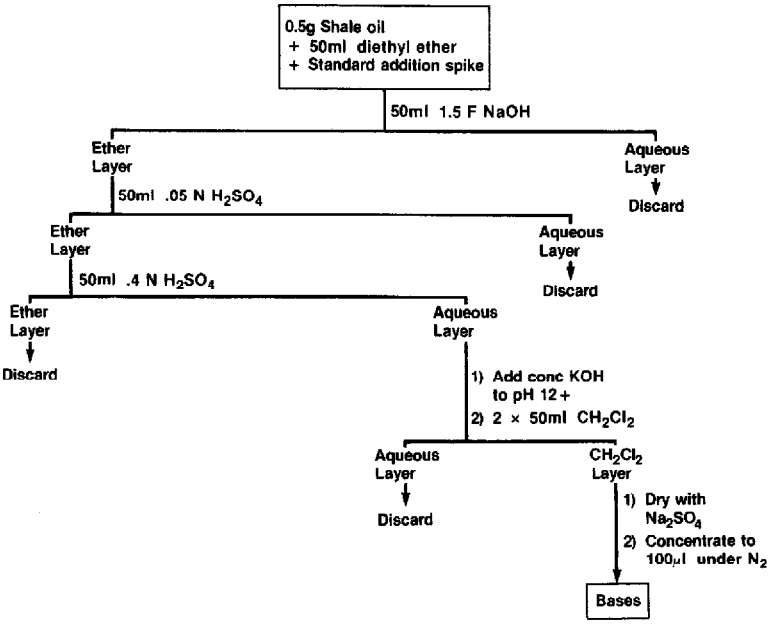


Fig. 1. Extraction procedure for basic nitrogen heterocycles.

The GC system consisted of two capillary columns interconnected by a low dead-volume switch which operated as described by Deans[15]. The construction and operation of this microswitch are shown in Fig. 2. The two analytical capillary columns were connected with a small diameter quartz capillary which fitted loosely inside the ends of each of the analytical columns. The column ends and pneumatic

* Certain commercial equipment, instruments, or materials are identified in this paper in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

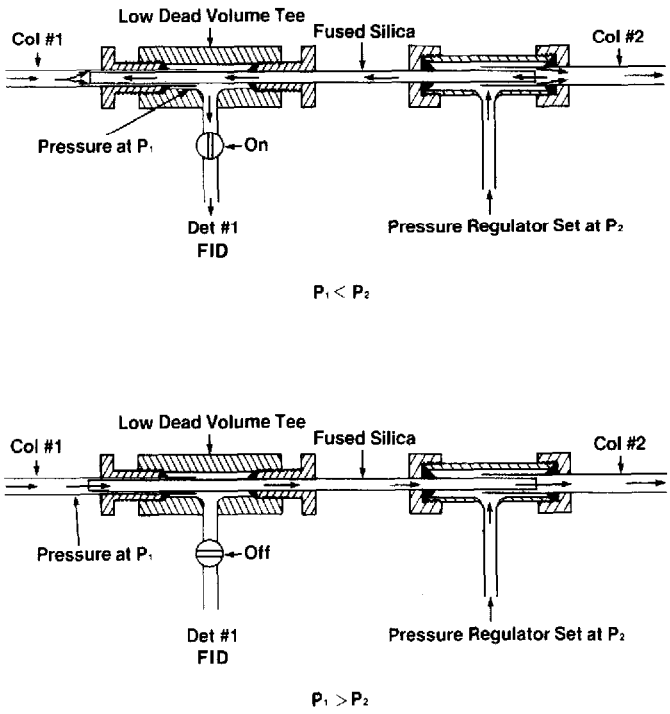


Fig. 2. Construction and operation of low dead volume microswitch. Upper part, transfer mode, effluent from column 1 transferred to column 2; lower part, vent mode, effluent from column 1 vented to detector 1.

microswitch were contained within two commercially available stainless-steel union tees. A low dead-volume tee located at the exit of the first column served as the exit for the vent line of the switch. This vent line led to the first flame ionization detector, allowing the elution from the first capillary column to be monitored (except when switched to the second analytical column). A low dead-volume, high-temperature valve in the vent line provided the off/on control for the switch. The control stem of the vent valve extended outside the chromatographic oven so that the valve could be adjusted while the oven was at its operating temperature. The second tee, located at the entrance to the second analytical column, was connected to a pressure controller which acted to maintain a constant pressure at the second column head. The entire switch assembly was wrapped with heating tape and maintained 100°C above the column oven temperature so that cold trapping could not occur in the switch.

The effluent from the first column was switched to the second column by turning off the valve on the vent line. In the "off" state, the gas flow can only proceed through the fused-silica transfer line and into the second column (Fig. 2a). If the control valve is then opened (Fig. 2b), the pressure in the first tee is reduced to the point where gas flows from the pressure regulator connected to the second tee, through the fused-silica transfer line and, along with the effluent of the first column, out through the valve to detector 1. In the "on" position, no effluent from the first

column can be transferred to the second column. The design of this switch ensures that when effluent is being transferred, it is only exposed to glass or fused-silica surfaces; and, when the effluent is vented, the transfer line connecting the two columns is completely swept by clean carrier gas from the auxiliary pressure controller.

An enhanced separation of analytes on a two-column, heart cutting apparatus can only be produced if the separation mechanisms of the two columns chosen are sufficiently different. For this reason, a non-polar column was selected as the first analytical column, since this column separates analytes according to their boiling points. A polar column was used as the second analytical column, since this column tends to retard polar analytes which interact more strongly with its stationary phase. Analytes with approximately equal boiling points (but with varying polarities) are eluted together from the first column and transferred to the second column where they are separated because of their polarity differences.

For this analysis, the first column was chosen to be a 20-m SE-52 (non-polar) capillary column, prepared in our laboratory by the method of Grob *et al.*[17]. The internal diameter of this borosilicate glass column was 0.32 mm, and the stationary phase film thickness was 0.25 $\mu$m. The seond column was a commercially procured 30 m $\times$ 0.32 mm I.D. fused-silica capillary column coated to a thickness of 0.25 $\mu$m with Carbowax 20M (polar). The uncoated fused-silica transfer line was 15 cm in length with an outer diameter of approximately 0.25 mm.

Prior to any analyses, standards of BQ and phenanthridine (PH) were chromatographed on the first analytical column to determine the proper retention time window to be used in the heart cutting operation. This window was determined to be between 4.5 and 5.7 min for the experimental conditions used. Phenanthridine is a naturally occurring nitrogen heterocycle found in the shale oil matrix. The area of this peak was ratioed to that of BQ in all standard addition calculations, so that errors due to varying injection volumes were mathematically corrected.

The NHET fractions were injected on the first column using a splitting injector maintained at 300°C and a split ratio of approximately 20:1. The oven temperature was maintained isothermally at 150°C until the heart cut was made. The switch was turned to the "off" position at the start of elution of the analyte window as previously determined. After the completion of the analyte transfer, the switch was opened and the temperature of the column oven was increased using a temperature program rate of 2°C/min to 220°C. The BQ and PH were fully separated by the second column.

## RESULTS AND DISCUSSION

To test the transfer efficiency of the column switch, an injection of the normal hydrocarbons $C_{12}$, $C_{13}$, $C_{14}$, and $C_{15}$, was made, and only *n*-$C_{14}$ was transferred onto the second column (Fig. 3). The $C_{14}$ peak shows no significant loss in resolution or intensity resulting from the heart cutting method.

The detector outputs of heart cutting of the N-heterocycles, are shown in Fig. 4. The top chromatogram is the detector output from the first (non-polar) column. The outwardly poor chromatographic separation was a result of an extremely large number of overlapping peaks and not due to low chromatographic efficiency. The measured efficiency of the non-polar column was greater than 1000 plates/meter. However, by transferring an appropriate two-minute portion of eluate from the first

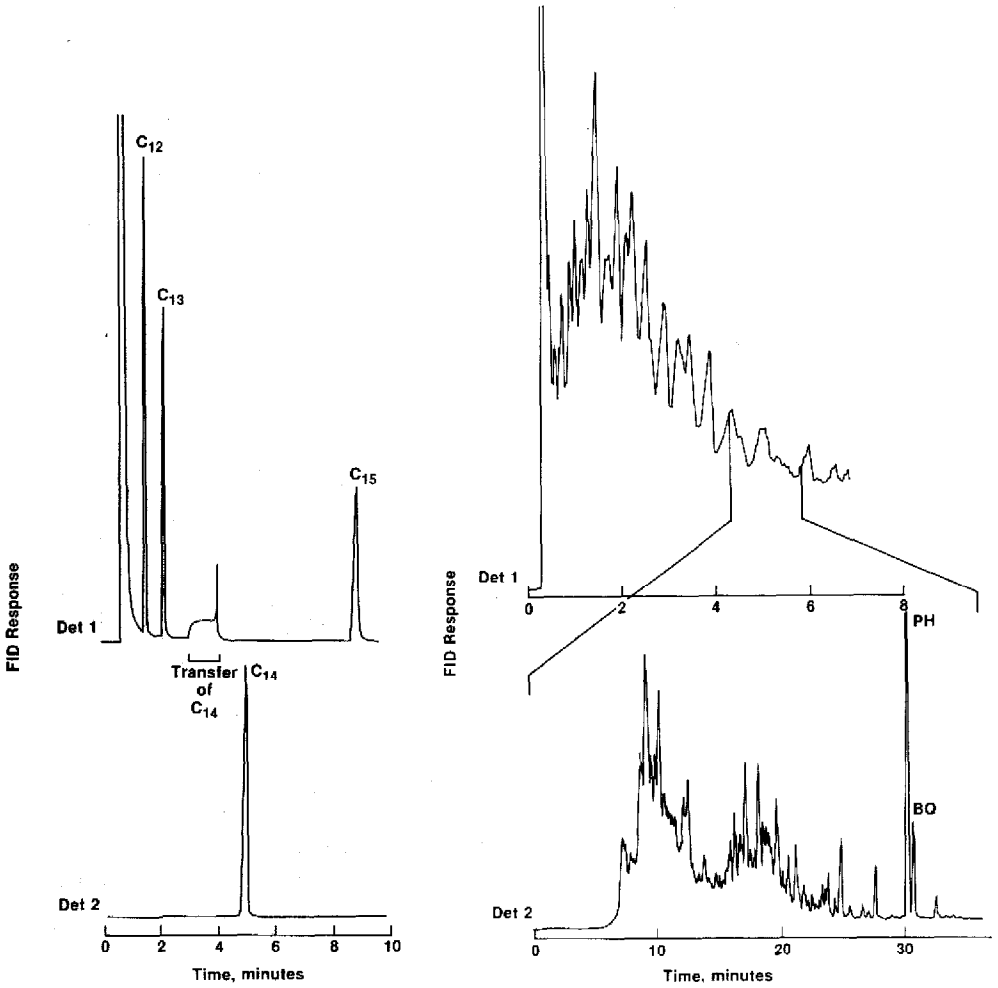


Fig. 3. Chromatogram of transfer of $n$-$C_{14}$ from non-polar SE-52 column to polar Carbowax column. Transfer mode initiated for $n$-$C_{14}$ only.

Fig. 4. FID chromatogram for separation of 5,6-benzoquinoline and phenanthridine. Top: detector output of the non-polar column. Bottom: detector output of the second, polar column. PH = phenanthridine, BQ = 5,6-benzoquinoline.

column to the second, polar column, baseline separation of PH and BQ was achieved on the second column. A plot of the area ratios of the BQ peak to the PH peak by the standard addition method is shown in Fig. 5. The BQ concentration present in the original shale oil sample is the negative value of the $X$ intercept. The results of a complete set of analyses, incorporating three replicates of each enriched sample, are shown in Table I. The concentration of BQ, determined from eight separate analyses, was 15 ± 1 $\mu$g/g. The concentration determined by independent analyses by HPLC was 16 ± 1 $\mu$g/g[16].

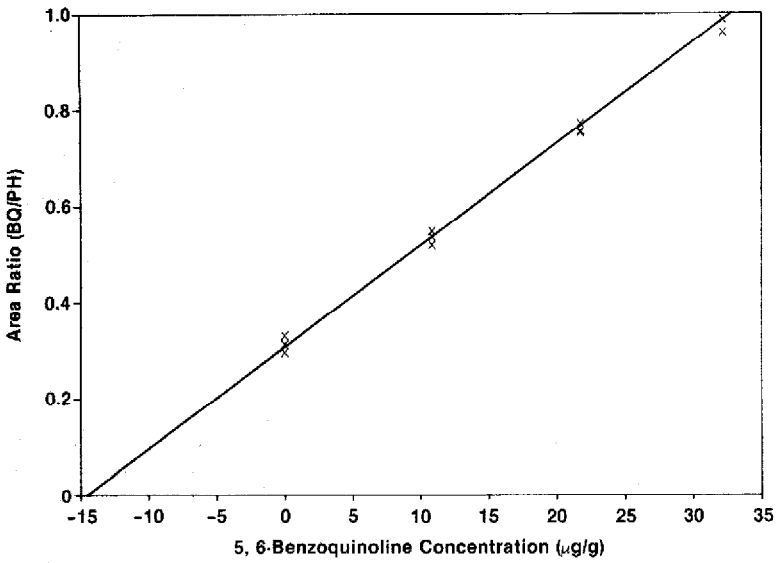


Fig. 5. Typical standard addition plot of the ratio of the 5,6-benzoquinoline area to the phenanthridine area *versus* the added concentration of 5,6-benzoquinoline. The *X*-intercept represents the native concentration found in this analysis set. Concentration = 14.55 μg/g; estimated error = 0.84; correlation coefficient = 0.997.

The results from this experiment and others have shown this technique to be generally applicable to complex matrices from which close isomer pairs are to be separated and quantitated. Computer control of the switching mechanism would increase method reproducibility. The computer would monitor the output from the first flame ionization detector and switch the effluent based on retention time and other chromatographic features. These improvements should make this method very useful as a quantitative tool in the future.

TABLE I

RESULTS OF A COMPLETE SET OF ANALYSES FOR 5,6-BENZOQUINOLINE IN SHALE OIL

| *5,6-Benzoquinoline (μg/g)* | *No. of data points per analysis* | *Estimated error** |
|---|---|---|
| 14.19 | 12 | 0.7 |
| 16.69 | 12 | 0.6 |
| 14.36 | 12 | 0.5 |
| 14.31 | 12 | 1.2 |
| 16.66 | 12 | 0.9 |
| 16.22 | 8 | 2.0 |
| 14.55 | 12 | 0.8 |
| 14.18 | 8 | 2.5 |
| 15.1 ± 1.2** | | |

* Error of *X*-intercept estimated from standard error of regression line at $Y = 0$.

** Sample mean and sample standard deviation (1 standard deviation).

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