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LIQUID CHROMATOGRAPHY-GAS CHROMATOGRAPHY PROCEDURE TO DETERMINE THE CONCENTRATION OF DIBENZOTHIOPHENE IN A CRUDE OIL MATRIX

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SUMMARY

The concentration of dibenzothiophene in SRM 1582, Wilmington crude oil, was determined using a technique which combines liquid chromatography and gas chromatography. In particular, liquid chromatography was utilized for initial sample clean-up and separation of the thiophenes. A dual-flame photometric detector specific for sulfur-containing compounds was used as the detector for gas chromatography. In order to further minimize possible sources of error due to the natural hydrocarbon matrix of the oil, a standard addition method was also utilized.

INTRODUCTION

While developing a plan to issue a Standard Reference Material (SRM)¹ from a Wilmington crude oil, dibenzothiophene (DBTP) was selected as one of the possible compounds to be certified. Although at least two different analytical methods are usually used for a SRM certification, only one will be reported at this time, namely a combined liquid chromatographic (LC)-gas chromatographic (GC) technique. The result of a second method, GC-mass spectrometry (MS), developed by a different group, is reported at the end of this article. The LC-GC technique was necessary because the complexity of the Wilmington crude oil made it impossible to determine the concentration of DBTP by a single chromatographic method. Even after an LC fractionation of the oil, the sample injected on the gas chromatograph was still too complex to measure accurately the DBTP with a flame ionization detector. Too many other compounds with similar retention times responded to the flame ionization detector and the use of sulfur-specific flame photometric detector (FPD) became mandatory.

Since 1966, when FPD was introduced by Brody and Chaney² as a sulfur- (or phosphorus-) specific detector for GC, numerous papers have been published which discuss the advantages and disadvantages of FPD for the determination of sulfur-containing species. First, there is the question of the exact relationship between the

chemiluminescent FPD response and the concentration of the sulfur compound³⁻⁶. The concentration of the sulfur compound is not linear with the FPD response but is approximately proportional to the square root of the response. The exact power of the response for linearity (linearization exponent) depends not only on the type of sulfur compound measured but also on the rates of flow of the hydrogen and oxygen (or air) to the flame, the ratio of oxygen to hydrogen³ and the detector geometry or design (for instance, single- *versus* dual-flame detector)⁶. Moreover, in determining the concentration of DBTP in a Wilmington crude oil matrix, two other effects, the continuum-light emission from carbon in the flame and the hydrocarbon quenching of the sulfur emission, have to be considered. The first effect increases the apparent response of the detector while the latter decreases the response. The selectivity of the detector for sulfur *versus* carbon response is greater than 10^3 for low sulfur concentration and greater than 10^6 at high sulfur concentration^{5,6}. The use of a dual flame photometric detector in the present investigation minimized the hydrocarbon quenching effect⁷.

In view of the above potential problems, it was imperative that the linearization exponent of the detector be determined for dibenzothiophene. Moreover, in order to take into account any small changes in conditions which might affect the value of this exponent from day to day, the calibration experiments were conducted on the same day as each sample analyzed. To reduce further possible errors due to the aforementioned factors, a standard addition method of analysis was used. Thus, the sample and the sample plus the additions were always analyzed in the same matrix environment.

EXPERIMENTAL

Liquid chromatography

A single-pump liquid chromatograph was used for initial sample clean-up⁸. A semi-preparative aminosilane column was utilized with a mobile phase of 1% (v/v) methylene chloride-hexane and the column eluent was monitored by a UV detector at 254 nm. Dibenzothiophene eluted from this column at 23 ml. A fraction of the injected Wilmington crude oil sample (100 μ l) was collected from 18 to 31 ml to ensure complete recovery of the DBTP and three other compounds naturally occurring in the oil which were used for volume correction (see procedure section below). This collected fraction (13 ml) was then evaporatively concentrated to *ca.* 300 μ l by flowing argon gas above the sample and finally, 1-4 μ l of this concentrate were injected into the gas chromatograph for analysis.

Gas chromatography

A gas chromatograph with a sulfur-specific flame photometric detector was used for the final analysis of the DBTP. This detector was a dual-flame version as described by Patterson *et al.*⁶ and was used in the direct mode. A broad-band pass-colored-glass filter with peak light transmission at 365 nm was used. The various gas flow-rates that were used for these analyses were those that were specified by the manufacturer: hydrogen at 140 ml/min; air No. 1 (for inner flame) at 80 ml/min; air No. 2 (for outer flame) at 170 ml/min; and helium make-up gas at 30 ml/min. Hydrogen was also the carrier gas through the wall-coated open tubular fused-silica

capillary column. A splitter flow-rate of 30 ml/min was used, but it was splitless for the first 30 sec after injection. The injection temperature and the detector temperature were maintained at 300°C. The following temperature program was used: 100°C isothermal for 1 min, then increased at a rate of 20°C/min to 140°C, then at 4°C/min to 160°C; finally, to clean the column, the temperature was increased at *ca.* 50°C/min to 260°C for 10 min.

Two different capillary columns were used during the course of this investigation. For the preliminary experiments and for the first three SRM samples, a 15 m × 0.25 mm I.D. × 0.25 μm film SE-52 column (J & W Scientific*) was used. However, after the analysis of the third SRM sample was completed, a new column was installed because the original column was no longer yielding acceptable resolution. A non-polar immobilized phase, 30 m × 0.25 mm I.D. × 0.25 μm film, DB-5 column (J & W Scientific) was installed. Except for slight changes in the temperature program to give acceptable resolution for this new column and in the pressure of the hydrogen carrier gas, all other parameters remained the same.

Materials and procedure

Commercial grade gases were employed throughout this study. Distilled-in-glass hexane was used as the solvent and also distilled-in-glass methylene chloride was used together with the hexane as the mobile phase for the LC sample clean-up. The dibenzothiophene was 99.7% pure (GC) and did not contain any measurable sulfur containing impurities. 2-Methylthiophene (2-M-DBTP) was used in the calibration solutions volume correction since it is similar in structure to DBTP and of the three possible methyl isomers available, it was the only one without an impurity of DBTP. Both 3- and 4-methylthiophene had such an impurity. In all calculations the ratio of DBTP to one of the three volume correction compounds was used to account for the different amounts injected into the gas chromatograph.

As mentioned above, the standard addition method was used to determine the concentration of DBTP in the Wilmington crude oil samples. For each determination, two sequentially numbered SRM vials of the oil sample (each vial contained *ca.* 1 g of oil) were opened, and *ca.* 0.5 g of oil sample was accurately weighed into each of three stoppered flasks (10 ml). A known amount of DBTP in hexane, about equal to the amount naturally present in the SRM, was added to one flask, twice that amount to the second container, and none to the third flask. A fresh solution of DBTP in hexane was prepared for each sample determination. Pure hexane was added to the first and third flasks so that the concentration of Wilmington crude oil was roughly the same in all three vessels (approximately one-half of the original concentration). After complete mixing, 100 μl from each vessel were then fractionated on the liquid chromatograph. The appropriate LC fraction which contained the DBTP and the volume correction compounds was collected, concentrated by evaporation of the solvent to *ca.* 300 μl, and injected into the gas chromatograph. Each fraction was run in triplicate.

The calibration experiments to determine the correct linearization exponent

* Certain commercial equipment, instruments, or materials are identified in this paper 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.

were run on the same day as each sample. Three calibration mixtures were prepared and contained dibenzothiophene in hexane with 2-M-DBTP added for GC injection volume correction. The concentration of 2-M-DBTP was the same in each calibration mixture while the relative concentration of DBTP was 1.0, 2.0 and 3.0 units, respectively. Again, each mixture was injected onto the gas chromatograph and run in triplicate.

RESULTS AND DISCUSSION

Because of the previously mentioned complexity of the Wilmington crude oil sample, it was imperative that a combined LC-GC technique be used as well as a sulfur-specific detector to determine the concentration of DBTP in the oil. Fig. 1 shows the type of chromatogram which results from the direct injection of Wilmington crude oil on a gas chromatograph even with a sulfur specific detector. A similarly complex type of chromatogram would be obtained if a sample were first fractionated on a liquid chromatograph and then injected on a gas chromatograph with a flame ionization detector. Fig. 2 shows the results of the combined LC-GC with a sulfur-specific detector on the gas chromatograph. This chromatogram shows very cleanly separated peaks for DBTP and for three other peaks which eluted after it. From a determination of the retention times of standards, the first and largest peak in the chromatogram after DBTP is 4-methyldibenzothiophene (4-M DBTP). The second

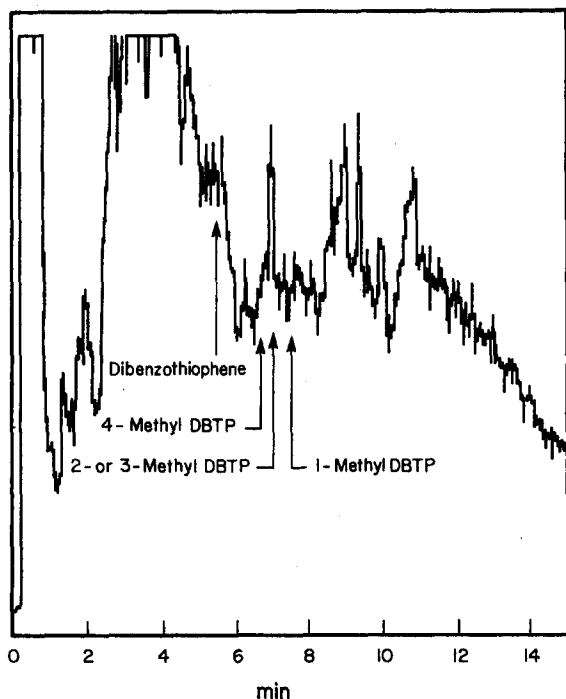


Fig. 1. Gas chromatogram of Wilmington crude oil utilizing a sulfur-specific detector, no preliminary sample clean-up on LC.

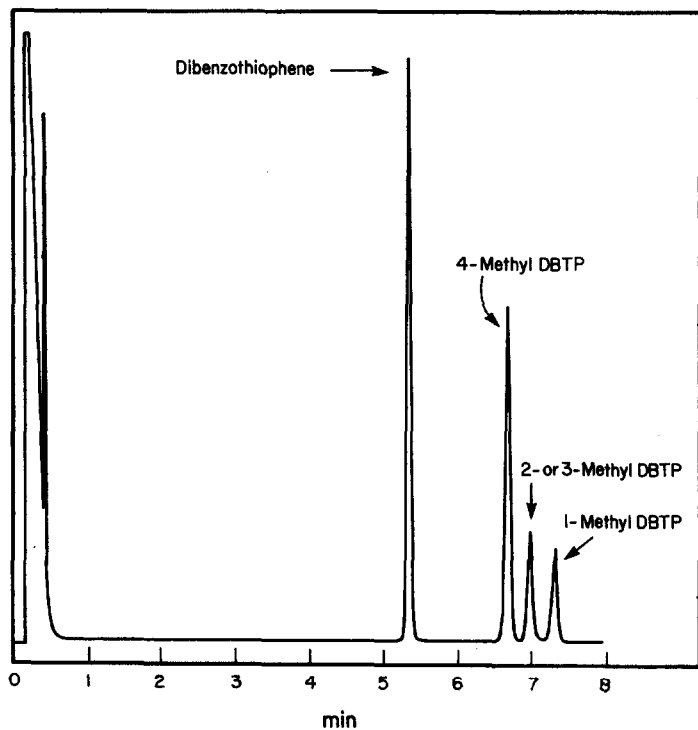


Fig. 2. Gas chromatogram of Wilmington crude oil using a sulfur-specific detector after sample partitioning on LC.

is either 2- or 3-methyldibenzothiophene. The third peak was identified only by retention indices⁹ as 1-methyldibenzothiophene. (A sample of 1-methyldibenzothiophene was not available for use as confirmation.) All three of these peaks were used initially for volume correction to calculate the concentration of DBTP in the oil samples. However, for the final results, the 4-M DBTP peak was used exclusively because it was the largest and gave the highest measured precision. The other two peaks were simply used as confirmatory checks. A summary of the DBTP concentrations is given in Table I. As can be seen from the data for all samples analyzed, the three values of DBTP concentration, calculated from the three different volume correction peaks, were within experimental error of each other.

The linearization exponent which was used for each sample analyzed was determined from a linear regression calculation for the calibration curve in which the logarithm of the DBTP concentration was plotted against the logarithm of the ratio of the response of DBTP to 2-M-DBTP. The slope of this straight line is the linearization exponent (see Table I, column 6). For the first three samples, the average value of this exponent was 0.536 ± 0.015 ; but after a new column was installed the average value of the exponent was 0.580 ± 0.007 .

This method assumes that the linearization exponent is essentially the same for 2-M-DBTP as for DBTP itself. The fact that the three isomers of methyl-DBTP, which were used as volume correction compounds in the analysis of the oil sample,

TABLE I
DIBENZOTHIOPHENE IN WILMINGTON CRUDE OIL

Sample	Column used	Concentration ($\mu\text{g/g}$)			Linearization exponent
		Comparison with peak 1*	Comparison with peak 2	Comparison with peak 3	
A	SE-52	$35.2 \pm 0.8^{**}$	34.4 ± 2.2	36.7 ± 1.9	0.520
B	SE-52	32.7 ± 0.7	31.9 ± 0.5	31.2 ± 0.9	0.550
C	SE-52	35.1 ± 0.7	35.1 ± 0.6	36.0 ± 0.7	0.538
D	DB-5	33.1 ± 1.2	32.4 ± 0.9	33.0 ± 0.5	0.580
E	DB-5	32.6 ± 2.8	28.7 ± 1.2	30.1 ± 1.2	0.588
F	DB-5	34.7 ± 0.8	33.5 ± 0.8	34.8 ± 1.5	0.583
G	DB-5	34.8 ± 0.5	33.8 ± 1.7	32.7 ± 2.1	0.578
H	DB-5	32.9 ± 0.8	32.5 ± 1.6	32.4 ± 1.1	0.571
Average		$33.9 \pm 1.2^{***}$	32.8 ± 2.0	33.4 ± 2.3	

* Values used in certification of SRM-1582.

** Calculated uncertainty from standard addition experiments with 95% confidence limits.

*** Sample standard deviation for the eight values of dibenzothiophene concentration reported above.

produced the same concentration of DBTP within experimental error would seem to support this assumption. Actually, since 4-M-DBTP was used as the volume correction compound for the sample while 2-M-DBTP was used in the calibration experiments to determine the linearization exponent, this technique also assumes that the linearization exponent is the same for both methyl dibenzothiophene isomers. Again, a comparison of the results from the three different isomers listed in Table I supports this assumption.

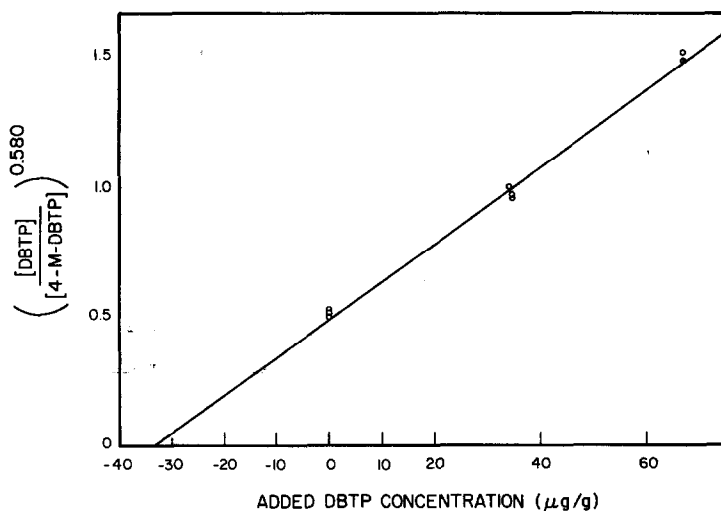


Fig. 3. Standard addition plot of $([\text{DBTP}]/[\text{4-M-DBTP}])^{0.580}$ versus the concentration of added DBTP for sample D.

The concentration of DBTP in each sample was calculated using the linearization exponent determined the same day under nearly identical conditions. The concentration of DBTP added to the three aliquots of each sample was plotted against the ratio of the volume corrected DBTP concentration raised to the power of the linearization exponent. A linear regression calculation of this plot gave an intercept whose negative value is the concentration of DBTP in the original sample. Fig. 3 shows such a plot for sample D using 4-M-DBTP as the volume correction compound. Similar plots were obtained for the other samples and using the other volume correction compounds. These results, which have been corrected for the purity of the DBTP, are given in Table I for all three volume correction compounds. However, because of the highest precision obtained with the 4-m-DBTP (peak 1), this result is considered more reliable, namely $33.9 \pm 1.2 \mu\text{g/g}$. Moreover, as further corroboration it should be mentioned that this result agrees very well with a GC-MS study¹⁰ in which the concentration of dibenzothiophene was determined for the same Wilmington crude SRM. In this study the average value for ten determinations on five ampoules was $32.9 \pm 1.7 \mu\text{g/g}$.

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