A Rapid Method to Determine Bunker C Fuel Oil in Marine Organisms

by NORMAN L. MORGAN

California Department of Fish and Game
Fish and Wildlife Water Pollution Control Laboratory
Rancho Cordova, Calif. 95670

A rapid method of analysis for Bunker C fuel oil in shellfish requiring less than four hours has been developed. Current methods (1-5) involve soxlet extractions and are for No. 2 fuel oil. These procedures are quantitative but time-consuming (59 hours). By the method presented here, Bunker C fuel oil has been demonstrated in tissue at the 0.5 mg/kg level. The method is a pentane-methanol extraction utilizing a blendor, followed by adsorption chromatography. After evaporation, the sample is quantitatively analyzed for fuel oil by gas chromatography. The use of gas chromatography (6-9) for fuel oil analysis is well documented.

In this investigation no attempts were made to identify the individual hydrocarbons. The method is to quantitatively identify Bunker C fuel oil in marine organisms.

Apparatus and Materials

Solvents

All solvents were analytical grade and redistilled in all-glass stills or were equivalent to Mallinckrodt® nano-grade.

Adsorbent Column

The glass adsorbent column was 19 mm I.D. and 150 mm in length, with a teflon ultra max valve. A sintered glass filter disc supported the adsorbent (Van Waters and Rogers' Cat. No. 21491-320).

Silica Gel

Silica gel 60-200 mesh (J.T. Baker Cat. No. 3405) suitable for chromatographic use was activated at 120°C for 18 hours and then deactivated with 5% water (weight to weight).

Alumina

Two hundred mesh alumina (Alcoa F-20®) was activated at 250°C for 18 hours and deactivated with 5% water (weight to weight).

Gas Chromatography

The equipment consisted of a Varian aerograph series 1800, dual flame gas chromatograph, with linear temperature programmer

Bulletin of Environmental Contamination & Toxicology,
Vol. 14, No. 3 © 1975 by Springer-Verlag New York Inc.

and a 1 mv. recorder. The five feet by 1/8 inch O.D. glass columns were packed with 5% Apiezon L on 60/80 mesh, acid-base washed Gas Chrom P.

Waring Blendor

A Waring Blendor was used to homogenize samples. The standard neoprene gaskets were replaced with teflon. The plastic cover was lined with aluminum foil to eliminate contamination to the extracts.

Procedure

Extraction

The muscle tissue and methanol were chilled in a refrigerator prior to extraction to prevent volatilization of solvents. A 50-gram sample of the chilled tissue was cut into 1 cm pieces and blended with 100 ml of chilled methanol for one minute. This mixture was then extracted with 100 ml of n-pentane for two minutes.

The n-pentane was filtered into a 500 ml separatory funnel using a glass funnel fitted with a glass wool plug. The methanol remaining in the n-pentane was removed by washing three times with 100 ml of distilled water containing two grams of sodium sulfate.

Adsorption Chromatography

The adsorption column was prepared by adding the silica gel to a height of 55 mm over n-pentane. The alumina was added next (55 mm) to the combined height of 110 mm. The n-pentane was drawn off and eluted with an additional four column volumes of n-pentane and discarded. The sample extract was added to the adsorption column and eluted with four column volumes of n-pentane.

The eluate was concentrated on a vacuum evaporator to approximately 2 ml. Following the addition of 0.2 ml chloroform, the vacuum continued until a change in pressure indicated that the n-pentane had been removed.

Gas Chromatography

The column was cooled to 100°C. After injection, the 100°C column oven temperature was maintained for one minute. The oven temperature was programmed from 100°C to 250°C at 6° per minute. The 250°C oven temperature was held for 15 minutes. The injector and detector temperatures were at 260°C. The sample injections were on column. The nitrogen carrier gas flow was 20 ml/minute, the air flow was 250 ml/minute, and the hydrogen flow was 20 ml/minute.

Results and Discussion

Shellfish tissue was "spiked" with 10 micrograms per gram of Bunker C fuel and analyzed by this method. This resulted in a net recovery of 80 percent of the fuel oil. Shellfish collected from a Bunker C fuel oil spill area were analyzed by the soxlet extraction procedure and by the method presented here. The analytical results of both methods were identical.

Shellfish tissue uncontaminated with oil was analyzed by this method. This served as a reference for those gas chromatographic peaks of the control shellfish that could be attributed to reagents. A blank containing all reagents was also eluted through the adsorbent column, evaporated, and injected into the gas chromatograph. The majority of those peaks in the control tissue chromatogram corresponded to those found in the reagent blank. Therefore, the peaks in the control tissue chromatogram were from reagents.

Shellfish were collected from a Bunker C fuel oil spill area and analyzed by this method. The gas chromatographic pattern obtained was similar to the Bunker C fuel oil pattern. The relative contribution of the different carbon numbers and isomers was very nearly identical. The major difference was a decrease of the less soluble higher molecular weight hydrocarbons.

Shellfish collected three weeks after an oil spill were found to contain 2.0 mg/kg of Bunker C fuel oil and 4.0 mg/kg after five months. At ten months after the spill, fuel oil residues in shellfish were absent, except the gas chromatogram did exhibit a broad background of unresolved hydrocarbons.

The effects of weathering of some fuel oils and their identification by gas chromatography have been studied (10-12). To determine if weathered Bunker C could be determined by gas chromatography, Bunker C fuel oil was applied to etched glass rods and subject to tidal action for over 100 days. When a portion of this weathered fuel oil was analyzed by gas chromatography, no identifiable peaks were obtained, only a broad background of unresolved hydrocarbons were found. This suggests that shellfish tissue collected ten months after the spill may have contained weathered Bunker C fuel oil. Additional detection methods may be necessary to determine weathered Bunker C fuel oil in marine organisms.

Acknowledgments

The author is grateful to Mr. Steven J. Meith for sample preparation, to Mr. John M. Ladd for reviewing this manuscript, and to the staff of the Fish and Wildlife Water Pollution Control Laboratory for their technical assistance.

References

1. BLUMER, M., G. SOUZA, and J. SASS. Mar. Biol. 5, 195 (1970).

2. CHIA, F.S. Mar. Biol. 2(7), 105 (1971).

3. CLARK, R.C. JR. and M. BLUMER. Limnol. Oceanogr. 12, 79 (1967).

4. CLARK, R.C. JR. and J.S. FINLEY. Proceedings of the 1973 Joint Conference on Prevention and Control of Oil Spills. API/EPA/ USCG, Washington, D.C., 13. March (1973).

5. WOODIN, S.A., C.F. NYBLADE and F.S. CHIA. Mar. Poll. Bull., 3(9), 139 (1972).

6. ADLARD, E.R. J. of the Inst. of Petrol., 58(560), 63 (1972).

7. ADLARD, E.R., L.F. CREASER and P.H.D. MATTHEWS. Anal. Chem. 44, 64 (1972).

8. COLE, R.D. Nature, 233, 546 (1971).

9. RAMSDALE, S.J. and R.E. WILKINSON. J. of the Inst. of Petrol. 54, 326 (1968).

10. BLUMER, M. and J. SASS. Sci. 176, 1120 (1972).

11. BLUMER, M., M. EHRHARDT and J.H. JONES. Deep-sea Rev. 20, 239 (1973).

12. PARKER, C.A., M. FREEGARDE and C.G. HATCHARD. Water Pollution by Oil, London: Inst. of Petrol., p. 237 (1971).