Identification and Quantification of Water-soluble Hydrocarbons Generated by Two-cycle Outboard Motors

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Abstract. A 7.0 horsepower (HP) and a 10.0 HP outboard motor were operated at 3,500 ± 200 rpm and 1,700 ± 200 rpm, respectively for 30 min in a 160 L tank of tapwater. Exhaust hydrocarbons were concentrated by passage through a C18 reverse phase extraction column, and eluted with either ethylacetate or acetonitrile. Gas-liquid and/or high pressure liquid chromatographic procedures were used for identification and quantification of eight hydrocarbons. Identities were confirmed for seven of the compounds by GLC/mass spectrometry. Four additional hydrocarbons were tentatively identified with these procedures. Aromatic compounds composed the majority of the hydrocarbons detected; a few aliphatics were present in trace amounts.

In the U.S. during 1977, 500,000 new outboard motors were purchased, with a total of approximately 7 million motors in use. Average size of the motors was 44.4 horsepower (HP) (U.S. Census Bureau 1979). Compared with other types of internal combustion engines, outboard motors are inefficient, releasing significant amounts of raw fuel mixture and fumes into the water (Muratori 1968; Stewart and Howard 1968; Ferren 1970; Jackivicz and Kuzminski 1973b). The chemical composition of gasolines used in outboard motors, as well as other refined fuels and crude oils, has been extensively studied (Howard and Ferguson 1961; Martin and Winters 1963; Schwartz and Brasseaux 1963; Snyder et al. 1963; Sanders and Maynard 1968; Coleman et al. 1973; Papazova and Pankova 1975; Di-Corcia et al. 1978). Because there is a substantial amount of gasoline in the exhausts of outboard motors, these exhausts contain many of the same hydrocarbons that are found in gasolines and oils. English et al. (1963) identified major pollutants in exhausts as nonvolatile oils (the lubricating oils in the fuel mixture), volatile oils (the gasoline in the fuel mixture), phenols, and lead. They did not identify specific hydrocarbons, nor the classes of hydrocarbons. Kuzminski et al. (1974) identified six water-soluble components of outboard motor exhausts, but they gave no quantitative data. Gschwend (1979) examined the temporal variations of volatile organic compound concentrations in coastal seawater from Vineyard Sound, MA., and found C2- and C3-benzenes were the most abundant compounds and their concentrations were 2 to 10 times higher than average immediately after summer weekends in which tourist and recreational activities were greatest. This corresponded to periods in which motorboats were used most heavily. Studies to determine the compounds in outboard motor exhausts are needed (Jackivicz and Kuzminski 1973a; Liddle and Scorgie 1980). Therefore, this preliminary study focused upon identification and quantification of water-soluble hydrocarbons in these exhausts.

Materials and Methods

Outboard Motors: Two two-cycle outboard motors were selected for study; a 7.0 HP 1972 single cylinder, air-cooled motor with a recycling system for re-ignition of unburned crankcase material, and a 10.0 HP 1954 two cylinder, water-cooled motor which exhausted crankcase residuals directly into the water. Both motors used the same 50:1 gasoline:oil fuel mixture and were in good operating condition. The gasoline was regular grade fuel obtained locally; a 50:1 two-cycle motor lubricant was used. Each motor was placed into a clean stainless steel tank

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filled to 160 L with tapwater and run for 30 min. The 7.0 HP motor was operated at 3,500 ± 200 rpm for 30 min and the 10 HP model at 1,700 ± 200 rpm, because operation at higher rpm's resulted in excessive agitation and water loss from the tank. Fuel consumption was measured volumetrically.

Sample Preparation: Water samples were taken from the bottom of the tank via a spigot, and filtration through a 0.22 nm Millipore filter followed by a 0.22 nm Millipore filter was started immediately to remove emulsified components. Hydrocarbons remaining in the aqueous phase after filtration were designated water-soluble fractions. All samples were kept refrigerated at 4°C in tightly sealed amber bottles until analysis, which was completed within 8 hr after collection. Water-soluble fractions were concentrated by a column containing pellicular silica coated with octadecasilane (C8, available from Waters Associates, Milford, MA under the tradename Sep-Pak). Each column was conditioned to the aqueous phase before use by passing 1 ml of ethylacetate, followed by 5 ml of distilled water through the column. Exhaust water samples (400 to 600 ml) were forced through the column. Hydrocarbons were eluted with 2 ml of ethylacetate or acetonitrile. Since solvent peaks frequently mask unknown peaks, the use of two solvents, each having a different retention time, was necessary. All solvents were spectral grade (Burdick and Jackson, Muskegon, MI). During filtration, a Sep-Pak was placed in the vacuum line to collect volatiles which might have been lost from the sample. These were eluted in the same manner as the dissolved hydrocarbons.

Hydrocarbon Concentration Determinations: A Beckman Model GC 45 gas-liquid chromatograph (GLC) equipped with a flame ionization detector was used for some analyses. A 244 cm stainless steel column (2 mm I.D.) was packed with 10% 1,2,3-Tris(2-cyanoethoxy)propane on 100/120 Chromosorb PAW (Supelco, Inc., Bellefonte, PA). Pertinent operating conditions were N2 column = 20 ml/min, H2 = 44 ml/min, air = 240 ml/min, carrier makeup = 60 ml/min, inlet temperature = 170°C, detector temperature = 170°C, and detector line temperature = 205°C. All analyses were performed isothermally at 80°C ± 2°C. Sample injection volumes were 0.2 µl.

An Altex Model 322 MP high pressure liquid chromatograph (HPLC) was also used, and the column (25 cm long with 4.6 mm I.D.) was packed with Lichrosorb C18 stationary phase on 10 µm support material (Altex Associates, Berkeley, CA). The column was protected by a guard column packed with Chromosorb LC-4 coated with C18 stationary phase (Johns-Manville, Denver, CO). A 70:30 ratio of acetonitrile and water at a flow rate of 1.5 ml/min was used as the mobile phase. Peaks were detected with a fixed wavelength ultraviolet detector operated at 254 nm. Samples were injected onto the chromatographic column with a 20 µl fixed loop injection valve. Data from both chromatographs were fed into a Spectra-Physics SP4000 data system and quantified by co-chromatography with known standards. Calibration was checked daily and tapwater and solvent blanks were run and subtracted from sample concentrations. Identification of the components was determined, in part, by comparison of retention times of the unknowns with those of known standards (Alttech Associates, Arlington Heights, IL) and by peak enhancement techniques.

To obtain molecular weights of the unknown compounds, 0.5 µl aliquots of the sample eluate were injected into a Varian/MAT 112S double focussing magnetic mass spectrometer equipped with a Varian 3700 gas chromatograph. A glass column 274 cm long by 2 mm I.D. was packed with 10% 1,2,3-Tris(2-cyanoethoxy)propane on 100/120 PAW. The mass spectrometer and gas-liquid chromatograph were interfaced with a glass jet-faced separator. The data system employed was an SS 200 Varian Spectral System. Pertinent operating data were: He carrier gas = 24 ml/min, injector temperature = 150°C, column temperature = 80°C, detector temperature = 200°C, and separator temperature = 190°C.

Results

Figure 1 shows a gas-liquid chromatogram of the hydrocarbons in exhausts from the 7.0 HP motor. Chromatograms similar in pattern, but with larger peak areas, were obtained from 10.0 HP motor exhausts. Seven different peaks, corresponding to seven individual water-soluble hydrocarbons were detected using GLC (peaks 3, 4, 6, 7, 9, 10, and 11). Peaks 1, 5, and 8 each contained a pair of compounds which could not be resolved by GLC. The concentration of benzene (peak not shown in Figure 1) was determined by separate chromatograms of concentrated exhaust hydrocarbons eluted with acetonitrile. Identified compounds and their concentrations are listed in Table 1; values are corrected for different recovery efficiencies determined for each compound in earlier experiments. Recoveries ranged from 46 to 69% (x = 62%). Recovery efficiencies were determined by using analytical standards under conditions similar to those in the experiments. Recovery experiment procedures have been described previously (Montz 1980; Puyear et al. 1981). Concentrations for the aromatic compounds obtained by HPLC were similar to those found by GLC.

Mass spectral analysis verified the identity of methylbenzene, ethyl-benzene, 1,2-dimethylbenzene, 1-methyl-2-ethyl-benzene, 1,2,4-trimethylbenzene, 1,2,3-trimethyl-benzene and benzene. Tentative identification was made for four additional hydrocarbons. 1,3-dimethyl-benzene and 1,4-dimethyl-benzene which had identical molecular weights and, using the chromatographic procedures with 1,3- and 1,4-dimethyl-benzene standards, had identical retention times. Thus, it was not determined whether one or both of these compounds were present in peak number 6 in Figure 1. The total concentration is reported in Table 1. Peak number 9 (Figure 1) also contained either one or both of a pair of hydrocarbons (1-methyl-3-ethylbenzene, 1-methyl-4-ethyl-benzene) having the same molecular weight and identical retention times. Again, the presence of one or both of these compounds was suggested by mass spectrometry. A third peak, number 1 in Figure 1, may have contained decane and dodecane, because the retention time of this peak matched that of corresponding...