Quantification of Water-Soluble Gasoline Fractions Using A Radioisotopic Standard With Direct Aqueous Injection-Gas Chromatography

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The increased contamination of aquatic environments with petroleum has necessitated the development of analytical methods to evaluate, qualitatively and quantitatively, the extent of such hydrocarbon pollution. Although fluorescence spectroscopy (GORDON et al. 1974) and infrared spectrophotometry (MALLEVIALLE 1974) have been used, gas liquid chromatography (GLC) has been the most widely used technique for analysis of aqueous solutions of petroleum hydrocarbons.

When measuring volatile organic matter in water by GLC, direct aqueous injection should be used whenever possible to prevent both the loss of some components and the introduction of extraneous peaks that may result from such concentration techniques as solvent extraction (ASTM 1974). NICHOLSON and MERESZ (1975) recommended direct aqueous injection-GLC for the analysis of volatile, halogenated organics in water.

A new GLC technique was devised to determine the amounts of individual water-soluble gasoline fractions (WSGFs) present in aqueous solutions. The technique described here permits direct aqueous injection of water samples without the problems associated with solvent extraction techniques (JELTES and VELDINK 1967, LYSYJ and RUSSELL 1974, MALLEVIALLE 1974), and provides more accurate quantification.

MATERIALS AND METHODS

Preparation of Solutions of WSGFs

Solutions of water-soluble components of gasoline were prepared by pipetting small quantities (0.1 to 100 mℓ) of gasoline or its individual fractions (benzene, toluene, xylenes) into 1-ℓ of distilled water in a 1-ℓ flask. The resulting mixtures were then stirred rapidly for 3 hr on a magnetic stirrer.

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The solutions were poured into 1-ℓ separatory funnels and allowed to separate for 16-18 hr. Following separation, the lower 950 mℓ of each solution were removed to a 1-ℓ flask and mixed for 2 hr to disperse the water-soluble components.

Gas Chromatography

A Barber-Colman 5000 (Nuclear Chicago, Chicago, IL) gas chromatograph with a flame ionization detector (f.i.d.) was used for analysis of water-soluble components in these solutions. Six-foot glass columns (2 mm I.D.) packed with 5% SP-1200/1.75% Bentone 34 on 100/120 Supelcoport (Supelco, Inc., Bellefonte, PA) were used for separation of the water-soluble components. The carrier gas was nitrogen. All analyses were done isothermally under the following conditions: Column temperature, 80°C; detector temperature, 220°C; injector temperature, 225°C; nitrogen flow rate, 25 mℓ/min. Samples (1-3 μℓ) were injected using a 5-μℓ Pressure-Lok liquid syringe with a reproducibility adapter (Model CG-130, Precision Sampling Corp., Baton Rouge, LA).

Qualitative analysis. Solutions of WSGFs were qualitatively analyzed by spiking the experimental solutions with analytical standards (Aromatic Hydrocarbons, Kit No. 25A, Polyscience Corporation, Niles, IL). Samples of the spiked solutions were injected onto the chromatographic column and the chromatogram was checked for peak enhancement or additional peaks to determine if the standard was one of the original water-soluble components. This procedure, discussed by ETTRE and ZLATKIS (1967), was used in combination with comparison of retention times with those of the known standards for identification of the water-soluble fractions in the water-gasoline mixtures.

Quantitative analysis. Three 1-μℓ samples of H^3 toluene (specific activity 1.02 mCi/mmol, New England Nuclear, Boston, MA) were added to each of three separate vessels containing 10 mℓ of distilled water. From each vessel, 2 1-μℓ samples were added to 6 mℓ of scintillation cocktail (Spectrafluor, Amersham/Searle Corp., Arlington Hts., IL) in separate 20 mℓ glass scintillation vials. These samples were then counted in a Packard Tri-Carb Scintillation Spectrometer to determine the amount of toluene present. Knowing the specific activity of the H^3 toluene, the spectrometer efficiency (58%), Avogodro's number, and 3.7×10^{10} dps/Ci, the results obtained in counts per minute were converted to molecules of toluene per μℓ sample.

Three separate 1-μℓ samples of the 1-μℓ H^3 toluene/10-mℓ water solutions were injected into the gas chromatograph. The area of the H^3 toluene peaks were measured on the chromatograms by planimetry (Gelman Planimeter). This area also represents the amount of H^3 toluene present in each of the 1-μℓ samples. If the number of molecules determined by the scintillation procedure is divided by the peak area of the chromatogram, one then knows the number of molecules per unit peak area for toluene.

This entire procedure was repeated 4 times to obtain an average number of molecules per unit peak area for toluene (Table 1). The mean value was used to determine the quantities of the other hydrocarbons present in the WSGF.

TABLE 1

Determination of the number of molecules (M) of H^3 toluene/unit peak area of chromatogram. Twelve separate samples of 1 μℓ H^3 toluene/10 mℓ H_2O were analyzed (3 on each of 4 dates). CPM= counts per minute; PA = peak area.

Date	CPM	PA ($in^2 \times 10^{-3}$)	M x 10^{13}/PA
1/18/76	352	11.5	1.40
	326	10.5	1.42
	375	14.3	1.20
1/9/76	139	8.0	0.79
	77	5.5	0.64
	165	8.5	0.91
12/28/75	154	9.0	0.79
	306	22.0	0.64
	76	3.5	0.99
11/9/75	280	9.0	1.42
	445	17.0	1.20
	325	19.0	0.78

Mean = $1.02 \pm 0.30 \times 10^{13}$ molecules/$in^2 \times 10^{-3}$

The method of comparing each peak with one standard peak is recommended if the concentration of only a limited number of components is required (ETTRE and ZLATKIS 1967). This method is in common use by petroleum hydrocarbon investigators (BOYLAN and TRIPP 1971, FARRINGTON and QUINN 1973). Provided that the external standard is chromatographed using identical operating conditions to those used for the unknowns, and provided that the compounds of interest are structurally similar and have relatively similar retention times, then the error involved will be at most 5% (W. E. GEIGER, personal communication). The compounds of interest in this study are benzene, toluene (methyl benzene), and xylenes (dimethyl benzenes) with retention times of 2-12 min.

The number of molecules per unit peak area determined for the toluene standard as described above was used to determine the concentration of individual components in the following solutions of WSGFs:

Gasoline - 1, 10, 20, 50 and 100 mℓ/ℓ water
Benzene - 1.0 and 1.59 mℓ/ℓ water
Toluene - 0.30 and 0.86 mℓ/ℓ water
Xylenes - 0.50 and 1.64 mℓ/ℓ water

Combinations:

.2 mℓ benzene, .2 mℓ toluene, and .2 mℓ xylenes/ℓ water
.2 mℓ benzene and .2 mℓ toluene/ℓ water
.2 mℓ benzene and .2 mℓ xylenes/ℓ water
.2 mℓ toluene and .2 mℓ xylenes/ℓ water

These solutions were chosen for analysis because they were used in previous toxicity (BERRY and BRAMMER 1976) and respiratory response (BERRY et al 1976) experiments with mosquito larvae. For each of the solutions examined, 3 samples were prepared as described above and 2(1-, 2-, or 3-μℓ) subsamples of each solution were subjected to analysis.

Detector response to a range of concentrations encompassing the levels tested above was examined. Mixtures of 1 μℓ samples of H^3 toluene, benzene and xylenes diluted in 25, 50, 75 and 100 mℓ of water were prepared. Three 1 μℓ samples of each dilution were analyzed gas chromatographically, and the resulting peak areas were measured. Detector response was linear for each of these monoaromatics.

RESULTS AND DISCUSSION

Comparison of retention times of unknown components with those of known standards, in combination with the technique of peak enhancement, demonstrated the presence of six monoaromatic hydrocarbons in solutions of water-soluble gasoline fractions. Under identical operating conditions, the variability in retention times of these compounds was at most 2%. Fig. 1 shows the appearance of a typical chromatogram produced from the analysis of the water-soluble fraction of 1 mℓ gasoline/ℓ water.

Quantities of the water-soluble components of gasoline determined from peak areas of chromatograms of various gasoline-water mixtures are reported in Table 2. Because of their small quantities and their relatively poor separation by the chromatographic column, ethylbenzene and the three isomers of xylene were combined for quantitative analysis. Thus the term xylenes, as used in this report, refers to ethylbenzene as well as p-, m-, and o-xylenes. The last column in Table 2 demonstrates an insignificant change in water-soluble aromatics when the amount of gasoline/ℓ water is increased 100-fold. This suggests that

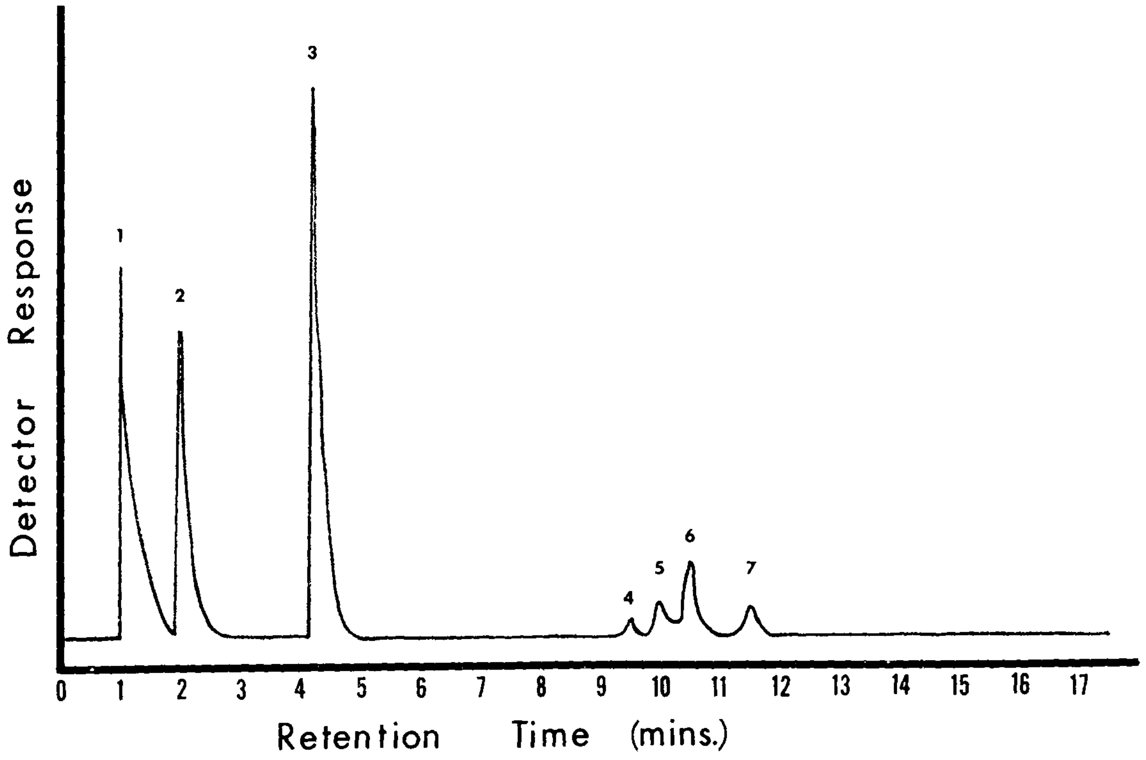

Fig. 1. A typical chromatogram of the water-soluble gasoline fractions in 1 mℓ gasoline/ℓ water. A 2μℓ sample was analyzed under operating conditions described in the text. Compounds by number: 1) water, 2) benzene, 3) toluene, 4) ethylbenzene, 5) p-xylene, 6) m-xylene, and 7) o-xylene.

TABLE 2

Quantification of water-soluble components of gasoline. Quantities determined from peak areas of chromatograms of various mixtures of gasoline/ℓ water are reported as molecules (M)/ℓ water and parts per million (ppm). Peak areas reported are the mean of 3 separate sample mixtures.

Gasoline/		Peak Area ± SE				M x 10^{19}/		
liter water	Component	in^2 x 10^{-3}		CM^2 x 10^{-3}		ℓ water	ppm	± SE
1 mℓ	Benzene	4.67	0.94	11.86	2.39	4.76	1.43	0.29
	Toluene	8.50	1.06	21.59	2.69	8.67	2.60	0.33
	Xylenes	9.50	0.35	24.13	0.89	9.69	2.91	0.11
10 mℓ	Benzene	7.00	0.35	17.78	0.89	7.14	2.14	0.11
	Toluene	10.13	0.27	25.73	0.69	10.33	3.10	0.08
	Xylenes	7.19	0.66	18.26	1.68	7.33	2.20	0.20
20 mℓ	Benzene	5.00	0.18	12.70	0.46	5.10	1.53	0.06
	Toluene	4.88	0.44	12.39	1.12	4.98	1.49	0.14
	Xylenes	4.50	0.18	11.43	0.46	4.59	1.38	0.06
50 mℓ	Benzene	12.50	0.88	31.75	2.24	12.75	3.83	0.27
	Toluene	10.00	0.88	25.40	2.24	10.20	3.06	0.27
	Xylenes	4.88	0.09	12.40	0.23	4.98	1.49	0.03
100 mℓ	Benzene	12.25	0.71	31.12	1.80	12.50	3.75	0.22
	Toluene	9.75	1.06	24.76	2.69	9.95	2.99	0.33
	Xylenes	5.38	1.50	13.67	3.81	5.49	1.65	0.46

TABLE 3

Quantification of water-soluble amounts of aromatics which comprise the water-soluble fractions of gasoline. Quantities determined from peak areas of chromatograms of various mixtures of aromatics/ℓ water are reported as molecules (M)/ℓ water and parts per million (ppm). Peak areas reported are the mean of 3 separate sample mixtures.

	Peak Area ± SE				$M \times 10^{19}$/		
Aromatic/liter water	$in^2 \times 10^{-3}$		$CM^2 \times 10^{-3}$		ℓ water	ppm ± SE	
1.59 mℓ Benzene	193.50	23.69	491.49	60.17	197.37	59.27	7.26
1.00 mℓ Benzene	42.00	0.71	106.68	1.80	42.84	12.86	0.22
0.86 mℓ Toluene	70.25	0.53	178.44	1.35	71.66	21.52	0.16
0.30 mℓ Toluene	32.50	4.24	82.55	10.77	33.15	9.95	1.30
1.64 mℓ Xylenes	45.50	1.77	115.57	4.50	46.41	13.94	0.54
0.50 mℓ Xylenes	25.87	1.06	65.71	2.69	26.39	7.92	0.33
0.20 mℓ Benzene,	13.50	0.00	34.29	0.00	13.77	4.14	0.00
+ 0.20 mℓ Toluene,	11.50	0.35	29.21	0.89	11.73	3.52	0.11
+ 0.20 mℓ Xylenes	13.00	1.41	32.02	3.58	13.26	3.98	0.43
0.20 mℓ Benzene,	20.00	0.71	50.80	1.80	20.40	6.13	0.22
+ 0.20 mℓ Toluene	20.00	0.71	50.80	1.80	20.40	6.13	0.22
0.20 mℓ Toluene,	12.25	0.95	31.12	2.41	12.50	3.75	0.29
+ 0.20 mℓ Xylenes	14.63	0.09	37.16	0.23	14.92	4.48	0.03
0.20 mℓ Benzene,	20.25	0.18	51.44	0.46	20.66	6.20	0.06
+ 0.20 mℓ Xylenes	16.50	0.35	41.91	0.89	16.83	5.05	0.11

the partitioning of these compounds between gasoline and water over the 100 mℓ range examined does not permit a significant increase in the amount of aromatics that go into solution.

Table 3 contains the results of the quantification of water-soluble amounts of aromatics comprising the water-soluble fractions of gasoline. The large differences in the amounts of specific aromatics that go into solution when the same initial quantity is added per ℓ water is probably due to partitioning differences. That is, toluene partitions differently in association with benzene than it does when combined with xylenes.

Because of the extreme sensitivity of the f.i.d. to toluene, it was impossible to use an undiluted standard. Toluene is not soluble in water in all proportions. Therefore, direct injection of a diluted toluene standard would not permit accurate quantification.

The use of a radioisotopic standard permits one to determine the amount of toluene in the diluted standard by liquid scintillation counting, and thus enables one to quantitatively determine the relationship between peak area and sample concentration. This method, when employed with direct aqueous injection-GLC, provides an easy, accurate technique for the quantification of water-soluble organics.

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