

NRL Report 6178

**Mass Spectrometric Determination
of the Aliphatic and Aromatic Content
of a Hydrocarbon Mixture**

F. E. SAALFELD

*Physical Chemistry Branch
Chemistry Division*

November 12, 1964



**U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.**

ABSTRACT

A simplified mass spectrometric technique has been devised for determining the aromatic content in hydrocarbon mixtures of the type that have been recovered from adsorptive carbon samplers exposed in the atmospheres of nuclear submarines. The method is based on the summation of ion currents at mass-to-charge ratios (m/e) of 27, 28, 29, 41, 43, and 57 for aliphatic hydrocarbons and 39, 51, 52, 77, 78, 91, 92, 105, 106, 119, 120, 133, and 134 for aromatic hydrocarbons. The mass spectrometric results agree reasonably well with the Fluorescence Indicator Adsorption analyses of the same samples.

While, due primarily to cost and operational complexity, no available mass spectrometers are suitable for shipboard operation, future developments in the field of mass spectrometry should be carefully observed for advances that make such use possible.

PROBLEM STATUS

This is a final report on this phase of the problem; work on other phases of the problem is continuing.

AUTHORIZATION

NRL Problem C07-02
Project RR 001-01-43-4804

Manuscript submitted September 17, 1964.

MASS SPECTROMETRIC DETERMINATION OF THE ALIPHATIC AND AROMATIC CONTENT OF A HYDROCARBON MIXTURE

INTRODUCTION

The accumulation of organic vapors and gases in closed habitable spaces such as nuclear submarines and, to a lesser extent, spacecraft is both a nuisance and a hazard. These vapors contribute a disagreeable odor and, more seriously, may contain compounds which exceed maximum allowable concentrations for continuous exposure. The bulk of the compounds identified have been hydrocarbons evolved from paints, fuels, or solvents used in the confined space (1).

While aliphatic hydrocarbons are of limited toxicity, the hydrocarbon mixture collected by carbon samplers on nuclear submarines has always contained an appreciable fraction of aromatic hydrocarbons (2). The presence of these compounds even in low concentrations constitutes a recognized hazard to personnel subjected to extended exposure (3).

None of the various instruments currently in use in nuclear submarines for atmosphere analysis or monitoring are capable of measuring the aromatic hydrocarbon content of the atmosphere, although instrumentation is being developed for total hydrocarbon analysis based on gas chromatographic techniques (4).

Mass spectrometric analysis has been advanced as a possibility for the determination of the aromatic content of hydrocarbon mixtures such as are found in nuclear submarine atmospheres but, at the present, there are no mass spectrometers suitable for shipboard use due to their cost and complexity. Developments underway elsewhere, primarily in conjunction with upper atmosphere sampling devices employing rocket-borne mass spectrometers, offer promise that these drawbacks may be reduced or eliminated.

THEORETICAL

Mass spectral analysis of organic compounds is based on the fragmentation of the organic molecules into characteristic ion fragments by means of a controlled intensity electron beam followed by determination of the relative abundance of fragments at various mass-to-charge (m/e) ratios. A neutral radical is formed concurrently with the positive ion but is not detectable by the collector system of the mass spectrometer. Every compound behaves in a characteristic manner; the relative abundances of the charged particles of various masses serve for identification and the size of the largest ion current serves for the quantitative estimation of the parent compound.

For application to aromatic class-analysis, the property of aromatic compounds to produce certain specific mass numbers in high yield is utilized. Aliphatic compounds produce another series of primary mass fragments. As defined in this work, any compound containing a benzene ring (either isolated or fused) in its molecular structure is considered to belong to the aromatic class. Any hydrocarbon lacking such a group is considered to be in the aliphatic class.

The three most abundant mass-to-charge ratios of some representative compounds that have been identified in the atmospheres of nuclear submarines are presented in Table 1. There is no similarity in the major fragments produced by the two functional classes of

Table 1
The Three Most Abundant Mass Spectral Peaks of Some
Hydrocarbons Identified in Submarine Atmospheres*

Compounds	Major Ion Fragments (m/e)		
	(1)	(2)	(3)
Aromatic			
Benzene (C ₆ H ₆)	78	52	51
Toluene (C ₇ H ₈)	91	92	39
Xylenes (C ₈ H ₁₀)	91	106	105
Ethylbenzene (C ₈ H ₁₀)	91	106	51
Ethyltoluenes (C ₉ H ₁₂)	91	120	39
Trimethylbenzenes (C ₉ H ₁₂)	105	120	119
n-Propylbenzene (C ₉ H ₁₂)	91	120	92
Diethylbenzenes (C ₁₀ H ₁₄)	119	105	134
Aliphatic			
n-Butane (C ₄ H ₁₀)	43	29	27
Isobutane (C ₄ H ₁₀)	43	41	42
n-Pentane (C ₅ H ₁₂)	43	42	41
Isopentane (C ₅ H ₁₂)	43	42	41
Cyclopentane (C ₅ H ₁₀)	42	70	55
n-Hexane (C ₆ H ₁₄)	57	43	41
Cyclohexane (C ₆ H ₁₂)	56	84	41
n-Heptane (C ₇ H ₁₆)	43	41	57
2,2,4-Trimethylpentane (C ₇ H ₁₆)	43	57	41
n-Octane (C ₈ H ₁₈)	43	57	29
n-Nonane (C ₉ H ₂₀)	43	57	41
n-Decane (C ₁₀ H ₂₂)	43	57	41
n-Undecane (C ₁₁ H ₂₄)	43	57	41
n-Dodecane (C ₁₂ H ₂₆)	43	57	41

*Relative abundance data obtained from American Petroleum Institute Research Project 44 reports.

compounds. The aromatic compounds listed give only 11 major m/e ratios, while the aliphatic compounds listed give 10 different ratios. There is some interference between hydrocarbon classes at masses of lesser importance but this is small compared to the total spectrum. As an example, *n*-heptane (C_7H_{16}) has an ion current peak at m/e 91, an aromatic fragment, but the contribution to this m/e ratio is only 0.01% of the aliphatic ion current at m/e 43 and 0.007% of the total ion current spectrum. Similarly ethylbenzene makes a contribution to the m/e 43 ion current but the contribution is only 0.19% of the ion current at m/e 91 and 0.002% of the total ion current. The three ion fragments listed in Table 1 for ethylbenzene account for 55% of the total spectrum, and those listed for *n*-heptane account for 44% of its spectrum (5). These examples are typical.

The fact that hydrocarbons of different classes form ions at different m/e ratios has been used in the petroleum industry for some time for class or "type" analysis (6). The procedure employed there is too involved for use on board submarines by nontechnical personnel, and has consequently been simplified in the following presentation.

EXPERIMENTAL PROCEDURE

The mass spectral analysis of organic mixtures typical of those found in nuclear submarines takes place in five basic steps.

1. A mass spectrometer calibration or sensitivity determination is made using *n*-butane as a standard. The ion current at mass 43 under normal operating conditions of the mass spectrometer is determined for a known pressure of *n*-butane.

2. The relative sensitivity of the system to the two hydrocarbon classes under consideration here is determined. This information can be found experimentally or obtained from data in the literature. Brown (7) has prepared a series of graphs for hydrocarbon classes in various molecular weight ranges which relate the sensitivity (ion current per micron pressure) for the characteristic aliphatic and aromatic mass numbers (m/e ratios) to that of the mass 43 peak of *n*-butane under equivalent conditions (ionizing current and excitation voltage) in the spectrometer. A condensation of this data is presented in Fig. 1 for C_7 , C_8 , C_9 , and C_{10} aromatic and aliphatic hydrocarbons. Similar calibration curves are available for other hydrocarbon groupings or classes. To use this data properly it is necessary to know the average number of carbon atoms per molecule in the mixture; this can be determined experimentally by conventional techniques (i.e., vapor density determinations). For these hydrocarbon mixtures, which were obtained by desorption of carbon exposed in the atmosphere of nuclear submarines, an average of nine carbon atoms per molecule was assumed for both the aliphatic and aromatic fractions. As is evident in Fig. 1, the simplified method described here is relatively insensitive to this parameter provided the average number of carbon atoms per molecule is similar for the two classes of hydrocarbons.

3. The unknown sample is introduced into the mass spectrometer and the sum of the ion currents associated with the characteristic aliphatic and aromatic currents is determined. The aliphatic ion currents are summarized at m/e ratios of 27, 28, 29, 41, 43, and 57; the aromatic ion currents of interest are at m/e ratios of 39, 51, 52, 77, 78, 91, 92, 105, 106, 119, 120, 133, and 134. These two sums could be presented automatically at the end of a run with the aid of a simple computer attachment.

4. The summed ion currents for the two individual groupings, aliphatic (ΣR) and aromatic (ΣAr), are converted to pressure readings by dividing by the sensitivity obtained for the C_9 hydrocarbons shown in Fig. 1 at the measured *n*-butane sensitivity.

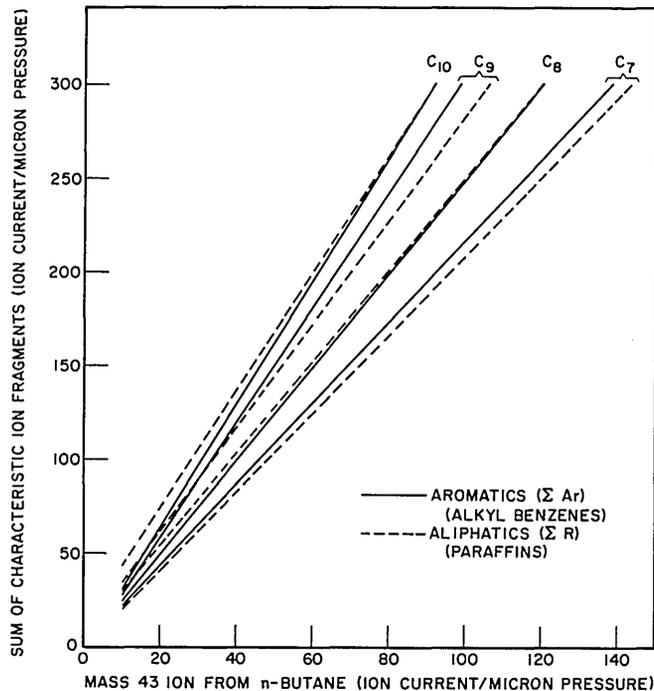


Fig. 1 - Sensitivity to the sum of characteristic aromatic and aliphatic ion fragments relative to sensitivity to mass 43 ion of n-butane

5. The two pressure readings are converted to relative liquid volumes by multiplying by the factors 1.78 and 1.33 for the aliphatic and aromatic types, respectively, which relate vapor densities to liquid densities (7). The relative liquid volumes can be converted readily to volume percents of aromatic and aliphatic compounds in the mixture.

RESULTS

The above procedure was checked experimentally by the analysis of a series of hydrocarbon mixtures which had been desorbed from carbon samplers exposed in operational nuclear submarines and which had previously been analyzed by a conventional technique, Fluorescence Indicator Adsorption (FIA), for aromatic and aliphatic content. All mass spectra were obtained on a CEC Model 21-103c mass spectrometer equipped with a 21-084 all-glass heated inlet system. The excitation energy was 70 volts and the ionizing current was $10\mu\text{amp}$.

The comparison of the mass spectrometric and FIA analyses is given in Table 2. The two sets of results, with one exception, are generally in excellent agreement. The reason for the one discrepancy is not apparent. Analytical time for each sample by the mass spectrometric technique, including that for manual handling of the data and calculation of results, was less than 15 minutes.

CONCLUSIONS

These analyses were carried out with a general purpose research instrument on hydrocarbon samples that had been adsorbed on carbon and later desorbed. It is conceivable that

Table 2
 Type Analysis of Hydrocarbon Samples from Nuclear
 Submarine Atmospheres by the Mass Spectrometric and
 Fluorescent Indicator Adsorption Techniques

Sample No.	Analytical Method			
	Mass Spectrometer		Fluorescent Indicator Adsorption	
	Aromatic (%)	Aliphatic (%)	Aromatic (%)	Aliphatic (%)
214	29.9	70.1	29.6	70.4
221	27.1	72.9	25.2	74.8
228	25.9	74.1	36.8	63.2
242	25.5	74.5	23.0	76.5
N-554	36.5	63.5	37.0	63.0
N-662	25.0	75.0	23.1	77.0
N-689	24.0	76.0	23.7	76.3

pecially constructed mass spectrometers could be designed to handle directly the air samples containing hydrocarbon contaminants and programmed to give direct readout of the analytical results.

These experiments indicate the feasibility of applying mass spectrometric techniques to characterize the aromatic content of hydrocarbon samples of the type encountered in nuclear submarine atmospheres. It should be possible to extend this procedure to the analysis of other classes of compounds having identifiable characteristics, e.g. halogen-containing compounds, olefins, etc.

At the present state of the art, it would not be practical to put a mass spectrometer on a submarine for routine monitoring purposes due to its excessive cost, specialized operational requirements involving electronics and high vacuum technology, and the necessity for extensive sample preparation involving adsorption and desorption from carbon samplers. Advances in the art of mass spectrometry are being made continuously so that this situation may change radically within the next few years and a suitable design for shipboard use may evolve.

ACKNOWLEDGMENT

The author is indebted to Dr. J.E. Johnson and Mr. A.J. Chiantella of the Fuels Branch for supplying the hydrocarbon samples and results of the FIA analyses.

REFERENCES

1. Piatt, V.R., Ramskill, E.A., and White, J.C., "Chemical Constituents of Submarine Atmospheres," NRL Report 5456, Jan. 1960
2. Johnson, J.E., "Organic Contaminants, Sampling and Analysis," Chap. 7 in "Third Annual Progress Report, The Present Status of Chemical Research in Atmosphere Purification and Control in Nuclear-Powered Submarines," Carhart, H.W., and Piatt, V.R., Editors, NRL Report 6053, Dec. 31, 1963
3. Carhart, H.W., and Piatt, V.R., "Chemical Constituents of Nuclear Submarine Atmospheres," Chap. 8 in "Third Annual Progress Report, The Present Status of Chemical Research in Atmosphere Purification and Control in Nuclear-Powered Submarines," Carhart, H.W., and Piatt, V.R., Editors, NRL Report 6053, Dec. 31, 1963
4. Johnson, J.E., Umstead, M.E., and Smith, W.D., "Nuclear Submarine Atmosphere, Part 2 - Development of a Total Hydrocarbon Analyser," NRL Report 6064, Jan. 30, 1964
5. "Mass Spectral Data," American Petroleum Institute Research Project 44
6. Brown, R.A., Taylor, R.C., Melpolder, F.W., and Young, W.S., *Anal. Chem.* 20:5 (1948)
7. Brown, R.A., *Anal. Chem.* 23:430 (1951)

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY <i>(Corporate author)</i> U.S. Naval Research Laboratory Washington, D.C. - 20390		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP	
3. REPORT TITLE MASS SPECTROMETRIC DETERMINATION OF THE ALIPHATIC AND AROMATIC CONTENT OF A HYDROCARBON MIXTURE			
4. DESCRIPTIVE NOTES <i>(Type of report and inclusive dates)</i> A final report on one phase of the problem.			
5. AUTHOR(S) <i>(Last name, first name, initial)</i> Saalfeld, Fred E.			
6. REPORT DATE November 12, 1964		7a. TOTAL NO OF PAGES 9	7b. NO. OF REFS 7
8a. CONTRACT OR GRANT NO. NRL Problem C07-02		9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6178	
b. PROJECT NO. RR 001-01-43-4804		9b. OTHER REPORT NO(S) <i>(Any other numbers that may be assigned this report)</i>	
c.			
d.			
10. AVAILABILITY/LIMITATION NOTICES Unlimited availability - Copies available from OTS - \$.50			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Dept. of the Navy (Office of Naval Research)	
13. ABSTRACT <p>A simplified mass spectrometric technique has been devised for determining the aromatic content in hydrocarbon mixtures of the type that have been recovered from adsorptive carbon samplers exposed in the atmospheres of nuclear submarines. The method is based on the summation of ion currents at mass-to-charge ratios (m/e) of 27, 28, 29, 41, 43, and 57 for aliphatic hydrocarbons and 39, 51, 52, 77, 78, 91, 92, 105, 106, 119, 120, 133, and 134 for aromatic hydrocarbons. The mass spectrometric results agree reasonably well with the Fluorescence Indicator Adsorption analyses of the same samples.</p> <p>While, due primarily to cost and operational complexity, no available mass spectrometers are suitable for shipboard operation, future developments in the field of mass spectrometry should be carefully observed for advances that make such use possible.</p>			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Mass spectrometry Ion currents Nuclear submarine atmospheres Carbon samplers Mass-to-charge ratio Aromatic hydrocarbons Aliphatic hydrocarbons Ion fragments Organic vapors and gases Class-analysis Excitation energy Fluorescence Indicator Adsorption Hydrocarbon mixtures						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.
- 2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.
- 2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.
3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.
4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.
6. **REPORT DATE:** Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.
- 8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.
- 8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.
- 9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.
- 9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).
10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.