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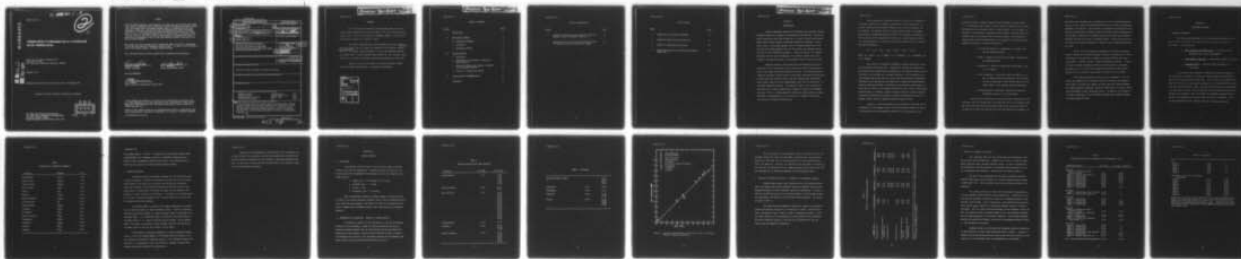
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**HYDROGEN CONTENT OF HYDROCARBON FUELS BY A LOW-RESOLUTION  
NUCLEAR RESONANCE METHOD**

Fuels and Lubrication Division (SF)  
Fuels Branch (SFF)  
Air Force Aero Propulsion Laboratory (AFAPL)

December 1977

Interim Technical Report for Period 20 July - 20 August 1977.

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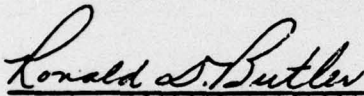
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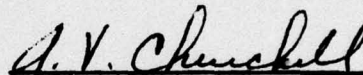
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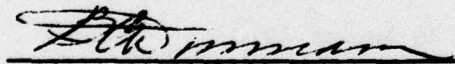


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1. REPORT NUMBER <b>14</b> AFAPL-TR-77-61	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER <b>7</b>
4. TITLE (and Subtitle) <b>6</b> HYDROGEN CONTENT OF HYDROCARBON FUELS BY A LOW-RESOLUTION NUCLEAR <del>MAGNETIC</del> RESONANCE METHOD	5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report. 20 Jul - 20 Aug 1977	
7. AUTHOR(s) <b>19</b> Ronald D. Butler	8. CONTRACT OR GRANT NUMBER(s)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Fuels and Lubrication Division (SF) Air Force Aero Propulsion Laboratory Wright-Patterson Air Force Base, Ohio 45433	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS PE 61102F <b>16</b> <b>17/S1</b> PROJ/TSK/WU 2303/S1/01	
11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE <b>11</b> Dec 1977	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	13. NUMBER OF PAGES 30	
	15. SECURITY CLASS. (of this report) UNCLASSIFIED <b>12/30 p.</b>	
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE		
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Elemental Analysis	Aircraft Fuels	JP-4
Hydrogen Content	Turbine Engine Fuels	JP-8
Nuclear Magnetic Resonance	Missile Fuels	JP-9
Nondestructive Testing	RJ-5	JP-10
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
A low-resolution (wide-line) nuclear magnetic resonance (NMR) technique has been evaluated for the direct, nondestructive determination of the hydrogen content of aircraft and missile fuels. The method is rapid and convenient, and requires minimal operator training. Accuracy and precision of the results compare favorably with the best microcombustion techniques. <b>K</b>		

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FOREWORD

This technical report describes work performed under a basic re- search program administered by the Fuels Branch (SFF), Fuels and Lubrication Division (SF), Air Force Aero Propulsion Laboratory (AFAPL). Project Scien- tist for this program is Dr. Ronald D. Butler.

The research described herein was performed by Dr. Butler from 20 July to 20 August 1977; the report was submitted for publication in Septem- ber 1977. The overall research program, a study of the detailed chemistry of aircraft fuels, is being conducted under Project No. 2303, Task No. 2303S1, Work Unit No. 2303S101 (Hydrocarbon Type Analysis Techniques for Jet Fuels).

Support of the Air Force Office of Scientific Research (AFOSR), Air Force Systems Command (AFSC), is gratefully acknowledged.

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## SECTION I

### INTRODUCTION

Ultimate (elemental) analysis of hydrocarbon fuels provides valuable information about their combustion characteristics and behavior. Data for the minor constituents sulfur and nitrogen are, of course, of particular interest because these elements produce undesirable atmospheric pollutants. Within recent years, it has become apparent that the elemental composition of the bulk fuel (the carbon:hydrogen ratio or, more simply, the hydrogen content) can also be a very informative parameter. Martel and Angello,<sup>1</sup> for example, have noted that the heat of combustion of an aviation turbine fuel can be estimated with good reliability if the hydrogen content of the fuel is known.

Elemental analysis, while based upon well-established analytical principles, has not been widely used in routine fuel testing laboratories because of the highly specialized techniques involved. The traditional micro-combustion procedure, which entails the very precise manipulation and weighing of micro-scale gas absorption trains, has been improved upon considerably within recent years by the gas chromatographic detection and quantitation of the sample combustion products. The analysis, however, still requires the unique ability to handle extremely small samples of volatile and flammable materials. Thus it is common practice, except where large numbers of samples would make it uneconomical, to use the services of commercial analytical laboratories for elemental analysis data.

Fuels chemists have found that hydrogen content can be estimated by correlating, empirically, a number of readily measured fuel properties, so that the inconvenience and expense associated with actual microanalysis can be minimized. The American Society for Testing and Materials, for example, has published a recommended procedure (D3343) for estimating the hydrogen content of any fuel from its measured API gravity ( $G$ ), volume percent aromatics ( $A$ ), and the average ( $V$ ) of the 10%, 50%, and 90% recovery points in the ASTM D86 bulk distillation:<sup>2</sup>

$$\%H = k_1G - k_2A + k_3AV + k_4GV - k_5GA + 10.56,$$

where  $k_1 = 0.06317$ ,  $k_2 = 0.041089$ ,  $k_3 = 0.000072135$ ,  $k_4 = 0.00005684$ , and  $k_5 = 0.0004960$ .

The Institute of Petroleum<sup>3</sup> recommends a similar calculation, using specific gravity and aniline point. Angello<sup>4</sup> has reviewed these methods and has found that the standard error of estimate for the hydrogen content of aviation fuels is on the order of 0.2 percent (absolute). This uncertainty is an order of magnitude greater than that of the best microanalytical determination. Furthermore, many laboratories have adopted the automated gas-chromatographic technique (ASTM method D2887) for defining the distillation characteristics of fuels, and the results do not compare directly with those from the conventional D86 distillation. Therefore, unless the analyst takes the trouble to perform an additional correlative calculation to obtain the appropriate values for  $V$ , hydrogen content cannot be computed directly by means of D3343.

Clearly, it would be desirable to have available a technique for the determination of the hydrogen content of fuels that would minimize the technical difficulties of the microanalysis method and the uncertainties of the

calculation method. Recently, Newport Oxford Instruments, Newport Pagnell, U. K., introduced a rapid, simple, and quite precise instrument for the direct determination of the hydrogen content of liquid samples. This instrument is basically a low-resolution, nonscanning nuclear magnetic resonance (NMR) spectrometer tuned to the frequency of the proton resonance. The manufacturer claims numerous significant advantages of this approach over classical micro-combustion techniques, including the following:

1. Accuracy and precision -- comparable to, or better than, the best absolute methods;
2. Speed -- analysis in less than ten minutes, including sample preparation time;
3. Flexibility -- ability to analyze any liquid sample, organic or inorganic;
4. Ease of operation -- macroscale sample (typically 10 to 30 gm), no special handling requirements, few instrument controls to manipulate, direct digital display of integrated signal, little operator training requirement;
5. Noninterference by heteroatoms, conductivity improvers, paramagnetic species, or dissolved oxygen.

The Institute of Petroleum has sponsored a careful evaluation of this instrument, and has concluded that it provides data that are in excellent agreement with values calculated using both the ASTM and IP correlation methods.<sup>5</sup> Although the IP study was extensive (more than 200 samples were analyzed), the

NMR results were evaluated only by comparison with the calculated ASTM and IP values; no "true" values from microcombustion analysis, or for pure reference standards, were obtained. Ford, Friswell, and Richmond<sup>6</sup> have partially filled this gap by reporting the hydrogen contents of aircraft fuels as determined by the NMR method, together with confirming analyses of several known reference materials covering a wide range of hydrogen content. These authors have verified that the instrument manufacturer's claims of high accuracy and precision are valid.

The Air Force Aero Propulsion Laboratory is currently conducting several in-house and contractual programs involving fuel chemistry, in which a large amount of reliable data is needed for selected aircraft fuels under investigation. Hydrogen content is among the properties required. In order to obtain the needed information within a short time and at a reasonable per-sample cost, we have procured a Newport Oxford wide-line NMR hydrogen analyser and have conducted a preliminary evaluation of the instrument.

This report describes the results of our investigation. For the purpose of establishing the confidence limits of the method, we analyzed a large number of aircraft fuel samples for which data were already available from three independent commercial analytical laboratories, or could be calculated from quality control laboratory results. In addition, we included in the study a broad range of pure reference materials whose elemental compositions were accurately known.

## SECTION II

## EXPERIMENTAL METHODS

## 1. INSTRUMENT PARAMETERS

The Newport Oxford analyser has only three operator-variable controls, none of which is critical to the analysis, but can be used to optimize the results. The controls are:

1. Radio Frequency (RF) Energy Input -- 12-position switch selectable from 6 to 500 microamperes;
2. Audio Frequency (AF) Gain -- continuously variable, 0 to 1000;
3. Integration Time -- 4-position switch selectable, 1 to 128 seconds.

The RF energy input parameter is potentially significant because of the likelihood of saturating the sample and thereby producing a nonlinear response and decreased signal-to-noise ratio. Ford, Friswell, and Richmond<sup>6</sup> confirm that this effect is particularly prominent for low-viscosity fluids, which have long nuclear relaxation times. Thus the RF input level must be maintained at a relatively low level. For low-viscosity fluids, including jet fuels, the manufacturer recommends a level of 20  $\mu$ amp; the experiments reported by Ford, Friswell, and Richmond<sup>6</sup> also indicate that this value is reasonable. All of the data reported here were therefore obtained at 20- $\mu$ amp energy input.

The AF Gain is "downstream" from the sample, and is simply a variable signal amplifier; it serves to provide a sufficiently strong signal for the integrator. While the manufacturer recommends an initial trial setting of 500 (50 percent of full scale), we found that a value of 900 was necessary in order to obtain reasonable four-figure readouts with most 25-gm samples of both reference materials and fuel samples. Presumably, this amplification does not affect the linearity of the response or the accuracy of the integration.

For maximum precision, a long integration time is advisable; although the signal strength can be integrated for periods as short as one second, we have followed the manufacturer's recommendation of 128 seconds.

Periodically, it is necessary to tune the proton resonance signal by means of a built-in oscilloscope and single tuning control. Once the instrument is warmed up and stabilized, this adjustment is needed only after several hours of continuous operation.

## 2. CALIBRATION

In operation, the analyser displays an integrated-signal value that is directly proportional to the number of protons, and thus the weight of hydrogen, in the sample cell. (It is also important to recognize that the instrument is only weakly dependent upon the *type* of hydrogen-containing sample in the cell.) If the instrument is calibrated with a known weight of a material whose hydrogen content is accurately known, then subsequent readouts can be converted directly to equivalent grams of hydrogen.

The instrument was calibrated with a series of known reference materials, rather than with only cyclohexane as the manufacturer recommends. This precaution was taken for two reasons. First, it is important to confirm that the instrument parameters are set so that saturation effects and nonlinearity, as mentioned above, will not distort the results. Second, we wished to confirm that the instrument response is not influenced appreciably by the compound types being studied, and thus the method is applicable to *all* types of aircraft fuels in which we are interested.

The materials used for calibrating the instrument are listed in Table 1 together with their known hydrogen contents. All of these materials were 99 percent or higher purity (Chemical Samples Company, Columbus, Ohio), and all gave consistent instrument calibration factors. Therefore, we are confident that compound types other than hydrocarbons can be used for calibration and that the method is applicable to the full range of hydrogen contents of these materials (4.5 to 16.1 percent).

Some comments are appropriate regarding the choice of calibration standards. The instrument manufacturer, and the Institute of Petroleum in its proposed operating procedure, recommend cyclohexane because this material very nearly resembles actual fuels in its physical and nuclear properties. For the analyst, however, it is not the ideal choice because of its high volatility (its normal boiling point is 81° C). Other materials are just as useful, and lack this disadvantage. However, some materials may not be suitable despite their apparent attractiveness. Low molecular weight alcohols, for example, should not be used because it is difficult to obtain truly anhydrous specimens, and they tend to be both hygroscopic and volatile. (Fortuitously, 2-ethoxy-ethanol, or ethyl cellosolve, is immune to the hygroscopicity problem because

TABLE 1

## COMPOSITION OF CALIBRATION STANDARDS

Material	Formula	% H
Chlorobenzene	$C_6H_5Cl$	4.48
Diphenyl ether	$C_{12}H_{10}O$	5.92
2-Chloroethanol	$C_2H_5OCl$	6.26
Benzyl alcohol	$C_7H_8O$	7.46
Toluene	$C_7H_8$	8.75
Tetralin	$C_{10}H_{12}$	9.15
Phenylcyclohexane	$C_{12}H_{16}$	10.06
Distilled water	$H_2O$	11.19
2-Ethoxyethanol	$C_4H_{10}O_2$	11.19
1-Pentanol	$C_5H_{12}O$	13.72
Cyclohexane	$C_6H_{12}$	14.37
Methylcyclohexane	$C_7H_{14}$	14.37
n-Hexadecane	$C_{16}H_{34}$	15.13
n-Dodecane	$C_{12}H_{26}$	15.39
n-Octane	$C_8H_{18}$	15.89
n-Heptane	$C_7H_{16}$	16.10

its hydrogen content -- 11.19% -- is exactly the same as water; reagent grade 2-ethoxyethanol could therefore be used as a calibration standard without regard to water contamination affecting the results.) The consideration of volatility also applies to the lower molecular weight alkanes.

### 3. OPERATING PROCEDURE

The Newport analyser accommodates standard 32 x 200 mm Nessler tubes as sample containers. For both the calibration standards and the fuel samples, sample weights on the order of 25 gms were found suitable and convenient. (While the instrument can be made direct-reading by varying the AF Gain and using exactly the same weight of standard and sample for each analysis, this approach is neither necessary nor convenient.) The sample to be analyzed (about 25 to 30 ml) is carefully introduced into a weighed sample tube, and the tube is stoppered tightly and reweighed.

The weighed sample is placed into the sample compartment and integration is started by means of a manual pushbutton control. After the 128-second integration period has elapsed, the total integrated signal is displayed on the instrument panel. If a calibration sample is being run, this value gives the instrument factor, i. e., signal counts per gram of hydrogen. For an unknown sample, the readout is converted to grams hydrogen, and that value divided by the sample weight to give the final result in %H by weight.

The analyser is internally programmed to continue integrating repetitively, so that a new reading appears on the display every 128 seconds; it is not necessary to restart the integration manually. For reasonable accuracy and precision, it is advisable to take five consecutive readings, although three readings are usually sufficient for routine work.

According to the manufacturer, the BCD output of the instrument can be used to drive a line printer, which can then automatically accumulate and preserve consecutive readings while the operator is preparing subsequent samples. In this way, the output of data is limited only by the operator's speed in taring and weighing the samples.

SECTION III

ANALYSIS RESULTS

1. CALIBRATION

The materials listed in Table 2, with their wide range of hydrogen contents, were used for calibration. Instrument parameters selected for the analysis were those recommended by the manufacturer, with the exception of the higher AF Gain:

1. Sample size -- 30 ml nominal (25 to 30 gms);
2. RF energy input -- 20  $\mu$ amp;
3. AF gain -- 900;
4. Integration time -- 128 seconds.

From 74 independent readings of standard samples selected from those in Table 2, the unified calibration yielded a value of 44.91 (standard deviation 0.35) counts per gram hydrogen. This factor was found to be unbiased with respect to sample type and hydrogen content, and so was used for all subsequent analyses.

2. CONFIRMATION OF CALIBRATION: ANALYSIS OF KNOWN MATERIALS

To confirm the validity of the calibration, as well as the longterm stability of the instrument, a number of reference materials were run as unknowns at random intervals over the entire period that actual unknown fuel samples were being analyzed. Results of these analyses are given in Table 2. To demonstrate the linearity of the instrument response and the agreement with theory, these results are also plotted and shown in Figure 1.

TABLE 2  
ANALYTICAL RESULTS FOR KNOWN MATERIALS

Material	%H, Known	%H, Found
2-Chloroethanol	6.26	6.29
		6.32
		6.30
		6.29
		6.26
		6.28
Phenylcyclohexane	10.06	10.11
		10.10
Distilled water	11.19	11.16
		11.14
		11.15
		11.14
		11.14
		11.14
		11.19
		11.22
		11.13
		11.19
		11.14
11.15		
11.19		
11.21		
11.14		
11.10		
2-Ethoxyethanol	11.19	10.86
1-Pentanol	13.72	13.78
		13.81
		13.78
Methylcyclohexane	14.37	14.36
		14.35
		14.33
		14.37
		14.37

TABLE 2 (Continued)

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Methylcyclohexane (contd.)		14.37
		14.32
		14.37
		14.33
Cyclohexane	14.37	14.37
n-Hexadecane	15.13	15.25
n-Dodecane	15.39	15.43
		15.47
n-Octane	15.89	15.85
		15.98
		15.88
		15.88

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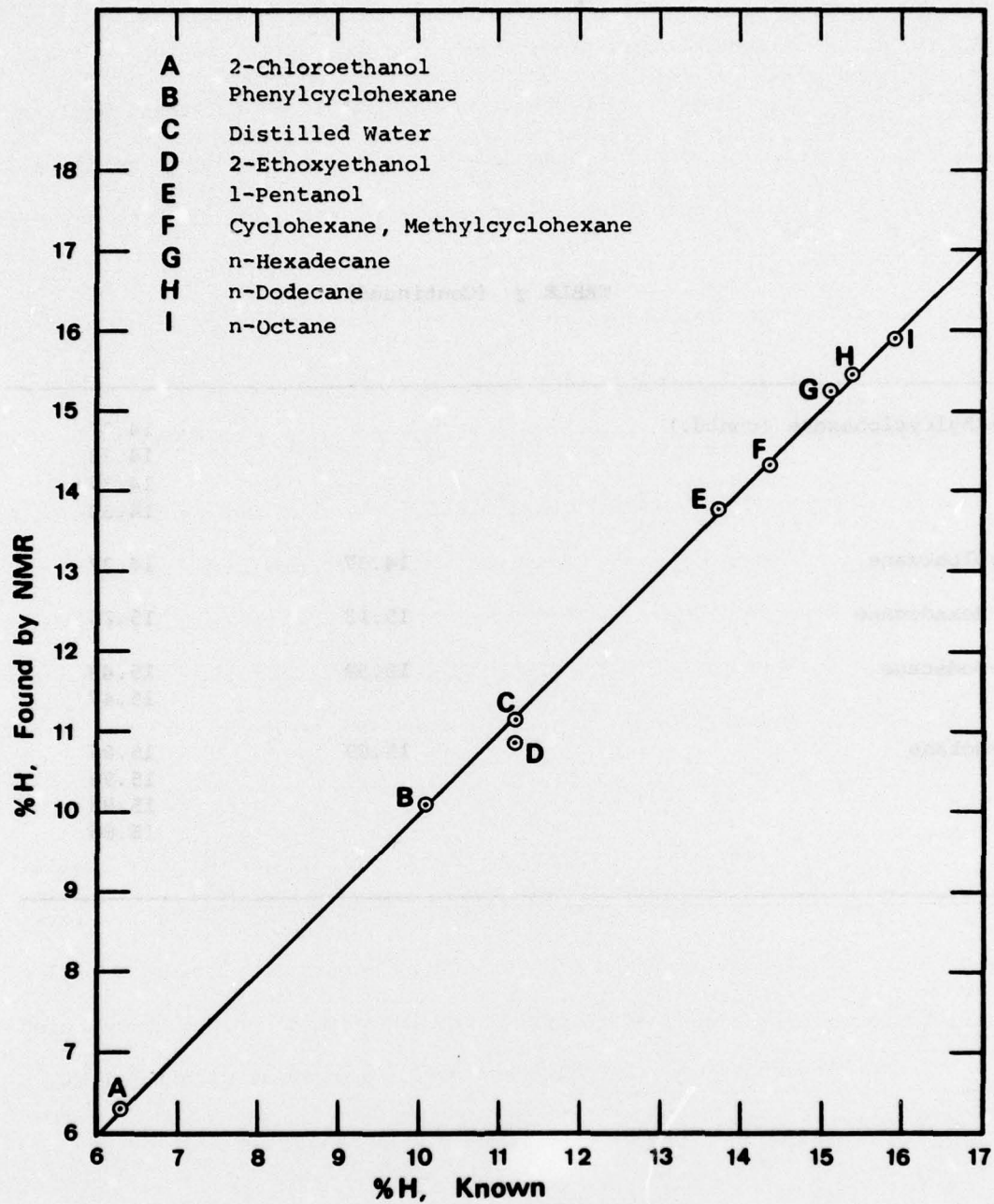


Figure 1. Agreement Between Known and Determined Values for Hydrogen Content of Reference Materials

With one exception (2-ethoxyethanol, which is in error by 0.33%), the agreement between the known and found values is excellent for these analyses. Precision is also good, with the standard deviation in most cases being well below 0.1% (absolute). Moreover, the stability of the instrument is verified by the fact that the calibration did not change noticeably during the ten days that the instrument was in continuous operation for this particular study.

### 3. ANALYSIS OF UNKNOWN FUEL SAMPLES: AGREEMENT WITH INDEPENDENT ANALYSES

Several turbine engine fuels, blending stocks, and synthetic blends, which were prepared for related combustion evaluation programs, had also been analyzed previously by three independent analytical laboratories. In order to check the new NMR technique in this laboratory against the conventional method, the same samples were analyzed using the Newport Oxford Analyser. The results are given in Table 3.

The traditional microcombustion technique is reputed to be capable of achieving an absolute accuracy of 0.3% (absolute) or better. With few exceptions, the reported values in Table 3 reflect a comparable precision. All of the values obtained in this laboratory by the NMR method could be considered excellent "consensus" values, in that they are in agreement with the best results from the commercial laboratories.

TABLE 3  
RESULTS OF INTERLABORATORY ANALYSES<sup>a</sup>

Sample Type	This Laboratory	Laboratory A	Laboratory B	Laboratory C
Conventional JP-4	14.48	14.53	14.66	14.66
	14.48	14.57	14.50	14.47
JP-4 Blended with Aromatic Blending Stock	12.17	12.07	11.66	12.48
	12.21	12.19	11.80	12.37
Conventional JP-8	13.97	13.94	13.93	14.25
		14.00	14.09	14.19
		14.00	13.93	13.77
		14.01	14.04	13.59
Mineral Seal Oil	14.27	14.14	13.73	---
	14.19	14.18	13.86	
JP-8 Blended with Mineral Seal Oil	14.03	14.05	13.90	14.16
	13.97	14.00	13.76	14.17
JP-8 Blended with Aromatic Blending Stock	12.32	12.18	12.16	12.66
	12.30	12.18	12.23	12.60

<sup>a</sup> Comparison of data taken in This Laboratory by the NMR technique; in commercial Laboratories A, B, C by the classical microcombustion technique.

#### 4. ANALYSIS OF UNKNOWN FUEL SAMPLES

This laboratory deals with both conventional and experimental fuels having widely varying chemistries. Common to all of them is a need for fundamental properties data, including hydrogen content. In order to demonstrate the versatility of the NMR technique, we performed routine analyses for a number of additional fuel specimens. These results are listed in Table 4.

For some of the conventional fuel specimens, sufficient data were available from quality control testing to calculate hydrogen content by means of ASTM Method 3343. These calculated values are also listed in Table 4 for comparison.

The synthetic fuels RJ-5, JP-10, and JP-9 provide the opportunity to calculate hydrogen content from their known compositions. Six batches of RJ-5 were analyzed separately and found to contain 9.92% (standard deviation 0.05%) hydrogen on the average. JP-10 is essentially a pure material having the molecular formula  $C_{10}H_{16}$ , from which a theoretical hydrogen content of 11.84% is calculated. JP-9 is a blend of methylcyclohexane (14.37% hydrogen), JP-10, and RJ-5; the hydrogen content of prepared blends of JP-9 can be easily calculated from the known quantities of the blending components. The calculated hydrogen contents for selected JP-9 blends, listed with the experimental values in Table 4, were obtained in this manner.

Agreement between the calculated and determined values for these fuels is demonstrated by the good linear correlation shown in Figure 2. Overall, it appears that the NMR technique provides results that are just as good as, if not superior to, those obtained either by microcombustion or calculation.

TABLE 4

## ANALYTICAL RESULTS FOR CONVENTIONAL AND EXPERIMENTAL FUELS

Sample Description	%H, Found	%H, Calcd. or Theor. <sup>a</sup>
JP-4 Type		
Sample 1, Blended with highly aromatic solvent	12.20	12.48
Sample 2, Refined from shale oil	14.49	14.54
Sample 3, Conventional	14.35	14.38
Sample 4, Conventional	14.44	14.40
Sample 5, Conventional	14.52	14.62
Sample 6, Conventional	14.35	14.35
Sample 7, Conventional	14.06	---
Sample 8, Conventional	14.61	---
Sample 9, Conventional	13.85	13.93
JP-5 Type		
Sample 1, Conventional, clay filtered	13.96	---
Sample 2, Refined from shale oil	13.83	---
JP-7 Type		
Sample 1, Conventional	14.58	
Sample 2, Conventional	14.63	14.49
Sample 3, Conventional	14.59	14.48
Sample 4, Conventional	14.48	14.43
JP-8 Type		
Sample 1, Blended with highly aromatic solvent	12.35	12.62
Sample 2, Blended with paraffinic light mineral oil	13.94	13.86
Sample 3, Conventional	13.94	13.57
Sample 4, Blended with paraffinic light mineral oil	13.98	13.86
Jet-A Type		
Sample 1, Conventional	13.86	---
Sample 2, Conventional	14.07	---
Sample 3, Conventional	13.61	---
Sample 4, Conventional	13.90	---
Sample 5, Conventional, clay filtered	14.27	---
Sample 6, Conventional	13.75	13.66
Sample 7, Refined from shale oil	13.85	13.75
JP-10 [exo-Tetrahydrodi(cyclopentadiene)]	11.98	11.84

TABLE 4 (Continued)

RJ-5		
Batch 1	9.94	---
Batch 2	9.84	---
Batch 3	9.98	---
Batch 4	9.88	---
Batch 5	9.92	---
Batch 6	9.93	---
JP-9 Blends (JP-10, RJ-5, and Methyl- cyclohexane)		
Blend 1	11.78	11.81
Blend 2	11.73	11.81
Blend 3	11.75	11.81
Blend 4	11.73	11.81
Blend 5	11.66	11.70
Blend 6	11.70	11.70
Blend 7	11.65	11.70
Blend 8	11.78	11.83
Blend 9	11.80	11.83
Blend 10	11.82	11.83

<sup>a</sup>Values for conventional fuels (JP-4, JP-5, JP-7, JP-8, and Jet-A) calculated by the correlation method, using ASTM D3343. Value for JP-10 calculated from the presumed molecular formula,  $C_{10}H_{16}$ . Values for JP-9 blends calculated from known compositions of the samples and hydrogen contents of the blending stocks.

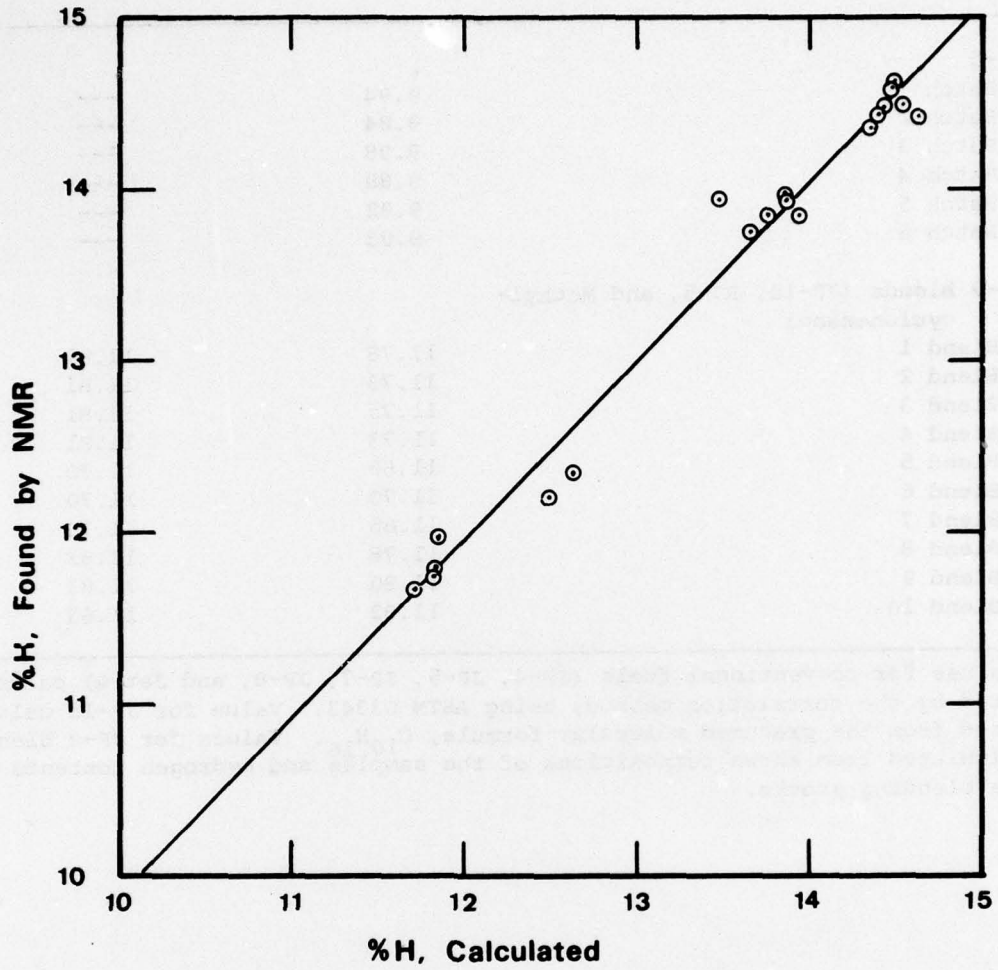


Figure 2. Agreement Between Calculated and Determined Values for Hydrogen Content of Unknown Fuel Samples

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

The data presented in this report support claims by previous workers that the wide-line NMR technique is entirely reliable for the determination of the hydrogen content of liquid samples. The method has numerous advantages, including ease of operation, a high level of accuracy and precision, and applicability to a broad range of sample types.

We have found that the results obtained with the NMR instrument are as precise as those provided by any other method. Data for known materials are in excellent agreement with theory, and a comparison of results from several commercial laboratories reveals that the NMR method is as accurate as the classical microcombustion technique. With careful technique, it also appears capable of significantly greater precision.

The wide-line NMR method can yield valid data at a relatively low per-sample cost, and for this reason alone it becomes attractive as a routine tool for laboratories interested in processing large numbers of samples. One considerable advantage is that suspect values can be redetermined quickly and economically; the instrument calibration can also be updated regularly by incorporating reference standards into the analysis schedule, thus further increasing the analytical precision.

The Institute of Petroleum has drawn similar conclusions following its exhaustive evaluation of the NMR technique.<sup>5</sup> In addition, IP recommends that hydrogen content be made a formal requirement in jet fuel specifications, replacing less precise tests such as smoke point, luminometer number, and aniline point. The IP study panel even suggests that hydrogen content alone may prove to be a more effective and reliable indicator of combustion behavior than either smoke point or aromatic content. Interlaboratory correlation studies may soon be undertaken to prove this point.

Routine laboratories now have available to them a valuable tool for directly determining a potentially useful quantity that has not been readily accessible previously. While the NMR method is by no means a complete elemental analysis system (it does not give data for carbon, nitrogen, oxygen, or sulfur), it does provide the most rapid and reliable route to the element of greatest interest in fuel technology. For this reason, it should be widely adopted by all laboratories dealing with the properties and behavior of hydrocarbon fuels.

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