NRL Report 6566

NMR Method for Determining Organic Loading of Charcoal

W. B. Moniz and C. F. Poranski, Jr.

Physical Chemistry Branch
Chemistry Division

June 2, 1967

NAVAL RESEARCH LABORATORY
Washington, D.C.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ABSTRACT

A proton NMR (nuclear magnetic resonance) method has been developed for determining the organic loading on adsorbent type charcoals. The NMR procedure compares in accuracy with the steam-desorption method, but it requires only a two-gram charcoal sample and a simple room-temperature carbon tetrachloride extraction. Certain contaminants and classes of contaminants may be identified directly from the NMR spectrum of the extract. The study employed 14 samples from the main carbon filters of nuclear submarines, whose organic loadings had been previously determined by the steam-desorption method.

Generally, NMR appears to be preferable to steam desorption for determining organic loading. However, since the NMR method does not detect fully halogenated compounds, it should not be used alone if unusually large concentrations of these contaminants are suspected.

The use of this method is restricted to a shore-based installation, since the size and weight of an NMR spectrometer preclude the use of this instrumentation aboard a submarine or spacecraft.

PROBLEM STATUS

Work on this phase of the problem has been completed; work on all other phases is continuing.

AUTHORIZATION

NRL Problem C07-04, Project RR 001-01-43-4806
NRL Problem C08-18, Project SF 013-08-03-4095

Manuscript submitted March 16, 1967.

NMR METHOD FOR DETERMINING ORGANIC LOADING OF CHARCOAL

INTRODUCTION

Conventional methods for determining the organic loading on adsorbent charcoals such as are used for air purification in nuclear submarines or spacecraft involve the use of heat and vacuum (vacuum desorption) (1) or superheated steam (steam desorption)(2). These methods suffer two major shortcomings, namely, long processing time and poor sensitivity. There is also the chance for product degradation during desorption, and with the steam method, the possibility of loss of low-boiling and water-soluble components. Identification of components requires the use of separative procedures, such as fractional distillation and liquid or gas chromatography. Processing of the desorbate can, of course, consume much effort if identification of several components is required.

High-resolution proton NMR (nuclear magnetic resonance) spectroscopy provides a sensitive and straightforward analytical method for the identification and quantitative measurement of hydrogen-containing materials. NMR can be applied to the analysis of many atmospheric contaminants collected on carbon adsorbents, provided a semiquantitative transfer of the adsorbate to a solvent can be effected; suitable NMR spectra are not obtainable directly from the carbon sample, because of the restricted motion of adsorbed molecules and the consequent broadening of spectral lines. The initial technique tried–displacing the adsorbed material from the charcoal with an excess of CCl_4–proved to be satisfactory. Carbon tetrachloride was chosen as the eluent, since it does not contain protons which might interfere with the subsequent NMR analysis. Two factors governed the choice of the charcoal to CCl_4 ratio: (a) the volume of CCl_4 should be kept small so that the extract will be as concentrated as practicable, resulting in maximum sensitivity; (b) for uniform desorption, the liquid level should cover the solid. The optimum combination was 1 ml of CCl_4 per gram of charcoal. Since the retention of CCl_4 by lightly loaded charcoal was substantial, a minimum sample size of 2 grams of charcoal and 2 ml of CCl_4 solvent was necessary to ensure enough extract for NMR analysis (0.5 ml). In the standardized procedure, the room-temperature displacement process requires only four hours.

The NMR method also provides a solution to the problem of identifying several classes of compounds without further processing of the desorbate. This result is possible because the proton NMR signals of compounds of greatest interest–aromatic, chlorinated, and aliphatic hydrocarbons–fall in distinctly different portions of the spectrum. It is fortuitous that methyl chloroform, a compound of particular current interest, produces a sharp signal in the NMR spectrum which is well separated from that of any other expected contaminants.

The accuracy of the NMR method and its utility for component identification were assessed using 14 charcoal samples of known organic loading, obtained from the main carbon filters of operational nuclear submarines.

EXPERIMENTAL PROCEDURE

Sample Preparation

In a 15- or 30-ml glass-stoppered weighing bottle are placed 2 g of charcoal and 2 ml of CCl_4 doped with 3 percent tetramethylsilane (TMS), which serves as an internal

lock signal for the NMR analysis. During the extraction, the weighing bottle is gently agitated on a shaker table. After the extraction period (four hours in the standardized procedure), the CCl_4 solution is decanted into a microfunnel containing a medium-porosity sintered-glass filtering disc; particulate matter is thus prevented from entering the NMR sample tube into which the funnel empties. The funnel is loosely stoppered during filtration to minimize evaporation of the extract. After approximately 0.5 ml of filtrate has collected in the NMR tube, it is capped and the liquid volume estimated to 0.01 ml by comparison with a height-of-fill scale which had been constructed by introducing known volumes of liquid into a similar precision NMR tube. To the sample tube is then added 2.83 percent vol/vol of the calibration standard, nitromethane. The tube is recapped, labeled, and sealed with Glyptal.

NMR Analysis

A high-resolution spectrum of the sample was run on a Varian HA-100 spectrometer using the 1000-Hz sweep width. Normally, the nitromethane peak is the tallest, and it is kept just on scale. In a heavily loaded sample, the aliphatic peak will be larger, and gain is adjusted to keep it on scale. Integrals were run in triplicate, using full pen deflection. Control blanks were run to make corrections for impurities in the nitromethane.

CALCULATION OF LOADING

One or more samples of known loading are necessary to convert the NMR data to organic loading. In the present work, the loadings of the 14 samples had been previously determined by the steam-desorption method. Two samples, C-242 and C-317, were used to calibrate the NMR method as follows. The integral of the nitromethane peak is an absolute quantitative reference, representing a specific number of protons per unit volume of solution. The sample integral represents a specific amount of desorbate per unit volume of solution. The ratio R of the sample integral to the nitromethane integral is than an absolute measure of the amount of desorbate. A correction for the dilution of the CCl_4 by the desorbate is incorporated in the calibration factor C, which is discussed below.

The amount of adsorbed water on the charcoal cannot be determined in either the steam-desorption or the NMR method. Independent studies (3) have shown that water content is inversely proportional to organic loading for typical submarine charcoals. Since a lightly loaded charcoal contains 6 to 7 percent by weight of water, the steam-desorption loadings for such charcoals will be spuriously low. The error amounts to about 0.4 percent absolute for 5-percent loading, which is smaller than the claimed accuracy of the steam desorption method. Therefore, in what follows, the water content of samples is neglected.

Because the charcoal sample which is used contains adsorbed organic components, not all of its weight represents charcoal. Therefore, in calculating the percent loading (which is based upon the weight of the "empty" charcoal), the weight of the organic loading must be subtracted from the total sample weight. Since R, as defined above, is proportional to the amount of desorbate, we can define CR as the absolute weight of organic loading per gram of loaded charcoal. The charcoal dry weight is then 1 - CR, and the percent loading is $100[CR/1 - CR]$. The calibration factor C depends upon the loading, because the dilution of the CCl_4 varies with the quantity of material desorbed. It also depends upon the extraction time, and becomes smaller as a larger fraction of the loading is desorbed. For each series of runs with fixed desorption time—that is, 1/2 hr, 4 hr, 20 hr, etc. —C vs R plots were calculated from the corresponding NMR data on charcoals C-242 and C-317, and their loadings as determined by steam desorption. Figure 1 shows the calibration for a four-hour extraction period.

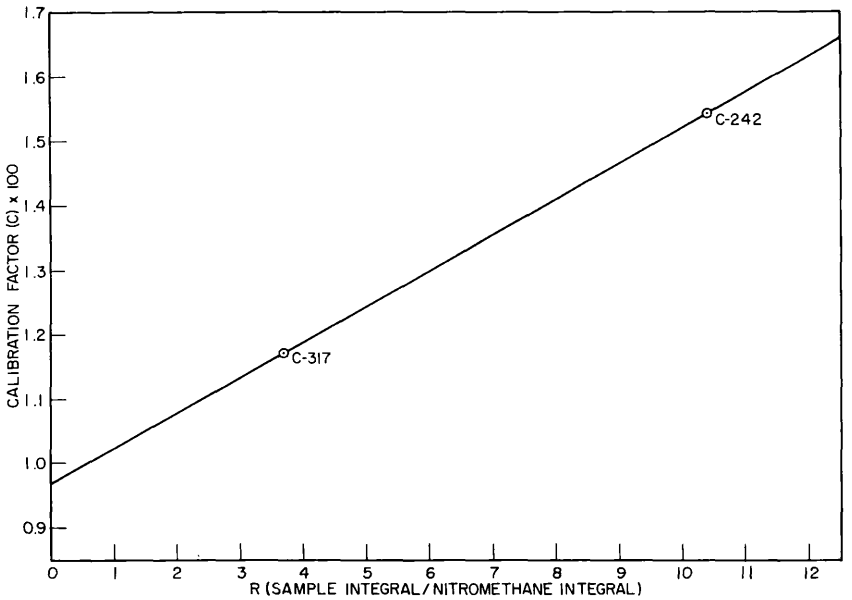


Fig. 1 - Calibration of the NMR method for determining charcoal loading, calibration curve for four-hour extractions

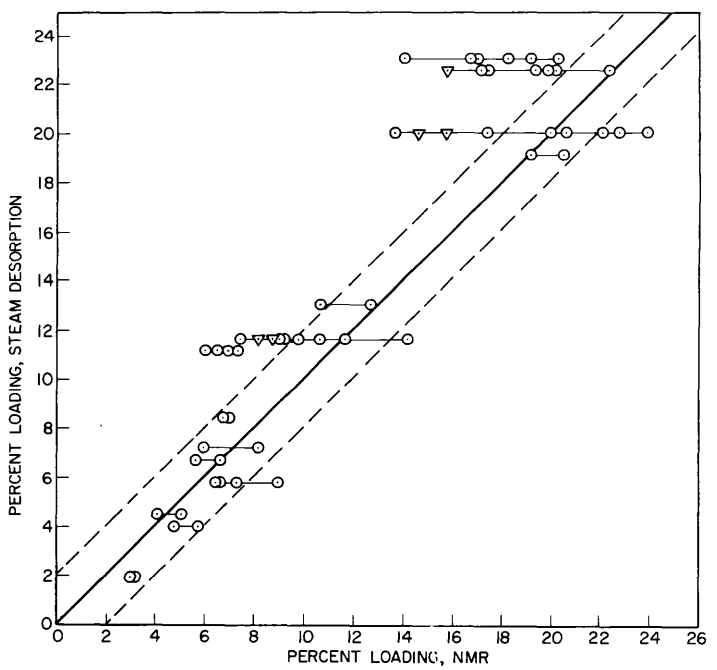


Fig. 2 - Determination of charcoal loading, steam-desorption results versus NMR results with 30-minute extractions. Points marked ▽ indicate a scale-up to 30-g charcoal samples.

The matter of extraction time was settled empirically. Although from the viewpoint of spectrometer sensitivity the concentrations of contaminants in the CCl_4 were satisfactory after only 15 or 30 minutes of extracting, the reproducibility was poor. In a series of runs with 30-minute extractions (Fig. 2), the results show scatter which is completely unacceptable for charcoal loadings greater than 10 percent. Since a scale-up to 30-g charcoal samples (points marked ▽, Fig. 2) showed that the scatter was probably not due to nonuniform loading or nonrepresentative samples, the only variable which remains is extraction time. Scaled-up samples of C-318 and C-320 were extracted for various

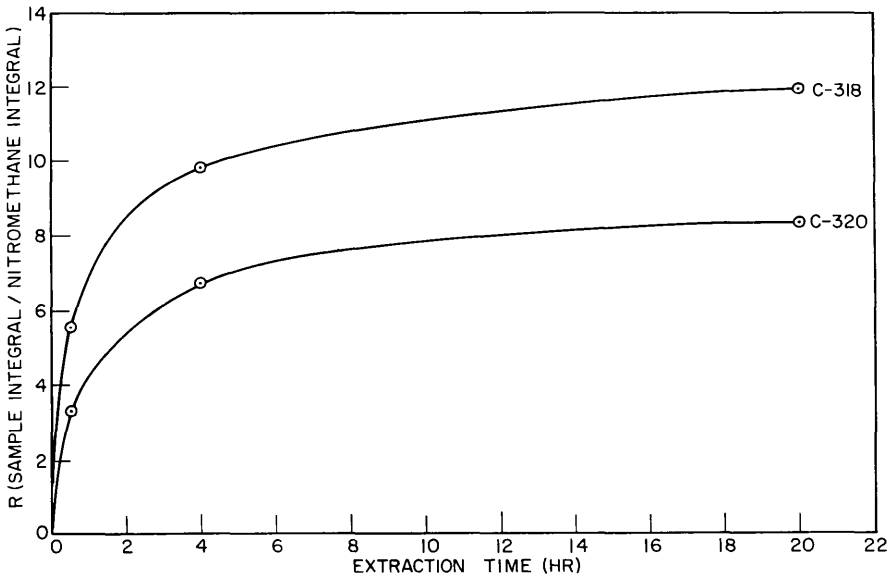


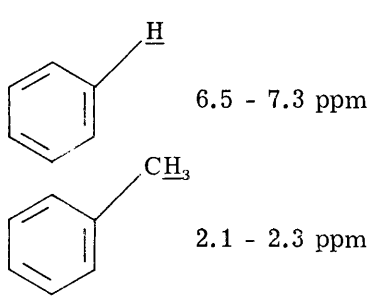
Fig. 3 - Variation of extract NMR integral with extraction time

periods, each time removing only sufficient solution to make an NMR determination. The quantitative data for these samples, corrected for the decrease in volume of CCl_4 as 1-ml aliquots were removed, are shown in Fig. 3 as plots of R (the ratio of sample integral to nitromethane integral) versus extraction time. It is apparent that for the first two hours of extraction, the slopes of the curves are very steep. Consequently, minor variations in technique or timing could be expected to affect the results seriously. The slopes of the two lines do not begin to parallel each other until after about four hours of extraction time. As a result of these experiments, an optimum extraction time of four hours was chosen.

RESULTS AND DISCUSSION

Qualitative Aspects

Differences in the chemical environment of protons give rise to shifts in the proton resonance frequencies (commonly called chemical shifts, or δ's). Additional structure is imposed on the proton spectra by spin coupling among chemically different nuclei within a molecule. However, by judicious choice of compounds, it is possible to devise mixtures whose NMR spectrum is illustrative of the characteristic spectral locations of various types of organic groupings. Figure 4 shows the spectrum of a mixture of 31 selected compounds. Of interest are the resonance positions of the following types of protons:



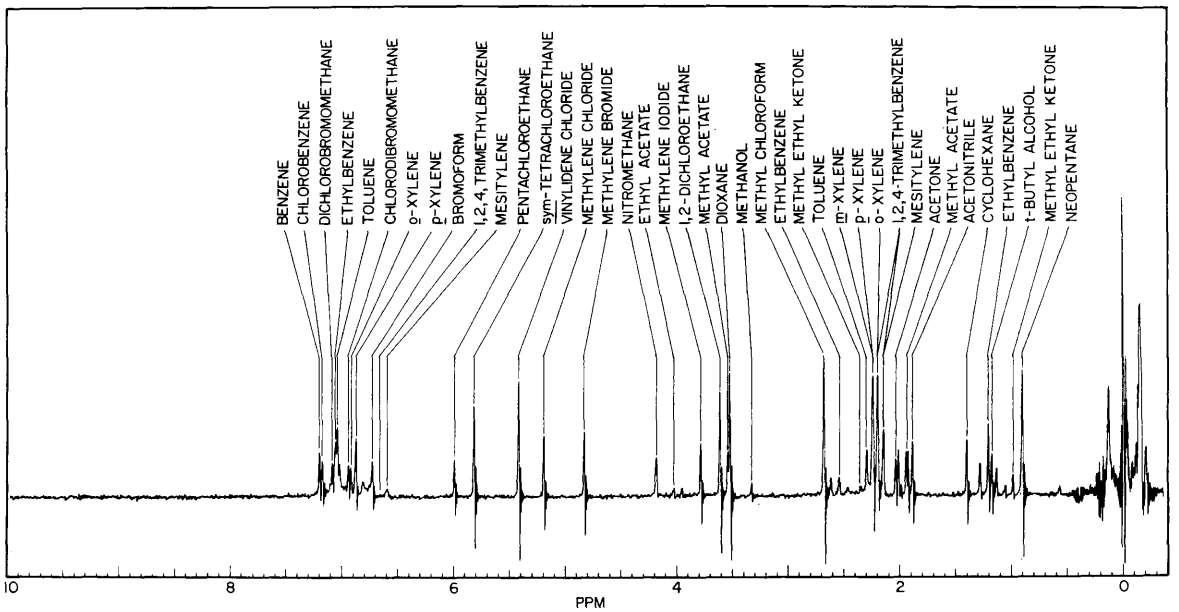


Fig. 4 - 100-MHz proton NMR spectrum of a mixture of selected compounds

$C\underline{H}_3CCl_3$	2.7 ppm
$RC\underline{H}_2X$ (X = halogen, –COOR, etc.)	3.6 - 5.4 ppm
$R-C\underline{H}_2-R$	1.4 - 2.6 ppm
$R-C\underline{H}_3$	0.9 - 1.3 ppm

These groupings occur in many molecules of interest in submarine atmospheres, and their signals are for the most part in well-separated regions of the spectrum. Fortuitously, the sharp methyl chloroform peak is not interfered with by any other anticipated component, and is readily identified. While the desorbate from a typical submarine charcoal is extremely complex in character, the NMR spectrum is easily analyzable in terms of aromatic-ring protons, aliphatic methyl and methylene protons, protons in methyl groups $\underline{\alpha}$ – to an aromatic ring (e.g., toluene, the xylenes, mesitylene, etc.), and methyl chloroform. Of course, it is completely useless for perhalogenated hydrocarbons. While F^{19} NMR is a possible point of attack for fluorine assay, it would probably be of marginal sensitivity, since the number of fluorine atoms per molecule is small, and the fluorocarbon content is usually low.

Quantitative Aspects

It is apparent from Fig. 2 that for organic loadings below 10 percent, the 30-minute extraction period gives sufficiently accurate results. Since, in general, the loading is not known beforehand, it is safer to employ the four-hour extraction period. As shown in Fig. 5, if the longer period is used, there is high probability that a single NMR determination will give a loading within ±2 percent absolute of that obtained by steam desorption. Since the latter method is subject to an error of ±1 percent absolute or more, the

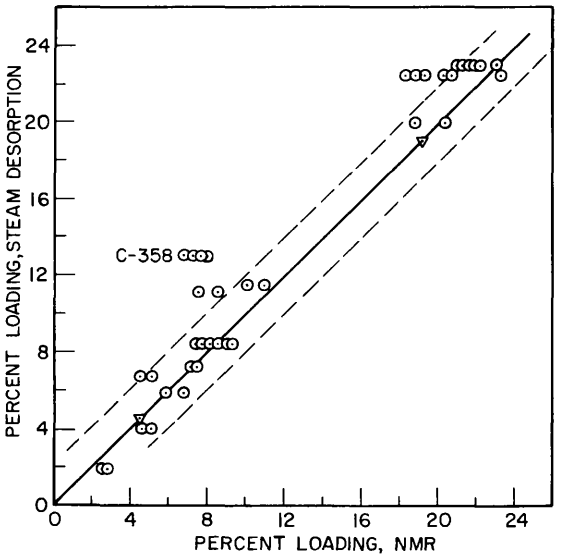


Fig. 5 - Determination of charcoal loading, steam-desorption results versus NMR results with four-hour extractions. The points marked ▽ are those for the two standardizing charcoals, C-317 and C-242.

NMR procedure may measure the actual loading no less accurately than does the steam-desorption technique.

Two major assumptions implicit in the NMR method for determining charcoal loading are (a) the fraction of loading which desorbs is independent of total loading, and (b) the makeup of the desorbate is the same for all samples. Judging by the approximate linearity of the plots of Figs. 2 and 5, both assumptions appear to be generally valid.

The anomalously low NMR loading of sample C-358 can be attributed to its high methyl chloroform content (33 percent by weight, determined by vapor phase chromatography (4)). A comparison of the NMR spectra of C-358 and that of a more typical sample, C-378, makes the difference obvious (Fig. 6). The methyl chloroform peak appears at 2.7 ppm. The number of protons (three) per methyl chloroform molecule is small compared to the number of protons in the typical C_{10} hydrocarbon (14 to 22, depending upon aromatic content). Thus, the sample integral for the extract of C-358 is smaller than it would be if its desorbate was of "normal" composition.

Large composition discrepancies in the NMR spectrum not only signal that the NMR loading calculation may be suspect, but, more importantly, that unusual contaminants and/or contaminant levels were present. The identity and approximate quantity of the anomalous components may, as was the case with C-358, be determined directly from the NMR information.

The Fuels Branch of the Chemistry Division recently employed the NMR method to study the loading and desorbate composition of a series of samples taken from the main carbon filters of Subron 15.* The low loadings of these charcoals allowed use of the 1/2-hr extraction period. The speed and ease of the NMR method permitted a comprehensive investigation of these charcoals with relatively small time and manpower requirements compared to those of conventional techniques.

CONCLUSIONS

The NMR method for determining the organic loading on submarine charcoals appears to be as accurate as the steam-desorption method, but requires a much smaller

*D.S. Jones and J.E. Johnson, private communication. To be published as an NRL Report.

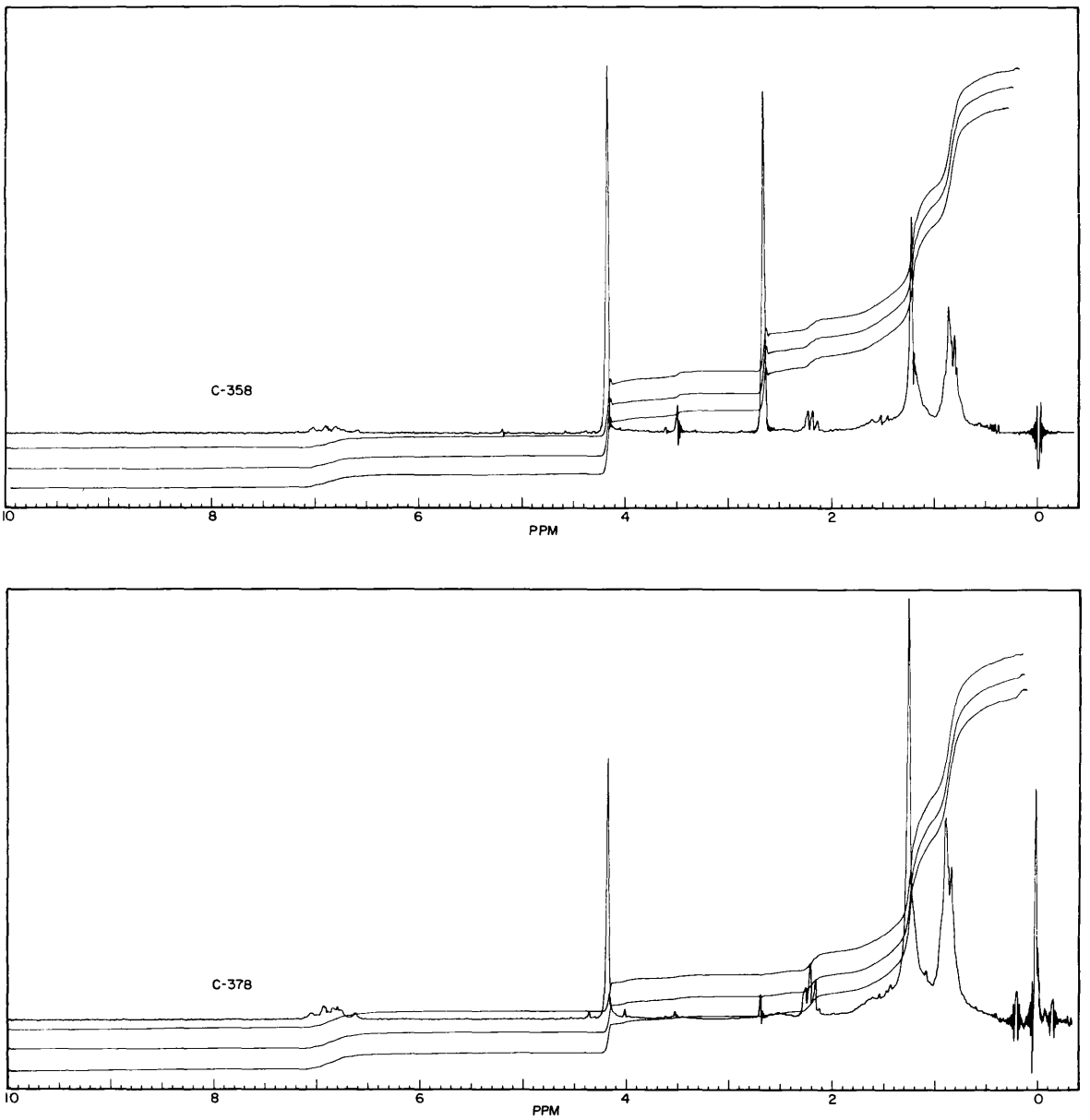


Fig. 6 - 100-MHz proton NMR spectra of CCl_4 extracts of carbon samples C-358 and C-378

sample, entails a simple, room-temperature extraction, and allows immediate identification of certain contaminants without any processing of the desorbate. While large variations from the typical desorbate compositions are detected if the contaminants contain protons, fully halogenated molecules go undetected. The NMR method should not be used alone, therefore, if larger than normal concentrations of the latter compounds are suspected.

Employment of the NMR method to study the loading and desorbate composition of charcoal samples from Subron 15 showed that considerable savings in manpower and time are possible, compared with conventional techniques.

ACKNOWLEDGMENTS

We are grateful to Dr. J.E. Johnson for supplying samples of the charcoals studied and for information concerning their history and loadings, and to Drs. L.B. Lockhart, Jr., and D.L. Venezky for most helpful discussions.

REFERENCES

1. Saunders, R.A., "Analysis of the Spacecraft Atmosphere," NRL Report 5816, Oct. 23, 1962

2. Nestler, F.H.M., and Smith, W.D., "Submarine Habitability - Atmosphere Sampling and Analysis," NRL Memo. Rept. 866, Oct. 1958

3. Venezky, D.L., and Moniz, W.B., "Method for On-Site Determination of Residual Adsorptive Capacity of Charcoals Used in Closed Environmental Systems," NRL Memo. Rept. 1710, Aug. 31, 1966

4. "Sample of Main Filter Carbon from USS Haddo (SSN 604), Report on," NRL Letter Report 6180-239:AJC:JEJ:ec, Dec. 18, 1964

Security Classification

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 (Corporate author) Naval Research Laboratory Washington, D.C., 20390	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

NMR METHOD FOR DETERMINING ORGANIC LOADING OF CHARCOAL

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

An interim report on the problem; work is continuing.

5. AUTHOR(S) (First name, middle initial, last name)

William B. Moniz and Chester F. Poranski, Jr.

6. REPORT DATE June 2, 1967	7a. TOTAL NO. OF PAGES 11	7b. NO. OF REFS 4
8a. CONTRACT OR GRANT NO. NRL Problems C07-04, C08-18 b. PROJECT NO. RR 001-01-43-4806 c. SF 013-08-03-4095 d.	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6566 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Navy (Naval Ship Systems Command, ONR) Washington, D.C.

13. ABSTRACT

A proton NMR (nuclear magnetic resonance) method has been developed for determining the organic loading on adsorbent type charcoals. The NMR procedure compares in accuracy with the steam-desorption method, but it requires only a two-gram charcoal sample and a simple room-temperature carbon tetrachloride extraction. Certain contaminants and classes of contaminants may be identified directly from the NMR spectrum of the extract. The study employed 14 samples from the main carbon filters of nuclear submarines, whose organic loadings had been previously determined by the steam-desorption method.

Generally, NMR appears to be preferable to steam desorption for determining organic loading. However, since the NMR method does not detect fully halogenated compounds, it should not be used alone if unusually large concentrations of these contaminants are suspected.

The use of this method is restricted to a shore-based installation, since the size and weight of an NMR spectrometer preclude the use of this instrumentation aboard a submarine or spacecraft.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Security Classification

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Nuclear magnetic resonance						
Organic loading						
Charcoal						
Spectroscopy						
Analysis						
Atmosphere contaminants						

DD FORM 1 NOV 65 1473 (BACK)

(PAGE 2)

Security Classification