NASA TECHNICAL MEMORANDUM

NASA TM X-53789

October 7, 1968

A METHOD FOR THE ANALYSIS OF HALOCARBON OIL CONTAMINATION IN COMPRESSED GASES

Propulsion and Vehicle Engineering Laboratory

NASA

George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

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By

Francis J. Carlin, Jr.

George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

ABSTRACT

A chromatographic method, utilizing an electron capture detector, has been developed for the detection of halocarbon oil contaminants in compressed gases. The lower limit of detection is 9×10^{-11} gm or 0.03 ppm. The upper limit of the detector is 3×10^{-9} gm or 0.9 ppm.

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RESEARCH AND DEVELOPMENT OPERATIONS

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SUMMARY

A chemical method is needed to analyze traces of halocarbon oil contamination in compressed gases. This report describes an electron capture-gas chromatographic detection system which gives linear response to halocarbon oil over the range of 9×10^{-11} gm (0.03 ppm) to 3×10^{-9} gm (0.9 ppm) Halocarbon Oil 208-4. Modifications of the sampling techniques may be required when sampling gases under field conditions.

INTRODUCTION

Compressed gases are used as pressurizing fluids and lubricants in various launch vehicle systems. Compressed nitrogen gas, which is used as a lubricant in the ST-124 stabilized platform on the Apollo Saturn IB and Saturn V launch vehicles, has very critical purity requirements. Contamination studies made with the gas bearings used in the ST-124 platform have shown that the long term operation of these bearings can be seriously affected if the aerosolized particle contamination (e.g., condensable hydrocarbons) exceeds 0.2 ppm by weight in the lubricating gas. It has come to the attention of this Center that the compressor pumps at Kennedy Space Center (KSC) for these gases employ a LOX-compatible halocarbon oil lubricant. Small amounts of this halocarbon lubricant have been found entrained in the nitrogen. This condition has not been a problem at this Center since the gas bearing nitrogen lubricant is obtained by the direct conversion of liquid to gas. The procedure [1] for the analysis of condensable hydrocarbon contamination in compressed gases is unsatisfactory for halocarbon oil analysis because it is possible to detect traces of halogenated contaminants only down to 0.4 ppm in the presence of a large excess of a chlorinated solvent such as the carbon tetrachloride used in the present procedure. Therefore, a more sensitive method for the analysis of halocarbon oil contamination in compressed gases is needed in addition to the present method. However, it should be noted that the additional procedure would not replace the requirement for assaying condensable hydrocarbons in compressed gases. In the case of gas bearing nitrogen, the purity level would still remain at 0.2 ppm condensable contamination by weight combining both condensable hydrocarbon and halocarbon concentrations.

The purpose of this work was to develop an analytical method capable of detecting and measuring accurately halocarbon oil contamination at the 0.2 ppm level. The most logical approach was a gas-liquid chromatographic procedure employing an electron capture detection system. Since the work of Lovelock [2,3,4] on the development of the electron capture detector, this extremely sensitive and specific detector has been used routinely for the analysis of traces of pesticides and other halogenated materials. The excellent separating power of gas-liquid chromatography and the extreme sensitivity of the electron capture detector have proven to be a powerful combination in solving analytical problems similar to the halocarbon oil contamination problem.

This report outlines the development of the gas chromatographic-electron capture detector system and its application to the halocarbon contamination problem. It was hoped that a combination of this detection system with the sampling techniques of the present method [1] would make a satisfactory analytical method for the analysis of halocarbon oil contamination in compressed gases.

INSTRUMENTATION

During the course of this investigation, a Micro Tek Model 150-G gas chromatograph equipped with an Ni^{63} high-temperature electron capture detector powered by an external pulsed dc voltage power supply was used. The response of the electron capture detector was measured by a Micro Tek electrometer, and the output of the electrometer was displayed on a one-millivolt recorder. To minimize detector noise, the 5 percent methane in argon carrier gas was passed through a molecular sieve, Type 5A, trap to remove moisture and hydrocarbon contaminants other than methane.

EXPERIMENTAL

A sample of a typical halocarbon oil used at KSC (Halocarbon Oil 208-4) was obtained for this investigation. To determine if small amounts of halocarbon oil could be detected, a series of very dilute solutions were made in hexane. (Halocarbon Oil 208-4 has a density of 1.8 gm/ml.) The various solutions were made as follows:

A. One microliter (1 μl) of Halocarbon Oil 208-4 was diluted to 100 ml with n-hexane. This solution contained 1.8×10^{-5} gm oil/ml or 1.8×10^{-8} gm/μl, or 27.4 ppm by weight.

B. Two milliliters of Solution A were diluted to 100 ml with n-hexane. This solution contained 3.6×10^{-7} gm oil/ml or 3.6×10^{-10} gm/μl, or 0.55 ppm by weight.

C. Two milliliters of Solution B were diluted to 100 ml with n-hexane. This solution contained 7.2×10^{-11} gm/μl, or 0.02 ppm by weight.

D. Ten milliliters of Solution A were diluted to 100 ml with n-hexane. This solution contained 1.8×10^{-6} gm oil/ml or 1.8×10^{-9} gm/μl, or 2.7 ppm by weight.

These solutions were used to determine the optimum working range for halocarbon oil detection and measurement and for determining the lower limit of detection for Halocarbon Oil 208-4.

The gas chromatograph was set up for analysis according to the parameters outlined in Table I. Several small injections (5 μl) of Solution A were made to determine if the electron capture detector would give adequate response for halocarbon oil. When Halocarbon Oil 208-4 was injected into the analytical column, at least 57 electron-capturing components were separated and detected. The major component of this group was used as a measure of halocarbon oil concentration in the solutions of Halocarbon Oil 208-4 in n-hexane.

To determine the proper settings for pulse width, pulse rate, and voltage output from the power supply to the electron capture detector, several 5 μl injections of Halocarbon Oil 208-4 in hexane (3.6×10^{-10} gm/μl) were used. Two of the parameters were held constant while the third was varied. The response for the halocarbon oil at every setting was recorded and measured. Each parameter was varied, in turn, while the two remaining were held constant. The combined parameters which produced the largest response for halocarbon oil were used in all subsequent work. The height of the component peak, measured in centimeters, was used as a measure of oil content.

After the optimum parameters had been determined, the linear dynamic range of the detector was determined by injecting increasing amounts of halocarbon oil and measuring detector response for each injection. A plot of the amount of oil injected versus detector response (on log-log paper) gave a visual presentation of the linear range of the detector, i.e., that region over which detector response was proportional to the amount of halocarbon oil passing through the detector (Fig. 1).

RESULTS

The gas chromatographic analysis for halocarbon oil contamination using electron capture detection appears to be satisfactory. The response of the Ni63 electron capture detector for Halocarbon Oil 208-4 is linear over the range of 9×10^{-11} gm to 3×10^{-9} gm of oil as shown in Table II and Figure 1. This corresponds to a range of 0.03 to 0.9 ppm halocarbon oil contamination in the compressed gas, following the sample procedure outlined in Reference 1.

Also, Halocarbon Oils 208 and 208-4 were chromatographed to determine any differences or similarities between the two blends. The components were detected by a hot wire thermal conductivity detector as each eluted from the analytical gas chromatography column. The major component of Halocarbon Oil 208-4 accounted for 54.6 percent (area %) of the total sample; 38 other components of this blend made up the remaining 45.4 percent. However, in Halocarbon Oil 208, only three components were detected; the major component, which had the same retention time as the major component of 208-4, represented 98.9 percent (area %), and the two minor components accounted for the remaining 1.1 percent of the Sample. Table III and Figures 2 and 3 illustrate these differences quite well.

The molecular weight of Halocarbon Oil 208 has been determined by mass spectrometry to be 386. This means that the limit of detection of the electron capture detector for Halocarbon Oil 208-4 is approximately 2.33×10^{-13} moles.

CONCLUSIONS

The detection system for traces of halocarbon oil contaminants outlined in this report is adequate for the analysis desired. The procedure is applicable for halocarbon oil concentrations of 0.03 to 0.9 ppm in the gas stream. The scrubbing solvent must be a hydrocarbon to prevent detector overloading. The analysis may be made by direct injection of the scrubbing solutions after they have been combined and diluted to a known volume. No concentration step is needed.

There is also a possibility that the analysis may be made on gas samples directly without the use of scrubbers. Analyses of vapor samples in the laboratory have been promising, but reproducible results have not been obtained because the Teflon-tipped gas-tight syringes suffer from "memory effects." That is, the halocarbon oil is adsorbed on the Teflon surfaces, and part of the adsorbed material is desorbed with each succeeding injection, thus producing a false response for the halocarbon oil. It is believed that this problem can be corrected by the use of a gas sampling valve and all-metal sample loops. However, actual gas samples are needed before this technique can be completely evaluated.

By gas chromatography with hot-wire thermal conductivity detection, major differences between Halocarbon Oils 208 and 208-4 were detected. Halocarbon Oil 208-4 contained a large percentage of high-boiling components, while Halocarbon Oil 208 contained none of these same components. Infrared analyses could detect only slight variations.

Based on laboratory work, this procedure appears to be satisfactory; however, modifications in sampling techniques may be required under field conditions.

TABLE I. INSTRUMENT OPERATING PARAMETERS

INSTRUMENT	Micro Tek Model 150-G, or Equivalent
DETECTOR	High-temperature Ni^{63} Electron Capture, 10 mCi
POWER SUPPLY	Micro Tek Electron Capture Power Supply in a Pulsed Mode
PULSE RATE	30 Microseconds
PULSE WIDTH	10 Microseconds
VOLTAGE OUTPUT	-50 Volts dc
ELECTROMETER SETTING	16×10^2 (1.6×10^{-9} amps Full Scale)
COLUMN	6-ft. x 1/8-in. od Stainless Steel, 5 Percent SE-30 Silicone Rubber on Chromosorb W (60/80 Mesh)
CARRIER	5 Percent Methane in Argon
FLOW RATE	43 ml/min at 40 psig
COLUMN TEMPERATURE	100°C
INLET TEMPERATURE	200°C
DETECTOR TEMPERATURE	280°C
RECORDER	1 Millivolt
CHART SPEED	30 Inches/Hour

TABLE II. RESPONSE DATA FOR HALOCARBON OIL 208-4

Sample	gm/μl	μl Injected	gm Injected	Peak Height, (cm)
1	1.8×10^{-8}	5.0	9×10^{-8}	342×10^{2}
2	3.6×10^{-10}	5.1	1.8×10^{-9}	182×10^{2}
3	3.6×10^{-10}	2.5	9×10^{-10}	102×10^{2}
4	3.6×10^{-10}	7.5	2.7×10^{-9}	228×10^{2}
5	3.6×10^{-10}	10.0	3.6×10^{-9}	266×10^{2}
6	7.2×10^{-11}	5.1	3.7×10^{-10}	39×10^{2}
7	7.2×10^{-11}	2.5	1.8×10^{-10}	21×10^{2}

TABLE III. ANALYSIS OF HALOCARBON OILS 208 AND 208-4

Sample	Peak Number	Peak Area	Area %
Halocarbon Oil 208-4	1	2	0.11
	2	44	2.33
	3	16	0.85
	4	94	4.98
	5	38	2.01
	6	17	0.90
	7	1030	54.59
	8	24	1.27
	9	124	6.57
	10	79	4.19
	11	8	0.42
	12	50	2.65
	13	1	0.05
	14	6	0.32
	15 16	26	1.38
	17	18	0.95
	18 19 20 21 22	152	8.06
	23 24 25 26 27	132	7.00
	28 29	21	1.11
Halocarbon Oil 208	2	14	0.65
	7	2142	98.89
	30	10	0.46

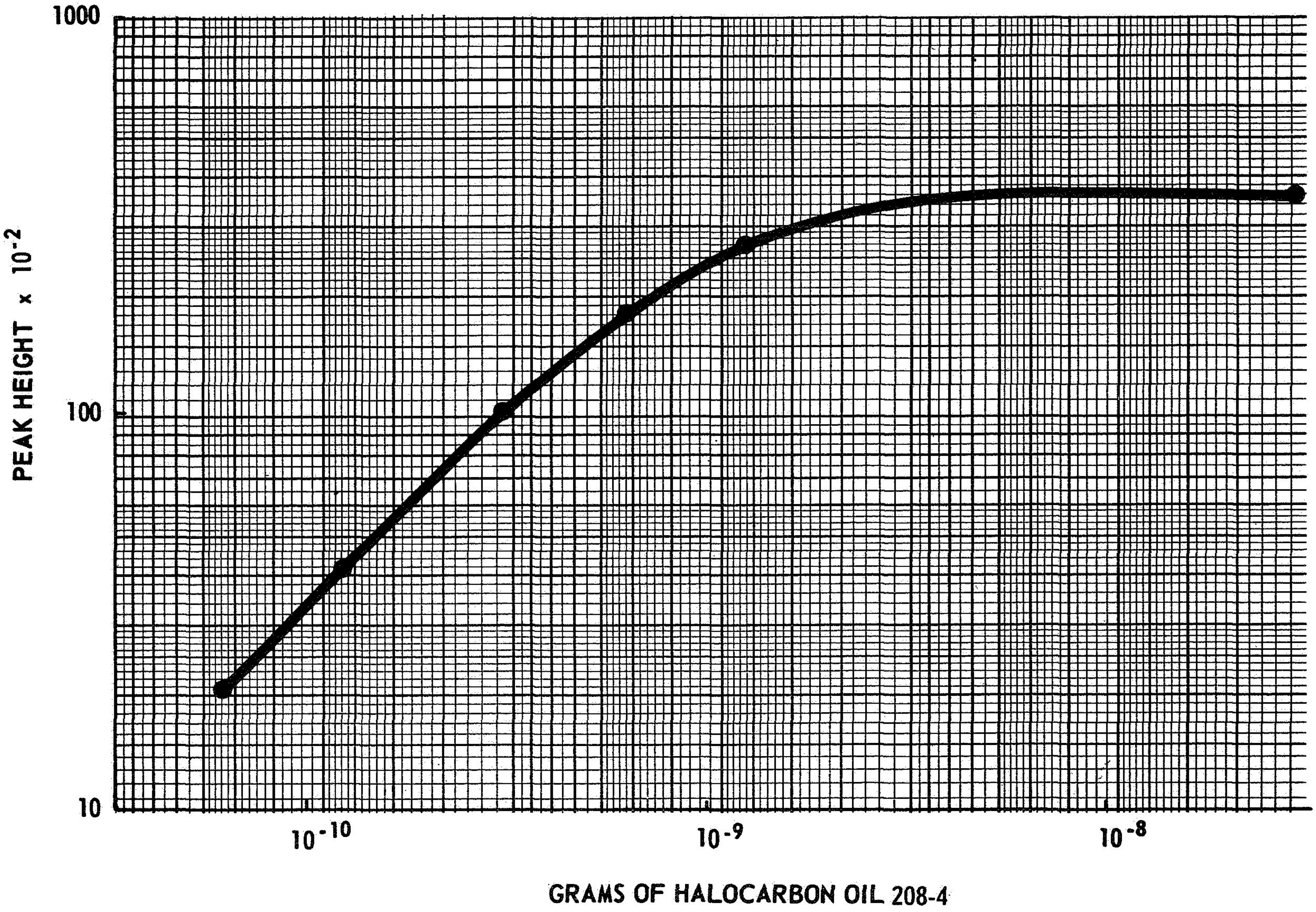

FIGURE 1 LINEAR DYNAMIC RANGE OF HALOCARBON OIL 208-4

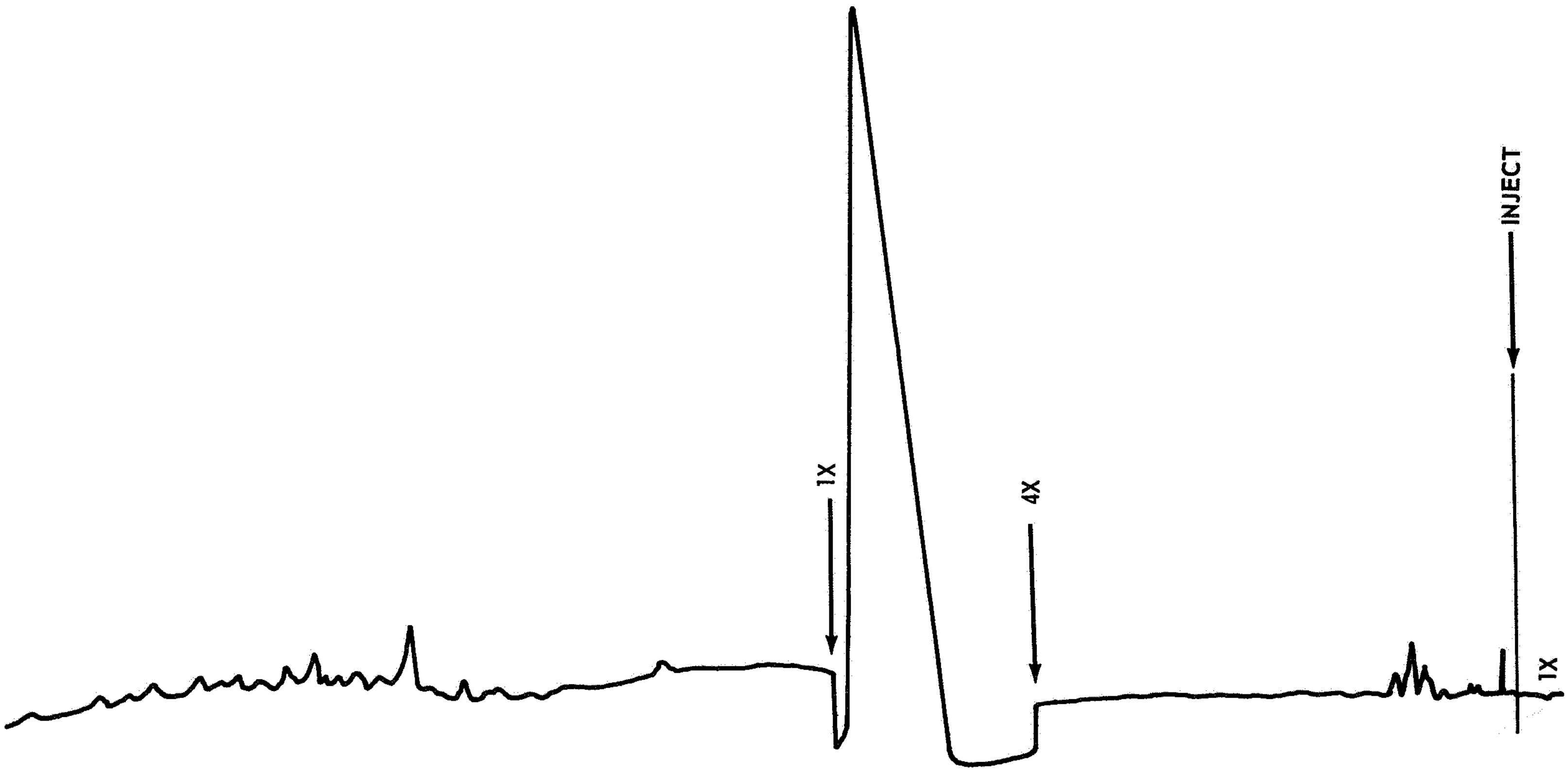

FIGURE 2 HALOCARBON OIL 208

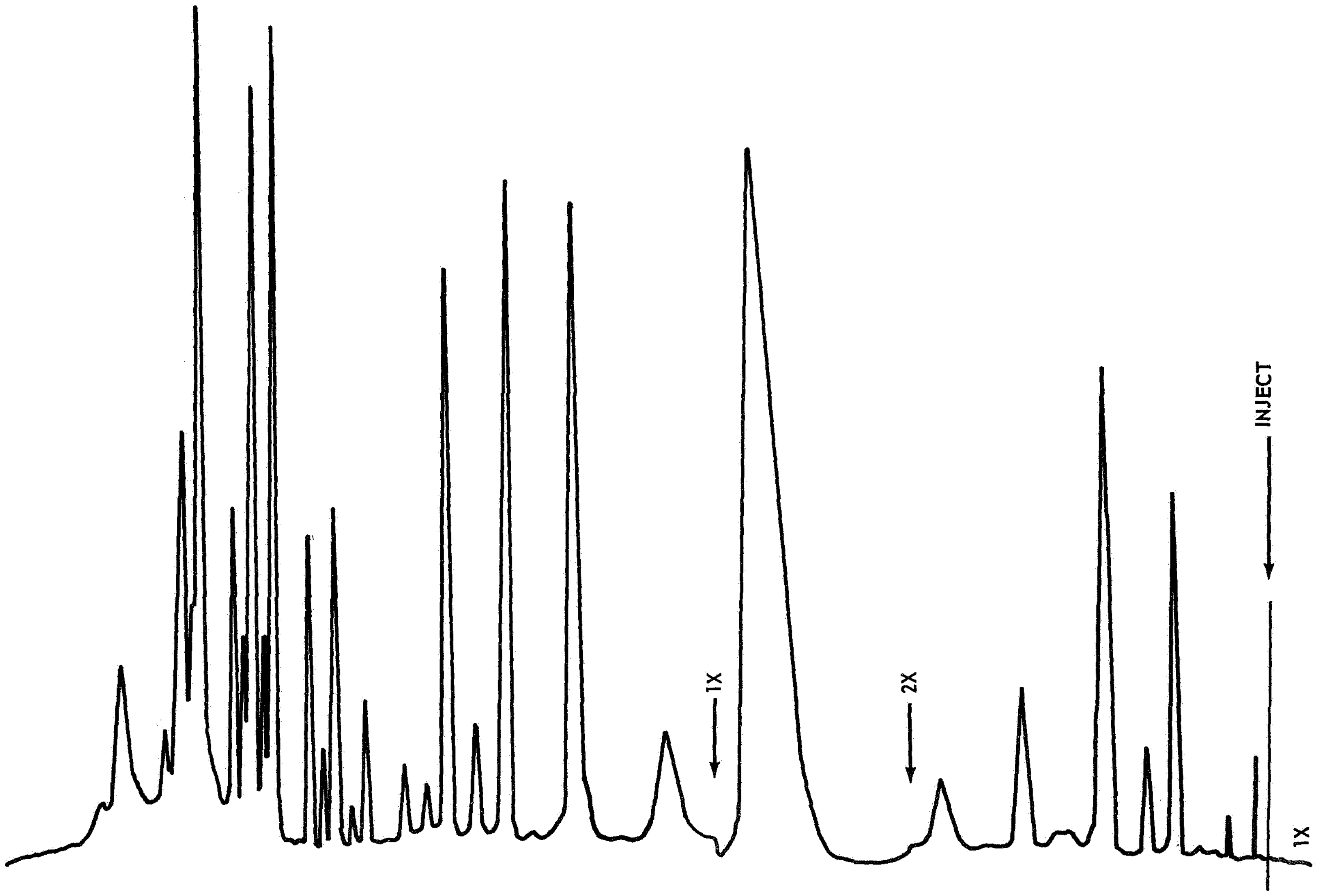

FIGURE 3 HALOCARBON OIL 208-4

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October 7, 1968 NASA TM X-53789

APPROVAL

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The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

J. R. Nunnelley

J. R. Nunnelley
Chief, Chemistry Branch

J. E. Kingsbury
Chief, Materials Division

W. R. Lucas

W. R. Lucas
Director, Propulsion & Vehicle Engineering Laboratory

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