NRL Report 6636

The SEALAB II Trace-Contaminant Profile

R. A. Saunders and R. H. Gammon

Physical Chemistry Branch
Chemistry Division

December 4, 1967

NAVAL RESEARCH LABORATORY
Washington, D.C.

This document has been approved for public release and sale; its distribution is unlimited.

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
ANALYTICAL METHODS	1
EXPERIMENTAL TECHNIQUE	2
RESULTS	3
SUMMARY	6
ACKNOWLEDGMENTS	7
REFERENCES	7

ABSTRACT

Adsorption of contaminants on activated charcoal was one of the methods used to sample the atmosphere of Sealab II. The contaminant material was later recovered by slowly heating the charcoal in an evacuated system and retaining the desorbate in liquid-nitrogen-cooled traps. The desorbate mixture was resolved with a vapor-phase chromatograph. The eluted components were passed directly into a rapid-scanning mass spectrometer for positive identification. Components were also collected from the effluent of the chromatograph and identified by means of their infrared spectra. Over 30 different compounds were identified in the charcoal desorbate. Added to those already known, the total number of atmospheric contaminants which have been identified in Sealab II now amounts to 40. These include refrigerants, saturated and unsaturated aliphatic hydrocarbons, cyclic aliphatic hydrocarbons, chlorinated hydrocarbons, and aromatic hydrocarbons. The characteristic feature of the Sealab II contaminant profile, like that of Sealab I, was a predominance of hydrocarbon contaminants. Some of the more prominent contaminants in the Sealab II atmosphere were cyclic aliphatic hydrocarbons which are not generally encountered as dominant trace contaminants in closed environmental atmospheres.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

NRL Problems C08-33 and C07-01
NAVSHIPSYSCOM Problem S4607
Project RR 001-01-43-4803

Manuscript submitted August 24, 1967.

THE SEALAB II TRACE-CONTAMINANT PROFILE

INTRODUCTION

The atmospheres of the Sealab series of manned underwater stations are of interest as part of a continuing NRL program of determining the organic trace contaminant profiles of closed environmental atmospheres. The atmosphere of Sealab I (1) was characterized by a predominance of hydrocarbon material, mainly saturated and unsaturated aliphatic hydrocarbons above C_7 in molecular weight. Some cyclic and aromatic hydrocarbons were also present. Over a hundred different compounds were recovered and identified or characterized. The presence of this material in the Sealab I atmosphere was attributed in part to oil-soaked paper dust filters in a pair of lithium hydroxide-carbon dioxide scrubber units, and partly to the normally present contaminant sources — for example, painted surfaces. Contaminants arising from less profuse sources in Sealab I were largely masked or spectrally hidden in the relatively large quantity and number of hydrocarbons from the sources mentioned.

ANALYTICAL METHODS

Two types of sampling procedure are generally used for the analyses of closed atmospheres. One is the direct chromatographic analysis of small samples of whole air (100 ml to 1 liter) taken from the source of interest, without recourse to concentrating techniques. Analyses of this type are usually made at the scene to monitor the concentration of a few known contaminants of particular interest and importance. Whole air samples may also be taken for subsequent analyses in the laboratory; these provide, also by direct chromatographic examination, more detailed qualitative and quantitative information regarding the more concentrated trace contaminants. The data from this type of analyses of the Sealab II atmosphere have been reported elsewhere (2).

Chromatograms of small whole air samples taken from closed environmental atmospheres typically display some 10 to 15 peaks, representing perhaps 20 to 40 different contaminants. For any given set of column conditions there are a number of compounds which have identical retention times; hence in the gas-phase chromatographic separation of any mixture which comprises a wide range of compounds, there will be instances where some of the components of the mixture are not separated from others. This fact diminishes the usefulness of the gas chromatograph as a positive means of identifying the constituents of such mixtures. True, the accuracy of identification can be increased by resolving the mixture on several different columns, but at the expense of a considerable increase in analytical complexity.

A more reliable method is to recover the material eluted from the column during the time interval of interest and to obtain its infrared or mass spectrum. This method affords a positive method of identification for most compounds. Having correctly identified the components of a mixture, quantitative data can be obtained from the original chromatograms.

Note: R.H. Gammon is now at Harvard University, Dept. of Chemistry, Cambridge, Mass.

A second sampling technique for analyzing environmental atmospheres is to concentrate the contaminants by separating them from the large volume of air in which they are diluted. One easy and simple method of accomplishing this is to pass the air through a suitable adsorbent such as activated charcoal, from which the contaminants can be recovered later. This method permits qualitative identification of a larger number of the less concentrated trace contaminants and was the method used to provide the sample for the analysis reported here. This procedure yields no information, however, about compounds for which charcoal has a very low affinity, e.g., methane and carbon monoxide. Moreover, without calibration the method is of limited value for the production of quantitative data.

EXPERIMENTAL TECHNIQUE

Samples were taken with the unit shown in Fig. 1. A 40-gram charcoal cartridge was exposed for ten hours at a flow rate of 1-1/2 cfm. Contaminants were recovered from the charcoal by very slowly heating it in an evacuated system and retaining the desorbate in liquid-nitrogen-cooled traps.

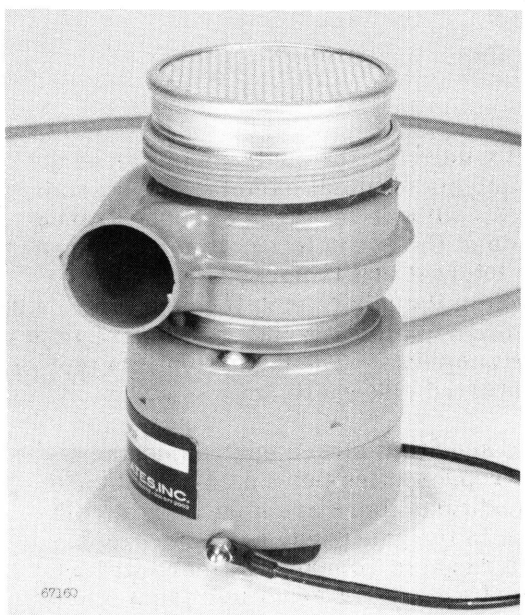

Fig. 1 - Activated charcoal air contaminant sampler

A detailed description of the methods used at NRL for analyzing environmental atmospheres has been given previously (3). Briefly, the desorbate mixture is resolved into its components with a vapor-phase chromatograph, the material represented by each peak of the chromatogram is collected from the column effluent in a separate collection trap and, finally, the collected material is transferred to an infrared or mass spectrometer for positive spectral identification.

A newer technique was additionally brought to bear in this case, one more advanced and with greater sensitivity. This method couples the output of a chromatographic column directly to the input of a rapid-scanning mass spectrometer. The equipment and procedures and the advantages of this method of analysis have already been described in detail (4,5). The particular rapid-scanning mass spectrometer used at NRL has a double ion source. One of the ion sources, energized with 20-volt electrons, serves as an extremely sensitive electron-impact detector for the chromatograph. The other source, energized with 70-volt electrons, gives rise to the mass spectrum. Since the chromatographic column effluent enters the two ion sources simultaneously, a mass spectrum can be obtained at any desired point instantaneously with the recording of any part of the chromatogram. Two or three seconds are sufficient to sweep through the mass range and record a mass spectrum, so that a spectrum can be obtained on the leading edge, at the peak, and on the trailing edge of most chromatographic peaks. Comparisons of these spectra indicate if the particular peak represented a single compound or more.

RESULTS

Figures 2 and 3 are chromatograms of the Sealab II charcoal desorbate. These chromatograms were recorded using the electron-impact detector (the 20-volt electron ionizing source of the rapid-scanning mass spectrometer). These chromatograms illustrate the reason for one of the necessary steps in an analysis of this type. Figure 2 is a chromatogram of an aliquot of the vapor portion of the desorbate exactly as it was recovered from the charcoal. The major component in this mixture is carbon dioxide, the concentration of which is two or three orders of magnitude greater than that of the other components. The amount of sample material which can be injected onto a chromatographic column or introduced into a mass spectrometer is limited, and if the sample is a complex mixture composed predominantly of one or two constituents, the absolute quantity of the other constituents present may be too low to permit identification. However, if the dominating component is removed from the sample or its concentration at least considerably reduced by low-temperature fractional distillation or, as was the case here, by passing the sample several times through a small bed of lithium hydroxide to remove the carbon dioxide, a much better chromatogram of the trace constituents is obtained, as shown in Fig. 3. Actually, the two chromatograms are not equivalent on a retention-time basis because the flow rate through the column in the second case was adjusted to enhance resolution. Both separations were effected with a 300-ft, 0.01-in. I.D., open-tubular column with a poly(propylene glycol) liquid phase (U.C. oil LB-550-X).

Spectra of many of the peaks in the chromatogram of Fig. 3 were obtained with the rapid-scanning mass spectrometer. On the basis of these spectra the compounds reported in Table 1 (column 1) were identified. A few additional compounds, minor constituents of unresolved pairs, were detected at low concentration, but were not identified with certainty and are not reported. Many of the compounds were also collected from the effluent of packed columns and their identity confirmed by means of infrared and mass spectra. The infrared and mass spectral identification of the refrigerants and the chlorinated hydrocarbons was supported by chromatographic retention-time measurements using a microcoulometric detector specific for chlorine-containing compounds (6). The major refrigerant in this

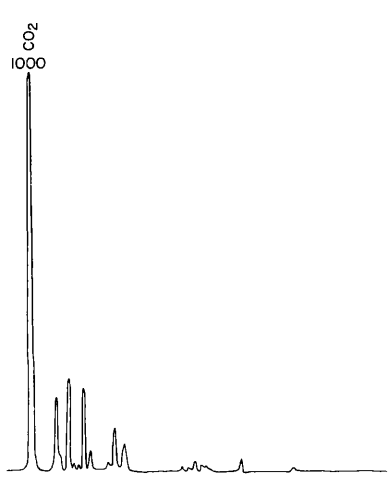

Fig. 2 - Chromatogram of Sealab charcoal desorbate

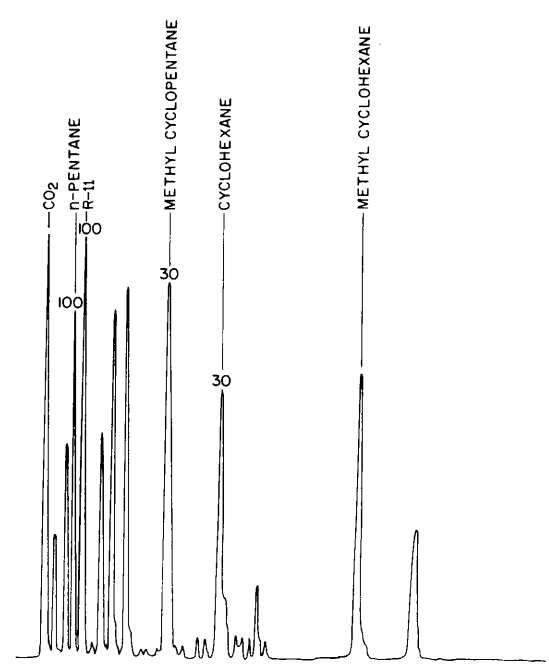

Fig. 3 – Chromatogram of Sealab desorbate after reducing the concentration of CO_2

Table 1
Contaminants Detected in the Atmosphere of Sealab II

Contaminant	Detected in	
	Charcoal Desorbate	Whole Air (2)
1. Carbon monoxide	(a)	x
2. Carbon dioxide	x	x
3. Ethyl alcohol		x
4. Acetone	x	
5. Trichlorofluoromethane (refrigerant-11)	x	
6. Dichlorodifluoromethane (refrigerant-12)	x	
7. Difluorochloromethane (refrigerant-22)	x	
8. Methylene chloride	x	
9. Vinyl chloride	x	
10. Vinylidene chloride	x	
11. Methane	(a)	x
12. n-Butane	x	
13. n-Pentane	x	
14. n-Hexane	x	x
15. n-Heptane	x	x
16. n-Octane	(b)	x
17. n-Nonane	(b)	x
18. Isobutane	x	
19. Isopentane	x	
20. Isohexane	x	
21. Isoheptane	x	
22. 3-Methylpentane	x	
23. 2,2-Dimethylpentane	x	
24. 2,3-Dimethylpentane	x	
25. 2,4-Dimethylpentane	x	
26. Isoprene	x	
27. 3,3-Dimethylpentane-1	x	
28. Cyclopentane	x	x
29. Cyclohexane	x	x
30. Methyl cyclopentane	x	x
31. Methyl cyclohexane	x	x
32. cis-1,2-Dimethylcyclopentane	x	
33. trans-1,2-Dimethylcyclopentane	x	
34. 1,1,3-Trimethylcyclopentane	x	
35. Benzene	x	
36. Toluene	x	x
37. Ethyl benzene	(b)	x
38. o-Xylene	(b)	x
39. m-Xylene	(b)	x
40. p-Xylene	(b)	x

(a) Activated charcoal has a low affinity for these compounds.
(b) These compounds had an unreasonably long retention time for the column and conditions used.

sample was R-11 ($CFCl_3$). The other two refrigerants detected were present in very small quantity. Higher molecular weight aliphatic hydrocarbons and aromatic compounds above toluene in molecular weight had unreasonably long retention times for the columns and column conditions used and, hence, none were detected in the charcoal desorbate.

However, several of these compounds were detected as a result of the chromatographic analyses of the whole air samples and are reported in Table 1.

The measured total hydrocarbon concentration* of the Sealab atmosphere was small, even though it contained a fairly large number of different hydrocarbon contaminants. The total hydrocarbon concentration rose to 15 mg/m^3 during the first ten days of the experiment, but dropped to less than 1 mg/m^3 after the main charcoal filter was changed. The concentration gradually increased during the final 35 days, although it never approached the higher levels which prevailed at first (2).

These figures are based on a sample pressure of one atmosphere. However, the pressure in Sealab was seven atmospheres. Therefore, the actual quantity of contaminant material per unit volume in Sealab was seven times higher than the values stated here.

The higher concentration which prevailed during the first ten days came about as a result of an omission in planned procedure. The charcoal in the main filter which was scheduled for replacement at the beginning of the experiment and every ten days thereafter was, in fact, changed only once – on the tenth day. The effect of that omission on atmospheric contamination has been discussed elsewhere (2). Some of the more volatile contaminants which were adsorbed on the main charcoal filter during the outfitting of Sealab II were later displaced or eluted from the charcoal and gradually re-entered the atmosphere during the first ten days. This steady contribution to the contaminant load gradually raised the total hydrocarbon concentration to a maximum near 15 mg/m^3 (normalized to one atmosphere pressure). Changing the charcoal filter on the tenth day eliminated this source of contaminants, and the concentration quickly fell to less than 1 mg/m^3. The kind of contaminants which were detected in whole air samples of the atmosphere before and after the filter change remained the same, however. The analytical charcoal sample was exposed on the thirtieth day of submergence – long after the main charcoal filter had been changed. The contaminants detected in the charcoal desorbate, therefore, were the volatile components actually off-gassed during submergence from material sources aboard Sealab and did not include any contaminant material which originated during the construction period.

As was the case with Sealab I and with most submarine atmospheres, most of the contaminants detected in Sealab II were hydrocarbons. The salient feature of the Sealab II trace contaminant profile, however, was the presence of a number of cyclic aliphatic hydrocarbons. A few of these compounds, in fact, were among the most predominant trace organic contaminants in the atmosphere of Sealab II. Compounds of this type were also found in the atmosphere of Sealab I, although in the profusion of other hydrocarbons present in that atmosphere, they were not as outstanding. Neither are these compounds outstanding in a typical submarine atmosphere. The presence of these cyclic compounds as dominant trace contaminants seems to be peculiar to the internal environment of Sealab II. Some effort at establishing the source of these compounds, therefore, seems to be warranted.

The two most obvious possible sources for such contaminants are painted surfaces and the adhesive used for applying cork insulation. The paint solvents used in Sealab were regular mineral spirits, which are rich (40 percent by volume) in cyclic hydrocarbons. However, the boiling range usually specified for such solvents, 150°C to 210°C typically, would presumably preclude all but traces of cyclic aliphatic hydrocarbons below C_7. A chromatogram of the lighter volatiles stripped at room temperature from a

*Total hydrocarbon concentration is defined as the weight of n-hexane per unit volume of air necessary to produce the same response in a hydrogen flame ionization detector as a unit volume of the sample atmosphere containing all its contaminants except methane and refrigerant-12.

sample of mineral spirits (taken from the Navy Supply System but of unknown prime source) not surprisingly failed to show the presence of compounds in this molecular weight range. California crude oils are known to contain a higher proportion of cyclic hydrocarbons than other crudes, however, and it has been suggested that paint thinners derived from such oils would contain more aliphatic cyclic compounds than a similar product derived from an oil of different origin. While this is undoubtedly true, such a solvent would be subject to the same boiling-range restrictions which, likewise, should minimize the concentration of cyclanes below C_7. Another source of cyclic aliphatic hydrocarbons in Sealab are the highly plasticized neoprene rubber diving suits. Oils rich in cyclic structures are favored for plasticizing neoprene because of their better degree of compatibility. These oils also are of a high boiling range and were found to contain no cyclanes below C_7.

The adhesive used to apply the cork insulation in Sealab II was furnished to comply with Military Specification Mil-A-18065A(SHIPS), which sets forth the requirements for an adhesive to be used for applying insulation to steel surfaces in poorly ventilated and dead-air spaces. The adhesive was a one-part waterproof cement based on a combination of resin and drying oil and a suitable nontoxic solvent. The more volatile components of the solvent were stripped from a sample of the adhesive at room temperature and examined with a combination gas chromatograph and rapid-scanning mass spectrometer. The volatile portion of the solvent was found to be a mixture of hydrocarbons including cyclopentane, methyl cyclopentane, cyclohexane, and methyl cyclohexane, the latter being one of the major components. Benzene, toluene, and the isomeric xylenes were also detected. A number of the remaining spectra were difficult to interpret, but the presence of normal- and isohexane was indicated along with normal- and isooctane and n-nonane. Since all of these compounds were also detected in the Sealab atmosphere, it is apparent that the cork-insulation adhesive could have been a major contributor to the Sealab II trace-contaminant pattern.

Specifications for the type of insulation adhesive used aboard Sealab require a Cleveland open-cup flash point of not less than 120°F, and the measured flash point (145°F) was well above this limit. However, the adhesive had a measured closed-cup flash point (Pensky-Marten) below room temperature. The low closed-cup flash point confirms the presence of volatile compounds, although the wide spread between the closed-cup and the open-cup measurements indicates that the volatile fraction of the solvent is a minor portion of the total solvent. Nevertheless, a sufficient quantity of the adhesive applied in a poorly ventilated space could generate enough highly flammable vapors to constitute a definite hazard during use.

The hydrocarbons which off-gassed from the sources mentioned dominated the Sealab II contaminant profile and probably obscured many contaminants stemming from less productive sources. It is suggested that in the future a longer drying time be permitted for paints and adhesives and that a fresh charcoal filter be installed before beginning submerged operations, to minimize contaminants from these sources, and thus uncover still unknown contaminants present at lower levels of concentration.

SUMMARY

Forty contaminants in the Sealab II atmosphere have been identified. Identifications were made both by the chromatographic analyses of whole air samples and by sampling the atmosphere with activated charcoal, resolving the recovered contaminant mixture with a vapor-phase chromatograph, and obtaining infrared and mass spectra of the separated compounds. In addition to the usual carbon monoxide, carbon dioxide, methane, and refrigerants, identified compounds included saturated and unsaturated aliphatic hydrocarbons, substituted and nonsubstituted cyclanes, chlorinated hydrocarbons, and low-molecular-weight aromatic hydrocarbons.

The outstanding feature of the Sealab II atmospheric contaminant pattern was the fact that a number of the more concentrated trace organic contaminants were cyclic aliphatic hydrocarbons. Compounds of this type have not been generally encountered as dominant contaminants in closed environmental atmospheres. One source for such compounds has been found to be the adhesive used for applying cork insulation. The volatile components off-gassed from this adhesive were apparently a major contributor to the Sealab II trace-contaminant profile.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Dr. Fred W. Williams of the Fuels Branch for confirming the identity of some of the halogen-containing compounds through use of his newly developed gas-chromatographic technique employing a microcoulometric detector. Thanks are also due Dr. Wilbur A. Affens of the Fuels Branch for determining the flash points.

REFERENCES

1. Saunders, R.A., "Contaminants in the SEALAB I Atmosphere," Report of NRL Progress, pp. 1-7, May 1965

2. Umstead, M.E. and Smith, W.D., "Trace Organic Contaminants in the Atmosphere of SEALAB II, Preliminary Report," NRL ltr rept 6180-89:MEU:WDS:ec, Ser 4516, June 8, 1966

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

4. Saunders, R.A. and Saalfeld, F.E., "Improved Methods for the Detailed Analysis of Trace Contaminants in Submarine Atmospheres," Chapter 5 in "Fourth Annual Progress Report - The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," Lockhart, L.B., Jr. and Piatt, V.R., editors, NRL Report 6251, March 1965

5. Saalfeld, F.E., "Rapid Analysis with a Gas Chromatograph-Mass Spectrometer Combination," Report of NRL Progress, April 1966, pp. 10-18

6. Williams, F.W., Umstead, M.E., and Johnson, J.E., "Determination of Trace Quantities of Halogenated Compounds," NRL Report in preparation

This page intentionally left blank.

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

THE SEALAB II TRACE-CONTAMINANT PROFILE

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

An interim report on the problem.

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

Raymond A. Saunders and Richard H. Gammon

6. REPORT DATE December 4, 1967	7a. TOTAL NO. OF PAGES 12	7b. NO. OF REFS 6
8a. CONTRACT OR GRANT NO. NRL Problems C08-33, C07-01 b. PROJECT NO. NavShipSysCom S4607 c. RR 001-01-43-4803 d.	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6636 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*	

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Navy (NavShipSysCom, ONR), Washington, D.C. 20360

13. ABSTRACT

Adsorption of contaminants on activated charcoal was one of the methods used to sample the atmosphere of Sealab II. The contaminant material was later recovered by slowly heating the charcoal in an evacuated system and retaining the desorbate in liquid-nitrogen-cooled traps. The desorbate mixture was resolved with a vapor-phase chromatograph. The eluted components were passed directly into a rapid-scanning mass spectrometer for positive identification. Components were also collected from the effluent of the chromatograph and identified by means of their infrared spectra. Over 30 different compounds were identified in the charcoal desorbate. Added to those already known, the total number of atmospheric contaminants which have been identified in Sealab II now amounts to 40. These include refrigerants, saturated and unsaturated aliphatic hydrocarbons, cyclic aliphatic hydrocarbons, chlorinated hydrocarbons, and aromatic hydrocarbons. The characteristic feature of the Sealab II contaminant profile, like that of Sealab I, was a predominance of hydrocarbon contaminants. Some of the more prominent contaminants in the Sealab II atmosphere were cyclic aliphatic hydrocarbons which are not generally encountered as dominant trace contaminants in closed environmental atmospheres.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Security Classification

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Atmospheric contaminants						
Analysis of atmospheric contaminants						
Habitability						
Sealab						
Trace organic contaminants						
Chromatograph						
Mass spectrometer						
Closed-space habitability						

DD FORM 1 NOV 65 1473 (BACK)
(PAGE 2)

GPO 934-315

Security Classification