63- 4

NRL Rep

CONSTITUTION AND SURFACE CHEMICAL PROPERTIES OF SEA SLICKS

PART 1 - BAY OF PANAMA

W. D. Garrett, C. O. Timmons, and N. L. Jarvis

Surface Chemistry Branch
Chemistry Division

and

R. E. Kagarise

Physical Chemistry Branch
Chemistry Division

May 23, 1963

DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH

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

CONTENTS

ABSTRACT

Samples of surface water have been collected from both slick and nonslick areas of the Bay of Panama by the screen method developed at NRL. The screen method samples the water surface to a depth of only 0.15 mm. Since this technique is nonselective, all constituents of the sea surface were effectively collected. Selective solvent extraction was used to concentrate and isolate the various organic materials from the sea water. The solvents were removed by vacuum pumping at room temperatures. Milligram quantities of organic waxes and oils, which were free of salt, water, and solvents, were obtained by this technique.

These slick constituents were subjected to infrared analyses, surface viscosity, surface-potential measurements, and force-area film-balance studies. In addition, fatty acid distributions were determined by gas chromatographic analysis. The data indicate that both slick and non-slick covered surface waters contain a similar mixture of surface-active chemicals. Extracted substances were identified as fatty acids, lipids, and nonpolar hydrocarbons, with some chemical unsaturation showing in the hydrocarbon portion of the organic molecules. The isolated material forms compressible, liquid-expanded films on water which appear to contain quantities of nonpolar material. Surface viscosities of the films were low, indicative of appreciable amounts of unsaturated fatty acids and esters. Gas chromatographic studies showed that each sample contained a complex mixture of saturated and unsaturated fatty acids containing from 8 to 20 carbon atoms. An average of approximately 16 carbon atoms per molecule was found.

PROBLEM STATUS

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

AUTHORIZATION

NRL Problem C02-18
Wep Task RUDC-4B-000/652-1/S031-01-00-231-3

Manuscript submitted January 31, 1963.

CONSTITUTION AND SURFACE CHEMICAL PROPERTIES OF SEA SLICKS

PART 1 - BAY OF PANAMA

INTRODUCTION

For many years there has been speculation about the nature and origin of natural slicks on the ocean. Scientific interest in these oceanic phenomena goes back to Thompson (1) who considered mechanisms to account for calmed areas on a rippled sea and Aitken (2) who studied the wave-calming effects of oily materials. In most cases a sea surface film exists as a monomolecular layer of polar organic molecules which may be derived from marine-biological sources. As surface convergences occur, the molecules of the surface layer are compressed and the resulting compacted area develops a measurable film pressure and exerts a damping effect on capillary waves.

Collection and analysis of the constituent chemicals in the sea surface has received little attention to date. Ewing (3) has described the collection of a surface scum from the pier of the Scripps Oceanographic Institution, San Diego, California. This foamy mixture had supposedly arisen from the compaction of a film beyond its collapse pressure. The scum was filtered and the dried solids were found to contain 27-percent organic matter. No analysis was made of the liquid or gaseous phases. Although several papers dealing with the analysis of specific chemical classes in subsurface water have been written (4-6), no further information exists in the literature as to the chemical nature of films on the ocean's surface.

This report is the first of a series concerned with the collection and identification of those materials which contribute to sea slicks. Upon isolation of the slick constituents, physical and chemical analyses and experiments were performed to develop a chemical picture of the ocean surface.

SAMPLE COLLECTION AND CONSTITUENT ISOLATION

Seven samples were collected from various stations in the Bay of Panama (Fig. 1) utilizing the surface sampling technique developed by Garrett (7). This method utilizes a metal screen enclosed by a frame to which handles are attached. The screen is placed into the water parallel to the surface, withdrawn, and drained into a 5-gallon polyethylene collection vessel. The operation was repeated until the vessel was filled. This technique removes a 0.15-mm-thick film of surface water and since the method is nonselective, all the organic constituents of the water are efficiently collected. The collected organic material was concentrated by the precipitation of a ferric hydroxide sol within the sample bottle. The organic constituents were occluded and adsorbed by the gelatinous precipitate which, after settling, was separated from the sea water. The supernatant sea water was discarded, and the concentrate acidified to a pH of 2 to dissolve the ferric hydroxide and to halt biological activity. The concentrated samples containing the organic material in aqueous suspension were frozen and packaged in dry ice for shipment from the collection location to the U.S. Naval Research Laboratory at Washington, D.C.

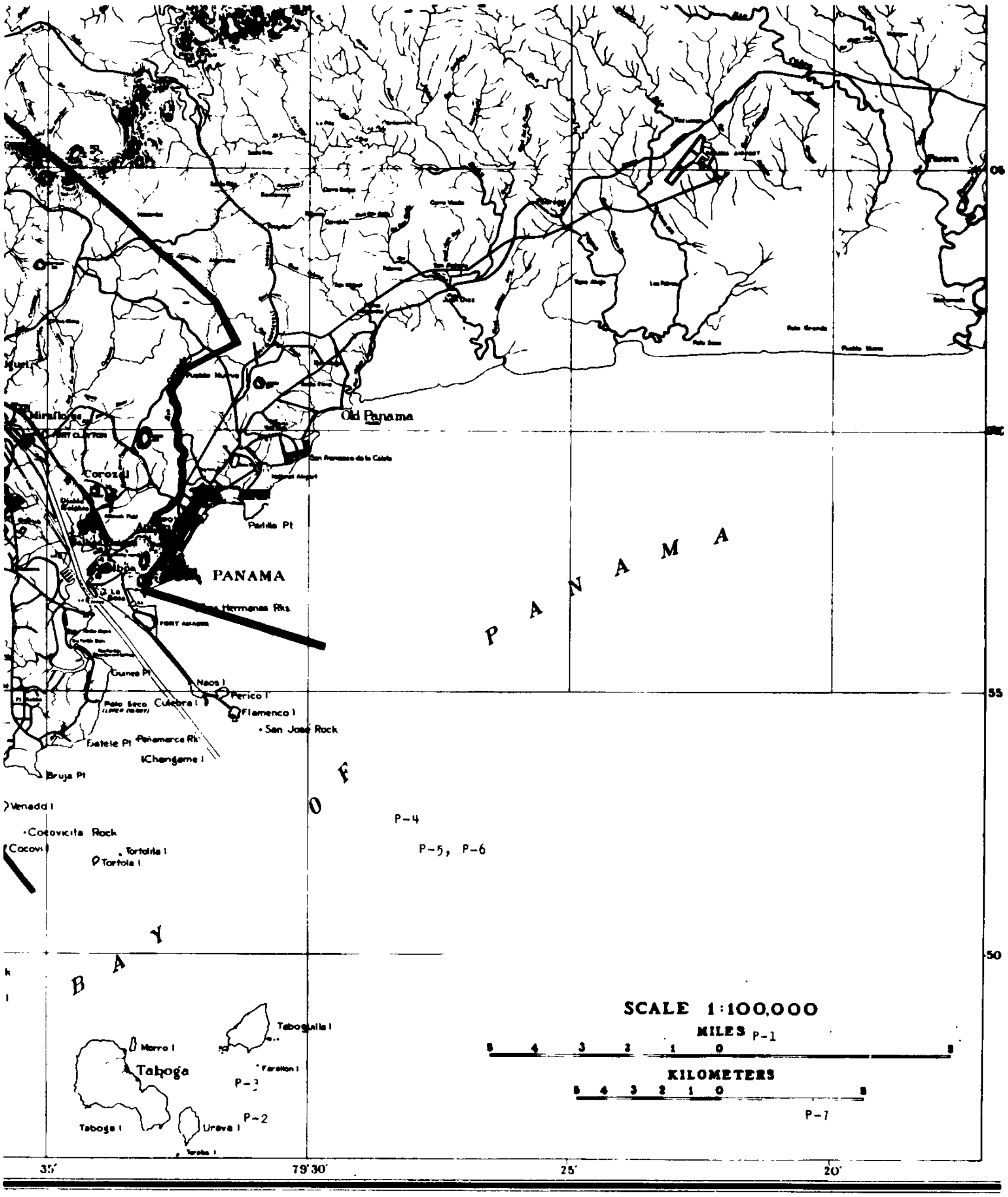

Fig. 1 - Surface sampling stations - Bay of Panama

Upon receipt, the slick samples were thawed and portions of the organic material extracted with a series of volatile organic solvents the remaining aqueous solutions being retained for future studies. The order of extraction used was petroleum ether, chloroform, benzene, and diethyl ether. These solvents met either ACS or AOCS specifications of purity and contained about 0.0002 percent "residue after evaporation." Before use they were further purified by distillation through a Vigreaux column to assure absence of any nonvolatile portions which might modify the analyses and properties of the slick components. Following extraction of the organic constituents of the slick materials, the individual solvents were removed under vacuum leaving the oils and waxes which had been present in the samples of surface water.

Table 1 lists the meteorological and oceanographic conditions observed at each sampling location. P-1 was collected under conditions where no visible slick existed although 1 to 2 dynes/cm surface pressure was measured in the area sampled. P-2 and P-3 were taken from the same slick. P-2 was taken from a compact surface scar, while by the time P-3 was collected, an increasing wind had streaked this slick into narrow bands aligned with the motion of the air. P-4, P-5, and P-7 were taken from individual slicks. These well-defined slicks were elongated areas aligned with the wind. P-6 was near-surface water taken in the same slick location as P-5 by slowly submerging the collection bottle.

Table 1
Samples From the Bay of Panama

Sample Designation (Fig. 1)	Pressure of Surface Film* (dynes/cm)	Depth (Fathoms)	Wind (mph)	Date	Time	Remarks
P-1	1 to 2	18	12	6 Feb. 62	0700	No visible slick
P-2	4	15	10	6 Feb. 62	0900	Compact surface scar
P-3	4	15	15	6 Feb. 62	1015	Same slick as P-2 with increased wind
P-4	6	10	3	7 Feb. 62	0720	Individual slick
P-5	6	10	3	7 Feb. 62	0810	Individual slick
P-6	6	10	3	7 Feb. 62	0830	Near-surface water from same slick as P-5
P-7	5	21	3	7 Feb. 62	0900	Believed to be oil slick from ship

*Surface film pressures were measured with calibrated spreading oils using the method of Adam (8).

The quantity of organic material isolated ranged from 2.5 to 13.1 mg and averaged about 8 mg per sample for six of the samples. Eighty milligrams were extracted from P-7. There appeared to be little correlation between the quantities of organic material isolated and the conditions under which sampling was performed.

Petroleum ether was not a particularly effective solvent for these slick constituents On the other hand, since chloroform and benzene were useful extractants, most of the organic matter was isolated through the use of these solvents. Yields from the diethyl ether extractions were low since this solvent was used as final extractant and most of the sought-after material had already been removed. A final chloroform extraction made for the purpose of testing the extraction efficiency did not yield a measurable quantity of organic material.

BIOLOGICAL CONTAMINATION

The presence of microbiological marine organisms in the sea surface samples will contribute some organic matter to the material recovered from the slick. Although acidification and freezing of the ferric hydroxide concentrate halts biological reproduction, the existing organisms might in part affect the analytical results. To determine the extent of this possible interference, raw 30-ml portions of each sample were placed into sterilized bottles, frozen, and shipped in dry ice. After thawing each sample, counts of viable bacteria and fungi were made by two independent techniques (9). These results, tabulated in Table 2, indicate that only a small number of biological entities existed in the collected samples. A rough calculation based upon generous assumptions showed that the maximum chemical contribution from these organisms is negligible in comparison to that from the slick itself.

Table 2
Counts of Bacteria and Fungi in Sea Water Samples
From the Bay of Panama

Sample Designation	Approximate Number of Colonies Developing Per mℓ	
	Bacteria	Fungi
P-1	<1	<1
P-2	130	20
P-3	<1	<1
P-4	5	<1
P-5	5	1
P-6	12	<1
P-7	1	2

INFRARED ANALYSIS OF SEA SLICKS

The use of infrared spectroscopy as a means of determining the chemical composition of materials is well known. This analytical technique is particularly useful for establishing the presence or absence of those structural units which have been correlated with characteristic infrared absorption bands. Many of the correlations, particularly those in the region of skeletal vibrations, are subject to considerable frequency variations with structural change. In both instances, the role of environment is important, since such factors as hydrogen bonding can appreciably alter the frequency of a given vibrational mode. Thus, the application of infrared spectroscopy to the elucidation of molecular structure must be carried out with caution, because structure-spectral correlation charts are not without limitations.

The materials extracted from the sea slicks, as described in the previous section, represent a rather difficult analytical problem. First, the amount of material available is limited, in several cases weighing less than 2 milligrams. Secondly, the materials are neither liquids nor solids but rather gummy waxes. Finally, they are not particularly soluble in carbon tetrachloride or carbon disulfide. For these reasons, it was impossible to make quantitative comparisons of the spectra, and only qualitative information was achievable.

The infrared spectra were obtained with a Beckman IR-5 spectrophotometer equipped with NaCl optics. The spectral region studied was from 2 to 16 microns. The materials were examined by spreading a small portion on the surface of a sodium chloride plate. The plate was then placed at the focus of a beam condensing unit in order to reduce the sample area needed to fill the radiation beam of the spectrometer.

Before discussing the observed spectra in detail, it seems desirable to make several general comments. First, the identification of unknowns is based primarily on the comparison of the spectrum of the unknown with the spectra of known materials. Provided one has a sufficiently complete collection of reference spectra, this can usually be achieved for single compounds of reasonable purity. In the case of complex mixtures, one can at best identify certain functional groups which may lead to a classification as to chemical type, e.g., hydrocarbon, carboxylic acid, amine, etc. Since the sea-slick samples are complicated materials, either because they are complex mixtures or large and multifunctional chemical compounds, it is not possible to make positive identifications. Therefore, the spectra have been interpreted on the basis of certain functional groups for which group frequency correlations are reasonably well established.

It is well known that most functional groups may be correlated with a number of infrared absorption bands. For example, the carboxyl group (-COOH) gives rise to bands at 3.1μ (OH stretching mode), 5.9μ (C=O stretching), and 7.9μ (OH bending mode). Rather than discuss the bands individually, they have been grouped together according to the functional group from which they arise. The results of such an analysis are shown in Table 3. Practically all of the observed bands are explainable in terms of the six functional groups shown. Group VI, which consists of bands at 6.02 and 13.5μ, is due to an unidentified functional group.

The alphabetic designations in the table give an estimate of the intensity of the bands due to the various groups. Thus, an S designation indicates a relatively high abundance of a particular functional group whereas a VW designation indicates a very low abundance.

As one would expect, all samples contain a relatively high abundance of CH_2 and CH_3 groups (Group I) since these are the basic components of most organic materials. The chloroform extract of P-7 was particularly high in CH_2 and CH_3 content and one must conclude that this material was essentially an aliphatic hydrocarbon oil.

The vinyl group (Group II) was observed in just two samples, P-2 and P-6. The bands characteristic of COO^-M^+ (Group III), COOH (Group IV), and COOR (Group V) are present, to some extent, in practically all of the samples. There does not appear to be any relationship between the intensities of these bands and the particular extracting liquid. However, the absence of such a relationship may be due to the qualitative nature of the spectral data.

Table 3
Summary of Spectral Results

Sample Designation	Strength of Functional Groups*					
	I	II	III	IV	V	VI
P-1, benzene	S[†]	A	M	S	M	S
P-2, benzene	S	S	M	S	M	S
P-2, CHCl$_3$	M	A	S	M	A	A
P-3, CHCl$_3$	M	A	S	M	W	A
P-4, benzene	M	A	S	W	S	A
P-4, CHCl$_3$	S	A	S	S	S	A
P-5, CHCl$_3$	S	A	S	M	M	A
P-6, CHCl$_3$	S	M	W	S	M	W
P-7, benzene	S	A	M	M	S	A
P-7, CHCl$_3$	S	A	VW	W	W	A

*Group I - Bands due to -CH$_2$ and -CH$_3$ groups - 3.48, 3.55, 6.93, 7.30, and 13.98μ
Group II - Bands due to HC=CH$_2$ vinyl group - 3.30, 6.12, 7.12, 10.12, and 11.05μ
Group III - Bands due to COO$^-$M$^+$ group - 6.32μ
Group IV - Bands due to -COOH group - 3.1, 5.9, 7.12, and 7.9μ
Group V - Bands due to -COOR group - 5.8 and 8.0μ
Group VI - Bands due to unknown group - 6.02 and 13.5μ
[†] S - Strong; M - Medium; W - Weak; VW - Very Weak; A - Absent

SURFACE CHEMICAL PROPERTIES

Force-Area and Surface Potential

Earlier work at this Laboratory has shown that Calanus, an abundant species of zooplankton, contains large amounts of surface-active materials which could form slicks if released to the surface of the sea (4). Since naturally occurring slicks may be composed of this or some similar material, it was of obvious interest to examine the surface chemical properties of the slick materials discussed in the previous section in order to shed additional light on their nature. The materials investigated were these slick samples or, in some cases, combinations of these samples.

The force – area characteristics of each sample were studied with a Langmuir-Adam type film balance. The film balance was made of Pyrex and had a trough 74 cm long, 12 cm wide, and 0.3 cm deep. Film pressures were measured with a Cenco torsion head equipped with a mica float and polyethylene end loops. The torsion head had a sensitivity of 7.69 degrees per dyne/cm. The edges of the Pyrex trough, the movable glass barriers, and the mica float were lightly coated with high-melting paraffin.

The vibrating condenser method (10) was used to measure surface-potential characteristics in conjunction with the film balance. The polished stainless steel electrode was cleaned in a Tide detergent solution, rinsed with greasefree distilled water, and dried at room temperature. The electrode was positioned about 2 mm above the substrate and gave potentials reproducible to ±2 mv. Synthetic sea water was used as the substrate (11). Each sample was spread from redistilled chloroform and all work was performed in a constant temperature room maintained at 20.0° ± 0.2°C.

Typical force-area and surface potential-area isotherms are shown in Figs. 2 and 3. Film pressures, in dynes/cm and surface potentials in millivolts, are plotted as a function of the specific area occupied per milligram of material. For additional reference, the estimated thickness of the film, on the basis of a density of 0.9 g/ml, is included at the top of each figure. A summary of film properties of each film is given in Table 4. These films were extremely fragile, i.e., they had to be compressed very slowly to avoid premature collapse.

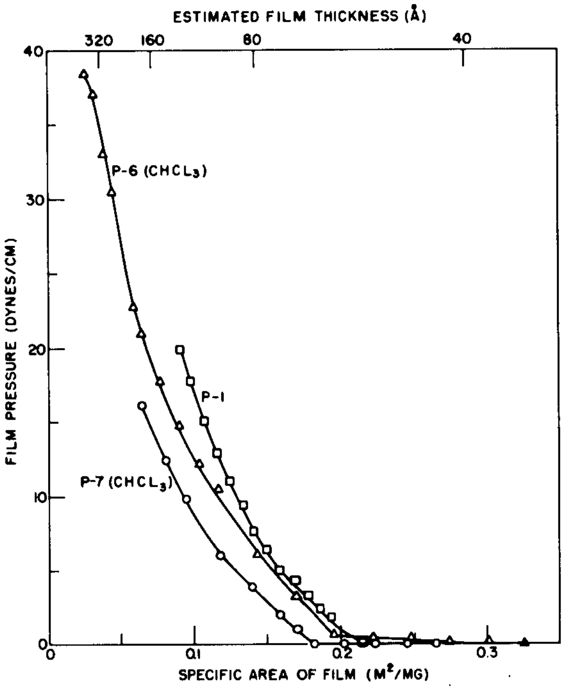

Fig. 2 - Typical force-area curves for Panama samples

P-1 formed a film with a limiting area of 0.21 m^2/mg and a collapse pressure of 19.8 dynes/cm. Collapse occurred at a specific area of 0.08 m^2/mg. The maximum surface potential obtained for this film was 225 mv. This film was fairly compressible, very fragile, and characteristic of a liquid expanded film. This film, as well as all others studied here, did not give a reversible force-area isotherm. The film had an estimated thickness of about 160A.

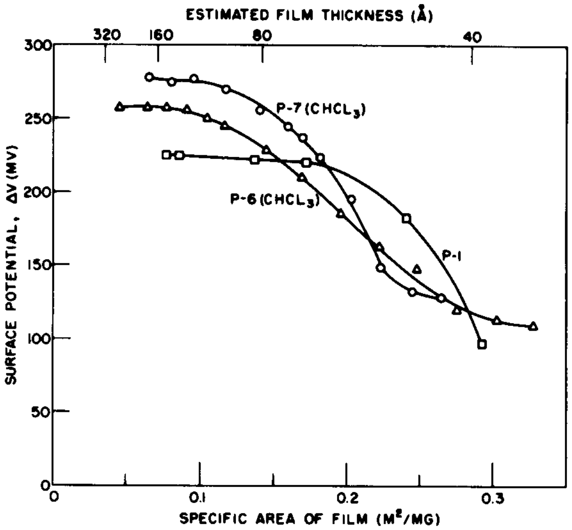

Fig. 3 - Typical surface potential-area curves for Panama samples

Table 4
Summary of Film Properties of Slick Samples

Sample	Limiting Area (m^2/mg)	Collapse Pressure (dynes/cm)	Area of Collapse (m^2/mg)	Maximum Surface Potential (mv)	Estimated Film Thickness (A)
P-1, benzene	0.21	19.8	0.08	225	160
P-2, benzene	0.12	12.5	0.04	243	300
P-2, $CHCl_3$	0.17	19.2	0.03	226	500
Combination*	0.27	17.6	0.11	279	100
P-6, $CHCl_3$	0.30	38.6	0.03	257	500
P-7, benzene	0.30	11.9	0.13	260	90
P-7, $CHCl_3$	0.18	16.1	0.07	277	160

*P-3, $CHCl_3$; P-4, benzene; P-4, $CHCl_3$; and P-5, $CHCl_3$.

The chloroform extract and benzene extract of P-2 also formed fairly fragile films though not as fragile as P-1. These two samples are very similar as might be expected since they came from the same slick. All formed rather compressible films with the same general properties. The benzene extract of P-2 formed a film having a limiting area of 0.12 m^2/mg, a collapse pressure of 12.5 dynes/cm, and a specific area at collapse of 0.04 m^2/mg. This area at collapse corresponds to an estimated film thickness of about 300A. The maximum surface potential obtained was 243 mv. The chloroform extract of P-2 formed a film having a limiting area of 0.17 m^2/mg, collapse pressure of 19.2 dynes/cm, and specific area at collapse of 0.03 m^2/mg. Maximum surface potential was 226 mv for P-2 (chloroform extract). This film was estimated to be on the order of 500A to 600A thick at collapse.

Because of their similar infrared spectra, several extracts were combined for surface property studies. A combination of these extracts from three slicks (Table 4) formed a fragile, slightly more expanded type film than those above. This film had a limiting area of 0.27 m^2/mg, a collapse pressure of 17.6 dynes/cm at a specific area of 0.11 m^2/mg, and a maximum surface potential of 279 mv. The film thickness at collapse was estimated to be about 100A.

Figures 2 and 3 show the film characteristics of P-6 (chloroform extract), the film-forming material extracted from subsurface water. This film had the highest collapse pressure of any observed in these samples. Collapse occurred at a film pressure of 38.6 dynes/cm at a specific area of 0.03 m^2/mg and an estimated film thickness of about 500A. The limiting area was 0.30 m^2/mg and the maximum surface potential was 257 mv.

P-7 (benzene and chloroform extracts (Fig. 4) formed fragile, liquid-expanded films. The limiting areas were 0.30 and 0.18 m^2/mg, collapse pressures were 11.9 and 16.1 dynes/cm, and specific areas at collapse were 0.13 and 0.07 m^2/mg, respectively. Maximum surface potentials were 260 and 277 mv and estimated film thicknesses were about 90A and 160A for the two samples.

It is difficult to be specific about the composition of these slick-forming materials from the data available. As each of these samples is a mixture of unknown materials, it is necessary to characterize them in general terms in light of their surface chemical properties.

The most obvious conclusion is the great similarity, with only few minor exceptions, of all the samples. For example, all samples formed compressible, fragile films of the liquid-expanded type. There are minor variations in the position of the isotherms along the area axis as a result of the amount of polar adsorbable material present. With the exception of P-6, which had a collapse pressure of 38.6 dynes/cm, all samples had collapse pressures ranging from 11.9 to 19.8 dynes/cm.

There is strong evidence that all of these samples contain large quantities of nonpolar material which was mechanically entrained by the film at low film pressures and squeezed out as the film is compressed. The fragility of the films attests to this as well as the extreme displacement of theforce-area isotherms toward low specific areas. Stearic acid, for example, which forms an incompressible, solid-type film, has a force-area isotherm which is displaced far to the right of those reported here. A stearic acid film collapses at a specific area of nearly 0.4 m^2/mg. Unsaturation in the molecule may displace the isotherm even farther to the right. An oleic acid film, for example, collapses at a specific area of nearly 0.6 m^2/mg.

The low specific areas observed for the slick samples lead to estimated film thicknesses of several hundred angstroms in most cases. These values are too large to be accounted for by monolayers (monolayers of close packed proteins are about 10A thick and those of stearic acid about 25A thick) and consequently, one must consider these films to consist of large amounts of nonpolar material which are forced up and out of the more polar material as the films are compressed.

The variations in collapse pressures do not correlate with the different polar species present as indicated by infrared data. These variations can be explained, however, by recalling that each of the samples is a mixture of several components. One of the effects on film properties of one or a combination of these components can be the increase or decrease of collapse pressure. Without knowing the identity or quantity of each component present, it is impossible to interpret precisely these collapse pressure variations.

The maximum surface potentials showed some variation ranging between 225 and 284 mv. Here again, there is no correlation between the data and the polar species present. Monolayers of acids and esters can be expected, generally, to have potentials of about 100 mv or less at the pH of the sea water substrate. Alcohol, amine, and amino acid monolayers, on the other hand, can have potentials as high as 400 to 700 mv. The magnitude of the surface potentials observed for the slick samples then may be explained as a dilution of the high potentials of alcohols, amines, and/or amino acids with the lower potentials of acids and/or esters and the negligible contribution due to the nonpolar hydrocarbons.

Surface Viscosity

The force-area and surface potential-area isotherms reported above are indicative of the orientation, compressibility, and surface activity of the samples, and may be useful in characterizing these surface-active materials. Another surface-chemical property of these materials which may be of interest is their surface viscosity. The surface viscosity of an adsorbed monolayer is related to the lateral forces of cohesion between the molecules, or in the case of long-chain polymers and proteins to the degree of intertwining of the chains.

The surface viscosity of the adsorbed material may play an important role in determining the behavior of natural slicks, inasmuch as it will determine the stress necessary to cause lateral movement of molecules within the film. If there is no lateral motion within the film, a layer of water to a depth of approximately 0.03 mm will also be motionless, because of the viscous drag exerted upon the water by the surface film (12). This viscous association between the adsorbed film and the thin layer of underlying water will certainly be a factor in determining the type of circulation or convective movement of surface water that will be present in the vicinity of a slick, and may also be a key to understanding damping of capillary waves by adsorbed films.

The surface viscosities of the sea slick samples from the Bay of Panama were determined using a deep, narrow canal viscometer like the one proposed by Nutting and Harkins (13). This method is capable of absolute surface viscosity measurements, and has a sensitivity of approximately 1×10^{-5} surface poise. The surface viscosities of the Panama samples reported here were all determined using synthetic sea water (11) as the substrate, at 20°C.

The collection of slick-forming materials taken from the Bay of Panama were divided into seven extracts as mentioned previously. The surface viscosity of each extract was found to be very low at all film pressures up to the point of collapse. The surface viscosity versus area per molecule curves for each of the samples were found to be very similar in shape as well as magnitude of viscosity. The η versus A curve for P-1 (benzene extract) as shown in Fig. 4 is representative of each of the slick-forming materials. The viscosities at 1 dyne/cm were generally around 0.00022 surface poise and at 10 dynes about 0.00044 surface poise. The η versus A curves leveled off at about 10 dynes/cm and very little change in surface viscosity was observed with further increase in film pressure. As an indication of the similarity of the surface viscosity values, the surface viscosity of each sample at 10 dynes/cm is listed in Table 5. The precision with which these surface viscosity measurements could be made was about ± 10 percent. On this basis the differences between the various samples are not significant.

It is difficult to interpret the surface viscosity data of the slick-forming materials for two reasons, the first being that our knowledge of the chemical composition of these materials is very limited. The second reason is that we have no information available on the surface viscosity of known compounds on sea water. For these reasons the surface viscosities of several well-defined reference compounds - oleic acid, triolein, bovine serum albumin, stearic acid, and cetyl alcohol - are compared in Fig. 5 with the surface viscosity of a typical Panama slick sample.

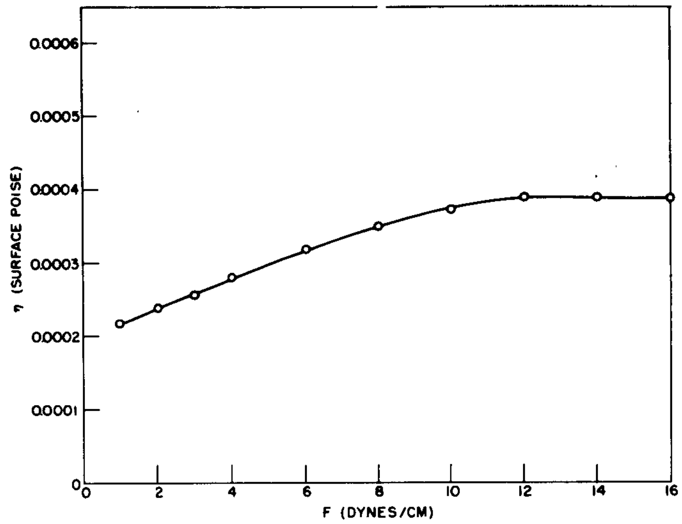

Fig. 4 - Surface viscosity versus film pressure for P-1 on synthetic sea water

Table 5
Surface Viscosity of Slick-Forming Materials
Collected From the Bay of Panama

Sample	Surface Viscosity at 10 dynes/cm (surface poise)
P-1, benzene	0.00044 ± 0.00004
P-2, benzene	0.00047
P-2, $CHCl_3$	0.00051
P-6, $CHCl_3$	0.00037
P-7, benzene	0.00038
P-7, $CHCl_3$	0.00040
Combined extracts (P-3, $CHCl_3$; P-4, benzene; P-4, $CHCl_3$; P-5, $CHCl_3$)	0.00049

As expected, stearic acid formed a solid film on sea water because of the presence of multivalent cations. Bovine serum albumin also gave a very high surface viscosity, which is typical of most proteins. Cetyl alcohol had a much lower surface viscosity than either of these, but was still several orders of magnitude greater than oleic acid, triolein, or P-1. The interesting comparison is between the last three samples, all of which had surface viscosities that agreed within the limits of experimental error at film pressures above 8 dynes/cm. Even at low film pressures the maximum difference between P-1 and oleic acid was still only 0.00008 surface poise.

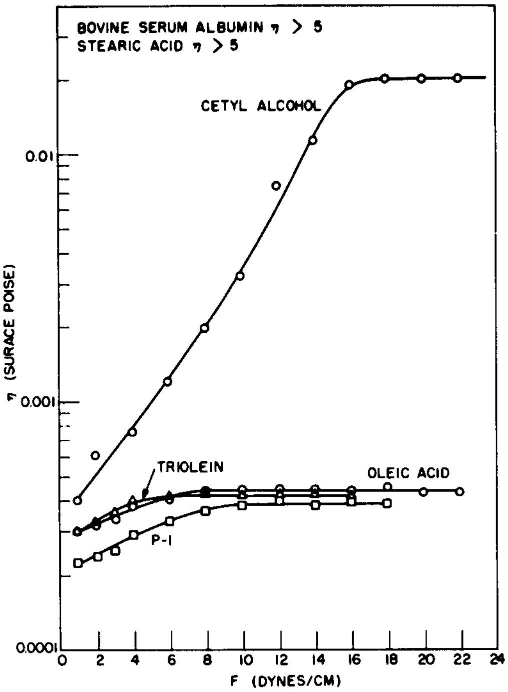

Fig. 5 - Comparison of surface viscosity versus film pressure curves for cetyl alcohol, triolein, oleic acid, and P-1 on synthetic sea water

FATTY ACID DISTRIBUTIONS

Since the infrared spectra strongly implied the presence of fatty acids and their esters in all of the samples, the distributions of specific saturated and unsaturated fatty acids were subsequently determined by gas chromatography (14). The samples were prepared for submission to the gas chromatograph by esterification with 10 ml of 2-percent H_2SO_4 in absolute methanol. P-7 was esterified for one hour at 60°C, and the remaining four samples overnight at 70°C. Five to six microliters of a hexane solution of the methyl esters were injected into the chromatograph column. A Craig polyester column (20-percent diethylene glycol succinate on Chromosorb W, 60/80 mesh) at temperatures of 208° to 215°C was used in these analyses. The column was 6 feet × 1/4 inch.

Table 6 lists the percentage distributions of various fatty acids for both saturated and unsaturated molecules. These values are percentages of the total fatty acid content of a sample. The percent of total fatty acids with respect to the entire slick sample was not determined. Also listed are values which correspond to unidentified chromatographic peaks. They are possibly due to branching of the hydrocarbon chain of the acid. Knowns were not available to definitely establish the identity of these undefined peaks. Although variations in the distribution exist between samples, the 14-, 16-, and 18-carbon fatty acids constitute the greatest percentage of material, with the average carbon chain length being approximately 16 for each sample.

Since marine organisms give fatty acid distributions which are characteristic for a particular species, it may be possible to relate data of the preceding kind to the types of biological entities responsible for sea slicks.

Table 6
Fatty Acid Distributions in Panama Samples
Determined by Gas Chromatography

Number of Carbons/Double Bonds	P-1, Benzene (percent)	P-6* (percent)	P-7* (percent)	P-1, Petroleum Ether (percent)	P-5* (percent)
8/0			1.30		
9/0	0.38		0.92		1.07
					0.90
10/0	0.13	0.45	0.34		0.12
11/0			1.04	0.35	3.50
		0.27		0.62	1.55
		5.06		0.10	
12/0	0.67		0.79	0.78	1.19
		0.92			
	0.50	1.46		0.39	
	0.19				
13/0			1.35	0.34	2.78
	0.64	5.24		2.15	3.18
14/0	24.99	3.88	10.39	11.31	9.23
	2.09		4.76		
	2.12	7.39		1.87	1.07
	1.12			3.71	4.18
15/0		5.47	4.10		
			6.96		
			0.60		
16/0	32.16	24.85	15.33	26.83	23.07
16/1	10.47	5.01	10.79	3.85	2.77
17/0	1.73	4.63	0.82	1.42	3.20
	0.66	5.81	12.10	0.78	2.20
			0.75		
			0.57		
18/0	5.97	16.85	7.81	9.48	12.62
			0.60		
			0.60		
18/1	8.95	7.67	6.93	3.19	3.82
18/2	7.20	5.01	3.05	32.72	23.55
19/0			6.11		
20/0			1.98		
Average number of carbons	15.8	15.9	16.0	16.4	15.9

*Represents the combined benzene and chloroform extracts of slick constituents from these samples.

DISCUSSION AND CONCLUSIONS

The surface-chemical properties of each of the slick samples studied are very similar with only a few exceptions. Each sample formed a more or less fragile, compressible, liquid-expanded-type film which collapsed at very small specific areas. The small specific areas at collapse and large estimated film thicknesses lead to the conclusion that the samples contained large amounts of nonpolar material which were forced out of the more polar material as the samples were compressed.

The maximum surface potentials obtained are higher than would be expected from hydrocarbons or from acids or esters alone, and lower than would be expected for alcohols, amines, or amino acids, and result from a dilution of the latter by the former. Recent qualitative data suggest that only a small amount of nitrogeneous material such as proteins or amino acids is present. However, preliminary thin-layer chromatography suggests that some alcohols and sterols exist in these samples.

These slick-forming materials were also shown to consist essentially of compounds whose surface viscosities are very low, which is consistent with the view that unsaturated fatty acids and triglycerides are major constituents of slick-forming materials. The low viscosities would not be expected if a considerable amount of protein were present in the samples.

In a previous report (15) it was postulated that the viscosity of a surface film might be a factor in determining its wave damping ability, and that a monolayer of high surface viscosity might be more effective than one of low viscosity. This may not be the case in view of the very low surface viscosities of the present samples of slick-forming materials. In fact, it is quite possible that films which adsorb at the sea/air interface will always have a low surface viscosity due to the abundance of long-chain saturated and unsaturated fatty acids or esters.

The infrared spectra may be interpreted to indicate the presence of a mixture of polar species containing long hydrocarbon chains. Nonpolar materials such as unoxidized hydrocarbons were also indicated. Although an unknown group and chemical unsaturation is present in a few samples, all slicks were similar in that they contain esters, free carboxyl, and ionic carboxyl functional groups. In general the slick constituents appear to be a complex mixture of lipids, free fatty acids, and nonpolar entities. The indication that P-7 is essentially an aliphatic hydrocarbon oil merely demonstrates the importance of extreme care in sampling. This sample quantity was unusually large (80 mg) – greater than would be anticipated from a surface monolayer. The sample may have been taken in an oil slick caused by the vessel used in the experiment. This sample probably contains some slick material but its spectrum is masked by the presence of the large amounts of hydrocarbons.

The presence of fatty acids was confirmed by the gas chromatographic analyses. A complex distribution of saturated and unsaturated fatty acids exists over a wide range of carbon chain lengths from 8 to 20. An average of 16 carbon atoms per molecule was found for each sample.

It is apparent from consideration of the collected data for P-1 and P-6 that much slick-forming material was present in nonslick areas and in subsurface water in the ocean area sampled. This is consistent with Leonard's suggestion (16) that the sea contains an abundance of surface-active material from natural sources which could adsorb at the surface and form slicks.

FUTURE RESEARCH

Further analyses of these samples will be conducted to establish their chemical and surface chemical properties. Thin layer chromatography will be used to uncover possible chemical species which cannot be detected by the described techniques. Elemental analysis for carbon, hydrogen, nitrogen, phosphorus, and sulfur will also be performed. The aqueous phase remaining after the extraction process will be examined for water-soluble materials with particular emphasis on proteins and amino acids.

More definite conclusions about the constitution and origin of slicks must await the conclusion of this analytical program. It may then be possible to relate the chemical entities in slicks to a specific marine-biological source. This might be accomplished, for example, through the comparison of fatty acid distributions between slick materials and organic detritus from known marine-biological species.

Additional sea surface samples both in and out of slicks will be required to furnish sufficient quantities of material for the planned analytical work. Such samples should be taken from various major water bodies in order to establish the variability of the properties of sea slicks.

Since relatively large surface potentials were obtained from films of the collected slick constituents, it may be possible to use such a measurement as a scanning tool for the location of areas of slick-forming material. In this regard, a seagoing device is being developed to measure and record the surface potential of the ocean.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the hospitality and assistance of Mr. Francis T. Brannan of the U.S. Naval Research Laboratory Tropical Exposure Site, and Mr. Charles R. Southwell and Mr. Charles Hummer of the NRL Canal Zone Corrosion Laboratory.

Important contributions to the biological aspects of this problem were made by Dr. John M. Leonard and Dr. Dorothea E. Klemme.

The gas chromatographic analyses of fatty acid distribution were performed by Mr. Albert Collier and associates of the A and M Marine Laboratory, Galveston, Texas.

REFERENCES

1. Thompson, J., Phil. Mag. 4th Series 24:247 (1862)

2. Aitken, J., Proc. Roy. Soc. Edinburgh 12:56-75 (1884)

3. Ewing, G., J. Marine Res. 9:161-187 (1950)

4. Timmons, C.O., and Jarvis, N.L., "A Chemical Characterization of Plankton Oil," NRL Memo. Report 1033, Mar. 1960

5. Williams, P.M., Nature 189:219 (1961)

6. Parsons, T.R., and Strickland, J.D.H., Science 136:313 (1962)

7. Garrett, W.D., "Collection of Slick-Forming Materials from the Sea," NRL Report 5761, Mar. 5, 1962

8. Adam, N.K., Proc. Roy. Soc. (London) B122:134 (1937)

9. Klemme, D.E., private communication

10. Zisman, W.A., Rev. Sci. Instr. 3:369 (1932)

11. "Lubricants, Liquid Fuels and Related Products; Methods of Inspection, Sampling and Testing," Federal Specification VV-L-791e, Method 4011.2, May 21, 1953

12. Schulman, J.H., and Teorell, T., Trans. Faraday Soc. 34:1337 (1938)

13. Nutting, G.C., and Harkins, W.D., J. Am. Chem. Soc. 62:3155 (1940)

14. Collier, A., "Fatty Acid Distribution of Certain Samples Submitted by Naval Research Laboratory, Washington, D.C.," special report to NRL from A and M College Marine Laboratory, Galveston, Texas, Nonr 2119 (03), Oct. 17, 1962

15. Jarvis, N.L., "Surface Viscosity of Monomolecular Films at Low Film Pressures, A Literature Survey," NRL Report 5743, Feb. 1962

16. Leonard, J.M., "Biological Oil Slicks, Part I – Literature Examination," NRL Memo. Report 955, July 1959

* * *

UNCLASSIFIED

Naval Research Laboratory. Report 5925. CONSTITUTION AND SURFACE CHEMICAL PROPERTIES OF SEA SLICKS. PART 1 – BAY OF PANAMA, by W. D. Garrett, C. O. Timmons, N. L. Jarvis, and R. E. Kagarise. 16 pp. & figs., May 23, 1963.

Samples of surface water have been collected from both slick and nonslick areas of the Bay of Panama by the screen method developed at NRL. The screen method samples the water surface to a depth of only 0.15 mm. Since this technique is nonselective, all constituents of the sea surface were effectively collected. Selective solvent extraction was used to concentrate and isolate the various organic materials from the sea water. The solvents were removed by vacuum pumping at room temperatures. Milligram quantities of organic waxes and oils, which were free of salt, water, and solvents, were obtained by this technique.

UNCLASSIFIED (over)

1. Ocean surfaces - Chem. anal.
I. Sea Slicks
II. Garrett, W.D.
III. Timmons, C.O.
IV. Jarvis, N.L.
V. Kagarise, R.E.

UNCLASSIFIED

Naval Research Laboratory. Report 5925. CONSTITUTION AND SURFACE CHEMICAL PROPERTIES OF SEA SLICKS. PART 1 – BAY OF PANAMA, by W. D. Garrett, C. O. Timmons, N. L. Jarvis, and R. E. Kagarise. 16 pp. & figs., May 23, 1963.

Samples of surface water have been collected from both slick and nonslick areas of the Bay of Panama by the screen method developed at NRL. The screen method samples the water surface to a depth of only 0.15 mm. Since this technique is nonselective, all constituents of the sea surface were effectively collected. Selective solvent extraction was used to concentrate and isolate the various organic materials from the sea water. The solvents were removed by vacuum pumping at room temperatures. Milligram quantities of organic waxes and oils, which were free of salt, water, and solvents, were obtained by this technique.

UNCLASSIFIED (over)

1. Ocean surfaces - Chem. anal.
I. Sea Slicks
II. Garrett, W.D.
III. Timmons, C.O.
IV. Jarvis, N.L.
V. Kagarise, R.E.

UNCLASSIFIED

Naval Research Laboratory. Report 5925. CONSTITUTION AND SURFACE CHEMICAL PROPERTIES OF SEA SLICKS. PART 1 – BAY OF PANAMA, by W. D. Garrett, C. O. Timmons, N. L. Jarvis, and R. E. Kagarise. 16 pp. & figs., May 23, 1963.

Samples of surface water have been collected from both slick and nonslick areas of the Bay of Panama by the screen method developed at NRL. The screen method samples the water surface to a depth of only 0.15 mm. Since this technique is nonselective, all constituents of the sea surface were effectively collected. Selective solvent extraction was used to concentrate and isolate the various organic materials from the sea water. The solvents were removed by vacuum pumping at room temperatures. Milligram quantities of organic waxes and oils, which were free of salt, water, and solvents, were obtained by this technique.

1. Ocean surfaces Chem. anal.
I. Sea Slicks
II. Garrett, W.D.
III. Timmons, C.O.
IV. Jarvis, N.L.
V. Kagarise, R.E.

UNCLASSIFIED

Naval Research Laboratory. Report 5925. CONSTITUTION AND SURFACE CHEMICAL PROPERTIES OF SEA SLICKS. PART 1 – BAY OF PANAMA, by W. D. Garrett, C. O. Timmons, N. L. Jarvis, and R. E. Kagarise. 16 pp. & figs., May 23, 1963.

Samples of surface water have been collected from both slick and nonslick areas of the Bay of Panama by the screen method developed at NRL. The screen method samples the water surface to a depth of only 0.15 mm. Since this technique is nonselective, all constituents of the sea surface were effectively collected. Selective solvent extraction was used to concentrate and isolate the various organic materials from the sea water. The solvents were removed by vacuum pumping at room temperatures. Milligram quantities of organic waxes and oils, which were free of salt, water, and solvents, were obtained by this technique.

1. Ocean surfaces - Chem. anal.
I. Sea Slicks
II. Garrett, W.D.
III. Timmons, C.O.
IV. Jarvis, N.L.
V. Kagarise, R.E.

UNCLASSIFIED

These slick constituents were subjected to infrared analyses, surface viscosity, surface-potential measurements, and force-area film-balance studies. In addition, fatty acid distributions were determined by gas chromatographic analysis. The data indicate that both slick and nonslick covered surface waters contain a similar mixture of surface-active chemicals. Extracted substances were identified as fatty acids, lipids, and nonpolar hydrocarbons, with some chemical unsaturation showing in the hydrocarbon portion of the organic molecules. The isolated material forms compressible, liquid-expanded films on water which appear to contain quantities of nonpolar material. Surface viscosities of the films were low, indicative of appreciable amounts of unsaturated fatty acids and esters. Gas chromatographic studies showed that each sample contained a complex mixture of saturated and unsaturated fatty acids containing from 8 to 20 carbon atoms. An average of approximately 16 carbon atoms per molecule was found.

UNCLASSIFIED

UNCLASSIFIED

These slick constituents were subjected to infrared analyses, surface viscosity, surface-potential measurements, and force-area film-balance studies. In addition, fatty acid distributions were determined by gas chromatographic analysis. The data indicate that both slick and nonslick covered surface waters contain a similar mixture of surface-active chemicals. Extracted substances were identified as fatty acids, lipids, and nonpolar hydrocarbons, with some chemical unsaturation showing in the hydrocarbon portion of the organic molecules. The isolated material forms compressible, liquid-expanded films on water which appear to contain quantities of nonpolar material. Surface viscosities of the films were low, indicative of appreciable amounts of unsaturated fatty acids and esters. Gas chromatographic studies showed that each sample contained a complex mixture of saturated and unsaturated fatty acids containing from 8 to 20 carbon atoms. An average of approximately 16 carbon atoms per molecule was found.

UNCLASSIFIED

UNCLASSIFIED

These slick constituents were subjected to infrared analyses, surface viscosity, surface-potential measurements, and force-area film-balance studies. In addition, fatty acid distributions were determined by gas chromatographic analysis. The data indicate that both slick and nonslick covered surface waters contain a similar mixture of surface-active chemicals. Extracted substances were identified as fatty acids, lipids, and nonpolar hydrocarbons, with some chemical unsaturation showing in the hydrocarbon portion of the organic molecules. The isolated material forms compressible, liquid-expanded films on water which appear to contain quantities of nonpolar material. Surface viscosities of the films were low, indicative of appreciable amounts of unsaturated fatty acids and esters. Gas chromatographic studies showed that each sample contained a complex mixture of saturated and unsaturated fatty acids containing from 8 to 20 carbon atoms. An average of approximately 16 carbon atoms per molecule was found.

UNCLASSIFIED

UNCLASSIFIED

These slick constituents were subjected to infrared analyses, surface viscosity, surface-potential measurements, and force-area film-balance studies. In addition, fatty acid distributions were determined by gas chromatographic analysis. The data indicate that both slick and nonslick covered surface waters contain a similar mixture of surface-active chemicals. Extracted substances were identified as fatty acids, lipids, and nonpolar hydrocarbons, with some chemical unsaturation showing in the hydrocarbon portion of the organic molecules. The isolated material forms compressible, liquid-expanded films on water which appear to contain quantities of nonpolar material. Surface viscosities of the films were low, indicative of appreciable amounts of unsaturated fatty acids and esters. Gas chromatographic studies showed that each sample contained a complex mixture of saturated and unsaturated fatty acids containing from 8 to 20 carbon atoms. An average of approximately 16 carbon atoms per molecule was found.

UNCLASSIFIED