

the enthalpies reported for synthetic systems (2), which are about 10 cal/g. The heat of transition measured in the membrane is 3.6 ± 0.4 cal per gram of lipid where the error represents the extremes of eleven measurements of three samples.

If we assume that the structure of the aqueous suspension of lipid is an unperturbed, two-dimensional bilamellar array (9), the enthalpy per gram of lipid should correspond to the heat of transition for a completely extended bilayer. Any perturbation of a continuous lipid bilayer in the membrane, such as permanent aqueous pores, penetrating protein, or hydrophobic association of lipid with protein, would disrupt the cooperative interaction of fatty acid chains and decrease the heat of transition. The ratio of the transition enthalpy per gram of lipid in membranes to that for the isolated protein-free lipids is therefore an indication of the proportion of the lipids in the membranes which are in the bilayer state. If this ratio is close to 1, the bilayer must be quite extensive. The observed ratio is 0.9 ± 0.1 , and suggests that 90 ± 10 percent of the lipid in the membranes is in the bilayer conformation. The calorimetric data, together with those from x-ray diffraction analyses (4), are thus consistent with the presence of an extensive lipid bilayer in the membrane of *Mycoplasma laidlawii* at growth temperature, and not with appreciable hydrophobic association of lipid and protein. However, the results do not eliminate the possibility that small amounts of protein might penetrate the bilayer.

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Atmospheric Oxygen in 1967 to 1970

Abstract. Observations of atmospheric oxygen in clean air between 50°N and 60°S , mainly over the oceans, yield an almost constant value of 20.946 percent by volume in dry air. Since 1910 changes with time over the globe appear to be either zero or smaller than the uncertainty in the measurements.

In May 1966, the late Lloyd Berkner urged the Office of the President's Science Advisor to measure oxygen in the clean atmosphere. He justified his request in a Memorandum for the File, which was prepared jointly with L. C. Marshall and dated 29 April 1966, entitled "Potential Degradation of Oxygen in the Earth's Atmosphere." Here it was noted "that fish in the Newfoundland Banks contain significant . . . quantities of herbicides and insecti-

cides." These, it was argued, derive from unicellular organisms, "the grass of the sea. . . . Thus, in the absence of more precise information, it must be assumed that the concentration of insecticides and herbicides in the fish of the sea arises from initial concentration by the photosynthetic organisms which are also the primary source of atmospheric oxygen. The problem is whether the herbicides and pesticides concentrated by the basic photosyn-

Table 1. Measured oxygen abundances, percent by volume (dry air).

Latitude	Longitude	Date collected	Analysis performed during			
			15 to 17 April 1969		9 to 11 April 1969	
			Value	S.D.	Value	S.D.
<i>In 1967 by the R.V. Oceanographer</i>						
49°00'N	007° 5'W	4/18			20.9457	±.0006
45°40'N	014°30'W	4/17	20.9463	±.0006		
42°09'N	019°19'W	4/16	20.9450	±.0017		
40°02'N	024°07'W	4/15	20.9450	±.0010		
36°08'N	031°08'W	4/14	20.9460	< ±.0001		
35°54'N	018°12'E	5/6	20.9460	< ±.0001		
35°54'N	018°12'E	5/6	20.9453	±.0012		
21°00'N	038°30'E	5/22	20.9460	< ±.0001		
21°00'N	038°30'E	5/22	20.9457	±.0006		
19°20'N	070°53'E	6/14			20.9427	±.0023
19°10'N	068°20'E	6/18			20.9487	±.0006
19°10'N	068°20'E	6/18			20.9440	±.0020
18°54'N	065°00'E	6/19			20.9450	±.0026
14°27'N	070°12'E	6/5			20.9487	±.0042
11°06'N	060°04'E	6/3			20.9493	±.0059
10°00'N	092°04'W	11/17	20.9460	±.0010		
10°00'N	092°04'W	11/17	20.9457	±.0006		
08°09'N	073°06'E	7/2			20.9457	±.0058
05°08'N	090°01'E	7/6	20.9463	±.0006		
00°49'N	092°00'W	11/22	20.9457	±.0006		
00°00'	106°10'E	8/10	20.9460	< ±.0001		
05°12'S	113°16'E	8/12	20.9463	±.0006		
09°52'S	115°06'E	8/14	20.9463	±.0006		
10°01'S	084°59'W	11/16	20.9463	±.0006		
15°02'S	113°01'E	8/17	20.9463	±.0006		
15°02'S	113°01'E	8/17	20.9437	±.0032		
20°00'S	115°01'E	8/18	20.9457	±.0006		
20°00'S	076°54'W	11/9	20.9463	±.0006		
25°20'S	112°01'E	8/20	20.9457	±.0006		
30°00'S	075°00'W	11/4	20.9457	±.0006		
30°25'S	114°50'E	8/23	20.9453	±.0012		
32°18'S	130°42'E	9/4			20.9450	±.0017
32°18'S	130°42'E	9/4	20.9453	±.0006		
34°16'S	149°58'W	10/18			20.9480	±.0020
35°00'S	165°00'W	10/15			20.9450	±.0061
35°00'S	135°00'W	10/20			20.9473	±.0012
35°00'S	135°00'W	10/20			20.9467	±.0015
37°42'S	180°00'W	10/12			20.9470	±.0010
Unknown	Unknown	Unknown			20.9457	±.0006
Unknown	Unknown	Unknown	20.9460	< ±.0001		
Unknown	Unknown	Unknown	20.9463	±.0006		
Unknown	Unknown	Unknown	20.9457	±.0006		
Unknown	Unknown	Unknown	20.9457	±.0006		
Unknown	Unknown	Unknown			20.9487	±.0006
Unknown	Unknown	Unknown			20.9457	±.0012
Unknown	Unknown	Unknown			20.9453	±.0012

thetic organisms can affect their population, thereby modifying the equilibrium concentration of oxygen in the earth's atmosphere." Each year about 0.05 percent of the atmospheric oxygen is renewed by photosynthesis of which over 60 percent derives from the oceans. It must be noted that the authors found "themselves in the dilemma that the extent of knowledge so far accessible to them is insufficient to demonstrate whether or not the problem is serious now or in the identifiable future."

In response to Berkner's request, the Environmental Science Services Administration and the National Science Foundation collected seventy-eight samples during 1967 and 1968 by the oceanographic vessels *Oceanographer* and *Eltanin*, both over the continental shelf and open ocean. The Analytical Chemistry Division of the National Bureau of Standards developed the method of analysis and determined the oxygen content.

Samples were collected, after drying, in one-liter evacuated stainless steel flasks. Previous experience had shown

that samples stored in similar containers suffered no detectable change of oxygen after storage for long periods of time, even at slightly elevated temperatures. The oxygen content of the samples was determined by repeated comparison with a gas of known oxygen content with the use of a modified Beckman oxygen analyzer (1). The oxygen contents of the comparison standards were derived from a primary standard which was determined by a gravimetric technique (2) as 20.959 percent by volume with an accuracy of 1 standard deviation of ± 0.006 percent by volume. The mean value of the primary standard and its uncertainty were obtained from 33 results selected from 36 determinations; all 36 results gave the same mean value but a standard deviation of ± 0.008 percent by volume.

Analytical results, sampling sites, and dates are given in Table 1. Three portions were taken from each sample and each measured at least ten times; the standard deviations for the samples in Table 1 derive from the set of three mean values. The averages for all 78

samples is 20.9458 percent by volume of dry air with a standard deviation of ± 0.0017 percent by volume. With one exception, 20.9527 ± 0.0012 percent by volume, the larger departures from the mean are generally associated with large standard deviations suggesting the analytical uncertainty as the source of variation. Values obtained during the second three days, 15 to 17 April, also average 20.9458 percent by volume but exhibit a smaller variability between samples, ± 0.0005 percent by volume, than those during the first 3 days. Increased familiarity with the instrument and its peculiarities after a thousand or so separate measurements probably explains this reduction in variability, although other less readily explained phenomena are undoubtedly present.

The recommended value for oxygen abundance of dry air from the more reliable oceanographic analyses is 20.946 percent by volume relative to a standard with an accuracy of ± 0.006 percent by volume. The precision or geographical variability, or both, is ± 0.0005 .

In February 1970, Hughes collected ten nearly identical samples from a relatively isolated rural site in western Maryland. The average value by the same method of analysis was found to be 20.946 ± 0.0018 percent by volume. In 1967 Hughes (2) reported an abundance of 20.945 percent by volume for a sample collected in the same region.

While new measurements may shed light on any future destruction of oxygen sources by pollution, comparison of present and past observations would indicate whether or not there has been any recent degradation of atmospheric oxygen. Many of the past measurements are reported to three decimal places but Paneth (3) contends that even the second decimal place is imperfectly given. Glueckauf (4) took a less pessimistic view and quoted 20.946 percent by volume as the probable value in his 1951 survey of previous work. We do not know the absolute error in past determinations of oxygen by the volumetric-chemical method but feel that there is some confidence in the third decimal.

There are only five measurements or series of measurements of the absolute oxygen abundance in the atmosphere between 1910 and 1967-70. The first of these was an extensive investigation during 1910-12 by Benedict (5) of the air near his laboratory in Boston as well as air obtained in flasks from isolated geographical areas. There are

Table 1 (continued).

Latitude	Longitude	Date collected	Analysis performed during				
			15 to 17 April 1969		9 to 11 April 1969		
			Value	S.D.	Value	S.D.	
<i>In 1968 by the R.V. Eltanin</i>							
33°30'S	126°10'E	9/8			20.9527	± 0.0012	
34°40'S	124°00'E	9/9			20.9470	± 0.0030	
35°11'S	121°25'E	9/10			20.9467	± 0.0006	
35°15'S	137°50'E	7/31	20.9460	± 0.0010			
35°15'S	137°50'E	7/31	20.9457	± 0.0006			
35°17'S	138°15'E	8/12			20.9443	± 0.0021	
35°18'S	137°43'E	10/7			20.9460	± 0.0010	
36°02'S	116°57'E	9/12			20.9453	± 0.0023	
36°02'S	116°57'E	9/12			20.9400	± 0.0052	
38°15'S	160°10'E	6/25	20.9457	± 0.0006			
38°15'S	160°10'E	6/25	20.9463	± 0.0006			
40°00'S	134°03'E	8/14			20.9480	± 0.0010	
41°52'S	117°04'E	9/14			20.9413	± 0.0042	
42°40'S	150°12'E	6/29	20.9457	± 0.0006			
43°03'S	147°22'E	6/30	20.9453	± 0.0012			
43°58'S	160°02'E	6/23	20.9457	± 0.0006			
44°42'S	145°31'E	7/1	20.9450	± 0.0017			
47°30'S	128°00'E	8/31			20.9460	± 0.0017	
47°30'S	128°00'E	8/31			20.9427	± 0.0021	
47°30'S	128°00'E	9/1			20.9470	± 0.0020	
47°30'S	128°00'E	9/1			20.9453	± 0.0012	
52°56'S	135°00'E	7/23	20.9460	± 0.0010			
53°36'S	122°30'E	9/28			20.9467	± 0.0021	
55°17'S	160°00'E	6/17	20.9463	± 0.0015			
57°00'S	160°04'E	6/16	20.9457	± 0.0006			
58°45'S	117°00'E	9/25			20.9427	± 0.0081	
59°57'S	167°53'E	6/10	20.9457	± 0.0006			
60°00'S	135°00'E	7/19	20.9463	± 0.0006			
60°00'S	128°00'E	8/24			20.9417	± 0.0035	
60°02'S	140°18'E	7/18	20.9457	± 0.0006			
60°10'S	145°00'E	7/17	20.9453	± 0.0006			
60°10'S	145°00'E	7/17	20.9457	± 0.0006			
<i>In 1970 16 kilometers west of Frederick, Maryland</i>							
39°35'N	77°32'W	2/21	20.944	20.949	20.946	20.946	20.947
			20.944	20.949	20.945	20.946	20.945

doubts concerning the validity of the flask samples. We, following Krogh (6), have used the mean of 212 direct laboratory analyses; 20.952 percent by volume. The variability among these samples was ± 0.007 percent by volume with no correlation to observed variations in weather conditions. Krogh suggested a correction of + 0.002 percent by volume for the formation of carbon monoxide in Benedict's apparatus; we believe this correction may be too high. On the other hand, Benedict appears to have reported the abundance of oxygen relative to the total of oxygen, nitrogen, and argon after removal of carbon dioxide. Since this is so, the oxygen abundance in the dry air with normal carbon dioxide would have been 20.946 rather than 20.952 percent by volume.

In 1919, Krogh (6) reported an abundance of 20.948 percent by volume for two analyses of atmospheric air in Denmark. In the early 1930's Carpenter (7) using equipment similar to that of Benedict analyzed over 1000 samples in eastern United States. The results are almost identical with those of Benedict, but it is not clear whether Carpenter used Benedict's uncorrected value, 20.939 percent by volume, as his standard since he was mainly concerned with variability. Carpenter concluded the oxygen abundance is constant, his standard deviation being about 0.003 percent by volume.

Six analyses of a single large sample collected west of Washington, D.C., by Shepherd (8) of the National Bureau of Standards in 1935 ranged from 20.935 to 20.950 percent by volume, the average being 20.946 percent by volume. In 1942, Lockhart and Court (9) reported oxygen abundances in Antarctica averaging 20.92 percent by volume and suggested that the low values might be unique to the location. Glueckauf pointed out that they performed no analysis of normal non-Antarctic air to confirm their procedures. To further cast suspicion, their carbon dioxide abundances were many times higher than that found in recent times. Table 1 does not suggest lower values approaching the Antarctica.

All reliable oxygen data since 1910 fall in the range 20.945 to 20.952 percent by volume. The change in atmospheric oxygen since 1910 has been either very small or zero. It is possible that there has been no change even in the third decimal but a more realistic assessment recommends no change in the second decimal place, there being little confidence in differences of the

third decimal place. Failure to detect changes in atmospheric oxygen may be consistent with Marshall's view that there is now less cause for alarm about the reduction in photosynthetic production of oxygen (10).

Several "doomsday" predictions for the eventual loss of the oxygen from the earth's gas mantle have been proposed and dismissed. Parson (11), for example, examined and rejected the views that oxidation of ferrous metals in lower oxidation states to their highest oxidation states and escape of oxygen from the top of the atmosphere would deplete the earth of its oxygen.

It is likely that the burning of fossil fuels would slightly diminish the oxygen content of the atmosphere. Benedict and Krogh showed that there were slight decreases in the oxygen abundance within cities coinciding with high carbon dioxide values. In fact, there is an approximate one-to-one correspondence in the opposite changes of carbon dioxide and oxygen gases when expressed as percent by volume.

Between 1910 and 1967 atmospheric oxygen should have decreased by 0.005 percent by volume as a result of the combustion of fossil fuels (12). But the uncertainty in both the 1910 and 1967-70 measurements prevents us from attributing significance to any coincidence between expected and observed changes in atmospheric oxygen. Extrapolating the depletion of oxygen due to fossil fuel burning to the day when all known recoverable reserves are consumed (13) leads to an abundance of about 20.8 percent by volume (14). The direct effects of this lower value on human respiration would be insignificant since it corresponds to an oxygen partial pressure change equivalent to a rise of about 75 m in altitude.

In summary, the 1967-70 abundance of oxygen in clean air, 20.946 percent by volume of dry air, is statistically the same as all the reliable measurements since 1910; the extreme range

among reported values is 0.007 percent of volume. The accuracy of the present oxygen standards is ± 0.006 percent by volume. This latter uncertainty rather than the geographic or instrumental variability may limit the detection of small changes of atmospheric oxygen in the future. Further periodic examination of the oxygen content is planned after more accurate standards are developed.

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Smog Aerosol: Infrared Spectra

Abstract. *Infrared spectra of smog aerosol are similar to those of sulfuric acid aerosol, but they do not show the prominent CH and carbonyl bands of organic aerosols from terpenes. Some features of the smog aerosol spectra are not present in the spectra from either type of synthetic aerosol.*

It has been clear for many years that the symptoms of photochemical air pollution (smog) are caused by a variety of chemical reaction products. One such product is ozone; it causes plant dam-

age, odor, rubber cracking, and probably respiratory discomfort, but it does not cause either eye irritation or light scattering. Almost all the reaction products so far identified are small mole-