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Submarine Application of Gas Chromatography for the Analysis of Dissolved Gases in Sea Water

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ABSTRACT

The instrument developed at NRL for the continuous stripping and periodic analysis of dissolved gases in water has undergone a very successful "sea trial" aboard an operating submarine. No unforeseen difficulties were experienced in the transition from laboratory to field operation. While the purpose of the test was not for collection of specific oceanographic data, the results correlate well with literature predictions for the ocean area surveyed. The equipment should have value for the routine collection of profile data on gas contents in the coming generation of submersible research vessels.

PROBLEM STATUS

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

AUTHORIZATION

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SUBMARINE APPLICATION OF GAS CHROMATOGRAPHY FOR THE ANALYSIS OF DISSOLVED GASES IN SEA WATER

INTRODUCTION

The apparatus and technique developed at this Laboratory for the determination of dissolved gases in liquids (1) has been subjected to its first oceanographic test or "sea trial." The test was conducted from 27 through 31 January 1964 aboard the USS SCAMP (SS(N)588) engaged in local operations off San Diego, California.

This apparatus was designed to accomplish direct sampling of sea water and analysis for oxygen, nitrogen, and carbon dioxide from a moving platform (submarine). This concept of chemical oceanographic data collection is unique in the area of dissolved-gas analysis. For this reason, the primary emphasis of this sea trial was on equipment performance rather than the quality of the oceanographic data. While no "umpire" analyses were attempted, a comparison with literature values for oxygen content data from this geographical area and for saturation values for atmospheric nitrogen content will be presented.

EQUIPMENT AND OPERATING CONDITIONS

The apparatus (Fig. 1) consisted of a spinning multiple-disk gas exchanger (stripper), multiport sample valve, gas chromatograph, 10 mv recorder (pressure stylus type to obviate inking problems associated with pressure changes in the submarine), and associated valves, flowmeters, and carrier-stripper gas supply (helium). This equipment and its operational parameters were as described in reference (1) except for the addition of a thermally stabilized base for the chromatograph. The only change from laboratory operation was that continuously flowing sea water was the sample source.

Briefly, a stream of sea water, flowing at a metered rate of 50 cc/min, passes through a stripping unit (Fig. 2) consisting of a series of spinning plastic disks which expose constantly renewed films of water to the stripping gas (helium) which is in constant counterflow at a metered rate of 50 cc/min. The efficiency of gas exchange in this unit is such that one pass-through "frees" the water of all its dissolved gas content. This "rich" gas then passes through the multiport sampling valve, the sequential operation of which allows known volume "cuts" to be injected into the gas chromatograph. The chromatograph separates the components of the sample into discrete portions which are presented to a thermal conductivity detector with recorder read-out. The time required for a given component to traverse the chromatographic separation columns denotes the identity of the individual gas and the magnitude of the deflection produced is a direct measure of its quantity. Appropriate calibration factors are then applied to establish the gas content of that sample in conventional units, e.g., cc's gas (STP) per liter of sea water.

The apparatus was installed on a service desk midway of and outboard of the circumferential passageway in the lower compartment of the auxiliary machinery space (AMS) of the SCAMP. Water source connection was made to the inboard vent lines of the starboard auxiliary sea water (ASW) pumps. The inboard vent line, manifolded to the discharge line of both pumps, "sees" ambient sea pressure at all operating times. An injection-temperature thermometer is located in the intake line just inboard of the pressure hull. Thus the sample water entering the analysis equipment has very low lag time

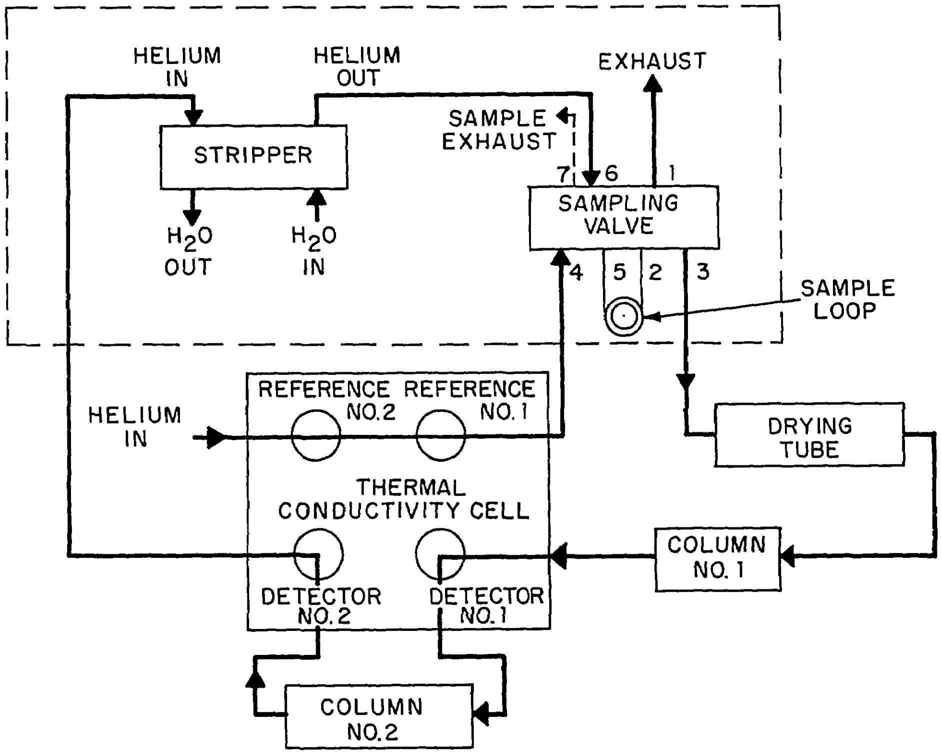

Fig. 1 - Block diagram of analyzer unit

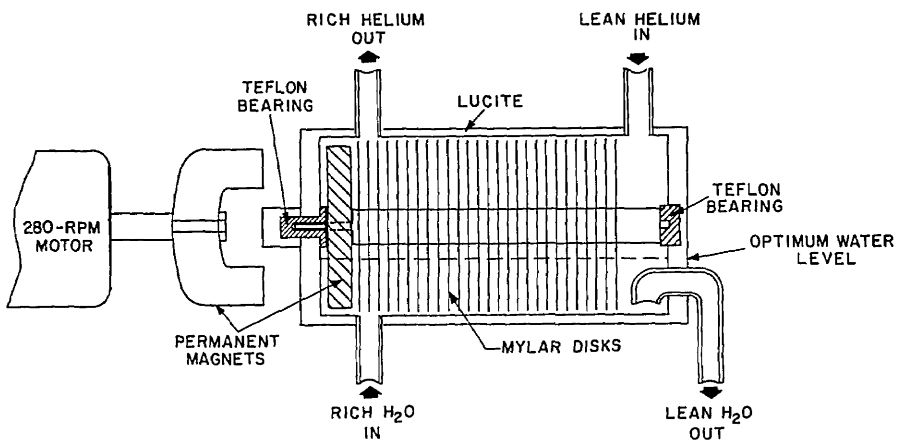

Fig. 2 - Multiple disk stripper

and is available at a minimum of about 8 psig (surface running = ca 20 feet keel depth). The feed pressure is a direct function of operating depth, and, as will be discussed, was the only source of difficulty encountered in this test.

The equipment was installed, and sampling was initiated at 1045, 27 January 1964, while the SCAMP was proceeding at periscope depth to the operations area. The first-day runs were for familiarization and "bug" elimination only.

It became apparent quickly that for keel depths of less than 60 feet there was insufficient hydrodynamic pressure to provide the required flow of 50 cc/min. The principal deterrent to adequate flow was a sintered metal filter in the feed line to the gas exchanger. This filter was removed and no further difficulty was encountered.

A "not-to-interfere" schedule, consistent with the SCAMP's operations, which would allow sampling under a variety of conditions was established. These conditions included rapid depth excursions and periods at various constant depths, both underway and laying to.

The only oceanographic parameters recorded were position, depth, and injection temperature. Geographically, the bulk of the sampling was performed in an essentially homogeneous area (Ref. 2) bounded by 32° to 32.6°N and 117.2° to 118°W. Sampling ranged from keel depths of 20 to 300 feet, and injection temperatures from 10° to 13°C. While not determined, typical salinities should have been in the range of 33.6 to 33.8 parts per thousand (Ref. 2).

Two sample loops were used in the course of the experiments, 2.48 and 5.54 cc (STP). The 5.54-cc loop, of course, gave higher peaks and less mathematical correction in the conversion factor. The larger sample, however, tended to give broader peaks and made peak height a somewhat less reliable means of computing the data. All oxygen values have been corrected for argon (Ref. 1) by the expedient of subtracting a somewhat arbitrary 0.3 cc/liter from each reading.

A total of 176 samples were analyzed, excluding the familiarization runs. The equipment was operated for a total of 18.5 hours over a three-day period, giving an average time of 6.3 minutes per sample, each sample yielding three bits of data: oxygen, nitrogen, and free carbon dioxide content.

As was stated initially, the lack of an "umpire" method for comparison and the avowed purpose of the experiment being an equipment operational checkout have rather limited the value of the data, per se. For this reason, the values are presented as average concentrations at the various depths along with the spread of the data (Table 1). Included are literature values for nitrogen saturation (Ref. 3) and for oxygen content in this region (ref. 2).

It is apparent from Table 1 that there is excellent agreement between the average oxygen-nitrogen contents and the literature values. This is probably fortuitous in view of the data spread. The probable cause of this spread will be discussed later. The carbon dioxide data are of questionable validity at this time, as will also be discussed later.

EQUIPMENT PERFORMANCE AND DATA DISCUSSION

The performance of the equipment and the direct adaptation of laboratory-derived techniques to shipboard operation was excellent beyond expectation.

An operational problem, not unpremeditated, involved the feed-pressure change occasioned by corresponding depth changes. Constant operator vigilance and appropriate valve adjustments were required to maintain a constant rate of water flow. The incorporation of a regulated flow gear pump or other pressure-insensitive metering device into the water feed to the stripper is a highly recommended addition for future instrumentation.

The local operations in which the submarine was participating required frequent excursions to and from various depths as well as some surfacing. In addition to the pressure effect already noted, these maneuvers also resulted in the rather rapid sampling of

Table 1
Oxygen, Nitrogen, and Carbon Dioxide Data

Number of Samples	Sampling Depth (ft)	Sample Temp. (°C)	Oxygen Content (cc/liter)			Nitrogen Content (cc/liter)			Carbon Dioxide Content (cc/liter)	
			Avg.	Spread	Literature Ref. 2	Avg.	Spread	Literature Ref. 3	Avg.	Spread
42	16	13.3	6.2	5.9-6.5	5.0-6.0	11.0	10.5-11.7	10.98	0.21	0.1-0.3
49	56	12.8	5.8	5.3-6.1	5.0-6.0	11.1	10.8-11.2	11.04	0.23	0.2-0.3
7	96	12.8	5.8	5.5-6.3	5.0-6.0	11.0	10.8-11.2	11.04	0.28	0.2-0.3
37	146	12.2	5.9	5.3-6.3	5.0	11.0	10.5-11.7	11.15	0.27	0.2-0.3
7	220	11.7	5.0	4.8-5.6	4.0-5.0	11.3	10.5-11.7	11.25	0.24	0.2-0.3
12	296	10.6	4.4	3.9-4.8	3.0-5.0	11.4	11.2-12.0	11.47	0.36	0.3-0.5

waters of various temperatures, salinity, and oxygen content. Combined with the normal "lag" due to the volume of the stripper these factors result in a non-equilibrium condition and a semi-integrated gas content read-out. Data taken at these times served to establish an "equilibrium adjustment" rate and are of little value analytically, although they are included in the tabulation. The indicated adjustment rate for the conditions encountered aboard the SCAMP was about fifteen minutes.

The application of this technique to a research-oriented mission on a submersible would, of necessity, allow for more continuous liaison between the scientist and crew. Such a cruise would also entail a program of operation aimed specifically at data collection at specific depths and positions. These two facts alone would eliminate nearly all of the cause for the doubtful data reported herein.

There is considerable doubt at this time as to the validity of any of the carbon dioxide data reported here and possibly of any literature values also. This gas is in equilibrium with dissolved carbonates and bicarbonates and is also a contributor to the equilibrium pH of a given mass of sea water. In fact, Harvey (Ref. 4) states that fixing any two of the quantities pH, free CO_2, and salinity, fixes the third. This being so, the removal of free CO_2 during sample stripping of necessity will shift one or both of the other quantities in an equilibrium readjustment. Depending upon the rate of shift, the free CO_2 content data are probably in error by some unknown amount. This situation does not appear to apply to fresh water analysis and is being investigated.

CONCLUSIONS

It is quite unique in the practices of chemical oceanography to have available a procedure for direct, in situ sampling and analysis of ocean waters in which no artifact such as temperature changes or long exposure to container walls affects the samples. While it is true that the jury-rigged sample intake utilized aboard the SCAMP did not completely eliminate pressure release effects, the point of pressure release was at the last valve before the stripper and any degassing that may have occurred should have been carried on into the stripper and thus not completely ignored as is the case in the cast type sampling. The speed of the analysis as well as the simultaneous collection of nitrogen and other gas content data are major improvements over other techniques. In this regard, gases such as hydrogen sulfide, carbon monoxide, and the lower hydrocarbons are also determinable by this technique, without modification.

On the debit side, the nature of sampling does not allow for multiple analysis. Consecutive analyses may be made in a given area, but these are not duplicates in the analytical sense. The technique of equating peak height to gas content is not the most accurate read-out; planimetry, while tedious, gives more accurate results. It is doubtful if data accurate to the second decimal place is attainable with this instrument. However, there is considerable question as to the validity of the present convention of reporting wet chemical data to two and even three decimal places–and, in sequential logic, to the importance attached to apparent oxygen content fluctuations of less than 0.1 cc/liter.

The instrument in its present form is capable of performing routine horizontal profile analyses on a moving or stationary submerged platform. Minor modifications (pumped samples) permit surface boat operations, and provision of an adequate sampling port on the coming generation of deep diving vessels would allow vertical profiling.

ACKNOWLEDGMENT

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