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Modification of the Ringrose Carbon Dioxide Meter

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ABSTRACT

A carbon dioxide meter manufactured in England by International Gas Detectors, Ltd., was in use in British submarines in 1956. When subjected via field tests to conditions prevailing on U.S. nuclear submarines, it failed to indicate properly after about two days. Upon careful evaluation of the instrument, NRL was able to suggest possible modifications to make the instrument more suitable and IGD appeared willing to cooperate with a modification project. A prototype Mark II featuring the best combination of changes subsequently suggested by both parties was built and independently evaluated. The English have already equipped their first nuclear submarine, Dreadnought, with four of the instruments. NRL work has shown that, with further minor alterations, the Mark II should be a very useful CO_2 meter on U.S. nuclear (and other) submarines. Five of the Mark II's are being purchased, four to be used for distribution and evaluation on submarines and the fifth for NRL use.

PROBLEM STATUS

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

AUTHORIZATION

NRL Problem C08-05
BUSHIPS Project SF-013-08-03, 4092, 4093, 4094, 4095

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REDESIGN OF THE RINGROSE CARBON DIOXIDE METER

The Ringrose carbon dioxide meter is an instrument manufactured in England by International Gas Detectors, Ltd. (IGD) for indicating the amount of CO_2 in the surrounding air from zero to five percent. The accuracy is about ±10% of the reading, and the response time is about five minutes. There is no interference from the air currents or temperature fluctuations normally encountered in living spaces, and the instrument is designed to compensate for pressure fluctuations that occur on a submarine. A first model (Fig. 1) of this instrument was put into service on British submarines in 1956 and was still giving satisfactory service when the U.S. Navy became interested in it in 1959.

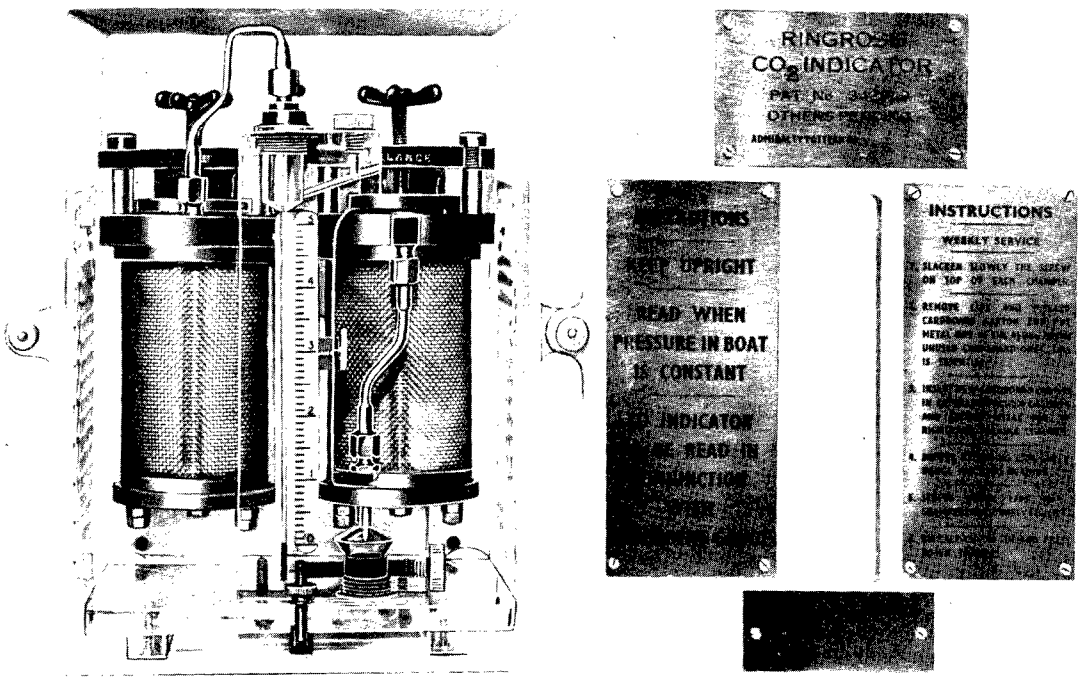

Fig. 1 - Ringrose CO_2 Meter, Mark I

The Ringrose meter consists basically of an oil-filled manometer with a cylindrical chamber at each end. These chambers have access to the atmosphere only through a semipermeable ceramic membrane. The chamber at the low-pressure end of the manometer contains a carton of carbon dioxide absorbent (soda lime), and the chamber at the high pressure end contains a carton of cotton batting impregnated with calcium chloride. All of the gaseous constituents of the surrounding air are free to diffuse in and out of the chambers through the ceramic membranes. However, when CO_2 enters the sodalime

chamber it is absorbed; this tends to develop a partial vacuum in that chamber–a condition indicated by the manometer. Since the degree of vacuum developed is proportional to the percentage of CO_2, the manometer reading becomes an indicator of this percentage. The $CaCl_2$/cotton chamber serves to balance the partial pressure of water vapor in each chamber and also to balance each end of the manometer against rapid external pressure changes.

In 1959 the Bureau of Ships purchased a Ringrose meter and submitted it to the Naval Research Laboratory for evaluation (1). The instrument was reported to be satisfactory in its operation with one reservation; it was sensitive to rapid or radical changes in the relative humidity. No test was made of the instrument's compensation for pressure changes or the service life of the chemical cartridges used in it.

By December of 1960 the Ringrose meter had been taken on two nuclear submarines (2,3) and a serious shortcoming became apparent. After one or two days of operation the reading of the instrument began to fall below the true CO_2 level; this trouble seemed to stem from the low relative humidity (ca 40%) prevailing on the nuclear submarines. It was suggested that LiOH might be substituted for sodalime. It was further stated that the instrument was superior to the Dwyer CO_2 meter in terms of convenience and ease of stowage. As a result of these conclusions, the Naval Research Laboratory was asked to study the use of LiOH and to investigate the principle for possible application to future designs of an atmosphere analyzer.

Since it seemed worthwhile to try to reduce the size and weight of the existing model of this instrument, an NRL model was designed and built to be used while attempting to develop more satisfactory chemical cartridges. The new instrument was made smaller, its weight was reduced by the use of aluminum alloy, and it made use of a Magnehelic mechanical pressure gage manufactured by F.W. Dwyer Company. It was quickly found that this pressure gage imposed an inordinately long period of equilibration to reach a given reading because of its considerable internal volume. Attempts to alleviate this, including the design and construction of a modified version of the gage having less internal volume, were unsuccessful. The alternative measure used with success was to design an oil-filled manometer that was spillproof (Fig. 2).

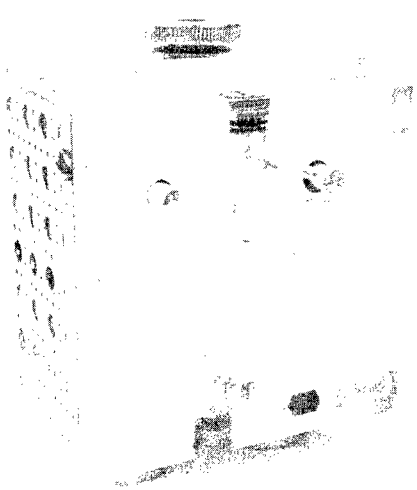

Fig. 2 - NRL Ringrose with plastic manometer

In the course of working with the NRL Ringrose meter, different dimensions made it necessary to fabricate new membranes. A number of these were made, some of clay and some of porcelain,–with only indifferent success. To have good sensitivity, one would want to develop the maximum possible pressure differential at a given CO_2 concentration. The NRL membranes never gave as high a differential as the IGD membranes, although the porcelain appeared identical to the English ceramic under a binocular microscope.

Work toward the substitution of LiOH for sodalime was fruitless. The problems of providing moisture compensation for this chemical were even worse than for sodalime. After attempting to use mixtures of LiOH with silica gel that had been equilibrated at relative humidities around 50% in the absorption chamber and the same gel alone in the compensation chamber without any success, LiOH was abandoned. It must also be compensated for because of the

generation of water by the carbonation reaction, but at the same time it must be in a specially prepared anhydrous form to absorb CO_2 at maximum efficiency.

When the work on the project had progressed to a point where the operation of this instrument and attendant problems in modifying it were better understood, a letter was sent to the English manufacturers informing them as to what was wanted. The manufacturers expressed the utmost willingness to cooperate on the project. At their request, a Magnehelic gage was sent along with some pelleted LiOH and silica gel of the type tested here. In April 1962, when the NRL meter had been quite thoroughly tested here, a member of the NRL group visited the company in Leeds, taking the NRL meter to show to them. They expressed considerable interest in the construction of this lightweight compact embodiment of their product. They also showed correspondence they had received from the Royal Naval Physiological Laboratory at Alverstoke wherein essentially the same shortcomings NRL had independently found in their production model were stated to be manifest in tests run at Alverstoke. The conference concluded with the decision that IGD would proceed with a Mark II design of the Ringrose meter incorporating a combination of the better features of the prototype of a new model that they had constructed (Fig. 3) and the NRL instrument (which was left there on loan for more detailed inspection).

A very important finding was brought up by the IGD people that NRL began to suspect only a week before. It was that the malfunctioning of the instrument when used in air of 50% relative humidity or less was caused by excess moisture in the sodalime as a result of the CO_2 reaction. This caused an excess partial pressure of water vapor to develop in the absorption chamber which overpowered the compensator and resulted in a progressive depression of the CO_2 reading below its proper level. At the time the switch to LiOH was suggested, it was believed that an unduly low moisture content of the sodalime, caused by evaporation to the dry air, was impairing the absorption of CO_2. Thus, the problem became one of inadequate compensation rather than impaired absorption.

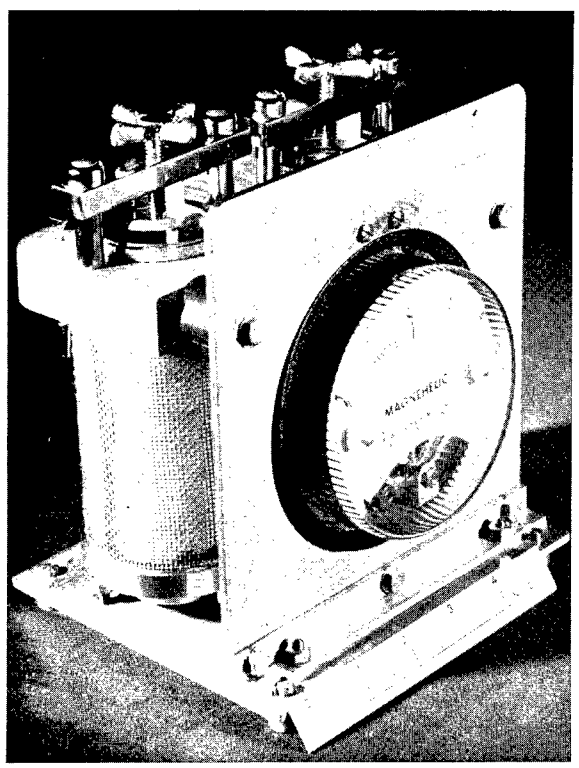

Fig. 3 - IGD "Interim Model"

During the year following this conference, IGD completed the design and prototype construction of the Mark II Ringrose meter (Figs. 4 and 5), accomplished suitable evaluation tests at the Alverstoke Laboratory (4), and had a published performance report from that laboratory in hand. NRL did little work during this period other than making the modification of a Magnehelic gage. In April of 1963, representatives of IGD delivered a prototype Mark II and discussed the state of the art with this Laboratory. The Mark II was left on loan for evaluation, and the NRL modified Magnehelic gage was taken back to the IGD plant to see if they could derive any benefit from its use on a Mark II meter.

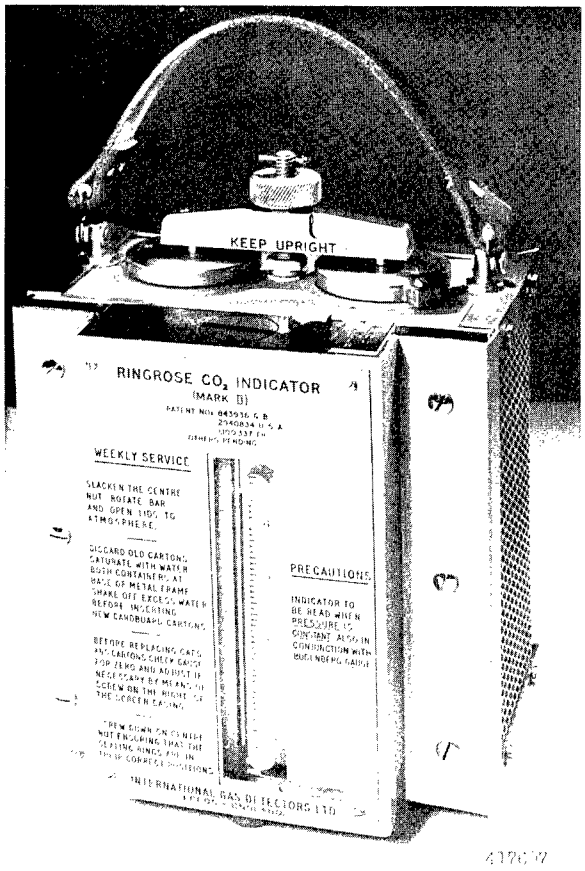

Fig. 4 - Ringrose CO_2 Meter, Mark II

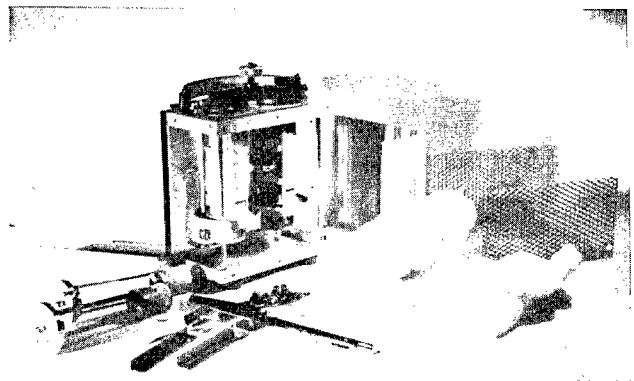

Fig. 5 - Exploded view of Mark II

Subsequent evaluation tests with this Mark II instrument showed up several minor difficulties that could be easily remedied but one additional trouble that looked more vexing. The minor difficulties were: the manometer leaked oil at the O-ring seal of the zero adjustment screw and at the closure of the oil reservoir; the rate of response to changes in CO_2 level was a bit slow (Fig. 6); the cartridge holders tended to bind with the holddown nut upon their removal; and the angle through which the manometer could be observed was limited by the machining for installation of the scale.

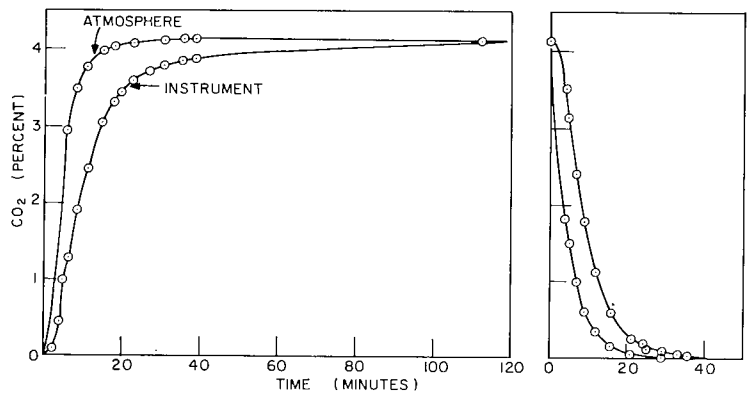

Fig. 6 - Equilibration of CO_2 meter reading. RH = 100%. Fresh cartridges from sealed polyethylene bag.

All of the above items are rather easily remedied but the more important difficulty was that the compensation for varying moisture in the carbon dioxide absorbent chamber was still not what it should be (Table 1 and Fig. 7). If the instrument was subjected to prolonged exposure at upscale levels of CO_2, the reading would gradually be depressed by excess moisture from the sodalime. To solve this problem IGD increased the depth of each chamber by about one inch and position cartridges of water-soaked cotton in each of these increased spaces. The NRL approach was to make the relative humidity in the two chambers of the instrument as near 100% as possible so that there could be no increase. In effect, this would simply be a step further in the direction IGD had started. It was found that sodalime with the high moisture content of 17% usually marketed in this country has a partial pressure of water above it such as to give about 90% relative humidity at room temperature. Then to balance this, one could use cotton batting soaked with a saturated solution of $ZnSO_4 \cdot 7H_2O$ which gives the proper partial pressure of water for 90% relative humidity. This could vary some with temperature but so can sodalime.

The zinc sulphate/moist sodalime system has been tried, and it does alleviate the problem to a considerable degree (Table 2). Apparently it does not quite eliminate the problem altogether (Fig. 8). If the readings of the instrument cannot be made to stay within the tolerance limit of ±10%, then perhaps the simplest alternative will be to reduce the range to 2.5%. Levels of CO_2 up around 4% or more cause the trouble, and there is some question as to whether the range must extend that far for the proposed use.

The prototype Mark II meter has been given shipboard trials on the SCAMP (SS(N)588) on two cruises. On the first test, the boat was operated at or near the surface and ventilated frequently, but the CO_2 level did reach 1.75% on occasion. Thus, the instrument was subjected to the most unsteady conditions it would be likely to encounter with regard to relative humidity, absolute pressure, and CO_2 concentration. Its performance was

Table 1
Downward Drift of Zero on Exposure to Upscale CO_2 Levels

Date	Ringrose Zero At Start (percent)	CO_2 Level (percent)		Time Held At Level (min)	Ringrose Zero At Finish (percent)
		Atm	Ringrose		
10/3/63	0.02	2.01	2.12	210	0.00
10/4/63	0.00	2.15	2.04	278	-0.03
10/7/63	0.02	4.30	4.40 4.79?	241	-0.05
10/8/63	-0.06	4.74	4.90	146	-0.11
10/9/63	-0.20				

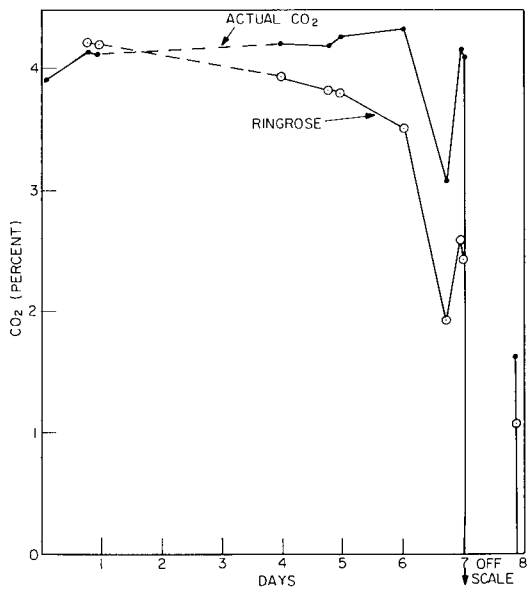

Fig. 7 - Drift of meter reading at 4% CO_2 with IGD cartons

considered satisfactory at all times. It was influenced by pressure changes but recovered in 5 minutes or so. Both the IGD (sodalime/$CaCl_2$) and NRL (moist sodalime/$ZnSO_4 \cdot 7H_2O$) carton systems were used and the pressure effects were with the latter, which hadn't been carefully adjusted as to volumes. The chambers of the meter were opened occasionally to check the manometer zero and when they were resealed, the time necessary to return to a proper reading never exceeded 5 minutes.

On the second trip the Ringrose meter was turned over to the ship's crew, who set it up and took all readings. The type of maneuvers this time led to a sustained CO_2 level of 1 to 1.8% for 6 days. The Ringrose reading was said to be slightly low at the start but more so at the end of the 6-day period (used only IGD cartons). Acceptance of the instrument by the ship's crew was good.

An order has been placed by NRL with Koehler Manufacturing Company of Marlboro, Massachusetts (American representative of IGD), for five Ringrose Mark II carbon dioxide meters incorporating all improvements of the past year. The instrument on

Table 2
Data on Zero Drift After Exposure to 4% CO_2

Date	Ringrose Zero At Start (percent)	CO_2 Level (percent)		Time Held At Level (min)
		Atm	Ringrose	
10/29/63	0.00	4.03	4.62	71
10/30/63	0.02	4.42	4.80	428
10/31/63	0.00	4.41	4.72	444
11/14/63*	0.03	3.91	4.28	371
11/15/63	0.03	3.81	4.18	432
11/18/63	0.03	3.87	4.22	387
11/19/63	0.03	3.95	4.30	441
11/20/63	0.02	3.87	4.13	398
11/21/63	0.02	3.97	4.10	467
11/22/63	0.00	4.19	4.45	340

*The instrument was inadvertently subjected to an RH of 5% for four days. It was necessary to add water to the compensator and to re-equilibrate the two cartridges.

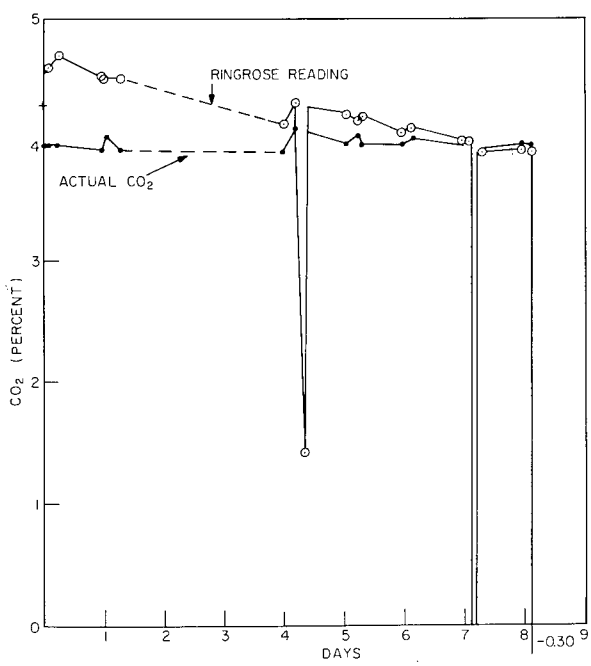

Fig. 8 - Drift of meter reading at 4% CO_2 with NRL cartons

loan from IGD during this time is to be returned. It is in good condition after a year of laboratory service, the only faults being the zero adjustment screw access sealed with paraffin, an upper manometer reservoir cap leak sealed with Apiezon Q putty, and a water cartridge badly corroded by being subjected to a saturated K_2CrO_4 solution for about a week. The leak at the manometer cap, very minute and difficult to locate, serves to emphasize the necessity of reasonably robust construction on this instrument. It was completely unusable until the leak was located. This leak appeared immediately upon return of the meter from its second SCAMP trip, involving shipment from San Diego, California.

In conclusion, this instrument has proved itself suited for the proposed use on nuclear (and other) submarines. It is simple, reliable, and requires little servicing. The necessity for training of crewmen in its use will be practically nil. Its cost is moderate, and the expected service life is unlimited, barring mistreatment. The weekly replacement of cartridges in the instrument should not pose any supply problem.

There are several ways in which this CO_2 meter could be incorporated into submarine usage. A meter could be carried to any part of the boat it was desired to monitor; a meter could be placed in a sealed chamber at a central location and provided with valved sample lines and a pump such as already exist for the Atmosphere Analyzer; or a separate instrument could be placed permanently in each location where CO_2 monitoring was necessary.

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