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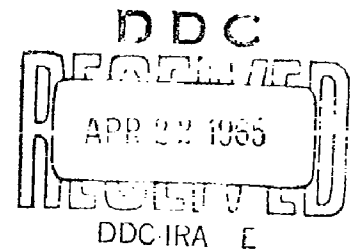
Studies of Submarine Carbon Dioxide Scrubber Operation:

Effect of an Additive Package for the Stabilization of Monoethanolamine Solutions

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ABSTRACT

Limited sea trials of a monosodium diethanol glycine-tetrasodium ethylenediaminetetraacetate (VFS-LDTA) additive package to stabilize monoethanolamine (MEA) scrubber solutions have been conducted aboard the USS ANDREW JACKSON and the USS JOHN C CALHOUN. For the one case where a direct comparison could be made, the additive package provided a 100-hour induction period before the formation of nonbasic nitrogen-containing compounds but no induction period was provided by VFS alone. VFS contents of the solutions decreased rapidly with time, but EDTA levels remained essentially unchanged.

The large copper contents of used scrubber solutions demonstrated the need for a deactivator such as EDTA. Iron contents were also substantial, but this metal is not considered as potent a degradative procatalyst as is copper.

Base stock MEA contained substantial proportions of copper and iron; make-up water samples contained no iron and little copper. MEA normalities were generally within acceptable limits, and in the one CALHOUN scrubber examined, up to 50% of the CO₂ in the rich MEA was removed in the stripper.

Recommendations are made to specify use of the VFS-EDTA package in scrubber solutions, and to take appropriate steps to minimize contamination of these solutions by copper.

PROBLEM STATUS

This is a final report on this phase of the problem; work is continuing on other aspects of the problem.

AUTHORIZATION

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

STUDIES OF SUBMARINE CARBON DIOXIDE SCRUBBER OPERATION:
Effect of an Additive Package for the Stabilization of
Monoethanolamine Solutions

INTRODUCTION

A study has been made recently of the factors affecting the stabilization of monoethanolamine (MEA) solutions used in submarine carbon dioxide scrubbers (1). It was reported that combined use of tetrasodium ethylenediaminetetraacetate (EDTA) and the currently employed additive, monosodium diethanol glycine (VFS), improved both the intrinsic stability of the amine and its resistance to copper-catalyzed degradation. This report deals with the results of limited sea trials of the additive package, and with related scrubber data.

To evaluate the operational characteristics of the MEA-VFS-EDTA system, two shipboard experiments were set up; the first early in 1964 on the USS ANDREW JACKSON (SSBN 619) (2), and the second in the latter part of 1964 on the USS JOHN C CALHOUN (SSBN 630). NRL personnel participated in the latter cruise.

SCRUBBER OPERATING CONDITIONS

The experiments on the ANDREW JACKSON were conducted in two phases, covering two patrols (3). At the start of each patrol, both scrubbers were freshly charged with conventional MEA-VFS solution; Scrubber 1 received in addition a charge of EDTA. Each additive was present in a concentration of 1.5%. Both scrubbers operated for 900 hours during Phase 1; during Phase 2, Scrubber 1 operated for 752 hours as compared to only 424 hours for Scrubber 2. Scrubber 2 was apparently very dirty at the commencement of Phase 1, as evidenced by the very dark color of the samples drawn immediately after startup. Since it was apparently not feasible to recharge the scrubber with fresh solution, the original solution remained in service for the time period stated. Because of the unknown nature and concentration of the contaminant no laboratory analyses of this solution were made.

The period of submersion of the CALHOUN was planned to be less than 300 hours. Under the circumstances, it was decided that sharing this time period between two scrubbers, i.e., one using VFS alone and the other using the VFS-EDTA additive package, would not be useful since differences in stability might not become apparent. Therefore, only Scrubber 1, employing the MEA-VFS-EDTA system was in continuous operation; Scrubber 2, containing only MEA-VFS, was used only briefly and intermittently as a backup when CO₂ levels became too high.

RESULTS

1. Additive Life -- CALHOUN scrubber samples were analyzed periodically for VFS and EDTA content. Surprisingly, the concentration of VFS decreased steadily until, after 84 operating hours, it was undetectable. The method of analysis, titration with lead nitrate, did not distinguish between loss of VFS

which was bound up with a more reactive metal and loss caused by deterioration of VFS to a nonchelating form. That the analytical method was not adversely affected by interfering salts was demonstrated by its ability to detect VFS after makeup additions of MEA-VFS to the used scrubber solution. The amount of recoverable VFS always decreased with time from the peak noted immediately after addition of a fresh charge of MEA-VFS to the solution. On the other hand, analysis for the EDTA content of the amine solutions revealed practically no loss during the period of scrubber operation.

As will be indicated in a subsequent section, the contaminant metal contents of the scrubber solutions were small when compared with the relatively large quantity of VFS present. Thus the VFS was not in the form of a non-titratable stable metal chelate; it appears probable that the additive was oxidized or otherwise converted to a nonchelating entity during scrubber operation. This assumption, it should be pointed out, does not necessarily preclude the possibility that the altered compound may still exert a stabilizing effect. For example, the oxidation products of phenothiazine, an excellent antioxidant for diester lubricants, are themselves useful stabilizers (4). At the present time, however, no firm conclusions can be drawn regarding the fate of VFS during scrubber operation.

2. Metal Contamination -- Spectrographic analysis of MEA solutions from both boats revealed the usual range of minor concentrations of metal contaminants (iron, nickel, chromium, copper, aluminum, calcium, silicone, magnesium, lead and tin). As in the earlier study (1) particular attention was paid to the first four of these metals - iron, nickel and chromium because they comprise the major material of construction of the scrubber, and copper because of its pronounced degradative effect on the amine. In general, the concentrations of metals found in the present samples were comparable with those from previously-examined scrubbers having equivalent operating times; a major exception was the iron content of the CALHOUN scrubber.

a. Nickel and Chromium -- None of the scrubber samples contained nickel or chromium in amounts exceeding 1 ppm. Such concentrations would not adversely affect the stability of the amine.

b. Iron -- Makeup water from both JACKSON and CALHOUN was iron-free, but the iron contents of the base stocks were surprisingly large, 112 and 240 ppm respectively. Makeup additions of the amine probably accounted for the major portion of the metal which accumulated in the solutions, Figure 1. Although the iron content of the ANDREW JACKSON scrubber solutions increased slowly and regularly with time, that of the JOHN C CALHOUN rose to high levels shortly after startup; thereafter, there was some fluctuation in level.

Previous laboratory experiments have shown (1) that MEA solutions containing 30 ppm of ferric iron, or much larger quantities of the bulk metal, were acceptably stable with VFS present, either alone or in conjunction with EDTA. What effect the iron concentration of more than 100 ppm found in the CALHOUN sample would have on the stability of the amine cannot be assessed with cer-

tainty. Iron, however, is not considered a potent degradative catalyst in the MEA system.

c. Copper -- As shown in Figure 2, copper contents of solutions from both boats showed comparable increases in concentration with time. The presence of EDTA would not affect the rate or extent of copper buildup, but previous laboratory data (1) indicate that the additive could be expected to limit sharply the adverse effect of the metal. The copper contents of the base stock amines from both boats were surprisingly high, 20 ppm in each case; the makeup water of each contained 1.5 ppm. Major sources of copper in the solutions are undoubtedly the base stock amine and makeup water, since the design of the scrubber precludes copper-bearing metal from coming in contact with the liquid, and airborne particulate copper is apparently not an important factor (5).

3. Nonbasic Nitrogen-Containing Compounds -- The oxidative degradation of MEA is manifested in part by the generation of nonbasic nitrogen-containing compounds (NBN). These products contain nitrogen in a form which is unreactive with carbon dioxide, and their concentration provides a useful measure of the extent of breakdown of the amine. Figure 3 shows that where a direct comparison could be made between scrubber solutions containing VFS alone, and the VFS-EDTA mixture (ANDREW JACKSON samples), the latter formulation was the more stable. This was demonstrated by an induction period of more than 100 hours before the appearance of NBN, whereas in the solution containing only VFS, NBN was generated immediately after the startup of the scrubber. Throughout the test period, the NBN levels of the latter samples remained significantly higher than those containing VFS-EDTA. The mixed additives-containing solution from the CALHOUN showed a significant early formation of NBN, but in the absence of reference data from a control solution containing only VFS, no useful conclusions can be drawn.

4. Normality Titrations -- The normalities of thirty-four amine samples from the JACKSON, covering both test programs, were determined potentiometrically. All values but one were between the acceptable limits of 3.0 N and 5.0 N, the exception being a Phase 1, Scrubber 2 sample whose normality was 5.8 N after 298 hours of operation.

5. Carbon Dioxide Content -- The efficient removal of carbon dioxide from the rich MEA is a critical factor in scrubber system operation. Some data on the efficiency of CO₂ stripping in the CALHOUN scrubber are reported in Table 1.

The theoretical CO₂ capacity of the amine is based on a value of 11.2 ml CO₂ for each milliequivalent of MEA, assuming that the carbonate is formed. This assumption is only approximately correct since some bicarbonate exists in equilibrium with the carbonate. The data indicate that the rich MEA is 50 to 75 percent saturated with carbon dioxide and that up to half of the total CO₂ is removed in the stripper.

TABLE 1

CARBON DIOXIDE CONTENT OF CALHOUN SCRUBBER SAMPLES
(VFS-EDTA MIXTURE)

Sample	Hours of Use	Normality	ml CO ₂ (Rich)	ml CO ₂ (Lean)	Theoretical CO ₂ Capacity
1	12	3.98	35.2	25.7	44.6
2	24	4.24	26.8	16.4	47.5
3	84	4.10	27.8	18.9	45.9
4	156	4.36	29.3	14.8	48.8
5	228	4.40	24.9	12.7	49.3
6	264	4.10	32.2	18.5	45.9

6. Recycling Pump Malfunction -- During the CALHOUN cruise, the efficiency of a scrubber recycling pump decreased during operation to such an extent that, after about 300 hours, replacement was necessary. Subsequent examination of this pump revealed that it hand-turned with difficulty, and that a tacky greenish deposit was present on the shaft. The working components of these pumps in contact with MEA are stainless steel; a copper-alloy sleeve bearing which supports the shaft is isolated from the solution by a seal. Although the cause of the pump failure was not definitely determined, it was possible that leakage past the seal may have permitted the amine to come in contact with, and to corrode the sleeve bearing. In the experience of the CALHOUN crew personnel, the average operational life of these pumps is about that observed in the present instance, 300 hours; their information was that other boats have had similar experiences with this pump.

SUMMARY AND CONCLUSIONS

Limited sea trials of a VFS-EDTA additive package for CO₂ scrubber solutions were conducted on the SSBN 619 and SSBN 630. Employing the generation of nonbasic nitrogen-containing compounds as a criterion of amine breakdown, in the only instance where a direct comparison could be made, the solution containing the mixed additive package showed a greater degree of stability than did the solution containing only VFS.

The quantity of unreacted VFS in the scrubber solutions decreased with time. The concentration of EDTA, on the other hand, remained substantially unchanged under the same operating conditions.

The incorporation of EDTA into the additive package to suppress the degradative action of copper appears to be well justified by the quantities of this metal encountered in the scrubber solutions. Considerable amounts of iron were also found in these solutions, probably originating in large part from the base stock amine. Although the presence of such concentrations of iron are not particularly desirable, the metal is not considered a potent degrader of the amine. Nonsignificant amounts of nickel and chromium were encountered.

Shipboard monitoring of the ANDREW JACKSON solution normalities generally maintained them within the desired limits of 3.0 N to 5.0 N. The JOHN C CALHOUN scrubber stripped up to 50% of the carbon dioxide content of the rich MEA. A recycling pump on the JOHN C CALHOUN failed after 300 hours of operation.

RECOMMENDATIONS

It is recommended that sea trials of the VFS-EDTA additive package be continued. However, the extensive laboratory and limited operational data accumulated to date justify early incorporation of this package into the MEA scrubber system. The copper content of scrubber solutions should be controlled by placing a copper limit requirement in the MEA procurement specifications, and by using battery-grade makeup water.

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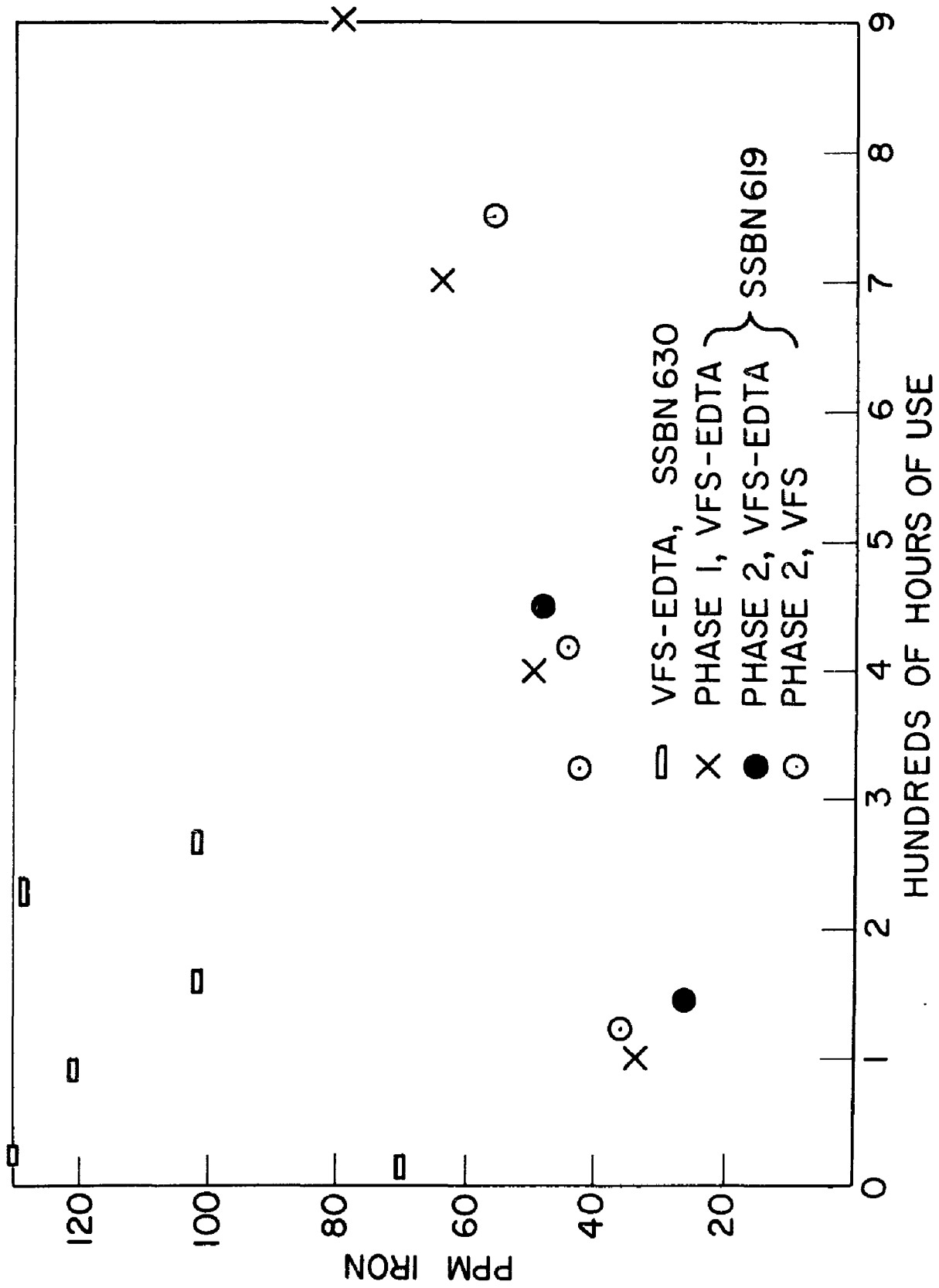


Figure 1 - Iron Content of Used Scrubber Solutions

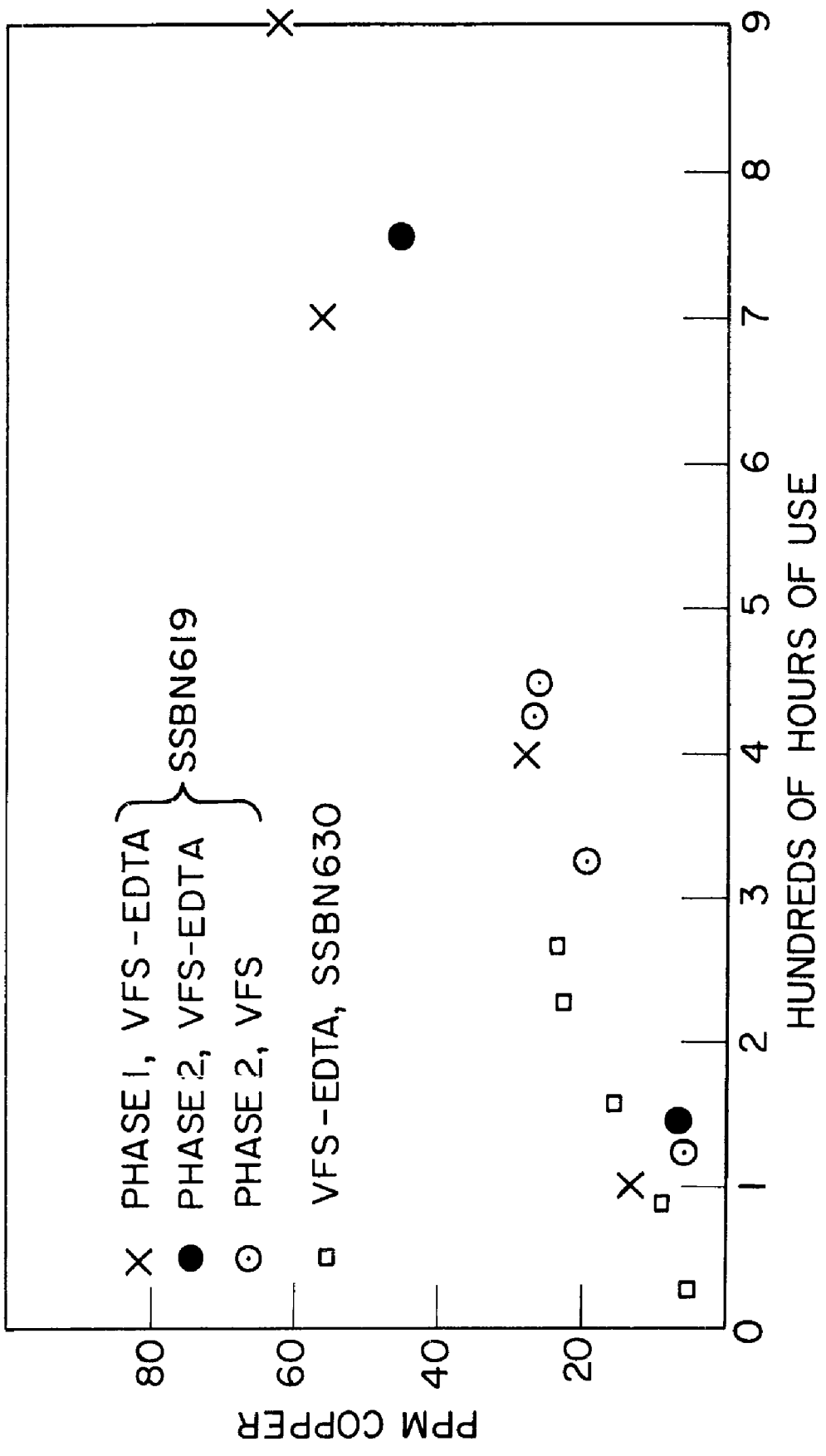


Figure 2 - Copper Content of Used Scrubber Solutions

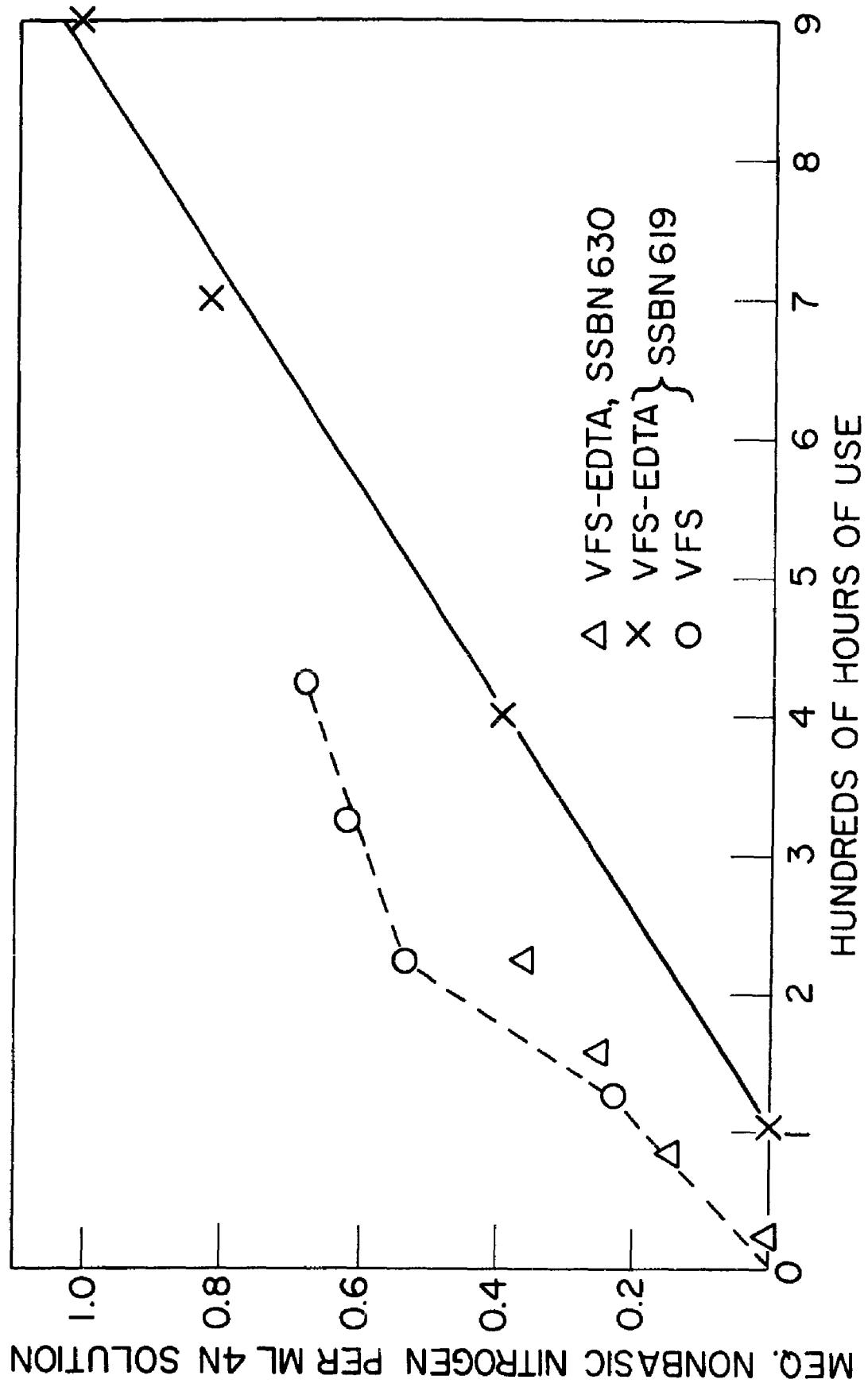


Figure 3 - Nonbasic Nitrogen Content of Used Scrubber Solutions

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